Semiempirical Modelling of a Nanostructured Photoanode Profile for Highly Efficient Water Splitting: Three Sublayers Concept

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Abstract

We present semiempirical modeling of conceptually new Cd$_x$Zn$_{1-x}$O/Ni$_y$Cd$_{1-y}$O based nanostructured photoanode, composed of three sublayers: Absorber (ABS), Grading (GRAD) and Barrier (BAR), for highly efficient photocatalytic water dissociation. Our modeling resulted into ABS made of Cd$_{0.55}$Zn$_{0.45}$O due to its favorable positions of the valence and conduction band on the water splitting potentials and a band gap $\sim$2.0 eV. The GRAD was composed of Cd$_x$Zn$_{1-x}$O with a gradual decrease of $x$ across the profile, resulting in a gradual band gap change from 2.0 to 3.1 eV. At the same time, GRAD provides the profile with an implanted electrical field that improves the hole survival rate. The BAR was engineered in a manner that provides 1 eV barrier in the conduction band. It was made of 50 nm thick Ni$_{0.4}$Cd$_{0.6}$O film with $E_g$ $\sim$3.0 eV. The BAR’s valence band is well aligned to the one of

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the GRAD, providing a barrier-free hole transport. In this paper, we prove that the proposed modeling of the three individual layers clearly represents a new paradigm for an improved efficiency for photoelectrochemical water splitting.

**Keywords:** Cd$_x$Zn$_{1-x}$O/Ni$_y$Cd$_{1-y}$O, photoanodes, water splitting, voltammetry, IPCE energy efficiency.

1 Introduction

Many efforts have been done for direct conversion of the solar energy into energy of chemical fuels (water reduction/oxidation to H$_2$/O$_2$). 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$_2$O$_3$ [4–6], Cu$_2$O [7], CoO$_x$ [8], TiO$_2$ [9], dual absorber of WO$_3$/Fe$_2$O$_3$ [10], etc. A typical PEC consists of a semiconductor photoelectrode that generates electron-hole pairs upon solar light absorption. The pairs are supposed to be separated and introduced into the hydrogen/oxygen evolution potentials, correspondingly. 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 candidate for a semiconductor electrode should satisfy some requirements: efficiently to absorb the solar spectrum at energies $\geq 2$ eV; 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); its conductivity to be considerable (noninsulating material) for minimization of the ohmic losses; to show good stability towards photo-corrosion; and last but not the list, the photoelectrochemical reaction occurs at a reasonable rate [12]. It has been demonstrated that ideal energy gap of the semiconductor for PEC water splitting is $E_g \sim 2$ eV [13], energy 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”, [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 PECs have been 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 for expanding the solar light harvesting spectrum towards the visible region, as in the case of double layered
ZnO-GaN [22] photoanode. Furthermore, complex PEC multilayers based on graded band gap Cd$_x$Zn$_{1-x}$O structures have been previously used for photoanodes by other authors [23]. However, this concept led to relatively poor PEC performance.

According to some previous exploration, the Cd$_x$Zn$_{1-x}$O system [24] 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 [25] 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 $x$ (gray box above ZnO’s VBM on Figure 1). Another research reported on the Ni$_y$Cd$_{1-y}$O alloying system that $E_g$ changed from 2.2 to 3.2 eV within the conductive alloying region.

![Figure 1](image.png)

**Figure 1** Overview of the band energies of semiconductors used for the proposed multilayered photoanode. This diagram is similar to LEGO blocks for semiconductor band engineering. The gray box above the ZnO VB maxima in the band offset diagram pertains to the up-lifting of the VBM with the increase of the Cd-substitutional fraction ($x$) in Cd$_x$Zn$_{1-x}$O [24, 25]. The band offset of SnO$_2$ (FTO) substrate TCO is given as well. Fermi stabilization level, $E_{FS}$ (–4.9 eV), and the water dissociation potentials, $\phi_{H^+/H_2}$ and $\phi_{O_2/H_2O}$, are also presented with level lines.
region \((0 < y < 0.6)\) [25]. It has been reported that in the same Ni-content region the CBM remained rather unaffected, but the VBM moved upwards as \(y\)-increased from 0 (pure ZnO) to 0.6.

Below we present the semi-empirical modeling of the three-sublayer concept applied on \(\text{Cd}_x\text{Zn}_{1-x}\text{O}/\text{Ni}_y\text{Cd}_{1-y}\text{O}\) alloy system and parameter optimization for highly efficient water-splitting in an optimized K-phosphate electrolyte (subject to different publication).

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 ABS (absorber layer), BAR (electron barrier layer) and GRAD (grading gap layer) on Figure 2. All these sublayers were synthesized by Radiofrequency (RF) sputtering (deposition conditions were given elsewhere [24–26]). Various profiles were synthesized due to the variation of sublayer’s thickness parameters \(a, b\) and \(g\), controlled by the deposition time, and the content parameters \(x\) and \(y\) correlated to the RF power of the corresponding target. All the five parameters \((a, b, g, x\) 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. The samples for the merits of the photoelectrochemical (PEC) studies were prepared as windows of a known area of approximately \(1 \times 1\) cm\(^2\), isolated with a non-transparent epoxy. Each profile was submerged into optimized 87% 1M \(\text{K}_2\text{HPO}_4\) and 13% 1M \(\text{Na}_2\text{SO}_3\) (known to act as a hole scavenger) with pH = 10 at the bottom of the 100 ml beaker with BAR facing...
the incident illumination. 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 $jV$s were recorded using single linear voltammetry sweeps in dark (D) and under light (L) at AM 1.5 G – 100 mW/cm$^2$ illumination conditions. The voltage sweep was set to 0.1 V/s. The reference electrode was Ag/AgCl (3M KCl) while a Pt-ribbon served as a counter electrode. By subtracting the dark (D) from the corresponding light (L) $jV$-characteristic the curves were turned into photocurrent density vs. voltage characteristics ($jV$).

3 Results and Discussion

3.1 Modelling

As described earlier, the ABS layer that is made of the Cd$_x$Zn$_{1-x}$O alloy is destined to harvest the photons of 2 eV energy from the solar spectrum. To engineer the band gap of the Cd$_x$Zn$_{1-x}$O for the required $E_{g}^{(CdZnO)} = 2$ eV [13] one has to resolve the bowing equation (1) for the CdO-ZnO system.

$$E_{g}^{(CdZnO)}(x) = E_{g}^{CdO}x + (E_{g}^{ZnO} - dx)(1-x)$$

The unknown parameter $x$ was evaluated by replacing the values of the bowing parameter, $d = 0.94$, the intrinsic band gaps of CdO and ZnO ($E_{g}^{CdO} = 1.3$ eV and $E_{g}^{ZnO} = 3.3$ eV) [24]. The realistic solution was $x = 0.55$. Hence, the Cd$_{0.55}$Zn$_{0.45}$O was selected for the ABS part of the three layer photoanode model. However, the thickness $a$ of the ABS remains to be evaluated in a customized photoelectrochemical experiment.

The graded gap sublayer (GRAD) is made of the same Cd$_x$Zn$_{1-x}$O alloy as the ABS. It stretches between the FTO-substrate and the ABS. It is deposited as a first layer over the FTO substrate, intended to absorb photons from 2.0 eV to 3.3 eV. Hence, the substitution fraction of Cd, $x$, in this sublayer gradually changes from $x_{\text{min}}$ (at the FTO margin) to $x_{\text{max}}$ (at the ABS margin). Naturally, $x_{\text{max}}$ should correspond to $x$ of the ABS (2 eV is achieved at $x = 0.55$) as shown in Figure 3. At the same time, GRAD sublayer furnishes the photoanode profile with an implanted electric field that enhances the hole-survival rate across the interface. GRAD was engineered in a manner that the Cd-fraction in the Cd$_x$Zn$_{1-x}$O profile gradually changes from $x_{\text{min}}$ (Cd-content at the side interfacing the FTO) to $x_{\text{max}}$ (Cd-content at the side interfacing the
Figure 3  Schematic band engineering of the three sublayer photoanode model: ABS, GRAD and BAR sublayers. Tentative band alignment within the multilayer and water oxidation and reduction potentials.

Sub-A). The other boundary value, $x_{\text{min}}$, remains to be determined through a customized experimental procedure. Finally, the electron barrier layer (BAR) was deposited on the top of the ABS (as depicted in Figure 2). It was synthesized 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 role of this sublayer is to furnish the CB with a barrier jump of about 1 eV at the solid-liquid interface (Figure 3). The selection of this particular ternary compound ($\text{Ni}_y\text{Cd}_{1-y}\text{O}$) was based on the findings that the VB minima of ABS ($\text{CdZnO}$) and BAR ($\text{NiCdO}$) are in an approximate alignment [24–26]. Hence, the photogenerated holes are expected to take a barrier-free route to the oxygen evolution potential $\varphi(\text{O}_2/\text{H}_2\text{O})$. Besides, both the alloys, CdZnO, and NiCdO have
binary endpoint compounds that are isostructural (polycrystalline-wurtzite) with grain sizes $\sim 16$ nm [24, 25] and $\sim 20$ nm [26] respectively, and are, therefore, convenient for building a conductive heterojunction. 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 Equation 2,

$$E_{g}^{NiCdO} = E_{g}^{NiO} y + (E_{g}^{CdO} - dy)(1-y),$$

we obtained a realistic solution for $y = 0.4$. Optimization of the thickness of BAR, $b$, was pursued experimentally.

The profiles synthesized and used for modeling/optimization photoelectrochemical experiments of the ABS, GRAD and BAR layers in the present study, are presented in Figure 4. The values were further summarized in Table 1. Figure 4 presents the variation of the Cd-content ($x$) across ABS and GRAD sublayers, both composed of Cd$_{x}$Zn$_{1-x}$O. Herein, Figure 4(a) describes the profiles of the same thickness of GRAD ($b = 135$ nm) but the variable thickness of ABS ($a = 0$–95 nm). Furthermore, Figure 4(b) shows the variation of the Cd-content across the set of profiles of approximately identical ABS ($a \sim 70$ nm), but different GRAD ($g = 135, 220$ and $280$). One should consider that the Zn-content across the profile is equal to $(1-x)$, assuming the stoichiometric transfer of the target material [26].

### 3.2 Thickness Optimization

As mentioned before, the role of electron barrier BAR made of Ni$_{y}$Cd$_{1-y}$O as a top layer over ABS is to prevent electrons from traversing across the solid/liquid interface into the oxygen evolution potential and recombine with the “photolysis working” holes, therein. The calculations for the demanded 1 eV high barrier using Equation 2 resulted into $y = 0.4$. However, the BAR thickness is limited by the occurrence of electron tunneling from the higher CB states. Hence, the thickness $b$ was optimized with BAR layers of same Ni-content (Ni$_{0.49}$Cd$_{0.51}$O) but various thickness $b$, deposited over the R744 profile (constant ABS & GRAD). The thicknesses $b$ were in the range from 0 to 85 nm. Herein, $b = 0$ denotes an absence of BAR. Again, the values of $b$ and $y$ were evaluated from RBS measurements on the BAR layer on glass substrates. The photo-$jV$-characteristics of these profiles are given in Figure 5(a) on the left. It is evident that the highest photocurrents yields were achieved for $b \sim 52$ nm. The supplemental Figure 5(a) on the right was derived from the one on the left. It presents the dependence of the photocurrent
Figure 4  Depth profiles (RBS results) of jointly ABS and GRAD layers. Change of the substitution Cd-fraction ($x$) in the Cd$_x$Zn$_{1-x}$O multilayer: (a) set of eight profiles with constant GRAD ($g = 135$ nm) but different ABS; (b) set of three profiles of constant ABS ($a = 70$ nm) but variable GRAD.

density at $+0.85$ V potential on the BAR thickness ($b$). The polynomial fit suggested that the optimum barrier layer thickness is $b = 40$ nm. It also appeared that further increase of $b$ induces higher ohmic losses, resulting into
photocurrent density fall. Further optimizations of BAR layer are possible with electrochemical surface modification of the optical and electrical properties of NiCdO alloy [27].

According to our calculations, the envisaged ABS band gap of 2 eV is achieved with $x = 0.55$. However, the thickness optimization of the ABS was accomplished by recording the photo-$jV$ characteristics for the profiles from Figure 3(a). Figure 5(b) on the left presents the photocurrent-voltage plots for profiles of different ABS thickness (0 nm $< a < 95$ nm). For these profiles BAR and GRAD sublayers were identical. Apparently, the photocurrent revealed a strong dependency on the ABS thickness. The supplemental Figure 5(b) on the right shows that the optimum ABS thickness responds to the Gaussian peak value at $a = 20$ nm. It is evident that the photocurrent density yields grow from 4 mA/cm$^2$ to 18.3 mA/cm$^2$ at 1.2 V potential as the ABS thickness attains its optimum value of 20 nm. This favorable thickness region could be associated to a reasonable trade-off between the need for a thicker absorber (greater absorption volume for 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. Further increase of the ABS ($a > 25$ nm) inflicted a fall in the photocurrent density to 3–4 mA/cm$^2$, suggesting that at this point the hole recombination process starts to prevail the photogeneration. Furthermore, from Figure 5(b) 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.
Figure 5  (a) Optimization of the thickness of the electron barrier (BAR) $\sim b \sim 40$ nm; (b) Optimization of thickness of absorber ABS $\sim a \sim 20$ nm; (c) Optimization of graded gap layer (GRAD) thickness ($g = 135$ nm).
Optimization of GRAD sublayer was carried out on the set of profiles from Figure 3(b), for which ABS thickness is identical \((a = 70 \text{ nm})\), and BAR is optimized \((y = 0.4, b \sim 40 \text{ nm})\), but their GRAD sublayer is with different thickness. According to Figure 3(b) and Eq. 1 the band gap within the GRAD 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 GRAD provided three different implanted electrical fields, and thus a different photocarrier life-times. The boundary values of the parameter \(x\) in GRAD of \(\text{Cd}_x\text{Zn}_{1-x}\text{O}\) for these three samples were \(x_{\text{min}} = 0\) (for pure \(\text{ZnO}\)) to \(x_{\text{max}} \sim 0.55\) (\(\text{Cd}_{0.55}\text{Zn}_{0.45}\text{O}\)). The thicknesses of the GRAD \((g)\) of these profiles were as follows: 135 nm, 220 nm, and 280 nm. The photo-jV curves, given in Figure 5(c), showed that the highest photocurrents were achieved for the thinnest GRAD \((g = 135 \text{ nm})\). This profile was designed to provide the highest implanted electrical field among the profiles of constant ABS-sublayer. The latter result shows that the steeper the gradient in the band gap across the GRAD sublayer, the better the photocurrent yield. Furthermore, comparing the photocurrents of the two profile groups from Figure 5(b) and Figure 5(c), one may easily spot the difference of two orders of magnitude in favor of those from Figure 5(b). Now, if one compares the photocurrents from Figures 5(b) and 5(c) of profile R836, depicted in Figure 3(a), and R840 on Figure 3(b) (please note that the two profiles have the same full thickness), one may notice the much lower photocurrent yield produced from R840. This could be explained by the existence of the highly resistive tail on the FTO side, i.e. \(\text{ZnO-rich profile section} (0 < x < 0.2) \) [24] of \(\text{Cd}_x\text{Zn}_{1-x}\text{O}\) that interfaces 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 GRAD interface with FTO. From all the above, it followed that the optimum thickness is \(g = 135 \text{ nm} \text{Cd}_x\text{Ni}_{1-x}\text{O}\) film, in which the Cd-substitutional fraction gradually changes from \(x_{\text{min}} = 0.2\) (reasonable conductivity \(\sim 10^{20} \Omega\text{cm} \) [24]) to \(x_{\text{max}} = 0.55\).

4 Conclusion

Our results proved that the three-sublayer photoanode depicted in Figure 3 clearly improved the photocatalytic dissociation performance. The modeling and the systematic optimization of the parameters of the proposed...
three-sublayer photoanode architecture resulted in the following structure: Absorbing layer (ABS) which is made of 20 nm thick Cd$_{0.55}$Zn$_{0.45}$O, providing the required band gap of 2 eV; Grading band gap layer (GRAD) which is designed from 135 nm thick Cd$_x$Zn$_{1-x}$O, where $x$ gradually changes from 0.2 to 0.55 (corresponding to photon absorption from 2 eV to 3 eV); and the electron Barrier layer (BAR), composed of 40 nm thick Ni$_{0.4}$Cd$_{0.6}$O film that prevents electrons to traverse into the water oxidation potential and recombine with the “working” holes therein. GRAD 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, and should be, therefore examined with other suitable pairs of ternary compounds.

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References


Biographies

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