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P-type NiO nanoparticles enhanced acetylene black as efficient counter electrode for dye-sensitized solar cells

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ABSTRACT

P-type nickel oxide acetylene black nanoparticles composite (NiO/AB) enables facile low cost counter electrode for dye-sensitized solar cells (DSSCs), prepared by simple chemical process and doctor-blading method. Nanocrystalline p-type NiO contributes in the improvement of holes conduction at the acetylene black surface and escalates the electrocatalytic activity, confirmed by our cyclic voltammetry and electrochemical impedance spectroscopy measurements. Owing to the improvement of electrocatalytic activity, the mutual porous acetylene black surface with p-type NiO nanoparticles counter electrode and dye-sensitized TiO_2 photoanodes yielded significantly enhanced power conversion efficiency of 7.75%, which is superior to that of 6.51% and 6.96% of AB and expensive Pt in our experiment respectively.

1. Introduction

Since the major breakthrough in 1991, dye-sensitized solar cells (DSSCs) have attained considerable interest among the scientists worldwide [1]. The low manufacturing cost advantages, environmental friendliness, and the large-area photovoltaic devices make them a potential alternative to conventional silicon-based solar cells [2,3]. Recently, the maximum reported laboratory power conversion efficiency (PCE) of DSSCs has been reached to 13% [4]. The design of conventional DSSCs is simple. It consists of dye attached mesoporous TiO_2 film onto fluorine doped tin oxide (FTO) photoanode, a spacer, counter electrode (CE) and an electrolyte solution [5]. In DSSCs, the CE is an important component and play critical role [6] i.e., for the catalytic iodine reductions and electron transfer. Usually noble metal platinum (Pt) coated FTO glass is used as a preferable CE in DSSCs to obtain high photovoltaic performances [7]. However, researchers also reported that weak corrosion resistance of Pt in an electrolyte solution containing iodide generates platinum iodides such as PtI_4 [8–10]. Therefore, it is necessary to investigate best CE materials for understanding low-cost DSSCs.

As an alternative inexpensive and abundant material to Pt metal, several other materials such as cobalt sulfide (CoS) [11], titanium nitrides (TiN) [12], carbon based material [13,14] and conducting polymers [15,16] have been employed as electrocatalyst for CE in DSSCs. Among all these candidates, carbonaceous materials have shown quite promising and remarkable performance owing to its availability in large amount, high catalytic activities, low cost and good chemical stability. However, to achieve good catalytic effect, the films of these carbon based counter electrode require usually thick (~15 μm) porous structure character as reported by Grätzel [17] but the conversion efficiencies are still insufficient as compared to that of Pt.

State-of-the-art, p-type nickel oxide (NiO) is well-known transition metal oxide and widely used as heterogeneous catalyst in chemical and petrochemical processes [18,19]. The wide band gap (ca. 3.6 eV) and exceptionally high ionization potential make them a potential candidate for several photo sensitizers [20–22]. He et al. used NiO film as photoactive electrode in DSSCs and yielded an open circuit voltage of 0.73 V [23]. Many efforts were attempted to attain better performance of NiO based photoelectrode but their power conversion efficiency is still insufficient [24,25]. Furthermore, NiO has been also used for DSSC CEs. Guai et al. obtained high power conversion efficiency (5.04%) of DSSCs with sulfur doped NiO CE [26]. Bajpai et al. used a CE made from NiO nanoparticles attached with graphene platelets and yielded an efficiency of 3.06% [27]. Okumura et al. employed NiO hybridized carbon film as an cathode for DSSCs, and attained a high efficiency (5.11%) [28]. The above efficiencies are still worse owing to its complex, expensive, two steps processes and also very thin carbon

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layer thickness, which strongly influenced the fill factor (FF) of DSSCs. As reported by Grätzel group, the thickness effect of carbon layer established strong relationship with improvement in FF [10].

To overcome all these inherent shortcomings, we report very simple and one step chemical method of NiO based DSSCs CE. As a CE material of DSSCs, p-type NiO exhibited superb catalytic activity because its valence band structure can easily collect holes from I_3^-/I^- and also have strong interaction with electrolytes of iodine based solution. However, due to its poor conductivity, NiO is required to combine with any electrically conductive component. For this reason, we introduce NiO with active conductive AB as CE composite.

Theoretically, Fig. 1(a) illustrates the schematic process of energy levels of the fabricated DSSCs for whole system. The energy levels are beneficial for efficient charge separation and transportation throughout the entire system. Due to structural imperfections in carbonaceous material, it provides more energy defects inside their band gap which is confirmed by our Raman analysis. These surplus energy defects play a pivotal role as intermediate states for charge transportation between electrolyte solutions and counter electrode of DSSCs [29,30]. Therefore, the added active sites justify the use of defected AB doped with NiO as efficient CE material in DSSCs. Additionally, it is also important that all component energy levels of NiO and AB nanoparticles are very close to each other, so it is feasible to use them as composite CE material in DSSCs. The combination of p-type NiO with conductive AB has not been reported for DSSCs CE before. Herein, p-type NiO enhanced AB CE was fabricated and studied. Moreover, two types of CE, including AB deposited on ordinary FTO glass and conventional Pt based CE were compared with our p-type NiO enhanced AB CE.

The structural and photovoltaic properties in this study indicate that the as-prepared NiO/AB CEs should be capable of working as efficiently as conventional Pt CE. In particular, the obtained power conversion efficiency (PCE) of NiO/AB under standard illumination condition (1.5G, 100 mW/cm^2) was 7.75%, which indicates promising potential applications for electrodes in DSSCs.

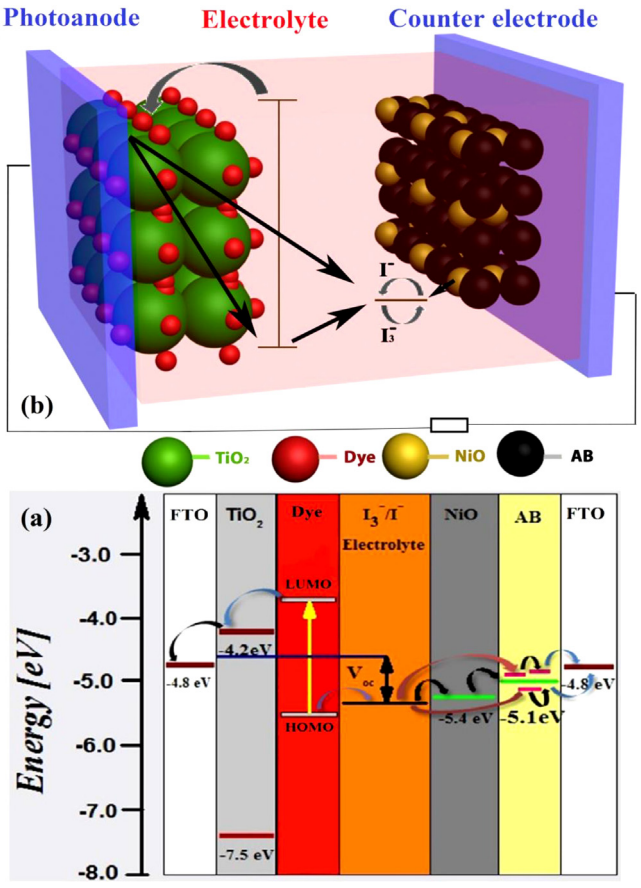

Fig. 1. (a) Schematic energy levels of fabricated DSSCs for whole system. The curved arrows depict possible paths for electrons and holes transport and (b) schematic illustration of DSSCs with TiO_2 photoanode and NiO/AB composite CEs in cross-sectional view.

2. Experimental

2.1. Reagents and materials

In our experiments, all chemicals and reagents were of analytical grade and used without any additional purification. Ethanol (C_2H_6O), terpineol ($C_{10}H_{18}O$), titanium tetrachloride ($TiCl_4$), ethyl cellulose and acetic acid (HAc) were purchased from Sinopharm Chemical Reagent Co., Ltd. Acetylene (99%) was obtained from Hubei Chuchengwei Chemical Co., Ltd. N719 (cis–bis (isothiocyanato) bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium(II) bis-tetrabutylammonium) was supplied from Solaronix. Fluorine doped tin oxide glass (FTO, 7 Ω/cm^2) was purchased from Nippon Sheet Glass Co., Ltd. and washed ultrasonically with laundry soap, acetone, Milli-pore water (18.2 MΩ cm) and ethanol for 15 min, respectively. Lithium iodide (LiI, 99.999%), iodine (I_2, 99.99%), $TiCl_4$. $3H_2O$ (99.99%), 1-methyl-3-propylimidazolium iodide (PMII, 98%), 4-tert-butylpyridine (4-TBP, 96%), *tert*-butyl alcohol (99.5%) and nickel oxide (NiO, 99.5%, 30 nm beads) were obtained from Aladdin. Acetonitrile (99.8%) and valeronitrile (99%) were bought from Alfa Aesar.

2.2. Fabrication of NiO/AB counter electrode

The AB was prepared by the pyrolysis method [31]. Typically, 1.5 g acetylene was heated at 680 °C in Ar atmosphere for 2 h and cooled to room temperature naturally to get the AB nanoparticles with size of about 50 nm. To obtain the optimal NiO/AB colloid paste, 0.90 g as-prepared acetylene black powder was mixed with 0.10 g nickel oxide, 0.2 ml acetic acid and some ethanol at room temperature under stirring. To attain fine dispersion, a measured amount of terpineol anhydrous (3 g) with 0.50 g ethyl cellulose was added into the above standard NiO/AB composite colloid paste. After stirring, the prepared homogenous mixture was grounded in a mortar and ultrasonication for 15 min, respectively. Subsequently, the NiO/AB composite slurry was deposited onto the patterned conducting layer of FTO glass by doctor-blading method. The resultant layer was dried at room temperature and then heated at 400 °C for 2 h using muffle furnace to remove the residual organic content and formed network of 3-D structure. The thickness and area of the film can be controlled by the height of transparent adhesive tape strip. For analysis and comparison purposes, AB film was also prepared under the same experimental conditions without the existence of NiO contents. Additionally, the conventional Pt CE was prepared according to the literature [32].

2.3. Fabrication of TiO_2 photoelectrode

The mesoporous TiO_2 suspension was synthesized according to the reported literature [33]. To prepare an ultrathin layer, the already cleaned conducting FTO glass was first dipped into 40 mM $TiCl_4$ aqueous solution and keep at 70 °C in air oven for 0.5 h. After washing, the high transparent TiO_2 suspension was applied on the treated substrate using one layer of magic scotch tape (with thickness of 50 μm) by doctor blade method and dried it in furnace at 300 °C for 0.5 h. After initial drying, the TiO_2 film color turns into