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Theoretical design and experimental synthesis of counter electrode for dye-sensitized solar cells: Amino-functionalized graphene

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ABSTRACT

For some specific catalytic reaction, how to construct active sites on two dimensional materials is of great scientific significance. Dye-sensitized solar cells (DSCs) can be viewed as one representative photovoltaics because in which liquid electrolyte with triiodide/iodide (I_3^-/I^-) as redox couples are involved. In this study, amino-functionalized graphene (AFG) has been designed according to theoretically analyzing iodine reduction reaction (IRR) processes and rationally screening the volcanic plot. Then, such AFG has been successfully synthesized by a simple hydrothermal method and shows high electrocatalytic activity towards IRR when serving as counter electrode in DSCs. Finally, a high conversion efficiency of 7.39% by AFG-based DSCs was obtained, which is close to that using Pt as counter electrode.

1. Introduction

Dye-sensitized solar cells (DSCs) have drawn extensive attention since 1991 due to their several advantages, such as low cost, easy fabrication, environmental friendliness, and high power conversion efficiency (PCE) [1]. To date, certified champion efficiency of more than 14% has been achieved [2]. Counter electrode (CE), one crucial component in DSCs, is responsible for collecting electrons from external circuit and reducing I_3^- into I^- in electrolyte [3–5]. Commonly, Pt (deposited on conductive substrate) is used as CE in DSCs. Although Pt has high catalytic activity and good conductivity, the limited reserve and high price hinder the large-scale production of DSCs [6–10]. Therefore, finding economical CE materials to replace Pt is meaningful. Ideal CE materials should have the following standards: high electrocatalytic activity and stability, good electronic conductivity, as well as feasibility in terms of large-scale production. To date, there have been many CE alternatives reported, including inorganic metal compounds, conducting polymers, alloys, and carbon materials that have shown promising properties as Pt-free CEs [11–18].

Given its excellent properties, such as high thermal conductivity, large surface area, high carrier mobility, and good mechanical strength, graphene has been intensively studied in the fields of energy conversion and storage [21,22]. In heterogeneous catalysis, pure graphene (or high quality graphene) does not serve as direct catalyst due to the lack of active sites [23]. Therefore, active sites should be constructed for some specific reactions, such as iodine reduction reaction (IRR) in DSCs. Some effective strategies could be used, such as doping with heteroatoms (e.g., oxygen [20,24], nitrogen [25–28], and boron [29]). Surface modification has proved to be another effective strategy to functionalize graphene and to obtain good CE materials in DSCs. However, according to recent reports, the guest chemicals used for surface modification on graphene are oligomers or macromolecules [19,30–33]. Currently, some key issues are put forward as follows: (i) Can small molecules be used for surface modification to obtain highly active sites on graphene? (ii) How can we obtain our expected materials more promptly?

In this study, we designed amino-functionalized graphene (AFG) by theoretically analyzing IRR processes and rationally screening the volcanic plot. Then, such AFG has been successfully synthesized by a simple hydrothermal method. Systematic characterizations were performed to identify its microstructures. As a CE in DSCs, AFG showed high electro-catalytic activity toward IRR. Finally, using AFG-based DSCs, a high conversion efficiency of 7.39% is achieved, which is close to that using Pt as CE (Scheme 1). Q2

2. Experimental

2.1. Computational method

All calculations have been performed at the B3LYP hybrid level of DFT using Gaussian 09 package. For simplifying calculations,

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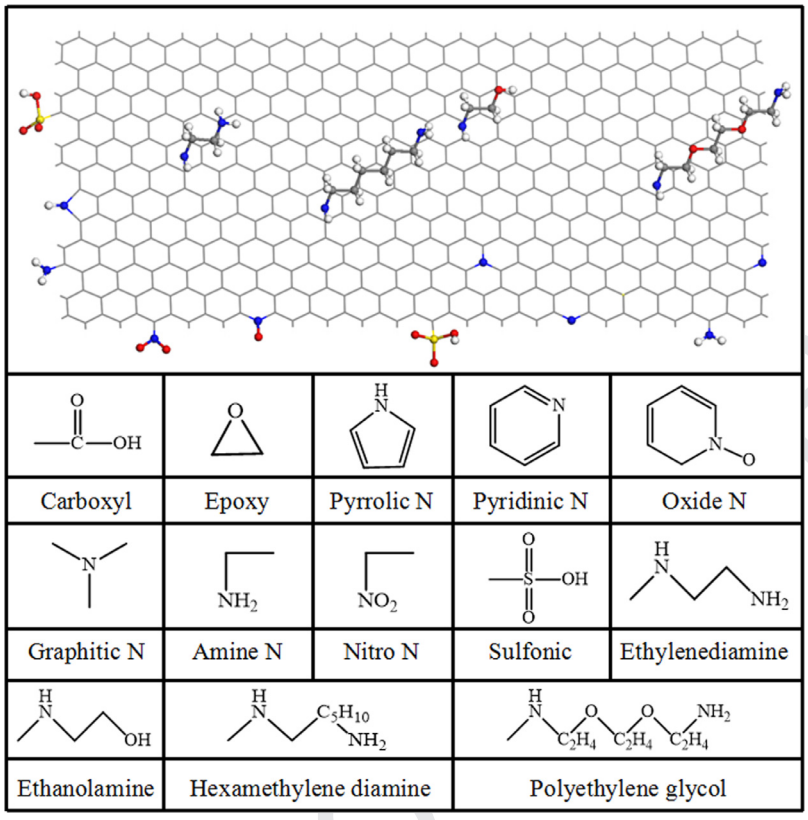

Scheme 1. General schematic model illustrating the different types of electrocatalysts (functionalized graphenes) for the I_3^- reduction reaction. Gray, red, blue and yellow balls represent carbon, oxygen, nitrogen, and sulfur atoms, respectively.

the structure of calculation model was simulated by graphene slab with nineteen hexagonal carbon rings, which are schemed in Fig. 1, and atoms on the edge of the graphene are terminated by hydrogen atoms. The optimized geometries were performed under the 6-31g(d,p) basis set with CPCM model. To simulate the real solution condition and ensure the reality of the DFT calculation, the acetonitrile solution was taken into consideration. The ionization energies (*IP*) is calculated as: $IP = E_{M+} - E_M$ [40], where E_{M+} and E_M are the energies of positive ion and neutral molecule at the ground state, respectively. The binding energy (E) is defined as the energy difference between system with iodine atom adsorbed (E_{total}) and the summation of iodine atom (E_1) and system (E_2): $E = E_1 + E_2 - E_{total}$. Basis set superposition error has been considered in the calculation of binding energy.

2.2. Experimental method

2.2.1. Synthesis of amino-functionalized graphene (AFG)

Preparation route of amino-functionalized graphene (AFG) is schemed in Fig. 2. First, further oxidation of graphene oxide (GO) suspension was obtained by ultrasonic dispersion and ozone oxidation in order to increase epoxy functional groups on graphene surface, one important preparation for the following ring-opening nucleophilic substitution reaction with ethylene diamine (EDA). Then, graphene oxide dispersion (90 mL, 1 mg/mL) was mixed uniformly with EDA (120 μL) and then sealed in a glass vial and heated for 6 h at 95 °C. After light reduction for 12 h, centrifuging, washing, and freeze-drying, AFG was produced [39]. For comparison, graphene (G) was got by direct thermal annealing of GO.

2.2.2. Preparation of counter electrodes (CEs)

First, we cleaned the FTO glass ultrasonically for 30 min using detergent solution, then followed by the second cleaning with deionized water for 30 min. After further and successive cleaning with ethanol, acetone, isopropanol (30 min for each), the FTO glass was immersed in isopropyl alcohol for use at our convenience. As the adhensive agent, the carboxyethyl cellulose solution was prepared by mixing ethyl cellulose (46070-250G-F, 0.9 g), ethyl cellulose (46080-250G-F, 0.7 g) and 18 mL ethanol thoroughly. Then, the slurry was magnetically stirred with 13 g terpineol for 12 h. Our CE material (GO, G, or AFG, 6 mg) was mixed with above carboxyethyl cellulose solution through grinding. The slurry was then transferred onto the FTO glasses using the doctor-blade method, finally with CE obtained by sintering at 500 °C for 30 min in N_2.

2.2.3. Fabrication of DSCs

The electrolyte was prepared by dissolving CuSCN (0.1182 g), BMII (1.5967 g), I_2 (0.0761 g), TBP (0.6761 g), LiI (0.0803 g) into 10 mL acetonitrile. Purchased TiO_2 photoanodes (Yingkou OPV Tech New Energy Co., Ltd, China, about 15 μm thickness) were heated to 80 °C and immersed in 0.5 mM anhydrous ethanol solution of N719 dye (Solaronix SA, Switzerland) for 24 h. The dye-loaded TiO_2 anodes and the CEs were separated by hot-melt Surlyn film (Surlyn, Yingkou OPV Tech New Energy Co., Ltd, China) of 45 μm thickness and sealed through hot-pressing (Heptachroma DHS-Eq 04, 125 °C, 30 s). Under the vacuum-assisted conditions, the electrolyte is injected through a small hole on the FTO glass. The sealed cells were used for the photocurrent–voltage test with an active area of 0.16 cm^2.

2.2.4. Characterization

The morphology of the samples was characterized with field-emission SEM (FEI NOVA NanoSEM 450) and TEM (FEI Tecnai F30). The X -ray diffraction (XRD) patterns were recorded on a D/Max2400 diffractometer. The surface characteristics of the samples were investigated using a ThermoFisher 6700 FTIR and

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