Semiempirical Modeling of a Three Sublayer Photoanode for Highly Efficient Photoelectrochemical Water Splitting: Parameter and Electrolyte Optimizations

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Below we present semiempirical modeling of conceptually new three-sublayer photoanode, composed of Absorber, Grading and Barrier sublayers, for highly efficient photoelectrochemical water dissociation. The modeling resulted into Absorber (Sub-A) made of $\text{Cd}_{0.55}\text{Zn}_{0.45}\text{O}$ due to its favorable positions of the band extrema to the water splitting potentials and a band gap ~ 2.0 eV. The Grading layer (Sub-G) was composed of $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ with a gradual decrease of x across the profile, changing from 0.2 to 0.55, aiming to photon absorption from 2.0 to 3.0 eV. At the same time, Sub-G furnishes the profile with an implanted electrical field that improves the hole-transport. The electronBarrier layer (Sub-B) deposited above the Sub-A, was engineered to provide 1 eV high barrier in the conduction band. It comprised of a 50 nm thick $\text{Ni}_{0.4}\text{Cd}_{0.6}\text{O}$ film with $E_g \sim 3.0$ eV with a valence band aligned to the one of the Sub-A, providing a barrier-free hole-flow. In this paper, we provide evidence that the proposed three-sublayer concept clearly represents a new paradigm for an improved efficiency for photocatalytic water dissociation. The highest photocatalytic activity of the optimized profile was achieved with an optimized electrolyte: 87% 1M K_2HPO_4 and 13% 1M Na_2SO_3 (known to act as a hole scavenger or sacrificial agent) at pH=10. A noteworthy feature of this study is that under optimized profile parameters and customized electrolyte conditions the photocurrent yields increased from ~ 0.05 mA/cm² to ~ 20 mA/cm² at +1.2 V for visible light. The observed Incident Photon-to-Current Efficiency (IPCE) was about 50% at a photon energy of 3 eV.

Keywords: CdZnO/NiCdO, photoanodes, photosensitivity, water splitting, voltammetry, IPCE

1. Introduction

Many efforts were made for the direct conversion of the solar energy into the energy of chemical fuels (for instance, water reduction to H_2). Various semiconductor photoelectrochemical cells (PEC) for water splitting (also known as photolysis or artificial photosynthesis) have been considered: TiO_2 based cell [1], $BiVO_4$ [2, 3], Fe_2O_3 [4-6], Cu_2O [7], CoO_x [8], TiO_2 [9], dual absorber of WO_3/Fe_2O_3 [10], etc. A typical PEC consists of a semiconductor photoelectrode that generates electron-hole pairs upon solar light absorption. There are several known approaches to achieve water photolysis [11] such as semiconductor-liquid junctions; dye molecules on the semiconductor/liquid surface; $p-n$ or Schottky junctions.

The ideal candidate for a semiconductor electrode should satisfy the following demands: (i) efficiently to absorb the solar spectrum at energies ≥ 2 eV; (ii) its valence band maximum (VBM) to be positioned somewhat higher than 1.23 V, and the conduction band minimum (CBM) somewhat lower than 0 V versus Normal Hydrogen Electrode (NHE); (iii) to reveal sufficient conductivity, minimizing the ohmic losses; (iv) demonstrates good stability towards photo-corrosion; (v) exhibits ample catalytic activity - the electrochemical reaction occurs at a reasonable rate [12]. It has been demonstrated that ideal semiconductor for PEC water splitting should have an optical band gap, $E_g \sim 2$ eV [13], corresponding to the sum of the theoretical water splitting thermodynamic potential of 1.23 V, plus the potential for replenishing the ohmic losses of the charge transfer across the PEC profile, losses called "overpotential", described by Tafel's equation [14], and Schottky losses.

Significant research interest in the PEC water splitting attracted ZnO. Despite of its wide gap of 3.3 eV, various forms of ZnO-based PEC devices have been extensively explored: ZnO nanowires with Ti-shells [15], N-doped ZnO [16], H-treated ZnO [17], C-doped ZnO [18], nano-forest textured ZnO [19, 20], ZnOSe [21]. The reason for ZnO alloying is expanding the solar light harvesting towards the visible region, as in the case of ZnO-GaN [22]. According to the recently published results, the most efficient photocatalytic devices were made on Si [23,24].

$Cd_xZn_{1-x}O$ multilayered structures have been previously used as photoanodes by other authors [25] whose design concept led to relatively poor PEC performance. However, according to some previous exploration, the $Cd_xZn_{1-x}O$ system [26]] within the range $0 < x < 0.60$ exhibited a gradual decrease of the direct gap from 3.3 to 1.9 eV, whereas the electron concentration grew from 10^{19} - 10^{20} cm^{-3} . For the concerning alloying region [27] it appeared that the CBM was rather fixed at about -5 eV relative to the vacuum level, while as the VBM moved up from -8.5 to -7.3 eV with the increase of x (purple box above ZnO's VBM on Figure 1). Another research, however, was conducted on the $Ni_yCd_{1-y}O$ alloying

system. Authors reported type-III extreme CBM offset, whereas the E_g changed from 2.2 to 3.2 eV. Some unpublished results of Walukiewicz et.al. showed that in the conductive alloying region of our interest ($0.4 < y < 0.6$) [28], the position of the VBM roughly matches the VBM of the Sub-A layer.

Also, it is a well-known fact that ZnO behaves as a stable compound under illumination in a neutral or alkaline solution [29, 30]. Similarly, NiO is stable in alkaline electrolytes [31]. However, the stability of CdO at $\text{pH} > 7$ has not been sufficiently studied in the past.

Below we introduce a novel three sublayer photoanode concept to be tested on a multilayer based on $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ and $\text{Ni}_y\text{Cd}_{1-y}\text{O}$ alloys. Furthermore, we applied semi-empirical modeling for evaluation of an optimum content and thickness of each sublayer. Also, we present the evidence for improvement of the photocatalytic performance with optimization of the content and thickness parameters of each of the three individual sublayers. The K-phosphate electrolyte conditions and the hole scavenger concentration were also optimized for highest possible efficiency.

2. Materials and Methods

The newly proposed $\text{Cd}_x\text{Zn}_{1-x}\text{O}/\text{Ni}_y\text{Cd}_{1-y}\text{O}$ photoanode structure comprises of three sublayers, denoted as Sub-A, Sub-B, and Sub-G, as depicted in Figure 2. All these sublayers were synthesized by Radiofrequency (RF) sputtering, using a dual anode system, with CdO and either ZnO or NiO targets into O_2/Ar atmosphere (20% O_2) onto industrially manufactured SnO_2 : F/glass and microscopy glass slides. The synthesizing conditions were described elsewhere [26-28]. Various profiles were synthesized due to the variation of sublayer's thickness parameters a , b and g , being controlled by the deposition time, and the content parameters x and y , controlled by the RF power of the corresponding target. All the five characteristic parameters of each sample (a , b , g , x and, y) were established from Rutherford Back Scattering (RBS) experiments, using 3.04 MeV He^+ incident ion beam, backscattering angle of 55° , and SIMNRA software for modeling the acquired spectra with the known interactions. Optical characterization was performed with a Perkin-Elmer Lambda 950 spectrometer within the spectral region between 320 and 800 nm. The absorption coefficient spectra were calculated, taking into consideration that the full profile thickness (d) is a sum of the three separate sublayer's thicknesses ($d=a+b+g$), all evaluated from the RBS thickness analysis. For the merits of the photoelectrochemical (PEC) studies, the samples were prepared as window-shaped electrodes of a known area, approximately $1 \times 1 \text{ cm}^2$. Their back FTO-electrodes were In-soldered with an insulated copper wire. To prevent the effect of other metallic elements on the cell performance, all the conductive contacts and the sides of the sample were insulated optically and

electrically with a non-transparent epoxy. A simple cell was formed by placing the sample in a beaker filled with an electrolyte, with its face (Sub-B layer) upwards. The illumination was always from up, illuminating first Sub-B (barrier layer) of the immersed cell so that the Sub-A layer harvests the largest portion of the incident light energy. Platinum stripe was used as an opposite electrode. The photocurrent density-voltage (jV) experiments were carried out on a three electrode setup, using a Gamry 600 potentiostat under AM1.5 illumination of a 150 W Xenon lamp. The light intensity on the profile surface was measured by a calibrated Solar Pyranometer, a product of Solar Ltd. The jVs were recorded using single linear voltammetry sweeps in dark (D) and under light (L) at AM 1.5 G - 100 mW/cm² illumination conditions. The voltage sweep was set to 0.1 V/s. The reference electrode was Ag/AgCl (3M KCl) while as a Pt-ribbon served as a counter electrode. The curves were turned into photocurrent density vs. voltage characteristics (jV) by subtraction of the dark (D) from the corresponding light (L) jV -characteristic. Also, the spectral dependence of photocurrent yield was measured using two electrode setup. The samples used therein were wired and then isolated/masked with nontransparent epoxy, allowing illumination to near square 0.5 x 0.5 cm² windows. The profiles were submerged into optimized K-phosphate electrolyte at the bottom of the 60 ml beaker in a manner that the Sub-B faced up the monochrome incident illumination. It has been reported that glass corrodes in an alkaline solution and contaminants, such as lead and silica, can influence the electrochemical activity on Pt-electrodes [32,33]. To minimize such a contamination at the solid-liquid interface, the electrolyte was frequently replaced with a fresh one (every 15 minutes). The incident light spectrum at the exact sample position was taken previously with a calibrated photodiode. Photocurrent spectral sensitivity was measured at 0 V potential (short-circuited samples @ 0V). Spectral dependence of the incident photon-to-current efficiency (IPCE) on the incident photon energy was evaluated for each profile. The initial photoelectrochemical tests were run with a K-phosphate buffer solution of pH=8 until the dedicated electrolyte optimization research was completed.

2. Results and discussion

The proposed model of an advanced photoanode is based on the 2D-nano-structured profile, comprising of three main sublayers, presented on Figure 2: Absorber (Sub-A), electron Barrier (Sub-B); and Grading gap (Sub-G) layer. Modeling of each sublayer will be pursued in two deferent stages, presented in separate sections: empirical and experimental.

2.1 Empirical modeling of the sublayers

The Sub-A is aimed to harvest the photons of 2 eV energy from the solar spectrum. Calculation of the x -value in the Cd _{x} Zn_{1- x} O, for which the Sub-A has an intrinsic band gap

$E_g^{(\text{CdZnO})} = 2 \text{ eV}$ [13] was made by resolving the bowing equation (Eq. 1) for the CdO-ZnO alloy.

$$E_g^{(\text{CdZnO})}(x) = E_g^{\text{CdO}}x + (E_g^{\text{ZnO}} - dx)(1 - x) \quad (\text{Eq. 1}).$$

The unknown Cd-content parameter x in the $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ alloy was evaluated by replacing the values of the bowing parameter, $d=0.94$, the intrinsic band gaps of CdO and ZnO ($E_g^{\text{CdO}} = 1.3 \text{ eV}$, and $E_g^{\text{ZnO}} = 3.3 \text{ eV}$) [24], as follows

$$2 = 1.3x + (3.3 - 0.94x)(1 - x).$$

We obtain a quadratic equation for the variable x , with solutions $x_1=0.54$ and $x_2=2.59$. The realistic solution was only the for $x=0.54$ since x can take only values between 0 and 1. Hence, the $\text{Cd}_{0.55}\text{Zn}_{0.45}\text{O}$ was selected for the Sub-A layer with a thickness a , remaining to be established experimentally.

The gap grading layer, Sub-G is deposited onto the FTO substrate. It is intended to absorb solar photons from 2.0 eV to 3.0 eV. Besides, it furnishes the profile with supplementary implanted electric field which is expected to enhance the hole-survival rate across the interface. As presented in Figure 2, the Sub-G was synthesized in a manner that the Cd-fraction in the $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ profile gradually changes from $x_{\min}$ (Cd-content at the side interfacing the FTO) to $x_{\max}$ (Cd-content at the side interfacing the Sub-A). The value of $x_{\max}$ is, however, determined with the x -value of the Sub-A ($x=0.55$). The other boundary value, $x_{\min}$, remains to be determined through a customized experimental procedure.

The electron barrier layer (Sub-B) was introduced in the profile as a top layer over the Sub-A (as depicted in Figure 2) because cells without Sub-B yielded poor photocatalytic activity. The role of this sublayer is to furnish the CBM with a tentative barrier jump of about 1 eV, relative to the CBM of Sub-A layer. Our later research, regarding optimization of Ni-content (y)(the factor that determines the E_g) will also justify the barrier height of about 1 eV). Sub-B was made of $\text{Ni}_y\text{Cd}_{1-y}\text{O}$ with a Ni-content (y) engineered to provide $E_g \sim 3.0 \text{ eV}$. The tentative selection of this particular ternary compound ($\text{Ni}_y\text{Cd}_{1-y}\text{O}$) was made from the findings that the both VBM of Sub-A (ZnCdO) and Sub-B (NiCdO) within the alloying regions of interest for this work are in an approximate alignment (unpublished results of W. Walukiewicz *et al.*). Taking into account that the interfacing alloys are set to $E_g(\text{CdZnO})=2 \text{ eV}$ and $E_g(\text{NiCdO})= 3 \text{ eV}$, it follows that a barrier jump of 1 eV is likely be formed in the CBM at the interface. Hence, the photogenerated holes are expected to take a barrier-free route to the oxygen evolution potential $\phi(\text{O}_2/\text{H}_2\text{O})$. Besides, both the alloys, CdZnO, and NiCdO have binary endpoint compounds that are isostructural (polycrystalline-wurtzite) with grain sizes ~ 16

nm [26,27] and ~20 nm [28] respectively, and are, therefore, convenient for building a conductive heterostructure. By replacing the following parameters: $d=-1.26$ [26], $E_g^{(NiCdO)}=3$ eV, $E_g^{NiO}=3.7$ eV and $E_g^{CdO}=2.2$ eV in the bowing Eq. 2,

$$E_g^{(NiCdO)} = E_g^{NiO}y + (E_g^{CdO} - dy)(1 - y) \quad (\text{Eq. 2}),$$

we obtain a quadratic equation for the variable y . The resolution is similar as for Eq.1. The realistic solution was $y=0.4$. Further, Sub-B optimization (using further improvement of y -value and the thickness- b) was pursued experimentally.

The results from the quantitative analysis with the RBS measurements are shown in Figure 3. The values were further summarized in Table I. Figure 3 presents the variation of the Cd-content (x) across the two $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ sublayers (A and G). Herein, Figure 3(a) depicts profiles of the same thickness of Sub-G ($b = 135$ nm) and a variable thickness of Sub-A ($a = 0 - 95$ nm). Furthermore, Figure 3(b) shows the variation of x across the thickness for profiles of approximately identical Sub-A ($a \sim 70$ nm), but different Sub-G ($g = 135, 220$ and 280). Assuming stoichiometric transfer of the target material, one should consider that the Zn-content across the profile is equal to $(1-x)$ [28].

2.2 Optical absorption and sensitivity

Figure 4 presents the optical properties of the photoanode profiles. Optical transmittance spectra are given in 4(a) and 4(b) and reflectance spectra, taken relative to the FTO/glass substrate are given in 4(c) and 4(d). The absorption coefficient spectra are presented on 4(e) and 4(f). The (a), (c) and (e) figures pertain to the optical properties of profiles of identical Sub-G but different Sub-A, and (b), (d) and (g) to those of identical Sub-A, but different Sub-G. Herein, the Sub-B layer deposited on the top of all the profiles was identical ($\text{Ni}_{0.4}\text{Cd}_{0.6}\text{O}$, thickness $b=50$ nm). From Figures 4(e) and 4(f), one can see that the examined photoanode profiles revealed exceptional absorption throughout the examined visible and UV region, whereas a notable contribution originated from photons of energies greater than 2 eV. As obvious from Figure 5(e), the profile with thickness $a=0$ nm for Sub-A layer revealed the highest absorption coefficient. This behavior could be ascribed to the fact that for $a=0$ nm the absorption coefficient results solely from the grading gap layer (Sub-G), engineered to absorb photons of energy between 2 and 3 eV. In addition, the well known thickness effect on the absorption coefficient may contribute, too.

Figure 5 presents the Incident Photon-to-Current Efficiency (IPCE) spectra. 5(a) presents the profiles of same Sub-A and different Sub-G, while 5(b) presents the profiles of same Sub-G and different Sub-A. One could see values for IPCE as high as 75% at photon energies greater than 3.4 eV, meaning that the both, Sub-B (NiCdO) and FTO-substrate also took part

in the UV part electron-hole pair photogeneration. The highest IPCE of all the tested profiles for photon energies of 3 eV throughout the broadest part of the spectrum exhibited the R837 profile. The R866 profile, which is, however, most similar to R837, was second best. The observed IPCE was about 50% at a photon energy of 3 eV.

2.3 Experimental parameter optimization

Optimization of multiple parameters of the three sublayers composite system is rather a complex procedure. However, the most convenient optimization method seemed the one at which one single parameter was variable while all the others were controlled. It seemed appropriate to start with the optimizations of the thickness (b) and the Ni-content (y) of the electron barrier layer (Sub-B).

As was mentioned before, the role of Sub-B composed of $\text{Ni}_y\text{Cd}_{1-y}\text{O}$ as a top layer over the Sub-A is the prevention of electrons from traversing across the solid/liquid interface into the oxygen evolution potential and recombine with the “photolysis working” holes, therein. Although the calculations for the demanded 1 eV high electron barrier resulted into $y=0.4$, further optimization within a wider y range ($0.4 < y < 0.6$) was carried out. Also, the thickness of Sub-B is limited by the occurrence of electron tunneling from the higher CB states. Hence, optimization of the two Sub-B parameters (thickness- b and Ni content- y) was pursued in two consecutive experimental steps, while as the thickness b was optimized first. For this purpose, Sub-B layers of constant Ni-content ($\text{Ni}_{0.49}\text{Cd}_{0.51}\text{O}$) and various thickness b ranging from 0 to 85 nm, were deposited over the R744 profile (constant Sub-A & Sub-G). Herein, $b=0$ denotes an absence of Sub-B. Again, the values of b and y were evaluated from RBS measurements on the Sub-B layer on glass substrates. The photoelectrochemical measurements, by means of photo- jV -characteristics of these profiles, are given in Figure 6(a). One may notice that at certain positive potential the photocurrent attains a peak value. After this potential point of a maximum photocurrent, the photogenerated holes start intensively recombine with the electrons at the interface, before they get to the oxygen evolution potential. Also, it is evident that the highest photocurrents yields were achieved for $b=24$ nm and 52 nm. The inset of Figure 6(b) represents the dependence of the photocurrent density (L-D) at +1.0 V anodic bias on the Sub-B thickness (b). The Gaussian fit suggested that the optimum barrier layer thickness is $b=40$ -50 nm. It also appeared that further increase of b induces higher ohmic losses, resulting in an abrupt fall in the photocurrent density. Once the thickness was optimized, several R744 profiles were topped with $\text{Ni}_y\text{Cd}_{1-y}\text{O}$ Sub-B of different Ni-contents (y) with the previously established optimum thickness ($b=50$ nm). The results of the photo- jV characteristics are summarized in Figure 6(b). Herein, the inset chart represents the

dependence of the photocurrent density at 1.0 V bias as a function of y . It appeared that the highest photocatalytic activity was observed on the profile for which $y \sim 0.4$, which is in line with the predicted value by applying Eq. 2. As expected, the higher Ni-contents induced growth of resistivity at the interface since the Ni-rich alloying region is insulating [28]. Hence, the observed abrupt fall of the photocurrent density with Ni-content growth.

All the future examinations were made on photoanode profiles of various Sub-A and Sug-G profiles but identical Sub-B (optimized: $b=50$ nm for the thickness and $y=0.4$ for the Ni-content in the $\text{Ni}_y\text{Cd}_{1-y}\text{O}$ film). However, because of the relatively poor photocatalytic activity of the explored multilayer profiles, before pursuing Sub-A and Sub-G optimizations it was essential to optimize the electrolyte.

2.4 Electrolyte optimizations

Due to the poor photocatalytic activity achieved in the previous experiments, different catalysts were tested for possible photocatalytic reaction enhancement. For this purpose, photo- jV measurements were made with the K-phosphate buffer (pH=8) electrolyte to which 2 Vol. % of either methanol or ethanol was added, and a nitrogen gas was purged. The results, however, showed insignificant catalytic enhancement. Also, the experiments with the pH=8 phosphate buffer solution were soon abandoned because of the intensive photoanode corrosion that was observed during voltammetry experiments. Hence, the fast film degradation enforced using electrolytes of alkalinity higher than pH=9. For this purpose, in our further experiments only dipotassium phosphate (K_2HPO_4) was used. Nevertheless, a considerable improvement of the photocatalytic activity was achieved by adding Na_2SO_3 , a chemical compound known as a hole scavenger (HS)[34], but also as a sacrificial reagent (SR), a chemical that is able to oxidize/reduce water even without the presence of a photocatalyst [35, 36]. Figure 7(a) presents the impact of the volume concentration of the 1M Na_2SO_3 added to the 1M K_2HPO_4 water solution on the photocatalytic activity of profile R866, topped with an optimized Sub-B layer. As obvious from Figure 7(a), the photocurrent density at +1.2 V photoanode potential remarkably grew from 0.5 mA/cm² to 18.5 mA/cm² as the volume concentration of the HS increased from 0 to 15%. Apparently, the further increase of the HS concentration invoked a photocurrent fall. The inset figure in Figure 7(a) presents the change of the Photocurrent density at photoanode potential of +1.2 V with the increase of HS concentration. The Gaussian fit revealed a peak at HS concentration of about 13 Vol.%. Further electrolyte experiments will be pursued with this optimum HS concentration. As shown in Figure 7(b) the impact of the electrolyte alkalinity of the K_2HNO_3 electrolyte with an optimized HS (Na_2SO_3) concentration is substantial. The natural acidity of the solution was about pH=9. Higher pH values were achieved by adding NaOH to the solution. Maximum photocatalytic activity is observed at pH=10 as obvious from the Gaussian fit within the inset of Figure

7(b). Finally, the impact of the molar concentration of the electrolyte is shown in Figure 7(c). As obvious from the inset of Figure 7(c), the higher the molar concentrations, the greater the yields in photocurrents. However, the photocurrents on the inset Figure 7(c) for photoanode potentials +1.0 V and +1.2 V tends to saturation at molar concentrations higher than 1M. As could be seen, for the increase in the electrolyte molar concentration from 0.0625 M to 1.0000 M the photocurrent density increased from 1.2 mA/cm² to 18.3 mA/cm² at photoanode potential +1.2 V.

Finally, one may conclude that the concerned photocatalysts composed of three sublayers NiCdO/CdZnO film, exhibited their maximum photocatalytic activity at 1 mol/L molar concentration, alkalinity pH=10, and optimum volume concentration of the 1M Na₂SO₃, used as a hole scavenger, of 13%.

Clearly, the motion of the photogenerated holes across Sub-A is governed by the diffusion law due to the gradient in concentration across the profile. On the other side, Sub-A borders with Sub-G, a sublayer that contributes to a complementary “driving” force, as it forms an implanted electrical field, therein. Hence, to minimize the recombination rates, one should consider reducing the photoanode’s thickness below the diffusion length for holes (L). One may argue that the thickness parameters a and g could be modeled theoretically, utilizing the carrier life-time measurements from time-resolved photoluminescence (TRPL). However, the high dark conductivity of these profiles inflicted a low relative photoconductivity, which prevented the experimentalists from obtaining useful TRPL measurements.

According to our calculations, the envisaged Sub-A band gap of 2 eV is achieved with $x=0.55$. However, the thickness optimization of the Sub-A was accomplished by recording the photo- jV characteristics for the profiles from Figure 3(a). Figure 8(a) presents the photocurrent-voltage plots for profiles of variable thickness of Sub-A (0 nm< a <95 nm). Sub-B and Sub-G for all these profiles were close to identical. Apparently, the photocurrent revealed a strong dependency on the Sub-A thickness. The inset of Figure 8(a) shows that the optimum Sub-A thickness falls responds to the Gaussian peak value at $a=20$ nm. It is evident that the photocurrent density yields grows from 4 mA/cm² to 18.3 mA/cm² at 1.2 V potential as the Sub-A thickness attains its optimum value. Please note that this favorable thickness region (15-25 nm) corresponding to the profiles R837 and R866, which is in line with the photosensitivity and IPCE results from Figure 5(a). This favorable thickness region could be associated to a reasonable trade-off between the need for a thicker absorber (the greater the absorption volume the higher photogeneration) on one side, and a requirement for a thinner absorber than the diffusion length ($a<L$), for a better hole survival rate, on the other side. As presented in the inset of Figure 6(a), further increase of the absorber thickness ($a>25$ nm) inflicted a fall in the photocurrent density to 3-4 mA/cm², suggesting

that the hole recombination process starts prevailing the photogeneration. Furthermore, from Figure 8(a) it is obvious that the current offset potential, being equal to the flat band potential, for the majority of the examined profiles was about 0.6 V - 0.7 V.

Optimization of Sub-G was carried out on the set of profiles from Figure 3(b), with identical Sub-A ($a=70$ nm), and same and optimized Sub-B, but different Sub-G. According to Figure 3(b) and Eq. 1 the band gap within the Sub-G changes from 3.3 eV to 2.0 eV, furnishing the profile with an internal electrical field at the same time. Hence, the three samples of different Sub-G provided three different implanted electrical fields, and thus different photocarrier lifetimes. The boundary values of the parameter x in Sub-G ($\text{Cd}_x\text{Zn}_{1-x}\text{O}$) for these three samples were $x_{\min}=0$ (for pure ZnO) to $x_{\max}=0.55$ ($\text{Cd}_{0.55}\text{Zn}_{0.45}\text{O}$). The thicknesses of the Sub-G (g) of these profiles were as follows: 145 nm, 220 nm, and 280 nm. The photo- jV curves, given in Figure 8(b) showed that the highest photocurrents were achieved for the thinnest Sub-G ($g=135$ nm), at the same time providing the highest implanted electrical field. Furthermore, comparing the photocurrents of profiles from Figure 8(b) and Figure 8(a), one may easily spot the difference of two orders of magnitude for those from Figure 8(a). Now, comparing the photocurrents of the two profiles of identical thickness (R836 from Figure 8(a) and R840 from Figure 8(b)) suggests that the low photocurrent observed might on R840 could result from the highly resistive ZnO-rich profile section ($0 < x < 0.2$) [26] of $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ interfacing the FTO substrate (Figure 3(b)). Such a heterojunction between semimetal and a semi-insulating alloy expectedly induces dramatic Schottky-barrier current loss. On the other hand, the same grading section endows solar light absorption in the region between 2.6 and 3.2 eV. However, it seemed reasonable to trade-off a fraction of the UV absorption for a reasonable conductivity across the Sub-G interface with FTO. From all the above, it followed that the optimum Sub-G should be about $g=135$ nm thick $\text{Cd}_x\text{Ni}_{1-x}\text{O}$ film, in which the Cd-substitutional fraction gradually changes from $x_{\min}=0.2$ (reasonable conductivity $\sim 10^{20} \Omega\cdot\text{cm}$ [26]) to $x_{\max}=0.55$.

3. Conclusion

In conclusion, we have proved that the three-sublayer photoanode clearly improves the water dissociation performance. Herein we also show that most significant role in the photoelectrochemical enhancement performance played the electrolyte optimization (HS-concentration, alkalinity, and molar concentration). Most remarkable growth in photocatalytic kinetics was, however, accomplished thanks to the optimized concentration of Na_2SO_3 , added to the K_2HPO_4 electrolyte as a hole-scavenger/sacrificial reagent. The systematic optimization of the parameters of the proposed three-sublayer photoanode architecture resulted in the following structure: Absorbing layer, Sub-A which is made of 20 nm thick $\text{Cd}_{0.55}\text{Zn}_{0.45}\text{O}$, providing the required band gap of 2 eV; Grading band gap, Sub-

G which is designed from 135 nm thick $\text{Cd}_x\text{Zn}_{1-x}\text{O}$, in which x -gradually changes from 0.2 to 0.55 (corresponding to photon absorption from 2 eV to 3 eV); and Sub-B, which is composed of 50 nm thick $\text{Ni}_{0.4}\text{Cd}_{0.6}\text{O}$ barrier that prevents electrons traverse into the water oxidation potential and recombine with the “working” holes therein. Sub-G also furnishes the photoanode with an implanted electrical field that increases the survival rate during the hole transport. The results showed that this new concept turned to be far more efficient for harvesting the solar illumination. Figure 9(a) shows a voltammogram - the photocurrent density versus potential of R870, a profile of optimized parameters ($a=20$ nm, $g=135$ nm, $x_{\min}=0.2$, $x_{\max}=0.55$, $b=50$ nm, $y=0.4$) in an optimized electrolyte (87% 1M K_2HPO_4 +13% 1M Na_2SO_3 , pH=9.8). The profile with the optimized parameters exhibited a photocurrent yield of 20 mA/cm^2 at 1.2 V potential. This high value is in agreement with the predicted value on the model (please check on the photocurrent at 1.2 V at $a=20$ nm on the Gaussian peak on the inset of Figure 8(a). Figure 9(b) depicts the optimized three sublayer profile with the band alignments among the utilized ternary compounds relative to the water red-ox potentials. It is noteworthy to mention that these, conceptually new, photoanodes also appeared to be photosensitive within the wavelengths range 300-600 nm. The maximum incident photon to current efficiency (IPCE) of $\sim 50\%$ at a photon energy of 3 eV was found for the most efficient profiles R837 and R866. Our results could be at some point comparable to those of the $\alpha\text{-Fe}_2\text{O}_3$ champion nanostructures for solar water splitting [37] However, corrosion challenges remain to be addressed in the future. The proposed photoanode model could be coupled with a Si-cell to form a highly efficient hybrid device [23,24,38]. Its optical properties could be further improved by electrochemical modification [39]. The modeling pattern is also applicable to other ternary alloyed junctions that satisfy the strict requirements [11] set for the photoanode materials.

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Caption to the Figures

Figure 1. Overview of the band energies for semiconductors used for the proposed multilayered photoanode. The purple boxes above the ZnO VB maxima in the band offset diagram pertain to the up-lifting of the VBM with the increase of the Cd-substitutional fraction (x) in $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ [24, 25]. The band offsets of TiO_2 and SnO_2 are also given for comparison. Fermi stabilization level, E_{FS} (-4.9 eV), and the water dissociation potentials, $\phi^{\text{H}^+/\text{H}_2}$ and $\phi^{\text{O}_2/\text{H}_2\text{O}}$, are also presented with level lines.

Figure 2. Three-sublayer general concept: (1) Absorber layer (Sub-A) with $E_g \sim 2.0$ eV and thickness a ; (2) Grading (Sub-G) layer $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ of thickness g , for x gradually changing from x_{min} to x_{max} and; (3) Electron barrier (Sub-B) layer of $\text{Ni}_y\text{Cd}_{1-y}\text{O}$ with thickness b .

Figure 3. Depth profiles (RBS results) of jointly Sub-A and Sub-G layers. Change of the Cd-content (x) in the $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ multilayer: (a) set of eight profiles with constant Sub-G but variable Sub-A; (b) set of three profiles of constant Sub-A but variable Sub-G

Figure 4. Visible spectra of the three-sublayer photoanode $\text{CdZnO}/\text{NiCdO}$ profiles: (a) transmittance spectra of the set of profiles with same Sub-G, but different Sub-A; (b) transmittance of profiles with same Sub-A but different Sub-G; (c) reflectance spectra of profiles with same Sub-G, different Sub-A; (d) reflectance spectra of profiles of same Sub-A, different Sub-G; (e) absorption coefficient spectra of profiles of same Sub-G, different Sub-A; and (f) absorption coefficient spectra of profiles of same Sub-A, different Sub-G. Sub-B is constant for all samples.

Figure 5. Incident Photon-to-current Efficiency (IPCE) spectra: (a) profiles of same Sub-G different Sub-A; (b) profiles of same Sub-A different Sub-G. All the sensitivity spectra were taken at short circuit conditions (@0 V bias vs. Pt-electrode).

Figure 6. Sub-B Parameters optimization. 6(a) Thickness- b optimization - photocurrent density for R744 profiles of a different Sub-B thickness, but identical y ($\text{Ni}_{0.49}\text{Cd}_{0.51}\text{O}$). Inset: Photocurrent density vs. b . Optimum Sub-B thickness is about $b \sim 50$ nm; 6(b) Ni-content optimization; photo- jV characteristics for profiles R744 topped with Sub-B with same thickness ($b \sim 50$ nm) but different Ni-contents (y). Inset: Photocurrent density as a function of the Ni-substitutional fraction (y) in $\text{Ni}_y\text{Cd}_{1-y}\text{O}$ layer. The Gaussian fit shows optimum Ni-content at $y = 0.4$.

Figure 7(a). Impact on the volume concentration of 1M Na_2SO_4 water solution in the 1M K_2HPO_4 electrolyte. Linear sweep voltammograms of profile R688.

Figure 7(b) Influence of the alkalinity ($\text{pH} > 9$) of the electrolyte with and optimized concentration of the HS on the photocatalytic activity of R838 photoanode profile, topped

with an optimized Sub-B. Inset: Photocurrent density versus the alkalinity at photoanode potentials of +1.0 V and +1.2 V (Gaussian fit-peak at pH=10).

Figure 7(c). Voltammograms representing the dependence of the photocurrent yields from R837 profile with an optimized Sub-B in an electrolyte that was optimized on the HS-concentration and pH on the electrolyte's molar concentration. Inset: Photocurrent dependence at a potential +1.0 V and +1.2 V on the molar concentration of the electrolyte.

Figure 8(a). Optimization of (*a*) the thickness of Sub-A: Photocurrent Density vs. voltage for profiles with same Sub-G and Sub-B but various Sub-A thicknesses ($0 < a < 95$ nm. Inset: dependence of the photocurrent at two different voltages (1.0 V and 1.2 V) as a function of *a*, and a Gaussian fit (maximum at $a=20$ nm)

Figure 8(b). Optimization of Grading layer - Sub-G thickness (*g*) and $x_{\min}$. Photocurrent Density for the multilayer profiles with identical Sub-A (same $a \sim 70$ nm) but different Sub-G.

Figure 9. Linear Sweep Voltammogram of R870, an optimized photoelectrochemical photoanode profile in optimized electrolyte. Photocurrent density was evaluated from the Light current density reduced by the Dark. Inset: R870 RBS profile of Sub-A and Sub-G.

Caption to the Table

Table I. $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ Sub-A and Sub-G parameters: *a*= thickness of Sub-A, *g*=thickness of Sub-G, $x_{\max}$ and $x_{\min}$ are the boundary Cd-contents of Sub-G, at the Sub-B and FTO margins, correspondingly.

Table I.

#	Profile	t=a+g [nm]	a [nm]	g [nm]	$x_{\max}$ [rel. un.]	E_g (min) [eV]	$x_{\min}$ [rel. un.]	E_g (max) [eV]
1	R744	290	70	220	0.61	2.0	0	3.3
2	R835	235	65	170	0.57	2.0	0.22	2.6
3	R836	210	40	170	0.57	2.0	0.20	2.7
4	R837	170	15	155	0.56	2.0	0.22	2.6
5	R838	150	0	150	0.53	2.1	0.20	2.7
6	R839	350	70	280	0.58	2.0	0	3.3
7	R840	210	75	145	0.56	2.0	0	3.3
8	R841	265	95	170	0.58	2.0	0.16	2.9
9	R866	165	25	150	0.58	2.0	0.20	2.7
10	R867	175	35	140	0.57	2.0	0.20	2.7
11	R868	145	10	135	0.55	2.1	0.20	2.7
12	R930	185	25	160	0.62	2.1	0.20	2.7

Fig. 1.

Fig. 2

(a)

(b)

Fig. 3.

(a)

(b)

(c)

(d)

Fig. 4

(e)

(f)

Fig. 4

Fig. 5.

Fig. 6.

Electrolyte Optimizations on R866 1M K_2HPO_4 & 1M "HS" Na_2SO_3

Variable: HS concentration

Fig. 7(a).

Electrolyte Optimizations with R838 in 87% 1M K_2HPO_4 + 13% 1M Na_2SO_3 + NaOH

Optimized Sub-B, Optimized HS-concentration

Variable: Electrolyte Alkalinity

Fig. 7(b)

Electrolyte optimizations with R837 87% K_2HPO_4 +13% Na_2SO_3
 Optimum Sub-B, Optimum HS, Optimum pH
Variable: Molar Concentration

Fig. 7(c).

Constant: Sub-B and Sub-G. Optimized Electrolyte
Variable: Sub-A ($a=0-95$ nm)

Fig. 8(a).

Fig. 8(b).

Optimized Multilayer Profile: R870(g=135 nm/a=20nm)b=50 nm y=0.4
Optimized Electrolyte: 87% 1M K₂HPO₄+13% 1M Na₂SO₃ pH=9.6

Fig. 9