Journal of Alloys and Compounds 688 (2016) 527–536

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Self-assembly of CeO_2 nanostructures/reduced graphene oxide composite aerogels for efficient photocatalytic degradation of organic pollutants in water

Jiha Choi, D. Amaranatha Reddy**, M. Jahurul Islam, Rory Ma, Tae Kyu Kim*

Department of Chemistry and Chemical Institute for Functional Materials, Pusan National University, Busan 609-735, Republic of Korea

A R T I C L E I N F O

Article history:
Received 31 October 2015
Received in revised form
20 July 2016
Accepted 21 July 2016
Available online 22 July 2016

Keywords:
CeO_2-Reduced graphene oxide aerogels
Degradation of Rhodamine-B
Simulated sunlight
Water remediation

A B S T R A C T

Reduced graphene oxide aerogels (RGAs) are excellent candidates for water remediation due to their lightweight, high surface area and high absorbance rate. Here, we report a simple green synthetic approach for the self-assembly of CeO_2-RGA aerogels using vitamin-C as the reducing agent. The photocatalytic degradation performance of the as-synthesized CeO_2-RGA aerogels was studied as a function of simulated sunlight irradiation, using the organic dye Rhodamine-B (RhB) as a test molecule. The CeO_2/RGA composites displayed highly enhanced photocatalytic activity in comparison to bare CeO_2 nanostructures. This enhancement is ascribed to efficient charge transfer from the CeO_2 nanostructures to the reduced graphene oxide (RGO) sheets due to the high degree of interconnectivity between the RGO and CeO_2 nanostructures. In addition, photoluminescence studies strongly support this charge separation mechanism. The microstructures and optical properties of the as-synthesized nanostructures were characterized using HRTEM, XRD, FTIR, XPS and DRS. These results demonstrated that the CeO_2 nanostructures are grown on interconnected three-dimensional RGO nanosheets. We believe that the findings of this study provide a versatile pathway to induce self-assembly of reduced graphene sheets with other semiconductor nanostructures in the form of lightweight aerogels for a variety of environmental applications.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Graphene has received a great deal of research attention since it was first reported in 2004 because of its high physical and chemical stability, thin two-dimensional (2D) atomic layers, high electrical conductivity, rapid electron transfer, strong absorption nature, superior thermal conductivity and high elasticity [1]. Graphene nanocomposites that combine these properties with other nanomaterials have seen use in applications such as energy storage, catalysis, and absorption [2,3]. However, when graphene nanosheets are constructed into 2D graphene layers, they tend to aggregate and restack in solution due to hydrophobic interactions, strong π-π interactions and van der Waals forces. This behavior limits electron and ion transport and causes the formation of much thicker multilayer graphene nanosheets, which leads to poor accessibility of the overall surface area [4]. In order to resolve these issues, self-assembled 3D reduced graphene aerogels (RGAs) have been recently developed [5]. RGAs not only retain their large accessible surface area but can also feature a wide range of porous structures from macropores to mesopores. As a result, RGAs have various potential applications in the fields of catalysis [6,7], water purification [8], energy storage and conversion [9], and oil absorption [8]. Combining the properties of graphene with those of other semiconductors for diverse applications is well-documented in the literature [10–16]. Recent research indicates that the synergetic effects between graphene aerogels and semiconductors can enhance overall material performance and give rise to new properties that are not found in either component [17]. Furthermore, these functional semiconductors can help to prevent the graphene sheets from aggregating into graphitic structures in order to retain the perfect properties of individual graphene sheets [18]. As a result, researchers have conducted photocatalytic experiments with the combination of graphene nanosheets and various semiconductor nanomaterials such as TiO_2 [19], P25 [20], BiOBr [21], ZnS

---

* Corresponding author.
** Corresponding author.
E-mail addresses: drreddy@pusan.ac.kr (D.A. Reddy), tkkim@pusan.ac.kr (T.K. Kim).

http://dx.doi.org/10.1016/j.jallcom.2016.07.236
0925-8388/© 2016 Elsevier B.V. All rights reserved.

[22], $W_{18}O_{49}$ [23] and Cu_2O [24].

Among these semiconductors, CeO_2 is a promising material because of its useful properties such as its non-toxicity, chemical stability, low cost, and high electron transfer capability, which originate from the two oxidation states present in the material. It currently sees use in catalysis, where it can act as both a catalyst support and a catalyst [25,26]. In addition, CeO_2 can be photoactivated by UV–Vis irradiation to degrade organic pollutants in the aqueous phase [27]. However, CeO_2 has a wide band gap ($E_g = 3.2$ eV) that limits its further application in the visible light region [28]. In order to make a visible light-driven photocatalyst with this material, methods such as doping with metal elements [29], forming composites [30] have been designed. Nevertheless, for environmental applications, a new, simplified method is still required to improve the efficiency of this photocatalyst. We believe that CeO_2 modified with RGAs could resolve these problems.

Here, we report for the first time, a simple green synthetic approach for the self-assembly of CeO_2/RGA using vitamin-C as the reducing agent. The performance of the as-synthesized nanostructures was investigated under simulated sunlight irradiation, using the photocatalytic degradation of the colored organic dye Rhodamine-B (RhB) as an example. The lightweight CeO_2/RGA nanocomposites exhibit enhanced photo-degradation ability and durability compared to bare CeO_2 nanostructures. The possible mechanism for the photocatalysis of dye degradation and the role of 3D RGO nanosheets were investigated on the basis of these experimental results. Finally, we believe that this work provides a template for the design of lightweight, recyclable graphene aerogel nanocomposites with excellent photoactivity and durability, meeting the requirements of future environmental and energy technologies.

2. Experimental

2.1. Preparation of graphene oxide

Graphene oxide (GO) was obtained from natural flake graphite using a modified Hummers method published previously [31]. In brief, 69 mL H_2SO_4 (98%) was carefully added to a mixture of 3 g graphite (1 wt% equiv.) and 1.25 g $NaNO_3$ (0.5 wt% equiv.) in a 1 L beaker, mixed in an ice bath for 1 h and cooled to 0 °C. While stirring, 9.0 g $KMnO_4$ (3 wt% equiv.) was slowly added over 30 min and then stirred for an additional 1 h, keeping the reaction temperature below 5 °C. The beaker was then placed in a water bath at 45 °C, and the solution was stirred for 1 h to form a thick paste. Subsequently, 138 mL of DI water was slowly added to produce a large exothermal reaction to bring the temperature to 98 °C; this temperature was then maintained for 30 min. A mixture of DI water (420 mL) and 30% H_2O_2 (10 mL) was then added to bring the temperature below 20 °C. Finally, the solution was filtered to collect the precipitate. The precipitate was washed several times with HCl (30%) and DI water. The aqueous GO solution was sonicated for 1 h, allowing for final collection of the GO.

2.2. Synthesis of CeO_2/reduced graphene aerogels

The CeO_2/RGA nanocomposites were chemically synthesized using an ultra-sonication assisted chemical method. In a typical synthetic process, 4 mg/mL of the above synthesized GO was added to 10 mL DI water and sonicated for 30 min to reduce the oxygen groups included in the GO. After that, 0.05 M of CeO_2 nanostructures were dissolved in this solution, which was again sonicated for 30 min. 0.1 g vitamin-C was then added and uniformly mixed, and the suspension was vigorously sonicated for another 15 min to obtain a homogeneous suspension. Finally, the suspension was left undisturbed and unstirred in a muffle furnace at 95 °C for 8 h. The resultant hydrogels were first purified in a large volume of distilled water for at least a week in order to wash out low molecular weight components of the system, including excess vitamin-C and its oxidized product dehydroascorbic acid. Finally, the purified hydrogels were freeze-dried for 24 h to ensure complete removal of water molecules.

2.3. Characterization

The morphologies and structural properties were examined using transmission electron microscopy (TEM; JEOL JEM-2100F) with an accelerating voltage of 200 kV. Phase determination of the as-prepared powders was performed using X-ray diffraction (XRD; PHILIPS X'Pert-MPD) with a Cu-Kα X-ray source. The surface chemical compositions were analyzed with using X-ray photoelectron spectroscopy (XPS; Thermo VG scientific multi lab -2000) an Al Kα X-ray source. Fourier-transform infrared (FTIR) spectra were obtained for structural characterization using a Nicolet 380 spectrophotometer scanning over a range of 4000 to 500 cm^{-1} with a spectral resolution of 4 cm^{-1}. Photoluminescence (PL) measurements were performed at room temperature using a Hitachi F-7000 fluorescence spectrophotometer. Optical absorption spectra were recorded using a UV–visible spectrophotometer (Shimadzu UV-1800). The nitrogen adsorption–desorption isotherm measurements for the samples were carried out at 77.35 K using a Tristar 3000 Micromeritics instrument to measure the surface area and porosity.

2.4. Photocatalytic experiments

The photocatalytic efficiencies of the CeO_2 and CeO_2/RGA materials were evaluated with regards to the degradation of RhB aqueous solutions under simulated solar irradiation. A 150 W Xe-lamp (Abet Technologies) with an AM 1.5G filter was used as the light source. For photocatalytic analysis, graphene aerogel nanocomposites was immersed in a 100 mL aqueous solution of RhB ($C_o = 10$ mg L^{-1}) and vigorously stirred in the dark for 30 min to reach an adsorption-desorption equilibrium. After that, the solution was exposed to simulated sunlight irradiation. Every 10 min, approximately 2 mL of the solution was collected and centrifuged at 9000 rpm for 15 min. The UV visible spectra of the supernatants were recorded to monitor the degradation behavior. The characteristic absorption peak of RhB at 554 nm was used to assess the extent of degradation. For the recycling process, the CeO_2-RGA nanocomposite photocatalyst was centrifuged, dried at 80 °C for 8 h and then reused for degradation of the same concentration of the RhB dye, up to 3 cycles. The mineralization ratio of RhB solution was determined by total organic carbon (TOC) value which was obtained by a TOC analyzer (TOC-VCPH, Shimadzu, Japan).

2.5. Photo electro chemical impedance analysis

Photo-electrochemical measurements were performed in a three-electrode system using a CHI 617B electrochemical workstation. A solar simulator equipped with an AM 1.5G filter and 150 W Xe lamp (Abet Technologies) was used as the irradiation source to produce monochromatic illuminating light. The output light intensity was adjusted to 1 sun (100 W/m^2) using 15151 low-cost calibrated Si reference cell (ABET technologies). The reference and counter electrodes were Ag/AgCl and platinum wire, respectively, and Na_2SO_4 aqueous solution served as the electrolyte. To prepare the working electrode, 10 mg of as-synthesized CeO_2 and CeO_2-RGA nanocomposites were first dispersed into ethanol (450 μl) and 50 μl Nafion mixtures using soft ultrasonic stirring to

Download English Version:

https://daneshyari.com/en/article/10656306

Download Persian Version:

https://daneshyari.com/article/10656306

Daneshyari.com