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# Synthesis of $Tb_4O_7$ complexed with reduced graphene oxide for Rhodamine-B absorption



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#### ABSTRACT

 $Tb_4O_7$  complexed with reduced graphene oxide composite (Tb–rGO) had been designed and fabricated by a facile thermal reduction method. The formation of  $Tb_4O_7$  particles and reduction of graphene oxide (GO) occurred simultaneously, and partial terbium ions would be complexed with rGO via oxygencontaining function groups on rGO sheets. Introducing of terbium ions could effectively tune the photoluminescence properties of rGO, and the composite exhibited the typical green emission of terbium ions as well as the blue self-luminescence of graphene entered at 440 nm. Moreover, Tb–rGO had demonstrated its high capability as an organic dye (Rhodamine-B) scavenger with high speed and efficiency. The findings showed the promising applications for large-scale removal of organic dye contaminants, especially in the field of waste water treatment.

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#### 1. Introduction

Addressing the severe water pollution arising from organic dyes is a challenge task [1]. Graphene-based materials have attracted tremendous attentions due to their good absorption ability for organic solvent, oils and organic dyes [2]. The commonly-used precursor for graphene, graphene oxide (GO), contained a series of reactive oxygen functional groups, which would be useful for the practical applications through chemical functionalizations [3]. The availability of oxygen functional groups allowed GO sheets to react with manifold materials to form functionally advanced hybrid macroassemblies with superior characteristics. These made GO be a possible starting material for immobilization of a large number of substances, such as rare earth metals, drugs, and inorganic nanoparticles [4,5].

Graphene combined with rare earth ions composites have been reported in very recent years. For example, europium (Eu) ions complexed with rGO had been created for the environmental protection for high absorption for organic dyes [4]. Terbiumcontaining GO was reported to be used for monitoring the hypochlorite [6]. Rare earth-based compounds displayed sharp emission bands; large stokes shifts, and a wide range of lifetimes as well as good chemical stabilities, which could be good candidate

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for graphene composites. Combined with rare earth would not only make the graphene luminescent, but also modify the inner structure of graphene.

In this work,  $Tb_4O_7$  complexed with reduced graphene oxide (Tb-rGO) composite was synthesized by a facile thermal reduction approach. The objectives of this study were: (1) to investigate the inner structure of Tb-rGO; (2) to investigate the photoluminescence (PL) of Tb-rGO; (3) to evaluate the adsorption ability of Tb-rGO for organic dye.

#### 2. Experimental

GO was prepared from flake graphite powder using the modified Hummers' method [7].  $Tb(NO_3)_3$  solution was obtained by dissolving  $Tb(NO_3)_3$  powders in the deionized water.  $Tb(NO_3)_3$  (15 ml of 0.3 mg ml<sup>-1</sup>) aqueous solution was slowly added into the GO solution (30 ml of 2 mg ml<sup>-1</sup>) and stirred for 20 min at room temperature to form the uniform system. After drying the water, the mixture was calcined at 500 °C under an H<sub>2</sub>/Ar (volume ratio 1:5) atmosphere with a flow rate of 3 ml/h for 30 min. Then, the chamber was slowly cooled to room temperature and the products were collected. rGO sample was also prepared without Tb component at the same synthesizing condition.

The morphology was characterized by scanning electron microscopy (SEM, Hitachi, S-4800) and transmission electron microscopy (TEM, Tecnai G2, FEI Company) with X-ray energy dispersive spectrometry (EDS). Raman spectroscopy was recorded

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using a Renishaw InVia Raman microscope with 532 nm laser. Xray photoelectron spectroscopy (XPS, PHI-5702, Physical Electronics) was performed using a monochromated Al-Ka irradiation. Fourier transform infrared spectrum (FTIR) was recorded on a Nicolet NEXUS 670 FTIR spectrometer. And the PL spectra were recorded using an FLS-920T fluorescence spectrophotometer equipped with a 450 W Xe light source and double excitation monochromators.

#### 3. Results and discussion

SEM image of Tb–rGO was provided in Fig. 1a. After the thermal reducing process, GO sheets were partially reduced to the folding and ripple rGO nanosheets, which naturally aggregated and stacked to multilayers. It was observed the particles grew on the surface of rGO nanosheets, and some of them were wrapped by the flexible rGO nanosheets. It is believed that during the reaction, the decomposing of  $Tb(NO_3)_3$  to terbium oxide  $(Tb_4O_7)$  and the reducing of GO occurred simultaneously. Some large particles dispersed in crumpled pieces of silk fabric could be also clearly observed in TEM image (Fig. 1b). Fig. 1c provided more detailed structural information of Tb–rGO. The image showed a well-defined  $Tb_4O_7$  particle with lattice spacing of 0.36 nm, which could be assigned to the *d*-spacing in the (111) planes of  $Tb_4O_7$  [8]. EDS spectrum (Fig. 1d) showed the distinctive existence of terbium in the composite.

Raman spectrum for Tb–rGO was shown in Fig. S1, the D peak and G peak of Tb–rGO were located at  $1368.4 \,\mathrm{cm^{-1}}$  and  $1595.5 \,\mathrm{cm^{-1}}$ . The G peak of Tb–rGO was noticed to have a red shift compared with the previous reported GO, implying not only the restacking of graphene sheets after the thermal reduction treatment, but also the modifying the coordination environment of the rGO nanosheets after complexed with terbium ions [9]. The existence of various oxygen functionalities (including the C=O, C–O–C, –OH and the Tb–O) would be attributed to the D peak. The I<sub>D</sub>/I<sub>G</sub> ratio for Tb–rGO is 0.88. And the presence of 2D peaks was also observed at 2935 cm<sup>-1</sup>, indicating the few-layered crystal structure of Tb–rGO. The FTIR spectrum for Tb–rGO was shown in Fig. S2. The peak at  $3440 \text{ cm}^{-1}$  could be attributed to the O—H stretching vibration, and the unoxidized sp<sup>2</sup> C=C bands located at  $1550 \text{ cm}^{-1}$ , indicating the conversion from GO to rGO. The absorption of  $1060 \sim 1180 \text{ cm}^{-1}$  and  $1630 \text{ cm}^{-1}$  could be assigned to the vibrations of C—O and C=O stretching vibrations. And the peak at  $571 \text{ cm}^{-1}$  would be attributed to Tb-O vibration [10]. From the above analysis, the remaining oxygen-containing groups would be effectively coordinated with partial terbium ions on the rGO sheets.

Fig. 2a shows the XPS results for Tb-rGO, detecting the existences of the carbon (C), oxygen (O) and Tb elements. High resolution of C 1s peak (Fig. 2b) could be decomposed into three components at 284.5, 285.1, and 287.9 eV. The main peak at the binding energy of 284.5 eV was assigned to sp<sup>2</sup> hybridized C atoms in graphene while the higher binding energy confirmed the presence of O-rich groups: epoxy/hydroxyls (C-O, 285.1 eV) and carbonyl (C=O, 287.9 eV) [11]. The O 1s peak (Fig. 2c) could be fitted with two components: the peak located at 530.7 eV originated from the Tb-OH bonds and the peak at 532.3 eV involved various functional oxygen groups including C-OH, C=O and O=C-OH [12,13]. The Tb 4d peak was shown in Fig. 2d, The peak at 150.1 eV was surely assigned to Tb (III) species. And the Tb (IV) species were suggested for the peaks at 156.9 eV and 167.5 eV [14]. The results indicated that the Tb ions could be in the mixed valence of Tb (III) and Tb (IV).

The emission and excitation spectra of the Tb–rGO were presented in Fig. 3a and b. A band ranging from 350 to 400 nm could be related to the direct excitation of the f–f transition of the Tb ions. Compared with that of Tb ions in inorganic compounds, the excitation band seemed to be slightly broad, which was probably induced by the diversity of the transitions state of Tb ions in composite [15]. The emission peaks in the green region were noticed when using 378 nm as the excitation wavelength including  ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$  (489 nm),  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  (545 nm),  ${}^{5}D_{4} \rightarrow {}^{7}F_{4}$  (580 nm),  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  (617 nm) transitions, respectively. And the emissions of terbium ions were proposed not only from Tb<sub>4</sub>O<sub>7</sub> particles but also from the terbium ions complexed with the rGO sheets. Our previous investigation for europium complexed with



Fig. 1. The SEM image (a), TEM image (b), high resolution TEM (c) and EDS for Tb-rGO (d).

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