



Dr. Biju Mani Rajbongshi

Ph.D (Solar Energy), M.Tech (Energy), M. Sc (Physics)

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Profile Summary

Research-oriented, dedicated and reliable professional with over 8 years of hands-on experience in the diverse fields of Renewable and Clean Energy Technology. My research capability to lead independent interdisciplinary research reflects on several research articles in international journals of high repute. More than One year of teaching experience also helps me to give my contributions to any organization in research, teaching, and international collaboration activities. Currently, I am looking for opportunities to be professionally associated with an organization of dynamic environment where my competence can be applied conscientiously for the benefit of the organization and my professional career.

Area of Interest

- Solar Energy Utilization: *solar photovoltaic, solar photocatalysis, and solar thermal*
- Fuel cell and hydrogen energy: *Polymer electrolyte membrane fuel cell, catalyst development, Testing, Operation at sub-freezing temperature, Electrode preparation*
- CO₂ conversion: *Catalyst development, conversion to value added fuel*
- Advance Energy Material: *Synthesis and characterization and application in energy system*
- Recycling of PV module: *Recycling of PV module and synthesis of value added energy material.*
- Battery and super capacitor : *Material development and application*
- Utility-scale solar PV power generation: *design and data analysis; loss analysis*

Professional Experience

A. Research and development (2017-2020): 3 years 8 months

Organization : IIT Delhi

Role: 1. Senior Research Fellow (February 2020-October 2020)

2. Project Engineer (February 2019-February 2020)

3. Post-Doctoral Fellow (February 2017-February 2019)

B. Teaching and Academic (2015-2016): 1 year 5 months

Organization : North Eastern Hill University, Shillong

Role : Teaching at UG level

Google scholar

<https://scholar.google.com/citations?user=JoLi-wwAAAAJ&hl=en&authuser=1>

Web of Science

ResearcherID: AAS-2725-2021

Publications

Journal: 16

Book Chapter: 02

Conference: 16

i10-index: 12

References

1. Prof. S K Samdarshi

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3. Dr. Sadhan Mahapatra

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Language

English, Hindi, Assamese

Permanent Address

Goreswar, Assam

Brief Description of Assignment

- **Senior Research Fellow**
 - Electrode preparation, cell fabrication, cell performance testing
 - Assisting and training master and graduate interns in their dissertation and lab work
 - Assisting divisional activities related to project: report preparation, purchasing equipment
- **Project Engineer**
 - Research and development on fuel cell, CO₂ conversion to syngas (Catalyst synthesis, characterization, and performance testing)
 - Project execution, monitoring, meeting project goal
 - Report writing, manuscript publication
- **National Post-Doctoral Fellow**
 - Research and development on dye-sensitized solar cells (Material development, characterization, solar cell fabrication, performance testing)
 - Project execution, monitoring, meeting project goal
 - Assisting master students in their master degree thesis
- **Teaching**
 - UG level courses on renewable energy (Theory and practical)
Alternative fuel for IC engine, Basic of Solar Energy Engineering, (, Solar Energy Laboratory, Nuclear Energy, Biomass and Bio-fuel laboratory.
 - Question paper preparation, answer script evaluation
- Work as an examiner in theory and practical examination

Sponsored Project Involved

1. **Project:** *Noble metal loaded TiO₂ based plasmonic nanostructures for dye sensitized solar cell*
Funding Agency : Science and Engineering Research Board, DST India
Role: Principle Investigator
Sanction No: PDF/2016/002109; Sanctioned Amount: Rs. 19.20 Lakh
2. **Project:** *Investigation of Non-assisted Low Temperature Start-up of PEM fuel cell*
Funding Agency : ISRO, India
Role: Senior Research Fellow
3. **Project:** *Smart Infrastructure for an Electric Vehicle Ecosystem*
Role: Project Engineer

4. **Project:** Synthesis and characterization of visible active ZnO photocatalyst for solar energy application

Funding Agency: CSIR, India

Role: Senior Research Fellow

Sanction No: 09/796/055/2014-EMR-I & dated 08/08/2014

Key Expertise

- Nano and quantum dot material synthesis
 - *OD (Quantum dot,) 1D (Nanorod, nanotube, nanowire, 2D (graphene nanosheet, nanofilm) and 3D (Nanoparticle) material*
 - *Synthesis methods are: Hydrothermal synthesis, Co-precipitation, Sol-gel technique, Chemical vapor deposition, Electro-deposition*
- Thin film preparation: *Dip coating, spin coating, solution casting, Spray coating*
- Solar cell fabrication: *Dye-sensitized solar cell, Organic solar cell*
- Solar photocatalytic waste water treatment: *Catalyst development, system design*
- Fuel cell : *catalyst development and performance testing*
- Electro-catalytic CO₂ reduction: *Liquid phase CO₂ reduction to CO*
- **Instrumentation techniques**
 - *Structural characterization:* X-ray Diffraction(XRD), Fourier transform infrared spectroscopy(FT-IR), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS)
 - *Physical characterization:* Pore-size distribution(BET-BJH) isotherms, Atomic force microscopy (AFM), Particle size analyser (PSA)
 - *Chemical characterization:* Gas chromatography (GC)
 - *Optical characterization:* UV-VIS Spectrophotometer, PL spectroscopy
 - *Morphological characterization:* Scanning electron microscopy-energy dispersive X-ray(SEM-EDX), Transmission electron microscopy (TEM)
 - *Stability Test:* Thermal gravimetric analysis/differential scanning calorimetry (TGA/DSC)
 - *Electrochemical characterization:* Cyclic voltammetry (CV), Linear sweep voltammetry (LSV), Electrochemical impedance spectroscopy (EIS), Chronopotentiometry chronoamperimetry
- **Software experience**
 - ImageJ, Xpert High score plus software, JCPDS (XRD data analysis), Origin. PVSyst

Academic Qualifications

| | |
|------------------------------|--|
| Ph.D in Energy Technology | Tezpur university, Assam, 2016 <i>Thesis title: Synthesis, characterization and engineering of novel visible active metal oxide photoactive material for solar photocatalysis application</i> |
| M. Tech in Energy Technology | Tezpur university, Assam, 2011 |
| M.Sc in Physics | Gauhati University, Assam, 2008 |
| B.Sc in Physics | Pub Kamrup college, Gauhati University, Assam, 2006 |

Book Chapters

- **Biju Mani Rajbongshi** and Anil Verma “Emerging Nanotechnology for third Generation Photovoltaic cells”, In: Nanotechnology: Applications in Energy, Drug and Food, Ed., Dr. Melvin Gan Jet Hong, Springer, ISBN: 978-3-319-99601-1.
- **Biju Mani Rajbongshi**, Photocatalyst: Mechanism, challenges and strategy for organic contamination degradation, In: Hussain-HSPM: Environment, Energy, Emerging applications and Sustainability, Elsevier, ISBN 978-0-12-819049-4.

SCI Journal Publications (Total Impact Factor>92)

1. Barnali Das, Ranjith G. Nair, **Biju Mani Rajbongshi** and S.K. Samdarshi, “Investigation of the photoactivity of pristine and mixed phase N-doped Titania under visible and solar irradiation” Material characterization, 83, 145-151, 2013 (Impact factor:4.3).
2. **Biju Mani Rajbongshi** and S K Samdarshi “Cobalt-doped zincblende–wurtzite mixed- phase ZnO photocatalyst nanoparticles with high activity in visible spectrum” Applied Catalysis B: Environmental, 144, 435-441, 2014 (Impact factor: 19.5)
3. **Biju Mani Rajbongshi** and S. K. Samdarshi “ZnO and Co-ZnO nanorods -Complementary role of oxygen vacancy in photocatalytic activity of under UV and visible radiation flux” Materials Science and Engineering: B,182, 21-28, 2014 (Impact factor: 4.05).
4. **Biju Mani Rajbongshi**, Anjalu Ramchiary and S. K. Samdarshi “Synthesis and characterization of plasmonic visible active Ag/ZnO photocatalyst” Journal of material science: Material in Electronics, 25, 2969–2973, 2014 (Impact factor: 2.5).
5. **Biju Mani Rajbongshi**, Anjalu Ramchiary, S. K. Samdarshi “Influence of N-doping on photocatalytic activity of ZnO nanoparticles under visible light irradiation” Materials Letters, 134, 111-114, 2014 (Impact factor: 3.4).

6. **Biju Mani Rajbongshi**, Anjalu Ramchiary, and S. K. Samdarshi “Investigation of visible light active Ag sensitized mixed phase TiO₂ photocatalyst for solar energy application” *Journal of Sol-Gel Science and Technology*, 72, 114–121, 2014 (Impact factor- 2.3)
7. **Biju Mani Rajbongshi**, S. K. Samdarshi, Bibha Boro, Multiphasic bi-component TiO₂– ZnO nanocomposite: synthesis, characterization and investigation of photocatalytic activity under different wavelengths of light irradiation, *Journal of material science: Material in Electronics*, 26, 377–384, 2015 (Impact factor: 2.5).
8. Bibha Boro, **Biju Mani Rajbongshi**, S. K. Samdarshi, “Synthesis and fabrication of TiO₂-ZnO nanocomposite based solid state dye sensitized solar cell” *Journal of Material Science: Material in Electronics*, 27, 9929-9940, 2016 (Impact factor: 2.5)
9. Samrat Paul, **Biju Mani Rajbongshi**, Birinchi Bora, Ranjith G Nair and S K Samdarshi “Organic photovoltaic cells using green-MWCNTs” *New Carbon Materials*, 32, 27-34, 2017 (Impact factor: 1.7)
10. Ranjith G. Nair, Abinash Das, Samrat Paul, **B. M. Rajbongshi**, S.K.Samdarshi, “MWCNT decorated V-doped titania: An efficient visible active photocatalyst” *Journal of Alloys and Compounds*, 695, 3511-3516, 2017 (Impact factor: 5.3)
11. Bibha Boro, B. Gogoi, **B.M. Rajbongshi**, A. Ramchiary, Nano-structured TiO₂/ZnO nanocomposite for dye-sensitized solar cells application: A review, *Renewable & Sustainable Energy Reviews*, 81, 2264-2270, 2018 (Impact factor: 14.98)
12. **Biju Mani Rajbongshi**, Anil Verma, Plasmonic noble metal coupled biphasic TiO₂ electrode for dye-sensitized solar cell, *Materials Letters*, 232, 220-223, 2018 (Impact factor: 3.4)
13. Karan Malik, **Biju Mani Rajbongshi**, Anil Verma, Syngas Production from Electrochemical Reduction of CO₂ at High Current Density using ZnO/CuO Nanocomposite, *Journal of CO₂ Utilization*, 33, 311-319, 2019 (Impact factor: 7.1)
14. Kumari, N., Gaurav, K., Samdarshi, S.K., A.S.Bhattacharyya, Paul S., **Rajbongshi, B.**, Mohanty, K. “Dependence of photoactivity of niobium pentoxide (Nb₂O₅) on crystalline phase and electrokinetic potential of the hydrocolloid” *Solar Energy Materials and Solar Cells* 208, 110408 (Impact factor: 7.3)
15. **Biju Mani Rajbongshi**, M. Shaneeth, Anil Verma “Investigation of Sub-zero Start-up of Polymer Electrolyte Membrane Fuel Cell using Un-assisted Cold Start Strategy” *International Journal of Hydrogen energy*, Impact factor: 5.8
16. S. Saha, **B. M. Rajbongshi**, V. Ramani, A. Verma, Titanium Carbide: An Emerging Electrocatalyst for Fuel Cell and Electrolyser, *International Journal of Hydrogen energy*, Impact factor: 5.8

Conference Papers

1. Biju Mani Rajbongshi, Samrat Paul and S. K. Samdarshi; "A review on polyaniline in organic solar cell" International congress on Renewable energy 2010, Chandigarh.
2. Biju Mani Rajbongshi, Samrat Paul and S. K. Samdarshi; "Green Synthesis of polyaniline nanoparticles" National conference of smart nanostructures 2011, Tezpur University,
3. Biju Mani Rajbongshi, Samrat Paul and S. K. Samdarshi; "Synthesis of carbon nanotube from Mustard oil" Indian Science Congress Association 2011, SRM Chennai.
4. Biju Mani Rajbongshi, Bibha Boro, and S K Samdarshi, "Synthesis and Characterization of Ti-Zn oxide composite photocatalyst" International seminar and workshop on Energy, sustainability and development, 2012, Sivsagar, Assam.
5. Bibha Boro, Biju Mani Rajbongshi and S.K. Samdarshi; "A review of Solid State Dye Sensitized Solar Cells" International congress on Renewable energy, 2012, Tezpur University.
6. Biju Mani Rajbongshi, Anjalu Ramchiary and S. K. Samdarshi, "Surface plasmon assisted visible active Ag/ZnO photocatalyst" International Conference on Nanotechnology 2013, Kolkata.
7. Biju Mani Rajbongshi, Anjalu Ramchiary, S.K. Samdarshi "Synthesis and characterization of visible active nitrogen doped ZnO" International conference on green energy and smart material through science, technology and management (GESM14) 2014, Guwahati.
8. Anjalu Ramchiary, Biju Mani Rajbongshi, S.K. Samdarshi "Investigation of the photo catalytic Performance of Fe- doped TiO₂ photo catalyst under visible light for solar energy utilization" International conference on green energy and smart material through science, technology and management (GESM14) 2014, Guwahati, India.
9. Biju Mani Rajbongshi, Samrat Paul, Influences of Fe doping concentration on the structural, optical and photocatalytic properties of TiO₂ nanoparticles" 1st Springer International Conference on Emerging Trends and Advances in Electrical Engineering and Renewable Energy, 2016, Sikkim, India.
10. Biju Mani Rajbongshi, Priyank Rajput and Anil Verma "Photocatalytic degradation of model textile dye in waste water using Fe doped TiO₂ photocatalyst" Industry Day 2017, IIT Delhi
11. Biju Mani Rajbongshi, Priyank Rajput and Anil Verma "Photocatalytic degradation of model textile dye in waste water using Fe doped TiO₂ photocatalyst" Industry Day 2017, IIT Delhi
12. Biju Mani Rajbongshi, Karan Malik and Anil Verma "Mixed phase Ag-TiO₂ nano- composite for electrochemical hydrogen evolution" ICEAR 2017, IIT Bombay.
13. Biju Mani Rajbongshi, Priyank Rajput and Anil Verma "Synthesis and characterization of Cu loaded mixed phase TiO₂ nanoparticles" ICEAR 2017, IIT Bombay
14. Biju Mani Rajbongshi, Priyank Rajput and Anil Verma "Facile synthesis and characterization of mixed-phase TiO₂ nanorod" OPEN HOUSE 2018, IIT Delhi.
15. Karan Malik, Biju M. Rajbongshi, Jay Pandey, Anil Verma, "Ni-Mn based Bimetallic Electro-catalyst

for Electrochemical Reduction CO₂ to Hydrocarbons” Chemcon 2018

16. Biju Mani Rajbongshi, Anil Verma “ Investigation of sub-zero temperature on polymer electrolyte membrane fuel cell” Chemcon 2019.

Academic Achievements

1. Senior Research Fellow, CSIR, India, 2014-2015
2. National Post-Doctoral Fellow, SERB, 2017-2019
3. First prize, Chemical Engineering Department, OPEN HOUSE IIT Delhi, 20

Professional Training

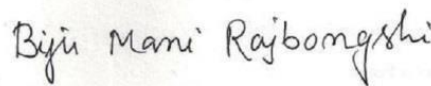
| S. No | Training | Organizer | Period |
|-------|--|----------------------------------|----------------------------|
| 1 | Short course on surface and porous material characterization | Anton Paar | 12th March, 2019 |
| 2 | Solar Photovoltaic: Fundamental, Technologies and application | IIT Bombay | 12th - 22nd December, 2011 |
| 3 | Functioning and Maintenance of Solar Radiation resource Assessment station | Centre of Wind Energy Technology | 3rd-4th July, 2014 |
| 4 | Nano fabrication Technologies | Tezpur University | 25th-26th April, 2015 |

Reviewer of Journal

- Journal of material science: Material in electronics
- Journal of Materials Science
- Indian Chemical Engineer
- Supper lattice and microstructure
- Applied Thermal Engineering

Declaration

I hereby declare that all the above mentioned information is true to the best of my knowledge.

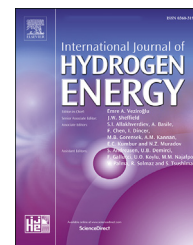


Place: Gurgaon, Haryana

Biju Mani Rajbongshi

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journal homepage: www.elsevier.com/locate/he

Investigation on sub-zero start-up of polymer electrolyte membrane fuel cell using un-assisted cold start strategy

Biju Mani Rajbongshi ^a, M. Shaneeth ^b, Anil Verma ^{a,*}

^a Department of Chemical Engineering, Indian Institute of Technology Delhi, New Delhi, India

^b Vikram Sarabhai Space Centre, ISRO, Thiruvananthapuram, India

HIGHLIGHTS

- Un-assisted cold start of PEMFC at different temperatures was studied.
- Cell performance loss due to cold start has been recovered by operating at 30 °C.
- Studied performance decay of MEA in freeze/thaw and sequential cold start cycle.
- Cold start temperature can affect the performance decay in freeze/thaw cycles

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PEMFC

Freezing

Cold start

Stability

ABSTRACT

The technical barriers for commercialization of polymer electrolyte membrane fuel cell (PEMFC) are the startup ability and survivability at sub-zero temperatures. Ice formation causes cold start fail and volume change damages the cell components leading to performance decay. Many strategies are used to assist successful cold start and to reduce the performance decay. But, unassisted cold start is very crucial and needs attention. Here, an experimental protocol is reported for successful unassisted cold start using low temperature gas purging at various temperatures (-5, -8, -10, -15, and -20 °C) as well as to recover temporary performance decay. The stability of the membrane electrode assembly is also studied in freeze/thaw and sequential cold start cycles. At temperature -10 °C, there is small performance decay after the 6th freeze/thaw cycle. However, the subsequent cold start cycle shows significant performance decay after the 6th cycle. Changes in microstructures and loss of hydrophobicity in the gas diffusion layer are attributed to the performance decay in both freeze/thaw and sequential cold start cycles. The effect of cold start temperature on the performance of a PEMFC in subsequent freeze/thaw cycles is also studied. It shows that depending upon the start-up temperature, the preferential ice formation can affect the performance decay characteristics.

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Introduction

Polymer electrolyte membrane fuel cell (PEMFC) has attracted significant attention as a potential candidate for automotive power supply. However, for the widespread applications of

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Plasmonic noble metal coupled biphasic TiO₂ electrode for dye-sensitized solar cell

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Sol-gel preparation

Biphasic

Surface plasmon resonance

Dye-sensitized solar cell

ABSTRACT

Biphasic (anatase-rutile) TiO₂ can play a significant role in photon harvesting and charge transport in Dye-sensitized solar cell (DSSC). However, fabrication of biphasic TiO₂ thin film for electrode is crucial at low temperature. This paper reports the fabrication of plasmonic Ag loaded biphasic TiO₂ electrode using sol-gel dip coating method to study the synergistic effect of surface plasmon resonance and homo-interface on photon harvesting and charge transport in DSSC. Structural and optical analyses confirm the phase composition and elevated absorption of the electrodes. Comparative study on the performance of DSSCs assembled with electrodes shows that Ag loaded biphasic TiO₂ enhanced 60% power conversion efficiency (PEC) compared to anatase TiO₂. This enhanced efficiency is mainly attributed to the reduced band gap, improved interfacial charge transfer, increased electron lifetime and retarded charge recombination.

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1. Introduction

Dye-sensitized solar cell is one of the most promising technologies for solar energy harvesting because of its simple fabrication process, flexibility and low cost as compared to silicon solar cell. Significant research work is being conducted on DSSC to increase PCE and stability. The critical limiting factor of mostly used semiconductor TiO₂ is light absorption in the UV region and high charge recombination due to the random way of electron transport [1]. In order to minimize recombination losses of electrons and improve PCE, Surface Plasmon Resonance (SPR) effect of noble metal nanoparticles (Ag, Cu, Au) is widely used in DSSC [2,3]. Recently, biphasic TiO₂ has been getting attention due to its excellent electronic and optical properties. It has been well accepted that biphasic TiO₂ can increase the efficiency in photocatalytic activity compared to anatase TiO₂ because of its improved photon harvesting and efficient charge transport. Reported studies show that biphasic TiO₂ also been used in DSSC, but in all these studies researchers used Degussa P25 (biphasic TiO₂) for the electrode fabrication. [4–6]. The critical analysis shows that none of the studies has been reported on the in-situ growth of biphasic TiO₂ coupled with noble metal for DSSCs electrode.

Therefore, in the present study, fabrication of Ag loaded biphasic TiO₂ electrode using sol-gel dip coating method has been

reported because generally used doctor blading or screen printing methods require different time consuming and complex process steps. The synergetic effect of homo-interface and SPR on TiO₂ based electrode is evaluated for DSSC.

2. Materials and methods

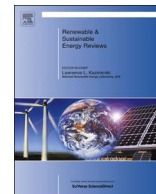
Sol-gel dip coating method has been employed for the fabrication of electrode. The detailed synthesis method and materials used, fabrication of DSSC, and characterization details are given in [supporting information](#).

3. Results and discussion

XRD spectra of TiO₂ (Fig. 1a) shows that T70 is purely in anatase phase corresponding to the peaks at $2\theta = 25.2^\circ$, 37.9° and 48.1° (JCPDS: 894921). T75 shows a very small peak for rutile phase at $2\theta = 27.5^\circ$ (JCPDS: 894920) apart from peaks of anatase phase which is further confirmed by Raman analysis. In Fig. 1b, AgT55 shows only anatase phase, however, AgT65 shows 37% anatase with 63% rutile phase (calculated using Spurr's equation). The phase transformation temperature from anatase to rutile (ATR) for bulk TiO₂ is 600–900 °C, but for the TiO₂ thin film, it is above 900 °C [7,8]. Here, we are getting ATR for TiO₂ at 750 °C may be because of thickness of TiO₂ films [9]. In case of AgT65, the ATR transformation temperature further reduces to 650 °C. Here, Ag played an important role in phase transformation. It has been

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Nano-structured TiO₂/ZnO nanocomposite for dye-sensitized solar cells application: A review



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Photo-anode
Solar cells

ABSTRACT

Dye-sensitized solar cell (DSSC), the third generation photovoltaic technology is most promising alternative photovoltaic technology due to low-cost, stable electrical generation, good temperature stability, non-toxic emission during manufacturing, rapid efficiency enhancement and wider flexibility in design. The present study reviews the advanced techniques and research trends of ZnO compotization with TiO₂ in different nano-structures. Performance efficiency gap between the conventional silicon solar cell and DSSC is an intensely promoted area of research. It results in an efficient photoanode which further leads to the improvement in DSSC. Their performance is further enhanced using engineered nanostructured metal oxide photoanode. The study emphasizes on nano-compotization of conventional titanium dioxide with other metal oxide in different structures. It is one of the active research technologies for efficient DSSC. Comparative performance study shows that three dimensional and hybrid nanostructured TiO₂/ZnO nanocomposite such as nanodonsuts, nanoflower and 3D hierarchical heterostructure have better performance. Their open circuit voltage, short circuit current, fill factor and efficiency lies in the range of 0.76–0.82 V, 3.24–16.70 mA/cm², 0.17–0.69% and 0.51–9% respectively. Thus they result in rapid electron transfer rate, slower charge recombination rate and higher surface area.

1. Introduction

Solar energy is a gift of nature to the living beings of the planet Earth. Since ancient days, it is being used in different forms and applications. Its knowledge and applications are growing linearly with development of technology. One of the promising solar energy harnessing techniques is the use of photovoltaic systems (PVs) [1]. It was in the year 1991, when Micheal Gratzel and Brian O'Regan made a remarkable development of Dye Sensitized Solar Cells (DSSCs). They have exceptional qualities of high photo-conversion efficiency, low-cost, flexibility and fine-tuned materials [2–6]. Since then DSSCs have drawn the attention of many researchers from the field of photo voltaic technologies. Its performance is measured in terms of photo-conversion efficiency, which in turn is dependent on rate of electron transfer. They are reported to be affected with change in crystallinity, morphology and surface area of the semiconductor [6]. Moreover the performance of DSSCs has been reported to be enhanced with:

a. Doping and/or sensitization to increase the absorption of solar light [7–10]

b. Nanocomposite of metal oxide through efficient charge separation e.g. Al₂O₃/TiO₂ [11], MgO/TiO₂ [12], ZnO/Al₂O₃ [13], TiO₂/ZnO [14], ZnO/SnO₂ [15].
c. Multi-structured semiconductor metal oxide for effective path for electron transport and higher surface area for dye absorption [16,17]

In addition to the conversion efficiency, for utilization and better commercialization of DSSCs good stability and easy fabrication also plays a vital role in its selection [18]. Amongst the above mentioned enhancement techniques, using composites of metal oxides has made its largest impact and is advantageous over bare use of n-type metal oxide semiconductors. The prime reason is the formation of hetero-junction structures. These structures can be different forms and possess the property of reducing the probability of photo-generated electron-hole recombination to a great extent. Nanocomposite materials constitute a good number of advantages like they are simple to manufacture, benign and low fabrication cost [19]. Researchers on the other hand are trying their best in finding the best combination of the nanomaterials for enhancing the properties and the performance of DSSCs using nanocomposite materials. Kanmani et al. reported core/

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Multiphasic bi-component TiO_2 – ZnO nanocomposite: synthesis, characterization and investigation of photocatalytic activity under different wavelengths of light irradiation

Biju Mani Rajbongshi · S. K. Samdarshi ·
Bibha Boro

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Abstract Nano-composite of biphasic (mixed phase) titania and monophasic (wurtzite) zinc oxide was synthesized by sol–gel method and characterized using, XRD, SEM, EDAX, TEM, UV–DRS PL and FTIR. The structural analysis from XRD reveals the formation of multiphasic TiO_2 – ZnO (TARZ) nanocomposite with TiO_2 in anatase–rutile mixed phase (TAR) and ZnO in wurtzite phase (ZW). The nano-composite with an average crystallite size of 15.3 nm shows a red shift in the absorption spectrum with the band-gap of 2.91 eV. The photoactivity of the composite TARZ in the degradation of methylene blue under UV and visible irradiation was found to be higher than the individual components. In UV irradiation nanocomposite shows 1.46 and 1.13 times higher photoactivity than TAR and ZW, respectively. But in visible irradiating it is 2 and 4 times higher than the TAR and ZW, respectively. Further, the study of the photocatalyst, under different near monochromatic light sources, indicates that the sharp increase in visible light activity may be attributed to the synergy of the components and the band-offset at the hetero-junction in addition to small particle size, and elevated and/or extended absorption spectrum.

1 Introduction

The nanostructures of titanium dioxide and zinc oxide, two of the most versatile semiconductor oxides, have consistently drawn attention for their potential applications in a number of photo-responsive processes (photocatalytic processes/hydrogen production) and devices (photovoltaic cells and optoelectronic devices/systems). In spite of that their utility is constrained due to narrow absorption band limited to the UV range of solar spectrum, and high probability for recombination of the photogenerated charge carriers [1–3]. While the extension in the absorption spectrum may be achieved through metal/non-metal doping, and/or dye/metal sensitization [4–7], the recombination may be inhibited through creation of lattice defects and/or band offsetting [8].

Plasmino et al. attributed the effectiveness of coupling of two semiconductors in reducing recombination in TiO_2 – ZnO composite [9] to the presence of lattice defect and band-offset at the heterojunction. Subsequently, a number of research work on this composite proved its effectiveness in the form of one and two dimensional structures grown with/without substrate [9–12]. Two of the closely related work on biphasic systems by Nair et al. [13] and Rajbongshi et al. [14] demonstrated identical effect in the phase couples of titania (anatase + rutile) and zinc oxide (wurtzite + zinc blende), respectively, ascribable to lattice defect and band offset at the homojunction. These biphasic systems not only have higher activity than their monophasic counterpart but an extended activity in the visible range as well. Consequently, replacing one of the components in the TiO_2 – ZnO composite system with its biphasic counterpart results a combination of homo- and heterojunction. Such a composite is expected to improve the performance of TiO_2 – ZnO system further. In fact some of

Electronic supplementary material The online version of this article (doi:10.1007/s10854-014-2410-4) contains supplementary material, which is available to authorized users.

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Cobalt-doped zincblende–wurtzite mixed-phase ZnO photocatalyst nanoparticles with high activity in visible spectrum



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ABSTRACT

The photoactivity of metal-oxide nanoparticles can be elevated and extended in the visible range through doping, sensitization, nanostructuration, and phase mixing. The present work reports synthesis of highly photoactive cobalt-doped mixed phase/biphasic zinc oxide nanoparticles with zinc-blende and wurtzite phases. The photoactivity of the nanoparticles, assessed through photocatalytic degradation kinetics of methylene blue and phenol, shows over 3 and 1.5 times more visible light photoactivity than monophasic (wurtzite) undoped ZnO and doped Co-ZnO counterparts, respectively. The increase in the activity is mainly attributed to red-shift in the absorption spectrum due to doping. But in the mixed phase (biphasic) Co-ZnO it is further complemented by the synergy of the interacting phases at the homojunction and the increase in oxygen vacancies at the surface which ensure availability of more photogenerated carriers by contributing in their generation and/or separation.

The synthesis of the novel mixed-phase photocatalyst has been done through a sol-gel based facile and single-step process wherein cobalt plays the unique role of dopant-cum-substrate.

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1. Introduction

Activity of a photocatalyst nanoparticle can be elevated and extended in the visible range using a number of strategies such as doping, sensitization, nanostructuration and phase mixing. While crystalline monophasic nanoparticles have been widely studied under doped/sensitized condition with robust and predictable characteristics, their biphasic/polyphasic counterparts, now being developed offer unique opportunities due to their novel characteristics which are useful for photocatalysis applications. Such a study on ZnO has not been reported because of obvious reasons. Out of the three known structural polymorphs of ZnO – wurtzite (hexagonal, WZ), zincblende (cubic, ZB), and rocksalt (cubic, RS) the wurtzite phase has received maximum attention of researchers due to the highest thermodynamic stability and ease of synthesis compared to pristine ZB and RS phases which are metastable. Thus getting a mixed phase ZnO with one or more metastable phase(s) becomes incrementally more challenging. Each of these metastable monophasic, due to its unpredictable physical and chemical properties, has been projected to be more exciting than the stable counterparts [1]. Due to its lower ionicity and higher crystallographic symmetry than the other polymorphs, ZB-ZnO is expected to have the advantage of low carrier scattering, higher

doping efficiency and higher optical gain [2] which, consequently, may impart superior optical and electronic properties to it. Due to these ZB-ZnO nanostructures are being considered as the future for development of a number of low-cost efficient devices such as LEDs, lasers, sensors [3], electronic memories [4], electrochromic displays [5] and applications such as photocatalysis [6], photovoltaics, spintronics [7], and piezoelectricity [8]. Lu et al. [6] concentrated on the study of dependence of photoactivity on hierarchical morphology of nanostructures. To the best of the authors' knowledge the photocatalytic performance study on mixed phase (biphasic) ZnO with ZB-ZnO has not been reported so far.

In general the attempts to synthesize metastable monophase of ZnO has puzzled the researchers because of the existence of mixed phase homojunctions in the yield. The attempts to synthesize ZB-ZnO employing techniques such as molecular beam epitaxy [9,10], metalorganic chemical vapour deposition [11], thermal oxidation of ZnS [12,13], sol-gel [14], thermal evaporation [15], solvothermal method [6], refluxing [16], and pulse laser deposition method [17] have invariably yielded biphasic nanomaterials such as ZB phase with WZ subdomains or vice versa [2,9,11–13,16,18,19]. Nevertheless, two important outcomes of these efforts are – One, these efforts have resulted in growth of novel ZB nanostructures like nano-tetrapods [20,21], nano-helices [22], nano-wires [5,15], and hierarchical pyramid made of nano-sheets [6] all with subdomains of the phase other than the bulk; and, two, they have further evidenced the existence of mixed phase. Caroff et al. [4] in their work on InAs polymorphs predicted interesting effects and

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