Journal of Power Sources 380 (2018) 142–148

Contents lists available at ScienceDirect

Journal of Power Sources

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

# Spectrum-enhanced Au@ZnO plasmonic nanoparticles for boosting dye-sensitized solar cell performance

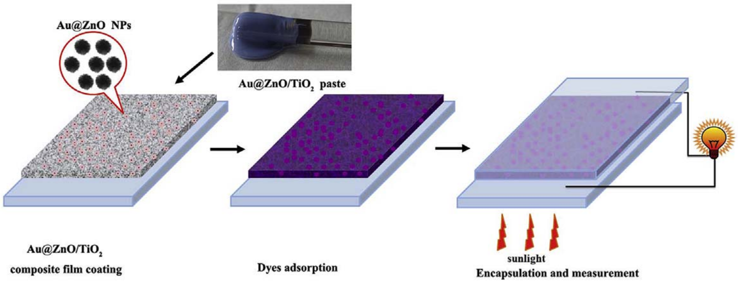
Qisheng Liu[a,*], Yunwei Wei[a], Malik Zeeshan Shahid[a], Mingming Yao[a], Bo Xu[a], Guangning Liu[a], Kejian Jiang[c], Cuncheng Li[a,b,**]

[a] *School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, China*
[b] *Key Laboratory of Chemical Sensing & Analysis in Universities of Shandong (University of Jinan), Jinan 250022, China*
[c] *Key Laboratory of Green Printing, Institute of Chemistry, Chinese Academy of Sciences (ICCAS), Beijing Engineering Research Center of Nanomaterials for Green Printing Technology, Beijing National Laboratory for Molecular Sciences (BNLMS), Beijing 100190, China*

## HIGHLIGHTS

- Novel spectrum-enhanced Au@ZnO plasmonic nanoparticles are developed.
- The optimized amounts of Au@ZnO are used to boost the DSSC performance.
- Enhanced SPR effects increase the light harvesting abilities of plasmonic DSSCs.
- Low recombination of charges is also responsible for the enhanced DSSCs.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

*Keywords:*
Dye-sensitized solar cell
Surface plasmon resonance
Power conversion efficiency
Nanoparticles

## ABSTRACT

Spectrum-enhanced Au@ZnO plasmonic nanoparticles (NPs) are developed for fabrication of the dye-sensitized solar cells (DSSCs), and their remarkable enhanced performances are achieved due to Surface Plasmon Resonance (SPR) effects. When being doped different blended amounts of the Au@ZnO NPs within the photoanode layers, various enhanced effects in the SPR-based DSSCs are exhibited. Compared with the power conversion efficiency (PCE, 7.50%) achieved for bare DSSC, device with doped Au@ZnO NPs of 1.93% delivers the top PCE of 8.91%, exhibiting about 20% enhancement. To elaborate the charge transfer process in the Au@ZnO NPs blended DSSCs, the photoluminescence (PL), electrochemical impedance spectra (EIS), etc are performed. We find that both the enhanced SPR absorption properties and the suppressed recombination process of charges contribute much to the improved performance of Au@ZnO-incorporated DSSCs.

## 1. Introduction

In recent decades, dye-sensitized solar cells (DSSCs) have attracted broad interest due to their low manufacturing and material costs. Benefiting from the pioneering works by Grätzel and co-workers [1], tremendous progress has being made in the design of the high-performance DSSCs for potential applications [2–6]. To gain the high-efficiency DSSCs, many alternative efforts, such as developments of strong light harvesting organic dyes, novel electrolytes, and optimized $TiO_2$ photoanode networks, etc., were adopted in DSSC applications [7–16]. However, the design of the novel structures for DSSCs or development of the new materials (such as organic dyes) for optimizing

---

[*] Corresponding author.
[**] Corresponding author. School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, China.
*E-mail addresses:* chm_liuqs@ujn.edu.cn (Q. Liu), chm_licc@ujn.edu.cn (C. Li).

https://doi.org/10.1016/j.jpowsour.2018.01.089
Received 6 November 2017; Received in revised form 25 January 2018; Accepted 30 January 2018

DSSCs performance might be difficult and tedious. Recent studies have shown that utilizing the Surface Plasmon Resonance (SPR) effects to enhance the light harvesting of DSSCs is indeed one of the promising ideas for boosting their performance [17–22]. Generally, under the incident light, the plasmonic nanomaterials with SPR effects will exhibit collective oscillations of electrons within the metal nanoparticels, which can increase the light harvesting of the dyes and facilitate generation of the photon-carries in the photoanode layers [17,18]. Thus, by introducing plasmonic nanoparticles into DSSC systems, the remarkable enhancements can be expected. Motivated by these ideas, tremendous efforts were devoted to developing the novel plasmonic materials for application in DSSCs [19–22]. Currently, most of the studies were focused on spheroidal plasmonic nanoparticles, which can only exhibit a narrow absorption spectrum band and have limited the light harvesting improvement of the dyes for the DSSCs. In contrast with the most used spheroidal SPR particles, the polyhedral noble metal nanoparticles (e.g. octahedral particles) can exhibit higher near-field enhancement around the octahedral corners, which subsequently can enhance their SPR effects greatly [23,24]. These non-spheroidal SPR particles, however, could not be directly introduced into $TiO_2$ photoanode layers in DSSCs: Firstly, the naked metallic SPR particles (such as Au) are good conductors, which can serve as recombination sites for photogenerated charge carriers during the fabricating process of DSSCs [25,26]; In addition, the naked metallic SPR particles may also easily encounter the corrosion caused by the liquid electrolytes (such as $I^-/I_3^-$ solution), which will destroy the stabilities of solar cells [27]. In order to solve the problems, a protective layer outside of metallic SPR cores is always indispensable before introducing them into the DSSCs. In this regard, the inorganic $TiO_2$ or $SiO_2$ materials are usually employed as a protective shell to meet the needs. As for $SiO_2$ materials, their insulating properties can minimize charge recombination [24], but its native nonconductivity will also inhibit efficient charge transfer within photoanodes [25]. As another alternative material, N-type semiconductor $TiO_2$ can function as both electron-transfer mediator and protective layer of the metallic SPR particles, and the SPR-core@$TiO_2$ based DSSCs have achieved tremendous successes [23,28,29]. Although, the Au@$TiO_2$ NPs for enhanced DSSCs were continuously reported, the interactions between the SPR cores and semiconductive shells and their relevant enhanced absorption properties have been not claimed clearly. Thus, developing novel shell-based plasmonic materials and investigating their SPR enhanced effects for promoting the DSSCs efficiency would be very meaningful for high-performance photovoltaic applications.

In this work, we developed novel spectrum-enhanced Au@ZnO plasmonic NPs, and successfully introduced them into nanocrystalline-$TiO_2$ photoanodes to improve DSSC performance. In the Au@ZnO plasmonic NPs, Au octahedrons instead of Au spheres were adopted as the cores due to its high near-field SPR enhancement around the corners [23]. Besides, the coated ZnO semiconductor layers outside of the Au octahedrons can further enhance their SPR absorptions greatly [30], which is important for improving the light harvesting of dyes in the DSSC systems. In addition, the ZnO shells can not only suppress the corrosion caused by the liquid electrolyte [31], but also the incorporation of Au@ZnO plasmonic NPs can be anticipated to suppress the charge recombination in its transfer process, and effectively favoring the collection of the separated charges in DSSCs. This work may be expected to open up new prospect in novel SPR nano-material applications for optimizing the DSSC performance.

## 2. Experimental

### 2.1. Synthesis of Au@ZnO core-shell NPs

The Au@ZnO core-shell NPs were prepared according to our previous report with minor modification [30]. As for the core Au NPs, octahedral Au NPs were firstly synthesized through a polyol process according to our previous work [32]. Subsequently, the coating process of ZnO shells was outlined as follows: 0.9 mL of 0.02 M $NaBH_4$ (0.018 mmol) aqueous solution was first added to 18 mL of 0.5 mM Au NPs solution, and the mixture was stirred under ambient condition for several minutes. Then, the 1.8 mL of 0.01 M $Zn(NO_3)_2$ (0.018 mmol) aqueous solution, 1.8 mL of 0.05 M NaOH (0.09 mmol) aqueous solution was introduced into the mixture above. After being stirred for a while, the obtained homogenous mixture of Au octahedrons and ZnO precursor was then reacted at 60 °C for 20 min. Finally, the product was separated out via centrifugation, and washed several times with water and ethanol consecutively. As for different coated thicknesses of ZnO shells, the concentrations of $Zn(NO_3)_2$, NaOH, as well as $NaBH_4$ can be adjusted according to their corresponding proportions.

### 2.2. Preparation of the Au@ZnO doped $TiO_2$ paste

The pure $TiO_2$ paste (Dyesol, OPV-18 NR-T, containing about 20% $TiO_2$) was purchased and used as received. As for blended $TiO_2$ paste, its synthesis process was outlined simply as follows: 50 mL of the Au@ZnO NP solution as prepared was first centrifugated and washed several times with absolute ethanol, and the last centrifugation was performed to remove most solvents for achieving the high concentration mixture (about 1 mL, containing about 7.8 mg Au@ZnO nanoparticles). In preparation of the Au@ZnO doped $TiO_2$ paste, the different amounts of Au@ZnO NPs as needed (for example: about 83 μL concentrated solution was introduced into 0.5 g $TiO_2$ paste for 0.65% $TiO_2$ layer) were introduced into $TiO_2$ pastes, and the mixtures were mixed to form the homogeneous plasmonic NPs doped $TiO_2$ pastes.

### 2.3. Fabrication of DSSC devices

The cleaned fluorine-doped $SnO_2$ conducting glasses (FTO) were first treated with 50 mM $TiCl_4$ aqueous solution at 70 °C for 30 min. After being cooled to room temperature, the samples were washed with water and absolute ethanol for several times. Then, the treated FTO glasses were sintered at 500 °C for 30 min under air conditions and subsequently cooled to room temperature slowly. Next, the Au@ZnO doped $TiO_2$ paste was coated onto the $TiCl_4$ pre-treated FTO glasses surface by doctor blade methods, and then was performed with a programmed heating procedure: (1) heating at 80 °C for 10 min; (2) heating at 120 °C for 10 min; (3) heating at 325 °C for 5 min; (4) heating at 385 °C for 5 min; (5) heating at 500 °C for 30 min; (6) cooling to room temperature naturally. The samples with $TiO_2$ films coated were then immersed in 0.5 mM N719 dyes solutions in mixed solvents of acetonitrile and tert-butyl alcohol (1:1 vol ratio) for 24 h to absorb the dyes. Then, the DSSCs with dyes loaded were sealed with Pt-coated conducting glass as the counter-electrode by heating with a hot-melt ionomer film (Surlyn, OPV-SN-45 TamaPoly). Finally, the traditional electrolyte solution ($I^-/I_3^-$) was injected between the electrodes before photoelectrochemical measurements.

### 2.4. Characterization methods

The morphology of the Au@ZnO NPs was recorded in JEOL, JEM-1400. UV-visible absorption spectrum was collected in Hitachi U-4100, which is equipped with an Edinburgh Xe900 xenon arc lamp as exciting light source. Luminescent spectra were carried out on an Edinburgh FLS920 phosphorimeter equipped with a continuous Xe-900 xenon lamp and an nF900 ns flash lamp. X-ray diffraction (XRD) spectra were measured on a Bruker D8 Focus X-ray diffractometer with Cu Kα radiation ($\lambda = 0.15418$ nm) by depositing the product on a glass slide. The current density–voltage (*I–V*) curves were recorded by ModuLab XM PhotoEchem (Solartron Metrology) with *I–V* photoelectrochemical measurement platform coupled with a 500 W xenon lamp as the light source, and the incident light intensity was 100 mW cm$^{-2}$ (the equivalent of one sun at AM 1.5) at the surface of solar cells. Intensity