EXECUTIVE SUMMARY

Entitled

"SYNTHESIS, CHARACTERIZATION AND PHOTOVOLTAIC PERFORMANCE OF INNOVATIVE NANOSTRUCTURED MATERIALS FOR SOLAR ENERGY CONVERSION"

Submitted to

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002

By

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UNIVERSITY GRANTS COMMISSION

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NEW DELHI – 110 002

EXECUTIVE SUMMARY ON UGC MAJOR RESEARCH PROJECT

(Ref. No. F. No. 41-376/2012 (SR) Dated 17.07.2012)

1. TITLE OF THE PROJECT

"Synthesis, characterization and photovoltaic performance of innovative nanostructured materials for solar energy conversion"

2. NAME AND ADDRESS OF THE PRINCIPAL INVESTIGATOR

Name: Dr. A. Vadivel Murugan, Associate Professor
Organization: Centre for Nanoscience and Technology,
Madanjeet School of Green Energy Technologies,
Pondicherry University (A Central University),
Dr. R. Venkatraman Nagar, Puducherry-605014.

3. NAME AND ADDRESS OF THE INSTITUTION

Name: Pondicherry University (A Central University)
Address: Centre for Nanoscience and Technology,
Madanjeet School of Green Energy Technologies,
Pondicherry University (A Central University),
Dr. R. Venkatraman Nagar, Puducherry-605014.

4. UGC APPROVAL LETTER NO. AND DATE

F. No. 41-376/2012 (SR) Dated 17.07.2012

5. DATE OF IMPLEMENTATION

17.07.2012

6. TENURE OF THE PROJECT

3 years from 2012 to 2015, extended till 31/03/2017.

7. TOTAL GRANT ALLOCATED

Rs. 11, 94,371.00/-

8. TOTAL GRANT RECEIVED

Rs. 11, 28,014.00/-

9. FINAL EXPENDITURE

Rs. 11, 43,239.00/-

10. TITLE OF THE PROJECT

"Synthesis, Characterization and Photovoltaic Performance of Innovative Nanostructured Materials for Solar Energy Conversion"

11. OBJECTIVES OF THE PROJECT

1. Synthesis and characterization of TiO_2 and ZnO as photoanode for dye sensitized solar cells (DSSCs).
2. Synthesis and characterization of transition binary metal alloy or metal sulfide consisting of Co/Ni/Ti/Mo/W/Fe/Bi and Cu with and without PEDOT, ID MWCNT and graphene to develop Pt-free counter electrode.

After successfully develop the materials, the project proposed to fabricate the dye sensitized solar cells (DSSC) device and measure the photovoltaic properties.

12. WHETHER OBJECTIVES WERE ACHIEVED (GIVE DETAILS)

All objectives were successfully achieved.

- (Objective-1 and 3) Synthesis, characterization and application of ZnO and TiO_2 as DSSC photoanode material.
- (Objective 2 and 3) Development of $NiCo_2S_4$ thiospinel/graphene nanohybrid as a novel sustainable counter electrode material for Pt-free DSSCs.

13. ACHIEVEMENTS FROM THE PROJECT

All the objectives proposed for this project has been successfully achieved. Various microwave-assisted synthesis, characterization and photovoltaic studies of innovative nanostructured electrode materials such as ZnO, TiO_2, Plasmonic nickel nanoparticles and $NiCo_2S_4$ for dye-sensitized solar cells application were successfully carried out. The results from the project on microwave-assisted synthesis of different electrode material can provide promising technological potential as the method is facile and energy efficient that can make the DSSC fabrication process easier with lesser time consumption and also highlights the importance of structure-morphological and device-architecture impact of different electrode materials on performance of DSSC. Thus, the aims and objectives of the project were successfully achieved and the synthetic methodology used in research are innovative, analysis of data were carried out effectively and the publications from this project proves the originality and international standards of the research work.

14. SUMMARY OF THE FINDINGS (IN 500 WORDS)

We have developed a facile controlled rapid synthesis for ZnO with micro-/nanostructures, TiO_2 and $NiCo_2S_4$ nanocrystals with different morphologies by energy efficient MWHT/ST processes within few minutes. The photovoltaic (PV) properties of various photoanodes of TiO_2 and ZnO based DSSCs were investigated in detail. The material characterization were done by standard characterization methods including XRD, SEM, TEM, PV, and EIS. From the synthesized materials, we have developed 2 types of innovative photoanode device configurations such as Nano-hybrid architecture and Bi-layer architecture & observed enhancement in the photovoltaic performance due to "size-mismatching" and "synergistic effect" particularly from two different ZnO morphologies. We have also synthesized different TiO_2 morphologies such as interconnected beads-like (IBL), square platelets-like (SPL), spindle shape-like (SSL), porous spheres-like (PSL) in different solvents (ethanol, mixture of ethanol+H_2O and HF) and size and shape-tuned Ni-NCs of mixed triangular and hexagonal morphological crystals with size ranging from 15 - 62 nm in ethylene glycol (polyol) medium. Using as synthesized TiO_2 nanocrystals, we have achieved 10-17% net enhancement in PCE for TiO_2 based DSSCs by incorporating different amounts of size-tuned Ni-NCs in electrolyte, by localized surface plasmon resonance of highly stable Ni-NCs. Both MW-ST synthesis protocol and Ni-NCs incorporation are highly advantageous over other reported procedures. The improvement in efficiency is entirely driven by improvement in J_{sc}. We have also successfully demonstrated the single-step synthesis of nanocrystallite-aggregates of $NiCo_2S_4$ thiospinels (NCS-1) within a short reaction time (15 min) by a novel microwave-solvothermal (MW-ST) approach without requiring any elevated temperature and reducing gas atmosphere, significantly lowering the manufacturing cost. Furthermore, one-step MW-ST *in situ* polyol-reduction of graphite oxide (GO) into GNS with inorganic precursors of NCS-1 at 200 °C within 15 min simplified the formation of NCS- 1/GNS hybrid. In order to understand morphological dependent electrocatalytic performance of $NiCo_2S_4$, we have successfully fabricated $NiCo_2S_4$ with tremella-like (NCS-2) and porous-bead-cum needle like morphologies (NCS-3) *via* a three-step oxide-route, MW-HT/ST processes. Among them, NCS-1 and NCS-1/GNS hybrid exhibits superior PCE rather than NCS-2 and NCS-3. The electrochemical results reveal synergistic effect between $NiCo_2S_4$ and GNS. The electrochemical impedance data revealed low R_{ct} and ohmic resistance of NCS-1/GNS hybrid CE, which correlates with the *J-V* and IPCE results. The high performance of the hybrid sample is accomplished *via* rich redox chemistry of nickel and cobalt ions, better conductivity and good adhesion from the synergetic coupling interaction at the interfaces of $NiCo_2S_4$ and graphene sheets. The $NiCo_2S_4$ nanocrystallite aggregates-decorated GNS hybrid as electrocatalyst offered excellent catalytic activity toward the tri-iodide reduction and a promising PCE of 7.98%, which is equivalent to the PCE value obtained for Pt CE (8.01%) under similar experimental conditions and it can outperform after further optimization, as a low-cost, Pt-free CE for DSSCs.

15. CONTRIBUTION TO THE SOCIETY (GIVE DETAILS)

In the present world, human life has remarkable dependence on clean energy sources and the challenge of global society is to find better ways to replace conventional energy by renewable sources and to avoid negative impact on environment, climate and health. In this regard, dye-sensitized solar cells (DSSC) have engrossed great consideration as the most powerful technology for solar energy conversion to electricity owing to their low-cost, environmental benignity and simplicity. Nano-architectured electrodes are playing crucial role in DSSC device performance. Consequently, various synthesis strategies are being adopted to design efficient electrode materials to enhance the system performance, during the recent years. The main emphasis of this project is to accomplish enhancement in power conversion efficiency (PCE) of DSSCs by implementing different aspects such as designing morphology controlled synthesis of nano/micro architecture electrode materials, DSSC device architecture modifications, effect of localised surface plasmon effect on improving the light harvesting efficiencies and finally replacing platinum by non-precious transition metal sulfide counter electrode. The selected microwave-assisted synthetic strategy is proved to be attractive and significantly reduced the reaction time and subsequently the fabrication cost *via* energy-efficient route. From, the materials synthesized, we have developed two types of innovative photoanode device configurations such as Nano-hybrid architecture and Bi-layer architecture and observed enhancement in the photovoltaic performance due to "size-mismatching" and "synergistic effect" particularly from two different ZnO morphologies. The new device architecture and PV performance study have potential contributions to the device engineers, as the method adopted can be easily followed. The developed $NiCo_2S_4$ counter electrodes will be a promising low-cost, earth-abundant electro-catalyst not only for DSSCs but also for various energy conversion and storage devices such as photocatalytic and supercapacitor applications.

16. WHETHER ANY PH.D. ENROLLED/PRODUCED OUT OF THE PROJECT

Yes, One Ph.D,

Details:

Name: R. Krishna Priya
Reg. No. 121600015
Centre for Nanoscience and Technology, Pondicherry University.

Thesis entitled: "Microwave-Assisted Synthesis, Characterization and Photovoltaic Studies of Innovative Nanostructured Electrode Materials for Dye Sensitized Solar Cells" (Ph.D awarded on 30-06-2017.

17. NO. OF PUBLICATIONS OUT OF THE PROJECT (PLEASE ATTACH)

Following five publications (Four RSC and 1 ACS) were made from this project:

1. R. Krishnapriya, S. Praneetha, and **A. Vadivel Murugan**, "Energy-efficient, microwave-assisted hydro/solvothermal synthesis of hierarchical flowers and rice grain-like ZnO nanocrystals as photoanodes for high performance dye-sensitized solar cells" ***RSC CrystEngComm.***, *17*, 8353-8367 (2015) **IF - 3.84.**

2. R. Krishnapriya, S. Praneetha, and **A. Vadivel Murugan**, "Investigation of the effect of reaction parameters on the microwave-assisted hydrothermal synthesis of hierarchical jasmine-flower-like ZnO nanostructures for dye-sensitized solar cells" ***RSC New J. Chem.***, *40*, 5080 – 5089 (2016) **IF - 3.28**.

3. R. Krishnapriya, S. Praneetha, Arul Maximus Rabel and **A. Vadivel Murugan**, "Energy efficient, one-step microwave-solvothermal synthesis of highly electro-catalytic thiospinel $NiCo_2S_4$/graphene nanohybrid as a novel sustainable counter electrode material for Pt-free dye-sensitized solar cells." ***RSC- J. Mater. Chem. C***, *5*, 3146--3155 (2017) **IF – 5.26.**

4. R. Krishnapriya, S. Praneetha and **A. Vadivel Murugan**, Microwave-solvothermal synthesis of various TiO_2nano-morphologies with enhanced efficiency by incorporating Ni nanoparticles in an electrolyte for dye-sensitized solar cells" ***RSC-Inorg. Chem. Front***, *4*, 1665–1678 (2017) **IF – 4.03.**

5. R. Krishnapriya, S. Praneetha S. Kannan and **A. Vadivel Murugan**, Unveiling the Co^{2+} Ion Doping-Induced Hierarchical Shape Evolution of ZnO: In Correlation with Magnetic and Photovoltaic Performance" ***ACS-Sustainable Chem. Eng.***, *5*, 9981-9992 (2017) **IF – 5.95**

8/4/19

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Energy-efficient, microwave-assisted hydro/solvothermal synthesis of hierarchical flowers and rice grain-like ZnO nanocrystals as photoanodes for high performance dye-sensitized solar cells†

R. Krishnapriya, S. Praneetha and A. Vadivel Murugan*

Received 21st July 2015, Accepted 15th September 2015

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www.rsc.org/crystengcomm

ZnO nanoparticles with different morphologies including marigold flower-like (MGFL), multipod jasmine flower-like (MPJF), sea urchin-rod flower-like (URFL), calendula flower-like (CDFL) and rice grain shape-like (RGSL) were successfully synthesized by decomposing either the $Zn(OH)_4^{2-}$ or $Zn(NH_3)_4^{2+}$ precursor in different solvents such as H_2O, ethylene glycol (EG) and ethanol (EtOH) *via* one-pot rapid microwave-assisted hydro/solvothermal (MW-HT/ST) methods. From the obtained ZnO, we have developed two types of innovative photoanode configurations such as the "nano-hybrid architecture" and the "bi-layer architecture" *via* integration and layer-by-layer coating of flower-like URFL-ZnO and RGSL-ZnO nanoparticles, respectively, for dye-sensitized solar cells (DSSCs). Interestingly, the URFL/RGSL-ZnO nano-hybrid architecture photoanode-based DSSCs showed remarkably enhanced power conversion efficiency (PCE) as high as 5.64% compared to DSSCs based on their individual components such as flower-like URFL-ZnO and RGSL-ZnO nanoparticles which exhibited PCEs of 2.05% and 0.95%, respectively. In contrast, two types of "bi-layer architecture" photoanodes which were composed of an RGSL-ZnO layer on top of URFL-ZnO and *vice versa* exhibited PCEs of 1.74% and 2.26%, respectively. It is revealed that the "hybrid architecture" exhibits superior enhancement in PCE when compared to the "bi-layer architecture" assembly and their respective individual bare ZnO components, which was mainly attributed to the synergistic effect of the two different morphologies when blended together at a "nanoscale" level. Indeed, superior light-scattering ability and anchoring of more dye molecules were provided by URFL-ZnO. The fast electron transport through better inter-particle and electronic contacts with the fluorine-doped SnO_2 glass (FTO) substrate was facilitated by RGSL-ZnO nanoparticles. Hence, the present investigation facilitates a promising way to enhance the efficiency of ZnO-based DSSCs by tuning different morphologies with innovative device architecture.

Introduction

Due to the rapid exhaustion of fossil fuels and increasing global energy demands, the development of alternative, sustainable and clean energy technologies has become a necessity to address these inevitable challenges. In this regard, finding a method to convert an enormous amount of sunlight into electrical energy happened to be appealing to satisfy the world energy demand. DSSC is a modern electrochemical energy conversion device that was inspired from nature by the breakthrough work of O'Regan and Gratzel in 1991.[1] Considerable attention has been paid to the development of DSSCs, due to their simple fabrication procedures coupled with relatively high power conversion efficiency, eco-friendliness and low cost production.[2–4] So far, DSSCs fabricated with TiO_2 nanoparticles have achieved overall conversion efficiency above 13%.[5] In the meantime, other n-type semiconducting oxides, such as ZnO, SnO_2, *etc.*, have been identified as promising photoanodes for DSSCs.[6] Among them, ZnO with different nanostructured morphologies has been investigated intensively due to its comparable band gap of 3.37 eV and facile synthesis. Moreover, there are many

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† Electronic supplementary information (ESI) available: Table showing experimental data for different ZnO morphologies and their grain sizes calculated by using Scherrer's equation, and figures showing the XRD pattern of hybrid photoanode films coated on FTO, Raman spectra of individual and hybrid ZnO, magnified FE-SEM images of ZnO flowers and BET surface area measurements, the Tauc plot from the diffuse reflectance spectra of the different hierarchical ZnO flowers and the combined *J–V* curve of the different hierarchical individual ZnO flowers as well as hybrid photoanode films. See DOI: 10.1039/c5ce01438g

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Investigation of the effect of reaction parameters on the microwave-assisted hydrothermal synthesis of hierarchical jasmine-flower-like ZnO nanostructures for dye-sensitized solar cells†

Ramachandran Krishnapriya, Selvarasu Praneetha and Arumugam Vadivel Murugan*

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A facile, energy-efficient microwave assisted hydrothermal (MW-HT) method has been demonstrated to synthesize hierarchical jasmine-flower-like ZnO nanostructures. The obtained product was characterized using structural, morphological and optical studies by X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), Raman spectroscopy, photoluminescence spectroscopy (PL) and UV-visible spectroscopy. The obtained results revealed that nanostructured ZnO possesses good crystalline properties and enhanced scattering ability. The nucleation and crystal growth mechanism for the synthesized ZnO has been investigated by changing the reaction parameters such as microwave power, reaction time and temperature. A systematic investigation has also been carried out on the influence of the reaction parameters upon the photovoltaic performance of fabricated ZnO-based dye sensitized solar cells (DSSCs). It has been observed that ZnO nanostructures prepared in the microwave assisted power mode (300 W at 10 min) exhibited a maximum power conversion efficiency (PCE) of 4.12%, which is significantly higher than that of commercially purchased ZnO with a PCE of 1.08%. This could be attributed to the unique hierarchical jasmine-flower-like morphological features of the ZnO nanostructures prepared using a rapid MW-HT method.

1. Introduction

Dye-sensitized solar cells (DSSCs), owing to their facile, unique hybrid architecture, relatively low-cost and an eco-friendly fabrication process, have been gaining significant attention as promising candidates for the future clean energy conversion technology.[1–5] The core part of DSSCs is made up of a wide band-gap semiconductor photoanode, where structural and morphological tuning significantly influences the cell performance by controlling light collection and charge transport.[5] Recently, several metal oxide-based semiconductors such as TiO_2, ZnO, SnO_2, Nb_2O_5, Bi_2O_3 *etc.* have been successfully investigated as photoanode materials for DSSCs. A benchmark power conversion efficiency of DSSC more than 12% was reported recently using porphyrin-sensitized TiO_2 with $Co^{2+/3+}$ redox electrolytes.[4]

Particularly, the ZnO based-photoanode has been gaining much attention, because of its direct and wide band gap (3.37 eV) in the UV spectral region, large exciton-binding energy (60 meV) which enables the persistence of excitonic emission over a wide range of temperatures, strong luminescence, high thermal conductivity as well as mobility ($\sim$115–155 $cm^2 V^{-1} s^{-1}$). Moreover, ZnO exhibits unique optical and electrical properties, which also make it a suitable candidate for many electronic, optoelectronic, sensor, piezoelectric and varistor devices.[6] There have been several scientific reports which demonstrated the successful use of ZnO nanostructures as DSSC photoanodes, however the power conversion efficiencies of ZnO-based DSSCs are found to be low when compared to TiO_2.[7] This is due to the dissolution of ZnO and the subsequent formation of a dye–Zn^{2+} complex under acidic conditions, leading to low electron injection from the dye to ZnO. This issue can be ameliorated by reducing the dye-sensitization time that avoids the possible formation of a dye–Zn^{2+} complex and use of dye molecules with fewer carboxylic groups.[8] In addition, the possibility of high electron mobility with reduced electron recombination in ZnO offers profuse scope to enhance the PCE of ZnO based DSSCs.

The PCE of ZnO mostly depends on its structure, morphology, aspect ratio, size, orientation and density of the crystal. Tremendous efforts have been made in recent years for the development of various organized complex, micro or hierarchical nanoarchitectures through self-assembly of nanoscale building blocks.

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† Electronic supplementary information (ESI) available: Tables S1–S9 showing detailed photovoltaic parameters calculated for five sets of DSSC devices fabricated using identical photoanode materials. See DOI: 10.1039/c6nj00457a

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Energy efficient, one-step microwave-solvothermal synthesis of a highly electro-catalytic thiospinel $NiCo_2S_4$/graphene nanohybrid as a novel sustainable counter electrode material for Pt-free dye-sensitized solar cells†

R. Krishnapriya,[a] S. Praneetha,[a] Arul Maximus Rabel[b] and A. Vadivel Murugan*[a]

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A sustainable rapid microwave-solvothermal (MW-ST) synthesis approach has been successfully demonstrated to develop thiospinel $NiCo_2S_4$ nanocrystals and their nanohybrids with graphene nanosheets (GNS) using transition metal-ions (Co^{2+}, Ni^{2+}) and thiourea as a sulfur precursor in the presence of graphite oxide (GO). The MW-ST method enables the nucleation and growth of cubic linnaeite-type thiospinel $NiCo_2S_4$ nanocrystals and simultaneous *in situ* ultra-fast polyol-reduction of GO to GNS and its hybridization within 15 min at 200 °C using ethylene glycol (EG) as the solvent. This process absolutely evades the use of toxic reducing agents or post solid-state sintering at elevated temperatures and subsequent sulphurization using toxic H_2S/Na_2S gases. The nanocrystallite aggregates (NCS-1)/GNS nanohybrid exhibited a remarkable electro-catalytic activity towards triiodide (I^-/I_3^-) reduction owing to improved electronic conductivity and synergistic effects at NCS-1 and GNS interfaces. The developed NCS-1/GNS nanohybrid as a novel counter electrode (CE) for Pt-free dye sensitized solar cells (DSSCs) demonstrated a high power conversion efficiency (PCE) of 7.98% in comparison to the conventional Pt CE of 8.01% under the same conditions. Hence, this work presents a scalable synthesis of an earth-abundant, thiospinel $NiCo_2S_4$/GNS nanohybrid CE *via* a facile single-step MW-ST process as a potential alternative to expensive Pt as a CE in DSSCs and other electrochemical clean energy systems.

1. Introduction

As a long-lasting solution for the rising global energy demand and associated environmental factors, the existing renewable energy technologies need to be developed using sustainable, low-cost and earth-abundant elements.[1–3] Among the existing technologies, dye-sensitized solar cells (DSSCs) that come under third-generation solar cells have attracted much attention due to their ease of fabrication, low-cost and better performance in diverse light conditions.[4] The power conversion efficiency (PCE) of a DSSC is categorically determined by its components (photoanode, counter electrode, dye and redox electrolyte). As a result, the development of efficient inorganic nanostructured electrode materials as well as their structural and morphological impact on the photovoltaic performance has become a major concern in the technological context.

A vital constituent of the DSSCs is the counter electrode (CE) which plays an important role in determining the PCE by harvesting electrons from the external circuit and serves as an electro-catalyst to regenerate redox species by reduction of I_3^- to I^-.[1–3] To ensure efficient functioning of DSSCs, an ideal CE material should possess the following prerequisites: high electro-catalytic activity, good conductivity, effective surface area, excellent long-term stability and compatibility with redox electrolytes.[5] Conventionally, a thin layer of noble metal platinum (Pt) coated on a fluorine-doped tin oxide (FTO) glass substrate has been used as a functional CE in DSSCs. However, the ease of corrosion by the redox species and lack of exposed surface area in addition to the expensive vacuum fabrication procedure (sputtering) for thin-film formation hamper the application of extremely expensive and rare earth element Pt for large scale commercialization in DSSCs. Therefore, the idea of designing and developing an economic, robust, earth-abundant CE as a suitable surrogate for Pt with significant electro-catalytic activity is one of the promising conduits.

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† Electronic supplementary information (ESI) available: DSSC device stability plots and synthesis procedure for GO, fabrication and characterization procedure for DSSCs. See DOI: 10.1039/c6tc04619c

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Cite this: DOI: 10.1039/c7qi00329c

Microwave-solvothermal synthesis of various TiO_2 nano-morphologies with enhanced efficiency by incorporating Ni nanoparticles in an electrolyte for dye-sensitized solar cells†

R. Krishnapriya, S. Praneetha and A. Vadivel Murugan *

Received 11th June 2017,
Accepted 14th August 2017

DOI: 10.1039/c7qi00329c

rsc.li/frontiers-inorganic

Dye-sensitized solar cells (DSSCs) have been fabricated with various nanostructured TiO_2 morphologies, including interconnected beads-like (IBL), square platelets-like (SPL), spindle shape-like (SSL), and porous spheres-like (PSL), synthesized in different solvents (ethanol, mixture of ethanol + H_2O and HF), and size and shape-tuned Ni-NCs of mixed triangular and hexagonal morphological crystals with sizes ranging from 15 to 62 nm in ethylene glycol (polyol) medium. These different TiO_2 and Ni-NCs were constructed *via* a rapid, facile microwave-assisted solvothermal (MW-ST) route. The application potential of these TiO_2 NCs as photoanodes unveiled excellent morphology-dependent PCEs (5.3% to 9.33%) using a conventional electrolyte and N719 dye as a photosensitizer. Subsequently, after impregnating Ni-NCs in the I^-/I_3^- electrolyte, the nanoparticles on the surface of each TiO_2 morphology acted as excellent scattering centers to provide a potential interface between TiO_2 and Ni-NCs and enhance both light absorption and scattering, leading to improvements in the PCEs to 5.8%, 8.37%, 9.19% and 10.02% for the PSL, SSL, SPL and IBL-based photoanodes, respectively. This enhanced PCE was accomplished by systematic optimization of factors such as the surface morphology of the TiO_2 photoanode and the size and concentration of the Ni-NCs in the electrolyte to attain the best advantages of scattering-induced effective light utilization and size-mismatching effects at the photoanode and Ni-NCs integrated electrolyte interface. The incorporated Ni-NCs effectively trap incident light and successively improve the rate of electron–hole pair formation and short circuit current (J_{sc}); they also exhibit excellent stability in the conventional I^-/I_3^- electrolyte over a period of 30 days.

1. Introduction

Dye-sensitized solar cells (DSSCs) have recently received significant scientific and technological attention because of their low cost and ease of fabrication. The size and morphology control of nanostructured semiconductor materials and their interfacial interactions after incorporation into DSSCs indeed play crucial roles in device enactment.[1] Extensive research efforts have focused on manipulation and effective utilization of incident light in order to foster the light harvesting efficiency (LHE) of DSSCs by enhancing visible light absorption through fabricating thick photoanodes, dimensionally modulated semiconducting oxides as scattering layers and back reflectors, modified sensitizers, co-sensitizers, size-mismatching/integrating of sub-micrometer-sized spherical structures in photoanodes, *etc.*[2–8] Among these perspectives, molecular engineering of the photosensitizer has increased the efficiency of these devices beyond 13%.[9] However, the novel design of semiconductor photoanodes is a simpler methodology to enhance the LHE and power conversion efficiency (PCE) of DSSCs.[10–16]

A promising practice to improve LHE and subsequently PCE is the incorporation of noble metal nanoparticles (Ag and Au) in the DSSC photoanode because they can increase scattering by the collective oscillation of electrons in the conduction band and can confine adequate sunlight within the photoanode.[17–20] Specifically, localised surface plasmon resonance (LSPR), *i.e.* the charge density oscillations confined to metallic nanoparticles by an electric field (light) at an incident wavelength where resonance occurs, resulting in strong light scattering, in the presence of intense surface plasmon (SP)

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†Electronic supplementary information (ESI) available: Table and figures showing Raman, FESEM and UV-Vis, experimental conditions to synthesize different TiO_2 and Ni-NCs, photovoltaic parameters of different TiO_2 morphologies-based DSSCs. See DOI: 10.1039/c7qi00329c

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Unveiling the Co^{2+} Ion Doping-Induced Hierarchical Shape Evolution of ZnO: In Correlation with Magnetic and Photovoltaic Performance

R. Krishnapriya, S. Praneetha, S. Kannan, and A. Vadivel Murugan*

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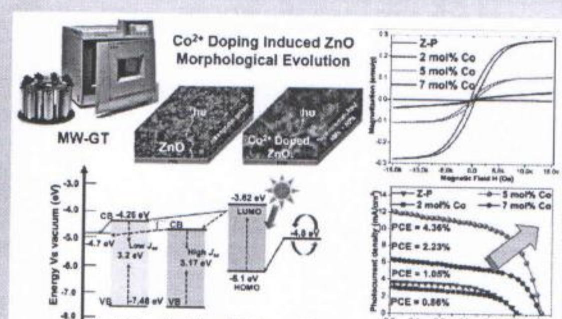
Supporting Information



ABSTRACT: A sustainable, rapid microwave-assisted glycothermal (MW-GT) method has been adopted for the synthesis of pristine ZnO and a series of $Zn_{1-x}Co_xO$ (x = 0, 0.02, 0.03, 0.05, 0.07, 0.10) within 15 min at 180 °C using ethylene glycol (EG) as solvent. The XRD results reveal that the altering of lattice parameters of ZnO by introduction of Co^{2+} ions and crystalline sizes of Co^{2+} doped ZnO samples decreased with increasing Co^{2+} ion content. A spectacular morphological change of ZnO from well-defined hexagonal prismoid to hierarchical flower-like 1-D nanorods-assembly upon increasing Co^{2+} ion concentration was perceived using FE-SEM and TEM analyses. After Co^{2+} ion inclusion into pristine ZnO, the width of the M−H loop significantly changes, where the diamagnetic behavior of ZnO changes from ferromagnetic to paramagnetic upon further increase in Co^{2+} ion content. Particularly, 5 mol % Co^{2+} ion doped ZnO sample shows enhanced photovoltaic performance in dye-sensitized solar cells (DSSCs) due to nanoscale level intermingling of two different 1-D nanorod-like morphology with particle-like morphology, resulting in size-mismatched combination-induced light-scattering effect, photoinduced charge-carrier formation by charge-transfer transitions of high spin Co^{2+} ions, and lower recombination resistance together with extended electron lifetime, which were deduced from UV−vis and impedance spectroscopy analysis, respectively.

KEYWORDS: *Cobalt doping, Microwave glycothermal, Zinc oxide nanocrystals, Hierarchical morphology, Dye-sensitized solar cells*

■ INTRODUCTION

Doping is the process of incorporating intentional impurities into the semiconductor nanocrystals (NCs) to modify their unique structural, optical, electrical, and magnetic properties. This approach is more promising yet challenging in semiconductor-based technologies and an effective way to tune the band gap to broaden its spectral absorption.[1−3] Recently, ZnO has become an attractive wider band gap semiconducting metal oxide and exhibits unique properties that provide both technological as well as eco-friendly benefits.[4−8] Various devices functioning with ZnO NCs include solar cells, field effect transistors, and photodetectors, which all affirmed their potential reliability in the development of electronics and clean energy systems. Significant efforts were made to improve ZnO materials as DSSC photoanode, because this material unveils higher electron mobility than TiO_2 and enables rapid transport of photoinjected electrons. The incident light absorption of ZnO occurs mainly in the UV region with spectral wavelength equal to or less than 385 nm. However, the visible light (400−700 nm) is mainly accountable for 45% of the total solar energy absorption, and the UV region accounts for less than 10%.[9] In this regard, there is a necessity to broaden the spectral absorption range to boost the solar cell performance.[10,11] On the other hand, morphology tuning as well as ZnO doped with appropriate metal ions have been demonstrated with considerable photovoltaic (PV) enhancement in the DSSCs.[12−15] Moreover, when the doped NCs are applied as photoanode materials for DSSCs applications, the dopants prevent the photo-oxidation and promote effective charge transfer of absorbed photons to solar energy conversion by the appropriate dopant concentration. In addition, dopants cause effective quick localization of photoexcitation followed by suppression of undesirable reactions at NCs surface, which synergistically contribute to enhanced PV performance in solar cells.[16] Doping of ZnO with various metal and nonmetal elements such as Li, B, and I, etc., were widely carried out to tailor the optical properties of photoanode in DSSCs.[17−19] Transition metal (TM) doped ZnO NCs have also been proven as suitable candidates in yielding extensive photoresponse in the visible region and are hence manifested as efficient photocatalysts for solar energy conversion and degradation of toxic water pollutants.[20−25] The photochemistry behind all of these processes is the excitation of a sub-band gap absorption by a d−d transition. Among various TM doped ZnO, Co^{2+}

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