

Supplementary Material (ESI) Journal of Materials Chemistry A

## Electronic supplementary information

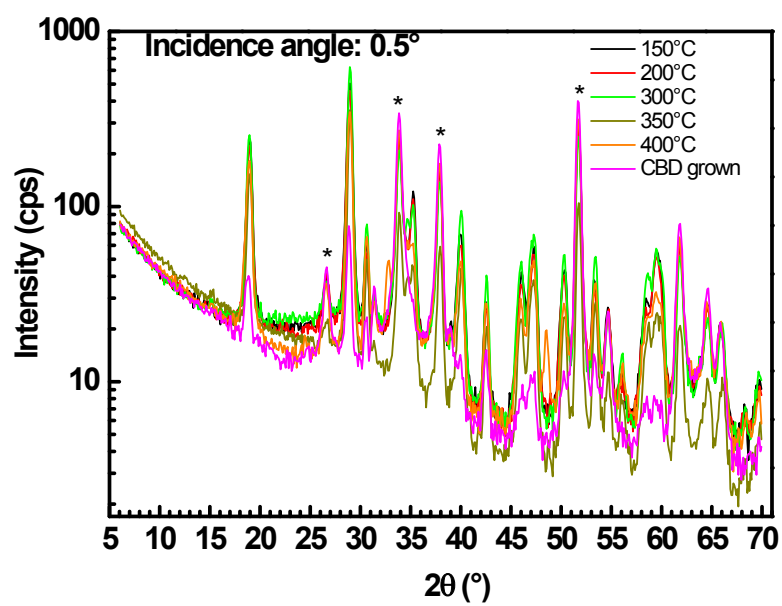
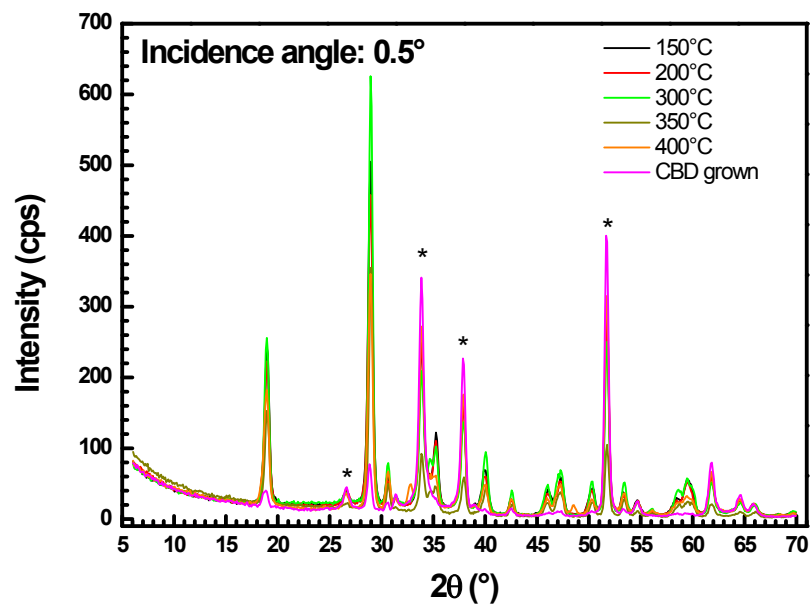
### Solution-Processed Multilayered BiVO<sub>4</sub> Photoanodes: Influence of Intermediate Heat Treatments on the Photoactivity

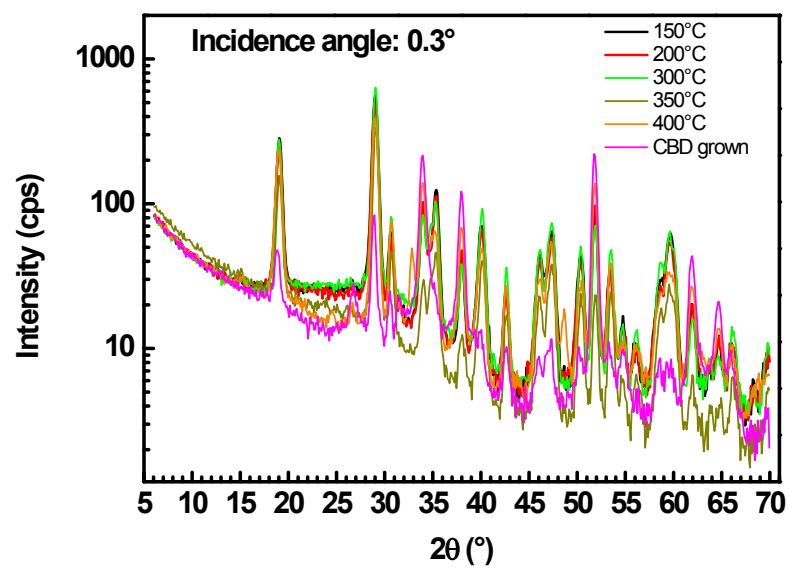
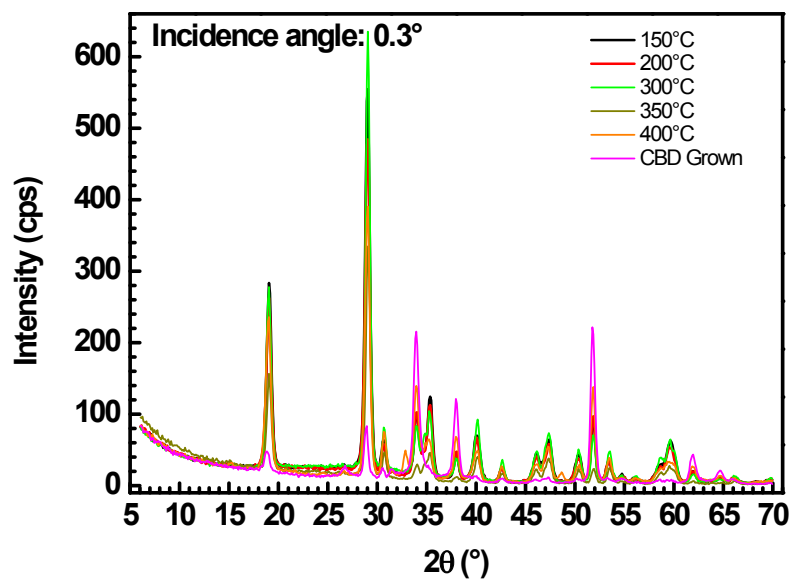
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#### **1- X-rays diffraction Studies.**

The BiVO<sub>4</sub> films thin were investigated by X-ray diffraction using a PANalytical X'pert PRO MRD in grazing incident geometry with three fixed angle (0.5°, 0.3° and 0.1°) using monochromatic Cu K $\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) and a scanning range ( $2\theta$ ) of 5-70°. The incident X-ray beam was conditioned by a 60 mm graded parabolic W/Si mirror with a 0.8° acceptance angle and a 1/16° divergence slit. The reflected beam was collected with a PW3011/20 sealed proportional point detector positioned behind a 0.27° parallel plate collimator. The results are shown in Figure S1. The peaks corresponding to the underlying FTO substrate, indicated by asterisks, decrease in intensity as the incidence angle decreases. The FTO peak around 25° is not anymore present. However the broad background which is assigned to the amorphous content in the BiVO<sub>4</sub> films, increases in intensity. This is clearly observed when the intensity is plotted on a logarithmic scale and even on the linear scale in the case of a grazing incident of 0.1°. At this angle, the beam is more focused on the BiVO<sub>4</sub> film and much less on the FTO substrate. It is important that all samples were measured under the same conditions.





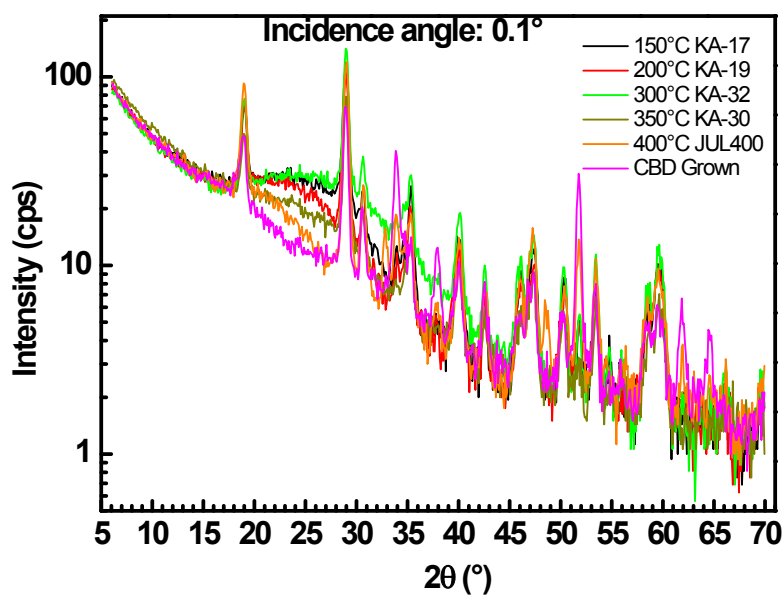
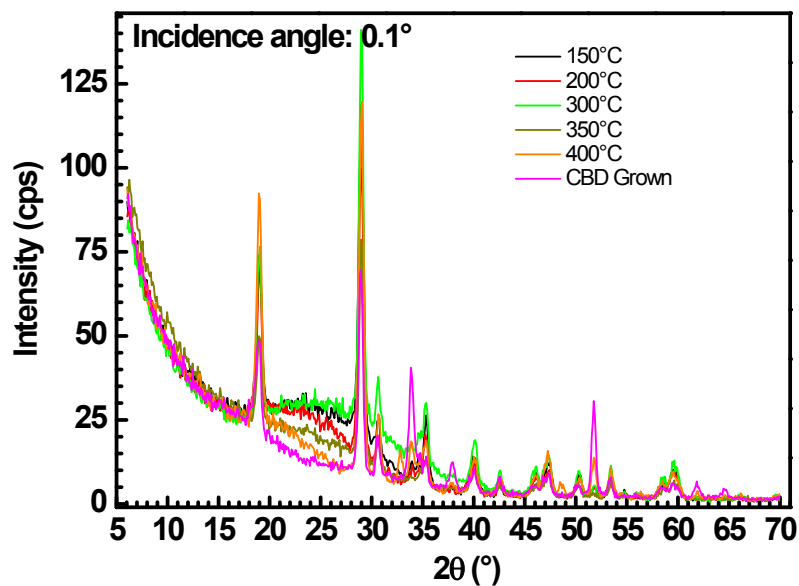


Figure S1. XRD data in grazing incident geometry with three fixed angle ( $0.5^\circ$ ,  $0.3^\circ$  and  $0.1^\circ$ ) for  $\text{BiVO}_4$  electrodes made with different pre-heating temperatures and a final heat treatment of  $460^\circ\text{C}$ . (b) Each graph is show first on a linear scale then on a logarithmic scale.

## 2- Effect of pre-heating temperature on the photo-electrochemical properties of BiVO<sub>4</sub> photoanodes

The effect of the preheating temperature  $T_{PR}$  on the photoelectrochemical properties of BiVO<sub>4</sub> in the absence of an efficient hole scavenger, such as hydrogen peroxide, is shown below in Fig. Xx. In this case, the highest anodic photocurrents are obtained for a  $T_{PR}$  value of 350°C under both front- and back-side illumination.

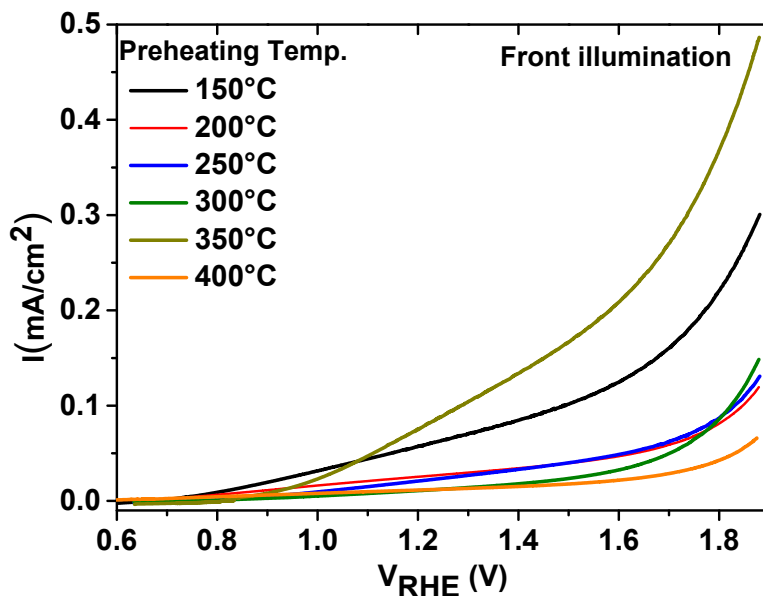


Figure S2. Photocurrent-voltage measurement of BiVO<sub>4</sub> processed at different  $T_{pr}$  values under AM1.5 front-side illumination. The scan rate is 10 mV/s and the electrolyte is a 0.5 M K<sub>2</sub>SO<sub>4</sub> solution buffered to pH 5.9

in the presence of H<sub>2</sub>O<sub>2</sub> the photoelectrode processed at  $T_{PR}$  of 350 °C still shows the highest photocurrent; under both front- and back-side illumination consistent with the results in the absence of H<sub>2</sub>O<sub>2</sub>. The BiVO<sub>4</sub> film processed at a  $T_{PR}$  of 400°C shows the second highest photocurrent in the presence of H<sub>2</sub>O<sub>2</sub>, despite showing the smallest photocurrent when H<sub>2</sub>O<sub>2</sub> is not present. The same trend is observed under both front- and back-side illumination.

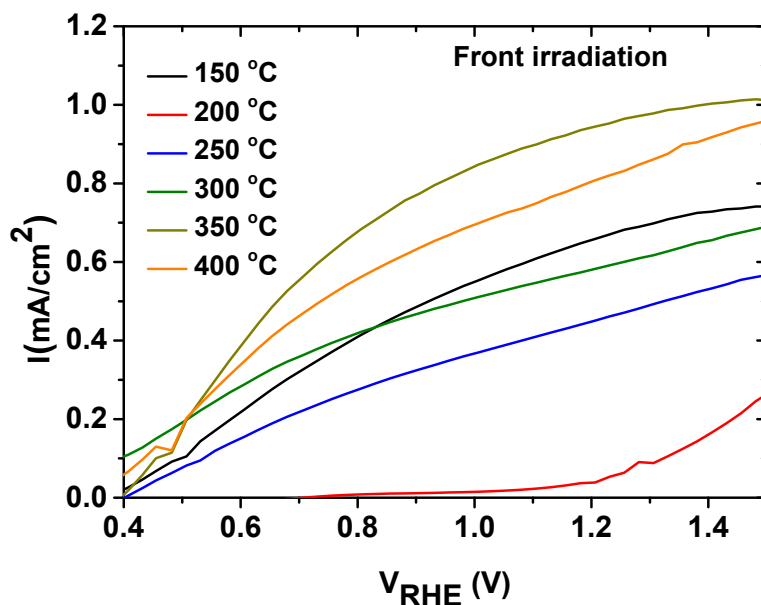


Fig. S3. Photocurrent-voltage measurement of non-doped BiVO<sub>4</sub> processed at different  $T_{pr}$  values under AM1.5 front-side illumination and in the presence of H<sub>2</sub>O<sub>2</sub>. The scan rate is 10 mV/s.

### **3. Scanning Electron microscopy Observation.**

The SEM observations indicate a clear effect of the intermediate heating on the morphology of the multilayer films. After deposition of a layer by spin-coating, the electrode is introduced in a pre-heated furnace in this case 350 °C and 300°C. In the case of 350°C, the films are highly porous but show a homogeneous morphology consisting of the same type of particles. However in the case of 300°C, the films are also porous but consist of two types of objects. Large particles in the form of plates with a relatively smooth surface and ill-defined aggregates consisting of much smaller particles. The films were introduced in a pre-heated furnace which means a very high heating rate. The temperature of 350°C is relatively high, leading to a very fast pyrolysis of the organics such acetate and alkoxide groups and the formation of the inorganic crystalline phase BiVO<sub>4</sub> while at lower temperatures, mass transfer takes place in the presence of some organic ligands leading to segregation and the formation of two phases and therefore the loss of the homogeneous mixing at the molecular level of Bi and vanadium precursors. Further heating of the films consisting of two phases does not lead to a single phase BiVO<sub>4</sub> at 460°C but to an additional amorphous content as shown by XRD.

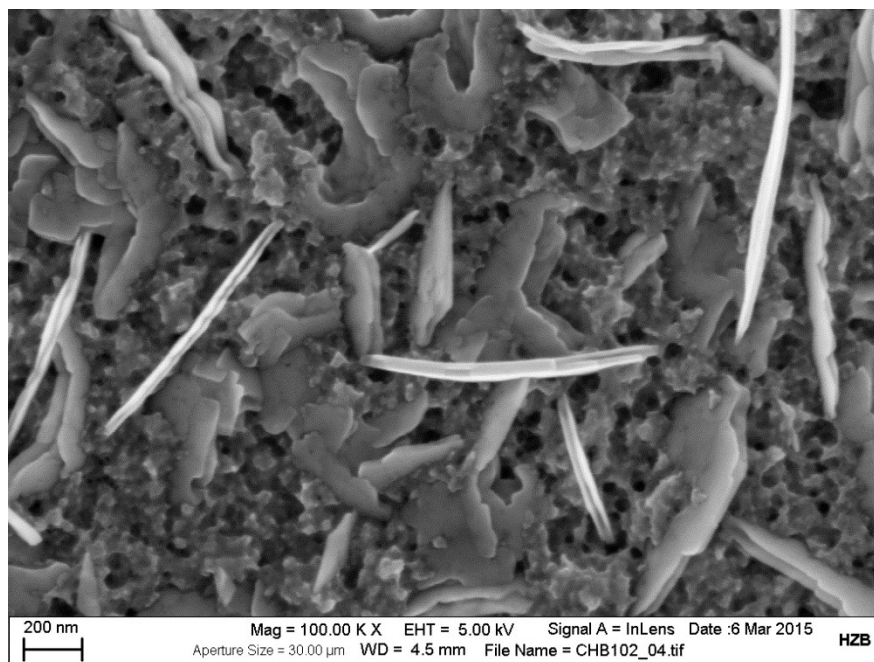


Figure S4. SEM images of multilayers processed at  $T_{pr}$  of 300 °C without further heating.

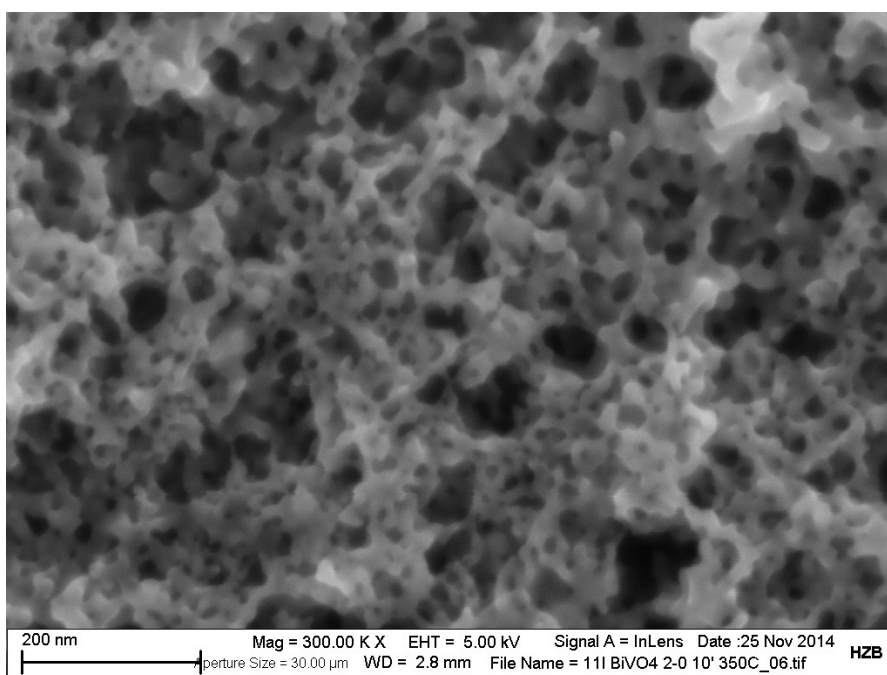
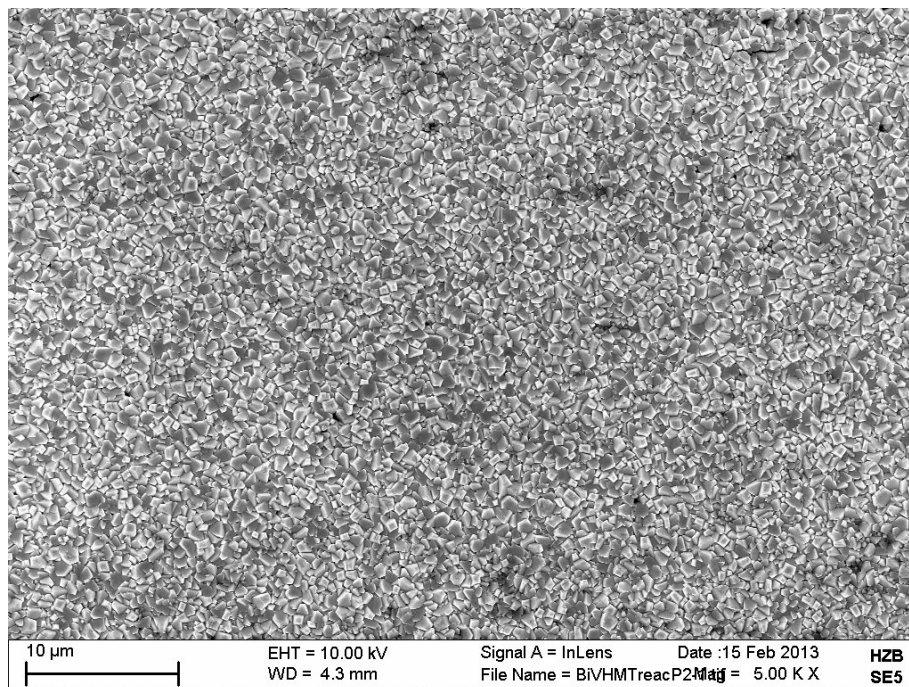


Figure S5. SEM image of multilayers processed at  $T_{pr}$  of 350°C without further heating.

#### 4. Chemical Bath Deposition technique.

The chemicals used for the chemical bath deposition technique include  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (98%, Fluka),  $\text{NH}_4\text{VO}_3$  (99.5%, Fluka), of hexamethylenetetramine (HMT). 99.5%, Fluka),  $\text{HNO}_3$  (p.A 65% Merck). The spin-coating method in this paper was used to deposit a single layer as a seed film and heated to  $460^\circ\text{C}$  for 2 hours. The FTO with the seed film was introduced in the bath containing 10 ml aqueous nitric acid solution (1.84 Mol/l) containing 2 mmol of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , 10 ml aqueous nitric acid solution (1.84 Mol/l) containing 2 mmol of  $\text{NH}_4\text{VO}_3$  and 90 ml aqueous nitric acid solution (1.84 mol/L), containing 6 mmol of hexamethylenetetramine (HMT). The substrate was heated for a period of 16 minutes to  $98^\circ\text{C}$  and kept for 48 minutes at this temperature. The film was kept in the bath during a cooling time of 55 minutes. After deposition and cooling, the substrate was removed from the chemical bath, cleaned thoroughly in distilled water and dried in air at ambient temperature.

The  $\text{BiVO}_4$  films grown directly on FTO by CBD were characterized by XRD and scanning electron microscopy. Figure S6 shows SEM micrographs of the same film at different magnifications. The low magnification micrograph (top) shows a homogeneous morphology of the polycrystalline CBD made film. The high magnification micrograph (middle) shows the film consisting of large well defined crystallites with vertices and facets. The last SEM micrograph shows the two parts of the FTO substrate with the seed film. The top part was not dipped in the CBD bath and consists of small crystallites of the  $\text{BiVO}_4$  seed film and the larger FTO crystallites. The part below shows the dipped part with larger  $\text{BiVO}_4$  crystallites grown by CBD. In contrast to the films made by spin-coating, they are relatively thin explaining the high intensity of the FTO peaks. However, the broad background between  $15^\circ$  and  $40^\circ$  of 2 theta values is much less pronounced or even not present.



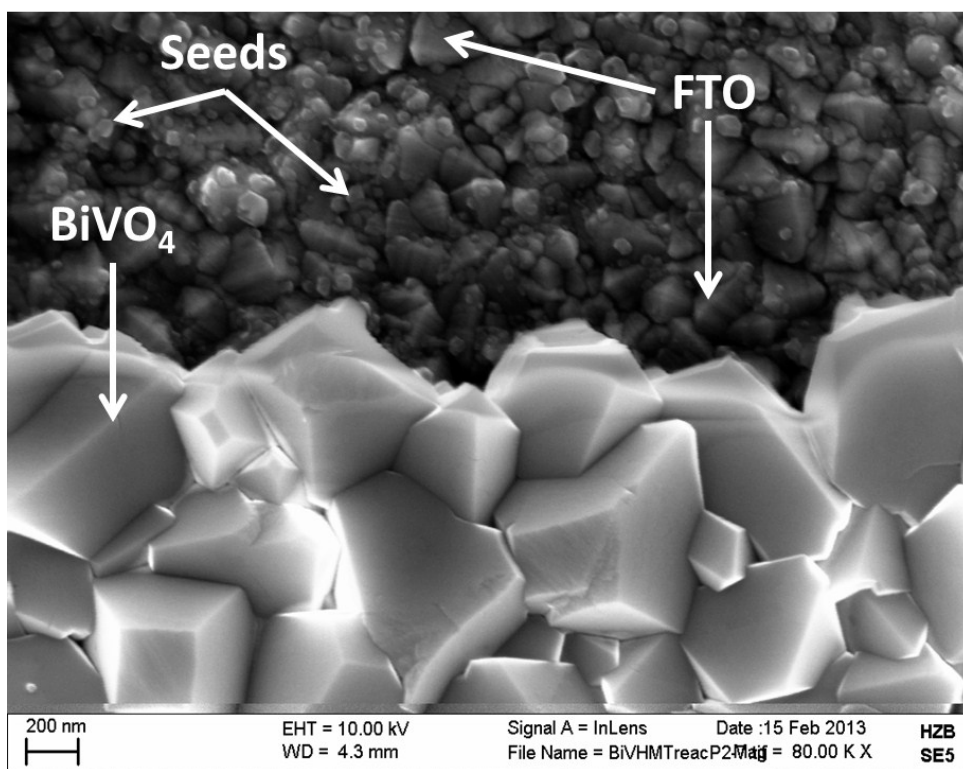
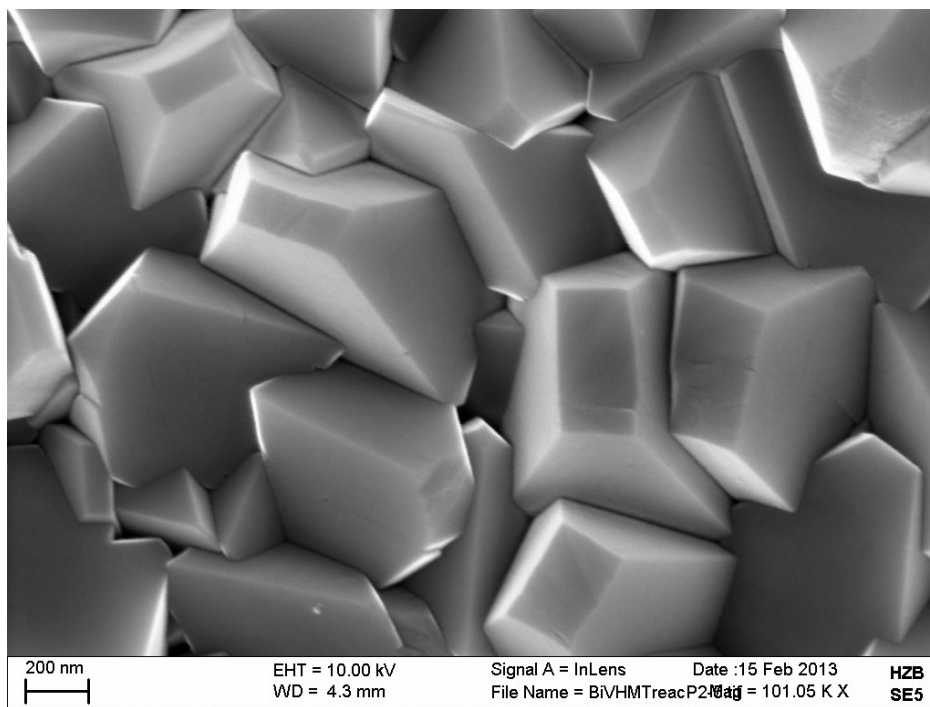


Figure S6. SEM images of CBD made films with different magnifications. The image below shows the FTO substrate with seeds deposited by spin coating.

## 5. SEM cross-section images

Figure S7 shows the SEM cross-section image of eight  $\text{BiVO}_4$  layers deposited on FTO substrate. The measured thickness is roughly 80 nm however, due to the high roughness of the FTO substrate (about 40 nm roughness) it is difficult to determine with high precision the  $\text{BiVO}_4$  film thickness. For this reason, we also used a silicon wafer as substrate to compare and determine the thicknesses of our films. Figure S8 shows the SEM cross-section image of eight  $\text{BiVO}_4$  layers deposited on a flat silicon wafer and the thickness measured in this case is about 78 nm. We also determined the thickness for 4 layers, 8 layers and 16 layers in order to determine roughly an average thickness of each layer.

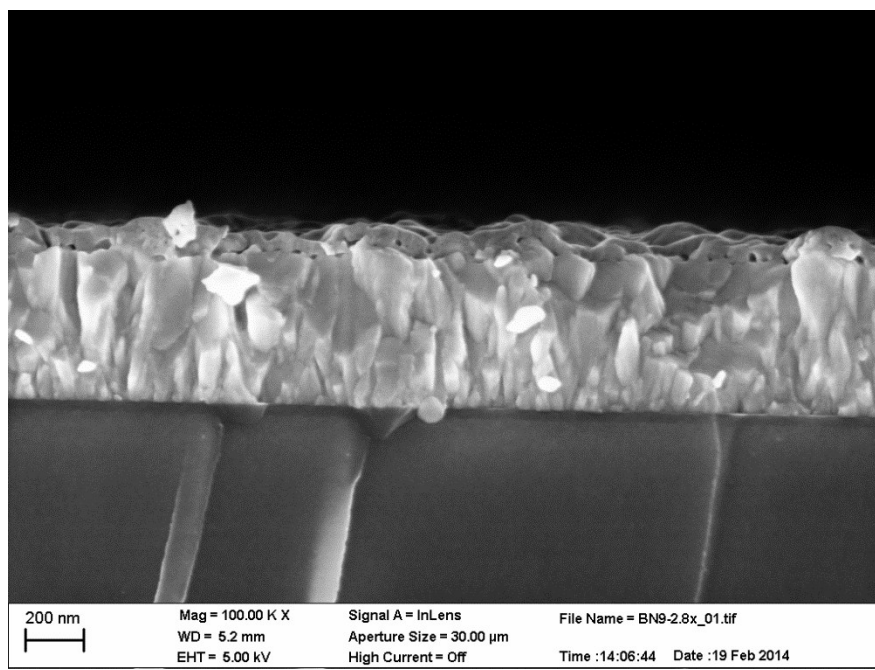


Figure S7. Cross section SEM image of 8 layers deposited on FTO. The thickness is roughly 80 nm.

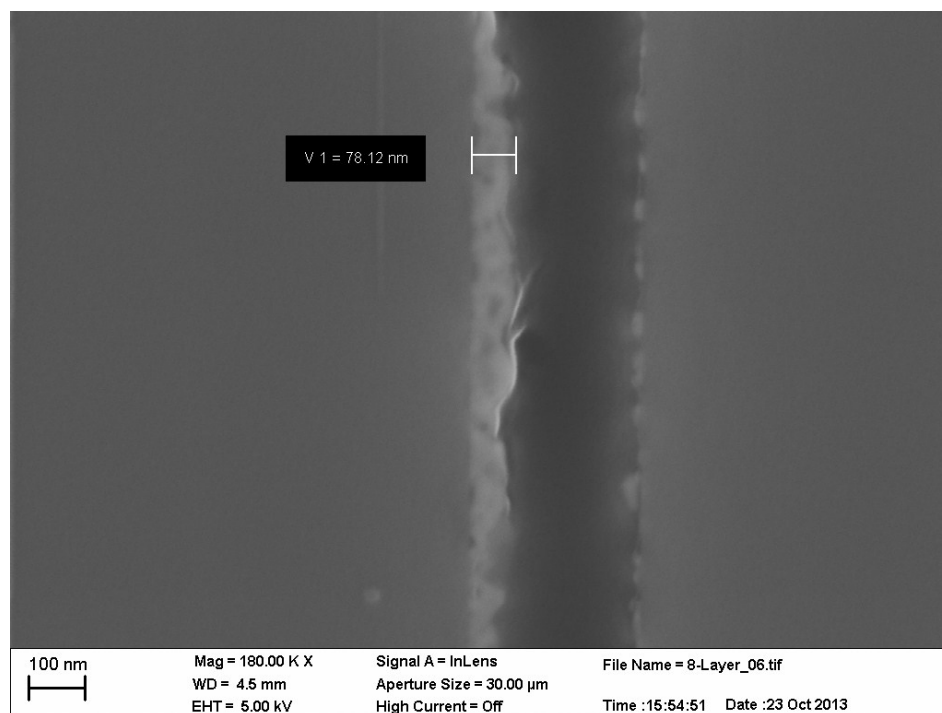


Figure S8. Cross section SEM image of 8 layers deposited on silicon. The thickness is roughly 7.8 nm.