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Design and fabrication of sandwich-structured α-Fe_2O_3/Au/ZnO photoanode for photoelectrochemical water splitting

Rich Kant*, Sandeep Pathak, Viresh Dutta

Photovoltaic Laboratory, Centre for Energy Studies, Indian Institute of Technology, Delhi, Hauz-Khas, New Delhi, India

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ABSTRACT

α-Fe_2O_3/Au/ZnO hetrostructured thin films were fabricated using chemical spray pyrolysis technique and implemented as photoanode for photoelectrochemical (PEC) water splitting. Photoactivity of α-Fe_2O_3/Au/ZnO electrodes for PEC water oxidation under solar radiation was efficiently improved as compared to that for α-Fe_2O_3, α-Fe_2O_3/Au and α-Fe_2O_3/ZnO electrodes. The α-Fe_2O_3/Au/ZnO photoanode displayed a significant increase in photocurrent density of 250 μA/cm^2, as compared to α-Fe_2O_3 (photocurrent density~27 μA/cm^2), at 0.5 V vs. SCE in 0.5 M NaOH under AM 1.5 G illumination indicating enhanced optical absorption and charge transportation. The presence of Au layer favored the charge transfer from α-Fe_2O_3 to ZnO via high energy coupled surface plasmons. The charge transfer kinetics was further improved by tuning of the surface plasmon resonance (SPR) band of Au nanoparticles (NPs) using electric field assisted spray pyrolysis. The maximum photocurrent density of 500 μA/cm^2 (at 0.5 V vs. SCE) was obtained for α-$Fe_2O_3$0.5 kV/Au/ZnO electrode. The optimized design using Au sandwiched layer between two different band gap semiconductors with creation of different hetrojunctions (α-Fe_2O_3/ZnO and ZnO/Au) presented a configuration with enhanced optoelectronic properties, which is highly useful for PEC water splitting.

1. Introduction

Utilization of solar energy as a sustainable renewable energy source can be considered as an alternative pathway to meet future energy demands. In this regard, PEC water splitting using semiconductor photoelectrodes is an attractive approach for production of clean and renewable fuel (H_2) which can provide for an energy storage option as well. A crucial role is played by the semiconductor photoelectrode, which creates the conditions (like photon absorption, electron hole pair generation, charge separation followed with reduction and oxidation processes by the photogenerated electrons and holes to produce H_2 and O_2 respectively) necessary for the hydrogen generation under light and a proper combination of materials is required for higher efficiencies in PEC. Recently, research has been focused on many semiconductor electrodes such as TiO_2, Fe_2O_3, ZnO, and WO_3 owing to their suitable characteristics of low cost, suitable band structure, stable and natural abundance [1–10]. However, it is difficult for a single semiconductor oxide to satisfy all the requirements of PEC water splitting. For example, ZnO, TiO_2 have favorable band edge positions for both water oxidation as well as reduction but are insensitive to the visible part of solar spectrum [11]. α-Fe_2O_3 is able to absorb in the visible part of solar spectra, however, its solar to hydrogen conversion (STH) efficiency is lower because of inappropriate position of conduction band i.e. not suitable for water reduction and poor charge transport properties due to short diffusion length (~ 4 nm) [12]. It has been reported in literature that STH conversion efficiency of PEC activity is mainly affected by having good optical absorption, suitable position of the energy levels according to water oxidation and reduction potentials in the band diagram and good charge transfer kinetics of the photocatalyst [13]. In this context, recent efforts have been made to develop hetrojunction based photoelectrodes to get an optimal configuration for practical PEC applications. Coupling two semiconductors having different band gaps prepared by different synthesis methods such as wet chemical, hydrothermal, atomic layer deposition, photochemical deposition, for creation of an optimized heterojunction [14–17],etc.,may lead to an enhanced efficiency of PEC devices, one of the reason being absorption of a larger portion of solar spectrum which is not possible with the individual semiconductors [18–21]. Designing a hetrojunction based photoanode contributes to enhanced PEC efficiency through red shift in band gap, improved charge separation via reducing recombination centers and increasing diffusion length of charge carriers [22]. Many reports are there in the literature on hetrostructures based on α-Fe_2O_3-$TiSi_2$, Fe_2O_3-AZO, Fe_2O_3-TiO_2, and Fe_2O_3-ZnO to improve optical absorption with proper band gap engineering as well as faster charge

* Corresponding author. Tel.: +91 1126596489.
E-mail address: richkant18@gmail.com (R. Kant).

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transportation [15,23–28]. Among these α-Fe_2O_3/ ZnO hetrostructures have also been investigated in literature for photocatalytic applications. Combining Fe_2O_3 and ZnO in form of hetrostructures (Fe_2O_3–ZnO) will result in improving light absorption covering UV to Visible region, facilitating charge transfer kinetics via reducing e^-h^+ recombination [17]. Liu et al. [29] synthesized Fe_2O_3/ ZnO tubular hetrostructure via photochemical deposition and found great improvement in photocatalytic activity. Guo et al. have demonstrated the efficient photodegradation of RhB dye ZnO/$ZnFe_2O_4$ core–shell NW arrays [14]. Moniz et al. [30] synthesized Fe_2O_3-TiO_2 composites by photodeposition method. The Fe_2O_3-TiO_2 composites yield a photocurrent density of 340 μA/cm^2 at 1 V vs. Ag/AgCl. Barreca et al. [31] reported vapor phase fabrication of ZnO hetrostructure followed by functionalization with Fe_2O_3 or WO_3 via radio frequency-sputtering for application in solar PEC water splitting. The ZnO-Fe_2O_3 photoanodes showed maximum photocurrent of 35 μA cm − 2 at 0.8 V vs. Ag/AgCl, whereas ZnO-WO_3 introduction resulted in a nearly twofold photocurrent increase (≈55 μA cm − 2 at 0.8 V vs. Ag/AgCl). The reason for enhancement in PEC performance has been attributed to enhanced separation of photogenerated charge carriers due to the intimate contact between the two oxides. Hernández et al. [32] showed application of the ZnO@TiO_2 core–shells for the PEC water-splitting reaction, which showed a maximum photocurrent density of 400 μA/cm^2 at 1.23 V vs. RHE.

In addition, sensitization of semiconductor surface with noble metals especially Au is another popular approach to enhance the photoelectric conversion through formation of semiconductor-metal Schottky junction and SPR effect [11,33–36]. In addition to this, Au nanoparticles also help to prevent corrosion during photoreaction [36]. For e.g. Zhang et al. [37] reported Au nanoparticles sensitized ZnO nanorod@nanoplatelet core–shell arrays. The photocurrent density of the modified electrode exhibited a photocurrent density of 60 μA/cm^2 at 0.6 V vs. SCE, much superior to pristine ZnO photoanode. Liu et al. [38] showed fabricated Au sensitized ZnO nanorods modified with Al_2O_3 overlayer (ZnO/Au/Al_2O_3) as a photoanode for PEC applications. ZnO/Au/Al_2O_3 photoanode yielded a photocurrent of 550 mA/cm^2 at 1.5 V vs. Ag/AgCl. But there are very few reports on using Au nanoparticles as an electron shuttle at interface of two semiconductors e.g. CdS–Au–TiO_2, ZnO–Au–SnO_2 [39,40]. Tada and his group demonstrated a high photocatalytic activity for CdS–Au–TiO_2 nanojunction system via vectorial electron transfer from TiO_2 to CdS using Au nanoparticles as compared to single and two component systems [39]. Li. et al. reported improved charge transfer across ZnO-Au-SnO_2 interface resulting in superior PEC performance with a maximum photocurrent density of 0.58 mA/cm^2 at 1 V vs. Ag/AgCl [40]. In order to better comprehend the different approaches being reported in literature, a summary of the current state of art on the ZnO based photoanodes is presented in Supplementary Table SI. To our best knowledge, there is no report on using Au nanoparticles (NPs) as an interlayer between α-Fe_2O_3/ZnO interfaces for application in PEC water splitting. Intercalating Au NPs in α-Fe_2O_3/ ZnO interface would be helpful in improving e^-h^+ separation, e^- transfer and electron collection efficiency.

In this study, for the first time a sandwich-structured α-Fe_2O_3/Au/ZnO photoanode is proposed for efficient PEC water splitting. Different thin film configurations (α-Fe_2O_3, α-Fe_2O_3/Au, α-Fe_2O_3/Au/ZnO) are fabricated using spray pyrolysis method and then PEC performance of their photoanodes is investigated separately. Further, an additional voltage of 0.5 kV is applied during spray deposition (Electric field assisted spray pyrolysis) of α-Fe_2O_3 film and its effect upon morphology of α-Fe_2O_3 thin film is highlighted and subsequently optoelectronic properties of the whole α-$Fe_2O_3$0.5 kV/Au/ZnO configuration are studied. Applying voltage during deposition itself play a major role in reducing the droplet size due to columbic fission, creating a uniform thin film [41]. This spray pyrolysis and electric field assisted spray pyrolysis method is a very simple, inexpensive, fast one step technique where NPs as well as thin film can be deposited [42]. This research reveals that the spray pyrolysis method could be an important method for low cost fabrication of hetrojunction based photoanodes for PEC applications.

2. Experimental

Spray pyrolysis set up used for deposition of thin films is described in detail elsewhere [43]. Indium tin oxide was used as substrate for deposition of thin films. The substrates were washed with soap solution and then ultrasonically cleaned in deionized (D.I) water, acetone and isopropanol, respectively and dried in air. The optimized deposition parameters used for all depositions: substrate temperature 400 °C, solution flow rate 4 ml/min and nozzle to substrate distance18 cm. Nitrogen was used as a carrier gas at a flow rate of 1.5 Kgf/cm^2.

2.1. α-Fe_2O_3 layer

For the preparation of α-Fe_2O_3 spray solution 0.1 M $FeCl_3$ was dissolved in ethanol. Approximately 7 ml of solution was sprayed on the heated substrate. An additional electric pressure was created on the spray droplets by applying DC voltage of 0.5 kV between the nozzle and a circular metal electrode.

2.2. Au layer

Spray solution for Au NPs was prepared by adding 0.5 mM chloroauric acid in D.I water. About 3 ml of spray solution was used for this deposition.

2.3. ZnO layer

For deposition of ZnO thin film, 0.3 M zinc acetate and 1.5 M ammonium acetate dissolved in methanol was used as precursor solution [44]. Approximately 7 ml of solution was sprayed for depositing ZnO thin film.

After the final deposition, all the films were annealed at 500 °C for 60 minutes.

3. Material Characterization

X-ray diffraction (XRD) patterns were obtained using Rigaku Minflex 600 ×-ray diffractometer equipped with CuKα incident beam (λ = 1.54 Å). Field emission scanning electron microscopy (FESEM) images were acquired with FEI Quanta 200 F scanning electron microscope operating at an accelerating voltage of 10 kV. The UV-Vis spectra were recorded on a LAMBDA L602008 spectrometer. Room temperature photoluminescence (PL) spectra were recorded using a fluorescence spectrophotometer (Horiba Lab RAM Evolution) with an excitation wavelength of 325 nm.

4. Electrochemical characterization

For electrochemical measurements, thin films of as prepared samples were converted into working electrodes (having active area of about 1 cm^2) by making ohmic electrical contacts using silver paste and copper wire with the exposed area of ITO substrate and then the uncovered area was enclosed with non-transparent and nonconducting epoxy resin. The electrochemical measurements were performed in a three-electrode PEC cell to obtain the current–voltage (I–V) characteristics, Mott–Schottky (M-S) and electrochemical impedance spectroscopy (EIS) measurements. The PEC study was performed on SP-300 Electrochemical Workstation (Biologic instruments, France) which is attached to class AAA solar simulator (Sol3A Oriel Newport USA) having an intensity of 100 mW/cm^2 (AM 1.5 G). Linear sweep voltammetry (LSV) scans under dark and visible light illumination performed under AM1.5 G illumination conditions and M-S measurement was carried out in the dark in the potential range −1.0 to +1.0 V vs.