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Great enhancement of electrochemical cyclic voltammetry stabilization of Fe_3O_4 microspheres by introducing 3DRGO

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ABSTRACT

Excellent electrochemical stabilities and superior electrocatalytic activities of inexpensive counter electrodes (CEs) play an essential role in the large-scale practical application of dye-sensitized solar cells (DSSCs). Herein, the spherical Fe_3O_4 was selected as a CE and high power conversion efficiency (*PCE*) of 8.76% was achieved, which was more than Pt's efficiency (7.80%). Unfortunately, the efficiency decreased expeditiously (from 8.76% to 7.88%) in three consecutive measurements. Cyclic voltammetry (*CV*) tests also reveal that the Ox1 and Red1 peaks of the CE disappear after a few cycles, which could be attributed to the fact that pure Fe_3O_4 was easily corroded in the electrolyte, and the catalytic activity was gradually lost after repeated tests. Here, a novel strategy is that Fe_3O_4 spheres are encapsulated within the 3D reduced graphene (3DRGO) networks to enhance the stability of CV. Three consecutive photovoltaic measurements demonstrate that PCE of the cell with Fe_3O_4@3DRGO nanocomposites as CE has been enhanced and the cell shows surprising stabilization (PCE = 9.10%, 9.07% and 9.05% in the three consecutive tests, respectively). The specific surface area of the composite is increased after introducing 3DRGO, which is helpful for electrons transferring rapidly from external circuit to the system of redox to catalytically reduce triiodide, and also decreases charge-transfer resistance. This work not only achieves the outstanding photovoltaic performance and stabilization, but also offers a promising strategy in constructing 3D nanomaterials with novel structure for wide energy applications.

1. Introduction

Dye-sensitized solar cells (DSSCs) as promising renewable energy source players have attracted much attention in the decades. In general, DSSCs is made of three key components: a dyed coated TiO_2 anode, an electrolyte and a counter electrode (CE). The main function of CE is to accelerate I^-/I_3^- redox couple and achieve the electric circuit in this system [1–8]. As we all know, Pt has excellent performance as a traditional CE in DSSCs, such as superior conductivity and excellent electro-catalytic activity for the reduction of I_3^- in the redox electrolyte. However, it not only is one of the most expensive and rare metal materials in the nature, but also can be corroded to PtI_4 in traditional I^-/I_3^- redox couple electrolyte, which will affect the long-term stability and seriously hinder the development of the industrialization of the DSSCs [9–11]. Hence, inexpensive Pt alternatives for CEs in DSSCs are very popular and attractive. At present, Many synthetic materials have been proven to be the potentially candidates for the replacement of Pt, such as conducting polymers, inorganic materials including transition metal sulfides, nitrides and carbides [12–15]. However, they have also brought a lot of pollution in the nature at the same time. Therefore, developing an economic, non-pollution, stable, effective and Pt-free CE is a necessary precondition for DSSCs.

Oxide is seldom used in the DSSC, due to poor electrical conductivity and low electro-catalytic activity for the reduction of I_3^- in the redox electrolyte. Whereas, as a typical layered transition metal oxide, Fe_3O_4 is a solid solution of FeO and Fe_2O_3. Owing to the difference in ion size, half of the Fe^{3+}cations fill in the smaller tetrahedral interstitial sites, and another half of Fe^{3+} and Fe^{2+}cations occupy the larger octahedral interstitial sites [16]. Therefore, Fe_3O_4 possess the excellent conductivity and its resistivity is much lower than any other metal oxides. It is also

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expected to have significant catalytic activity due to the typical mixed valence metal ions, $Fe^{2+}$and Fe^{3+}. Simultaneously, the morphology and specific surface area of the material is easy to control in order to effectively contact with electrolyte and accelerate the transmission of electrons, leading to high conductivity and catalytic activities. For these reasons, Fe_3O_4 is widely used in the field of lithium ion batteries [17], supercapacitor [18] and wave absorption material [19]. Recently, another iron oxide Fe_2O_3 as CE materials for DSSCs showed high photovoltaic efficiencies of 4.60% [20].

In addition, composites of inorganic compounds and carbon materials also have the ability of enhancing the electro-catalytic performance of the CEs. For example Cu_2O/RGO [21], AgInZnS-graphene oxide [22] and Co_3O_4@RGO, the composite Co_3O_4@RGO with high electrical conductivities, excellent catalytic activities and superior electrochemical stabilities were reported and enhanced photovoltaic property of DSSCs was achieved [23]. As a consequence, the electro-catalytic activity was improved due to electron-transport network provided by the carbon-based materials to speed up the electronic transmission. Unfortunately, to the best of our knowledge, Fe_3O_4 is seldom used in DSSC, and the reported power conversion efficiency of the cell equipped with Fe_3O_4/RGO as CE is not ideal either [24].

Herein, we presented a facile one-step solvothermal synthesis of the uniform Fe_3O_4 microspheres in situ encapsulated with three dimensional reduced graphene (3DRGO). This configuration can prevent Fe_3O_4 from being easily corroded by electrolyte and have the catalytic activity of Fe_3O_4 microspheres almost retained. Three consecutive photovoltaic measurements demonstrate that PCE of the cell with Fe_3O_4@3DRGO nanocomposites as CE has been enhanced and the cell shows surprising stabilization (PCE = 9.10%, 9.07% and 9.05% in the three consecutive tests, respectively). This result is far superior to the performance of pure Fe_3O_4 as CE (whose PCE rapidly decays from 8.76% to 7.88% in three consecutive measurements) and also higher than Pt's value (7.80%). Besides, the composite shows amazing corrosion resistance to electrolyte during 25-cycle CV tests at 25 mV/s scanning speed. In contrast to the pure Fe_3O_4, the oxidation/reduction peak shape and the peak-to-peak width E_{pp} of the composite almost do not show any variation after 25-cycle CV tests, which is highly consistent with consecutive photovoltaic measurements. Moreover, Fe_3O_4@3DRGO nanocomposites are low-cost, environment-friendly and can be produced at large scale. Therefore, Fe_3O_4@3DRGO should be an excellent candidate to replace conventional Pt CE in DSSCs. Details of the results and discussions are elaborated as follows.

2. Experimental

2.1. Materials

All chemicals used in this study were analytical grade and used without further purification.

Ferric chloride hexahydrate ($FeCl_3\cdot 6H_2O$), ethylene glycol, diethylene glycol, sodium acetate, trisodium citrate were all purchased from Aladdin Industrial Corporation. Deionized water was obtained from electrothermal distiller and was used in all experiments.

2.2. Preparation of Fe_3O_4 microspheres

The Fe_3O_4 microspheres were prepared by a simple one-step hydrothermal method [25]. As a typical method, $FeCl_3\cdot 6H_2O$ (0.95 g, 3.0 mmol) and trisodium citrate (0.05 g) were first added to ethylene glycol (20 mL) with vigorous stirring (180r/min). Another 40 mL solution of diethylene glycol containing 4.0 g of sodium acetate was then added with intense magnetic stirring (180r/min). The two different solutions were mixed and stirred until they were homogenous. After that, the mixture was stirred vigorously with 240r/min for 30 min and then divided equally and transferred into four Teflon-lined stainless-steel autoclaves with a capacity of 100 mL. The four autoclaves were heated at 200 °C for 6 h, 8 h, 10 h and 12 h, respectively. After cooling to room temperature, the black precipitates were obtained with magnetic decantation and washed with water for six times, and dried at 50 °C for overnight in a vacuum. According to the following measurements, we found that the product heated for 10 h shows the best performance (please refer to Supporting Information in detail). The following discussion is based on Fe_3O_4 microspheres heated for 10 h.

2.3. Synthesis of Fe_3O_4@3DRGO hybrids

The graphene oxide nanosheets (GO) were synthesized by a modified Hummers procedure [26,27]. To prepare Fe_3O_4@3DRGO hybrids, GO (250 mg) was dispersed in ethylene glycol (30 mL) and stirred vigorously, and then the mixed solution was treated with ultrasound for 30 min to form a homogeneous solution. Later, $FeCl_3\cdot 6H_2O$ (0.95 g, 3.0 mmol) and trisodium citrate (0.05 g) were added to the homogeneous solution. And in the meantime another solution of diethylene glycol (20 mL) and sodium acetate (2.0 g) was obtained under intense magnetic stirring. The two different solutions were stirred until they were homogenous. After that, two solutions were mixed together and stirred vigorously for 30min. The mixed solution was transferred into Teflon-lined stainless-steel autoclaves with a capacity of 100 mL. Subsequently, the sample was heated at 200 °C for 10 h to form a graphene-based 3D hydrogel. After cooling to room temperature, the composites were obtained by magnetic decantation and washed with ethanol and deionized water for four times. Finally, the products were processed with freeze drying a night to maintain the 3D frame structure, and Fe_3O_4@3DRGO hybrids were thus obtained. In addition, fabrication of Fe_3O_4@2DRGO and electrochemical stabilization were also introduced in Supporting Information.

2.4. Fabrication of Fe_3O_4@3DRGO counter electrodes

At the beginning, the fluorine-doped tin oxide (FTO) transparent glass substrates (NSG, $13\ \Omega sq^{-1}$) were ultrasonically cleaned sequentially in absolute ethyl alcohol and then stored in isopropyl alcohol. Fe_3O_4@3DRGO composite (0.04 g) and pure Fe_3O_4 microspheres powders (0.04 g) were used as raw material to prepare CEs. Fe_3O_4@3DRGO composite was ground with poly ethylene glycol powder (0.01 g) and 1 mL of absolute ethanol with a mortar to form a gelatin microspheres powders. CE coats were prepared by a doctor-blade method on the FTO glass substrates with subsequent natural drying and annealing at 400 °C for 60 min under a flowing of nitrogen gas environment. After natural cooling to room temperature, Fe_3O_4@3DRGO CE was obtained. For pure Fe_3O_4 CE, the procedure was the same.

2.5. Assembly of DSSCs

A sandwich DSSC device is combined of a dye-sensitized photoanode TiO_2, the as-prepared CEs, and liquid electrolyte. The commercial photoanodes with an actual area of $0.5 \times 0.5\ cm^2$ TiO_2 film (Dalian HeptaChroma Solar Tech Co, Ltd) were dipped in N719 (Dalian HeptaChroma Solar Tech Co, Ltd) dye solution overnight at room temperature, then cleaned with ethanol and dried in the air. The liquid electrolyte was composed of 0.1 M LiI, 0.12 M I_2, 1.0 M 1, 2-dimethyl-3-propylimidazolium iodide and 0.5 M 4-*tert*-buylpyridine in acetonitrile solution. The two electrodes were clipped