



Water soluble reduced graphene oxide as an efficient photoluminescence quencher for semiconductor quantum dots



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ABSTRACT

Chemically derived water soluble reduced graphene oxide (rGO) is synthesized via a two-step reduction approach assisted with sulfonation. X-ray photoelectron spectroscopy confirms the removal of oxygen-related groups from GO. The obtained rGO can effectively quench the photoluminescence (PL) of CdTe quantum dots. Concentration- and volume-dependent quenching behaviors are investigated to reveal the quenching mechanism. The Stern-Volmer plot shows exponential dependence on the rGO concentration, indicating that “sphere of action” model works when the extent of quenching is large.

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1. Introduction

Graphene has proven to be a promising candidate for many optoelectronic applications ever since its discovery and large-scale synthesis, owing to its unique electronic structure and outstanding properties [1–5]. Recently, it was realized that graphene can extract photoexcited electrons from semiconductor quantum dots (QDs) very efficiently [6,7]. Such a feature is highly desired in either photovoltaic solar cells or ions, biomolecules and bacteria sensing [8] based on photoluminescence (PL) quenching. It has been reported that graphene [9,10], graphene oxide [8,11], or graphene-metal composites [12] can behave as PL quencher for various luminescent materials.

As a luminescence quencher, generally graphene should be water soluble because most of the quenching applications use solution as the media. However, the water solubility of most graphene prepared by various methods is low. So far great efforts have been made to improve the water solubility of graphene. For examples, Stankovich et al. [13] reported polymer coating of graphene. Ruoff et al. [14] and Li et al. [15] reported the synthesis of reduced graphene oxide (rGO) by hydrazine hydrate reduction. However, such rGO inclines to aggregate because most of the hydrophilic groups

on the graphene surface will be removed during the reduction. To resolve this problem, covalent [16] and noncovalent [17,18] functionalization methods were used to synthesize water soluble graphene. However, most researchers used the toxic reducing agents for the chemical reduction of GO. Recently, novel approaches to water soluble graphene-based materials have been developed. For examples, Tian et al. [19] reported a fast and green exfoliation strategy for large scale production of water dispersible few layer graphene through a controllable edge oxidation and localized gas bubbling process. Hu et al. [20] reported method of hyper-branched polyol functionalization to synthesize water soluble GO.

Sulfonation represents an effective approach to water soluble graphene [21–24]. Sulfonated graphene can not only recover relatively sp^2 carbon domains but also introduce charged SO_3^- units to the graphene surfaces. Thus, the sulfonated graphene was water-soluble and was prevented from heavy aggregation in water. Moreover, sulfonated graphene have two main advantages: i) it shows extremely high adsorption capability [21] and ii) it can be completely non-luminescent when compared with most luminescent GO or r-GO [25]. These advantages make it an excellent candidate for fluorescence quenching. In this work, we demonstrate the improvement of water solubility of rGO via a sulfonation reaction. The produced rGO solution exhibits good PL quenching ability as demonstrated by mixing it with various CdTe QDs that have different emission wavelength. We find that the PL quenching can be described by the modified Stern-Volmer equation when the

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extent of quenching is large.

2. Material and methods

The water soluble rGO was chemically derived from graphene oxide (GO) by a two-step reduction approach assisted with sulfonation, as schematically shown in Fig. 1a. GO was synthesized by the well-established modified Hummers method [26]. For the first-step reduction, the GO solution with concentration of 0.5 mg/ml and pH value of ~ 10 was placed into 80 °C water bath. NaBH_4 dissolved in deionized ice water was then added into the GO solution to trigger the reduction. The reaction was lasted for 1 h. The product, labeled as rGO', was obtained by centrifugation, and then dispersed in deionized water for sulfonation. The diazonium salt solution was made by mixing NaNO_2 (5 mg) and p-aminobenzenesulfonic acid (50 mg) powders with 500 μl 1 M HCl solution. The sulfonation was carried out in ice bath for 2 h to obtain sulfo-rGO'. The residual p-aminobenzenesulfonic acid was then removed by dropping 5% wt Na_2CO_3 solution. For the second-step reduction, sulfo-rGO' solution was placed in 100 °C oil bath, and then reduced by 85% hydrazine hydrate for 24 h. The product was then centrifuged twice at 8500 rpm for 15 min. The deposit was finally dispersed in deionized water to obtain water soluble rGO. The synthesis procedure produces water soluble rGO with good reproducibility.

The luminescent material used in this study is CdTe QDs with emission wavelengths at 544, 584, 630, and 756 nm. The CdTe QDs were synthesized by colloidal method after the procedures reported in ref.16, using $\text{Cd}(\text{NO}_3)_2$ and NaHTe solution as the

precursors and mercaptopropionic acid as the capping agent. The reaction was carried out at 100 °C for 1–90 min, and the QD size thus the emission wavelength can be tuned by the reaction time. Details of the synthesis can be found in Ref. [27].

The morphology, optical properties and composition of the samples was examined by atomic force microscope (AFM, Seiko SPI-3800N), Raman scattering (Jobin Yvon HR800) and X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250). PL measurements were performed on a FLS920 fluorescence spectrometer (Edinburgh Instruments) at room temperature, using 325 nm He-Cd laser as the excitation source.

3. Results and discussion

Fig. 1b shows the AFM image of GO prepared by the modified Hummers method. The thickness is about 2 nm, indicating that the GO sheets are bilayer. Raman scattering spectrum (Fig. 1c) shows two characteristic bands for graphene [28], that is, the G-band at 1590 cm^{-1} corresponding to the first-order scattering of the E_{2g} mode and the D-band at 1330 cm^{-1} corresponding to the second order of zone-boundary phonons in defected graphite. The vibration modes of 2D, D + G, and 2G can also be observed. Fig. 1d shows the XPS C1s core level spectrum of the rGO. The spectrum exhibits a prominent peak at 284.6 eV corresponding to C=C bond in graphene. The oxygen-related peaks, C–O and C=O bonds in the region of 286.5–288.0 eV, are almost absent. The results indicate that the oxygen-related groups of GO has been removed after two reduction processes and our rGO is graphene-like.

It should be noted that chemically derived GO is generally

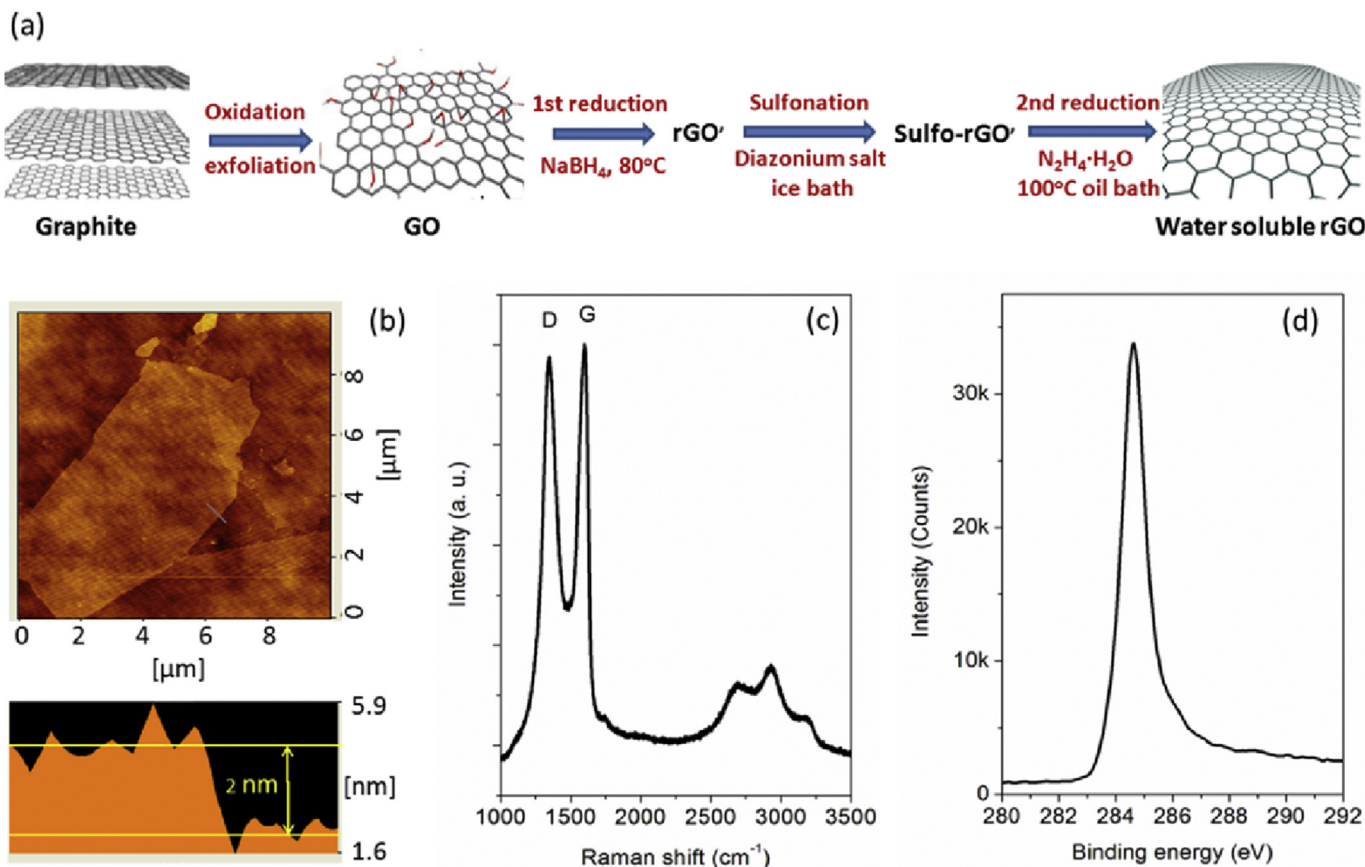


Fig. 1. (a) Schematic diagram for the synthesis procedures of water soluble rGO. (b) AFM image of GO. The thickness is about 2 nm. (c) Raman scattering spectrum of rGO. (d) XPS C1s core level spectrum of rGO.

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