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Hybridization of graphene oxide with commercial graphene for constructing 3D metal-free aerogel with enhanced photocatalysis

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ABSTRACT

The electrical conductivity and charge carrier mobility of reduced graphene oxide (RGO) based 3D aerogel using graphene oxide (GO) as precursor is often restricted by the intrinsic population of defects and thus disruption of 2D π-conjugation in the domain of RGO sheets. Here, we report a facile and efficient approach to improve the electrical conductivity of RGO aerogel by introducing highly conductive commercial Elicarb graphene (EGR). GO acting as a "macromolecular surfactant" can be used to simultaneously resolve the intrinsic drawback of low solution dispersibility of EGR and provides the basic skeleton for solution-processable synthesis of RGO@EGR-Eosin Y (RGO@EGR-EY) metal-free 3D aerogel composites. The as-synthesized RGO@EGR-EY aerogel with superior electrical conductivity facilitates more efficient separation and transfer of photogenerated charge carriers, and consequently exhibits much higher photocatalytic activity than RGO-EY aerogel. It is hoped that our current work could open promising prospects for the rational utilization of highly conductive commercial graphene to fabricate graphene-based aerogel for enhanced photoredox applications.

1. Introduction

Three-dimensional (3D) graphene-based aerogel, by virtue of its many interesting physicochemical properties, has proved itself as an exciting monolith material for constructing high-efficiency photocatalyst for practical applications of solar energy conversion [1–6]. Such a 3D porous monolith structure can afford the large accessible surface area, easy recyclability and efficient light harvesting ability due to the multi-reflection within interconnected open-framework, which benefits for facilitated adsorption and photoreaction [7–9]. Moreover, 3D porous structure of aerogel can substantially inhibit the aggregation or stacking of subunits, thus exposing more active sites for catalytic surface reaction [10,11]. Regarding the synthesis of graphene aerogel-based photocatalysts, graphene oxide (GO), owing to its amenable and flexible solution processability is often adopted as the precursor of graphene aerogel. Under hydrothermal treatment or in the presence of reducing agents, GO can be reduced to graphene and in situ self-assembled into a 3D architecture with the $\pi-\pi$ stacking and hydrogen bonds between nanosheets [9,12]. However, the electrical conductivity and charge carrier mobility of reduced GO (RGO) aerogel is remarkably decreased, which is because the large population of defects of RGO results in considerable disruption of the 2D π-conjugation in the domain of RGO sheets [13,14]. And this in turn results in the fact that the net improvement efficiency of RGO aerogel-based photoactivity is often restricted [15–17]. Therefore, one important strategy for enhancing the photocatalytic performance of RGO aerogel-based photocatalyst is to improve the electronic conductivity of the cross-linked 3D framework composed of RGO sheets by the use of selective viable approaches.

Commercial Elicarb graphene (EGR), which is manufactured on a large scale *via* a high-shear exfoliation process in liquid phase, has attracted great attention in recent years [18,19]. Being different from the oxidation-exfoliation-reduction approach, the high-shear exfoliation process includes neither the strong oxidation of graphite nor the subsequent reduction process, which results in the EGR possessing less structural defects and superior electrical conductivity [20,21]. Therefore, coupling the highly conductive commercial EGR with RGO aerogel could be a feasible approach to improve the electronic conductivity of 3D framework of RGO aerogel. However, owing to the intrinsic hydrophobic nature of EGR, the direct dispersion of EGR in water has been generally considered unattainable [22]. To process EGR in benign solvents, the surfaces of EGR have to be modified either covalently with solvent-liking functional groups or by coating with surfactant or solvent-liking polymers [23–25]. However, a fundamental tradeoff of such strategy is that it tends to sacrifice the intrinsic material properties of EGR for enhanced processability. Surface coating usually introduces hard-to-remove and insulating surfactants or polymers, while covalent

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functional groups inevitably break the π-conjugated carbon surfaces [26–28].

Notably, apart from the role as the precursor to make graphene, Huang's group recently has highlighted the new multifaces of GO as "a big macromolecular surfactant" to disperse insoluble materials such as graphite and carbon nanotubes [14,29–32]. The oxygen-containing groups render GO sheets hydrophilic and highly dispersible in water, whereas the aromatic regions offer active sites to interact with the graphite and carbon nanotubes through π-π supramolecular interactions [26,33]. Therefore, it will be a feasible approach to disperse EGR in solution phase by using GO as the surfactant, and this approach can realize the purpose of killing two birds with one stone. On the one hand, the utilization of GO as a dispersing agent can generate a clean, electrically addressable carbon–carbon interfaces in the final composite because GO can be cleanly converted to RGO without producing hard-to-remove byproducts. On the other hand, GO can provide a basic skeleton to directly construct the EGR doped RGO (RGO@EGR) aerogel composites.

Against this background, we herein report the rational synthesis of a series of metal-free EGR doped RGO-Eosin Y aerogel (RGO@EGR-EY aerogel) photocatalysts with different weight addition ratios of EGR, during which GO acting as surfactant has been used to disperse EGR in the wet-chemistry synthesis process. The as-obtained RGO@EGR-EY aerogels possess the robust characteristics of 3D monolith, but exhibit the distinctly improved electrical conductivities as compared to RGO aerogels. The photoactivity assay under identical reaction conditions highlights that the RGO@EGR-EY aerogels exhibit much higher visible light activity than RGO-EY aerogel. It is expected that this work could open up new frontiers for improving the electrical conductivity of the 3D framework of RGO aerogel by utilizing commercial, highly conductive graphene and constructing more efficient aerogel-based photocatalyst for artificial redox catalysis.

2. Experimental

2.1. Materials

Hydrochloric acid (HCl), concentrated sulfuric acid (H_2SO_4, 98%), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2, 30%), Eosin Y (EY) were all obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Graphite powder was supplied by Qingdao Zhongtian Company, China. Elicarb graphene (EGR) was obtained from Thomas Swan Co. Ltd. (UK). All reagents were used as received without further purification. The deionized (DI) water used in the experiment was from local sources.

2.2. Preparation of graphene oxide and RGO-EY aerogels

Graphene oxide (GO) was synthesized from natural graphite powder by a modified Hummers method [34–37]. The preparation of RGO-EY aerogels was based on a facile one-step hydrothermal method. The primary difference of synthesis protocols from previous work [38] was that the hydrothermal treatment temperature in this work was 180 °C because it can yield the more mechanically robust 3D aerogels. The details are presented in the Supporting Information.

2.3. Preparation of RGO@EGR-EY aerogels

The preparation process of RGO@EGR-EY aerogels is illustrated in Scheme 1. EGR was dispersed using GO as surfactant with the assist of ultrasound. Typically, the given amount of EGR was added into 10 mL deionized water, and the resulting mixture was sonicated for 0.5 h to form a uniform dispersion. Then, a certain amount of GO suspension was added into the EGR dispersion and sonicated for 4 h to form a uniform GO@EGR dispersion. The total mass of GO@EGR was maintained at 30 mg. After that, 4 mL of the EY aqueous (0.5 mg/mL) solution was added into the above mixtures. DI water was added into the above mixtures to a volume of 30 mL. After being stirred for 6 h, the mixture was transferred into a 50 mL Teflon-lined autoclave and subjected to hydrothermal treatment at 180 °C for 12 h. The as-prepared RGO@EGR-EY hydrogels were taken out with tweezers, washed several times with deionized water, and treated by freeze-drying. Finally, the RGO@EGR-EY aerogels with different weight ratios of EGR (5%, 10%, 15%, 20%) were obtained. For the comparison purpose, the RGO@EGR aerogel was also synthesized *via* the same procedure without the addition of EY.

2.4. Characterization

X-ray photoelectron spectroscopy (XPS) analysis was completed on a Thermo Scientific ESCA Lab 250 spectrometer equipped with a mono chromatic Al Kα (X-ray source), a multiaxial sample stage and a hemispherical analyzer. The calibration of the binding energies was based on the C 1s peak at 284.6 eV. A Nanoscope IIIA system was used to measure the atomic force microscopy (AFM) spectra. Scanning electron microscopy (SEM, FEI Nova NANOSEM 230) and transmission electron microscopy (TEM, FEI Tecnai G2 F20 S-TWIN) were used to determine the morphology and microscopic structure of the samples. The electrical conductivity measurement of graphene (RGO and EGR) was performed by measuring the resistivity-pressure curve (R-P curve) using a four-point probe technique on a ST2722 (Suzhou Jingge Electronic Co., P. R. China) power resistivity tester. A Renishaw inVia Raman System 1000 with a 532 nm Nd:YAG excitation source was employed to collect the Raman spectra at room temperature. The nitrogen adsorption-desorption isotherms and Brunauer-Emmett-Teller (BET) surface areas were measured on a Micromeritics ASAP2010 equipment. The photoluminescence (PL) spectra were obtained using an Edinburgh Analytical Instrument PLS920 system. The contact angle of the prepared membranes was analyzed using a contact angle goniometer (OCA-20, Dataphsics, Germany).

Photoelectrochemical measurements were performed in a home-made three electrode quartz cell with a PAR VMP3 Multi Potentiostat apparatus. A Pt plate was used as the counter electrode, and Ag/AgCl electrode was used as the reference electrode. The working electrode was prepared on fluorine-doped tin oxide (FTO) glass that was cleaned by ultrasonication in ethanol for 30 min and dried at 80 °C. Typically, 5 mg of the sample powder was ultrasonicated in 0.5 mL of ethanol to disperse it evenly to get a slurry. The slurry was spread onto FTO glass, whose side part was previously protected using Scotch tape. After air drying, the working electrode was further dried at 100 °C for 2 h to improve adhesion. Then, the Scotch tape was unstuck, and the uncoated part of the electrode was isolated with epoxy resin. The exposed area of the working electrode was 0.25 cm^2. The electrochemical impedance spectroscopy (EIS) measurement and cyclic voltammograms were carried out using a CHI-660D workstation, (CH Instrument, USA) in the three electrode cell in the presence of 0.5 M KCl solution containing 0.01 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1) under open circuit potential conditions. The photocurrent measurement was carried out on a BAS Epsilon workstation without bias and the electrolyte was 0.2 M aqueous Na_2SO_4 solution (pH = 6.8) without an additive. The visible light irradiation source was a 300 W Xe arc lamp system equipped with a UV-CUT filter ($\lambda > 420$ nm).

2.5. Photocatalytic reduction of Cr(VI)

The photocatalytic reduction of Cr(VI) over the as-synthesized graphene-organics aerogels was performed in an aqueous solution under the irradiation of visible light. A graphene-EY aerogel sample and 60 μL of triethanolamine (TEOA, sacrificial agent) were added into 50 mL of 20 mg L^{-1} aqueous solution of Cr(VI) in a quartz vial. Prior to irradiation, the above suspension was kept in the dark for 1 h to establish adsorption-desorption equilibrium between the photocatalyst