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Photoreduction of graphene oxide enhanced by sacrificial agents



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ABSTRACT

In this work, the photoreduction of graphene oxides (GOs) was carried out in the presence of a sacrificial agent of $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ and triethanolamine (TEA) separately in the solution. The photoreduction of GOs was enhanced with the addition of the sacrificial agent, which was examined in terms of reduction extent and needed reduction period. The quench of the GO emission was observed in the photoluminescence spectra of both GO solutions with $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ and TEA. Although both sacrificial agents facilitated the charge transfer in the irradiated GO solutions, the aggregation of GO/reduced GO (RGO) occurred in the $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ -contained solution during photoreduction, which limited further photoreduction of GOs with the assistance of $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$. By keeping good dispersion characteristic during the whole process, the photoreduction efficiency of GO in the presence of TEA was therefore superior to that with the assistance of $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$.

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1. Introduction

Graphene, which is the two-dimensional (2D) sp^2 carbon network has attracted great interests because of its extraordinary electronic, thermal and mechanical properties. Combining with the characteristics of high surface area and natural abundance, graphene is a promising material for use in sensor [1,2], supercapacitor [3–5], solar cell [6–8], and photocatalyst [9–11], etc. Therefore, many research efforts have been devoted to the synthesis of graphene [12–16]. The most widely used route to the large batch of this 2D material begins with the chemical exfoliation of graphite to graphene oxides (GO) followed by the reduction of the GOs.

The modified Hummers method is a convenient route to synthesize bulk quantities of GOs by oxidation of graphite [17]. GOs contain many oxygen functional groups on the basal planes and edges, which make it strong hydrophilic in nature and well-dispersed in organic solvent. On the other hand, the electrical conductivity of GO is considerably inferior to that of graphite (graphene) because of the conversion of the planar sp^2 to sp^3 carbon in the presence of oxygen functional groups. By the reduction of GO to the reduced GO (RGO), the electrical conductivity of the 2D material can be somewhat restored through the recovery of sp^2 binding sites in RGO [18,19]. However, the dispersibility of RGO in organic solvent is significantly decreased due to the removal of the oxygen functional groups. Different approaches have been developed to

produce electrically conductive RGO, including chemical, electrochemical, thermal, and photo-reductions of GOs [12,20–26].

Photoreduction of GO using UV or visible light has drawn growing attention as an alternative route to produce RGO because of not only its mild and green-process characteristics but also the possible realization of patterned RGO on the GO sheet through the way of photolithography [22,27]. Photochemical and photothermal reduction mechanisms may take place individually or simultaneously during photoreduction of GO [28–31]. In the case of photochemical reduction, a photocatalyst such as TiO_2 nanoparticles (NPs) is usually added in the GO solution [32]. Photoelectrons for reduction of GO are transferred from irradiated photocatalyst. It has been demonstrated that photochemical reduction of GO can also be conducted in the absence of photocatalyst. The electron-hole pairs can be generated by band gap excitation of GO and that self-reduction of GO can therefore be achieved by the photogenerated electrons in its conduction band. Moreover, the self-photoreduction of GO can be enhanced in the presence of hole scavenger in the solution [33].

In this work, the photoreduction of GO was performed in the presence of sacrificial agents of $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ and triethanolamine (TEA) individually in the solution. The performances of the sacrificial agents were examined by the evolutions of reduction extents of the GOs. The reduction extents of GOs were investigated by UV–vis absorption spectroscopy, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) and thermogravimetric analysis (TGA). The photoreduction of GOs was significantly enhanced with the addition of the sacrificial agent in the GO solution. The role of hole scavenger of the agents was confirmed by the quench of the GO emission observed in the photoluminescence

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(PL) spectra of the solutions. By keeping good dispersion characteristic during the whole process, the photoreduction efficiency of GO in the presence of TEA was superior to that with the assistance of $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$.

2. Experimental

2.1. Preparation of graphene oxides

Graphite oxide was prepared by a modified Hummers method [17]. A pretreatment of the graphite powder was conducted by following procedure. 1 g of graphite powder was mixed with 1 g of $\text{K}_2\text{S}_2\text{O}_8$, 1 g of P_2O_5 , and 7.5 mL of concentrated H_2SO_4 and the mixture was stirred for 0.5 h at 90 °C. The solution was then kept at 80 °C for another 4.5 h followed by being diluted with DI water to 200 mL and being left for 1 h. The solution was filtered and washed with 1000 mL of DI water. The remained solid was then dried in a vacuum for 12 h. Graphite oxide was synthesized from the pre-treated graphite powder. 1 g of pre-treated graphite powder was added in 39 mL of concentrated H_2SO_4 stirred in an ice bath for 0.5 h. KMnO_4 was slowly added into the stirring solution which was kept at a temperature lower than 10 °C. The solution was then heated at 35 °C for 2 h. 500 mL of DI water was added into the stirring solution, which was conducted in an ice bath for keeping the temperature lower than 50 °C. Then 50 mL of 30% H_2O_2 was added into the solution. After staying for 12 h, the solution was filtered and washed with 500 mL of 10% HCl and DI water. The remained graphene oxide was dried in a vacuum for 24 h. The GO solution with a concentration of 0.1 mg/mL was prepared by dispersing GO in the DI water for further photoreduction process.

2.2. Photoreduction of graphene oxides

For the photoreduction of GO, sacrificial agents of $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ and TEA were individually added into the GO solution. The safety issues in operating with TEA have been addressed in [Supplementary data](#). The concentrations of $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ sulfur redox couple in the GO solution are 3.5 mM/2.5 mM which are the maximum for free of the aggregation of GO. The concentration of TEA in the GO solution was optimized to be 10 Vol% ([Supplementary data](#)). The pH value of each GO solution was adjusted to be 12 to prevent from the aggregation of GO during photoreduction. The photoreduction of the 20 mL of GO solution was carried out under a UV irradiation in a wavelength range of 280–450 nm with an intensity of 1 W cm^{-2} . The GO solution was bubbling by an argon flow during photoreduction. The product was collected and purified by dialysis for a week [34]. The molecular weight cut-off (MWCO) of the dialysis tubing (Cellu Sep T2) is 7–8 kD. After dialysis, the solution was filtered and washed with DI water. The remained reduced graphene oxide was dried in a vacuum for 24 h. The reduced GOs (RGOs) were then dispersed in ethanol for further characterization.

2.3. Characterizations of graphene oxides and reduced graphene oxides

The UV–vis absorption spectra of the GO and RGO solutions were measured using a UV–vis spectrophotometer (VARIAN Cary-100). The chemical bonding states of the GO and RGO products were investigated by X-ray photoelectron spectrometer (ULVAC-PHI, Kanagawa, Japan) using Al $K\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$). The photoemission of the GO solutions with and without sacrificial agent was measured in a photoluminescence spectroscopy (integrated by Protrustech Co., Ltd.) using an excitation wavelength of 405 nm. Fourier transform infrared (FTIR) spectra of the GO and RGOs were measured with a spectrometer (Nicolet 6700, Thermo Fisher). The GO and RGO powder were ground with KBr and then

were pressed to the pellets. Thermogravimetric analysis (TGA) was performed using a TG analyzer (TA Instrument, Model 2050) under nitrogen gas flow (100 mL min^{-1}) at a heating rate of 5 °C min^{-1} .

3. Results and discussion

3.1. Characterizations of reduced graphene oxides

The photoreduction of GO solution with sacrificial agent was conducted under UV irradiation. $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ and TEA were individually added into the GO solutions and their performances serving as the sacrificial agent were examined at a temperature of 25 °C. For comparison, a maximum amount of $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ was added into the solution in which GO is still well-dispersed without aggregation. On the other hand, the concentration of TEA was optimized as described in [Fig. S1a \(Supplementary data\)](#). The reduction extents of GOs were first examined by UV–vis absorption spectroscopy. As shown in [Fig. 1a](#), the UV–vis absorption spectrum of GO solution (0.1 mg/mL) displays a $\pi \rightarrow \pi^*$ absorption peak at 230 nm with a $n \rightarrow \pi^*$ characteristic shoulder at 300 nm [35]. After 10 h UV irradiation, a red shift from 230 nm to 260 nm is obtained in the absorption spectrum of solution without sacrificial agent. With the addition of sacrificial agents, significant shifts of the $\pi \rightarrow \pi^*$ absorption peak to 265 nm and 268 nm are observed in the spectra of the solutions in the presence of $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$, and TEA, respectively, as illustrated in [Fig. 1a](#). The shift of the $\pi \rightarrow \pi^*$ absorption to the longer wavelength of the characteristic graphene indicates that graphite-like structure was significantly repaired by the photoreduction of GO with the assistance of the sacrificial agent. The UV–vis absorption results suggest that these agents play a role as the hole scavenger and therefore the photocharge separation efficiency in the GO is improved in the presence of these sacrificial agents. As a result, self-reduction of GO is enhanced in the presence of the sacrificial agent.

[Fig. 1b](#) shows the evolutions of $\pi \rightarrow \pi^*$ absorption peak position of the photoreduced GO solutions in the presence of $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ and TEA individually. It reveals that with the addition of $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$, the $\pi \rightarrow \pi^*$ absorption peak position of RGO solution is measured at 265 nm after 3 h UV irradiation and the absorption position is kept at the same value as extending the reaction period to 10 h. In the case of TEA addition, the $\pi \rightarrow \pi^*$ absorption peak position of RGO solution can reach 267 nm over 1-h treatment, as shown in [Fig. 1b](#). While the reduction is further proceeded, the $\pi \rightarrow \pi^*$ absorption peak at 268 nm is observed after 10 h treatment. The UV–vis absorption measurements indicate that the performance of TEA is superior to $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ as a sacrificial agent. Moreover, when the reaction temperature is elevated to 53 °C, the reaction time can be significantly reduced to 1 h for achieving the reduction extent with the $\pi \rightarrow \pi^*$ absorption peak at 268 nm. [Fig. S1b \(Supplementary data\)](#) illustrates that the $\pi \rightarrow \pi^*$ absorption peak at 240 nm was observed in the UV–vis absorption spectrum of the GO solution with TEA at 53 °C in the dark for 1 h, indicating that TEA itself is not an efficient reduction agent for the formation of RGOs. TEA in the photoreduction of GO process is therefore suggested to mainly serve as the hole scavenger.

XPS was employed to analyze the GO and RGO samples to further learn the details of the reduction degree of RGOs by the sacrificial agent-assisted photoreduction method and the results are shown in [Fig. 2](#). [Fig. 2a](#) shows the C 1s XPS spectrum of the GO, in which the peaks with binding energies of 284.6 eV, 286.7 eV, and 288.5 eV are respectively corresponding to the C–C, C–O (epoxide and alkoxy), C=O (carboxyl, and carbonyl) bonds [19,36]. It reveals the existence of oxygen-containing functional groups in the GO sample. [Fig. 2b](#) and [2c](#) display the C 1s XPS spectra of the samples

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