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Semiempirical modeling of a three sublayer photoanode for highly efficient photoelectrochemical water splitting: Parameter and electrolyte optimizations

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ABSTRACT

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 $Cd_{0.55}Zn_{0.45}O$ 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 $Cd_xZn_{1-x}O$ 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 electron Barrier 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 $Ni_{0.4}Cd_{0.6}O$ film with E_g~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% 1 M K_2HPO_4 and 13% 1 M 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/cm^2 to ~20 mA/cm^2 at +1.2 V for visible light. The observed Incident Photon-to-Current Efficiency (IPCE) was about 50% measured at a photon energy of 3 eV.

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~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

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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 Fig. 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 stabile compound under illumination in a neutral or alkaline solution [29,30]. Similarly, NiO is stabile in alkaline electrolytes [31]. However, the stability of CdO at 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 $Cd_xZn_{1-x}O$ and $Ni_yCd_{1-y}O$ 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.

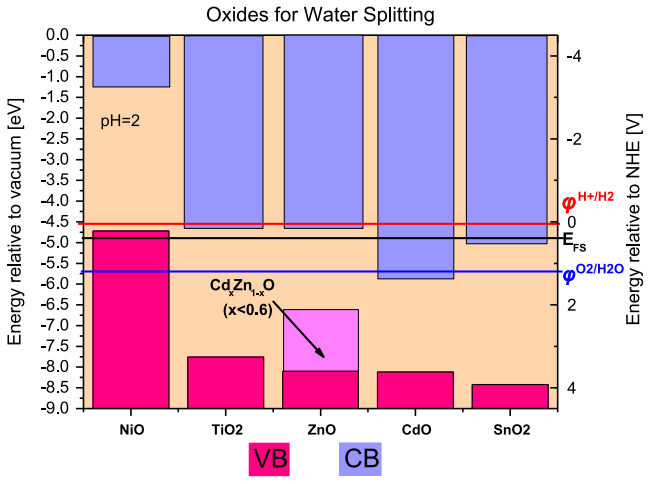

Fig. 1. Overview of the band energies for semiconductors used for the proposed multilayered photoanode. The pink box above the ZnO VB maxima in the band offset diagram pertain to the up-lifting of the VBM with the increase of the Cd-substitutional fraction (x) in $Cd_xZn_{1-x}O$ [24,25]. The band offsets of TiO_2 and SnO_2 are also given for comparison. Fermi stabilization level, E_{FS} (-4.9 eV), and the water dissociation potentials, ϕ^{H+/H_2} and ϕ^{O_2}/H_2O, are also presented with level lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Materials and methods

The newly proposed $Cd_xZn_{1-x}O/Ni_yCd_{1-y}O$ photoanode structure comprises of three sublayers, denoted as Sub-A, Sub-B, and Sub-G, as depicted in Fig. 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 1×1 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

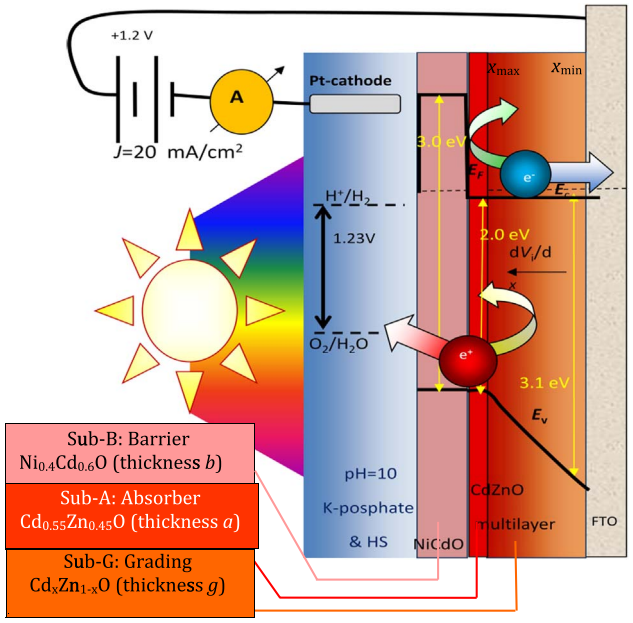

Fig. 2. Three-sublayer general concept: (1) absorber layer (Sub-A) with $E_g \sim 2.0$ eV and thickness a; (2) grading (Sub-G) layer $Cd_x Zn_{1-x}O$ of thickness g, for x gradually changing from x_{min} to x_{max} and; (3) electron barrier (Sub-B) layer of $Ni_yCd_{1-y}O$ with thickness b.