

Study on charge transfer processes in thin-film heterojunction between cuprous oxide and hematite



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ARTICLE INFO

Keywords:

Hematite
Cuprous oxide
Heterojunction
Charge transfer
Z-scheme
Solar energy conversion

ABSTRACT

Low cost, abundantly available, stable and environmentally friendly metal oxide semiconductors are of particular interest in the area of solar energy conversion. In the present study thin-layered heterojunction, composed of iron (III) oxide and copper (I) oxide was formed on conductive glass substrate using spray-pyrolysis and electrodeposition techniques. X-ray diffraction, scanning electron microscopy, electrochemical impedance spectroscopy and potentiometry were used to characterize and analyze the chemical composition, surface morphology and the processes of light-induced charge transfer between the oxide phases.

It was found that under illumination effective separation of photoinduced charge carriers across $\text{Fe}_2\text{O}_3/\text{Cu}_2\text{O}$ interface occurs. It has been demonstrated that the experimental results are consistent with the so-called Z-scheme mechanism of charge transfer, when photoelectrons from the conduction band of Fe_2O_3 transfer through the heterojunction to recombine with photoholes in the valence band of Cu_2O .

1. Introduction

Continually increasing importance of renewable energy resources promotes active search for semiconductor materials and their composites for efficient solar energy conversion. Low cost, efficiency and stability are among the main requirements posed for these materials. Application of metal oxides for both photovoltaic and photoelectrochemical (PEC) conversion has been attracting more and more attention recently [1–6], because they are chemically stable, environmentally friendly, not-expensive and less prone to photocorrosion in aqueous solutions compared to group III-V or II-VI semiconductors. Hematite ($\alpha\text{-Fe}_2\text{O}_3$) and cuprous oxide (Cu_2O) are among those earth abundant, not toxic, low cost, small band gap ($E_g \sim 2$ eV) and widely investigated semiconductor oxides. Both are of particular interest from the viewpoint of solar hydrogen generation via photoelectrochemical water splitting: p-type Cu_2O as photocathode [7,8] and n-type Fe_2O_3 as photoanode [9,10] for PEC reduction and oxidation of water molecules, respectively. Numerous studies have been devoted to understanding the p-type conductivity of cuprous oxide and it has been established that it originates from the presence of copper vacancies, which have the lowest formation energies under both Cu-rich-O-poor and Cu-poor-O-rich conditions [11]. Main problem associated with the use of Cu_2O in photoelectrochemical energy conversion is related with intrinsic instability of the semiconductor, predetermined by the fact that oxidation and reduction potentials of Cu_2O phase lie within the bandgap [12],

whereas the main drawback of hematite is very short hole diffusion length [13]. Though the performance of individual oxides has been extensively investigated, the heterojunction between these materials has not been explored much so far. It is known that iron (III) and copper (I) oxides form the so-called type II heterojunction with a staggered band alignment [14,15]. Such heterostructures are of particular interest from the photocatalytic point of view due to effective separation of photo-generated charge carriers across the junction between two oxide phases [16,17]. Sharma et al. [18,19] have used spray pyrolysis method to deposit thin layered $\alpha\text{-Fe}_2\text{O}_3/\text{Cu}_2\text{O}$ heterojunction on ITO/glass substrate. Photoelectrochemical measurements revealed photoanode behavior of the fabricated heterostructures and the PEC performance of the heterojunction in oxygen evolution reaction under anodic bias was demonstrated to be more efficient compared to that of individual oxides spray-pyrolyzed on ITO substrate. In [20,21] heterojunction between Cu_2O and $\gamma\text{-FeOOH}$ or Fe_2O_3 was formed using electrodeposition technique and photovoltaic characteristics of such solar cell were tested. Short circuit current densities ranging between 0.74 and 1.58 mA cm^{-2} and open-circuit voltage of 38–108 mV was reported. Recently, the heterojunction between iron oxide and copper oxides has attracted the attention of scientists working in the area of CO_2 reduction. In [22] hydrothermal synthesis has been applied for the deposition of Cu_2O on the surface of $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles and the activity of the composite photocatalysts towards reduction of CO_2 in gas phase has been explored. CO has been reported to be the main product under

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visible light illumination. Li et al. [23,24] have formed Fe_2O_3 nanotubes by means of anodizing Fe foil, decorated them with Cu_2O or CuO and investigated their performance in photoelectrochemical reduction of CO_2 . Methanol and ethanol were the two major products of reduction process.

In the present study we used the combination of spray-pyrolysis and electrodeposition methods to form thin bilayered heterojunction between Cu_2O and Fe_2O_3 oxides on conducting glass substrate. To the best of our knowledge thus formed heterostructure of iron (III) and copper (I) oxides has not been explored so far. The processes of light-induced transfer of charge carriers across the oxide interface were investigated and compared with results reported in literature [22].

2. Experimental

2.1. Formation of oxide layers

Thin layers of Ti-doped Fe_2O_3 were formed on glass/FTO ($5\text{--}7\ \Omega/\text{sq}$) substrate using the method of spray-pyrolysis. Self-made spray pyrolysis equipment was employed. Before spraying, the surface of the substrate was cleaned in hot Piranha solution (3:1 mixture of concentrated H_2SO_4 and 30% H_2O_2 – a highly corrosive and hazardous etchant) and washed thoroughly with deionized water. The precursor solution was prepared by dissolving $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in the mixture of HCl and 2-propanol. The resulting solution was then added to the mixture of TiCl_3 and H_2O_2 . The molar concentrations of the components in the final solution were as follows: 0.05 M FeCl_3 , 0.032 M TiCl_3 , 0.07 M HCl, 0.8 M 2-propanol, 1.2 M H_2O_2 . The precursor solution was sprayed onto the glass/FTO substrate, which was maintained at $475 \pm 15\ ^\circ\text{C}$ using the hot plate. Argon of ultra-high purity grade (99.999%) was used as carrier gas and the flow rate was $5\ \text{L}\cdot\text{min}^{-1}$. Titanium salt was added into spraying solution as a dopant, because it is an established fact, that Ti doping increases the conductivity of hematite films improving significantly their photoelectrochemical performance [13,25–28].

Layers of cuprous oxide were electrodeposited onto glass/FTO or glass/FTO/ Fe_2O_3 substrates ($1.0 \times 1.5\ \text{cm}^2$) from acetate electrolyte containing 0.1 M $\text{Cu}(\text{CH}_3\text{COO})_2 + 0.25\ \text{M}\ \text{CH}_3\text{COONa}$, pH 5.6, at $50\ ^\circ\text{C}$. Similar procedures were reported in [29–32]. Prior to electrodeposition, the surface of Fe_2O_3 was subjected to mild etching in 5% solution of H_2SO_4 . The electrodeposition was performed in a water-jacketed three electrode cell by means of scanning the working electrode potential from E_{ocp} (open-circuit potential) to $-0.3\ \text{V}$ (Ag/AgCl) and backwards at the rate of $0.5\ \text{mV}\ \text{s}^{-1}$. Platinum plate was used as counter electrode and Ag/AgCl/sat. KCl, connected to the cell via the salt bridge, was used as reference.

All solutions used in the experiments were prepared from reagents of analytical grade and deionized water.

2.2. Characterization of oxide layers

2.2.1. Scanning electron microscopy, X-ray diffraction and absorption measurements

The surface morphology of the oxide layers as well as film thickness were investigated using Helios NanoLab dual beam workstation equipped with X-Max $20\ \text{mm}^2$ energy dispersion spectrometer (Oxford Instruments). The cross-sections of the samples were produced applying focused ion beam (FIB) technique. Pt layer of $0.7\ \mu\text{m}$ thickness was e-beam deposited on the sample surface before sectioning with Ga^+ focused beam.

XRD patterns of the films were measured using an X-ray diffractometer SmartLab (Rigaku) equipped with 9 kW rotating Cu anode X-ray tube. Grazing incidence (GIXRD) method was used in 2θ range $20\text{--}80^\circ$. An angle between parallel beam of X-rays and a specimen surface (ω angle) was adjusted to 0.5° . Phase identification was performed using software package PDXL (Rigaku) and ICDD powder diffraction data-base PDF-4+ (2014 release).

Absorption spectra of Fe_2O_3 and Cu_2O layers formed on glass/FTO substrate were recorded using Perkin Elmer Lambda 35 UV/VIS spectrophotometer and glass/FTO as reference sample.

2.2.2. Electrochemical impedance measurements

The electrochemical impedance measurements were performed in dark, using three-electrode cell, solution of 0.5 M Na_2SO_4 and electrochemical measurement system Solartron 1280 C with frequency response analyser (AMETEK, Inc). FTO/ Fe_2O_3 and FTO/ Cu_2O samples were used as working electrodes, whereas reversible hydrogen electrode in the working solution (RHE) and Pt wire were used as reference and counter electrodes, respectively. All potential values further in the text refer to RHE. The conversion to standard hydrogen electrode (SHE) scale can be done using the following relationship: $E_{\text{vs. SHE}} = E_{\text{vs. RHE}} - 0.059\ \text{pH}$. The electrochemical impedance spectra were recorded under the open-circuit potential in potentiostatic mode with the AC voltage amplitude of $\pm 5\ \text{mV}$. The frequency range from 20 kHz to 0.1 Hz was explored. The Mott-Schottky plots of Fe_2O_3 and Cu_2O films were obtained by sweeping the potential from 0.6 V to 1.4 V and from 0.95 V to 0.4 V, respectively at frequency of 5 kHz and scan rate of $5\ \text{mV}\ \text{s}^{-1}$.

2.3. Photoelectrochemical measurements

Photoelectrochemical behavior of oxide layers was investigated using the above-described three-electrode cell and the solution of 0.1 M KOH. The processes of photoinduced charge transfer across $\text{Fe}_2\text{O}_3/\text{Cu}_2\text{O}$ interface were studied in a two-electrode setup. Indium contacts were used for the measurements as illustrated schematically in Fig. 1. The surface of working electrodes was illuminated with high intensity discharge Xe-lamp with 6000 K spectrum and calibrated with a silicon diode to simulate AM 1.5 illumination ($\sim 100\ \text{mW}\ \text{cm}^{-2}$) at the sample surface. The variation of the open-circuit potential or voltage under illumination was measured using potentiostat/galvanostat AUTOLAB 302.

3. Results and discussion

3.1. Phase composition, surface morphology and optical absorption of oxide films

Composition of the oxide layers was investigated using X-ray diffraction (XRD) technique. XRD patterns of iron and copper oxides, spray-pyrolyzed and electrodeposited, respectively, on conducting glass substrate are shown in Fig. 2. In the case of iron oxide (Fig. 2a), the diffraction peaks at $2\theta = 33.15^\circ, 54.06^\circ, 57.44^\circ, 62.44^\circ, 69.59^\circ$ and 71.94° can be indexed to (1 0 4), (1 1 6), (1 2 2), (2 1 4), (2 0 8) and (1 0 10) planes of $\alpha\text{-Fe}_2\text{O}_3$ hematite phase, respectively (ICDD PDF 1–80–2377), whereas those at $2\theta = 26.71^\circ, 38.14^\circ, 51.92^\circ, 62.2^\circ, 66.22^\circ$ and

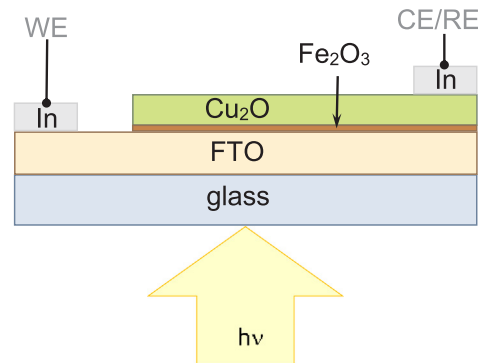


Fig. 1. Schematic cross-sectional image of layered $\text{Fe}_2\text{O}_3/\text{Cu}_2\text{O}$ heterojunction with indium contacts used for experiments; WE – working electrode, CE/RE – shorted counter and reference electrodes.

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