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Nanostructured $BaTiO_3/Cu_2O$ heterojunction with improved photoelectrochemical activity for H_2 evolution: Experimental and first-principles analysis

Dipika Sharma[a], Sumant Upadhyay[a], Vibha R. Satsangi[b], Rohit Shrivastav[a], Umesh V. Waghmare[c], Sahab Dass[a,*]

[a] Department of Chemistry, Dayalbagh Educational Institute, Agra 282 110, India
[b] Department of Physics & Computer Sciences, Dayalbagh Educational Institute, Agra 282 110, India
[c] Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560 064, India

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ABSTRACT

Nanostructured $BaTiO_3/Cu_2O$ heterojunction electrodes with varying thickness of Cu_2O thin films were synthesized using spray deposition of porous cuprous oxide films onto the surface of spin coated nanostructured thin films of $BaTiO_3$. First-principles based density functional theory calculations have been done for the first time on the band offsets of $BaTiO_3/Cu_2O$ heterojunction interface and effective mass of electron and hole for bulk $BaTiO_3$ and Cu_2O, exhibited better separation of the photogenerated charge carriers at the $BaTiO_3/Cu_2O$ interface. Experimental results on photoelectrochemical activity of $BaTiO_3/Cu_2O$ heterojunction in the photoelectrochemical cell for water splitting reaction validate the theoretical results. Maximum photocurrent density value of 1.44 mA/cm^2 at 0.95 V/SCE was observed for $BaTiO_3/Cu_2O$ heterojunction photoelectrode with 442 nm thickness. Photo-generated charge carriers apparently transfer more easily in $BaTiO_3/Cu_2O$ heterojunction than that in pristine Cu_2O and $BaTiO_3$.

1. Introduction

Various Strategies have been attempted to improve performance of photoelectrodes in the Photoelectrochemical splitting of water including dye sensitization [1] or using inorganic sensitizers [2], doping [3,4], swift heavy ion irradiation [5], use of heterojunction or layered systems [6,7]. Overall performance of PEC water splitting process is limited by efficiency of photogenerated charge carriers separation and their rate of electron transfer to the reaction site [8–10]. An efficient charge separation at the interface is still a challenge before the researchers and scientific community at large. Bilayered/heterojunction system of metal oxide semiconductors is one of the recent strategies towards improving the performance of the photocatalyst with inherent merits [11–20]. Use of *p-n* heterojunction as a building block for nanodevices [21–25] is preferred over single semiconductors [26], because *p-n* junction creates a region with potential gradient near which electrons in n-type semiconductors and holes in p-type semiconductors are depleted, and potential gradient thus generated facilitates the separation of charge carriers thereby reducing the recombination of electrons and holes. $BaTiO_3$ can be consider as a good photoelectrode for photoelectrochemical water splitting as it has high resistance to corrosion and photocorrosion in aqueous media and well-matched energy band edges with the redox level of water, However, $BaTiO_3$ band gap is about 3.2 eV and it mostly absorbs in the ultraviolet region of spectrum with a small amount of visible light [27] Combination of n-type $BaTiO_3$ with p-type semiconductor such as Cu_2O, MoS_2, CuO to form *p-n* heterojunction can be a effective way to improve the absorption in visible light and separation of photogenerated charge carriers. Among these p-type semiconductors Cu_2O is highlighted due to its low band gap (Eg = 2.2 eV) and promising material for conversion of solar energy into electrical or chemical energy [28]. Moreover, one of the physical quantities that play an important role in characterizing the interface of semiconductor heterojunction systems is the band offset, i.e., relative position of the energy levels on both sides of the interface. Difference between the positions of the top of the valence bands and bottom of the conduction bands of the two materials is valence band offset (VBO) and conduction band offset (CBO) respectively. These band discontinu-

* Corresponding author.
E-mail addresses: vibhasatsangi@gmail.com (V.R. Satsangi), waghmare@jncasr.ac.in (U.V. Waghmare), drsahabdas@gmail.com (S. Dass).

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ities play a fundamental role in deciding the transport properties of heterojunction systems. With this idea, this paper presents the First-principles density functional pseudopotential calculations on the band offsets of $BaTiO_3/Cu_2O$ heterojunction interface and effective mass of electron and hole for bulk $BaTiO_3$ and Cu_2O to explain the better separation of the photogenerated charge carriers at the $BaTiO_3/Cu_2O$ interface and their experimental validations on photoelectrochemical response of nanostructured $BaTiO_3$ thin films modified by overlayering of Cu_2O with varying thickness. Prepared $BaTiO_3/Cu_2O$ heterojunction photoelectrodes were also characterized for their structural, electrical and optical properties to assess the mechanism by which this concept influences the photoelectrode performance.

2. Experimental

Copper(II) acetate [$Cu(CH_3COO)_2{\cdot}H_2O$, Aldrich 98%], Dextrose [Fisher 99.5%] and isopropanol [$(CH_3)_2CHOH$, Qualigens 99.5%] were used for cuprous oxide synthesis. For the synthesis of $BaTiO_3$, barium acetate [$Ba(CH_3COO)_2$, Aldrich 99%], titanium(IV) isopropoxide [$Ti(OC_2H_4CH_3)_4$, Aldrich 99%], 2-methoxyethanol [$CH_3OCH_2CH_2OH$, Aldrich 99.3%] and glacial acetic acid [CH_3COOH, Qualigens, 99.5%], were used as precursor solution.

2.1. Preparation of photoelectrode

2.1.1. Preparation of nanostructured $BaTiO_3$ thin films

Nanostructured thin films of $BaTiO_3$ were deposited on ITO (Sn: In_2O_3) glass substrate using sol-gel spin coating method. The precursor solution comprising of barium acetate [$Ba(CH_3COO)_2$] and titanium isopropoxide [$Ti(OC_2H_4CH_3)_4$] dissolved in glacial acetic acid (CH_3COOH) and 2-methoxyethanol ($CH_3OCH_2CH_2OH$). Initially an appropriate ratio of solid-state barium acetate was dissolved in glacial acetic acid. In second step stoichiometric amount of titanium isopropoxide was dissolved in 2-methoxyethanol with stirring at 70 °C for 30 mins and cooled to room temperature. Both solutions were then mixed with each other for making stoichiometric, transparent, and stable Barium titanate precursor. The films were spin coated on ITO at 2000 rpm for 20 s and sintered at 600 °C for 2 h [29]. Finally films were slowly cooled to room temperature inside the furnace. One third length of ITO substrate was initially covered by transparent tape to establish the electrical contact to convert them into electrodes. Synthesis of $BaTiO_3$ thin films from acetate precursor shown in the following flow chart:

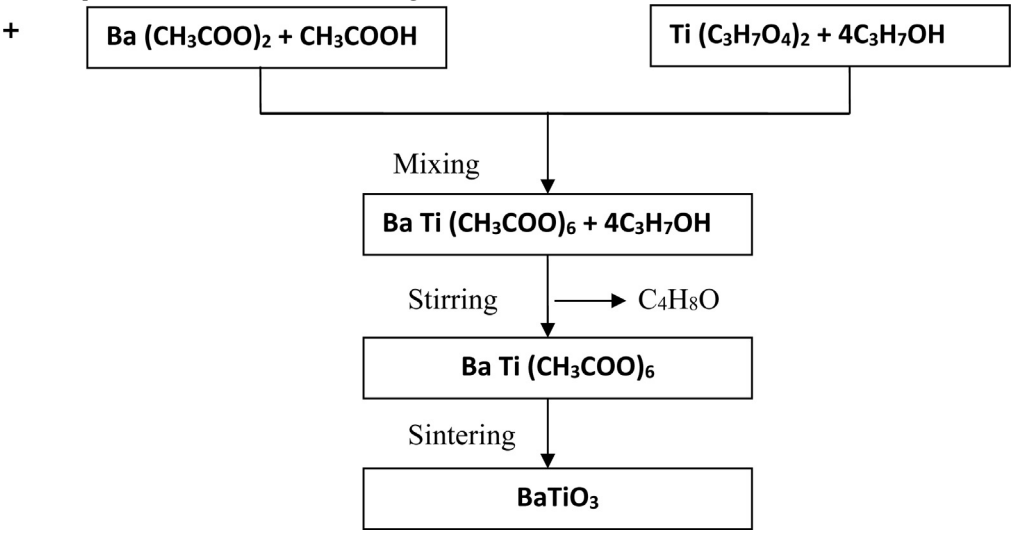

Table 1
Thicknesses with other details of samples.

Film thickness (nm)				
S.no.	Cu_2O	$BaTiO_3$	overall thickness	Acronym
1	142	–	142	A
2	–	156	156	B
3	142	156	298	C
4	286	156	442	D
5	307	156	463	E
6	541	156	697	F

2.1.2. Preparation of $BaTiO_3/Cu_2O$ heterojunction thin films

Nanostructured $BaTiO_3/Cu_2O$ heterojunction thin films were obtained by deposition of Cu_2O thin film layer with varying thickness over the predeposited $BaTiO_3$ thin film by spray pyrolysis method (Holmarc, India). The precursor solution containing of Copper(II) acetate monohydrate ($Cu(CH_3COO)_2{\cdot}H_2O$), and Dextrose dissolved in water were used as starting compounds. In addition 20 vol% of 2-propanol [$(CH_3)_2CHOH$ (Qualigens 99.5%)] was added to the above described aqueous solution. Detailed methodology has been reported elsewhere [30]. To optimize the photoelectrochemical response of $BaTiO_3/Cu_2O$ heterojunction thin films, 15, 30, 45 and 60 s spray periods were tried for the deposition of Cu_2O thin films. The possible chemical reactions for the formation of Cu_2O crystal are shows given below:

$$Cu(CH_3COO)_2.H_2O \xrightarrow{aq} 2Cu^{2+} + CH_2COO^- + H_2O$$

$$2Cu^{2+} + C_6H_{12}O_6 + H_2O \rightarrow 2Cu^{+} + C_6H_{12}O_7 + 2H^{+}$$

$$2Cu^{+} + 2H_2O + OH^{-} \rightarrow Cu_2O + 4H^{+} + H_2O$$

Thicknesses with other details of samples prepared have been summarized in Table 1. To use $BaTiO_3/Cu_2O$ heterojunction thin films as photoelectrode in PEC cell, electrical contacts were obtained using silver paste and copper wire, from the uncoated area of the conducting glass substrate. The area of contact was later covered with non-transparent and non-conducting epoxy-resin (Hysol, Singapore). The effective area of the photoelectrode available for illumination was 1.0 cm^2.

3. Characterization

Cross-sectional and surface morphology of samples was characterized using field emission scanning electron microscope