Electrochimica Acta 226 (2017) 10–17

Contents lists available at ScienceDirect

Electrochimica Acta

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

Ozonization, Amination and Photoreduction of Graphene Oxide for Triiodide Reduction Reaction: An Experimental and Theoretical Study

Hongyu Jing, Suzhen Ren*, Yantao Shi, Xuedan Song, Ying Yang, Yanan Guo, Yonglin An, Ce Hao*

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, 116024, Liaoning, China

ARTICLE INFO

Article history:
Received 28 October 2016
Received in revised form 26 December 2016
Accepted 29 December 2016
Available online 31 December 2016

Keywords:
Dye-sensitized solar cells
Counter electrode
Graphene-based catalysts
DFT calculation
Photovoltaic performance

ABSTRACT

This work proposes a mild and environmentally-friendly approach to prepare a highly efficient functional graphene (termed as AGO-hv) using methods of ozone oxidation, solvothermal synthesis, and photoreduction. The use of ozone oxidation in the first step can effectively increase the interlaminar distance between graphite oxide sheets, and create active sites for nucleophilic attack on the epoxy carbon from ammonia. The amino groups were successfully grafted on the surface of graphene as evidenced by the amidation reaction, with a maximum nitrogen content of 10.46 wt% and a C/N molar ratio of 8.46. After further photoreduction of the aminated graphite oxide (AGO), the residual oxygen functionalities, such as C-OH, were effectively removed and the conductivity of the graphene sheet was further recovered. The dye-sensitized solar cell (DSC) exhibited a power conversion efficiency (PCE) of 7.51% based on AGO-hv counter electrode (CE), close to that of Pt counterpart (7.79%). The experimental results indicated that the amidation and photoreduction processes were significantly facilitated by the initial ozonization of graphene oxide, and this process significantly improved the electrochemical activity and the conductivity of graphene oxide. Density functional theory (DFT) calculations revealed that AGO-hv had the lowest ionization energy (a better electron-donating ability) and also suitable binding energy with I atoms as well. The combination of ozonization, amination and photoreduction is an efficient route to obtain electrocatalysts with desired compositional distributions and performance for triiodide reduction reaction in DSCs.

1. Introduction

Dye-sensitized solar cells (DSCs) have received much attention due to their low cost, easy fabrication and high efficiency of solar energy conversion [1,2]. These promising photovoltic devices (including a green device of aqueous DSC) are assembled with a TiO_2 photoanode, a counter electrode (CE), and a redox couple electrolyte [3–7]. Herein, we focus on the designing of CE component in the liquid I_3^-/I^- electrolyte using acetonitrile as the solvent. It is well-known that the selected CE in DSC should exhibit high electrical conductivity and electrocatalytic activity for the regeneration of the redox couple. Presently, platinum is one of the most appealing CEs owing to its excellent electrocatalytic activity and high power conversion efficiency (PCE) in DSCs. However, platinum is extremely rare and expensive material, which hinders its large-scale application for DSCs. Alternatives to Pt include carbonaceous materials such as conducting polymers, graphene, and derivatives that are readily available and inexpensive [8–13].

The high specific surface area and excellent conductivity make state-of-the-art carbon materials, such as graphene, promising candidates as an alternative material to platinum [14]. However, pristine graphene sheets are hydrophobic and also exhibit low catalytic activity due to the lack of catalytic active sites for the iodine reduction reaction (IRR) [15]. To address this problem, heteroatoms such as nitrogen, boron, and sulfur have been added to modulate the catalytic activity of graphene. Fang et al. prepared boron-doped graphene by thermal annealing of graphite oxide (GO) with B_2O_3, which has shown a PCE of 6.73% as a CE for DSCs [16]. Nitrogen-doped graphene (NrG) was obtained by Hou et al. via thermal annealing of a mixture of GO and cyanamide at 900 °C in N_2 atmosphere, which was subsequently utilized as an alternative to the Pt electrocatalyst for DSCs with the PCE of 5.4% [17]. Song et al. prepared a series of nitrogen-doped porous graphene foams (NPGFs) by hydrothermally treating a mixed

---

* Corresponding authors.
E-mail addresses: rensz@dlut.edu.cn (S. Ren), haoce@dlut.edu.cn (C. Hao).

http://dx.doi.org/10.1016/j.electacta.2016.12.190

solution of GO and ammonia with optimal PCE of 4.5% for the iodide-based electrolyte [18]. Xue et al., developed three-dimensional (3D) N-doped graphene foams (N-GFs) by annealing the freeze-dried graphene oxide foams (GOFs) in ammonia, and found that the resultant DSCs showed a PCE as high as 7.07% [19]. Additionally, other chemical methods to synthesize N-doped graphene have been reported, including chemical vapor deposition, nitrogen plasma treatment, and the reduction of graphene oxide in ammonia or nitrogen gas [20]. Of these, chemical functionalization is considered the most effective method to modify the catalytic activity of graphene [21].

From both theoretical and experimental points of view, we report functionalized graphene, produced by the oxidation of graphene oxide with ozone, amination by inorganic amines of ammonia via solvothermal synthesis, and further photo-reduction by ultraviolet light. In order to enhance the amount of amino groups and prevent the aggregation of the GO, numerous nucleation sites were introduced by ozonization. After reaction with ammonia, the amino groups were grafted onto the preoxidized graphene oxide (GO-O_3) via nucleophilic substitution. This modified amination could decrease the damage of the *sp*^{2} network of the graphene sheet without sacrificing its conjugative structure. In this case, the amount of oxygen-containing groups in aminated graphite oxide (AGO) were relatively high, thus the residual $-$OH functional groups would be removed via light reduction. The obtained electrocatalyst was denoted as AGO-hv.

DFT calculations were used to elucidate the mechanisms of IRR on the synthesized AGO-hv. To the best of our knowledge, the interactions between the functional groups from functional graphene and iodine species have been rarely studied as a critical factor in DSCs. The identification of what type of functional groups serves as the catalytic active site would facilitate the rational design of electrocatalysts for DSCs. Both DFT calculations and experimental results revealed that enhanced performance was partly correlated with the increase in pyridine-like species. The pyridine N and amide moieties introduced may be exploited as the main anchoring site for the IRR. The superior properties of AGO-hv are due to the appropriate binding energy of iodine on the functional group with high conductivity and excellent charge transfer resistance, which improves the PCE (7.51%) to close to that of Pt (7.79%) in the liquid I_3^-/I^- redox couple electrolyte.

2. Experimental and theoretical methods

2.1. Preparation of catalysts and corresponding CEs

The GO-O_3 was synthesized by bubbling a certain amount of O_3 gas into a GO aqueous suspension by controlling the oxidation time. AGO were synthesized via the modified solvothermal reaction route, using ammonia as nitrogen source, and benzyl alcohol as solvent for the amination of GO-O_3 and introduction of amino groups [22]. Then, AGO-hv CEs were prepared by coating AGO films on the FTO glasses and subjected to UV illumination. The preparation of AGO-hv CEs is schematically shown in Scheme 1 (see the Supporting Information for detailed descriptions).

The sample of AGO-0 was also prepared based on the above procedures from GO without the addition of O_3. Those mentioned samples were also compared to a sample of reduced graphene oxide (rGO) that was produced by a common thermal reduction method described elsewhere [23]. The thickness of all the graphene-based CEs were optimized about 8–10 μm. Additionally, a Pt electrode (200 nm thick) was obtained by drop-casting 0.5 mM H_2PtCl_6/ethanol solution on a FTO glass substrate. Subsequently, the FTO glass was sintered in a muffle furnace at 450 °C for 30 min.

2.2. Structural characterization

The obtained samples were characterized by means of X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), UV–vis absorption spectroscopy, elemental analysis, and X-ray photoelectron spectroscopy (XPS). The details on material characterization are presented in the Supporting Information.

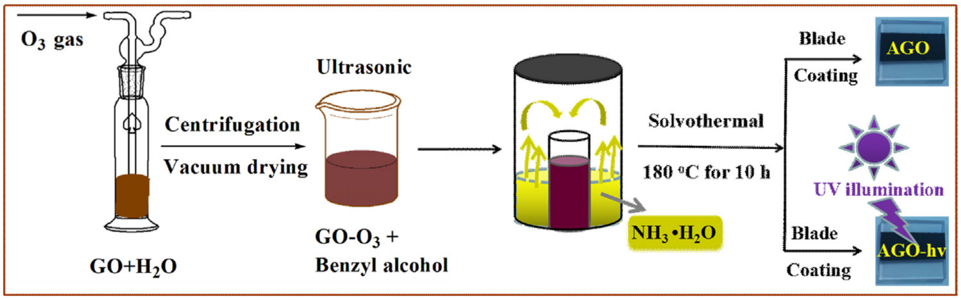
2.3. Electrochemical measurements

The current density-voltage (*J*-*V*) curves of the DSCs were measured to estimate the photovoltaic performance, which was conducted under simulated AM 1.5 illumination (100 mW cm^{-2}, Solar Light Co., INC., USA). The electrochemical properties were investigated by CV, EIS, and Tafel-polarization measurements. The details are presented in the supporting information.

2.4. Computational methods

All calculations were performed using Gaussian 09 package based on DFT methods with the B3LYP hybrid functional [24] and 6–31 g (d, p) basis sets [25] for C, H, N and lanl2dz [26] for I atom. The edges of the graphene sheets are terminated by H atoms [27]. The FT-IR spectroscopy (scaled by 0.961) of the models were calculated based on the geometric optimization. Solvation effects were taken into account using the conductor-like polarizable continuum model (CPCM) [28] for all calculations.

The ionization energy (*IP*) is calculated as: $IP = E_M^+ - E_M$, where E_M^+ and E_M are the energies of a model with positive charge and a neutral molecule without charges on the ground state [29]. The binding energy (E_b) between I and the binding site is defined as: $E_b = E\ (\text{Site}) + 1/2\ E\ (I_2) - E\ (\text{I/Site}) + E\ (\text{BSSE})$. BSSE (basis set superposition error) correction has been taken into account in all the calculations of binding energy [30]. The *E* (I/Site), *E* (Site) and *E* (I_2) represent the total energy between I and the site, the energy of AGO-hv, and the energy of the isolated I_2 molecule. All the models are shown in the most stable configuration and acetonitrile solvent effects are also taken into account.



Scheme 1. Schematic illustrations of preparation of AGO-hv CE using ozone oxidation, solvothermal synthesis and light irradiation method.