**Dipika Sharma**
Department of Physics
Indian Institute of Technology, Delhi
New Delhi, India
+91 9758754920 (Mob.),
dipika.sharma286@gmail.com

## EDUCATION

- **Working as Institute Post Doc fellow** at Department of physics, Indian Institute of technology Delhi, India (11/10/2018-present).
- **National Post Doc fellow**, under the supervision of Prof. B.R. Mehta Department of physics, Indian Institute of technology Delhi, India (10/02/2017-10/10/2018).

  **Project Title: Heterojunction photoelectrocatalysts: Effect of Structure and Composition Imperfections on Photoelectrochemical splitting of water for solar hydrogen generation**
- Ph.D. in Chemistry from Dayalbagh Educational Institute (Deemed University), Agra, India

  **Thesis Title** : **Experimental & First-Principles Theoretical Studies on Nanostructured Bilayered Semiconductors Systems in Photoelectrochemical Splitting of Water**

  **Thesis Advisor:** Prof. Sahab Dass, Dept. of Chemistry, Dayalbagh Educational Institute, Agra

  **Thesis Co-Advisor:** Prof. Umesh V. Waghmare, Theoretical Sciences Unit, JNCASR, Bangalore, India

- **Master of Philosophy in Chemistry** with 9.31 CGPA from Dayalbagh Educational Institute, Agra, India-282 110 in 2012.
- **Master of Science in Chemistry** with 9.45 CGPA from Dayalbagh Educational Institute, Agra, India-282 110 in 2011.
- **Bachelor of Science in Chemistry** with 81.2 % from Dayalbagh Educational Institute, Agra, India-282 110 in 2010.

## RESEARCH EXPERIENCE

- Photoelectrochemical Splitting of Water for Solar Hydrogen generation
- Synthesis of Nanostructured Materials
- Electrochemical Energy Conversion, *Ab initio* methods based on density functional theory (DFT)

## INSTRUMENTS HANDLED

- X-Ray DIFFRACTOMETER (XRD) (BRUKER AXS D8 ADVANCE,GERMANY)
- UV-Vis SPECTROPHOTOMETER (SHIMADZU, JAPAN)
- POTENTIOSTAT (PAR VERSTAT II, U.S.A.), Zahner Electrochemical work station
- LCR METER (AGILENT TECHNOLOGIES, U.S.A.)
- SOLAR SIMULATOR (AM 1.5)
- ATOMIC FORCE MICROSCOPY (AFM) (NANOSURF EASY SCAN, SWITZERLAND)
- HIGH TEMPERATURE MUFFLE FURNACE (METREX, INDIA)
- PEC SET-UP CONSISTING OF LIGHT SOURCE INCLUDING SOLAR SIMULATOR AND $H_2$ COLLECTION ASSEMBLY

## SOFTWARES USED

- QUANTUM-ESPRESSO (PWSCF)- Open-Source Package for Research in Electronic Structure simulation, and optimization
- XCRYSDEN (Crystal Structure Visualization-Software)
- XMGRACE
- ORIGIN

## HONORS AND AWARDS

1. *Awarded with INSPIRE scholarship for Higher Education (SHE)(DST, New Delhi) from 2007 to 2012.*
2. *Awarded with INSPIRE fellowship for Ph.D Program (DST, New Delhi), 2014*
3. *Awarded with International travel support (ITS) (DST, New Delhi), 2015 to attend SPIE Conference in San Diego from 28th August to 1St September 2016.*

## JOURNAL PUBLICATIONS

## PUBLICATIONS

### *IN JOURNALS*

1. **Dipika Sharma,** and B.R. Mehta, Nanostructured $TiO_2$ thin films sensitized by $CeO_2$ as an Inexpensive Photoanode for enhanced photoactivity of water oxidation, ***Journal of Alloys and Compounds,*** 749, 2018, 329-335. **(IF=3.7)**

2. **Dipika Sharma,** Rishibrind Kumar Upadhyay, Biswarup Satpati, Vibha R. Satsangi, Rohit Shrivastav, Umesh V. Waghmare, and SahabDass, Electronic Band-offsets across $Cu_2O/BaZrO_3$ Heterojunction and its Stable Photo-Electro-Chemical Response: First-principles Theoretical Analysis and Experimental Optimization, **Renewable energy**, 113 (2017) 503-511. **(IF=4.9)**

3. **Dipika Sharma**, Sumant Upadhyay, Rohit Shrivastav, Vibha Satsangi, Umesh V. Waghmare, Sahab Dass, Nanostructured $BaTiO_3/Cu_2O$ heterojunction with improved Photoelectrochemical Activity for $H_2$ Evolution: Experimental and First-Principles Analysis, ***Applied Catalysis B: Environmental*** 2016, 189, 75-85. **(IF=11.698)**

4. **Dipika Sharma**, Sumant Upadhyay, Rohit Shrivastav, Vibha Satsangi, Umesh V. Waghmare, Sahab Dass, Improved Photoelectrochemical Water Splitting Performance of $Cu_2O/SrTiO_3$ Heterojunction Photoelectrode, ***Journal of Physical Chemistry C***, 118, 25320-25329, 2014. **(IF=4.587)**

5. **Dipika Sharma**, Sumant Upadhyay, Rohit Shrivastav, Vibha Satsangi, Sahab Dass, Nanostructured Ti-$Fe_2O_3/Cu_2O$ heterojunction photoelectrode for efficient hydrogen production, ***Thin Solid Films***,574, 125-131, 2015. **(IF=1.99)**

6. **Dipika Sharma,** Anuradha Verma, Rohit Shrivastav, Vibha Satsangi, Sahab Dass, Nanostructured $SrTiO_3$ thin films sensitized by $Cu_2O$ for Photoelectrochemical Hydrogen Generation, ***Int. Journal of Hydrogen Energy***, 39, 4189-4197, 2014. **(IF=4.22)**

7. **Dipika Sharma**, Vibha R. Satsangi, Rohit Shrivastav, Umesh V. Waghmare and Sahab Dass, Understanding the photoelectrochemical properties of Nanostructured $CeO_2/Cu_2O$ Heterojunction Photoanode for Efficient Photoelectrochemical Water Splitting, ***International Journal of Hydrogen Energy***, 41,2016, 81339-813350. **(IF=4.22)**

8. **Dipika Sharma**, Sumant Upadhyay, Vibha R. Satsangi, Rohit Shrivastav, Umesh V. Waghmare and Sahab Dass, Ni-doped $Cu_2O$ thin films for solar-hydrogen generation: Experiments & First-principles analysis, ***Advanced Science Letter***, 22, 780-784, 2016. **(IF=1.25)**

9. **Dipika Sharma**, Sumant Upadhyay, Surbhi Choudhary, Vibha R. Satsangi, Rohit Shrivastav, and Sahab Dass, Enhancement of Photoelectric Conversion Properties of $\alpha$-$Fe_2O_3/Cu_2O$ Bilayered Photoanode, ***International Journal of Materials, Mechanics and Manufacturing***, 2: 51-55, 2014.

10. Rishibrind Kumar Upadhyay, **Dipika Sharma**, Fe doped BaTiO 3 sensitized by Fe 3 O 4 nanoparticles for improved photoelectrochemical response, Materials Research Express, 2018. **(IF=1.16)**

11. Sumant Upadhyay, **Dipika Sharma**, Vibha R. Satsangi, Rohit Shrivastav, Umesh V. Waghmare, Sahab Dass, "Experimental and First-principles Theoretical Studies on Ag-doped Cuprous Oxide as Photocathode in Photoelectrochemical Splitting of Water", ***Journal of Materials Science***, 49 (2), 868-876, 2013. **(IF=2.599)**

12. Sumant Upadhyay, **Dipika Sharma**, Vibha R. Satsangi, Rohit Shrivastav, Umesh V. Waghmare, Sahab Dass, "Spray pyrolytically deposited Fe-doped $Cu_2O$ thin films for solar hydrogen generation: Experiments & first-principles analysis", ***Materials Chemistry and Physics***, 160, (2015) 32-39. . **(IF=2.99)**

13. Surbhi Choudhary, Anjana Solanki, **Dipika Sharma**, Nirupama Singh, Sumant Upadhyay, Rohit Shrivastav "Photoelectrochemical water splitting using bilayered $ZnO/SrTiO_3$ photoelectrodes", ***Int. J. Mod. Phys***. 22 (2013) 545-551. . **(IF=1.0)**

14. Anuradha Verma, Anupam Srivastav, Anamika Banerjee, **Dipika Sharma**, Shailja Sharma, Udai Bhan Singh, Vibha Rani Satsangi, Rohit Shrivastav, Devesh Kumar Avasthi, Sahab Dass, "Plasmonic Layer Enhanced Photoelectrochemical Response of $Fe_2O_3$ Photoanodes", ***Journal of Power Sources***, 315, 152-160, 2016. . **(IF=6.945)**

15. Anuradha Verma, Anupam Shrivastav, **Dipika Sharma**, Anamika Banerjee Shailja Sharma, Vibha Rani Satsangi, Rohit Shrivastav, Devesh Kumar Avasthi, Sahab Dass, "A Study on the Effect of Low Energy Ion Beam Irradiation on Au/ $TiO_2$ System for its Application in Photoelectrochemical Splitting of Water" ***Nuclear Instruments and Methods in Physics Research Section B Beam Interactions with Materials and Atoms***, 2016, 379, 255-261. . **(IF=1.34)**

## CHAPTERS IN BOOKS

1. Nanostructured α-$Fe_2O_3$ Thin Film Coupled with Bioinspired CoAc Catalyst in Artificial Photosynthesis for Hydrogen Generation. Authored by – Anamika Banerjee, Anupam Srivastav, Anuradha Verma, **Dipika Sharma**, Shailja Sharma, Vibha Rani Satsangi, Rohit Shrivastav and Sahab Dass Published in Industrial Applications of Nanostructured Materials (Bloomsbury Publishing India Pvt. Ltd.) edited by V. Rajendran, R. Suriyaprabha and K.E. Geckeler. ISBN: 978-93-85436-93-2 (2015), 205-208.

## POSTER/ORAL PRESENTATIONS

1. **Dipika Sharma**, Experimental and first-principles studies on $BaZrO_3$/CuO heterojunction in photoelectrochemical splitting of water, Proceedings of DAE-BRNS 4$^{th}$ Interdisciplinary Symposium on Materials Chemistry (ISMC-2012); 11-16 Dec: BARC, Mumbai.
2. **Dipika Sharma**, Enhancement of photoelectric conversion properties of α-$Fe_2O_3$/$Cu_2O$ bilayered photoanode, ICNST, 2013, 16-17 Sep, New Delhi.

3. **Dipika Sharma**, Nanostructured $BaTiO_3/Cu_2O$ heterojunction thin films for Photoelectrochemical Splitting of water, Proceedings of Direction to Materials Science (DMS), 2013, 1-3 December, JNCASR-Bangalore.
4. **Dipika Sharma**, Nanostructured $SrTiO_3/Cu_2O$ heterojunction thin films for Photoelectrochemical Splitting of water, Global summit, (FICCI), 2013, 25-26-July, New Delhi.
5. **Dipika Sharma**, Ni-doped $Cu_2O$ thin films for solar-hydrogen generation: Experiments & First-principles analysis, Nanocon, 2014, BhartiyaVidhya Peeth- 13-14 October, Pune.
6. **Dipika Sharma**, Nanostructured $BaTiO_3/Cu_2O$ heterojunction with improved Photoelectrochemical Activity: Experimental and First-Principles Analysis, National Conference on Frontiers at the Chemistry-Allied Sciences Interface (FCASI), 2015, 14-16 March, University of Rajasthan, Jaipur
7. **Dipika Sharma**, Nanostructured $CeO_2/Cu_2O$ Heterojunction Photoanode for Efficient Photoelectrochemical Water Splitting, ICEFN, 2016, 27-29 March- Kumaun University, Nainital.
8. **Dipika Sharma**, Nanostructured $BaTiO_3/Cu_2O$ heterojunction with improved Photoelectrochemical Activity: Experimental and First-Principles Analysis, International Conference on Nanostructuring by Ion Beams (ICNIB), 2015, 23-25 November, Amar Hotel, Agra.
9. **Dipika Sharma**, Band-offsets at $BaTiO_3/Cu_2O$ heterojunction and enhanced photoelectrochemical response: Theory and experiment, SPIE Optics + Photonics for Sustainable Energy, 28$^{th}$ August to 1$^{st}$ September 2016, San Diego, California United States.
10. **Dipika Sharma**, Nisha. Kodan, B. R. Mehta, Nanostructured $TiO_2$ thin films sensitized by $CeO_2$ as an Inexpensive Photoanode for enhanced photoactivity of water oxidation, Nano India, 15-17 March, IIT Delhi, 2017.

11. **Dipika Sharma**, B. R. Mehta, Nanostructured $Cu_2O/PbTiO_3$ Heterojunction For Photoelectrochemical Hydrogen Generation, ICONSAT,21-23 March, Centre for Nano and Soft Matter Sciences, Bengaluru, 2018.

- **Invited Talk as women Nano scientist on "**Nanostructured $TiO_2$ thin films sensitized by $CeO_2$ as an Inexpensive Photoanode for enhanced photoactivity of water oxidation" ICONN17, 9-11 Augtust, SRM University, Chennai, 2017.

**Ph.D RESEARCH WORK:**

Photoelectrochemical (PEC) method is considered to be a safe option for hydrogen generation. A conventional PEC cell is established with a semiconductor photoanode and platinum (Pt) cathode in the electrolyte solution. To achieve efficient splitting of water, the semiconductor photoanode must meet the following criteria. (i) It should be photochemically stable with good corrosion resistance in aqueous solution; (ii) Its conduction band edge should be more negative than the $H_2$ evolution potential and a valence band edge should be more positive than the $O_2$ evolution potential; (iii) It should have strong absorption in the solar spectrum region; (iv) It should be a high quality material with low density of defects for efficient charge transfer and (v) It should be low-cost. Unfortunately, to date, there is no such material that can satisfy all above requirements simultaneously.

To improve the performance of photoanode or photocathode various attempts have been made in advances of design, fabrication, and modification of semiconductor nanostructured materials. **Bilayered/heterojunction system of metal oxide semiconductors is one of the recent strategies adopted towards improving the performance of the photocatalyst with inherent merits.**

The aim of the my Ph.D work was to develope a theoretical model for heterojunction systems using DFT calculations and validating the same by experimentally preparing heterojunction thin films and then performing PEC studies.

**HETROJUNCTION SYSTEM STUDIED**

**a.** $SrTiO_3$-$Cu_2O$ **b.** $BaTiO_3$-$Cu_2O$ **c.** $Cu_2O$-$BaZrO_3$ **d.** $Cu_2O$-$SrTiO_3$ **e.** Ti-$Fe_2O_3$-$Cu_2O$ and **f.** $CeO_2$-$Cu_2O$ heterojunction

**Post Doc Work:** Physical and chemical methods for the deposition of various metal oxides and 2D layered materials and their characterization techniques such as XRD, SEM, and UV-visible for the improved photoelectrochemical applications.

## RESEARCH INTEREST

My research interests include the development of efficient semiconductor photoelectrode with recent preparation techniques such as Rf- sputtering, molecular epitaxy, pulse laser deposition etc. and its modification such as layering with bio-inspired catalyst, use of precious metals such as platinum, ruthenium, and iridium as catalysts attached to a semiconductor, ***use of 2D graphene based metal oxide semiconductors (as single oxides, mixed/layered oxides),*** and gradient doping for efficient Hydrogen production. I would also like to perform first principles electronic structure investigation for providing theoretical understanding of the performance of semiconductor with respect to water splitting as the photoelectrode properties of a material strongly depend on the electronic structure of the material.

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# Nanostructured $TiO_2$ thin films sensitized by $CeO_2$ as an inexpensive photoanode for enhanced photoactivity of water oxidation

Dipika Sharma*, B.R. Mehta**

*Thin Film Laboratory, Department of Physics, Indian Institute of Technology, New Delhi, 110016, India*

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ABSTRACT

Nanostructured $CeO_2/TiO_2$ bilayer thin films were fabricated by sequential deposition of $CeO_2$ on $TiO_2$ with varying the thickness of $CeO_2$ using sol–gel spin-coating method. All samples were characterized by XRD, SEM, and UV–Visible absorption spectroscopy with an inspiration to use them as photoanode in photoelectrochemical splitting of water. The $CeO_2/TiO_2$ bilayer with the optimized thickness of $CeO_2$ and $TiO_2$ showed enhanced photoelectrochemical response of 2.1 mA $cm^{-2}$ at 0.95 V/Ag/AgCl as compared to pristine $CeO_2$ and $TiO_2$. The improved photocurrent density of $CeO_2/TiO_2$ bilayer probably due to rapid transfer of charge carriers or electrical gradient at $CeO_2/TiO_2$ interface. This scalable and cost effective work with stable PEC performance of $CeO_2/TiO_2$ also shows the potential for realistic PEC applications.



## 1. Introduction

Solar hydrogen generation by solar water splitting in PEC cells is the most forward-looking method in the recent time on account of hydrogen being widely accepted as clean energy carrier [1,2]. This solar-to-hydrogen conversion process initiated from the first PEC water splitting response of titanium dioxide ($TiO_2$) by Honda and Fujishima in 1972 [3]. Nowadays, $TiO_2$ is well known semiconductor as photoanode due to its suitable band positions, abundant, non-toxic, and stability. However, previous studies on $TiO_2$ have found that its wide band gap of 3.2 eV absorbs only UV part of the solar spectrum and high recombination rate of photogenerated electron–hole pairs due to its short diffusion length of charge carriers are main drawbacks that limited the photocatalytic activity and visible light response of $TiO_2$ [4,5]. In this regards, extensive surveys have been carried out on refining the photoelectrochemical response of $TiO_2$. Among the numerous techniques coupling of $TiO_2$ with other low band gap semiconductor with matching band edges positions will be potential method to improve the utilization of visible light and facilitation of photo-generated electrons and holes separation [6–11]. Recently, a nontoxic and inexpensive rare earth material, Cerium dioxide ($CeO_2$) has been received extensive attention in photocatalysis as photoelectrode because of its wide range of band gap (2.6–3.4 eV) depending on the composition or method of preparation [12,13]. Excellent photocatalytic ability of $CeO_2/TiO_2$ nanocomposite materials has already been shown the extended photo-response of $TiO_2$ to the visible light region and good thermal stability [14,15]. In present work, nanostructured $CeO_2/TiO_2$ bilayer thin films were synthesized through a low cost spin coating method with varying thickness of $CeO_2$. The resulting $CeO_2/TiO_2$ bilayer exhibit remarkably improved photoresponse than pristine $CeO_2$ and $TiO_2$ in 0.1 M NaOH. Pristine $CeO_2$, $TiO_2$ and $CeO_2/TiO_2$ bilayer thin films were also characterized for structural, electrical and optical properties with an objective of understanding the improved PEC performance of $CeO_2/TiO_2$ bilayer.

## 2. Experimental

### 2.1. Synthesis of $TiO_2$ thin films

Nanostructured $TiO_2$ thin films were deposited using sol gel spin coating method on conducting glass substrate (ITO). Diethanolamine, Titanium isopropoxide (TTIP) and ethanol were used as precursors and solvent respectively. Precursors were dissolve in ethanol and stirred for 3 h on a magnetic stirrer, resulting in

* Corresponding author.
** Corresponding author.
*E-mail address:* dipika.sharma286@gmail.com (D. Sharma).

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# Electronic band-offsets across $Cu_2O/BaZrO_3$ heterojunction and its stable photo-electro-chemical response: First-principles theoretical analysis and experimental optimization

Dipika Sharma [a], Rishibrind Kumar Upadhyay [b], Biswarup Satpati [c], Vibha R. Satsangi [d], Rohit Shrivastav [a], Umesh V. Waghmare [e], Sahab Dass [a,*]

[a] Department of Chemistry, Dayalbagh Educational Institute, Agra, India
[b] Department of Applied Physics, Delhi Technological University, New Delhi, India
[c] Surface Physics & Material Science Division, Saha Institute of Nuclear Physics, Kolkata, India
[d] Department of Physics & Computer Sciences, Dayalbagh Educational Institute, Agra, India
[e] Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore, India

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ABSTRACT

$Cu_2O$ has been shown to be highly active as a cathode in photo-electro-chemical (PEC) reduction of water to generate hydrogen fuel using sunlight. However, $Cu_2O$ is susceptible to photo-corrosion when exposed to an electrolyte and needs to be protected by an over-layer of a suitable material, and its performance depends sensitively on its interface with the over-layer, and hence to the method of deposition. Here, we use first-principles theoretical analysis of the electronic structure of $Cu_2O/BaZrO_3$ interface, and show that valence and conduction bands are favourably aligned to absorb light and catalyse the Hydrogen Evolution Reaction. We then present experiments with spray pyrolytically deposited $Cu_2O$ films and spin coated over-layer of $BaZrO_3$, and optimize its PEC performance with thickness of $Cu_2O$ film. We find a maximum photocurrent density of 1.25 mA/cm$^2$ at 0.95 V/SCE for an overall thickness of 458 nm, and demonstrate that the photocurrent remains stable over a long period of time. Demonstration of scalable and cost effective deposition of $Cu_2O$ and $BaZrO_3$ with stable PEC performance and understanding of the mechanism of charge separation across the $Cu_2O/BaZrO_3$ interface developed here should facilitate further optimization of $Cu_2O/BaZrO_3$ films for realistic PEC applications.



## 1. Introduction

Generation of hydrogen by photoelectrochemical (PEC) water splitting using sun light illumination is simpler and environmentally friendlier than the catalytic reforming of hydrocarbon fuels [1,2]. Although considerable research within the past decade has been devoted into PEC water splitting, fabrication of a stable and efficient photo-electrode with Solar to Hydrogen (STH) efficiency of more than 10% required for practical applications still remains a challenge. To make this technique commercially viable, the electrode material, for example a semiconductor, must be of low-cost; it should be synthesized/fabricated in energy efficient manner with abundant elements using scalable techniques [1–5]. Use of bilayered/heterojunction system of metal oxide semiconductors with inherent merits is one of the recent strategies towards improving the performance of the photocatalyst in the recent years [6–11]. Among various semiconductors, copper oxides are attractive because they are photoactive and can be processed by industrially proven low-cost method such as spray pyrolysis, with copper being an abundant material. Cuprous oxide ($Cu_2O$) is an inexpensive and promising material as a photocathode in PEC for $H_2$ evolution through water splitting [12–14], and is also used in gas sensors [15], electronics [16] and lithium ion batteries [17]. Its electronic band gap of 2.3 eV [18,19] allows for visible light absorption, and a favourable position of its conduction band relative to redox potential of hydrogen evolution reaction provides a potential of about 0.7 V as driving force for water reduction [20]. However, a major technical issue associated with $Cu_2O$ is its relatively short electron diffusion length (30–100 nm) [21] and high recombination rate, i.e. electrons and holes excited by incident light

* Corresponding author.
E-mail address: [illegible] (S. Dass).

[illegible]

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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:* [illegible] (V.R. Satsangi), [illegible] (U.V. Waghmare), [illegible] (S. Dass).

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# Improved Photoelectrochemical Water Splitting Performance of $Cu_2O/SrTiO_3$ Heterojunction Photoelectrode

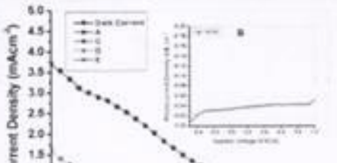
Dipika Sharma,[†] Sumant Upadhyay,[†] Vibha R. Satsangi,[‡] Rohit Shrivastav,[†] Umesh V. Waghmare,[§] and Sahab Dass*[,†]

[†]Department of Chemistry, Dayalbagh Educational Institute, Agra 282 110, India

[‡]Department of Physics & Computer Sciences, Dayalbagh Educational Institute, Agra 282 110, India

[§]Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560 064, India

ABSTRACT: Nanostructured thin films of $Cu_2O$ modified by overlayering $SrTiO_3$ with varying thickness have been studied for the first time as photoelectrode in photoelectrochemical (PEC) water splitting. Effective mass calculations for electrons and holes in bulk $SrTiO_3$ and $Cu_2O$ using DFT first-principles have also been attempted to explain the enhanced charge separation at $Cu_2O/SrTiO_3$ interface. All samples were characterized using XRD, SEM, and UV−vis spectrometry. The influence of surface modification of $Cu_2O$ with varying thickness of $SrTiO_3$ on PEC performance has been investigated. Photocurrent density for $Cu_2O/SrTiO_3$ heterojunction with overall thickness of 343 nm at 0.8 V/SCE was found to be 2.52 mA $cm^{-2}$ which is 25 times higher than that of pristine $Cu_2O$ (0.10 mA $cm^{-2}$ at 0.8 V/SCE). Theoretical studies showed that the electrons in $SrTiO_3$ had large effective masses as compared to electrons in $Cu_2O$ at conduction band minima indicating weak mobility of photogenerated electrons in $SrTiO_3$ and strong mobility in $Cu_2O$ leading to improved separation of charge carriers resulting in the enhancement of photocurrent densities at the $Cu_2O/SrTiO_3$ heterojunction.




## ■ INTRODUCTION

Photoelectrochemical (PEC) method is considered to be a safe and highly promising method for hydrogen generation due to several reasons: (a) PEC technology is based on solar energy, which is a perpetual source of energy, and uses water which is a renewable energy resource, (b) PEC technology may be used on both large and small scales, and (c) PEC technology is relatively uncomplicated.[1] Various methodological attempts have been carried out toward enhancing the efficiency of PEC water splitting including heterojunction systems,[2] doping,[3] dye sensitization,[4] swift heavy ion irradiation,[5] etc. Use of a heterojunction semiconductor system (as photoelectrode) is a promising strategy attempted to improve the efficiency of PEC cell. A heterojunction of two semiconductor materials, one with wide band gap and another with low band gap, having a staggered band-edge alignment (i.e., type-II band alignment) in which the valence band (VB) of one semiconductor is positioned (energetically) between the valence band (VB) and conduction band (CB) of another semiconductor, and its CB is positioned above the VB and CB of other semiconductor, can improve separation of photogenerated charge carriers leading to enhanced photoactivity of photoelectrodes. The small band gap semiconductor is also responsible for visible light absorption and sensitizes the wide band gap material through electron or hole injection.[6] Among the various metal oxides, strontium titanate ($SrTiO_3$), on account of its favorable properties, becomes a favorable candidate to be used as photoanode in the PEC splitting of water.[7,8] $SrTiO_3$ has perovskite cubic structure with good flatband potential and photovoltage (Voc) indicating its ability to photolyze the water.[9−13] On the other hand $SrTiO_3$ is a wide band gap material, and absorbs in the UV region which limits its efficiency toward photoelectrochemical splitting of water. It is expected that heterojunction of $SrTiO_3$ with a small band gap material such as $Cu_2O$,[14] CdS,[15] and $\alpha$-$Fe_2O_3$[16] may overcome its limitation of absorption in UV region. In the present study modifications were attempted on $Cu_2O$ with $SrTiO_3$ (both possess cubic crystal structure with lattice constant of about 4.26 and 3.905 Å, respectively), by making the ITO/$Cu_2O$/$SrTiO_3$ heterojunction thin films with varying thickness of $SrTiO_3$. Prepared $Cu_2O/SrTiO_3$ heterojunction photoelectrodes were also characterized for their structural, electrical, and optical properties. Effective mass calculations for charge carriers using first-principles density functional theory (DFT) were also carried out for the first time to understand the charge separation mechanism at $Cu_2O/SrTiO_3$ interface.

## 2. EXPERIMENTAL SECTION

**2.1. Preparation of $Cu_2O$ Thin Films.** Nanostructured thin films of $Cu_2O$ were deposited on the conducting glass substrate (ITO) using simple spray-pyrolysis (Holmarc, India) method. For this spray precursor, copper(II) acetate mono-

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# Understanding the photoelectrochemical properties of nanostructured $CeO_2/Cu_2O$ heterojunction photoanode for efficient photoelectrochemical water splitting

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

[a] *Department of Chemistry, Dayalbagh Educational Institute, Agra 282 005, India*
[b] *Department of Physics & Computer Sciences, Dayalbagh Educational Institute, Agra 282 005, India*
[c] *Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560 064, India*

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ABSTRACT

Nanostructured thin films of $CeO_2$ sensitized by overlayering thin layers of $Cu_2O$ with varying thickness have been studied for the first time as photoelectrode in photoelectrochemical (PEC) water splitting. Effective mass calculations for electrons and holes in bulk $CeO_2$ and $Cu_2O$ using first principles based on Density Functional Theory (DFT) have also been attempted to explain the enhanced charge separation at $CeO_2/Cu_2O$ heterojunction interface. All samples were characterized by X-ray diffractometer (XRD), Scanning Electron Microscope (SEM), Atomic Force Microscopy (AFM) and UV–Visible spectrophotometer. The photoelectrochemical activity of the samples was investigated in a three electrode quartz cell system and maximum photocurrent density of 2.89 mA $cm^{-2}$ at 0.7 V/SCE was obtained for the $CeO_2/Cu_2O$ heterojunction with overall thickness of 397 nm. Improved conductivity and better separation of the photogenerated charge carriers at the $CeO_2/Cu_2O$ heterojunction as compared to individual components may be responsible for the higher photocurrent density. The possible mechanism for the enhanced photocurrent density has been explained using heterojunction model based on density functional theory calculations.



## Introduction

Solar hydrogen generation from photoelectrochemical water-splitting reactions has received much attention on account of hydrogen being widely accepted as clean energy carrier [1–3]. The main challenge in this area is to find a suitable semiconductor exhibiting efficient splitting of water in photoelectrochemical (PEC) cell. Various modification techniques have been carried out towards improving the photoelectrochemical activity of semiconductor for splitting of water such as doping [4], heterojunction systems [5] dye

* Corresponding author. Fax: +91 562 2801226.
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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Self attested
Dipika

**CONTACT DETAILS OF REFEREES FAMILIAR WITH MY WORK.**

| | First Referee | Second Referee | Third Referee |
|---|---|---|---|
| **Name** | PROF. SAHAB DASS | PROF. UMESH WAGHMARE | PROF. B.R. MEHTA |
| **Email ID** | drsahabdas@gmail.com | waghmare@jncasr.ac.in | brmehta@physics.iitd.ac.in |
| **Contact** | +91-9219695960 | +91-9448287711 | 09891076842 |
| **Address** | Head, Dept. of Chemistry, Dayalbagh Educational Institute, Agra, India | Theoretical Sciences Unit, JNCASR, Bangalore, India | Dean, Research and Development (R & D) Department of Physics Indian Institute of Technology Delhi New Delhi- 110016, India |

**DECLARATION:**

**I hereby declare that the above written particulars are correct to the best of my knowledge.**

**Dipika Sharma**