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Nitrogen-doped porous carbon prepared by a facile soft-templating process as low-cost counter electrode for High-performance dye-sensitized solar cells

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ABSTRACT

Nitrogen-doping porous carbon (NPC) with high surface area is prepared by a simple soft-templating method and explored as a low-cost counter electrode for dye-sensitized solar cells. Nitrogen adsorption analysis shows that the as-prepared NPC has a high surface area and mesoporous structure. Electrochemical impedance spectroscopy test shows a low charge-transfer resistance of 0.77 $\Omega\,cm^2$ for NPC electrode in iodide/triiodide redox electrolyte. Such excellent electrocatalytic activity can be attributed not only to good surface properties including high surface area and mesoporous structure but also to nitrogen doping in NPC framework. Among various nitrogen species in the NPC framework, pyridinic and quaternary nitrogen are considered to contribute significantly to the electrocatalytic activity. A conversion efficiency of 7.09% is achieved for dye-sensitized solar cells with NPC counter electrode at one sun illumination, which is comparable to that of the cell with Pt counter electrode. These results reveal that the NPC electrode is a promising counter electrode candidate for dye-sensitized solar cells.

1. Introduction

Since pioneering report of dye-sensitized solar cells (DSCs) by O'Regan and Grätzel in 1991, these photovoltaic systems have shown great potential for the development of solar cells due to their low cost, simple fabrication process, good stability, and relatively high conversion efficiency [1–3]. Typically, a DSC consists of a dye-sensitized porous semiconductor photoanode, an electrolyte containing an iodide/triiodide (I^-/I_3^-) redox couple, and a counter electrode. The counter electrode in DSCs plays a key role in terms of transferring electrons from external circuit to I^-/I_3^- redox species used as a mediator to regenerate the sensitizer after electron injection [4]. Thus, the counter electrode for a well-operating DSC should possess high electric conductivity, superior electrocatalytic activity, and good chemical stability. Currently, Pt counter electrode has been widely used as a counter electrode in DSCs due to its excellent electrocatalyitc activity for triiodide reduction and high conductivity [5–7]. Nevertheless, Pt is expensive and suffers from a long-term stability problem under highly corrosive I^-/I_3^- redox couple. Therefore, much effort has been made to replace Pt in DSCs with low-cost and high-stability alternatives including inorganic metal compound [8–10], conducting polymer [11–13], and carbonaceous materials [9,14].

Carbon-based materials, such as carbon black [15], porous carbon [16–19], graphene [20–22], and carbon nanotubes [23–25], have recently attracted much attention as practical materials for the counter electrode in DSCs because of their low cost, high resistance against corrosion, and good catalytic activity and conductivity. In particular, porous carbons hold considerable appeal for counter electrodes because of their

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high accessible surface area, large pore volume, and tunable pore structure. Several authors have shown that the pore structure of many carbonaceous materials have significant advantages for counter electrode application in DSCs [16,18]. However, the electrocatalytic performance of these porous carbon counter electrode still cannot match up to that of Pt electrode, and then the conversion efficiency of DSCs with porous carbon counter electrode is still insufficient.

To improve the photovoltaic performance of DSCs with porous carbon counter electrode, one of the key points is to improve the electrocatalytic performance of the porous carbon counter electrode. Recently, many researchers showed that the nitrogen doping is an attractive approach for effectively enhancing electron-transfer properties and chemical reactivity of carbon materials [26,27]. Nitrogen-doped carbon nanotubes and graphene have been used as the counter electrode in DSCs to show even higher electrocatalytic activity relative to Pt electrode [28–30]. We previously demonstrated that nitrogen-doped mesoporous carbon (NMC) prepared by a hard-templating method could be used as a favorable counter electrode for DSCs [31]. Nevertheless, the hard-templating approach usually involves multiple steps consisting of synthesis of template, impregnation with carbon precursor, carbonization, and etching of hard template, which limits its practical application. However, a facile soft-templating approach was recently developed for the preparation of porous carbon and would provide an opportunity for potential application of porous carbon in energy storage and conversion [16,32]. In this study, nitrogen-doped porous carbon (NPC) was prepared by a facile method using melamine-formaldehyde resin as carbon and nitrogen precursors and Pluronic F127 as template and explored as the counter electrode in DSCs. The NPC-based DSC has similar photovoltaic performance as that of Pt-based device in terms of the open-circuit voltage, the short-circuit current density, and the conversion efficiency. Electrochemical measurements demonstrated that NPC counter electrode exhibited an excellent electrocatalytic activity for I_3^- reduction, indicating that NPC electrode is a promising low-cost alternative for the application in counter electrode of DSCs.

2. Experimental

2.1. Preparation of NPC counter electrode

NPC was prepared by a soft-templating approach using melamine-formaldehyde resin as precursor and Pluronic F127 as template. In brief, 25 g melamine was added to 50 ml of formaldehyde solution (37 wt%) under stirring. The obtained milky solution was then heated at 80 °C for 30 min to form a clear solution. After adjusting the pH value of above solution to 4.5 by the addition of HCl, 22 g Pluronic F127 was added and thoroughly dissolved in the solution. The mixture was cured at 65 °C for 3 h, and then heated at 80 °C for 12 h. The obtained polymer was carbonized in a furnace under nitrogen atmosphere by a stepwise heating at 400 °C and 700 °C for 2 h, respectively, with a heating rate of 2 °C min^{-1}. Finally, NPC was obtained. For comparison, a porous carbon (PC) without nitrogen doping is prepared from phloroglucinol-formaldehyde resin through the same procedure as that for the NPC sample.

To prepare NPC electrode, NPC paste was first prepared by grinding 0.1 g NPC sample with 0.1 ml tetrabutyl titanate, 0.1 ml of 10% Triton X-100 aqueous solution, and 7 ml n-butanol in a mortar. The NPC electrode was fabricated by coating above paste on fluorine-doped tin oxide (FTO) glass using a doctor-blade method and heating at 300 °C for 15 min. PC electrodes were prepared through the same procedure as that for the NPC electrode.

2.2. Fabrication of DSCs

A porous nanocrystalline TiO_2 film with the thickness of 12 μm was deposited on FTO glass by doctor blade method and then sintered at 450 °C for 30 min. The sintered TiO_2 electrode was immersed into 0.5 mM N3 dye solution in ethanol for 12 h at room temperature. Afterwards, the electrode was rinsed with absolute ethanol and dried in the air. The DSC was fabricated by assembling the dye-sensitized porous TiO_2 electrode and the counter electrode into a sandwich-type cell. The interelectrode space was filled with the I^-/I_3^- electrolyte that consists of 0.4 M LiI, 0.05 M I_2, 0.4 M 1-methyl-hexylimidazolium iodide, and 0.4 M 4-tert-butylpyridine in 3-methoxypropionitrile.

2.3. Measurements and characterization

The pore texture of the sample was characterized by N_2 adsorption at 77 K using Micromeritics ASAP 2020 instrument. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method and the pore size was determined using the Barrett–Joyner–Halenda (BJH) model. The morphology of the product was investigated by transmission electron microscopy (TEM, JEM-2011). X-ray diffraction (XRD) measurement was performed on a Bruker D8 Advance X-ray diffractometer with Cu K_α radiation. X-ray photoelectron spectroscopy study was carried out on an ESCA lab 220I-XL spectrometer with Al K_α radiation. The photocurrent–voltage characteristics were measured on a Keithley 2602 Source Meter at a solar simulator illumination (AM 1.5, 100 mW cm^{-2}). The incident light density was measured with a standard Si solar cell. The active area of the cell is 0.2 cm^2. Electrochemical impedance spectroscopy (EIS) measurement was carried out on the symmetric thin-layer cell using a Solartron 1255B frequency response analyzer equipped with a Solartron 1287 electrochemical interface system at zero bias potential and 10 mV of amplitude. Tafel polarization measurement was performed on a CHI660D electrochemical workstation in a symmetric dummy cell. The scan rate was 50 mV s^{-1}.

3. Results and discussion

The pore-structure properties of as-prepared carbon samples were investigated with N_2 adsorption–desorption analysis at 77 K. The nitrogen adsorption–desorption isotherms and the corresponding pore size distributions obtained by BJH model for the NPC and PC are shown in Fig. 1. The nitrogen isotherms for both carbon samples show similar type IV isotherm with an obvious H2 hysteresis loop.