

UNDERSTANDING PHOTOELECTROCHEMICAL WATER OXIDATION REACTION ON BiVO_4 -BASED PHOTOANODES

By

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This is to certify that I have examined this copy of a master's thesis by

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*Dedicated to my mom first and foremost,
Then my dearest brother, my closest friends and my love
Thank you.*

ABSTRACT

Photoelectrochemical (PEC) cells are devices that convert the energy of the sun to chemical energy via splitting water to H_2 and O_2 . During solar water splitting, oxygen evolution reaction (OER) takes place on the (photo)anode and hydrogen evolution reaction (HER) takes place on the (photo)cathode. The poor activity of photoanodes in the oxygen evolution reaction is one limiting factor in widespread use of PEC systems. Another factor is the inefficient utilization of the charge carriers. Hence, there is a need for active photo absorber materials to build more functional photoanodes. To match the efficiency of OER to the HER oxide semiconductor photo absorbers with ability to evolve oxygen are often utilized. Semiconductors with suitable light absorption properties in the visible light spectrum, good catalytic properties, adequate electron/ hole mobility and carrier lifetime, high chemical stability and low-cost are required for effective use of PEC devices.

Bismuth vanadate ($BiVO_4$), an n-type semiconductor, has gained much attention for its use as a photoanode in water splitting reactions, due to its relatively narrow band gap ($E_g = 2.4$ eV) among other metal oxide semiconductor photoanodes and suitable band edge positions with respect to OER electrochemical potentials [1]. Higher PEC activities from $BiVO_4$ -based photoanodes could be obtained via morphology control, doping and the addition of co-catalyst facilitating the oxygen evolution kinetics.

In this study, $BiVO_4$ photoanode films were prepared via hydrothermal synthesis method. Between direct growth and powder deposition onto FTO coated glass substrates methodologies, direct growth was found to be the best approach. Tungsten (W) dopant was incorporated to improve the electronic properties, and subsequently water oxidation kinetics and best activity was obtained from 2.0at% W-doped $BiVO_4$ samples. For further enhancement iridium oxide (IrO_x) co-catalyst was loaded on $BiVO_4$ via atomic layer deposition (ALD) method with water and ozone as oxidizers. Best water oxidation activity was obtained from low coverage (30 ALD cycles) water-oxidized IrO_x co-catalyst decorated on $BiVO_4$ with 1.73 mA/cm^2 current density at 1.23V under simulated solar light illumination. The effect of hydrothermal reaction time and temperature were also investigated, and the sample preparation was optimized to 2h reaction time at 180°C to get the best photocatalytic performances from the $BiVO_4$ photoanodes. It was found that crystallinity and morphology could be modified by using different surfactants. It was

shown that increased homogeneity in morphology distribution and crystallinity did not improve the photocurrent densities for the BiVO₄ photoanodes.



OZET

Fotoelektrokimyasal (PEC) hücreler, suyu H_2 ve O_2 'ye ayrıştırmak suretiyle güneş enerjisini kimyasal enerjiye çeviren cihazlardır. Güneş enerjili su ayrışması sırasında (foto) anot üzerinde oksijen evrimi reaksiyonu (OER) gerçekleşir ve (foto) katot üzerinde hidrojen açığa çıkarma reaksiyonu (HER) gerçekleşir. Oksijen evrimi reaksiyonundaki fotoanotların zayıf aktivitesi, PEC sistemlerinin yaygın kullanımında bir sınırlayıcı faktördür. Diğer bir faktör ise yük taşıyıcıların verimsiz kullanımıdır. Bu nedenle, daha işlevsel fotoanotlara için etkin foto emici materyallere ihtiyaç duyulmaktadır. OER'in verimliliğini, HER'in verimliliğinin seviyesine çekebilmek için oksijeni evrimleştirme yeteneğine sahip oksit yarı iletken ışık soğuran malzemeler sıklıkla kullanılır. Görünür ışık spektrumunda uygun ışık soğurma özelliklerine, iyi katalitik özelliklere, yeterli elektron / boşluk hareketliliği ve yük taşıyıcı ömrüne, yüksek kimyasal kararlılığa ve düşük maliyetli fotoanotlar PEC cihazlarının etkili kullanımı için gereklidir.

Bir n-tipi yarı iletken olan bizmut vanadat ($BiVO_4$), diğer metal oksit yarı iletken fotoanotlara göre nispeten dar bant boşluğu ($E_g = 2.4$ eV) ve uygun bant sınırları nedeniyle su ayırma reaksiyonlarında fotoanot olarak kullanımı için çok dikkat çekmiştir. OER potansiyelleri ile ilgili pozisyonlar (2). $BiVO_4$ tabanlı fotoanotlardan elde edilen daha yüksek PEC aktiviteleri, morfoloji kontrolü, doping ve oksijen evrim kinetiklerini kolaylaştıran yardımcı katalizör ilavesi ile elde edilebilir.

Bu çalışmada, $BiVO_4$ fotoanode filmleri hidrotermal sentez yöntemi ile hazırlanmıştır. FTO kaplamalı cam substratlar üzerinde doğrudan büyütme ve üzerine toz birikimi arasında metodolojileri, doğrudan büyütme en iyi yaklaşım olarak bulunmuştur. Su oksidasyon kinetiklerini geliştirmek için tungsten (W) katkısı kullanıldı ve en iyi aktivite 2.0at% W-katkılı $BiVO_4$ örneklerinden elde edildi. Daha fazla iyileştirme için, iridyum oksit (IrO_x) yardımcı katalizörü, su ve ozon oksitleyicileri ile ALD yöntemi kullanılarak fotoanotlara yüklenmiştir. En iyi su oksidasyon aktivitesi, simüle edilmiş güneş ışığı aydınlatması altında 1.23 mA / cm²'de 1.23 V'de RHE'ye karşı oksijen akışı altında suyla oksitlenmiş IrO_x yüklü (30 ALD döngüsü) $BiVO_4$ 'ten ısıtılma işleminden sonra elde edilmiştir. Hidrotermal reaksiyon süresi ve hidrotermal sıcaklığın etkisi de araştırılmış ve $BiVO_4$ fotoanotlarından en iyi fotokatalitik performansları elde etmek için 180 ° C'de 2 saat reaksiyon süresine sahip olacak şekilde optimize edilmiştir. Kristalinite ve morfolojinin farklı sürfaktan kullanımı ile modifiye edilebileceği bulunmuştur. Morfoloji

dağılımı ve kristallikte artan homojenliğin, BiVO₄ fotoanotları için foto akımlarını iyileştirmediği gösterilmiştir.



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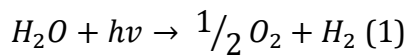
CHAPTER 1

INTRODUCTION

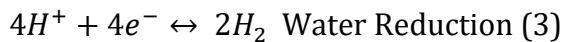
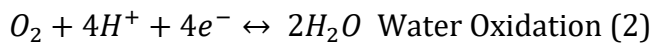
1.1 Photoelectrochemical Water Splitting

As the world started to go towards a more carbon-free fuel production and consumption, solar energy resources are in the center of attention more than ever. In fact, sunlight has the highest theoretical potential to be a primary source of earth's renewable energy [2]. Since Fujishima and Honda demonstrated artificial water splitting in 1972 using a photoelectrochemical (PEC) cell with TiO_2 as photoanode and Pt as photocathode, many studies have been conducted on artificial water splitting to obtain H_2 and O_2 [3]. However, to utilize sunlight efficiently and produce hydrogen and oxygen that can be used as renewable energy source, three main points need to be optimized: capturing of sunlight, converting it into electrochemical energy and adequately storing the products in a way that can eventually be mass-produced and distributed [4].

Generating hydrogen and oxygen from water by directly using sunlight is a phenomena found in nature, called natural photosynthesis [5]. The devices used in the laboratory environment to split water into oxygen and hydrogen perform an artificial photosynthesis or photoelectrochemical (PEC) water splitting. Water splitting reaction is quite demanding with the standard Gibbs free energy change ΔG° of 1.23 eV [1]. The reaction in acidic environment can be summarized as follows (1) [6]:



This reaction, in fact, consists of two half reactions that are the oxidation of water taking place on the photoanode and reduction of water on photocathode as shown in equations (2) and (3) [5]:



Eq. (2) and (3) show that oxidation process must create four electron-hole pairs per one molecule of O_2 and reduction two electron-hole pairs per one molecule of H_2 . This corresponds to $4 \times 1.23 \text{ eV} = 4.92 \text{ eV}$ and $2 \times 1.23 \text{ eV} = 2.46 \text{ eV}$ standard Gibbs free energy values, respectively [7]. The basic mechanism of the PEC water splitting depends on the

photoexcited charge carriers formed upon irradiating a photoanode or photocathode. They are usually prepared with semiconductors following the example of TiO_2 photoanode used by Fujishima and Honda, in the form of electron (e^-)- hole (h^+) pairs inside the semiconductor material [3,5]. To achieve water splitting, materials with band gaps higher than 1.23 eV and, since it also needs to absorb light in the visible region, lower than 3.0 eV should be used as photoanodes and/or photocathodes in the PEC cell system [6].

The PEC water splitting cell design is made up of three main components, a semiconductor photoanode (n-type) or a semiconductor photocathode (p-type) as the light absorber, a counter electrode, usually Pt, and a reference electrode, usually silver/silver chloride electrode [1].

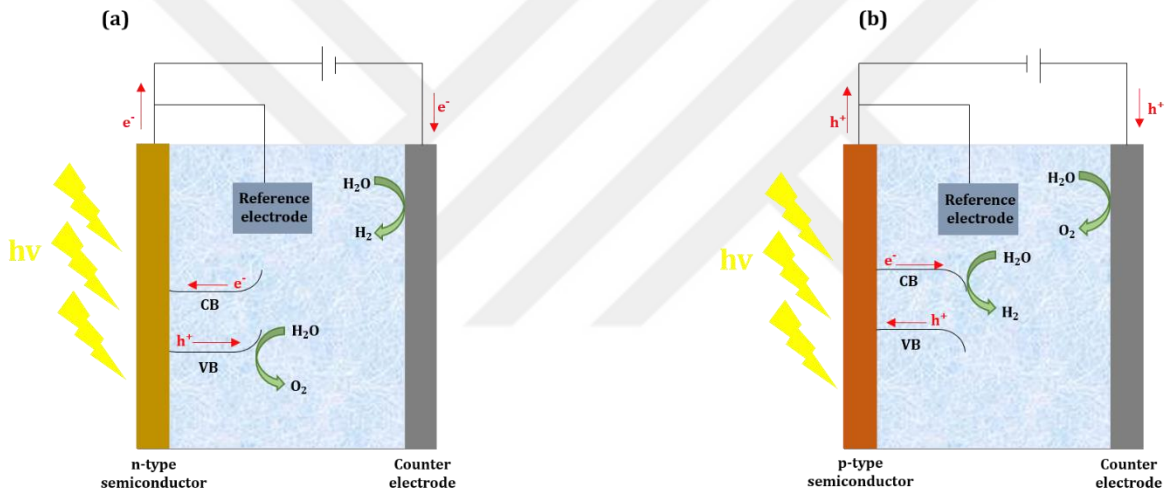


Figure 1.1.1: Schematic illustration of a typical PEC water splitting cell structure with an n-type semiconductor photoanode (a) and a p-type semiconductor photocathode (b), and basic working principle of it. Adapted from [1].

As Figure 1 emphasizes, the basic working principle of the PEC water splitting cell is that at first, the photoelectrode is excited by illumination with a light source, usually simulating the sun, therefore with a 1 sun intensity, while being immersed in an electrolyte. The electrolyte is usually chosen according to certain pH ranges and anion and cation types. After illumination, electron-hole pairs will be generated by the photoelectrode, and they will be separated and moved to the particular electrode for the reduction and oxidation of water [8]. As it is seen in Figure 1(a), photoexcited holes gather on the photoanode surface and oxidize water into oxygen which is referred to as oxygen evolution reaction (OER), and the electrons are transferred to the counter

electrode for water reduction. Similarly, Figure 1(b) shows that electrons are accumulated on a photocathode whose surface is then assisting in hydrogen evolution reaction (HER), while oxygen is produced on the counter electrode [9].

Though the design of an efficient PEC system is straightforward, there are various factors to be considered while creating real life applications of this cell. Other processes might take place on the surface and inside the bulk of the photoelectrodes, such as the recombination of electron-hole pairs which do not take part in the water redox reactions and reduce the efficiency of PEC system altogether. There might also be losses at the liquid-semiconductor electrode interface due to concentration and kinetic overpotentials required for the HER and the OER [7]. To reduce these losses and increase the efficiency while lowering the external bias that needs to be applied to overcome these potentials, researchers created many different designs for photoanodes and cathodes, especially to create a band gap of 1.6-2.4 eV which is required to account for all the losses described above [7]. The following section mentions the different types of semiconductors used and their different combinations, as well as morphology and structure optimizations in more detail, with some focus on BiVO_4 and TiO_2 as they have been the focus materials of the study being presented here.

1.2 Photoabsorbers

To achieve a high water splitting efficiency in PEC cells, the photoelectrodes that are being used should be optimized into the great photoabsorbers of solar light, as well as being capable of separating and transporting photoexcited electrons/holes while driving redox reactions effectively. Ideally, a good semiconductor material chosen as photoelectrode is abundant and low-cost, environmentally friendly and have high chemical stability to withstand real-life applications in PEC cells [1,10].

Various semiconductor materials have been widely investigated so far, from (oxy)nitrides and (oxy)sulphides to metal oxides with appropriate band gaps [6,8]. For (oxy)sulphides and (oxy) nitrides, the existence of N and S elements make them unstable as photoelectrodes due to photohole-induced self-oxidation [1]. To the contrary, the metal oxides that were investigated comprise a diverse group of materials, including TiO_2 , ZnO , WO_3 , BiVO_4 , Fe_2O_3 , Cu_2O and many more examples [11–15]. The reason behind the

spotlight the oxides have been given is that they are usually inexpensive, relatively stable, nontoxic and easily prepared even on a larger scale [16].

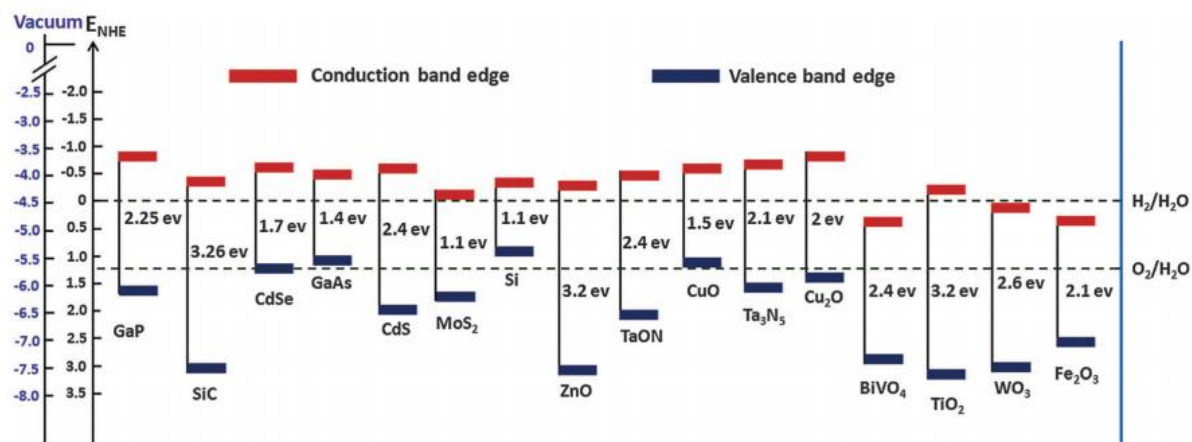


Figure 1.2.1: Band edge positions of some semiconductors; in an aqueous electrolyte at pH=0 relative to normal hydrogen electrode (NHE). For comparison the HER and OER redox potentials are also presented. Reproduced from [1,17].

Figure 2 shows various types of metal oxides often used in PEC cells. As it was mentioned before, band gap position and band gap energy (E_g) of the semiconductor is pivotal to achieving good efficiencies in PEC water splitting cells. As Figure 2 is also illustrating, n-type semiconductors such as BiVO₄ and WO₃ whose band gaps are relatively narrow, thus suitable for efficient sun light absorption, also have conduction band edges lower than HER potential but higher than OER potential, accompanied by valence band edges lower than OER potential. Among all the semiconductors shown in Figure 2, TiO₂ has been investigated most intensively as a PEC photoanode as a result of its nontoxicity, availability, chemical stability and diverse synthesis methods with well-established mechanisms [1]. The most substantial setback of TiO₂ is that in its two most common crystal phases, rutile ($E_g = 3.03$ eV) and anatase ($E_g = 3.18$ eV), it only absorbs solar light in the ultraviolet (UV) region, which comprises only 5% of the solar spectrum [18]. However, unlike wide band gap semiconductors, the ones with narrower band gaps such as BiVO₄ ($E_g = 2.4$ eV), WO₃ ($E_g = 2.6$ eV) etc. show light absorption in the visible region, therefore are considered to be good candidates as photoanodes [1,13,14].

Apart from the solar light absorption directly related to the band gap energy of a semiconductor, narrow band gap semiconductors are also limited by low separation of electrons and holes, along with fast surface recombination of electrons and holes [16]. To overcome these limitations, many different designs were developed for metal oxide-based

photoanodes. The most common and straightforward method of modification is to dope the metal oxide with an element to increase charge transfer and increase the separation of the photoexcited charges, however in this case the original structure of the metal oxide might change, and the impurity sites would act as charge recombination centers instead, therefore worsening the photocatalytic activity of the electrode as a counter effect [1,19]. Nonetheless, many advances in manufacturing much photoanodes with enhanced PEC activities have been made by n-doping and n-type metal oxide, one commonly studied example being W-doped BiVO_4 [14,20,21]. It is seen in density functional theory calculations that tungsten substitutes for V^{5+} as W^{6+} , thus is an n-type dopant in BiVO_4 structure [14,22]. PEC activity measurements performed in electrochemical cell set ups and Mott-Schottky plots, which are basically derived from an equation that relates the capacitance to the applied voltage over a semiconductor-electrolyte junction, presented in several studies indicates increase in the majority charge carrier density in BiVO_4 photoanodes caused by tungsten doping [14,20,21]. One example where the increase in charge carriers caused by introducing W to BiVO_4 structure is Gamelin group showing a cathodic shift in the onset potential for long-term PEC water oxidation at pH=8 [14,16,23]. There are other methods of improving the activities observed for semiconductor photoelectrodes such as surface modifications by adding a co - catalyst on the surface or covering it with a protective layer, or even surface passivation, all of which have specific effects that lead to a better observed activity in PEC measurements. Though the details of all these methods will not be introduced in this study, co-catalyst addition to the photoanode surface and how it effects the activity of the semiconductor photoanodes will be further mentioned in the following sections.

The attraction BiVO_4 gathered as a potential photoanode in PEC water oxidation reactions mainly stem from its appropriate band gap energy (2.4 eV), non-toxicity and very high activities for water oxidation under visible light illumination [16,24]. Though BiVO_4 has three well-known polymorph structures: monoclinic scheelite ($E_g = 2.4$ eV), tetragonal scheelite ($E_g = 2.34$ eV) and tetragonal zircon ($E_g = 2.4$ eV); in 1998, Kudo's group, followed by many studies, showed that monoclinic scheelite structure shows the highest PEC activities under solar light illumination [16,24,25]. To make this material, and any material of interest for PEC reactions, work even better, many parameters can be optimized such as the chemical composition, as suggested by the doping of BiVO_4 previously, morphology, size, crystal structure etc. to obtain various physicochemical

properties that contribute to the effective photogenerated electron-hole separation and transfer parts of the water splitting reaction on photoelectrodes used in PEC cells [1]. Thus, one method that has been utilized widely and is still being investigated intensively is to form hetero-nanostructures between two metal oxides, allowing one to make use of the properties belonging to both materials [1].

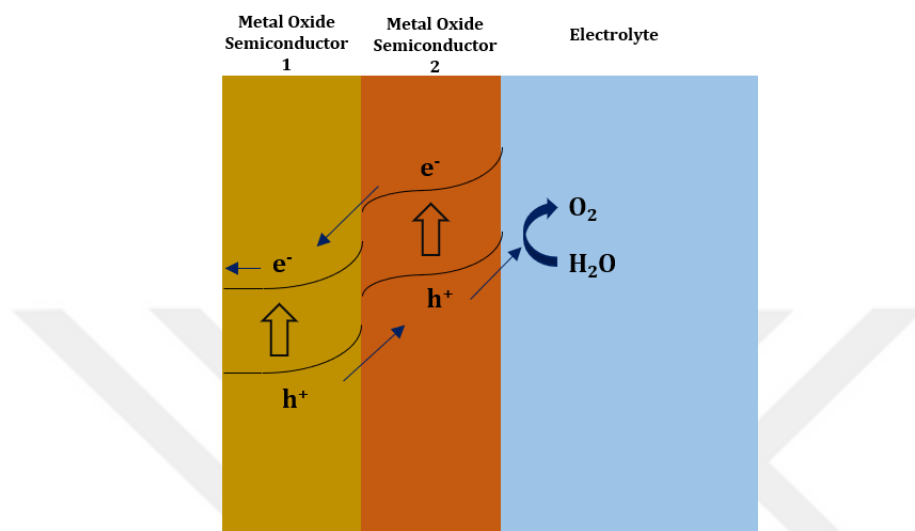


Figure 1.2.2: A schematic representation of heterostructured-photoanode with heterojunctions between the different metal oxides and the basic working principle of it for water oxidation (OER). Adapted from [1].

When two different metal oxides are coupled as a guest and host semiconductors, referred to as metal oxide semiconductor 1 and 2 in Figure 3, respectively, heterojunctions form between the semiconductors. These heterojunctions can effectively increase light absorption of the photoanode, significantly enhance the charge separation rate since they would suppress the electron-hole recombination and the life time of the charge carriers. That process would lead to improved PEC water splitting performance, usually observed and reported in the form of current density (mA/cm^2) [1,17]. Figure 3 shows the generally proposed mechanism of heterojunctions helping charge separation in the photoanode system as a basic scheme. There are many heterostructures that are investigated for this purpose such as $WO_3/BiVO_4$ [26–28] and $TiO_2/BiVO_4$ [15,29]. In both composite photoanode designs, TiO_2 and WO_3 bring chemical stability and decrease photocorrosion during PEC reactions as they are much more stable semiconductors when compared to $BiVO_4$ [1,27,29]. Pilli et al. showed that the 1D- $WO_3/BiVO_4$ structures they prepared showed improved photocurrent density of $2.45 mA/cm^2$ is greater than the measured photocurrent values of pristine $BiVO_4$ and 1D- WO_3

they had prepared [1,30]. This type of improvement in measured photocurrent densities for $\text{WO}_3/\text{BiVO}_4$ composites have been observed and reported in other studies as well; they have been mostly attributed to the charge carrier recombination suppression along with better separation of electron-hole pairs formed by photoexcitation [27,31].

As for $\text{TiO}_2/\text{BiVO}_4$ composite photoanode structures, apart from TiO_2 being stable in a wide range of pH values, Peidong Yang et al. suggested that it also has a relatively negative flat band potential of $\sim 0.2\text{V}$ vs. RHE therefore does not limit the photovoltage that can be obtained from BiVO_4 while providing a driving force for electron transfer [29]. They have also reported using spectroscopic and electrochemical characterization methods that TiO_2 and BiVO_4 are good candidates for making an efficient composite photoanode because of the thermodynamically favorable band alignment between them [29]. There has been some really comprehensive studies regarding the effect of different morphologies and structures of TiO_2 on its PEC activity regarding the change in charge carrier pathway, charge carrier amount and the changing surface area and surface tension in various morphologies making it possible to diminish the activity by becoming charge recombination centers instead of improving the efficiency [18]. However, optimizing certain structures for this material might provide advancement in the photocurrent densities or PEC activity behavior in a unique way. For instance, few studies suggested the tuning TiO_2 into 1D nanorod or nanotube structures might allow them to serve as direct charge transport paths for the charge carriers, therefore suppressing electron-hole recombination and leading to increased photocurrent values [15,32]. Thus, using nanorod type of 1D high surface area morphologies in $\text{TiO}_2/\text{BiVO}_4$ composites, or even tuning the morphology of BiVO_4 alone might bring advancements to a possible PEC water splitting cell with these materials as photoanodes. In tuning morphologies, various preparation methods and their wide range of parameters come into consideration. Though not all of them can be mentioned in this study, relevant preparation methods and their importance to this work will be mentioned in the following titles.

1.3 Co-Catalysts

In addition to the aforementioned modifications for the n-type semiconductors for improvement of their efficiency or their measured PEC activities, one other method has recently gained increasing attention: co-catalyst loading on the surface of the photoanode semiconductor. It has been reported in various studies that surface-functionalized co-

catalysts, such as oxygen evolution catalysts (OEC) for OER on photoanode surface, can improve water redox reactions kinetics since OER and HER reactions are both multiple electron transfer reactions leading to a high kinetic demand for completion [1,33]. Various photocatalysts have been loaded on photoelectrodes over the years, however most studied photoelectrodes remain to be BiVO_4 , along with WO_3 and TiO_2 . In relation, among various photocatalyst materials, Co-based ones have been studied most intensively, usually in the form of Co-Pi catalysts [14,34]. Several groups reported that depositing Co-Pi catalysts, or different catalysts such as NiOOH or FeOOH catalysts, even the recent rising star of the co-catalyst investigation, Iridium oxide catalysts, enhanced the O_2 evolution efficiency of the photoanode of interest, usually BiVO_4 and WO_3 [33,35–37].

Co-catalysts usually are reported to enhance the oxygen evolution activity and photocatalytic current density by promoting charge separation and transport on the semiconductor surface, therefore suppressing the surface recombination of the charge carriers [14,35–38]. Thus far there are three mechanisms that have been proposed for the way a co-catalyst helps improve the OER efficiency of a photoanode in a PEC cell: First, the most straightforward role proposed for a catalyst is also considered for co-catalysts; it might be reducing the activation energy of the rate-determining step of the four electron transfer oxidation reaction leading to improved kinetics for the OER due to the increased rate of the charge transfer to the electrolyte [39]. Secondly, it might be passivating the recombination centers on the photo absorber surface and inhibiting the surface recombination, as aforementioned [39]. The final mechanism that is commonly proposed is that the co-catalyst might be influencing the band bending of the semiconductor as it forms a Schottky-type junction on its surface, leading to improved charge separation [39]. As mentioned above, there has been many reports introducing improved photocatalytic activities and measured current densities for the semiconductor photoabsorbers of any kind using co-catalyst loading on their surface, and they have reported one or multiple of the reasons described above for the mechanism it helped their system through. However, there has yet to be a thorough understanding of the actual mechanism co-catalysts help a PEC cell photoanode or cathode, even a method to differentiate between the three types of pathways that are theorized for the activity of the OECs. Recently, Carolin Zachaus et al. released a study they performed solely for this purpose in which they studied the working mechanism of Co-Pi catalyst loaded on BiVO_4 using intensity modulated photocurrent

spectroscopy (IMPS) technique [39]. Through their experiments, they have concluded that Co-Pi, unlike what many published studies reported in the past, does not in fact enhance the charge transfer rate by acting as a classical catalyst on the BiVO₄ surface, but instead it suppresses charge recombination, leading them to believe that BiVO₄ is already thermodynamically active towards water oxidation reaction, thus its limited photocurrents do not primarily stem from slow oxygen evolution kinetics, but from surface charge recombination [39]. Their study suggests that there should be more investigation into the fundamental understanding of the surface reactions and the mechanisms of all the happenings that take place during a water splitting reaction in PEC cells. This study only presents results for two specific kind of materials when they are used together, but studies including different co-catalysts, such as Cobalt Oxide and Iridium Oxide prepared via various methods like ALD, metalorganic deposition etc. onto the surfaces of different types of photoanodes. In this study, the ALD method will be investigated further as part of the loading method chosen for loading co-catalysts onto the focus photoanode materials of this study, BiVO₄. Also, effects of different preparation methods and details of hydrothermal preparation for BiVO₄ photoanodes will be further mentioned.

CHAPTER 2

EXPERIMENTAL

2.1 Electrode Preparation:

2.1.1 Hydrothermal Method

Hydrothermal processes can be defined as heterogenous chemical reactions occurring in aqueous solutions under high pressures and mild temperatures to dissolve and recrystallize materials [40]. Hydrothermal synthesis is advantageous to produce fine powders with controlled particle size, high crystallinity, controlled morphology/microstructure and good reproducibility, along with being environmentally friendly compared to most methods for producing BiVO₄-based photoanodes [40]. The environmentally favorable aspect of hydrothermal method stems from its possibility to produce fine particles under mild temperature conditions, therefore limiting the energy consumed during production [40–42].

Hydrothermal synthesis of particles from any material is, though advantageous in some respects, is not without its limitations. The said limitations often arise due to the sensitivity of the produced particles to even the smallest change in the pH, temperature, reaction time, solvent use, solubility etc. properties of the materials used in the system [40]. Hence, countless studies have been conducted so far evaluating the effect of each of these aspects in the final product produced from various materials that are used. Most relevantly, BiVO₄ photoanodes have been investigated in-depth for the effect of hydrothermal reaction temperature [41,43], hydrothermal mixture pH [44–47], use of various surfactants [41,48–50] and effect of many other parameters on the morphology and structure of the end product. These studies mostly revealed that even though changing even one parameter in the hydrothermal system resulted in drastic changes in the morphology, thus photoelectrochemical and some physical properties of the materials, the exact path in which these changes are caused is not clearly determined [40]. To determine the exact pathway for the effect of changing a specific parameter, the exact formation mechanism for the BiVO₄ particles and the exact role each parameter plays in it should be determined initially. However, to this day, the exact formation mechanism for the crystal growth of materials inside a hydrothermal reaction system is not revealed, as

the hydrothermal kinetics and the formation of intermediate phases also remain mostly a mystery [40,51].

Hydrothermal synthesis of BiVO_4 is usually performed using nitrate salt of Bismuth along with usually ammonium salt of vanadium as the precursors, added with some templating agents such as ethylene glycol, CTAB, PVP, SDBS [49,52,53]. However, it is also possible to perform this synthesis without any soft templates like these organic solvents. In one study published in 2009, Zhou et. al. demonstrated that it is possible to obtain highly crystalline BiVO_4 with uniform morphology can be obtained with addition of a simple salt such as K_2SO_4 as the directing agent, instead of using complex organic solvents that might later cause a decrease in the activity if remains in the structure after synthesis [54]. However, this method that was used for obtaining powder product is not directly applicable to grow BiVO_4 films on substrates such as FTO coated glass. For this purpose, formation of seed layer on the surface and ordered growth of crystals on top of that seed layer is required. So far, these types of films are only produced via assisted hydrothermal synthesis using the templating agents mentioned above.

Much like its powder form counterpart, the exact formation mechanism behind the film growth of BiVO_4 or any other material obtained via hydrothermal method is not revealed yet. However, most studies refer to the crystal growth mechanism called Ostwald Ripening [47,55]. In one study by F. Li et. al., it was explained that according to Ostwald's step rule, the formation mechanism for the microparticles in the BiVO_4 -based photoanode is such that the initial nucleation occurs to form a seed layer, then nanoparticles are formed with further aggregation. Later, these smaller particles are in fact consumed to be used in the formation of larger aggregates. The shape, size and packing arrangement of the larger aggregates determine the final morphologies, such that if the outer aggregates are packed more densely, the formation of hollow structures are more likely. The packing arrangement in this study was related directly to the pH of the reaction mixture, indicating that at lower pH smaller particles are formed, leading to higher possibility for the formation of non-hollow morphologies [47]. However, it has been demonstrated that the formation of various shapes and morphologies is possible through varying the reaction temperature, templating agent and other parameters, as mentioned before. Therefore, it can be concluded that further studies following the formation mechanisms and the role of every parameter in each step should be investigated more in detail to

arrive at a certain conclusion for the effect of any parameter on the hydrothermal reaction of BiVO_4 formation.

One aspect remains true for the hydrothermal synthesis of BiVO_4 -based photoanodes that it is an environmentally favorable method due to low temperatures and availability to use non-toxic solvents, as well as easily applicable and cost-effective since it uses very low amounts of each material. This method is also favored in producing BiVO_4 photoanodes for water splitting and other photoelectrochemical applications due to its ability to directly produce monoclinic crystal structure without any post treatments, providing good control in obtaining pure phase films and powders [56]. Since the monoclinic scheelite structure is found to be the most active phase of BiVO_4 for PEC applications due to its suitable band gap properties, it can be said that hydrothermal synthesis of BiVO_4 -based photoanodes to study PEC water splitting reactions on is quite the beneficial choice of preparation method.

2.1.1.1 Experimental Procedure for Hydrothermal Synthesis of Pristine and Metal Doped BiVO_4 Films:

All chemicals used in the hydrothermal synthesis procedures were of analytical grade and used without further purification. All chemicals are obtained from Sigma-Aldrich. In a typical synthesis; $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.5 mmol) in 10 mL HNO_3 (1M) and 5 mL Ethylene Glycol (EG) is mixed with NH_4VO_3 (0.5 mmol) in 10 mL NaOH (0.5M) and 5 mL EG to be stirred for 30 minutes. The precursor solution was transferred to a Teflon-lined stainless-steel autoclave with 80 mL volume. FTO coated glass substrates were put inside the Teflon beaker with coated side facing upwards. The autoclave was sealed and heated at 180°C for 12h. After the autoclave was cooled to room temperature, the substrates that were then coated with a yellow thick layer are taken out and left to dry in air. After drying, the substrates were annealed at 500°C for 2h in air before being tested for PEC activity.

For modified samples preparation procedure was altered such that:

For investigating the effect of W-doping, H_2WO_4 was added to the reaction mixture with varying amounts; for 1.0at% doping 0.00158g, 1.5at% doping 0.00237g, 2.0at% doping 0.00316g and 2.5at% doping 0.00396g.

For varying hydrothermal reaction temperature, the autoclave was heated at 110°C, 130°C, 150°C and 180°C without changing any other parameter in the synthesis protocol, for both pristine and W-doped samples.

For varying hydrothermal reaction time, the reaction for pristine BiVO_4 was proceeded for 2h, 4h, 6h, 8h, 9h, 10h, 11h, 12h without changing any other parameter in the synthesis protocol. Similar change in the reaction times were also performed for 2.0at% W-doped samples with 2h, 4h and 6h reaction times, since these showed the most recognizable changes in the morphology for the pristine sample investigation.

For investigating the effect of templating agent (surfactant), the added surfactant was changed in the reaction mixture; Ethylene Glycol (EG) and Cetyltrimethylammonium bromide (CTAB) (0.018g) added together, only CTAB added (0.018g), EG and PVP (polyvinylpyrrolidone) (0.020g) added together and only PVP added (0.020g). No other parameter is changed in the protocol.

For investigating the powder samples, the same protocol was followed without putting FTO substrate inside the autoclave. The powder is collected by separating it from the solution with centrifugation at 2000 rpm for 20 minutes and washing twice with dI-water at 2000 rpm for 20 minutes each.

For 2.0at% Molybdenum and 2.0at% Tungsten doping in preparation of powder samples, 0.00316g of tungstic acid (H_2WO_4) and 0.00308g of sodium molybdate dihydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) are added to the reaction solutions without any other change to the initial protocol.

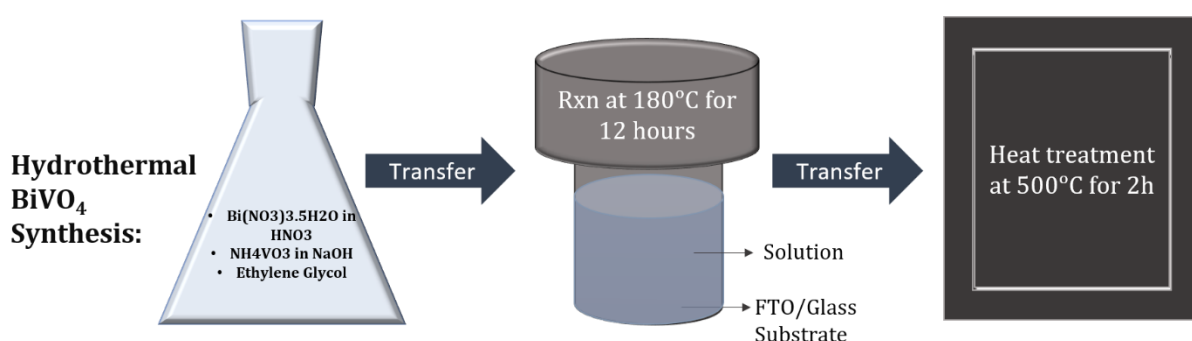


Figure 2.1.1.1.1 Schematic representation of the hydrothermal synthesis procedure used and modified in this study.

2.1.2 ALD Method

Atomic layer deposition (ALD) is an effective thin-film deposition method which is similar to chemical vapor deposition (CVD) technique, only it is composed of sequential, self-limiting surface reactions caused by exposure of the substrate to each gaseous precursor separately [57,58]. More specifically, ALD is based on reactions between two or more gaseous precursors, and the reactants are kept separated via evacuation and/or purge steps so as to avoid gas phase reactions that are also seen in the similar CVD method, and each react with surface functional groups [57,58]. This process is self-limiting and the unreacted precursors and by-products are removed in the purge steps mentioned above; this completes what is called an “ALD cycle” [57]. By repeating this process, continuous films and uniformly dispersed metal or metal-oxide nanoparticles can be obtained, depending on the surface properties of the substrates and precursors such as surface functional groups and wetting properties of the deposited materials [57,58].

ALD method has many advantages over various other methods that are used to deposit materials as thin films or as protective layers, interfacial layers, co-catalysts on thin films such as sol-gel methods, electrodeposition etc. No other method for thin film production can compete with the conformality ALD provides on high aspect structures [59]. Another outstanding advantage of ALD is the precise thickness control at monolayer level, excellent step coverage along with the conformal deposition caused by self-limiting character of the surface reactions [59]. Since the precursors will absorb and desorb from the surface when the reaction is completed, the deposition will be very conformal and the fact that the reactions are driven to completion in each cycle will lead to a quite continuous film growth [57,59]. As a result of these advantages, as well as good reproducibility, ALD has been utilized more and more as a way of producing efficient and precise synthesis of catalysts with improved activity, stability and selectivity [57]. Since it is possible to deposit precursors on variety of morphologies from pores to nanorods, ALD method has been specifically tuned to deposit catalysts onto different substrates to be used in a multitude of research areas [57].

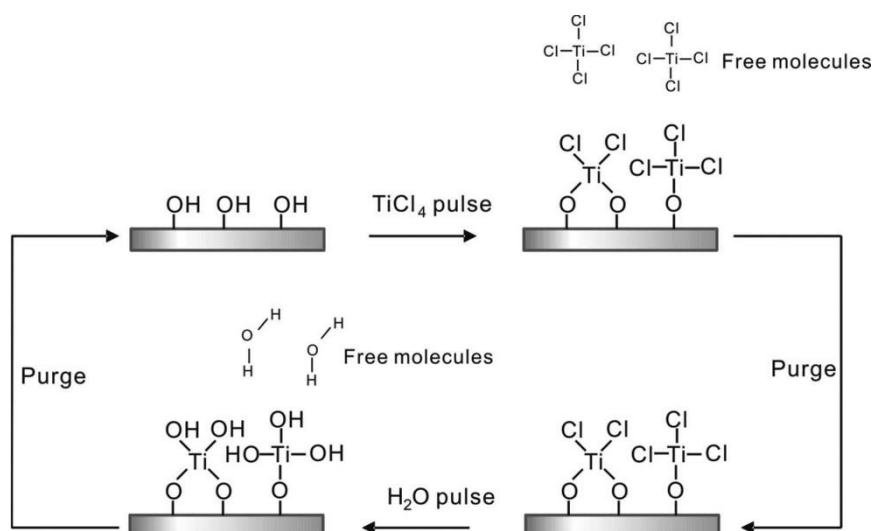


Figure 2.1.2.1: Basic scheme of an ALD cycle using TiCl_4 and H_2O as precursors to deposit TiO_2 onto a surface. Reproduced from [57].

In PEC water splitting reactions, ALD method is commonly used to produce very efficient and improved photocatalysts with the help of layers deposited by this method to function as top (protective) layers, interfacial layers, or co-catalysts on the surface of the substrates. Most commonly studied materials that are used in ALD are TiO_2 , Cobalt oxide and Iridium Oxide deposition, owing to their chemical stabilities in different pH conditions, band gap energies and band gap properties [60–65].

In photoanodes, such as BiVO_4 that is being studied in this work, the oxidation of the electrode material might sometimes compete with the water oxidation half reaction, thus causing photo corrosion or electrode surface passivation [65]. In this case, a suitable protective layer that can be coated on top of the electrode surface is useful to obtain longer lasting photoanodes [65,66]. For this purpose, TiO_2 is a very suitable material due to its appropriate band gap, chemical stability and the fact that in its amorphous phase, the electronic defects in its structure might increase the conductivity, leading to a decrease in the tunneling effects that decrease the conductivity and photocurrents in the electrodes [63,65,66]. The increase in conductivity obtained by ALD deposition of TiO_2 as a top layer can be tuned by n-type doping, such as manganese doping or post-heat treatments, as from a chemical perspective, the conductivity it provides to the photoelectrode is usually attributed to the reduction of Ti^{4+} cations to the Ti^{3+} state [63,65]. This way, increased stabilities in acidic medium, as well as in more basic medium than the regular pH range the photoanodes are confined in for water oxidation

reactions (around pH 7-9) are reported in various studies via transient photocurrent and other PEC measurement methods [63,65].

Deposition of photoelectrochemically active materials onto photoanodes are not limited to using them as protective or passivating top coats. Noble metal-based oxygen evolution catalysts like IrO_2 and RuO_2 generate some of the highest water oxidation half reaction performances, however they are inherently expensive due to their low-abundance [67]. Even with these shortcomings, Iridium oxide deposition as co-catalysts has been investigated notably, and various ALD processes are reported to create different thicknesses, crystal structures and orders as well as different chemical forms such as ending a cycle with ozone, water or hydrogen [58,61,62,68]. However, there has still been a significant amount of work dedicated to developing low-cost, first-row transition metal oxide oxygen evolution catalysts in recent years [67]. Among many metal oxide OECs, cobalt oxide emerged as an efficient water oxidation co-catalyst and it can operate under neutral conditions, though there are a few setbacks to this situation [67]. According to the literature, the most active form of this electrocatalyst is equivalent to a disordered form of heterogenite, $\text{CoO}(\text{OH})$ [60]. Though this co-catalyst was also tested under neutral pH conditions using buffers, along with basic ones using 1M KOH solutions, there has been evidence suggesting the formation of $\text{Co}(\text{IV})$ species and decreasing $\text{Co}(\text{II})$ species under working water oxidation conditions [69]. There are reports of cobalt, and other active abundant OECs such as Ni and Fe and their oxides, being highly stable against chemical corrosion under basic pH conditions [70]. On the other hand, there is also studies suggesting that cobalt catalyst that is deposited on the surface via ALD method might dissociate and stop showing any activity under bicarbonate-buffered KOH solution conditions (pH~9.5) [71]. In spite of the pH sensitivity problem that effects the work of a co-catalyst that is deposited onto a photoanode surface, some significant improvements in the photocatalytic activities in terms of measured photocurrents and TAS (transient absorption spectroscopy) measurements that allow monitoring of the photo-generated holes are observed and reported using cobalt-based materials on photoanodes by utilizing ALD method [72]. James Durrant et. al. previously reported that Co-Pi deposition onto BiVO_4 does indeed improve the water oxidation performance of BiVO_4 photoanodes, however it does so not using the catalytic function of CoPi on the anode surface, rather the cathodic shift in the onset potential is caused because the recombination surface-accumulated holes with the bulk electrons (back electron/hole recombination) is

suppressed [72]. By utilizing the outstanding structure control property of ALD method, Sharp et. al. loaded a biphasic cobalt-based layer on p*-n-Si substrate by depositing Co₃O₄ nanocrystals conformally and then depositing a disorder surface layer of Co(OH)₂ which led them to observe the longest photocatalytic stability performance of 72h [70].

2.1.2.1 Experimental Procedure for Iridium Oxide Coating on BiVO₄ Photoanode Films:

In ALD coating of IrO₂ onto BiVO₄ photoanodes, iridium (III) acetylacetonate (Ir[O₂C₅H₇]₃) as the precursor for the reactant while deionized water and ozone were used as the two different oxidants. The precursor temperature was set to 185°C. Nitrogen gas (N₂) was used as carrier gas. Film thickness (or cycle number), precursor temperature, pulse times and purging time in between the pulses, were optimized by trying out and analyzing different values via characterization methods. The recipes that were used in ALD method for iridium coating onto the photoanodes are as follows for ozone and water terminated samples:

Instruction	Value	Unit	
Flow	20	sccm	
Stop Valve		0	
Flow	20	sccm	
Pulse	0.3	sec	Water
Wait	2	sec	
Stop Valve		1	
Flow	20	sccm	
Wait	3	sec	
Stop Valve		0	
Flow	20	sccm	
Pulse	0.5	sec	Iridium Source
Wait	2	sec	
Stop Valve		1	
Wait	60	sec	
Flow	20	sccm	
goto	50	cycles	

Instruction	Value	Unit	
Flow	20	sccm	
Stop Valve		0	
Flow	20	sccm	
Pulse	0.01	sec	Ozone
Wait	2	sec	
Stop Valve		1	
Flow	20	sccm	
Wait	3	sec	
Stop Valve		0	
Flow	20	sccm	
Pulse	0.5	sec	Iridium Source
Wait	2	sec	
Stop Valve		1	
Wait	60	sec	
Flow	20	sccm	
goto	50	cycles	

CHAPTER 3

CHARACTERIZATION METHODS

3.1 Electrochemical Characterizations of BiVO₄-based Photoanodes:

Photocurrent measurements of the samples in this study were carried out using a three-electrode setup made up of a platinum counter electrode, Ag/AgCl (1M KCl) reference electrode and the photoanode that is prepared as the working electrode via a VSP-300 BioLogic potentiostat. An LCS-100 solar simulator was used as the light source for under illumination measurements, with 1.0 SUN AM (100 mW/cm²) 1.5G output that is obtained from a 100 W Xenon Arc Lamp.

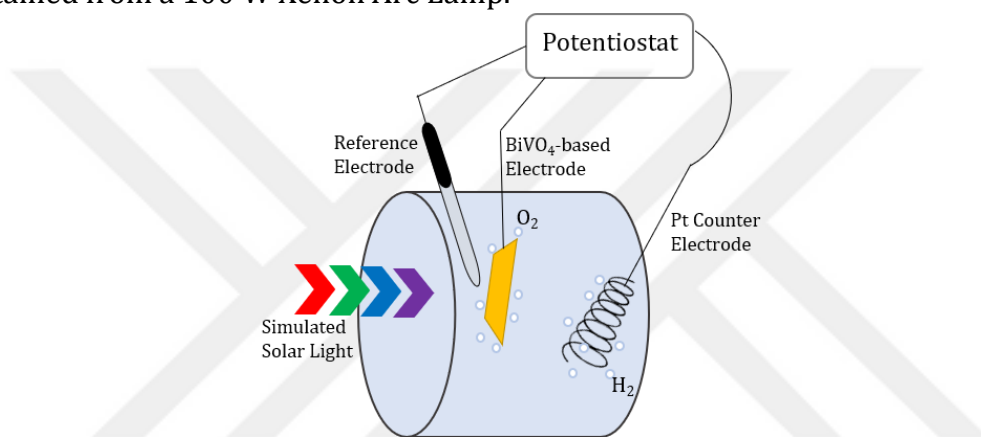


Figure 2.2.1: Basic scheme for the three-electrode cell system used for electrochemical measurements of the BiVO₄-based photoanodes.

The measured potentials are converted to *versus* reversible hydrogen electrode using the Nernst equation:

$$V_{RHE}(V) = V_{Ag/AgCl}(V) + 0.059 \times pH + V_{Ag/AgCl}^0$$

Where V_{RHE} is the applied potential versus RHE; $V_{Ag/AgCl}(V)$ is the applied potential versus Ag/AgCl/sat'd KCl reference electrode during measurements; $V_{Ag/AgCl}^0$ is the standard potential of the reference electrode.

CVs (cyclic voltammetry) and LSVs (linear sweep voltammetry) were recorded at 80mVs⁻¹ scan rate in the potential range -0.6V to 1.0V vs. Ag/AgCl (corresponding to 0.0V to 1.6V vs. RHE) in pH=7 electrolyte made up of 1M potassium phosphate buffer with 0.5M sodium sulfite as hole scavenger, and without scavenger.

Transient photocurrent density measurements are performed in pH=7 electrolyte made up of 1M potassium phosphate buffer with 0.5M sodium sulfite as hole scavenger,

using chronoamperometry (CA) and LSV methods of potentiostat. In CA, 5 minutes of measurement is taken at 0.0V vs Ag/AgCl and at a certain higher bias that corresponds to the applied potential-driven photocurrent in the measurements. In LSV mode, again a sweep in the potential range of -0.6V to 1.0V vs. Ag/AgCl (corresponding to 0.0V to 1.6V vs. RHE) was performed. In both cases, a timed home-made chopper was used to cut off the light source in 10 seconds intervals.

Electrochemical Impedance Spectroscopy (EIS) measurements were performed in pH=7 1M potassium phosphate buffer with 0.5 M sodium sulfite as hole scavenger, as well as buffer without any hole scavenger. Measurements were performed using the open circuit potential (OCV) technique of the VSP-300 BioLogic potentiostat. Measurements are taken under illumination via the solar simulator.

3.2 Physical Characterizations of BiVO₄-based Photoanodes:

3.2.1 X-Ray Diffraction Patterns (XRD):

X-ray diffraction patterns of samples were collected using Bruker D8 Advance X-Ray Diffractometer using grazing incidence angle at 1 theta degree with 1 nm slit width and 0.02 increment over 2 hours. Powder sample analyses were performed using Bruker D2 Phaser X-Ray Diffractometer.

3.2.2 Raman Spectroscopy:

Raman spectroscopy information of the thin film samples were collected via Renishaw Invia Raman Microscope using 532 nm and 633 nm excitation laser source.

3.2.3 UV-Visible Spectroscopy

UV-Vis spectrums for the films are obtained via Shimadzu UV-3600 UV-VIS-NIR Spectrophotometer in absorption and diffuse reflection and specular modes. Kubelka-Munk transformation provided by the device software was used to obtain absorption spectra from reflectance measurements. Kubelka-Munk function is summarized as follows:

$$f(R_{\infty}) = \frac{(1-R_{\infty})^2}{2R_{\infty}} = \frac{K}{S}$$

Where R_{∞} is absolute reflectance, K represents absorption coefficient and S represents scattering coefficient [73].

3.2.4 Field Emission-Scanning Electron Microscope

SEM images are obtained via Zeiss Ultra Plus Field Emission Scanning Microscope.



CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Effect of W-Doping in hydrothermally-synthesized BiVO₄ photoanodes:

Tungsten metal doped BiVO₄-based photoanodes were prepared by hydrothermal synthesis method for which the details are described in experimental section previously. All samples are annealed at 500°C for 2h before being used in electrochemical activity tests as well as in most physical characterizations. XRD patterns for the pristine and 2.5at% and 1.0at% W-doped BiVO₄ samples are given in Figure 4.1.1. Standard XRD patterns for BiVO₄ (JCPDS 83-1699) and WO₃ (JCPDS 88-545), as well as FTO (JCPDS 30-1375) were used to assign the peaks to the corresponding structures. XRD patterns of all photoanodes are consistent with the monoclinic scheelite crystal structure of BiVO₄ found in crystallography database. The peaks seen at around 18.5° and 35° for all samples confirm the presence of monoclinic phase (s-m) rather than tetragonal (s-t), which is also in accordance with the expectations from BiVO₄ samples heat-treated at 500°C [74–76].

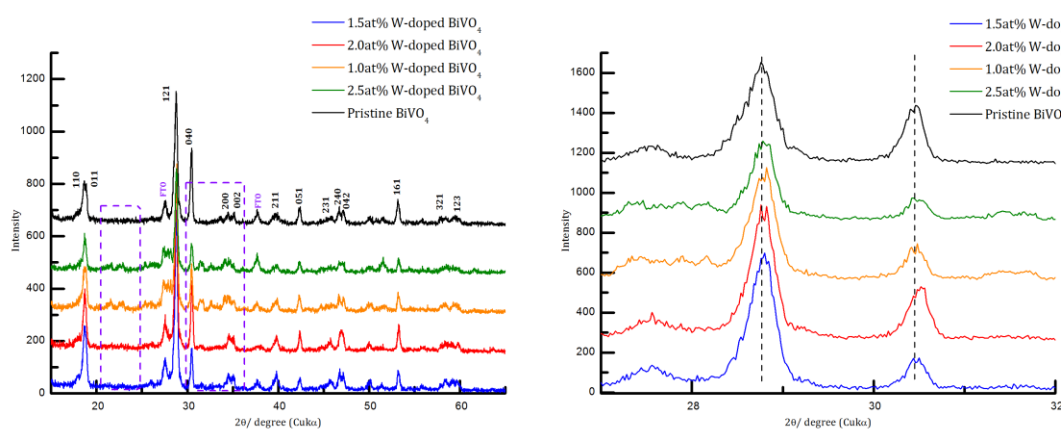


Figure 4.1.1: Grazing Incidence XRD patterns for the pristine and W-doped BiVO₄ photoanodes prepared by hydrothermal synthesis method and annealed at 500°C for 2h. The green dotted lines are highlighting the significantly changed regions for the doped samples compared to the pristine BiVO₄.

The splitting seen in the peak at 35° indicates there is no tetragonal phase with significantly high crystallinity is present in the sample structure [74]. It has been previously reported that the exposed facets of BiVO₄ can significantly influence the photocatalytic activity, specifically it has been known for a while that samples with more

exposed (121) facets often show higher photocatalytic activity [77]. Yet, recent studies for higher photocatalytic activity observed in samples with higher crystallinity and more exposed (040) facets have also been reported [44,78]. There is an increase in the relative intensity of the peak at 30.5° which represents the (040) facet of the monoclinic BiVO_4 structure found in the samples. This peak indicates that addition of W into the structure slightly increases the preferential growth towards this facet, although it also increased the growth in (121) orientation. Also, the FWHM (full-width at half-maximum) of the peaks at 30.5° decreases in doped samples compared to pristine BiVO_4 , indicating possibly lower crystallinity for these samples [79]. However, no change in FWHM and peak position/ degree are observed for (121) peak at 28.7° among the samples while the peak at 30.5° shows a shift towards higher degrees as the doping level increases (Fig. 4.1.1b). This shift might be caused by the incorporation of W^{+6} dopant into BiVO_4 by substituting V^{5+} , leading to a distortion in the crystal structure which would also be in accordance with the interpretation that the crystallinity of the samples rather increase as the doping level increases since the relative intensities of the peaks are also observed to increase [45,74,79]. This conclusion also coincides with the FE-SEM images obtained from these samples which indicate that more well-defined and homogenously-distributed morphology are observed in the doped samples compared to the pristine BiVO_4 .

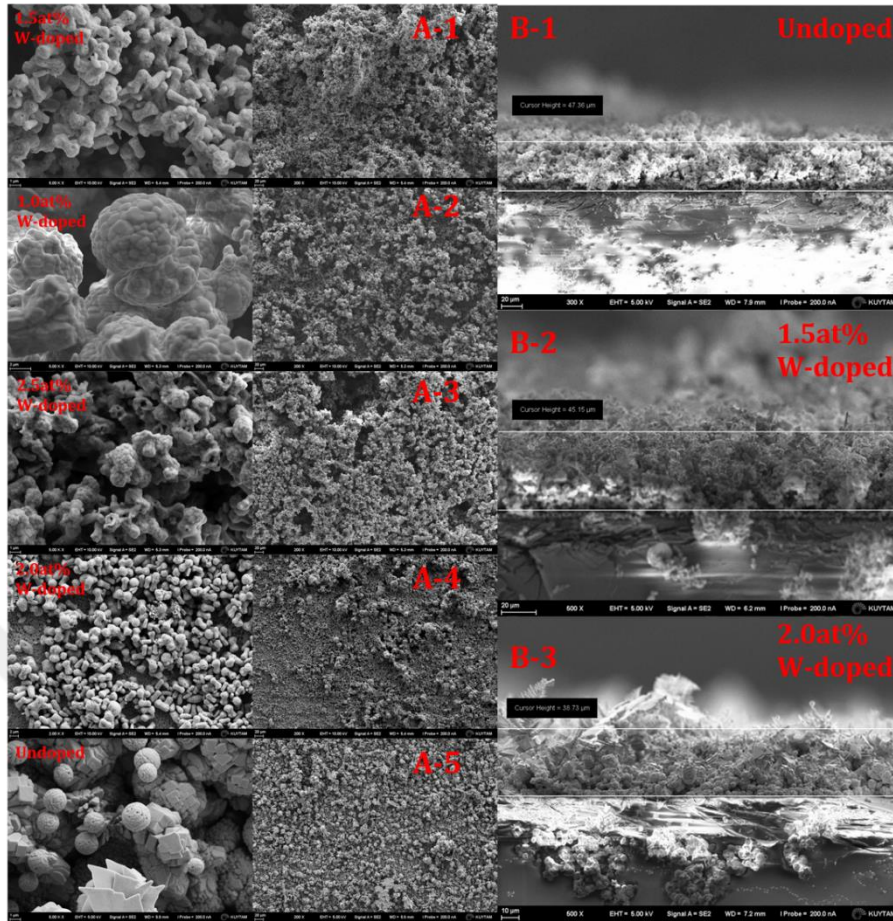


Figure 4.1.2: FE-SEM images of W-doped BiVO_4 film surfaces compared with pristine BiVO_4 samples (A). A decrease in the number of large clusters composed of 3D-rod like arrays is seen as doping level increases. Cross-section and thicknesses of 1.5at% and 2.0at% doped samples are also compared (B).

Figure 4.1.2 shows that the optimum separation between these 3D-rod like structures and most homogenous distribution of them on the surface is observed for 2.0at% doped sample which is in accordance with the PEC data (J-V curves), as well as UV-absorption, Raman and XRD data for the physical characterization, as this sample shows high crystallinity, good doping and most significant change in the absorption spectrum cut-off at around 520 nm (Figure 4.1.3). It is also observed that low doping level like 1.0at% does not induce significant change in morphology and particle size distribution, whereas higher doping levels show visible decrease in the formation of large clusters with various sizes and shapes that are seen in both pristine and W-doped samples with low doping levels. Moreover, the higher doping level samples show better connectivity between the 3D thick rod-like geometries that are observed [80]. These geometries are thought to be responsible for the increase in PEC activities along with other factors as they seem to be

increasing homogeneity, interconnectivity, and order in the sample morphology. This idea is also supported by the observation that after a CV measurement, the large cluster-type geometries are seen to have disappeared or significantly decreased over the sample surface for the 2.0at% W-doped sample, indicating that the reduced and most useful/efficient sample morphology is the 3D rod-like shapes that are distributed over the samples and the formation of these geometries increase with increased doping levels.

According to the conclusions that are drawn so far, it is expected that due to presence of W-dopant, the electron transport properties and charge carrier densities will increase, thus will suppress electron-hole recombination, and increase photocurrents for water oxidation. However, there are a few more observations that present for the XRD patterns that can be further related to other characterization results. The most important one is that even though crystallinities seem to have improved and the crystal structure seems to have changed conforming that W is indeed doped into BiVO_4 in the regions depicted with green dotted lines, some peaks are seen to appear and/or get stronger as the doping level increases. When compared with the literature data for WO_3 XRD patterns, it appears that tungsten oxide gives peaks in 20° - 25° degree region as well as at around 35° similar to the peaks observed in our XRD patterns [81–83]. These peaks mostly resemble the patterns that are reported for monoclinic structure of WO_3 so, it is possible that in addition to acting as a dopant, W addition might have created $\text{WO}_3/\text{BiVO}_4$ junction on the surfaces of 3D-like structures that are observed in FE-SEM images; presented in Figure 4.1.2 [83]. This might also help explain why front-side illumination is not improved as much as the back-side illumination for the J-V curves of W-doped BiVO_4 photoanodes. Possibly, n-doping indeed created the intended effect which increased charge carrier density and decreased electron-hole recombination during the charge transfer to the surface from the FTO side. This is also observable from the change in absorbance band edge in the UV-Visible Spectra as dopant is introduced into the structure (Figure 4.1.3). Even though this leads to an increase in the photocurrent densities that are obtained under front and back illumination slightly, it might be that front-side illumination is disrupted by the $\text{WO}_3/\text{BiVO}_4$ junctions that are probably in-homogenously distributed amongst the 3D hierarchical structures of the samples. Also, presence of WO_3 in the structure might even be preventing charge carrier transfer through the sample and decreasing electron-hole separation by creating recombination centers inside the bulk [80]. Therefore, it can be concluded that even back-side illumination is below its

actual maximum photocurrent density that can be reached by only W-doping effect in the structure. Even though, Ao et. al. reported in an 2018 article, a photocurrent as high as 5mA/cm² at 1.23V vs. RHE from the hierarchical structures they obtained purely as WO₃/BiVO₄ heterojunctions, there are no reports of photocurrent densities that high for only the effect of W-doping into BiVO₄ structure [84]. So, it might be that these two effects together do not improve the PEC efficiency of a BiVO₄ photoanode very well. However, we see that it is still possible to utilize the benefits of n-doping in these samples from the J-V curves (Figure 4.1.4) and transient photocurrent (TPC) curves (Figure 4.1.5).

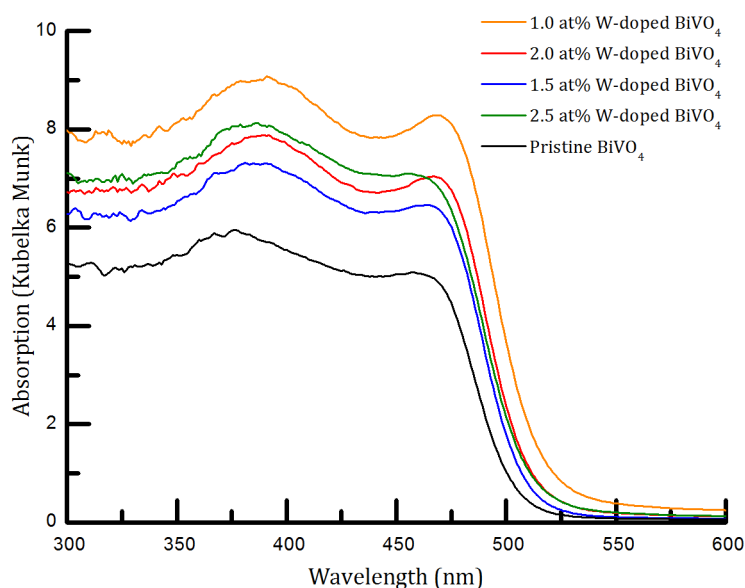


Figure 4.1.3: UV-Visible absorption spectra of pristine and W-doped BiVO₄ samples; obtained by DRS measurement mode and transformed into UV-Visible data via Kubelka-Munk transformation.

Up to this point, our findings indicate that an optimum doping level exists for these samples and 2.0at% W-doping provides the best results for optical band gap/ UV-Vis light absorption. Moreover, improvement in the photocurrent densities is supported in Raman spectra along with these characterization results as well (Figure 4.1.4). In Figure 4.1.3, UV-Vis absorption spectra indicate that the change in the light absorption of the material is not linearly following the increase in n-doping level, and 2at% W-doped sample shows absorption edge at a higher wavelength (525 nm) compared to the pristine sample (500 nm), followed by three other doping levels that are found to have absorption edges at the same wavelength (520 nm). This indicates that there is a change in the band gap of the BiVO₄, thus W dopant is indeed incorporated into the structure. However, the non-linear

change also indicates that the doping is not homogenous throughout the structure or the theory that WO_3 is present in the structure and somehow effects light absorption is disrupting the otherwise would-be-linear trend in UV-Vis absorption spectra obtained from these samples. Along with these reasons, there has also been many reports indicating that after an optimum doping level, the added materials start to decrease the light absorption properties, as well as PEC efficiencies of BiVO_4 -based photoanodes [45,79,85]. The exact reason behind this phenomenon is not yet known, however the reported effect is also observed in this study as the aforementioned non-linear trend in UV-Vis absorption spectra, as well as Raman spectra of these samples.

Raman spectra of four different doping levels of W into BiVO_4 are compared with the pristine sample in Figure 4.1.4. The intense characteristic peak at 824.2 cm^{-1} are attributed to $\nu_s(\text{V-O})$ symmetric stretching modes with shoulders at around 714.7 cm^{-1} and 645.03 cm^{-1} representing anti-symmetric stretching modes, $\nu_{as}(\text{V-O})$ [85]. The symmetric A_g bending mode of vanadate ion $\delta_s(\text{VO}_4^{3-})$ and anti-symmetric B_g bending mode of vanadate ion $\delta_{as}(\text{VO}_4^{3-})$ are near 329.3 cm^{-1} and 367.07 cm^{-1} , respectively [85,86]. Peaks in all the spectra presented in Figure 4.1.4 are in accordance with the monoclinic BiVO_4 structure data that has previously been reported in the literature [79,85,86]. It is seen that a slight blue shift in the characteristic peak at 824.2 cm^{-1} which is attributed to $\nu_s(\text{V-O})$ and in the bending mode peaks (Figure 4.1.5) occurs in the Raman spectra for the four different W-doped samples compared to the pristine BiVO_4 [85]. This indicates that there is indeed an incorporation of W^{+6} ions into the bismuth vanadate crystal lattice, therefore extending the V-O bond length since W ions substitute V ions in the crystal sites, and the monoclinic structure of BiVO_4 is disrupted even more as the doping increases, since the shift is stronger in 2.0at% W-doped sample than 1.0at% W-doped sample [56]. However, the peak positions are found to be at around the same point for both 1.5at% and 2.0at% W-doped samples, while 1.0% W-doped sample shows a smaller blue shift as expected from its lower doping level, 2.5at% W-doped sample however, shows an irregular change in its structure while the peak position is the same as the 1.0at% W-doped sample. This finding is similar to what was observed in UV-Visible absorption spectra. This irregularity might be again explained by the irregular doping of the sample throughout the surface and/or bulk, as well as the unexplained phenomena where the dopant starts to affect the physical properties of the sample in a negative way after a certain level, thus decreasing the PEC water splitting performance as well as the light

absorption properties as observed in the results of these characterizations. The fact that no peaks related to WO_3 structure are found in the Raman spectra eradicates the previously stated suspicion that some $\text{WO}_3/\text{BiVO}_4$ micro-heterojunctions are formed in the 3D/ hierarchical structure of the photoanode leading to a disruption in the charge carrier transfer through the sample as well as in the light absorption through the surface during front illumination [83]. The FWHM values presented in Table 4.1.1 for the peak at 824.2 cm^{-1} shows that doping decreases this value compared to pristine sample. Unlike all the other results, the decrease in this value is seen to be reversely proportional and regular compared to the doping level; smallest value belongs to the 2.5at% W-doped sample, followed by 2.0at%, 1.5at% and 1.0% doped samples and the largest value is observed for the pristine sample. This indicates that 2.5at% W-doped BiVO_4 sample shows the highest uniformity in structural distribution among all the samples, followed by 2.0at% W-doped, and undoped sample indeed shows the lowest uniformity. This information also coincides with the morphology investigation done via FE-SEM (Figure 4.1.2), where the most uniform distribution of morphologies was observed for 2.5at%, 2.0at% and 1.5at% W-doped samples, while 1.0at% doped and pristine samples showed more of the irregularly distributed large cluster type morphologies along the surface.

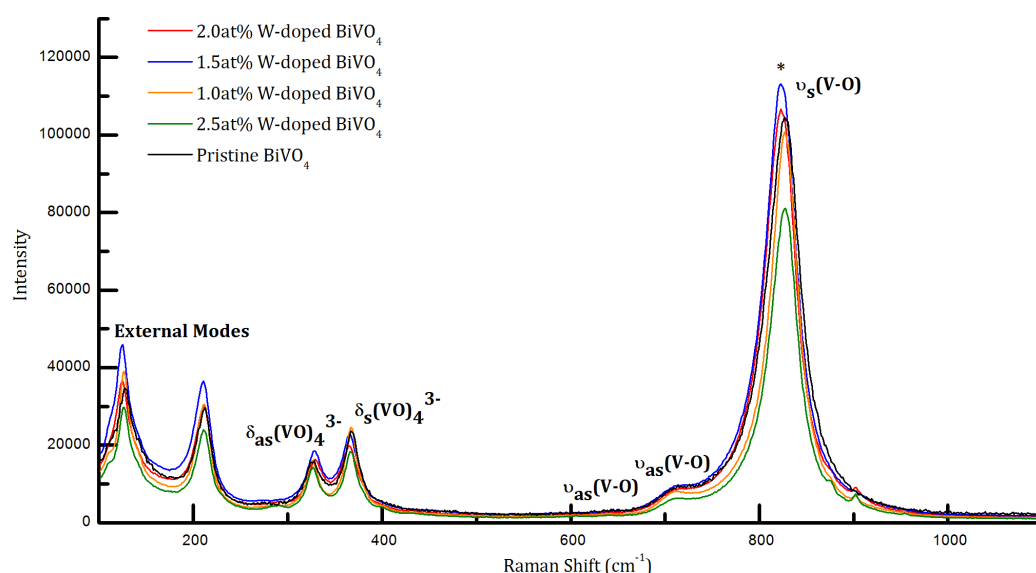


Figure 4.1.4: Raman spectra of samples prepared with different levels of doping via hydrothermal method: 2.0at% (red); 1.5at% (blue); 1.0at% (orange); 2.5at% (green); pristine (black).

Sample	FWHM (at 827 cm ⁻¹)
Pristine BiVO ₄	29.80
2.0at% W-doped BiVO ₄	27.97
1.5at% W-doped BiVO ₄	28.02
2.5at% W-doped BiVO ₄	26.87
1.0at% W-doped BiVO ₄	28.70

Table 4.1.1: Full-Width Half-Maxima of the characteristic peak at 824.2 cm⁻¹ wavelength for the four doped and pristine BiVO₄-based photoanode samples.

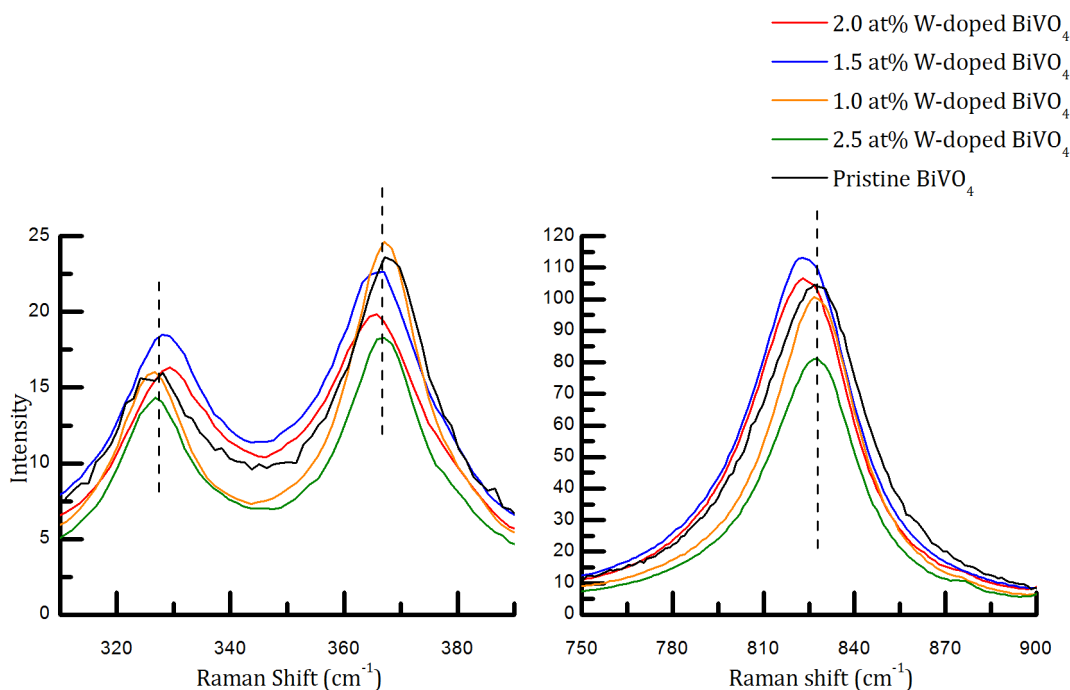


Figure 4.1.5: Zoomed in representation of the peaks at 824.2 cm⁻¹ (right) and at 367.1 cm⁻¹ and 327.3 cm⁻¹.

In Figure 4.1.6, photoelectrochemical activities of the doped and undoped BiVO₄-based photoanode samples are presented in terms of current density-potential (J-V) curves obtained via CV measurements under front and back illumination as well as in dark. Significantly higher photocurrents were observed for the back illumination of all the samples with 2.0at% W-doped sample showing up to 14.8% higher photocurrent densities under backside illumination compared to front-side illumination. The highest activity behavior was seen for 2at% W-doped BiVO₄ photoanode, followed by 1.5at%W-doped sample with the photocurrent density values of 0.74 mA/cm² vs RHE and 0.66 mA/cm² at 1.23 vs RHE, respectively, compared to the pristine sample that shows almost an insignificant activity with photocurrent density of 0.026 mA/cm² at 1.23V vs. RHE potential. These two samples are followed by 2.5at% and 1.0at% W-doped samples with

0.45 mA/cm² and 0.21 mA/cm² at 1.23V vs RHE, respectively. This trend in the actives match the change absorption band edges seen in UV-Visible absorption spectra as well as the shifts seen in Raman spectra that are previously evaluated. The more visible change observed in backside illumination is due to the poor electron transport inside the BiVO₄ photoanode that limits the frontside illumination activity, but decreases its effect under backside illumination since electron densities increase because of the light absorption of FTO substrate along with the photoanode semiconductor material and the electron transfer pathway is shorter compared to the frontside illumination due to the thickness of the film (~17 -40 μm) (Figure 4.1.2 (b)), thus improving the transfer of negative charge carriers [45,87]. This also indicates that electron transfer is more of a limiting factor in the PEC water splitting activity of BiVO₄-based photoanodes compared to the hole transfer pathway [45]. Introduction of an n-type dopant such as tungsten (W), increases the free electron concentration and increases the photogenerated charge carrier mobility through the photoanode to be used in PEC water splitting reaction, and such an effect is observed as the increased photocurrent densities in CV measurements (Figure 4.1.6) with almost 28 times higher photocurrent density in 2.0at% doped sample at 1.23V vs RHE compared to pristine samples as well as in transient photocurrent (TPC) measurements over a fixed time (Figure 4.1.7) [14,45,80,87].

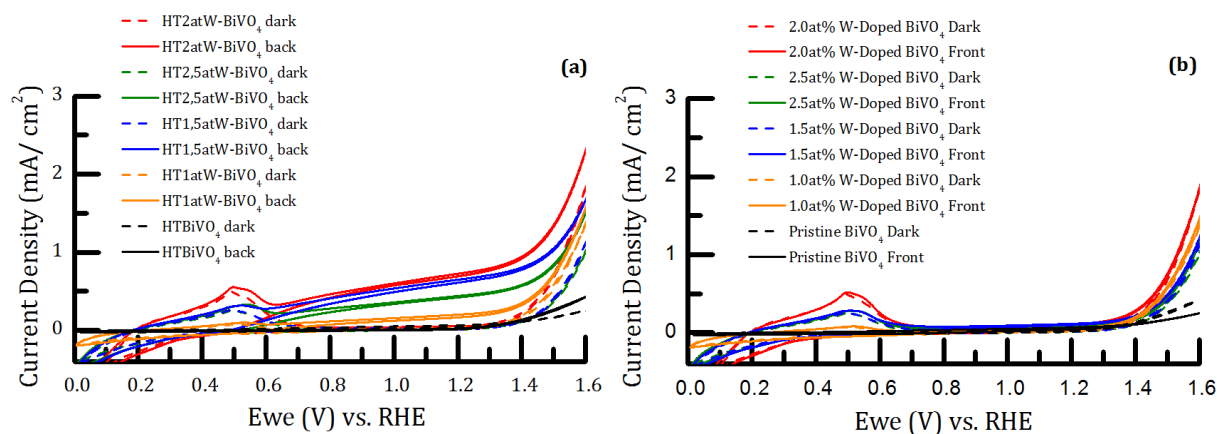


Figure 4.1.6: Cyclic Voltammetry (CV) measurements under dark, front (b) and back (a) illumination for the pristine and W-doped (2at%, 2.5at%, 1.5at% and 1at%) BiVO₄ photoanodes prepared by hydrothermal method and annealed at 500°C for 2h. Electrolyte used for measurements is 1M KPi buffer (pH=7.0) with 0.5M Na₂SO₃ as hole scavenger.

In Figure 4.1.7, it is seen that at 1.23V vs RHE, 2.0at% doped sample has an increase of almost 6 times in back illumination photocurrent densities compared to pristine sample, while at 0.6V vs RHE the increase is also significant with a magnitude of around 5 times of the pristine sample's photocurrent density. Even though W-doping increased the photocurrent densities obtained from PEC measurements due to increased charge carrier densities and mobility, the increase in the free electrons in the doped samples due to the presence of W^{6+} instead of V^{5+} in the crystal lattice of $BiVO_4$ might cause higher possibilities of photogenerated hole recombination, both on the surface and in the bulk depending on the doping levels [45]. Therefore, as the doping level is above an optimum level, such as 2.0at% doping level found to be the best in terms of activities and physical characterizations in this study, dopant might create a counter effect by decreasing the PEC activities of the $BiVO_4$ -based photoanode. This effect is observed by the decrease in photocurrent densities obtained for 2.5at% W-doped $BiVO_4$ samples in J-V curves and transient photocurrent measurements compared to the 2.0at% W-doped samples. In the transient photocurrents, the overall stability of the doped samples is seen to be quite close to each other with around %4 maximum change throughout 4 minutes of measurement for all samples (Figure 4.1.7 (a-d)). This indicates that doping of the $BiVO_4$ -based photoanodes delivers stability under front and backside illumination for PEC activities. It is also seen that the spikes that lowers from higher photocurrent values into a steady-state current after turning on light are more pronounced in samples with low-doping levels compared to higher levels like 2.0at% and 2.5at% doped samples for both applied bias values (Figure 4.1.7 (a-d)). In both low and high applied anodic potentials, none of the doped samples showed any visible/significant negative spikes, however in especially high applied potentials, positive spikes are visible for samples with low doping levels. This might be attributed to the understanding that for $BiVO_4$ -based materials, surface, and bulk hole recombination/ photogenerated charge carrier recombination is a major limiting factor in its PEC water splitting activity, however with the influence of n-doping the background electron concentration, i.e. donor concentration is increased, decreasing both bulk and surface recombination rates up to a point [14,45,87–89]. As the doping level increases, the spikes observed in the TPC plots decrease since surface accumulated holes are presumably utilized by the electrolyte more efficiently as their recombination with the bulk electrons of the photoanode is decreased [14,45,87–89]. Another possible mechanism in which doping helps increase the surface hole utilization efficiency by the

electrolyte might be that it removes the surface trapping states, thus lowering the number of surface accumulated holes(69–71). These assumptions are supported by the observation that the visible spikes in TPC plots at both moderate and high potential bias with back illumination become less pronounced as the doping level increases (Figure 4.1.7 (b,d)). However, these spikes are almost invisible for front illumination at both biases for all samples, confirming that transfer of photogenerated charger carriers, especially electrons, are still limited in the BiVO₄ photoanodes by the material property, as well as the thickness of the films even after doping. However, this is not the entire uptake from the photoelectrochemical test results presented here. A possible counter effect of high level doping was aforementioned regarding the observed decrease in the photocurrent densities in 2.5at% doped sample compared to 2.0at% and even 1.5at% doped sample. It was suggested that this decrease might be caused by the high number of free electrons in the samples brought by the W⁶⁺ addition to the lattice creating an increased probability for being recombination centers for the surface accumulated holes in the BiVO₄ photoanodes, therefore decreasing the measured photocurrent over a range of applied bias [14,45,87–89]. This suggestion was previously reported as a result of various studies and is seen to be supported by the J-V curves in Figure 4.1.6, however perhaps not entirely supported by the TPC plots in Figure 4.1.7. If the main reason for the photocurrent drop in 2.5at% W-doped sample was the increase in hole recombination on the surface and perhaps bulk of the sample with high level of W doping, then sharper spikes for the TPC measurements would be expected from this sample when it is singularly evaluated [14,45,87–89]. However, this sample shows very slightly visible spikes at both high and low biases both when considered singularly and compared with lower doping level samples. In fact, the surface accumulated hole behavior obtained from these spikes are seen to show a quite linear trend with respect to the doping level unlike the ones seen in all the other characterizations; the surface hole recombination is seen to be decreased as the spikes are becoming less pronounced with increasing doping level. Therefore, it might be suggested that the improvement that is obtained by n-doping in BiVO₄ photoanodes are indeed limited by an optimum doping level that should be determined for the study at hand, however the exact reason behind this limitation cannot be solely based on the creation of new recombination centers for the photogenerated

holes on the photoanode, rather it should be investigated further though that is beyond the extent of this study at the moment.

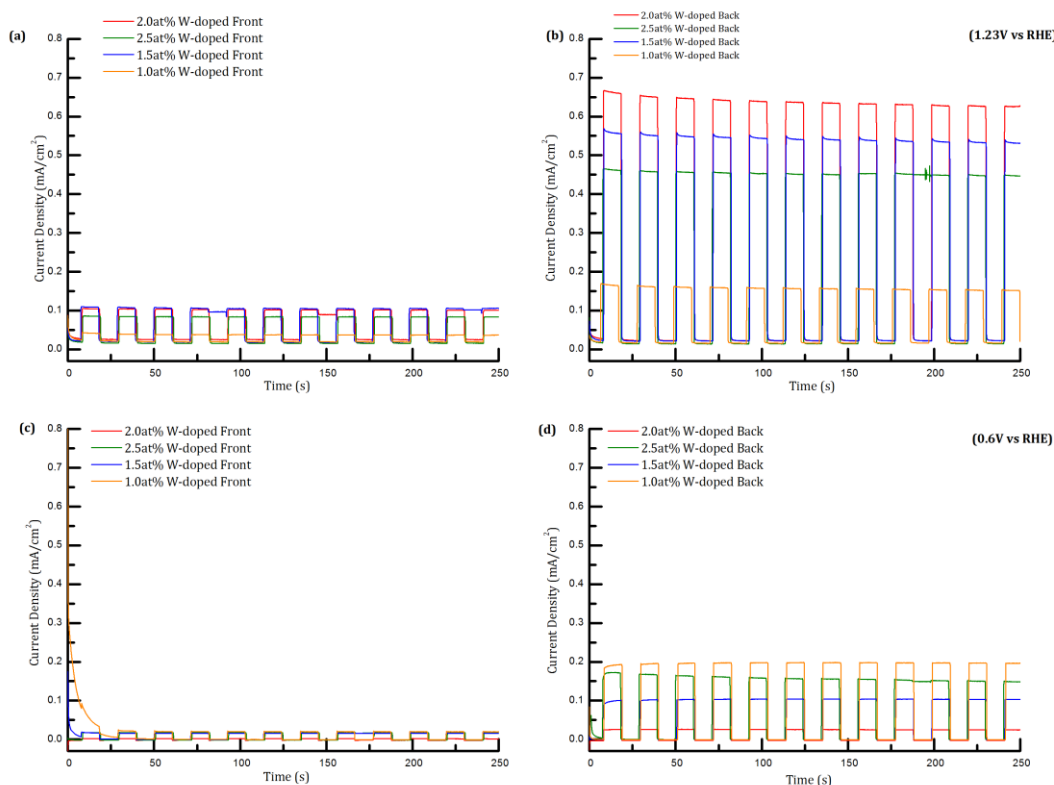


Figure 4.1.7: Transient photocurrent density measurements (TPC) for the pristine and W-doped BiVO₄ photoanodes with different doping levels at 1.23 vs RHE (a, b) and 0.6 vs RHE (c, d) bias with front (a, c) and back (b, d) illumination measured for 4.16 min. Electrolyte used for measurements is 1M KPi buffer (pH=7.0) with 0.5M Na₂SO₃ as hole scavenger.

4.2 Effect of Reaction Time for Pristine and W-doped BiVO₄ Photoanodes:

Thickness and morphology of the film has a significant influence on the measured PEC activities as well as the optical and physical properties of BiVO₄-based photoanodes. Thickness control is still one of the important factors in improving the PEC activities of BiVO₄-based photoanodes since, as was evidenced by the J-V curves (Figure 4.1.6) for the samples mentioned in Section 4.1, the front and back illumination photocurrents differ significantly when the sample thickness is larger than the optimum carrier path length for the photogenerated electrons and holes to travel efficiently between the sample bulk and surface to be utilized by the electrolyte-photoanode surface interface to perform the four electron water splitting reaction [90]. Thus, it is important to be able to tune with

the thickness of the sample, if possible, to improve its efficiency. However, for the hydrothermal synthesis method even the slightest change in the protocol might create critical changes in the structure with visible consequences in physical and electrochemical characterizations, therefore creating controlled changes in morphological structure is quite the challenge for this method [91]. For this purpose, effect of reaction time was investigated using the exact same protocol with unchanged variables other than time for both pristine BiVO_4 and W-doped BiVO_4 -based photoanodes. For the investigation using W-doped photoanodes, only 2.0at% and 1.5at% doped samples were prepared and investigated as these two samples showed the best improvement among other doping levels for PEC activity and photocurrent density in J-V and TPC measurements.

For pristine BiVO_4 photoanodes, samples with reaction time varying from 2h, 4h, 6h, 8h, 9h, 10h, 11h to the regular reaction time of 12h that is used in the initially prepared protocol were prepared. These samples were initially investigated via FE-SEM imaging both to observe the particle formation mechanism during the hydrothermal synthesis reaction of BiVO_4 on FTO coated glass substrate surface and to investigate if any change is occurring in the overall sample thickness as the reaction time increases. As shown in Figure 4.2.1, the size of the particles in all the samples remain in the micron range with irregular size distribution among the microparticles ranging from $\sim 1\mu\text{m}$ to $\sim 5\mu\text{m}$. The morphology is also seen to vary in terms of geometries in all the samples both throughout the surface of a singular sample and amongst the different samples with varying reaction times. In all the samples with reaction times from 6h to 12h, large shapes resembling pine tree needles and leaves are seen to be infrequently distributed along the sample surface. These types of structure formation are not observed for samples with 2h and 4h reaction times, indicating that as the reaction time increases sample morphology tends to become more inhomogeneous. This information is important in terms of determining an optimum reaction time for the hydrothermal procedure with which all samples are to be prepared for further investigations into ways of improving PEC efficiency of the BiVO_4 -based photoanodes prepared via hydrothermal method. It is also observed that in the first two hours of this hydrothermal synthesis reaction, the initial seed formation creates rod-like shapes made up of nano-sized particles, i.e. 3D microrods and these shapes are mostly distributed along the surface with horizontal position. In the literature, there are few reports of pristine BiVO_4 photoanodes that could be designed to have rod-like structure

using hydrothermal method and in all of these reports the rods are similarly reported to be horizontal to the surface and to have 3D-structures similar to the samples produced in this study [43,56,92]. Following this, as the reaction time increases the formation of plate-like structures after the morphing of these nanorods to form larger clusters are observed, and it can even be seen that after 10h reaction time the growth only seems to occur on the corners of these plates, increasing the apparent surface area. It might be expected that this type of increase in the surface area would increase the PEC activity, and this type of improvement has even been reported in the literature before [56,91]. However, it can also be expected that the formation of plate-like structures randomly on the surface and even inside the bulk of these BiVO_4 photoanode films might prevent the activity instead, as these plates might indicate the existence of surface defects that could act as surface recombination centers for photogenerated electrons and holes, decreasing the PEC activity and dominating any improvement that might have achieved from increased surface area [56]. Also, even though the formation of 3D ball-like large assemblies are visible in all the samples, their frequency seems to increase over time. These large clusters might also prevent effective electron transfer throughout the sample to the surface and might even affect the surface hole accumulation by creating recombination centers as they also seem to disrupt the homogeneity of the sample surface.

It is seen in Figure 4.2.2 that UV-Visible absorption edges of the samples do not change as the reaction time increases, indicating that the optical band gap of the samples remains the same throughout the hydrothermal reaction. This indicates that electronic structure of the sample does not change from the start of a hydrothermal synthesis reaction through the end (12h in our protocol) for the BiVO_4 -based photoanodes prepared following a similar protocol to this study. It also implies that even though FE-SEM study suggests there could be meaningful change in the light absorption properties of the samples as the morphologies seem to slightly differ between different reaction times causing different geometries and homogeneity along the surface, the optical band gap of the samples do not seem to be affected significantly after the initial formation of the BiVO_4 particles in an hydrothermal reaction with changing time (Figure 4.2.2). Thus, any change that could be observed in PEC activities would only be related to the changes in electronic mobility and charge carrier transfer properties of the sample caused by the increasing crystallite size and decreasing lattice strain as the hydrothermal time progresses instead of the surface

area values for the visible geometries in the SEM images for pH=1 reaction condition of hydrothermal synthesis of BiVO_4 photoanodes [91].

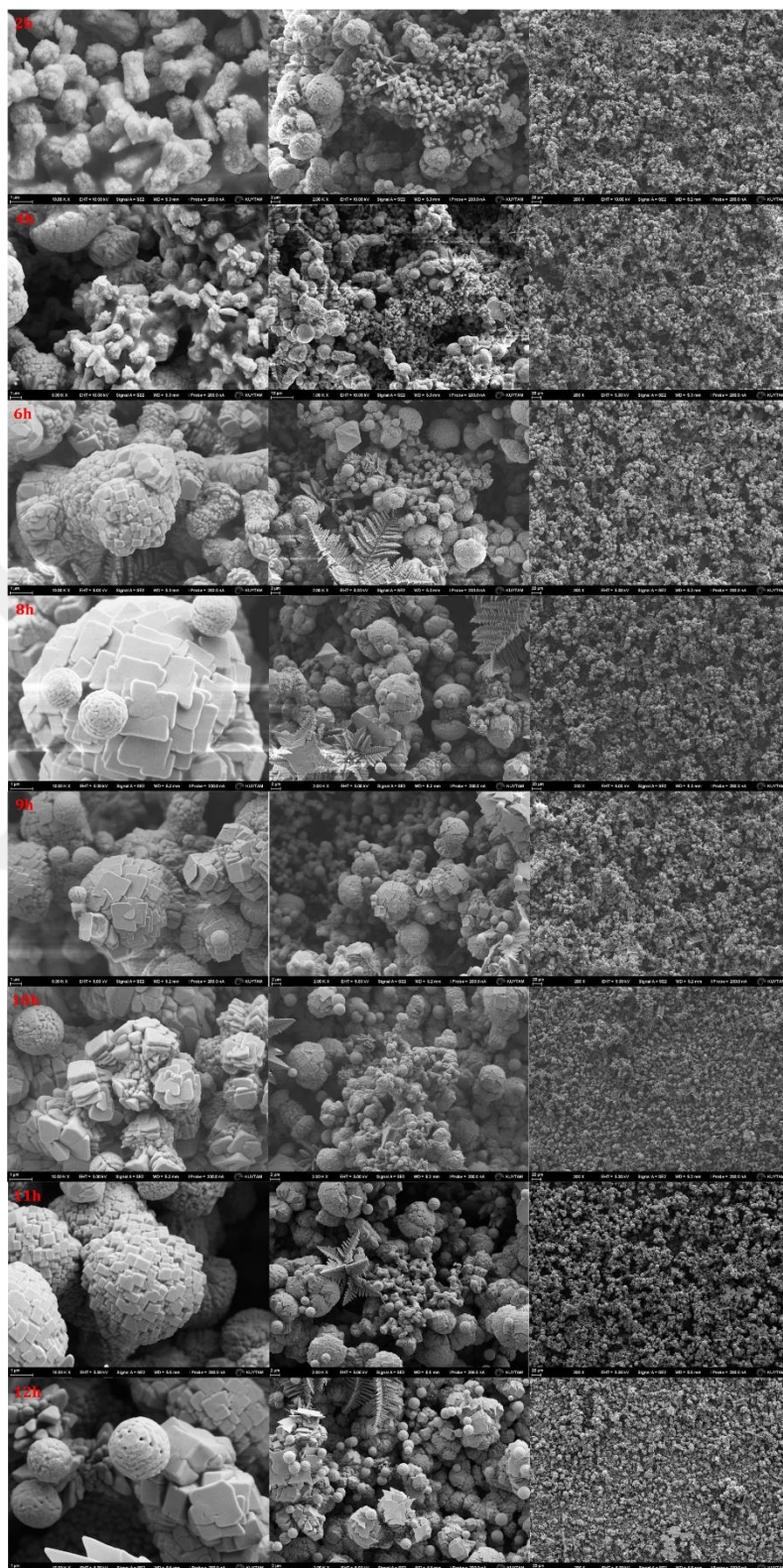


Figure 4.2.1: FE-SEM images of the surface of pristine BiVO_4 samples with differing reaction times from 2h to 12h (from top to bottom) prepared by hydrothermal method.

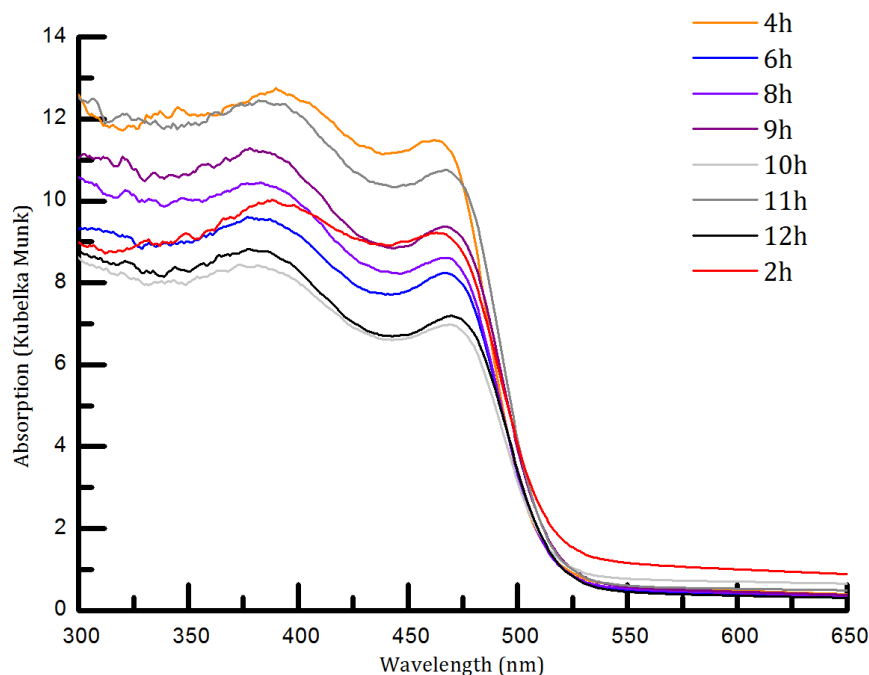


Figure 4.2.2: UV-Visible Absorption spectra of the pristine BiVO_4 photoanodes with various reaction times prepared via hydrothermal method. Samples are measured as-prepared (without annealing) to match with the FE-SEM data. Absorption data is obtained by using Kubelka-Munk transformation on the Reflectance data measured via DRS (diffuse reflectance spectroscopy).

The increase in crystallite size and decreasing lattice strain, i.e. increasing crystallinity, as the hydrothermal reaction time progresses was also indicated by the Raman data obtained for these samples (Figure 4.2.4) [91]. It is seen that there is a slight red shift in the characteristic peak for symmetric stretching of (V-O) at $\sim 826.7 \text{ cm}^{-1}$ as the reaction time progresses for these samples. This is also in accordance with the FE-SEM data obtained as the reaction time progresses, size of the particles, i.e. crystallite size, is seen to get larger. The FWHM values for the Raman peaks of symmetric (V-O) stretching for the various reaction time samples of pristine BiVO_4 photoanodes are also indicative of the increasing crystallite size and the decreasing uniformity. The FWHM values are seen to be decreasing as the reaction time proceeds from 2h to 12h with two deviations from this trend at 8h and 11h reaction time samples (Table 4.2.1). These deviations might have been caused by the slight differences that occur between different Raman measurements, or might have been a result of the inhomogeneous crystal/ particle formation that takes place during hydrothermal film growth, which was also observed in FE-SEM images, as

well as in PEC measurements for the W-doped samples previously. The overall trend seen in the Raman spectra confirms the previously hypothesis that rather than the visible surface area of the particles in hydrothermally prepared BiVO₄-based photoanodes, the crystallite size and lattice strain are the primary change that can influence the physical properties of the material, thus possibly the PEC activities. In Figure 4.2.3, All the peaks in the Raman spectra for all the samples are attributed to the expected values for monoclinic bismuth vanadate structure that are reported in the literature with no other visible impurity peaks such that: the intense characteristic peak at 827.6 cm⁻¹ are attributed to $\nu_s(\text{V-O})$ symmetric stretching modes with shoulders at around 713.6 cm⁻¹ and 643.8 cm⁻¹ representing anti-symmetric stretching modes, $\nu_{as}(\text{V-O})$ [85]. The symmetric A_g bending mode of vanadate ion $\delta_s(\text{VO}_4^{3-})$ and anti-symmetric B_g bending mode of vanadate ion $\delta_{as}(\text{VO}_4^{3-})$ are near 327.8 cm⁻¹ and 367.1 cm⁻¹, respectively [85,86].

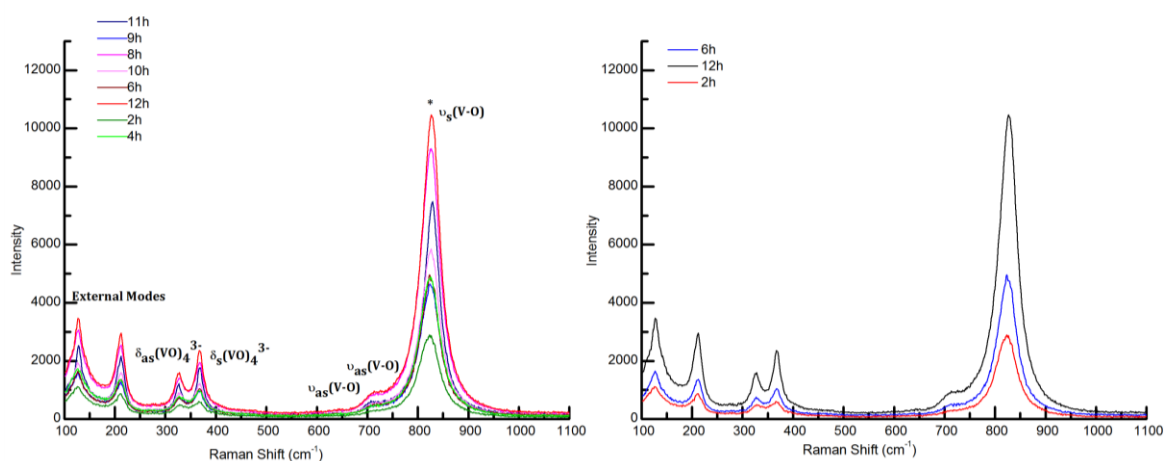


Figure 4.2.3: Raman spectra of the pristine BiVO₄ photoanodes with various reaction times prepared via hydrothermal method. Samples are measured as-prepared (without annealing) to match with the FE-SEM data.

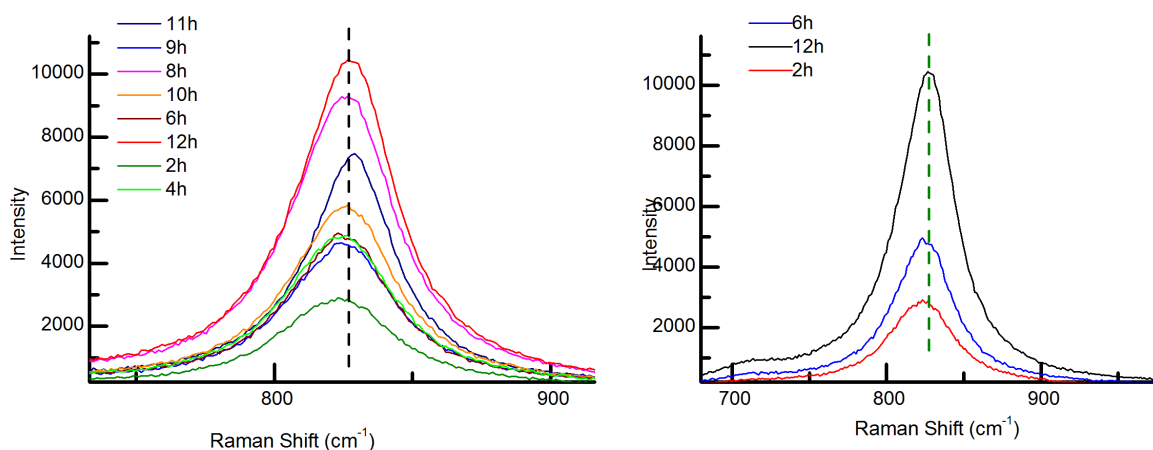


Figure 4.2.4: Zoomed-in Raman spectra of the pristine BiVO_4 photoanodes with various reaction times prepared via hydrothermal method comparing the characteristic monoclinic bismuth vanadate peak at 826.7 cm^{-1} . Samples are measured as-prepared (without annealing) to match with the FE-SEM data.

Sample	FWHM (at 826.7 cm^{-1})
2h BiVO_4	51.3
4h BiVO_4	51.3
6h BiVO_4	51.3
8h BiVO_4	45.9
9h BiVO_4	47.6
10h BiVO_4	46.3
11h BiVO_4	40.2
12h BiVO_4	43.5

Table 4.2.1: FWHM (full-width at half-maxima) values of all the different reaction time samples for the pristine BiVO_4 photoanodes are calculated from the characteristic peak at 826.7 cm^{-1} in their Raman spectra.

It is seen in GI-XRD patterns for 2h and 12h reaction time samples of pristine BiVO_4 photoanodes that the crystallinity indeed increases as the reaction time progresses, as indicated by the Raman spectra of the various reaction time samples, in a way that favors growth in the (004) direction ($\sim 31^\circ$). This was previously observed in W-doped samples with varying doping levels, indicating that during hydrothermal growth of BiVO_4 films, growth in this direction is preferred, thus revealing information about the growth process. This type of growth behavior for BiVO_4 during hydrothermal reaction was also previously reported in literature [91,93]. XRD patterns also indicate monoclinic scheelite structure for the BiVO_4 crystals, again supporting the Raman spectra data (Figure 4.2.5).

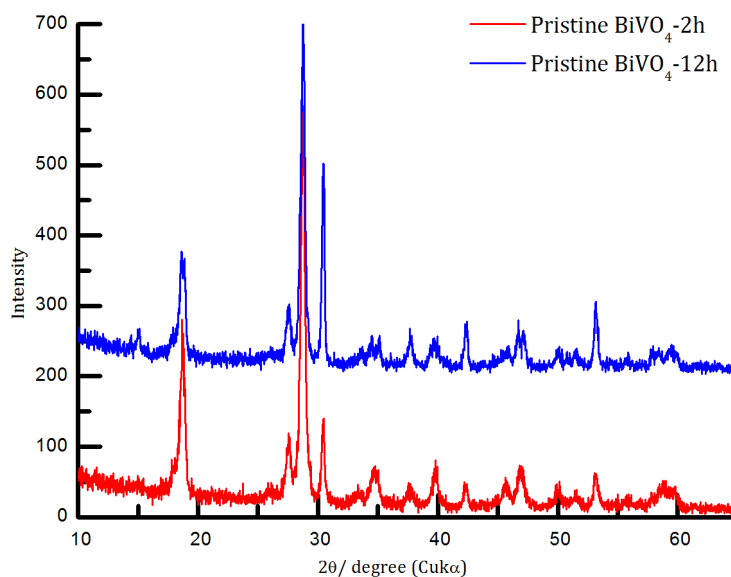


Figure 4.2.5: GI-XRD patterns for pristine BiVO_4 photoanode films prepared via hydrothermal synthesis method with varying reaction times, 2h (red) and 12h (blue). Standard XRD pattern for monoclinic BiVO_4 with JCPDS 83-1699 pdf number is used.

In light of the investigation for the crystal formation process during the pristine BiVO_4 -based photoanode film growth via hydrothermal synthesis route, it was observed that optical band gap, i.e. light absorption properties, of the samples are not affected by the reaction time, though the crystallinity and particle size, along with the surface homogeneity are seen to be affected, therefore possibly influencing the PEC activities as these factors are related to the electron transfer pathway throughout the sample. However, in the cross-section investigations for the pristine BiVO_4 samples with varying reaction times done via FE-SEM imaging, no significant change in the film thickness was observed, along with the finding that the thickness of the samples does not remain same throughout the films (Figure 4.2.6). This indicates that, other than the homogeneity and crystal size of the samples, changing hydrothermal reaction time does not provide any area for improvement for PEC performance of pristine BiVO_4 -based photoanodes. Then PEC performance improvement from only changing the reaction time of pristine BiVO_4 -based photoanodes is not expected, however for W-doped samples the changes in the crystallinity and homogeneity provided by lowered reaction time might prove to have significant effect on PEC performances.

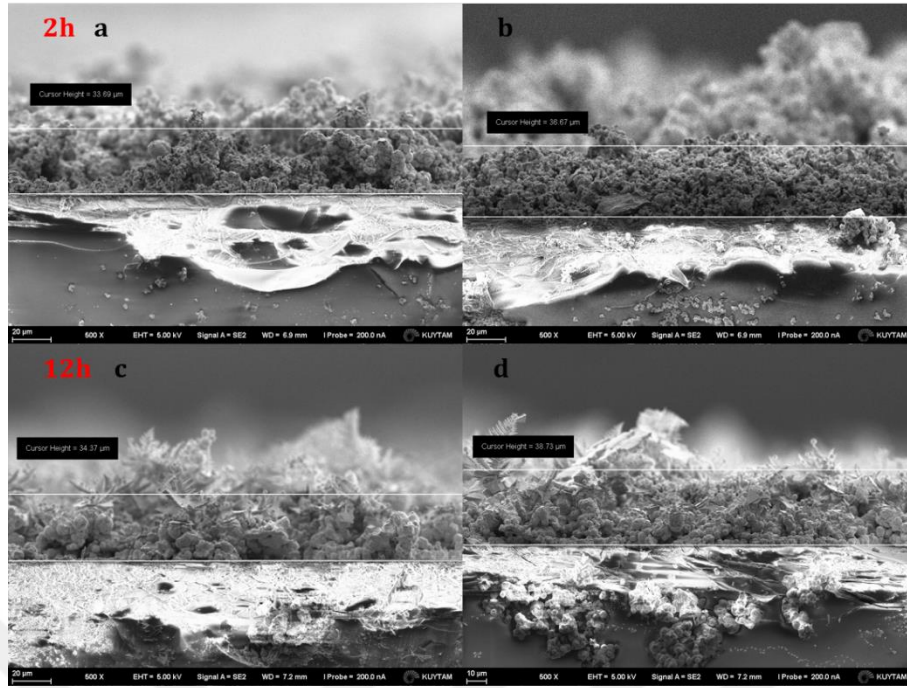


Figure 4.2.6: FE-SEM cross-section images for pristine BiVO_4 films grown via hydrothermal synthesis method with 2h (a) and 12h (b) reaction times.

The practical improvement that shortening the reaction time provides is that it shortens the sample preparation time. Considering the findings for pristine BiVO_4 samples, the effect of reaction time on W-doped samples was also briefly investigated. 1.5at% and 2.0at% W-doped samples were chosen for trials as they showed the best PEC performance and physical properties in the doping level effect study previously. For varying reaction time, based on the pristine sample study, 2h, 4h and 6h reaction times were chosen since they showed the best homogeneity and mostly rod-like geometries in their morphologies with reduced sample preparation times.

In Figure 4.2.7, Raman spectra for the 2.0at% and 1.5at% W-doped BiVO₄-based photoanodes with varying hydrothermal reaction times from 2h to 6h are presented. For all the samples, Raman peaks were attributed to the monoclinic BiVO₄ structure as follows: the intense characteristic peaks at 827.8 cm⁻¹ and 825.4 cm⁻¹ for 2.0at% and 1.5at% W-doped samples, respectively, are attributed to ν_s (V-O) symmetric stretching modes with shoulders at around 711.1 cm⁻¹ and 709.8 cm⁻¹; 643.8 cm⁻¹ and 635.1 cm⁻¹ representing anti-symmetric stretching modes, ν_{as} (V-O) [85]. The symmetric A_g bending mode of vanadate ion $\delta_s(\text{VO}_4^{3-})$ and anti-symmetric B_g bending mode of vanadate ion $\delta_{as}(\text{VO}_4^{3-})$ are near 335.4 cm⁻¹ and 368.4 cm⁻¹; 326.7 cm⁻¹ and 369.7 cm⁻¹, respectively [85,86].

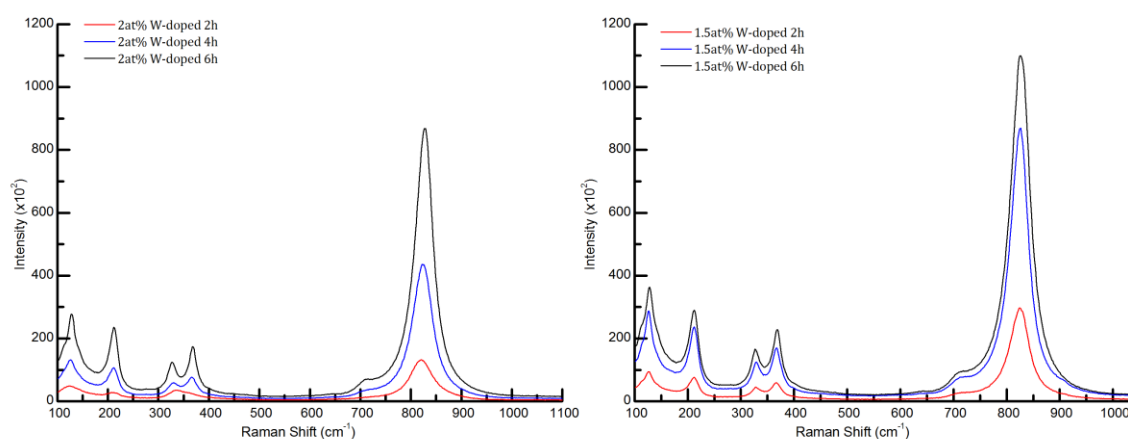


Figure 4.2.7: Raman spectra of the 2.0at% (left) and 1.5at% (right) W-doped BiVO₄ photoanodes with various reaction times (2h, 4h, 6h) prepared via hydrothermal method. Samples are annealed at 500°C for 2h before measurement.

For both doping levels, slight red shift is observed for the samples as the reaction time progresses, which is in accordance with the data obtained for the pristine BiVO₄ photoanodes (Figure 4.2.8). This red shift, especially highlighted on the characteristic peaks at ~827 cm⁻¹ for both samples, indicates that the V-O bond length is being shortened, thus the crystallinity is increasing with the reaction time [56,94]. This observation is in accordance with the results previously obtained for the pristine BiVO₄ photoanodes with varying hydrothermal reaction time, confirming that W-doped samples are showing a similar crystal growth process during hydrothermal synthesis. The effect of crystal growth time is more pronounced in doped samples as the red shift is more visible in these samples, and this corresponds to the expectations from these samples since the doping

effect is also influencing the V-O bond length and lattice strain. When the FWHM values of these peaks are also considered for both doping levels with varying reaction times, it is also seen that shorter reaction time yields less crystallinity in the samples, as was also observed for the pristine samples via both FE-SEM images and Raman spectra (Table 4.2.2). This result was expected as it was seen for pristine BiVO_4 that as the reaction proceeds over time, more defined morphologies start to form, such as plates with sharp edges or pine-like leaf type geometries. However, Table 4.2.2 shows that the trend in decreasing FWHM values is not linear through 2h, 4h and 6h reaction times for both 2.0at% and 1.5at% W-doped samples, instead 4h reaction time is found to yield the highest crystallinity when the sharpness of the V-O symmetric stretching peak at $\sim 827 \text{ cm}^{-1}$ is considered. This irregular change might be caused by uneven doping of the sample throughout the entire film, as was also considered to be a reason behind the irregular PEC activities and physical characterization results for the different doping level studies presented in section 4.1. Uneven doping would eventually lead to irregular formation pathways for the crystals in BiVO_4 films, therefore leading to a non-linear trend in the Raman peak intensities and sharpness. Contrarily for pristine BiVO_4 two samples with 8h and 11h reaction times also showed deviation from linear decrease of FWHM values with increasing reaction time, therefore indicating that the irregular crystal growth of hydrothermally produced BiVO_4 -based films is not only caused by addition of dopant, rather it is an inherent result of the difficulty in controlling crystal size, morphology and shape distribution in hydrothermal method [93].

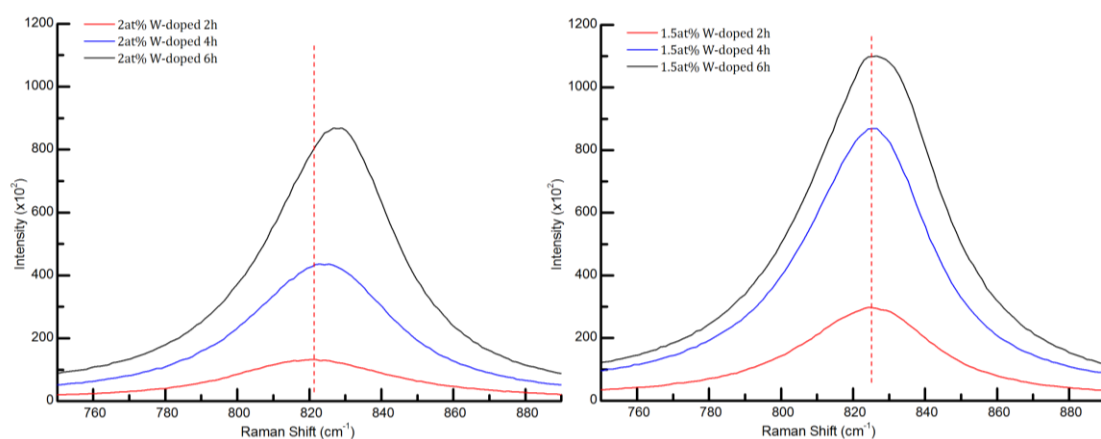


Figure 4.2.8: Zoomed-in representation of the Raman spectra for 2.0at% (left) and 1.5at% (right) W-doped BiVO_4 photoanodes with varying hydrothermal reaction times

(2h, 4h, 6h); characteristic V-O stretching modes at $\sim 827\text{ cm}^{-1}$ are highlighted and their peak positions are considered among the changing reaction times for both doping levels.

Sample	FWHM (at 827.8 cm^{-1})	Sample	FWHM (at 825.4 cm^{-1})
2.0at% W-doped BiVO_4 - 2h	54.90	1.5at% W-doped BiVO_4 - 2h	46.70
2.0at% W-doped BiVO_4 - 4h	30.46	1.5at% W-doped BiVO_4 - 4h	41.80
2.0at% W-doped BiVO_4 - 6h	42.77	1.5at% W-doped BiVO_4 - 6h	44.75

Table 4.2.2: FWHM (full-width at half-maxima) values of all the different reaction time samples for the pristine BiVO_4 photoanodes are calculated from the characteristic peak at $\sim 827\text{ cm}^{-1}$ in their Raman spectra.

UV-Visible absorption spectra, in Figure 4.2.9, indicates that no considerable change is seen for the absorption edges among various reaction time samples of W-doped samples with two different doping levels. This indicates that optical band gap of the W-doped samples does not change significantly by varying the reaction time, a finding like the one in pristine BiVO_4 studies for the effect of hydrothermal reaction time. This information also coincides with the findings from the previously evaluated Raman spectra for these photoanodes, as well as the PEC water splitting activities obtained for them via cyclic voltammetry (CV) and transient photocurrent (TPC) measurements (Figure 4.2.10 and Figure 4.2.11).

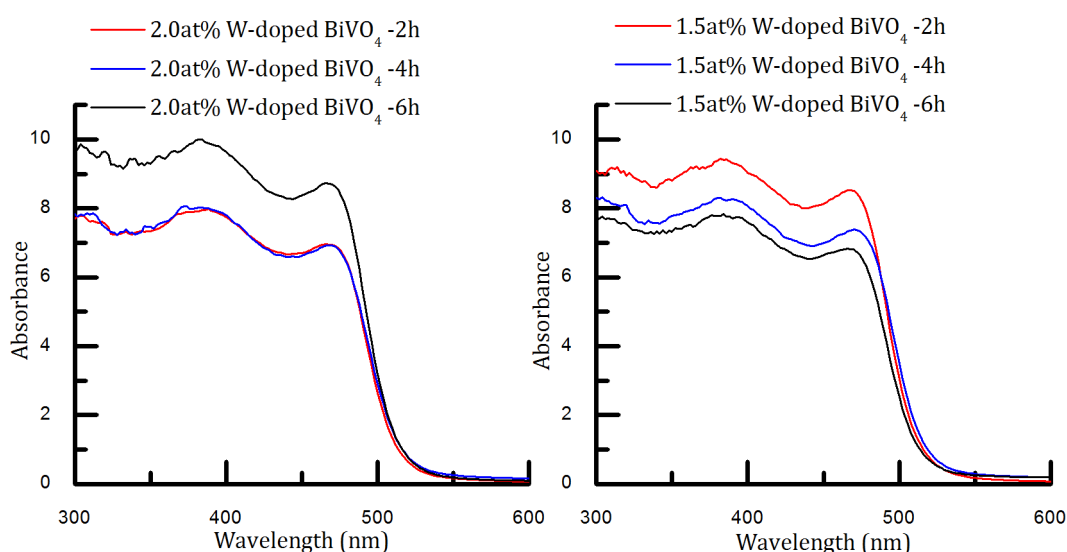


Figure 4.2.9: UV-Visible Absorbance spectra for 2.0at% (left) and 1.5at% (right) W-doped BiVO_4 -based photoanodes with varying reaction times (2h, 4h 6h). Absorbance

data is obtained by using Kubelka-Munk Transformation after measuring reflectance via DRS (diffuse reflectance spectroscopy) method.

In Figure 4.2.10, photocurrent density-potential (J-V) curves obtained via cyclic voltammetry method under dark and back illumination, for 2.0at% and 1.5at% W-doped samples with varying hydrothermal reaction times are showed. It is seen that for 2.0at% W-doped samples, films with 2h hydrothermal reaction time shows the highest photocurrent density for the activity behavior observed in 0.5V-1.23V vs RHE potential region under backside illumination with solar simulator, with 1.10 mA/cm² value at 1.23V vs RHE. It is followed by 6h and 4h samples with photocurrent densities of 0.83 mA/cm², and 0.63 mA/cm² at 1.23V vs RHE applied bias, respectively. When the onset potentials for the various reaction times of 2.0at% W-doped samples are compared it is seen that the photoanodes with 4h and 6h reaction times shows this point at around 0.507V vs RHE potential, followed by 2h sample with 0.517V vs RHE. For 1.5at% W-doped samples, films with 4h hydrothermal reaction time shows the highest photocurrent density for the activity in the 0.5V-1.23V vs RHE potential range under backside illumination, with photocurrent density value of 0.85 mA/cm²; 4h sample is followed by 6h and 2h reaction time samples with 0.54 mA/cm² and 0.37 mA/cm² photocurrent densities at the same potential value. Onset potentials are seen to be quite close to each other, similar to 2.0at% W-doping level case, with 4h reaction time having 0.51V vs RHE, followed by 6h and 2h samples with 0.55V vs RHE value for this point. Considering this information, it can be said that the onset potentials are not significantly affected by the changing hydrothermal reaction time, whereas the photocurrent densities can be influenced to increase by reducing reaction times for both doping levels. It is seen that, for 2.0at% W-doped samples, the highest photocurrents are obtained for the lower reaction time of 2h and the decrease in photocurrents are not proportional to the reaction time since the photoanode with 4h reaction time showed the lowest photocurrents. The change in the photocurrents is not a linear trend for 1.5at% W-doped samples as well, however the highest photocurrents are obtained for 4h reaction time sample, followed by 6h, then 2h reaction time sample. While the photocurrent change trend matches the FWHM data obtained from the Raman spectra of 1.5at% W-doped samples, since 4h sample indicated the highest crystallinity via its low FWHM value, the trend in seen for 2.0at% W-doped samples do not quite match this FWHM trend seen for their Raman spectra. Therefore, it can be concluded that change in crystallinity is not the only source for the change in PEC

activities for samples with various hydrothermal reaction times. Although progressing reaction time increases crystallinity, the mobility of photogenerated charge carriers and the efficiency with which they are utilized on the surface of these photoanodes are apparently not singularly controlled by that factor. Considering the information obtained from CV curves, TPC curves also provides some support for the commentary about the surface reactions differing between differing doping level samples with similar crystallinity trends for increasing reaction times.

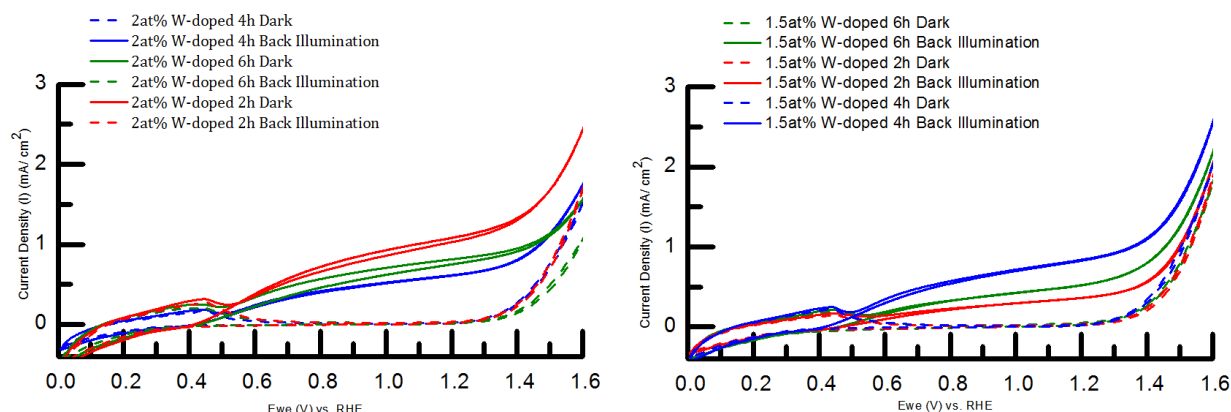


Figure 4.2.10: Cyclic voltammetry curves showing photocurrent density (mA/cm^2) vs potential (V vs RHE) values for 2.0at% (left) and 1.5at% (right) W-doped BiVO_4 photoanodes with varying reaction times (2h, 4h and 6h) under dark (dotted lines) and backside illumination (filled lines) are presented along with pristine BiVO_4 photoanode photocurrents for comparison. Electrolyte used for measurements is 1M KPi buffer (pH=7.0) with 0.5M Na_2SO_3 as hole scavenger.

In Figure 4.2.11, transient photocurrent densities (TPC) for 1.5at% and 2.0at% W-doped BiVO_4 photoanodes with 2h and 6h reaction times at 0.6V and 1.23V vs RHE applied bias with front and backside illuminations are presented. In Figure 4.2.11 (a) and (c), it is seen that for both reaction times and doping levels, around 10x increase in photocurrents from front to back illumination of the samples at 0.6V vs RHE applied bias is obtained, while (b) and (d) shows that at 1.23V vs RHE, both 1.5at% and 2.0at% doped samples with 2h and 6h reaction times around 3x increase in the photocurrents are obtained. This indicates that the difference between the amount of photogenerated charge carriers/surface accumulated holes produced, are the same for all the samples, which is expected since the film thicknesses are not significantly changed with reaction time or doping. Similarly, for all the samples, it is seen that negative spikes are quite insignificant/ not

visible, indicating that recombination of the photoinduced charge carriers are mostly suppressed for all the samples for both front and back illumination. When the 2.0at% W-doped and 1.5at% W-doped samples at both high and low bias are compared, it is seen that 2.0at% doped samples show much more visible positive spikes that are reduced to steady state current shortly after the light is turned on, compared to 1.5at% doped sample. This trend seems unexpected when the doping level study presented in section 4.1 is considered, since that study yielded the conclusion that as the doping level increases surface hole recombination becomes more suppressed, therefore producing less pronounced spikes [87–89]. However, as the reaction time is decreased to produce less crystalline samples, though with possibly more homogeneity in morphology distribution, it is seen that this behavior is also changed, leading to much sharper spikes for the sample with higher doping level under both high and low applied bias. This indicates that 2.0at% W-doped sample with decreased reaction time, i.e. decreased crystallinity, produces a much larger amount of photogenerated electrons and holes are produced more rapidly and then separated to turn into accumulated holes on the surface, therefore accumulation of electrons from the electrolyte, however the lifetime of these accumulated holes are rather short leading us to believe that back recombination rate of these photogenerated charge carriers might also be increasing in these samples [93]. However, for lower doping level, the change in the amount of photogenerated charge carriers are seen to be not affected as drastically as it did for 2.0at% doped samples with changing reaction time.

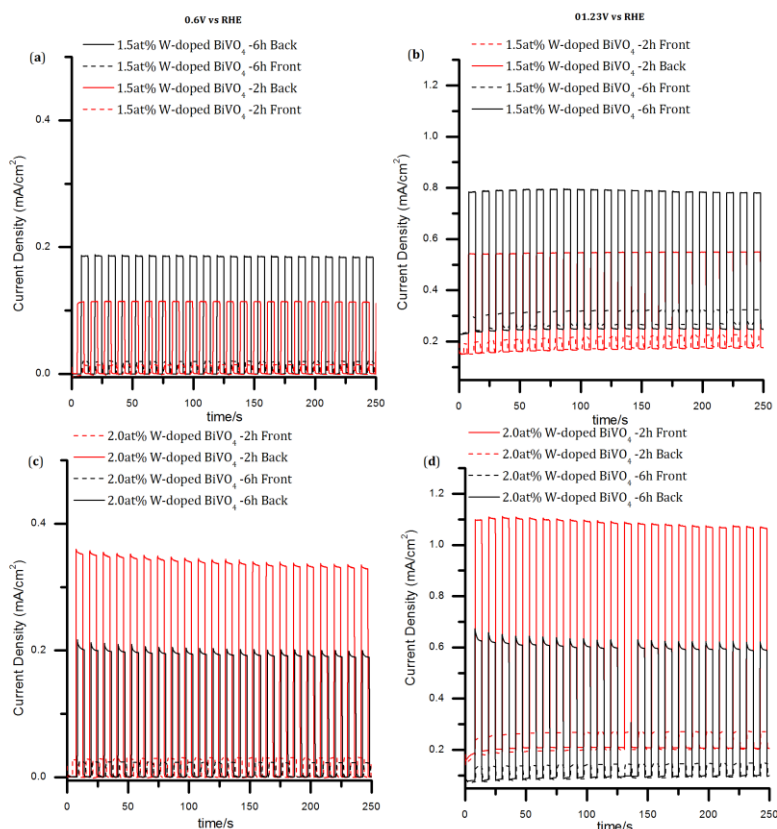


Figure 4.2.11: Transient photocurrent densities (TPC) for the 1.5at% (a, b) and 2.0at% (c, d) W-doped BiVO_4 photoanodes; at an applied bias of 0.6V vs RHE (a, c) and 1.23V vs RHE (b, d) with front and back illuminations. Electrolyte used for measurements is 1M KPi buffer (pH=7.0) with 0.5M Na_2SO_3 as hole scavenger.

When photocurrent stabilities of all the samples are considered from the transient photocurrent measurements over 4.2 minutes, they seem to be quite close to each other and all samples show good stability over time. It is seen that 2.0at% W-doped sample shows improved photocurrents for the low reaction time compared to the film grown with extended time, whereas 1.5at% doped sample shows the opposite effect. This mismatch between the effect of reaction time on samples with different doping levels of W into the BiVO_4 structure matches with the CV data and the evaluations of the transient J-V curves of these samples (Figure 4.2.11).

When all the results are considered, it was concluded that 2.0at% W-doped sample with 2h hydrothermal reaction time shows the best improvement for the PEC photocurrent densities, therefore should be used for further investigations to improve the PEC activities of BiVO_4 -based photoanodes produced via hydrothermal synthesis method.

4.3 Effect of Reaction Temperature on Pristine and W-doped BiVO₄ photoanodes:

In order to improve the PEC efficiency of hydrothermally prepared BiVO₄-based photoanodes, several methods have been utilized and reported so far in the literature such as addition of dopants [74,79,89], pH control [92,93], using different surfactants [41,48] or the tuning of the thermodynamic aspects of the hydrothermal synthesis method such as varying temperature [43,95] or reaction time. All of these changes that can be made in a hydrothermal synthesis protocol designed for growth of BiVO₄ can influence the crystallite size, lattice strain, morphology shape and distribution, as well as film thickness and defect sites in the structure; therefore can lead to changes in the charge transfer and separation as well as the charge carrier recombination on the surface, which is one of the main limiting factors for PEC performance in BiVO₄ films. Even the slightest change in these properties of a BiVO₄ photoanode film has been reported to cause significant changes in the PEC performances and obtained photocurrent densities at similar applied voltage ranges [44,56,79,93]. In this prospect, after tuning the best working doping level, 2.0at% in this study, for W dopant in the BiVO₄ films prepared in this study, and optimizing the best reaction time (determined to be 2 hours) to get even higher photocurrents from these samples, effect of hydrothermal reaction temperature on 2.0at% W-doped was investigated to determine if an improvement in the PEC performance could be obtained. Pristine BiVO₄ samples were investigated alongside these samples for comparison.

In Figure 4.3.1, Raman spectra of the 2.0at% W-doped and pristine BiVO₄ photoanodes showed that all the peaks can be attributed to monoclinic scheelite structure of BiVO₄ for varying hydrothermal reaction temperature samples of both photoanodes as follows: The intense characteristic peaks at 830.0 cm⁻¹ and 825.0 cm⁻¹ are attributed to ν_s (V-O) symmetric stretching modes of pristine and 2.0at% W-doped samples, respectively, with shoulders at around 708.4 cm⁻¹ and 638.4 cm⁻¹ as well as 710.5 cm⁻¹ and 643.2 cm⁻¹ representing anti-symmetric stretching modes, ν_{as} (V-O); the symmetric A_g bending mode of vanadate ion δ_s (VO₄³⁻) and anti-symmetric B_g bending mode of vanadate ion δ_{as} (VO₄³⁻) are near 326.3 cm⁻¹ and 368.2 cm⁻¹ as well as 366.9 cm⁻¹ and 328.8 cm⁻¹, respectively [85,86].

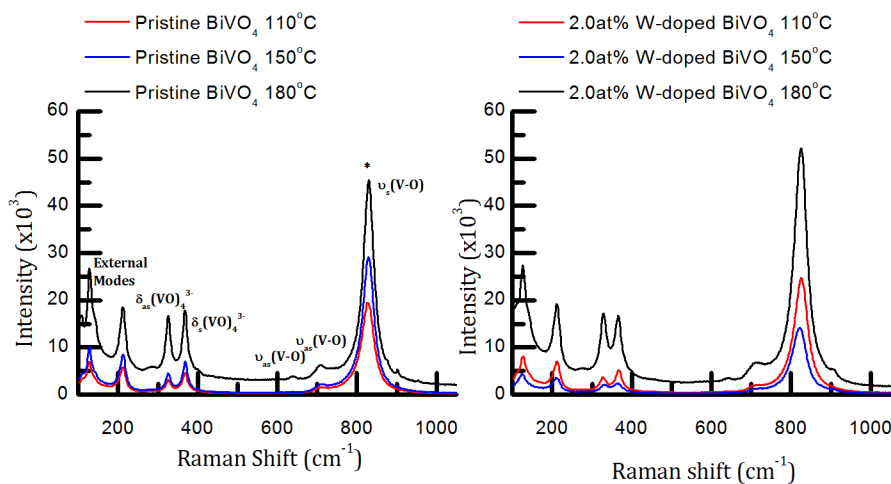


Figure 4.3.1: Raman spectra for the pristine (a) and 2.0at% W-doped BiVO₄ photoanodes with varying hydrothermal reaction temperatures (110°C, 150°C and 180°C) for 2h reaction time.

In Figure 4.3.2, the peaks at $\sim 820\text{ cm}^{-1}$ are showed up-close for all the samples. For pristine sample (Figure 4.3.2 (a)), a blue shift is seen for 130°C and 150°C samples compared to the films prepared at 180°C reaction temperature, which is the original protocol used for the hydrothermal synthesis of BiVO₄ films in this study; while a very slight similar shift is observed for 110°C reaction temperature sample. This shift indicates that as the reaction temperature is increased, the bond length of V-O bond in the structure is shortened, increasing the crystallinity of the samples [56,94]. It is also seen that the peak sharpness increases with increasing temperature, confirming that crystallinity and uniformity of the samples indeed increases. For the 2.0at% W-doped BiVO₄ photoanode, the effect of temperature seems to slightly differ from the pristine samples (Figure 4.3.2 (b)). Like pristine sample, W-doped sample also has the lowest blue shift for the 110°C reaction temperature sample compared to 180°C, followed by a more visible shift seen for 150°C sample. This sample also shows a sharper peak than 150°C and 110°C samples, again contrary to the pristine sample findings, indicating that 2.0at% W-doped BiVO₄ films grown at 130°C hydrothermal reaction temperature have higher crystallinity caused by decreased V-O bond length compared to other reaction temperatures. This peak shift is accompanied by the increase in the distance between the peaks representing the deformation modes of the VO₄³⁻ tetrahedron in their structures, as shown in Figure 4.3.3 (b). When these peaks are considered, it is seen that the intensities and FWHM of these peaks decrease, as well as showing slight decrease between the two peaks, at reaction

temperatures lower than 180°C for the 2.0at% W-doped sample. The sharpness and shift in these peaks are representative of the variations in VO_4^{3-} tetrahedron geometry, therefore indicating that reaction temperature influences the local sites on the surface of these BiVO_4 films [56]. Therefore, the decrease in the sharpness and relative intensities as well as the distance between these two peaks at lower reaction temperatures indicate that lower temperatures produce BiVO_4 films with lower distortion around the VO_4^{3-} , therefore around the Bi^{3+} cation [56]. According to a study conducted by Kudo et. al. to investigate the effect of structural changes on the PEC activities of BiVO_4 photoanodes, even the slightest change in the distortion level at these local structures on the surface of these photoanodes can significantly influence the delocalization of the electrons in the structure, therefore the efficiency of the photoinduced charge transfer and separation throughout the film [56]. Therefore, it is expected that the samples with higher degree of distortion are expected to show higher PEC activities under illumination. For 2.0at% W-doped sample, it is seen that 180°C sample shows the highest crystallinity and quite high distortion in the VO_4^{3-} tetrahedron region where lone pair distortion on Bi^{3+} is also proportionally effected [56]. This sample is followed by 150°C sample, as the two modes for VO_4^{3-} tetrahedron seem to be closer to each other even though their relative intensities have decreased, indicating the degree of distortion is increased even without the observation of increased relative peak intensities. This sample is also seen to have lower crystallinity indicated by the slight blue shift in its V-O symmetric stretching mode at around 820 cm^{-1} . Then, 110 °C sample is seen to have even smaller shift in its V-O symmetric stretching mode compared to 150°C sample, indicating relatively good crystallinity compared to it, accompanied with a slight decrease between the modes representing deformation modes of VO_4^{3-} tetrahedron that is lower than the one seen in 150°C sample indicating higher degree of distortion in the VO_4^{3-} tetrahedron region where lone pair distortion on Bi^{3+} is also proportional [56]. According to these results, the PEC results for the activity evaluation of these samples is expected to show the highest activity for either 150°C or 110°C as they seem to have higher degree of distortion, therefore better delocalization of electrons throughout the structure. However, actual PEC measurements under dark and back illumination show deviation from this expectation.

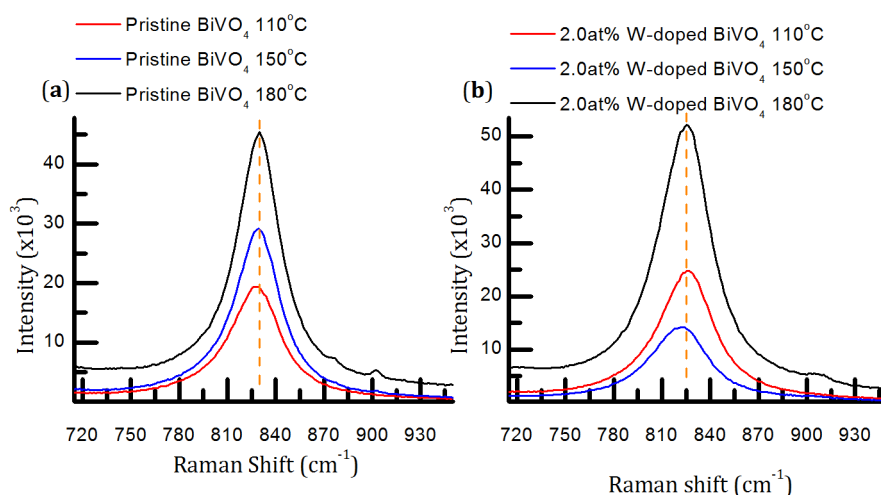


Figure 4.3.2: Zoomed-in Raman spectra for the pristine (a) and 2.0at% W-doped (b) BiVO_4 photoanodes with varying hydrothermal reaction temperatures (110°C, 150°C and 180°C) for 2h reaction time; characteristic V-O symmetric stretching peak at $\sim 820 \text{ cm}^{-1}$ is highlighted for analysis of Raman shift among the samples, as well as peak intensity/ FWHM change.

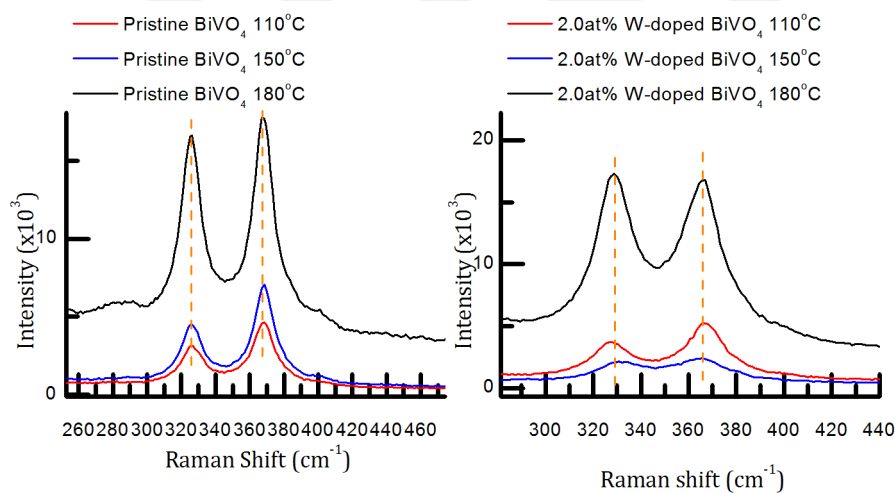


Figure 4.3.3: Zoomed-in Raman spectra for the pristine (a) and 2.0at% W-doped BiVO_4 photoanodes with varying hydrothermal reaction temperatures (110°C, 150°C and 180°C) for 2h reaction time; VO_4^{3-} symmetric and antisymmetric bending modes at ~ 360 and $\sim 320 \text{ cm}^{-1}$ are highlighted for analysis of Raman shift among the samples, as well as peak intensity/ FWHM change.

Figure 4.3.4 shows that GI-XRD patterns for both pristine and W-doped BiVO_4 films with varying hydrothermal reaction temperatures shows monoclinic scheelite structure

peaks, in accordance with the Raman spectra obtained for these samples. It is also seen for both pristine and doped samples that 180°C reaction temperature produced higher crystallinity since the peaks are seen to have smaller FWHM and higher relative intensities in the XRD patterns. This information also coincides with the Raman spectra for these samples, in which highest crystallinity regarding FWHM and Raman shift at characteristic peaks, are observed for 180°C reaction temperature conditions. The (004) ($\sim 31^\circ$) direction is favored more at higher temperatures, indicating higher PEC activities due to better delocalization of electrons throughout the BiVO_4 crystals [56].

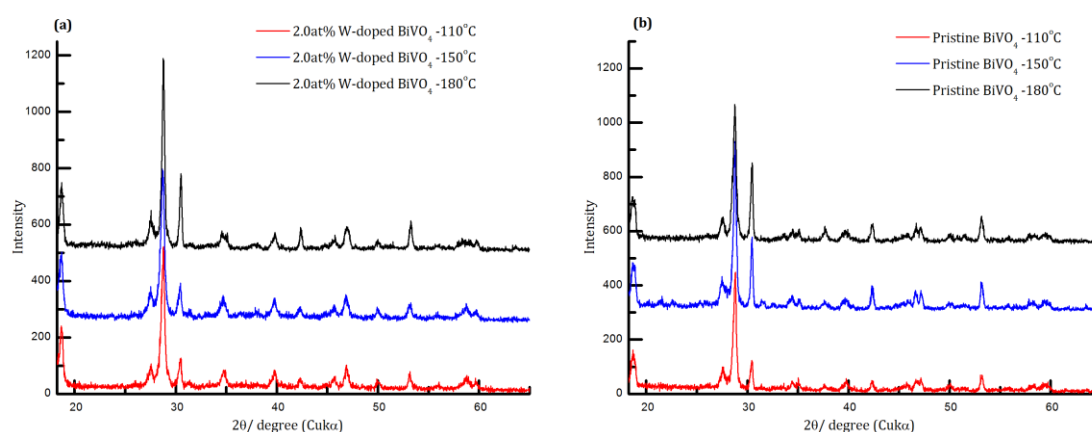


Figure 4.3.4: GI-XRD Patterns for Pristine (a) and 2.0at% W-doped (b) BiVO_4 photoanodes with varying hydrothermal reaction temperatures are presented. Standard XRD patterns for monoclinic BiVO_4 with JCPDS 83-1699 pdf number are used.

In Figure 4.3.5, photocurrent density – potential (J-V) curves for the 2.0at% W-doped BiVO_4 samples with varying hydrothermal reaction temperature are shown. It is seen that unlike the expectations based on the Raman spectra analysis for these samples, the highest activity behavior is obtained for the photoanode prepared at 180°C reaction temperature with 1.37 mA/cm^2 at 1.23V vs RHE potential, followed by 150°C, 110°C and 130°C reaction temperature samples with 0.46 mA/cm^2 , 0.41 mA/cm^2 and 0.31 mA/cm^2 at 1.23V vs RHE potential, respectively. This indicates that even though the degree of distortion around the VO_4^{3-} , thus Bi^{3+} is a significant factor effecting the photogenerated charge transfer and separation in BiVO_4 films, crystallinity of the particles in these photoanode films grown by hydrothermal synthesis method is also a strong influence on the PEC performance for water splitting. It is seen that even though 150°C and 110°C showed better geometries for improved electron mobility inside the samples due to

increased degree of distortion, films grown at 180°C showed higher PEC activities, possibly owing to their improved crystallinity compared to other samples in this group. Among the samples with lower hydrothermal synthesis temperature than 180°C, films grown at 150°C showed the highest activity, followed by 110°C and 130°C. It was previously observed in Raman spectra that 150°C sample has slightly lower crystallinity compared to 110°C sample, however has a much higher lattice distortion in the VO_4^{3-} region. This indicates that the changes in the geometries of local electron donor sites in BiVO_4 in favor of easier delocalization of electrons might become a more dominant influence on the PEC performance than the effect of crystallinity and uniformity in some cases for the W-doped BiVO_4 photoanodes grown via hydrothermal route. However, the presence of dopants and other possible changes on the surface of these films caused by hydrothermal temperature, reaction time, use of different surfactants etc. might come together to form synergistic effects on the PEC performance that cannot be easily detected by physical characterization methods. Thus, further studies on each of these aspects, as well as their holistic effect on the PEC performance and the water splitting reaction pathways on the surface of BiVO_4 -based films are still necessary.

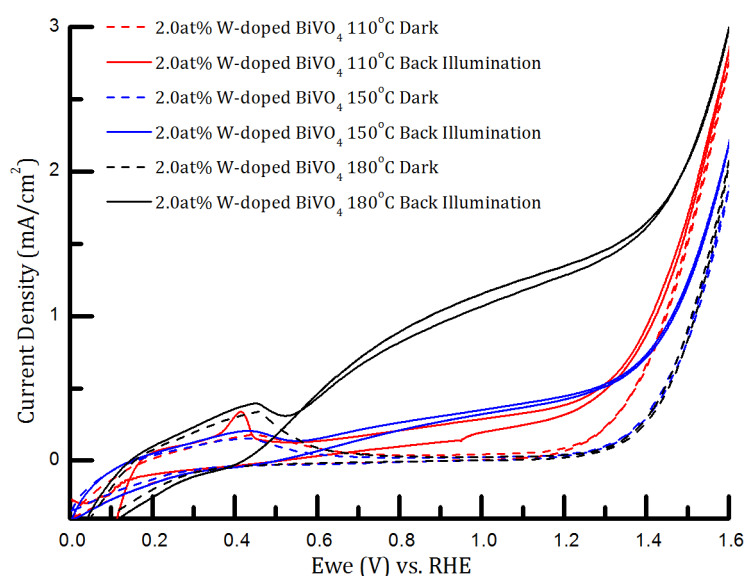


Figure 4.3.5: Cyclic voltammetry (CV) curves for 2.0at% W-doped BiVO_4 photoanodes with varying hydrothermal reaction temperatures (110°C, 130°C, 150°C, 180°C) over an applied potential range of 0.0V to 1.6V vs RHE under dark (dotted lines) and backside illumination. Electrolyte used for measurements is 1M KPi buffer (pH=7.0) with 0.5M Na_2SO_3 as hole scavenger.

4.4 Effect of Iridium Oxide Catalyst Loading via ALD Method:

4.4.1 Effect of Different ALD Cycles:

To investigate the effect of co-catalyst layer thickness on BiVO₄-based photoanode films, samples with varying ALD cycles for deposition of iridium oxide on the surface were prepared. An initial data set with 30, 50 and 200 ALD cycles coating of iridium oxide by using water precursor alongside was prepared using 10 cycle spin coated BiVO₄ photoanode films. After this data set, a secondary set was prepared with varying preparation methods such that spin coated pristine BiVO₄ film, hydrothermally grown pristine BiVO₄ film; hydrothermally grown 2.0at% and 1.5at% W-doped BiVO₄ films were utilized as these samples are previously studied to improve their PEC activities and photocurrent densities. For these samples, both the effect of various ALD cycles (30 and 100 cycles) and use of varying oxidizing agent alongside iridium source, such as water and ozone, on the obtained photocurrent densities are investigated.

Figure 4.4.1.1 shows that among the first set of samples with spin coated BiVO₄ films, 30 ALD cycle IrO_x coated one show the activity behavior in the 0.6V-1.2V vs RHE region under backside illumination compared to its dark current among all the samples. It has a photocurrent density of 1.03 mA/cm² at 1.23V vs RHE, followed by 50 ALD cycle IrO_x coated, 200 ALD cycle IrO_x coated, and bare BiVO₄ with no co-catalyst coating samples with 0.96 mA/ cm², 0.95 mA/ cm² and 0.86 mA/ cm² photocurrent densities at 1.23V vs RHE applied potential, respectively. Also, the onset potentials in the CV curves seem to be decreased in all the co-catalyst loaded samples compared to the pristine spin coated BiVO₄ films which has ~0.58V vs RHE onset potential. In comparison to the pristine sample, 30 ALD cycle, 50 ALD cycle and 200 ALD cycle shows a slight decrease in the onset potentials as the thickness of the loaded co-catalyst; i.e. the number ALD cycles, increases. 0.56V vs RHE, 0.57V vs RHE and 0.57V vs RHE onset potential values have been obtained from 30 ALD cycles, 50 ALD cycles and 200 ALD cycles IrO_x catalysts, respectively. The negative shift in the onset potentials and increase in the photocurrent densities can be attributed to the effect of IrO_x co-catalyst loaded to the surface. Iridium oxide catalyst loaded on the BiVO₄ photoanode is seen to improve the oxygen evolution kinetics for water splitting on the surface since the onset potentials are shifted to more negative values, indicating lowered water oxidation overpotential [1,37]. It can also be said that IrO_x catalyst loading onto the surface of BiVO₄ photoanodes have improved the photocurrent densities by

improving charge carrier separation and suppressing the hole recombination on the photoanode surface, therefore increasing charge transfer to the electrolyte for being used in oxygen evolution reaction.

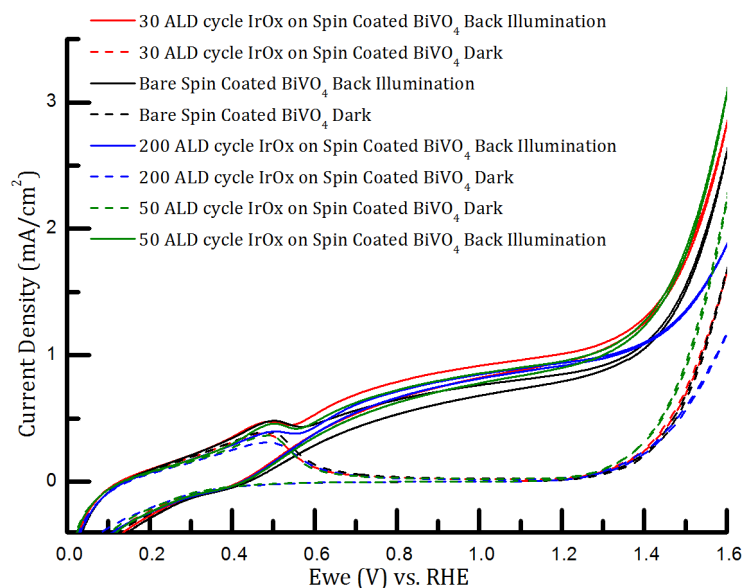


Figure 4.4.1.1: Photocurrent-potential (J-V) curves for the first data set with varying ALD cycle numbers for the IrO_x co-catalyst loading to the surface of 10 cycle spin-coated BiVO₄ samples, obtained via cyclic voltammetry measurements in dark (dotted lines) and under backside illumination (solid lines). 30 (red), 50 (green) and 200 (blue) ALD cycles of IrO_x loaded samples are compared with samples without catalyst (black). Electrolyte used for measurements is 1M KPi buffer (pH=7.0) with 0.5M Na₂SO₃ as hole scavenger.

After these observations, a second sample set with 30 and 100 ALD cycles IrO_x co-catalyst loaded pristine spin coated and hydrothermally-grown BiVO₄ along with W-doped hydrothermally-grown BiVO₄ photoanode films were prepared. These samples were prepared by using both water and ozone as oxidizing agents along with iridium source during ALD coating.

For the 10 cycles spin coated BiVO₄ films, Raman and UV-Vis spectra indicated the monoclinic scheelite structure of BiVO₄ with optical band gap values close to the literature value of ~2.4 eV for the bare and Iridium oxide co-catalyst loaded samples with varying ALD cycles and oxidizers (Figure 4.4.1.2(a, b)). Only 100 ALD cycle samples show slight increase in the absorption edge compared to other samples, though not a very significant change in the optical band gaps, thus indicating that light absorption property is not the

superior reason behind the changing PEC activities among these samples. Figure 4.4.1.2 (c, d) shows that there are no significant shifts in the characteristic peaks of BiVO₄-based photoanodes indicating IrO_x catalyst loading did not impact the crystal structure and order in the spin coated samples. This is expected to be the case, unlike the hydrothermal samples, since hydrothermally-prepared samples have 3D-structures and uneven distribution of various pores in throughout the surface.

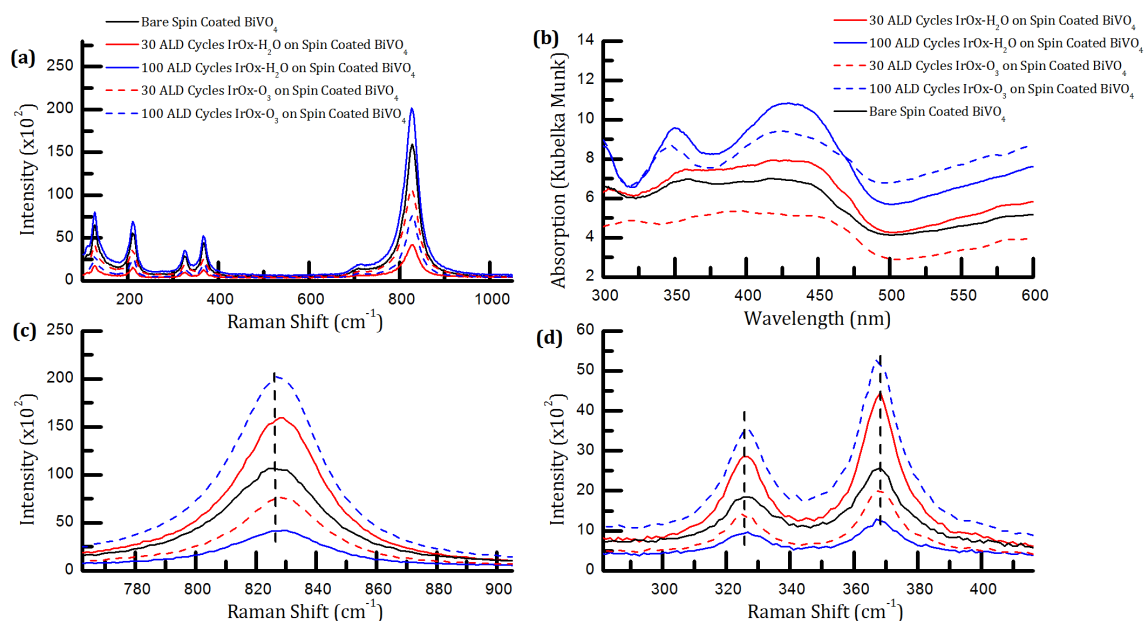


Figure 4.4.1.2: Raman spectra (a) and UV-Visible spectra (b) of Spin Coated BiVO₄ photoanode films loaded with IrO₂ co-catalyst via ALD method using varying ALD cycle numbers (30 (red) and 100 (blue)) and varying oxidizers (ozone (dotted lines) and water (solid lines)). Zoomed in regions for the characteristic Raman shifts of monoclinic BiVO₄ for V-O symmetric stretching at ~820 cm⁻¹ (c) and for VO₄³⁻ tetrahedron's symmetric and asymmetric deformation modes at ~320 cm⁻¹ and ~360 cm⁻¹ (d) are also given for evaluation of peak shifts and changes in sharpness.

Figure 4.4.1.3 shows that varying the oxidizing agent during ALD deposition of IrO₂ catalyst onto the spin coated BiVO₄ photoanodes has different effects on the photocurrent densities measured for these samples in dark and under backside illumination. It is seen that the samples prepared with water as the oxidizing agent shows slightly higher photocurrent densities in the 0.6V - 1.2V vs RHE applied bias region compared to the samples prepared with ozone as the oxidizer. For the water oxidized samples, it is seen that both 30 ALD cycle IrO_x deposited and bare samples have ~1.03 mA/cm² at 1.23V vs RHE, while 100 ALD cycle IrO_x deposited one has around 0.7 mA/cm² photocurrent value.

The 30 ALD cycle IrO_x deposited and bare samples also have $\sim 0.1\text{V}$ vs RHE smaller onset potential than 100 ALD cycles deposited sample. A similar trend is seen for the ozone oxidizer samples. 30 ALD cycles deposited and bare samples have around 0.98 mA/cm^2 at 1.23V vs RHE photocurrent densities while 100 ALD cycles deposited one has $\sim 0.6\text{ mA/cm}^2$. Also, at 1.23V vs RHE applied bias, bare sample has the smallest onset potential, followed by a 0.5V vs RHE shift to higher positive anodic potential of 30 ALD cycles deposited sample, finally by 0.5V vs RHE more increase in the onset potential of 100 ALD cycles deposited sample.

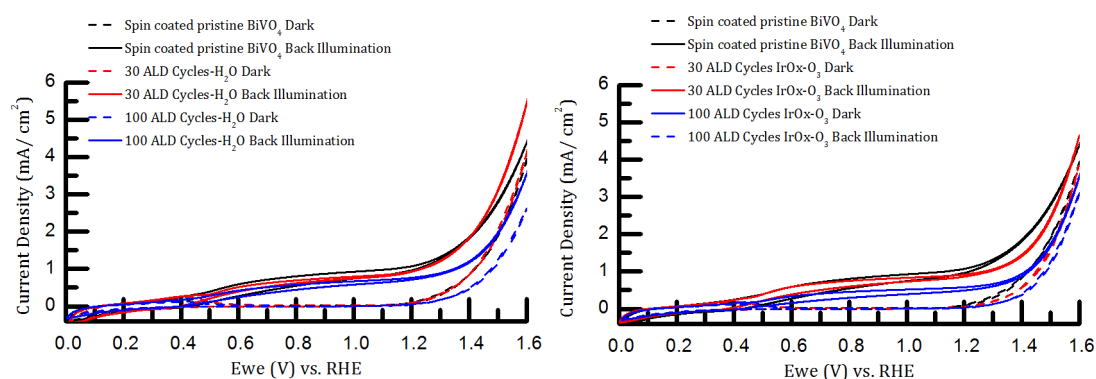


Figure 4.4.1.3: Cyclic Voltammetry (CV) curves for various ALD cycles of IrO_x catalyst loaded on Spin Coated pristine BiVO_4 with water (left) and ozone (right) as the oxidizing precursors. Photocurrent densities are measured in dark (dotted lines) and under backside illumination (solid lines). 30 (red) and 100 (blue) ALD cycles of IrO_x loaded samples are compared with samples without catalyst (black). Electrolyte used for measurements is 1M KPi buffer ($\text{pH}=7.0$) with $0.5\text{M Na}_2\text{SO}_3$ as hole scavenger.

The trends seen in the J-V curves indicate that Iridium oxide deposition via ALD method might have led to the passivation of the surfaces of spin coated BiVO_4 photoanodes, since the on-set potentials are seen to be decreased, accompanied with a decrease or no-change in the photocurrents of the activity behavior region of $0.6\text{V} - 1.2\text{V}$ vs RHE after catalyst deposition. This trend does not change between varying oxidizers, thus does not deviate from the theory that the surfaces might have been passivated. When the transient photocurrent densities (TPC) are considered for this set of samples (Figure 4.4.1.4), it is indeed observed that indeed for all samples with the thicker catalyst layer, i.e. 100 ALD cycle deposited, show lower photocurrent densities indicating blockage of charge carrier transfer between the electrolyte and the photoanode surface to some degree. However, only for water oxidized samples, 30 ALD deposited sample shows slight

improvement in the photocurrent densities compared to bare BiVO_4 under both low (Figure 4.4.1.4 (b)) and high applied bias (Figure 4.4.1.4 (d)), indicating optimizing the co-catalyst thickness on the surface of the BiVO_4 photoanode might be a key point in increasing PEC efficiency with the help of an OEC. In all catalyst loaded samples, the stability of the samples seems to be slightly increased with no current spikes at the point of light being turned on, indicating the surface might indeed have been passivated, or at least the charge carrier transfer or the surface recombination might be limited by the IrO_x co-catalyst, which is possible as evidenced by previous studies [1,70].

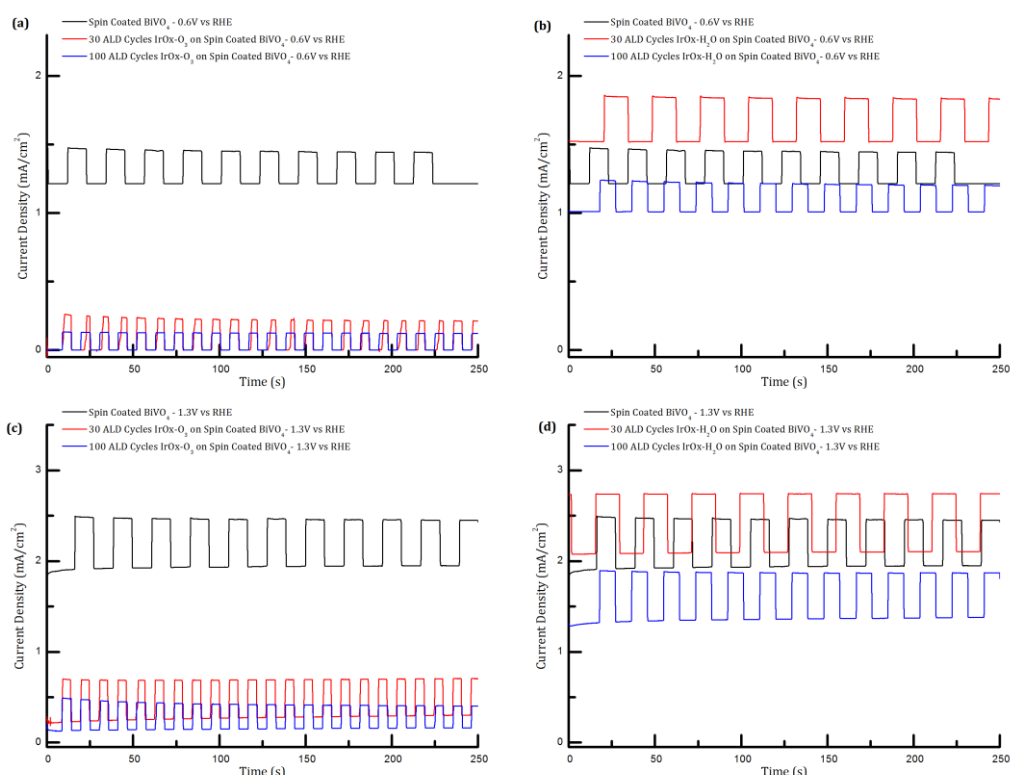


Figure 4.4.1.4: Transient photocurrent density (TPC) vs Time (J-s) currents for Spin Coated BiVO_4 photoanodes with 30 (red) and 100 (blue) ALD cycles of IrO_x catalyst loaded via ozone (a, c) and water oxidizers (b, d). Transient photocurrents are measured under low applied bias of 0.6V vs RHE (a, b) and high applied bias of 1.3V vs RHE (c, d). Electrolyte used for measurements is 1M KPi buffer (pH=7.0) with 0.5M Na_2SO_3 as hole scavenger.

For the hydrothermally-prepared pristine BiVO_4 films, Raman and UV-Vis spectra indicated the presence of monoclinic scheelite structure of BiVO_4 with optical band gap values close to the literature value of ~ 2.4 eV for the bare and iridium oxide co-catalyst loaded samples with varying ALD cycles and oxidizers (Figure 4.4.1.5). It is seen in UV-

Visible Absorption spectra that the absorption edges do not really change throughout this sample set (Figure 4.4.1.5 (b)), and only 100 ALD cycles IrO_x deposited with water oxidizer sample shows slight shift towards visible region in the absorption cut-off, meaning a slight increase in the optical band gap. Raman Spectra shows that all samples show the characteristic peaks of monoclinic scheelite structure of BiVO_4 and no peaks indicating other structures as seen in the samples Figure 4.1.1.5 (a)). When evaluated more closely, 30 ALD cycles IrO_2 loaded with ozone oxidizer on pristine BiVO_4 sample shows a red shift in V-O symmetric stretching mode at 818 cm^{-1} while all the other catalyst loaded samples only show a slight blue shift in comparison to the bare pristine sample (Figure 4.1.1.5 (c)). This trend is also seen for the VO_4^{3-} tetrahedron region, shown in Figure 4.1.1.5 (d), and the drastic change in 30 ALD cycles IrO_2 loaded with ozone oxidizer sample is seen here as the two peaks representing symmetric and asymmetric modes have merged into one peak at 345 cm^{-1} . This merged peak indicates that a different geometry for the VO_4^{3-} is formed in this sample, accompanied by a longer V-O bond length indicated by the blue shift [85,94]. This bond lengthening is seen in all samples; however, no sample shows the drastic change seen in the VO_4 tetrahedron region, indicating presence of a stronger oxidizer like ozone compared to water, might be not only helping oxidize the iridium source but also changing the oxidation states of the surface groups in BiVO_4 photoanode.

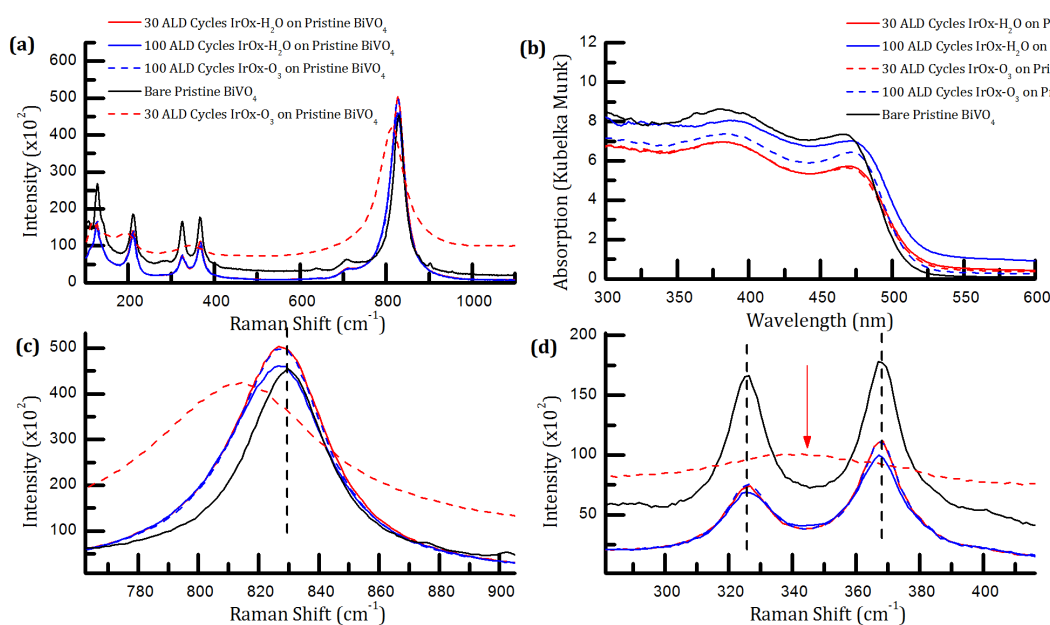


Figure 4.4.1.5: Raman spectra (a) and UV-Visible spectra (b) of Hydrothermally-prepared pristine BiVO_4 photoanode films loaded with IrO_2 co-catalyst via ALD method

using varying ALD cycle numbers (30 (red) and 100 (blue)) and varying oxidizers (ozone (dotted lines) and water (solid lines)). Zoomed in regions for the characteristic Raman shifts of monoclinic BiVO_4 for V-O symmetric stretching at $\sim 820 \text{ cm}^{-1}$ (c) and for VO_4^{3-} tetrahedron's symmetric and asymmetric deformation modes at $\sim 320 \text{ cm}^{-1}$ and $\sim 360 \text{ cm}^{-1}$ (d) are also given for evaluation of peak shifts and changes in sharpness.

Figure 4.4.1.6 shows that no significant activity behavior is observed for the samples in this set under backside illumination compared to their dark currents. However, a slight decrease of 0.2V vs RHE in the onset potentials are observed for the samples with IrO_2 catalyst on their surface for both water and ozone oxidizer case compared to the bare pristine BiVO_4 photoanode. Only for the 30 ALD cycles IrO_x loaded with ozone oxidizer case, a very slight increase in the photocurrent density in the 0.6 – 1.3V vs RHE applied bias region compared to other samples under back illumination. This deviation in the behavior of 30 ALD cycles deposited with ozone oxidizer sample compared to other samples matches with the aforementioned Raman spectra results.

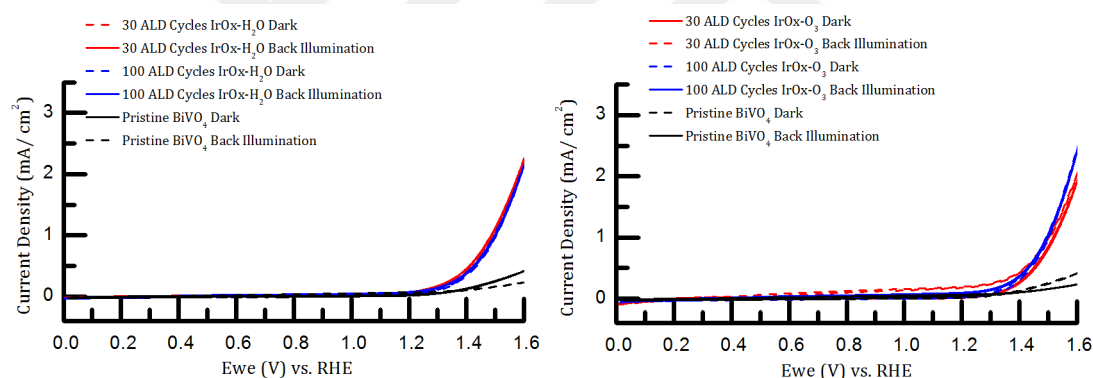


Figure 4.4.1.6: Cyclic Voltammetry (CV) curves for various ALD cycles of IrO_x catalyst loaded on hydrothermally-grown pristine BiVO_4 with water (left) and ozone (right) as the oxidizing precursors. Photocurrent densities are measured in dark (dotted lines) and under backside illumination (solid lines). 30 (red) and 100 (blue) ALD cycles of IrO_x loaded samples are compared with samples without catalyst (black). Electrolyte used for measurements is 1M KPi buffer (pH=7.0) with 0.5M Na_2SO_3 as hole scavenger.

Considering the J-V curves for this set of samples, the TPC curves seem to coincide with the results obtained from them, as well as the Raman spectra observations. Figure 4.4.1.7 shows that even though the photocurrent densities are at around the same values for high (c, d) and low (a, b) applied bias for the samples with varying oxidizers, the ozone

samples show much significant increase in the current densities for thinner catalyst layer (30 ALD cycles) compared to the thicker one than seen for the water samples. This coincides with the observation that ozone oxidized IrO_2 loaded BiVO_4 photoanodes show more significant changes in their structures as indicated by the blue shifts in their Raman peaks. Also, it is seen that the current spikes seen at the moment of illumination that are relieved into steady state current are more pronounced in the water oxidized samples at low applied bias (b) compared to the ozone oxidized samples at the same applied voltage (a). This indicates that the formation of photoinduced charge carriers on the surface is high in water oxidized samples, however their lifetimes are short, leading to the conclusion that the surface recombination might not be limited as well as it is in ozone oxidized samples showing better stability over the same period of time. This difference might be caused by the possible change in the BiVO_4 photoanode structure itself caused by the strong ozone oxidizer, as also indicated by the physical characterizations.

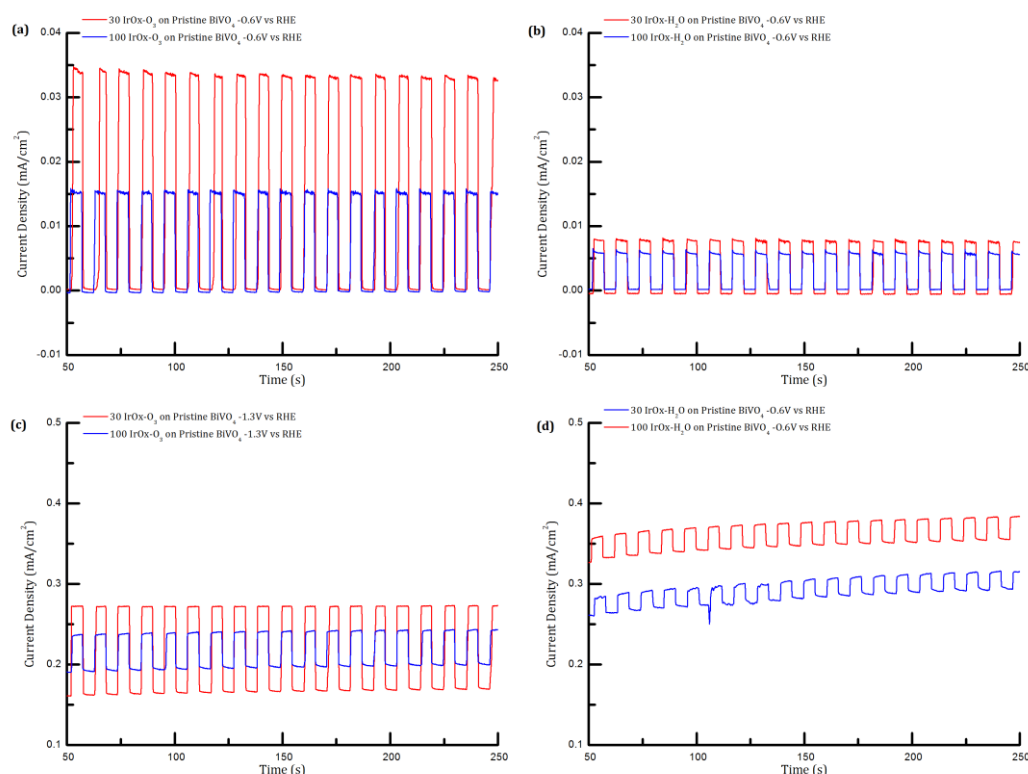


Figure 4.4.1.7: Transient photocurrent density (TPC) vs Time (J-s) currents for Pristine BiVO_4 photoanodes with 30 (red) and 100 (blue) ALD cycles of IrO_x catalyst loaded via ozone (a, c) and water oxidizers (b, d). Transient photocurrents are measured under low applied bias of 0.6V vs RHE (a, b) and high applied bias of 1.3V vs RHE (c, d).

Electrolyte used for measurements is 1M KPi buffer (pH=7.0) with 0.5M Na₂SO₃ as hole scavenger.

For the hydrothermally-prepared 2.0at% W-doped BiVO₄ films, Raman and UV-Vis spectra indicated the monoclinic scheelite structure of BiVO₄ with optical band gap values close to the literature value of ~2.4 eV for the bare and Iridium oxide co-catalyst loaded samples with varying ALD cycles and oxidizers (Figure 4.4.1.8). As seen in Figure 4.4.1.8 (b), no significant change is detected in the absorption edges, thus optical band gaps are unchanged for the samples in this set. When Figure 4.4.1.8 (b, c, d) are evaluated, it is seen that only 100 ALD cycles IrO_x loaded with water oxidizers on 2.0at% W-doped BiVO₄ sample shows slight red shift, indicating slight decrease in V-O bond length for this sample. The samples prepared with ozone oxidizers also show slight merging of the VO₄³⁻ deformation modes compared to other samples, coinciding with the effect using a strong oxidizer on the BiVO₄ photoanodes observed in the previous sample sets.

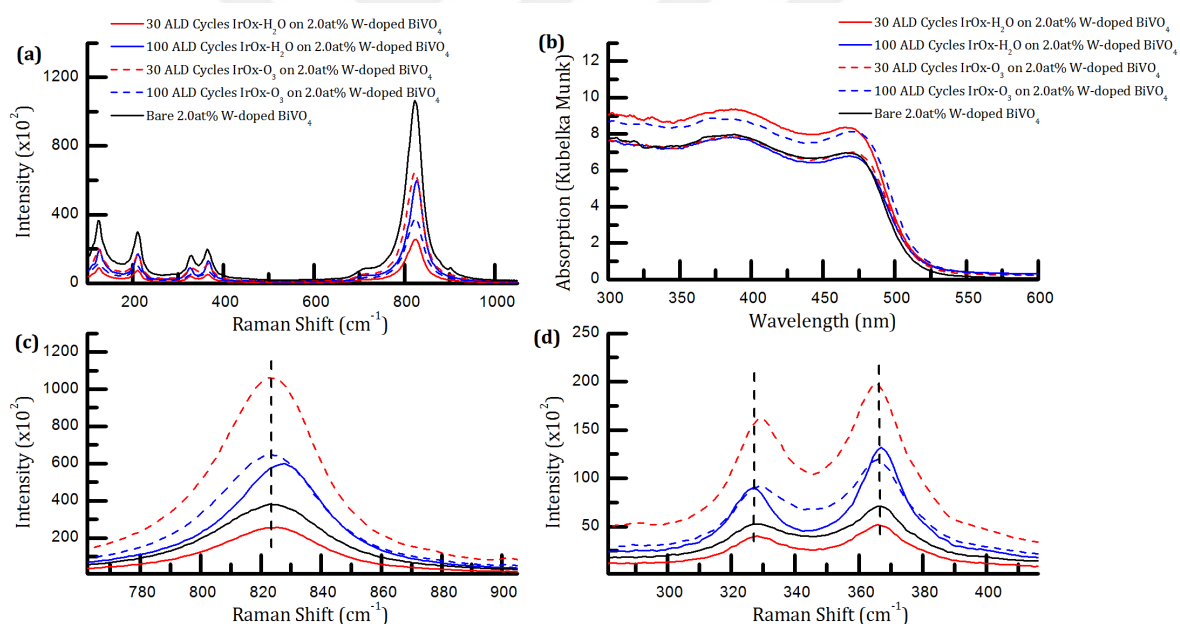


Figure 4.4.1.8: Raman spectra (a) and UV-Visible spectra (b) of Hydrothermally-prepared 2.0at% W-doped BiVO₄ photoanode films loaded with IrO₂ co-catalyst via ALD method using varying ALD cycle numbers (30 (red) and 100 (blue)) and varying oxidizers (ozone (dotted lines) and water (solid lines)). Zoomed in regions for the characteristic Raman shifts of monoclinic BiVO₄ for V-O symmetric stretching at ~820 cm⁻¹ (c) and for VO₄³⁻ tetrahedron's symmetric and asymmetric deformation modes at ~320 cm⁻¹ and ~360 cm⁻¹ (d) are also given for evaluation of peak shifts and changes in sharpness.

Photocurrent density – voltage (J-V) curves for this sample set matches with the previous sample sets as well as the physical characterization results for this set, indicating higher increase in the photocurrent densities in the activity behavior region of 0.6-1.2V vs RHE for the water oxidized samples compared to the ozone ones by 0.1 mA/cm². For this sample set, unlike the previous samples, the co-catalyst loaded samples showed higher onset potentials compared to the bare samples, and the photocurrent densities are seen to be almost the same as the bare samples with 0.9V and 0.8V vs RHE for water and ozone oxidized sample sets, respectively.

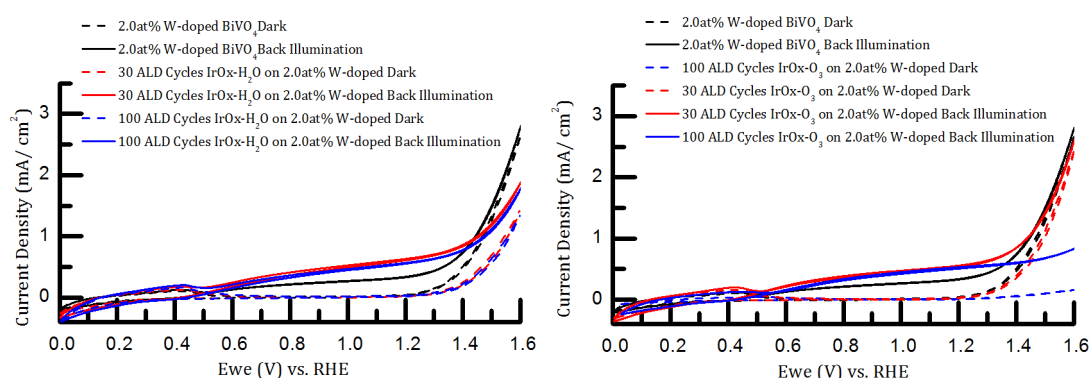


Figure 4.4.1.9: Cyclic Voltammetry (CV) curves for various ALD cycles of IrO_x catalyst loaded on hydrothermally-grown 2.0at% W-doped BiVO₄ with water (left) and ozone (right) as the oxidizing precursors. Photocurrent densities are measured in dark (dotted lines) and under backside illumination (solid lines). 30 (red) and 100 (blue) ALD cycles of IrO_x loaded samples are compared with samples without catalyst (black). Electrolyte used for measurements is 1M KPi buffer (pH=7.0) with 0.5M Na₂SO₃ as hole scavenger.

Consistent with the previous sample sets, Figure 4.4.1.10 shows that ozone oxidized samples show higher stability compared to the water oxidized samples, indicated by the less pronounced spikes that occur at the moment of light being turned on for the ozone samples. Again, similar to previous sample sets, all the samples in this set shows similar photocurrent densities at low (a, c) and high (b, d) applied bias for both oxidizing agent samples, and the increase in the photocurrent densities compared to bare is more significant for the ozone samples compared to water ones. However, only in the ozone oxidized samples at low applied voltage (4.4.1.10 (a)), 100 ALD cycle sample shows

higher photocurrent than the 30 ALD cycles sample. This deviation in behavior might also be related to the use of strong oxidizing agent ozone.

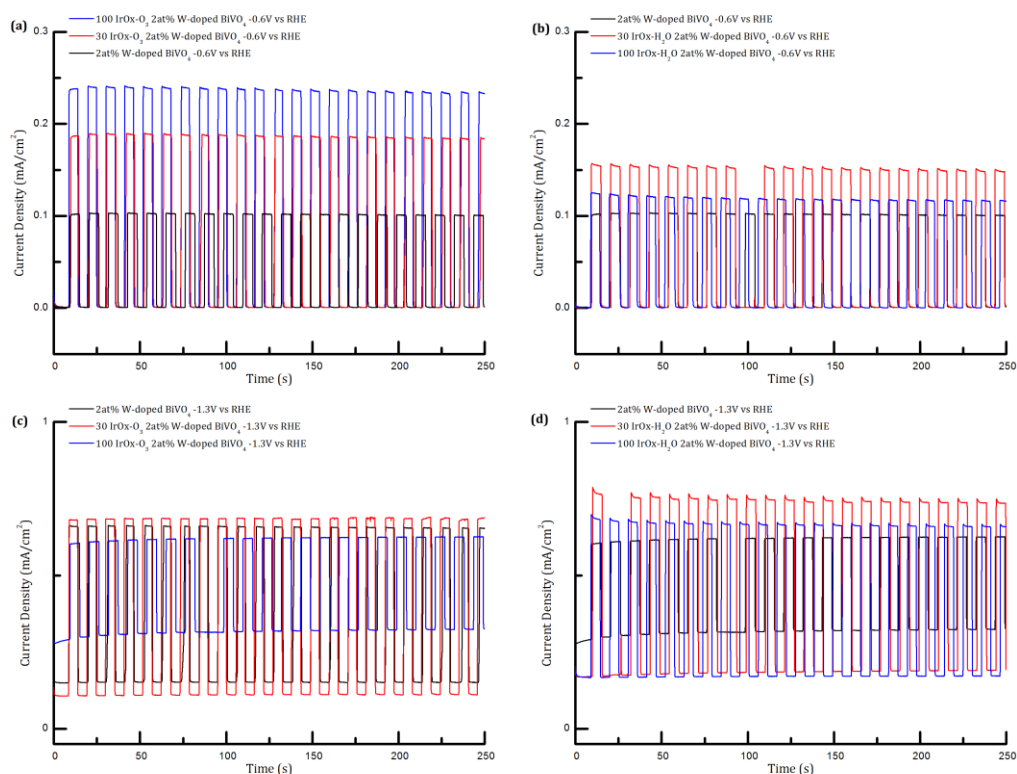


Figure 4.4.1.10: Transient photocurrent density (TPC) vs Time (J-s) currents for 2.0at% W-doped BiVO₄ photoanodes with 30 (red) and 100 (blue) ALD cycles of IrO_x catalyst loaded via ozone (a, c) and water oxidizers (b, d). Transient photocurrents are measured under low applied bias of 0.6V vs RHE (a, b) and high applied bias of 1.3V vs RHE (c, d). Electrolyte used for measurements is 1M KPi buffer (pH=7.0) with 0.5M Na₂SO₃ as hole scavenger.

For the hydrothermally-prepared 1.5at% W-doped BiVO_4 films, Raman and UV-Vis spectra indicated the monoclinic scheelite structure of BiVO_4 with optical band gap values close to the literature value of ~ 2.4 eV for the bare and Iridium oxide co-catalyst loaded samples with varying ALD cycles and oxidizers (Figure 4.4.1.11). When the Raman spectra is evaluated more closely, it is seen that again only the 100 ALD cycle IrO_x loaded with water oxidizer sample shows slight red shift in the V-O symmetric stretching peak at ~ 840 cm^{-1} , indicating a shortening in the V-O bond, like the 2.0at% W-doped BiVO_4 photoanodes case. This indicates that W-doped BiVO_4 photoanodes are influenced by the co-catalyst loading slightly differently than pristine samples, possibly since doping is also affecting the V-O bond in the crystal lattice of BiVO_4 . Other than this sample, no significant shift in the characteristic peaks are visible for the various samples in this set (Figure 4.4.1.11 (c, d)).

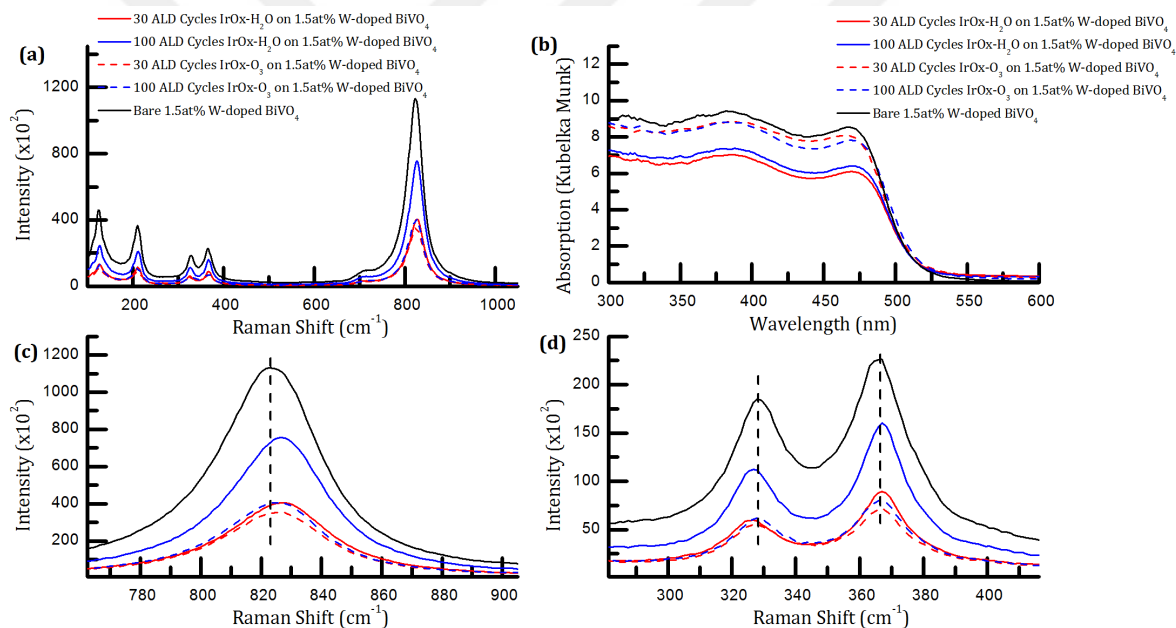


Figure 4.4.1.11: Raman spectra (a) and UV-Visible spectra (b) of Hydrothermally-prepared 1.5at% W-doped BiVO_4 photoanode films loaded with IrO_2 co-catalyst via ALD method using varying ALD cycle numbers (30 (red) and 100 (blue)) and varying oxidizers (ozone (dotted lines) and water (solid lines)). Zoomed in regions for the characteristic Raman shifts of monoclinic BiVO_4 for V-O symmetric stretching at ~ 820 cm^{-1} (c) and for VO_4^{3-} tetrahedron's symmetric and asymmetric deformation modes at ~ 320 cm^{-1} and ~ 360 cm^{-1} (d) are also given for evaluation of peak shifts and changes in sharpness.

Cyclic voltammetry curves for the 1.5at% W-doped sample set shows that for water oxidized samples, 30 and 100 ALD cycles IrO_2 loaded ones show the same activity behavior and photocurrent densities in 0.6V-1.3V vs RHE region, which is $\sim 0.3 \text{ mA/cm}^2$ higher compared to the photocurrent density observed for the bare sample under backside illumination (Figure 4.4.1.12). The onset potentials for the catalyst loaded samples are seen to have shifted towards lower anodic potentials as well. It is also seen that for ozone oxidized samples, 100 ALD cycles loaded sample shows the highest photocurrent density of $\sim 1.0 \text{ mA/cm}^2$, followed by 30 ALD cycles loaded and bare samples at the same current density value of $\sim 0.6 \text{ mA/cm}^2$ at 1.23V vs RHE applied bias. 100 ALD cycles catalyst loaded sample shows a shift in the onset potential towards lower anodic potentials compared to the other two samples in the ozone oxidized sample set, much like the trend seen in the water oxidized sample set for the 1.5at% W-doped BiVO_4 photoanodes. The 100 ALD cycle IrO_2 loaded samples showed higher photocurrent densities in the set for 1.5at% W-doped samples, unlike any of the previous sample sets for this co-catalyst loading study, This high PEC activity behavior is also in accordance with the slight red shift seen for these samples in their Raman spectra, which are not observed this clearly for the other sample sets, indicating increasing crystal lattice distortion in the structure, therefore easier delocalization and transfer of electrons throughout the sample during photocatalytic reactions [56].

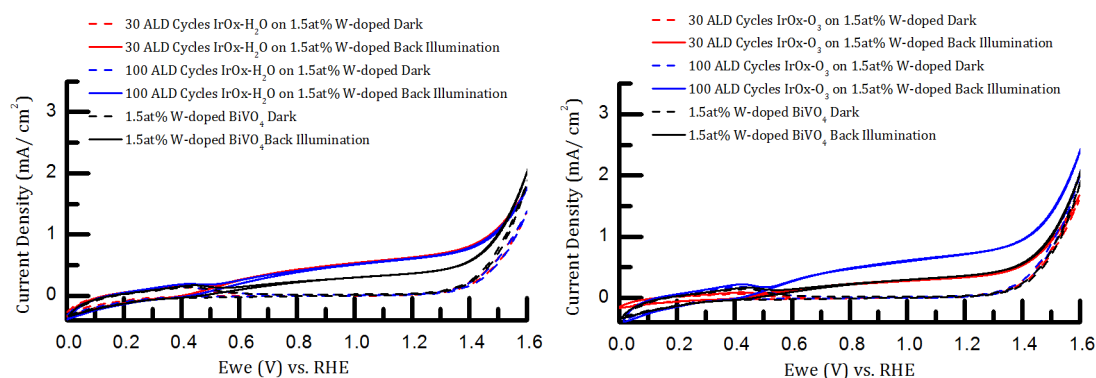


Figure 4.4.1.12: Cyclic Voltammetry (CV) curves for various ALD cycles of IrO_x catalyst loaded on hydrothermally-grown 1.5at% W-doped BiVO_4 with water (left) and ozone (right) as the oxidizing precursors. Photocurrent densities are measured in dark (dotted lines) and under backside illumination (solid lines). 30 (red) and 100 (blue) ALD cycles of IrO_x loaded samples are compared with samples without catalyst (black).

Electrolyte used for measurements is 1M KPi buffer (pH=7.0) with 0.5M Na₂SO₃ as hole scavenger.

Transient photocurrent (TPC) measurements for this sample set is seen to be in agreement with the J-V curves obtained, indicating increased photocurrents for the 100 ALD cycle loaded samples at low (a) and high (b) applied bias for ozone oxidized sample, and for water oxidized samples the difference between the 30 and 100 ALD cycle loaded samples are seen to be decreased compared to previous sample sets. Similar to previous sets, the stability of the ozone oxidized samples is seen to be better compared to water oxidized ones, indicated by the less pronounced spikes under initial illumination moment. Also, the life time of the accumulated holes generated by light absorption is seen to be decreased for the 1.5at% W-doped samples with water oxidized ALD IrO₂ co-catalyst loaded onto their surfaces under low and high bias (b, d) compared to the 2.0at% W-doped samples, indicating that n-doping and co-catalyst loading effects need to be optimized if they are to be applied together as their joint influence might different from their individual effect on the activity behavior and photocurrent densities of BiVO₄ photoanodes.

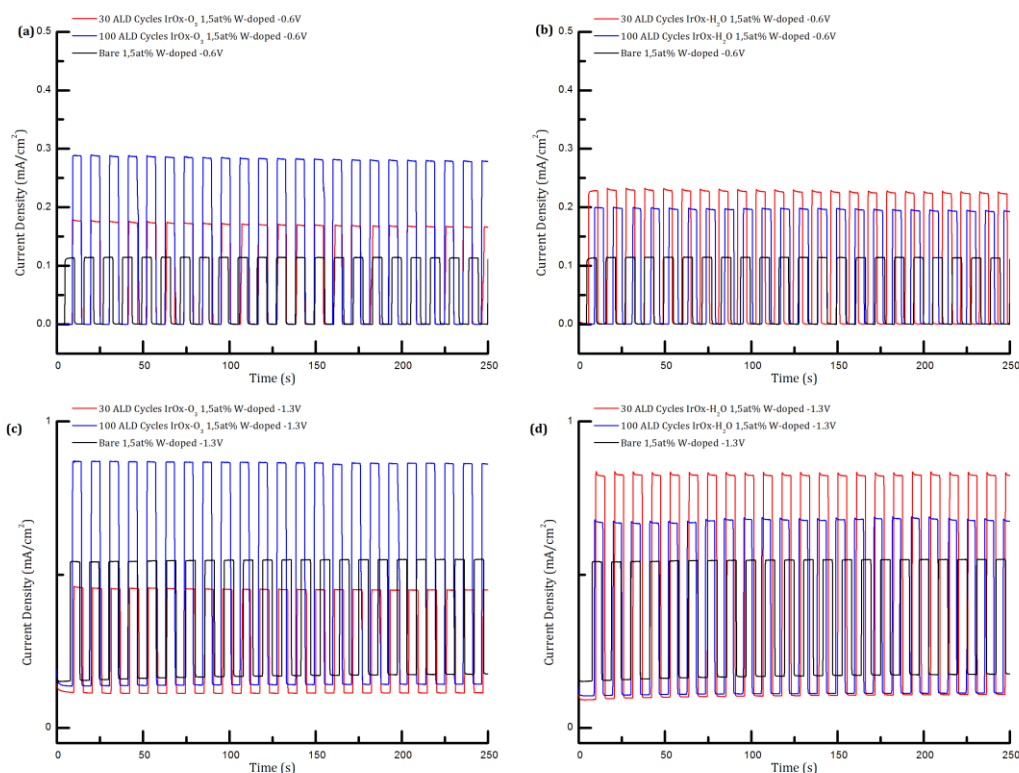


Figure 4.4.1.13: Transient photocurrent density (TPC) vs Time (J-s) currents for 1.5at% W-doped BiVO₄ photoanodes with 30 (red) and 100 (blue) ALD cycles of IrO_x

catalyst loaded via ozone (a, c) and water oxidizers (b, d). Transient photocurrents are measured under low applied bias of 0.6V vs RHE (a, b) and high applied bias of 1.3V vs RHE (c, d). Electrolyte used for measurements is 1M KPi buffer (pH=7.0) with 0.5M Na₂SO₃ as hole scavenger.

4.4.2 Effect of Post-Heat Treatment:

For the BiVO₄ photoanodes that are prepared with the spin coating method that are used for comparison with hydrothermally-prepared photoanodes in the co-catalyst loading effect as demonstrated in the previous section, a study for the effect of post-heat treatment on catalyst loaded samples were also conducted. In this study, 30 and 50 ALD cycles IrO_x loaded spin coated BiVO₄ photoanodes were prepared with water as the oxidizer in the ALD process. These samples, along with spin coated photoanodes without any catalyst loaded, were heat treated at 200°C for 1h under oxygen flow. It was seen that post-heat treatment significantly increased the effect of co-catalyst on the BiVO₄ photoanodes in terms of increased photocurrents and on set potentials that are shifted to lower anodic potentials. It is seen that for both heat-treated and as prepared bare BiVO₄ samples, ~0.81 mA/cm² at 1.23V vs RHE are obtained under backside illumination. However, when the Iridium catalyst loaded samples are heat treated under oxygen flow, the increase in the potentials that indicate that presence of co-catalyst is indeed increasing the PEC activities are much more pronounced. Figure 4.4.2.1 (b) shows that 30 ALD cycles IrO_x coated sample has 1.08 mA/cm² and 50 ALD cycles coated sample has 0.98 mA/cm² at 1.23V vs RHE potential; whereas (a) shows that 30 ALD cycles coated sample has 1.73 mA/cm² and 50 ALD cycles coated sample has 1.23 mA/cm² at 1.23V vs RHE potential. This indicates that post-heat treatment under oxygen flow almost doubles the positive influence IrO_x catalyst provides on the surface of these BiVO₄ photoanodes. The most probable reason behind this might be that IrO_x that is loaded onto the surface by using water oxidant is thoroughly oxidized by the post heat treatment under O₂ flow. This would provide well distributed metal oxide on the photoanode surface without any unoxidized iridium that might lead to hole blockage, thus a decrease in the photocurrents. It would in fact allow the co-catalyst to perform its role in improving charge separation and allowing surface accumulated holes to be used more efficiently in the oxygen evolution reaction. However, completing the oxidation of all the iridium loaded to the surface might not be the only effect this post-heat treatment under oxygen flow has on the

photoanodes. It is seen that although the photocurrents for the backside illumination of heat treated and as prepared bare BiVO_4 samples are almost the same, the onset potential is seen to be lowered for the heat-treated sample. It is seen that the onset is shifted from $\sim 0.60\text{V}$ vs RHE to 0.45V vs RHE, leading us to believe that oxygen treatment might be improving the BiVO_4 based photoanodes in itself, thus allowing for other improvement methods such as co-catalyst loading, to be expressed more intensely in the PEC activities. The exact nature of this improvement is not known yet, however one observation can be made that the oxidation peak at around 0.45V vs RHE in Figure 4.4.2.1 (b) seems to disappear after the post heat treatment, indicating that surface of BiVO_4 itself could be oxidized and leading to an improvement in the onset potentials for this reason. Further investigation on the effect of post-heat treatment on BiVO_4 -photoanodes as bare and IrO_x co-catalyst loaded should be conducted for various preparation methods of BiVO_4 photoanodes to gain more insight on this matter.

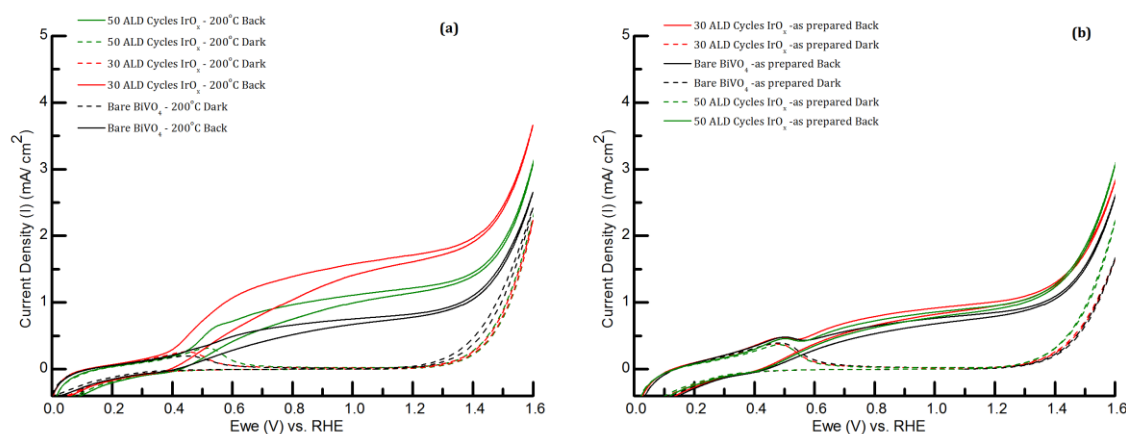


Figure 4.4.2.1: Photocurrent density – potential (J-V) curves for the bare (black), 30 (red) and 50 (green) ALD cycles IrO_x loaded spin coated BiVO_4 samples with (a) and without (b) post-heat treatment at 200°C for 1h under oxygen flow. Cyclic voltammetry measurements are taken in dark (dotted lines) and under backside illumination (solid lines). Electrolyte used for measurements is 1M KPi buffer (pH=7.0) with 0.5M Na_2SO_3 as hole scavenger.

4.5 Effect of Surfactant Use on pristine BiVO_4 photoanodes:

4.5.1 Effect of various surfactants during hydrothermal synthesis reaction:

During the studies optimizing the conditions for the hydrothermal synthesis of BiVO_4 photoanode films with improved efficiency, effect of using varying surfactants

other than ethylene glycol that is initially determined for the synthesis protocol. The significant effect that various surfactants have on the morphology of hydrothermally grown BiVO_4 films on substrates such as FTO coated glass that is used in this study has been well documented in the literature [1,41,49,93,96]. Considering the literature and the investigations presented so far in this study, it was decided to investigate the effect of varying templating agent on morphology and PEC activities by using the two most commonly used surfactants for hydrothermal synthesis of BiVO_4 other than ethylene glycol (EG) that is initially used for all the sample preparation so far, hexadecyltrimethylammonium bromide (CTAB) and polyvinylpyrrolidone (PVP).

In Raman spectra for pristine BiVO_4 photoanode films prepared by adding only ethylene glycol (EG) as indicated by the protocol that has been followed so far, as well the ones prepared by adding both CTAB and EG, only CTAB, both PVP and EG, and only PVP, all the peaks assigned were attributed to the monoclinic scheelite structure of BiVO_4 . This indicates that crystal structure does not change by varying templating agent (Figure 4.5.1.1). The peaks assigned for the full Raman spectra for the sample with only CTAB, only PVP, EG+CTAB, EG+PVP and only EG in the hydrothermal synthesis solution are as follows: the sharp characteristic peaks attributed to $\nu_s(\text{V-O})$ symmetric stretching modes are at 830.3 , 829.1 , 827.9 , 824.2 , 820.6 cm^{-1} , respectively, with shoulders at 707.4 cm^{-1} and 643.8 cm^{-1} ; 709.8 cm^{-1} and 640.1 cm^{-1} , 711.1 cm^{-1} and 640.0 cm^{-1} ; 711.1 cm^{-1} and 640.0 cm^{-1} ; 706.1 cm^{-1} and 640.0 cm^{-1} representing anti-symmetric stretching modes, $\nu_{as}(\text{V-O})$, respectively [85]. The symmetric A_g bending mode of vanadate ion $\delta_s(\text{VO}_4^{3-})$ and anti-symmetric B_g bending mode of vanadate ion $\delta_{as}(\text{VO}_4^{3-})$ are near 368.5 cm^{-1} and 325.5 cm^{-1} , respectively, for all the samples [85,86].

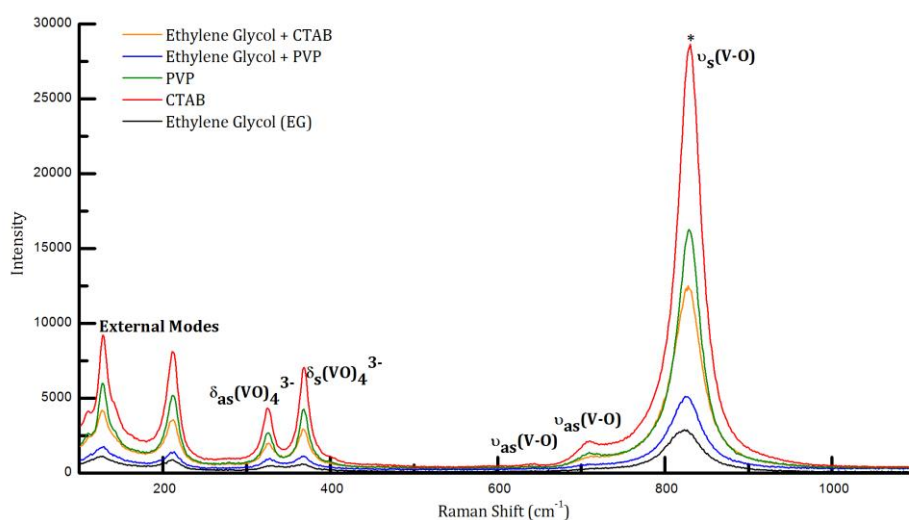


Figure 4.5.1.1: Raman spectra for BiVO₄ grown with varying templating agents in the hydrothermal reaction: both ethylene glycol (EG) and CTAB additive (orange), both EG and PVP additive (blue), only CTAB additive (red), only PVP additive (green) and only EG additive (black).

When the deformation modes for VO₄³⁻ tetrahedron and symmetric stretching mode of V-O bond are considered more closely in Figure 4.5.1.2, it is seen that photoanodes prepared with only CTAB and PVP, followed by CTAB+EG and PVP+EG samples show slight red shift compared to the films prepared only with EG. This indicates that the V-O bond is shortened, thus creating a more ordered structure for these the samples by the use of these surfactants. It is also seen from the FWHM values of the symmetric stretching mode for V-O bond at ~830 cm⁻¹ (Table 4.5.1.1) that this value is decreased considerably by use of CTAB and PVP along with EG, as well as their singular use in the hydrothermal synthesis. This indicates that the use of CTAB and PVP increases the crystallinity of the pristine BiVO₄ films that are grown via hydrothermal method. Indeed, this change is also confirmed by the morphology study conducted via FE-SEM imaging of these photoanodes (Figure 4.5.1.3).

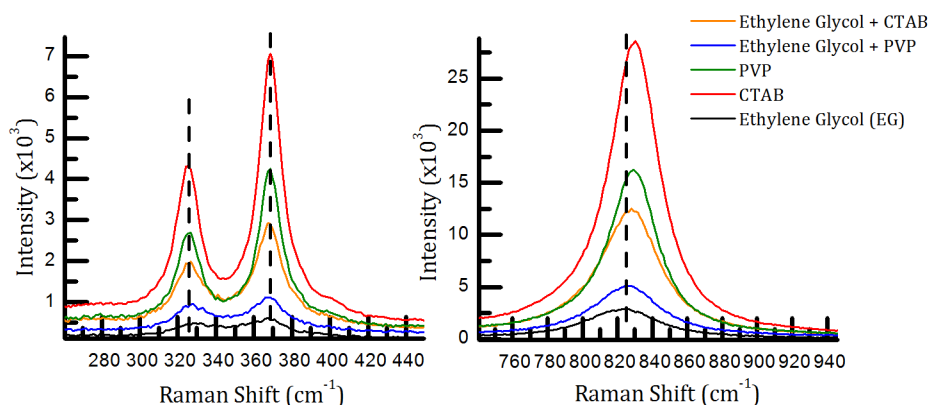


Figure 4.5.1.2: Zoomed in regions of the Raman spectra for BiVO₄ grown with varying templating agents in the hydrothermal reaction: both ethylene glycol (EG) and CTAB additive (orange), both EG and PVP additive (blue), only CTAB additive (red), only PVP additive (green) and only EG additive (black). The low frequency region with symmetric and asymmetric bending modes for VO₄³⁻ tetrahedron (left) and the characteristic symmetric stretching mode for V-O bond at ~820 cm⁻¹ (right) are highlighted.

Sample	FWHM (at $\sim 820\text{ cm}^{-1}$)
Pristine BiVO ₄ with CTAB	34.21
Pristine BiVO ₄ with PVP	33.14
Pristine BiVO ₄ with EG + CTAB	41.05
Pristine BiVO ₄ with EG +PVP	45.55
Pristine BiVO ₄ with EG	51.06

Table 4.5.1.1: Full-width at half-maxima (FWHM) values for the V-O stretching mode at $\sim 820\text{ cm}^{-1}$ of all the samples prepared with varying templating agents in the hydrothermal solution are presented.

FE-SEM images presented in Figure 4.5.1.3 shows that the morphology is much more homogenous and visibly more crystalline in the samples prepared with CTAB only. These samples show a singular geometry of thin 3D squares along the surface with no other shapes, making the morphology much more homogenous than other samples. Early stages for the formation of square 3D plate-like structures is also visible in CTAB+EG case as well, however these are seen to be not as well-defined in particle shape as the only CTAB case, seeing they remained as small particles making up large clusters with less separation between the individual geometries. This might indicate better connectivity between the particles, therefore improved pathway for electron transfer throughout the sample compared to only CTAB case where the crystallinity and visible surface area of the particles are much more improved, yet some degree of connectivity might have been lost between the BiVO₄ particles, therefore creating a possibility for decreased PEC activity for these samples. For the only PVP case, it also seen that the crystallinity and the presence of edges for the particle geometries in the morphology is improved compared to PVP+EG case, since some plate-like structures are visible for only PVP case among the 3D peanut-like morphologies made up of not well-defined smaller particles. Also, for PVP+EG case, it is seen that these peanut-like geometries only reached their early formation phase, remaining as still seemingly well-connected yet larger clusters on the surface. These large clusters and visible non-uniformity throughout the surface morphology are also visible for only EG case. Then, it can be concluded that CTAB has a much stronger influence on directing crystal growth to be better defined, more uniform and well separated than PVP has, while presence of EG in fact promotes crystal growth in a way that provides much better connectivity with smaller edge-less crystals lumped into larger clusters shaped like peanuts [91]. The strong directing ability of CTAB as an effective surfactant to promote self-aggregation into defined uniform crystalline particles with various geometries is

well-documented [50,93,97,98]. In fact, it has been suggested that addition of CTAB to a hydrothermal synthesis solution containing bismuth and vanadium sources might be influenced by the presence of Br in the structure of CTAB, therefore making it not only a templating agent, but also a source of Br which can react and bond with Bi^{3+} ions in the solution. Recently, there were even reports of synthesis routes developed to further control the morphology of BiVO_4 particles in a photoanode film by forming BiOBr first by addition of CTAB and bismuth source first, then addition of vanadium source in water or any solvent [49,93,97]. These studies proposed a mechanism for the interactions inside a solution with CTAB and bismuth sources, suggesting that bismuth ions first reacts and binds to the Br end of the CTAB molecule, being fixed to further react with oxygen and vanadium to form bismuth vanadate and leave the CTAB molecule, and owing to the fixed position of Bismuth ions, the crystal growth for BiVO_4 takes a much strongly directed pathway, therefore leading to higher crystallinity and uniformity in photoanode films produced with CTAB assist [50]. When the obtained FE-SEM images along with Raman spectra for the photoanodes prepared in this study are considered again, this formation mechanism seems to be supported as CTAB addition to the hydrothermal solution even in the presence of another templating agent like EG showed increased crystallinity and uniformity throughout the film surface.

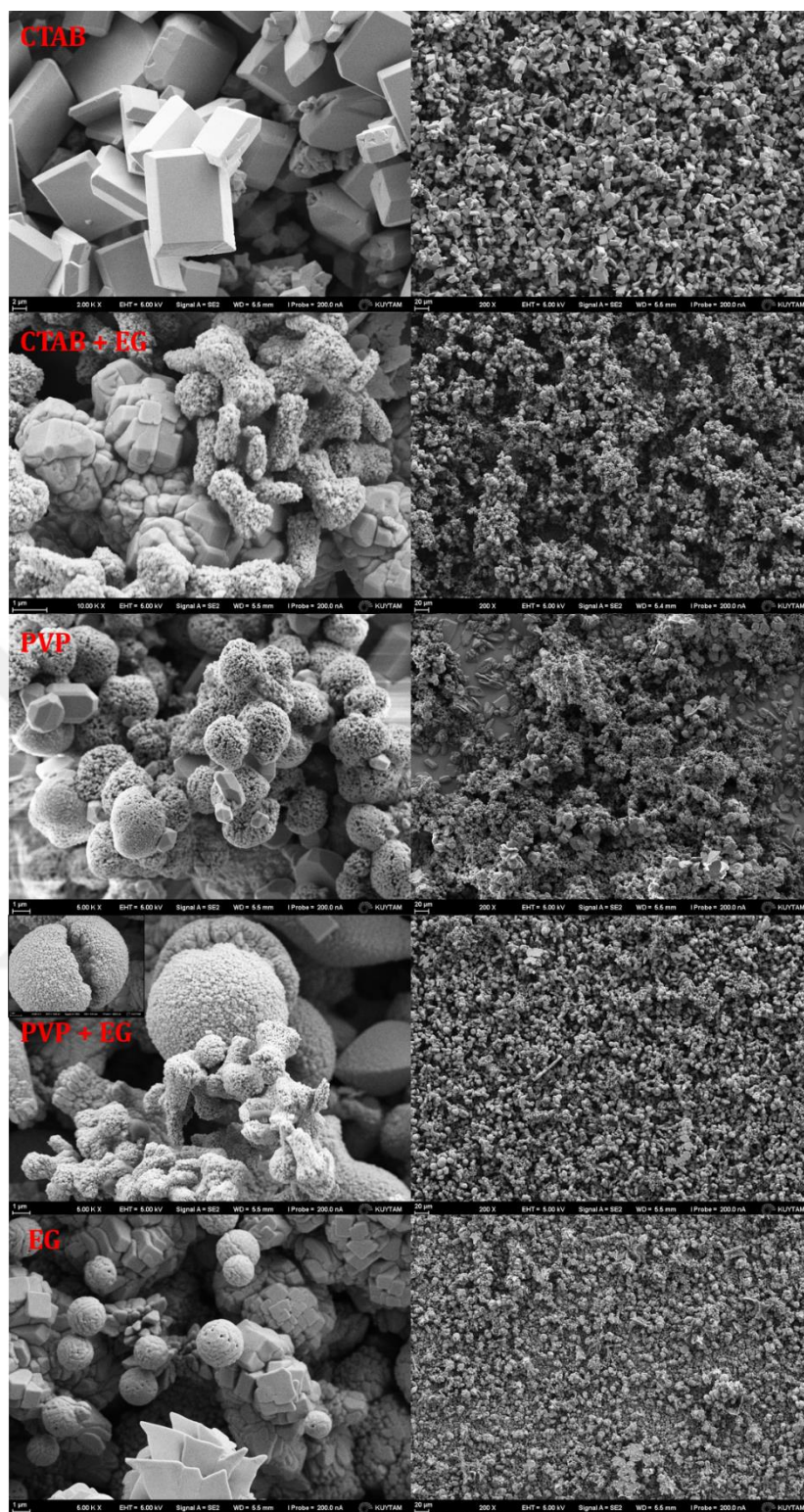


Figure 4.5.1.3: FE-SEM images of the surfaces of pristine BiVO_4 photoanode films prepared via hydrothermal method using various surfactants: (from top to bottom) CTAB, CTAB and EG, PVP, PVP and EG, EG.

In Figure 4.5.1.4, UV-Visible Absorption spectra for the samples prepared with various templating agents are shown, obtained via Kubelka-Munk Transformation of the

Diffuse Reflectance Spectra (DRS) of the samples. It is seen that the absorption edge of only CTAB sample is at the highest wavelength, while CTAB+EG, only PVP and PVP+EG samples are at a slightly lower wavelength than this sample, but still at a higher point than only EG sample. This indicates that, only CTAB sample has slightly larger optical bandgap than all the other samples, followed by samples with CTAB+EG, PVP, PVP+EG samples with around the same optical band gap, and finally only EG sample with the lowest band gap among all the samples. The change in the optical band gap property of the same material with different morphologies can be attributed to the effect of changing crystal size and uniformity, which can influence the defect sites and other physical properties that might participate in the mechanism in which the material absorbs visible light [50]. Therefore, the increase in the light absorption in the visible region for the samples with varying surfactant addition than only EG suggests that band gap is directly affected by the morphology control of the materials. However, all the samples still show optical bandgaps that are appropriate for good light absorption in the visible range to be utilized in PEC water splitting reactions [93].

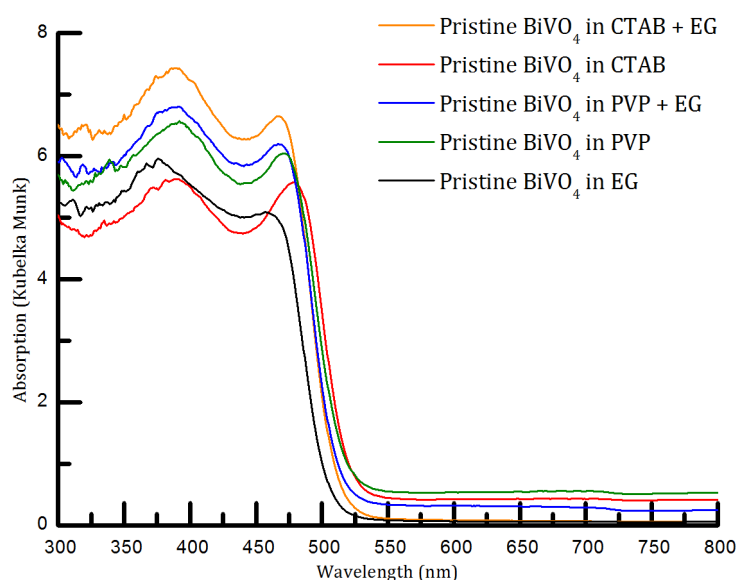


Figure 4.5.1.4: UV-Visible absorption spectra for the pristine BiVO_4 photoanode films grown via hydrothermal method using various surfactants: only CTAB, both CTAB and EG, only PVP, both PVP and EG, only EG. Absorption spectra are obtained via Kubelka-Munk transformation of the measured DRS data of the samples.

In photocurrent density measurements for these samples in dark and under backside illumination, cyclic voltammetry method was used over a potential range of 0.0V

to 1.6V vs RHE. At the first look, Figure 4.5.1.5 shows that no visible improvement in the PEC activity behavior in the 0.6V to 1.23V vs RHE region under backside illumination compared to their dark currents, except for the sample prepared with only PVP as the templating agent. At 1.23V vs RHE, the photocurrent densities for the samples prepared with CTAB only, CTAB+EG, PVP only, PVP+EG and EG only are as follows: 0.0996 mA/cm², 0.1000 mA/cm², 0.3120 mA/cm², 0.1088 mA/cm², 0.0720 mA/cm², respectively. Onset potentials seem to not show any improvement among the samples compared to only EG sample with around 0.6V vs RHE, except for only PVP sample which seems to have onset potential of around 0.4V vs RHE. This indicates that PVP only sample shows the highest amount photogenerated charge carriers with the best charge separation and transfer among all the samples. This finding coincides with the FE-SEM findings indicating better connectivity and higher uniformity in the film prepared with only PVP compared to other films. When the UV-Visible spectra are also taken into account, it can be concluded optical band gap is not as strong of an influence on the PEC activities of pristine BiVO₄ based photoanode films as the uniformity and connectivity of the morphologies, since PVP only sample showed slightly lower optical band gap compared to only CTAB sample. Also, it can be said that crystallinity increase may not always improve the PEC activity as it might also decrease electron mobility throughout the sample by extending charge carrier pathways as indicated by the slight red shift that was seen in the Raman spectra for the samples in the deformation mode region of the VO₄³⁻ tetrahedron region indicating less lattice strain, which is associated with less electron delocalization in the structure as also discussed in the results for the effect of reaction time on pristine and W-doped BiVO₄ photoanodes. However, as was evidenced for the different effect of reaction time on the PEC activities of pristine and W-doped BiVO₄ films earlier, it can be said that the effect of different surfactant use might not show the exact trend that is observed for the pristine samples. Thus, for improving W-doped BiVO₄-based photoanodes prepared using a similar hydrothermal synthesis protocol outlined in this study, further evaluation of the exact nature behind the PEC improvement observed for the different surfactant use during the hydrothermal synthesis reaction, as addition of a dopant might affect the reaction pathway in which the surfactant influences the crystal growth.

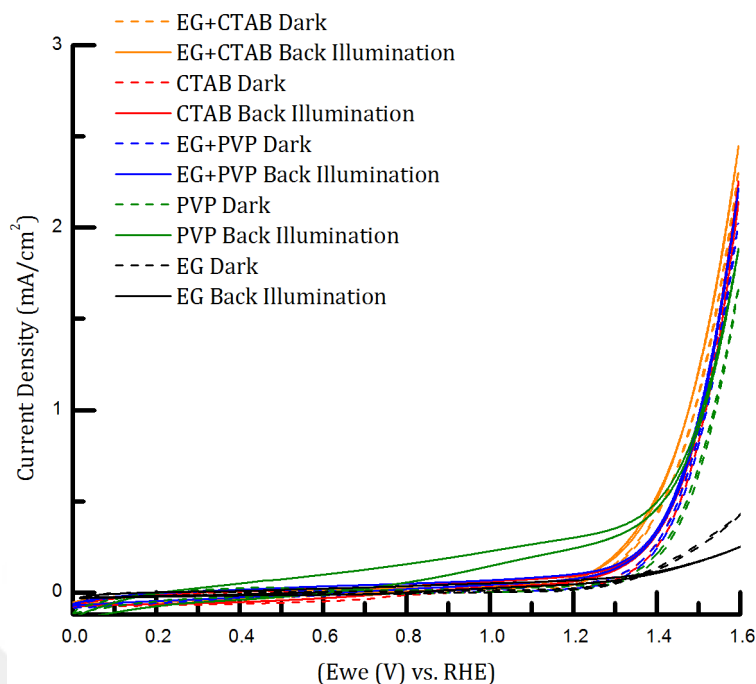


Figure 4.5.1.5: Cyclic voltammetry (CV) curves for the pristine BiVO_4 photoanodes prepared via hydrothermal method with varying templating agents. Electrolyte used for measurements is 1M KPi buffer (pH=7.0) with 0.5M Na_2SO_3 as hole scavenger.

4.5.2 Depositing Hydrothermally-prepared BiVO_4 powders onto the FTO/Glass substrate:

In PEC water splitting studies conducted for BiVO_4 -based photoanode films, there are two common methods to prepare the photoanodes; (i) directly growing the BiVO_4 particles on a substrate such as FTO coated glass that is used in our studies, via methods such as hydrothermal synthesis, electrodeposition etc. and (ii) depositing the already produced BiVO_4 particles on the substrate using techniques such as spin coating, drop casting etc. [34,99,100]. While the BiVO_4 -based photoanodes that are directly grown on the FTO coated glass were being utilized for effect of changing parameters of hydrothermal synthesis reaction, n-doping and co-catalyst loading on the surface, the PEC activities and photocurrents of BiVO_4 powders prepared using the same hydrothermal synthesis protocol fixed on the FTO substrates were also investigated to determine any changes in the physical or electrochemical differences for these type of photoanodes.

Pristine BiVO_4 powders were synthesized using the untuned hydrothermal recipe that is initially described in the experimental section. The BiVO_4 powders that are

obtained from the synthesis was then made into a suspension solution to be drop casted onto the FTO coated surface of the glass substrate. For preparation of a suspension solution from the powders, initially ethanol was used, however these samples did not show good connectivity both among the powder particles and the FTO coated surface of the glass, leading to very non-uniform looking films that immediately peeled off the surface when dipped into the electrolyte for PEC measurements.

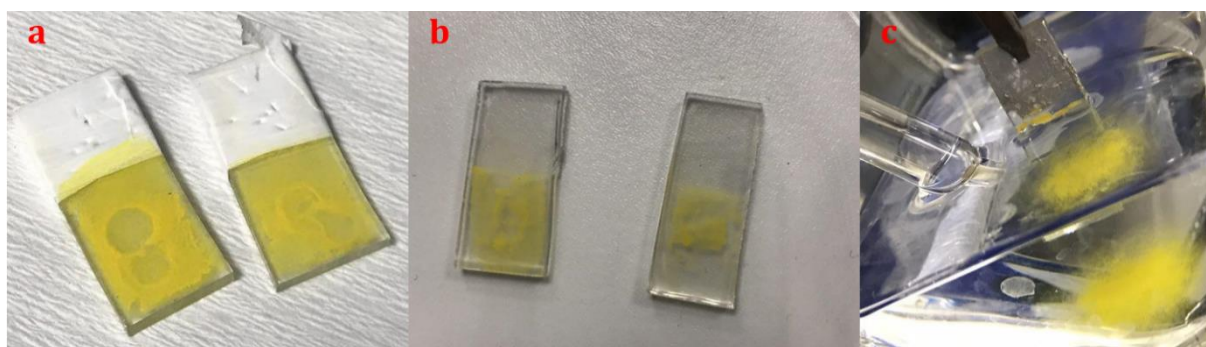


Figure 4.5.2.1: Images of the BiVO_4 photoanode films samples prepared via drop casting a suspension solution of the hydrothermally synthesized BiVO_4 powders in ethanol. Samples are seen before being dried (a), after drying (b) and when dipped into the electrolyte (c) for PEC measurements. (Electrolyte being used is 1M KPi buffer (pH=7.0) with 0.5M Na_2SO_3 as hole scavenger)

Upon these observations, ethylene glycol (EG) was utilized to prepare suspension solutions from the BiVO_4 powders. These solutions immediately showed improved homogeneity for the prepared films when dropcasted, as they also formed much dense suspension solutions. The higher viscosity of EG glycol compared to ethanol might have caused the observed increase in the particle connectivity among the film and between the film and FTO substrate, as the films prepared using EG peeled off only slightly throughout all the various trials performed for this method (Figure 4.5.2.2).

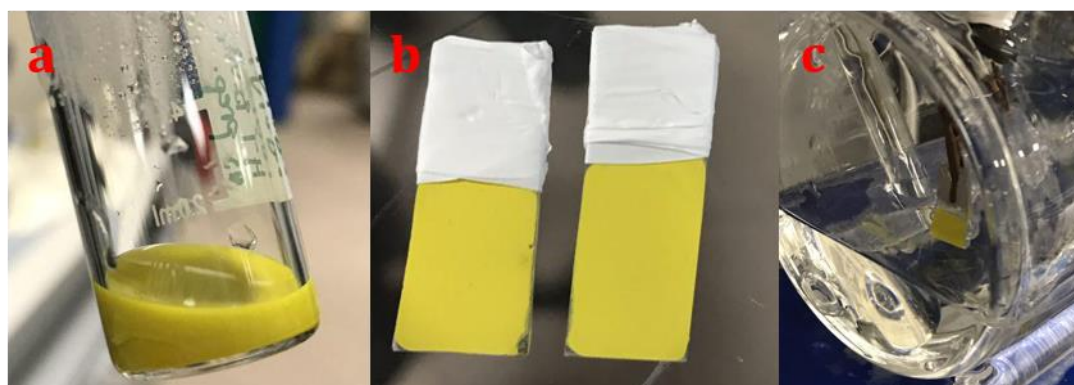


Figure 4.5.2.2: Images of the BiVO₄ photoanode films samples prepared via drop casting a suspension solution of the hydrothermally synthesized BiVO₄ powders in ethylene glycol (EG). The powder in EG suspension solution is seen (a); along with after being drop casted and dried on FTO surface (b) and when dipped into the electrolyte (c) for PEC measurements. (Electrolyte being used is 1M KPi buffer (pH=7.0) with 0.5M Na₂SO₃ as hole scavenger)

Based on these observations, further investigations for the use of powder BiVO₄ in photoanode film production on FTO coated glass substrate were conducted. The effect of film thickness through changing the amount of powder being suspended in a fixed volume of EG solution and the effect of n-dopants, namely W and Mo, into the hydrothermally-prepared powders were investigated. The effect of annealing the powders before and after being deposited onto the FTO surface were also recorded during the experiments.

Powder XRD taken from the pristine BiVO₄ powders showed monoclinic scheelite structure, indicating that using the same hydrothermal procedure both the powders and direct film growth on FTO substrate provides the same structure for BiVO₄ under the same conditions. Along with this, the Grazing Incidence XRD taken from the samples with powders deposited onto FTO substrate showed the same pattern for the monoclinic scheelite structure that is seen for both directly-grown films on the substrate and the powders before being deposited onto the substrate, indicating that after the hydrothermal synthesis of BiVO₄, its crystal structure is not effected by the physical procedures applied to deposit it as a film. For all the samples that are prepared into films, the peak positions are found to be same, except for the loose powder, which shows a slight shift towards higher degrees. This shift can be interpreted as the loose powder, compared to films grown or fixed on FTO substrate, having differing lattice distortion in the structure. However, since this shift is observed for all the peaks of the powder, along with increased intensities, it might be concluded that this shift is caused by the differences in the measurement method for powder XRD, compared to GI-XRD, and powder has higher crystallinity than the films, as expected, since the crystals would be less distorted than inside a BiVO₄ film. It is also seen that annealing the films made by drop casting BiVO₄ powders that are not annealed onto the FTO substrate leads to decreased crystallinity, indicating that the intense sintering of the particles might be creating a counter-effect in the crystallinity [101]. Therefore, annealing of BiVO₄ when only performed once seems to

be an effective tool in improving crystallinity, thus easing the charge transfer pathways for the photogenerated charge carriers to be used in PEC water splitting reactions.

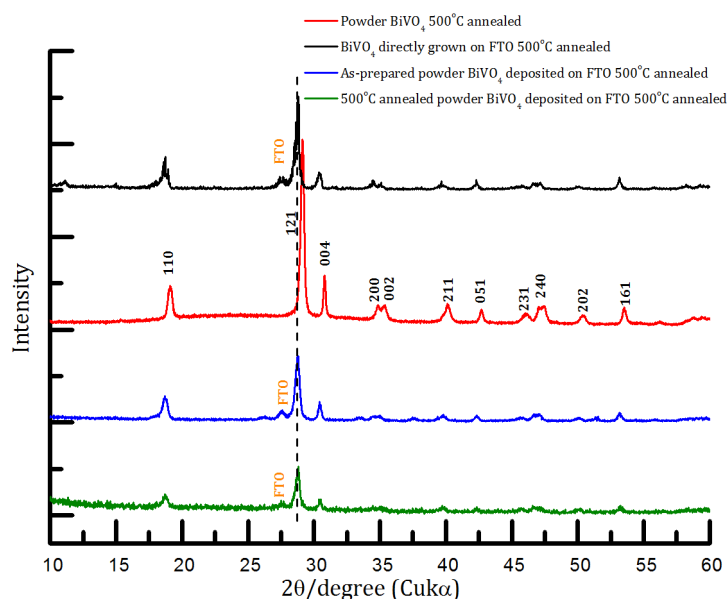


Figure 4.5.2.3: Powder and Grazing-Incidence XRD for the hydrothermally-prepared BiVO_4 photoanodes; fine powder heat treated at 500°C for 2h (red), film directly grown in hydrothermal reactor and heat treated at 500°C for 2h (black), as-prepared powder drop casted onto FTO and heat treated at 500°C for 2h (blue) as well as powder annealed at 500°C for 2h drop casted onto FTO and heat treated again at 500°C for 2h (green) are shown. Standard XRD pattern for monoclinic BiVO_4 with JCPDS 83-1699 pdf number is used.

In Figure 4.5.2.4, it is seen that absorption edges for films prepared from annealed powders and films directly grown on the substrate later to be annealed at the same temperature (500°C for 2h) are seen to be same, while only the as prepared directly grown film of pristine BiVO_4 shows a slight shift to the higher wavelength values, indicating slightly larger optical band gap for not annealed samples. It is well-documented that annealing BiVO_4 prepared via almost any method at 500°C or higher temperatures will change the crystal structure and order of crystallinity, leading to improvements or decrease in prospective PEC activities by influencing the charge carrier pathways, thus charge separation and transfer efficiencies in the photoanodes [97]. Therefore, it can be said that after an initial annealing of BiVO_4 at 500°C will create the well crystalline monoclinic scheelite structure and so long as the temperature remains the same, further annealing will not change the crystal structure of the samples. Only slight decrease in the

crystallinity might be caused by the intense sintering of the particles, as observed in XRD results.

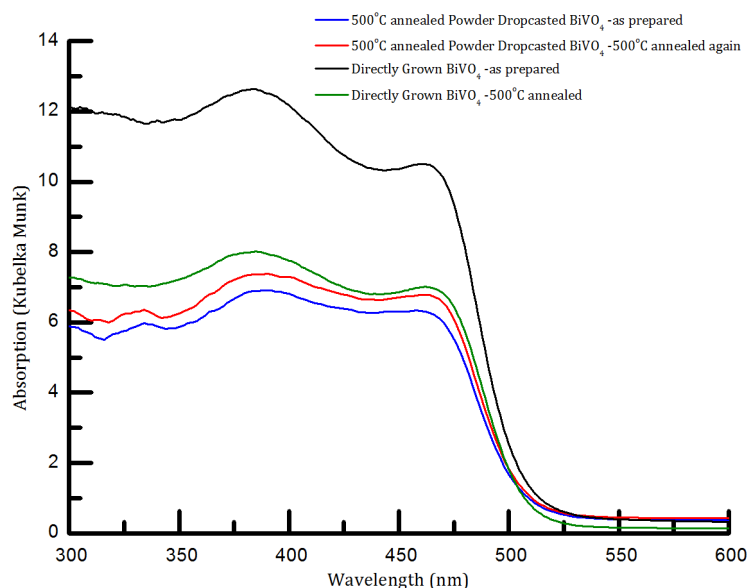


Figure 4.5.2.4: UV-Visible spectra obtained for hydrothermally synthesized BiVO_4 films grown directly on the FTO substrate (black and green) and drop casted onto the FTO substrate from its powder form (red and blue) are presented. For the directly grown films, samples that are heat treated at 500°C for 2h after synthesis (green) and left as-prepared (black) are shown. For the drop casted films, powders annealed at 500°C for 2h were used to prepare the films that are annealed at 500°C for 2h (red) and left as-prepared (blue).

In Figure 4.5.2.5, Raman spectra for a directly grown BiVO_4 and a film prepared by fixing BiVO_4 powder onto the substrate are being compared. As the XRD data also indicated, all the peaks for both samples are attributed to monoclinic scheelite structure of BiVO_4 . The peaks assigned for both spectra are as follows: the sharp characteristic peaks attributed to $\nu_s(\text{V-O})$ symmetric stretching modes are at 826.6 cm^{-1} with shoulder at 711.0 cm^{-1} representing anti-symmetric stretching mode, $\nu_{as}(\text{V-O})$ (68). The symmetric A_g bending mode of vanadate ion $\delta_s(\text{VO}_4^{3-})$ and anti-symmetric B_g bending mode of vanadate ion $\delta_{as}(\text{VO}_4^{3-})$ are near 367.0 cm^{-1} and 328.0 cm^{-1} , respectively(68,69). It is also seen that for the sample prepared from the powder, the relative peak intensities and sharpness are greater than the one that is directly grown on the substrate. This indicates that the crystallinity of the powder sample is increased compared to directly grown sample, however the crystal structures remain the same for both samples as no significant peak shift is observed in the Raman spectra. These outcomes also agree with the XRD

results which indicated increased crystallinity for powder samples but no change in crystal structure.

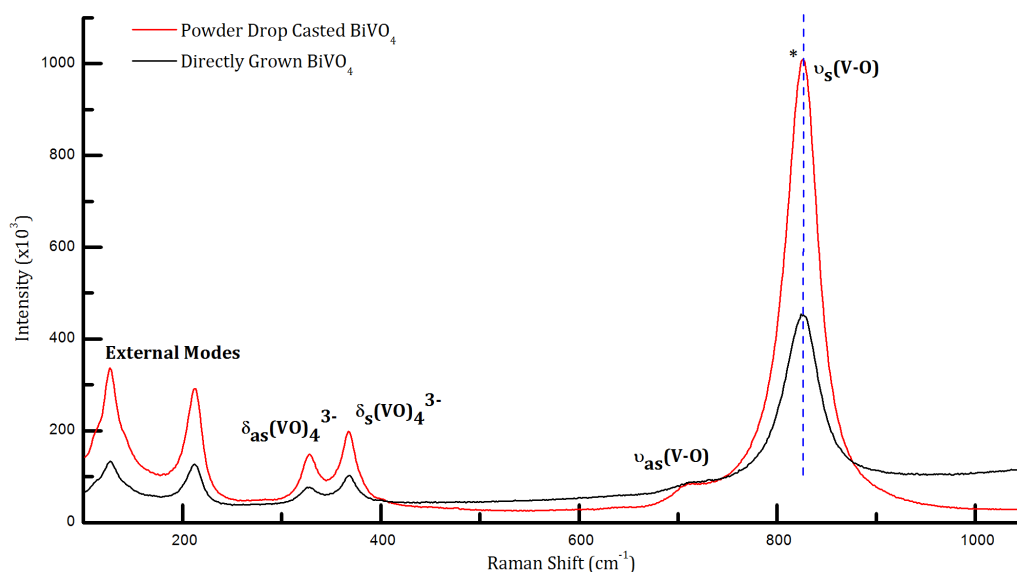


Figure 4.5.2.5: Raman spectra for the pristine BiVO₄ films prepared by directly growing the film on FTO substrate (black) and fixing the powder form onto FTO substrate (red) using hydrothermal synthesis method.

Considering the physical characterizations, PEC activities for both powder-drop casted and directly grown pristine BiVO₄ are expected to be close to each other in dark and under illumination. In Figure 4.5.2.6, the photocurrents obtained from these samples in dark and under backside illumination showed that for both samples no visible activity behavior in the applied potential range of 0.0V-1.6V vs RHE is observed. For both samples the onset potentials seem to be quite large for both measurement conditions, however for the powder deposited sample, it is seen that the onset potential is decreased by 0.2 V vs RHE, compared to the 1.4V vs RHE onset of the directly grown sample. The low activity and high onset potential are both observed for all the pristine BiVO₄ photoanodes prepared by hydrothermal method in this study, therefore the low activities here might be caused by the intrinsic limitations of pristine BiVO₄.

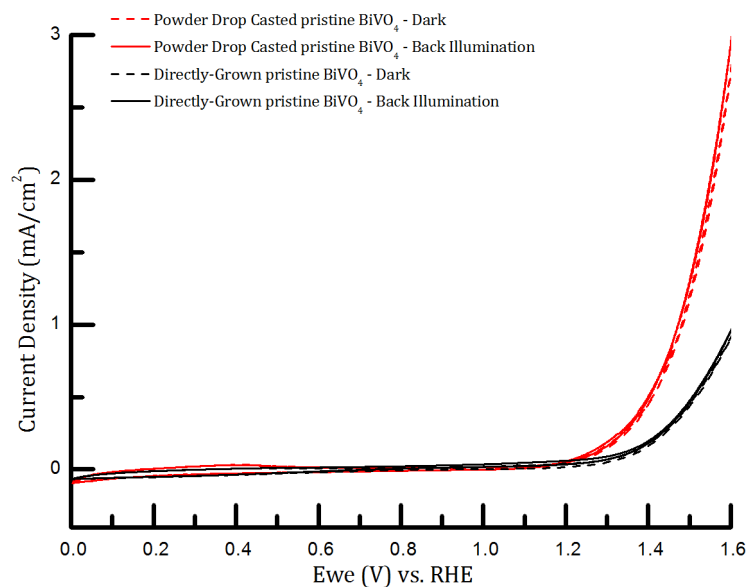


Figure 4.5.2.6: Photocurrent density – applied potential (J-V) curves for powder deposited (red) and direct growth (black) films of pristine BiVO_4 photoanodes obtained via cyclic voltammetry measurements under dark (dotted lines) and backside illumination (solid lines). Electrolyte used for measurements is 1M KPi buffer (pH=7.0) with 0.5M Na_2SO_3 as hole scavenger.

After the first observation that the low photocurrent densities measured from drop casted samples might be caused by the limiting nature of BiVO_4 for the efficient charge carrier separation and high surface charge recombination leading to low PEC activities, the powders were added with n-dopants, namely W and Mo, to overcome these disadvantages. Doping is known to significantly improve pec activity for reasons such as increasing conductivity, suppressing hole recombination on the photoanode surface by increasing charge carrier transport and separation efficiency [80]. This method was employed since significant improvements for measured photocurrent densities under backside illumination were obtained for the W-doped directly grown BiVO_4 films prepared via hydrothermal method previously. During hydrothermal synthesis of the powders, 2at% Mo and 2at% W doped powders were prepared and drop casted onto FTO substrates. It is seen from Raman spectra presented in Figure 4.5.2.6 (b) that for all the samples; W-doped, Mo-doped and pristine, monoclinic scheelite structure of BiVO_4 is obtained. The peaks that are attributed to the said structure are such that; the sharp characteristic peaks attributed to $\nu_s(\text{V-O})$ symmetric stretching modes are at 826.6 cm^{-1} with shoulder at 711.0 cm^{-1} representing anti-symmetric stretching mode, $\nu_{as}(\text{V-O})$ (68). The symmetric A_g bending mode of vanadate ion $\delta_s(\text{VO}_4^{3-})$ and anti-symmetric B_g bending

mode of vanadate ion $\delta_{as}(\text{VO}_4^{3-})$ are near 367.0 cm^{-1} and 328.0 cm^{-1} , respectively(68,69). When the deformation modes of VO_4^{3-} tetrahedron for both W-doped and Mo-doped samples are considered, a slight red shift in the symmetric bending mode and a slight blue shift in the asymmetric one is observed for both samples compared to the pristine BiVO_4 , though the shift is not very clear due to the saturation of the peaks, possibly caused by the sample thickness and strict packing of the powder. The shift might be due to distortion of the VO_4^{3-} tetrahedron by incorporation of W and Mo dopants to replace some the V^{5+} ions and change the lattice distortion in the structure. It is also seen that W-dopant shows this change more significantly than Mo-dopant, which can be attributed to the larger ionic size of W^{6+} compared to Mo^{6+} , thus leading to larger distortion in the crystal structure compared to Mo-doping [102]. It is also seen in UV-Visible absorption spectra for these samples (Figure 4.5.2.6 (a)) that the absorption edges for the doped samples and the pristine BiVO_4 differs from each other, and the samples with different dopants also differ from each other. The slight shift to the visible region in the absorption edges in doped samples compared to undoped BiVO_4 has been observed in previous studies as well and is attributed to the changing crystal lattice strain and crystal size leading to changes in optical band gap properties. It is also seen that two different dopants have varying effects on these properties of BiVO_4 supporting the similar findings from Raman spectra.

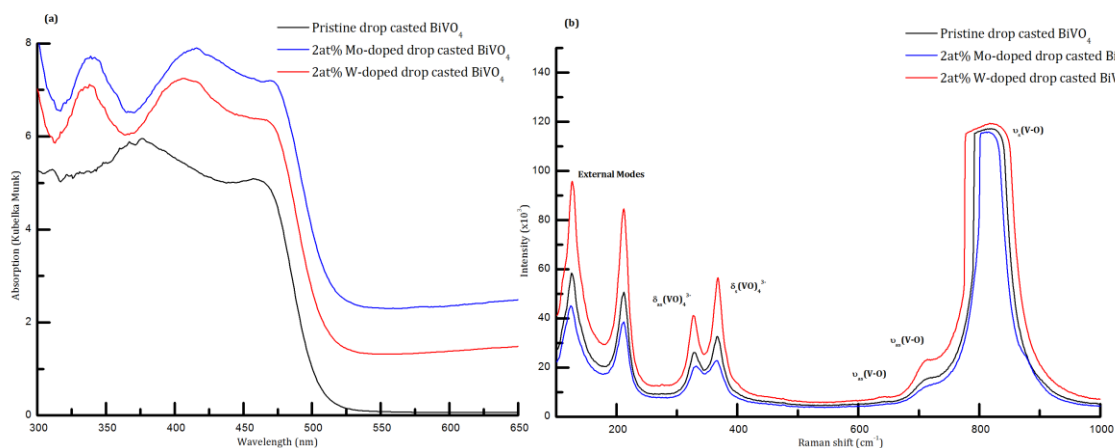


Figure 4.5.2.6: (a) UV-Visible Absorption spectra and (b) Raman spectra of 2.0at% W-doped (red), 2.0at% Mo-doped (blue) and pristine (black) BiVO_4 photoanode films prepared by drop casting hydrothermally grown powders onto FTO are presented. Absorption spectra are obtained by using Kubelka-Munk transformation on the diffuse reflectance spectra that are measured.

Figure 4.5.2.7 shows the photocurrent density – applied bias (J-V) curves obtained via cyclic voltammetry measurements for the pristine, 2at% W-doped and 2at% Mo-doped BiVO₄ films prepared by drop casting the hydrothermally-synthesized powders onto FTO substrates. It shows that the photocurrent densities are not improved by n-doping, which is unusual considering n-doping has been well-documented to increase the charge carrier densities in n-type semiconductors like BiVO₄ [74,89,99]. This indicates that the issue for the low photocurrents in the photoanodes prepared by drop casting BiVO₄ powders onto FTO substrate might be caused by another factor than just the intrinsic limitations of BiVO₄, such as low connectivity between the film and the substrate. However, it has been previously reported that physical methods used to make photoanode films of BiVO₄ from powder particles suffer from very low electron-hole separation yields, therefore producing very low photocurrents under solar light illumination [93]. In fact, the photocurrent densities and the onset potentials are seen to be even worsened in the doped samples; as onset potentials are increased by 0.5V vs RHE and overall photocurrent densities are seen to be decreased by around 1 mA/cm². Thus, along with substrate-film coating connectivity, the nature of the powder form BiVO₄ might be somehow acting as a limiting factor in achieving higher photocurrents and better PEC activities in this study.

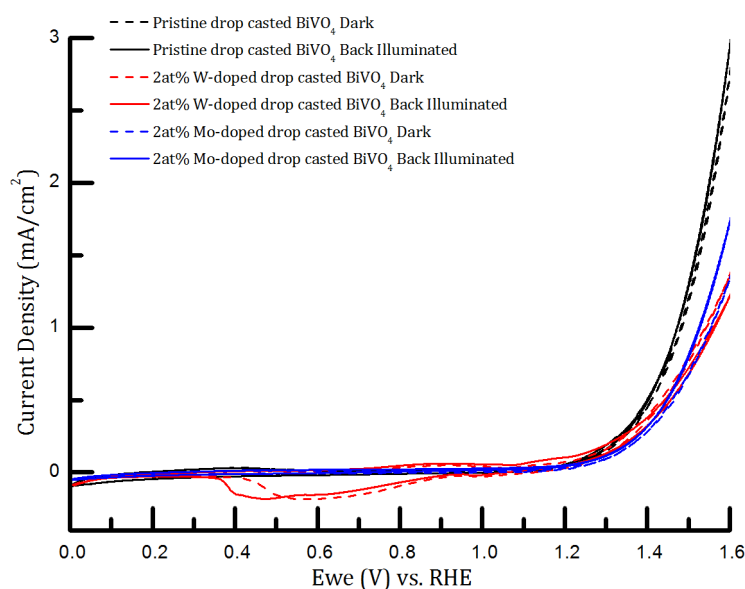


Figure 4.5.2.7: Photocurrent density – applied potential (J-V) curves for powder deposited films of pristine (black), 2at% W-doped (red) and 2at% Mo-doped (blue) BiVO₄ photoanodes obtained via cyclic voltammetry measurements under dark (dotted lines)

and backside illumination (solid lines). Electrolyte used for measurements is 1M KPi buffer (pH=7.0) with 0.5M Na₂SO₃ as hole scavenger.



CHAPTER 5

CONCLUSIONS

In this study, BiVO₄-based photoanodes were prepared via hydrothermal synthesis method and studied for the effect of both hydrothermal preparation parameters and structural and surface alterations. Initially, preparation method was investigated. It was found that depositing powder BiVO₄ prepared via hydrothermal synthesis onto the FTO/glass substrate instead of directly growing the film on the substrate remains to be problematic due to low connectivity between the powder and the substrate as these samples showed no activity under solar light illumination. Then the effect of n-type doping to obtain higher photocurrents for water oxidation under simulated solar light illumination was investigated by adding tungsten (W) to the hydrothermal synthesis mixture. These photoanodes revealed that there is an optimum tungsten doping level for obtaining increased photocurrents, and for our samples this optimum level was determined to be 2.0at% W-doped BiVO₄. Raman Spectroscopy and XRD results showed changes in the local bonding environment and the crystal structures indicating that W is indeed incorporated into the BiVO₄ structure. Also, UV-Visible spectra supported the change in the absorption edges. The highest photocurrent values were obtained from 2.0at% W-doped sample, followed by 1.5at% W-doped sample, however a significant decrease in 2.5at% W-doped sample's J-V curve was observed, confirming that there is a limit for optimum doping level to obtain the improved PEC water oxidation activity. Transient photocurrent data showed that exact reason behind this limitation cannot be solely based on the creation of new recombination centers for the photogenerated holes by tungsten doping. After this point, it was also determined that extended reaction times do indeed increase the crystallinity in the BiVO₄ films, however the activities are not always directly proportional to the change in their crystallinity, thus 2 hours reaction time found to be optimum for the pristine and 2.0at% W-doped BiVO₄ films prepared in this study. The effect of varying reaction temperature and surfactant type during hydrothermal synthesis of the photoanodes also showed that these aspects change the PEC activities obtained from BiVO₄ photoanodes. The changing hydrothermal synthesis reaction time showed that the lowest reaction temperature to obtain higher photocurrent densities from BiVO₄ films in this study is 180°C. Meanwhile, the use of various surfactants proved that each surfactant provides distinctive morphologies, however more

homogenous and crystalline structures do not necessarily equal high PEC performance.

Composition	Preparation Method	Strategy	Activity (photocurrents at 1.23V vs RHE (mA/cm ²))	Authors, Year	Reference
BiVO ₄ - (001) orientation	Laser ablation	Epitaxy/ crystal orientation	6,10	Zheng et. Al. March 2018	[103]
BiVO ₄ - W - WO ₃	Electrochemical deposition	composition/ heterojunction	5,00	Jing-Ping et. Al. June 2018	[84]
BiVO ₄ /FeOOH/NiOOH	Electrodeposition	heterostructure/ protective layer	4,70	Choi et. Al. January 2018	[100]
CoPO ₃ /pGO/LDH/BiVO ₄	spin coating/ solution deposition	composite structure	4,45	Li et. Al. January 2018	[104]
Mo- (0.9 Bi:V)BiVO ₄	sol-gel method	Bi:V molar ratio change and doping	4,20	Shin et. Al. January 2018	[45]
Fe ₂ O ₃ -BiVO ₄	electrodeposition	heterojunction	3,50	Wang et. Al. April 2018	[105]
BiVO ₄	hydrothermal method	surfactant addition effect	1,65	Chiang et. Al. March 2017	[106]
BiVO ₄	hydrothermal/ solvothermal method	effect of solvent/ morphology	0,90	Leung et. Al. October 2017	[93]
WO ₃ -BiVO ₄	hydrothermal method	heterostructure	0,50	Qurashi et. Al. February 2017	[28]
WO ₃ -BiVO ₄	hydrothermal method	heterostructure	0,11	Qurashi et. Al. November 2016	[27]
BiVO ₄	sonochemical assisted hydrothermal method	solvent and method effect	0,07	Qurashi et. Al. December 2016	[107]

Table 5.1: A review of the highest photocurrents obtained from BiVO₄-based photoanodes under solar light illumination at 1.23V vs RHE applied bias.

So far, the highest photocatalytic activity belonged to 2.0at% W-doped BiVO₄ sample. For IrO_x co-catalyst loaded onto various BiVO₄ photoanodes via ALD method to obtain higher photocurrents, it was seen that preparation method and n-doping influences the improvement that is obtained from the co-catalyst. In all these samples, ozone oxidized iridium oxide loaded samples showed less improvement compared to water oxidized samples. Among W-doped and pristine hydrothermally-prepared BiVO₄, as well as spin coated BiVO₄, low coverage (30 ALD cycles) iridium oxide coated spin coated BiVO₄ show the best activity with 1.20 mA/cm² at 1.23V vs RHE and 2.0at% W-doped sample showed the highest one among hydrothermal samples with 0.65 mA/cm² at the same potential. It was found that heat treatment under oxygen significantly improved the photocurrents that can be obtained from IrO_x co-catalyst loaded BiVO₄ photoanodes, as well as decrease the onset potentials noticeably, even for the bare BiVO₄ samples. Low coverage IrO_x loaded BiVO₄ (30 ALD cycles) showed the highest photoelectrochemical activity in this study with 1.73 mA/cm² at 1.23V vs RHE. When compared with the literature results representing the highest reported photocurrents for BiVO₄-based photoanodes (Table 5.1), it is seen that our results are lower than the highest reported value of 6.1mA/cm², however when compared with the highest photocurrent density for a BiVO₄ photoanode prepared via hydrothermal method, it is seen that 4.20 and 1.65 mA/cm² are the best results in the literature. When compared, the findings of this study representing the highest photocurrent density obtained from the BiVO₄-based photoanodes prepared, they are seen to be second highest among the highest reported literature data. Overall, the best photocatalytic activity was obtained for low coverage IrO_x catalyst loaded spin coated BiVO₄ after heat treatment under oxygen flow and a detailed study on photoelectrochemical and physical properties of BiVO₄-based photoanodes have been conducted in this study. Our findings confirmed and added to the fundamental knowledge on the water oxidation mechanisms, specifically on BiVO₄-based photoanodes.

CHAPTER 6

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