



# A facile route to porous beta-gallium oxide nanowires-reduced graphene oxide hybrids with enhanced photocatalytic efficiency



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## ABSTRACT

A facile route was developed to fabricate porous beta-gallium oxide nanowires ( $\beta$ -Ga<sub>2</sub>O<sub>3</sub> NWs)-reduced graphene oxide (rGO) hybrids using  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> NWs and graphene oxide (GO) as raw materials. The characterization results indicate that supercritical water can act as an efficient reductant to situ-reduce GO into rGO, and porous  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> NWs can further attach on the surface of as-reduced rGO through a strong coupling forces between the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> NWs and rGO. The photocatalytic performance of the hybrids can be obviously improved (about 74%) for the decomposition of methylene blue (MB) solution after coupling with 1 wt% rGO compared with the pure  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> NWs. The enhanced photocatalytic activity can be attributed to the synergistic effect of extended optical absorption band, the enrichment of MB molecular on the rGO and the valid inhibition of recombination of photo-generated electron-hole pairs induced by the strong coupling interaction between rGO nanosheets and porous  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> NWs.

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## 1. Introduction

As is well known, heterogeneous semiconductor photocatalysts such as TiO<sub>2</sub> [1], CdS [2] and ZnO [3] have been considered as a cost-effective materials for water remediation due to their great potentials for converting photon energy into chemical energy [4,5]. Among the various semiconductors, wide band-gap  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> ( $E_g = 4.9$  eV) [6] has exhibited a promising prospect in photocatalytic fields because of its good charge separation and high mobility of the photo-generated electrons [7]. For instance, Zhao et al. [8] found that the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanorods exhibited special photocatalytic properties for degrading the toluene to nontoxic substances which could improve the indoor air quality. Hou et al. [6] further reported that the porous  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> showed efficiently photoactive performance for mineralizing benzene to CO<sub>2</sub>.

However, the low photocatalytic activity of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> originated from the rapid recombination of photo-generated electrons and holes results in a limited practical application of Ga<sub>2</sub>O<sub>3</sub>. Therefore, it is necessary to explore new strategies to improve the

photocatalytic efficiency by reducing the recombination rate of the charge carriers. On one hand, various synthetic strategies including microwave plasma chemical vapor deposition [9], physical evaporation [10], arc discharge method [11] and hydrothermal method [12] have been attempted to prepare the nanostructured gallium oxide with large surface area and small size due to the structure sensitive property of catalysts in the photocatalytic system. Among these methods, a relatively simple wet chemical process using an organometallic ingredient [13] as the single ingredient was employed to prepare the precursor of the porous  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. Moreover, the porous materials have exhibited superior photocatalytic performance due to their large surface area. For instance, Yu et al. [14] fabricated the porous ZnO hollow spheres which showed high efficiency and stability in terms of dyes degradation. The porous TiO<sub>2</sub> with high performance for environmental and energy applications was further clarified [15].

On the other hand, graphene has high specific surface area and excellent optical, electrical, thermal and mechanical characteristics [16–18] due to its one-atom thick and two-dimensional honeycomb lattice structure [19], which makes it to be one of the most popular materials for the preparation of high performance hybrids with other functional semiconductors. In view of the significantly improved photocatalytic activity of other wide bandgap semiconductors coupled with rGO, such as GaN-rGO compounds [20,21],

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SiC-rGO hybrids [22,23], ZnO-rGO composites [24,25], ZnGa<sub>2</sub>O<sub>4</sub>-rGO complexes [26]. In order to improve the photocatalytic properties, we here develops a novel hydrothermal route to synthesize porous  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> NWs-rGO hybrids. In the facile hydrothermal process, supercritical water is used as solvent and reductant, which can successfully avoid the severe aggregation of the rGO [27] and the usage of toxic reactants. The photocatalytic efficiency of the different contents of rGO in the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> NWs-rGO hybrids was evaluated by the degradation of the MB solution under UV irradiation compared with the pure  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, and the corresponding photocatalytic mechanism is proposed in detail.

## 2. Experimental

### 2.1. Synthesis of the porous $\beta$ -Ga<sub>2</sub>O<sub>3</sub> NWs-rGO hybrids

To prepare the porous  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> NWs-rGO hybrids, graphene oxide (GO) was firstly prepared from natural graphite powder (99.95%) by the modified Hummers' synthetic strategy [28]. The porous  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> NWs were synthesized by a two-step route including a typical hydrothermal route using gallium acetylacetonate as a single-source organometallic ingredient at 150 °C for 8 h and an annealing treatment by further calcining the products at 800 °C for 2 h in air. Then, 0.2 g of the porous  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> NWs was added into the calculated amount of GO solution (0.1 wt%) obtained by ultrasonic dispersion of GO (0.1 g) in DI water (1 L) for 3 h. The mixture was then transferred into a 50 ml of Teflon-sealed autoclave and maintained at 150 °C for 6 h after vigorous stirring for 2 h. Finally, the products were obtained by centrifugation, washed with DI water and anhydrous alcohol for several times and then fully dried in vacuum at 60 °C for 12 h. The amount of graphene in the porous  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> NWs-rGO hybrids was controlled to be 0, 0.5, 1, 2 and 5 wt% and the corresponding samples was labeled as  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>,  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>-rGO (0.5 wt%),  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>-rGO (1 wt%),  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>-rGO (2 wt%) and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>-rGO (5 wt%), respectively.

### 2.2. Characterization

The powder X-ray diffraction (XRD) patterns were obtained on an X'pert PRO X-ray diffractometer with Cu K $\alpha$  radiation in a scan range of 5–80°. The sizes and morphologies of the samples were carried out by an S-4800 field emission scanning electron microscope (FESEM, Hitachi, Japan) with an acceleration voltage of 10 kV. The nanostructure and combination of the samples were characterized by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). The Raman spectra were measured by a LabRAM Aramis Raman spectrometer (Horiba Jobin Yvon, France) with an excitation wavelength of 532 nm. UV-vis absorption spectra were also acquired by a UV-visible spectrophotometer (UV-2550, SHI-MADZU, Japan).

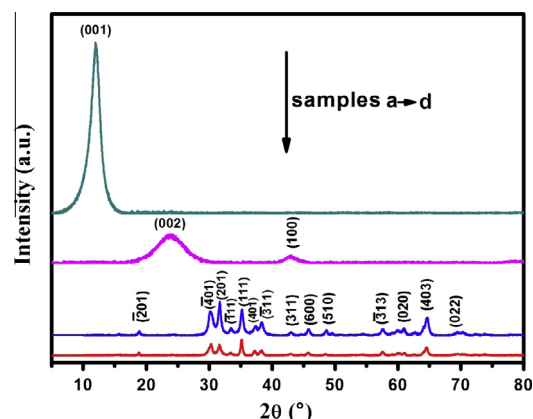
### 2.3. Photocatalytic activity

The evaluation of the adsorptivity and photocatalytic efficiency of the as-prepared samples was conducted by degrading the organic dyes at ambient temperature [29]. In a typical process: 20 mg catalytic materials was dispersed into 100 ml MB solution with the concentration of 10<sup>-5</sup> ml<sup>-1</sup> in a 200 ml beaker with a diameter of ca. 8 cm. The solution was kept in the dark under vigorous stirring for 30 min to reach the adsorption-desorption equilibrium and then the mixture was exposed under a mercury lamp (power is 500 W and main wave crest is 365 nm) for 1 h with a surface irradiation intensity of 4 mW/cm<sup>2</sup> examined by a radiometer. A certain amount of dye solution was sampled and centrifuged once every 10 min to measure the concentration changes of the MB dyes by a UV-vis spectrophotometer.

## 3. Results and discussion

### 3.1. Morphology and microstructures

The effective reduction of GO to rGO and successful preparation of the porous  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> NWs-rGO composites with enhanced photocatalytic activity can be confirmed by the following various strategies. Only a sharp characteristic diffraction peak at  $2\theta = 11.5^\circ$  (Fig. 1Sa) clearly demonstrates the accuracy of GO prepared by modified Hummers' method. Two wide diffraction peaks at ca. 24.1° and 42.8° corresponding to rGO (002) and (100) planes are obviously observed in Fig. 1Sb, which indicates the effective reduction of GO nanosheets to rGO by the hydrothermal treatment [30]. With increasing temperature and pressure, the supercritical



**Fig. 1.** XRD patterns of (a) GO, (b) rGO, (c) porous  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> NWs and (d) porous  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> NWs-rGO (1 wt%) hybrids.

water can exhibit strong reducing power during hydrothermal reaction, resulting in the cleavage reactions of various heterolytic bonds [31]. As a consequence, the bonds between the aromatic regions of GO and the functional groups of —OH, —C=O, and —COOH can be destroyed by supercritical water. Therefore, the hydrothermal reduction mechanism of GO nanosheets can be attributed to the deoxygenation/dehydration reaction of GO.

As shown in Fig. 1Sc, all the diffraction peaks can be indexed to the pure monoclinic phase of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> according to JCPDS: 41-1103. The sharp and strong peaks indicate that the as-prepared  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is well crystallized. However, no diffraction peak of rGO can be observed in the XRD patterns of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>-rGO hybrids (Fig. 1Sd) compared with the pure  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> samples, which is due to the destructive regular stacks and the limited amount of rGO in the hybrids [32].

As shown in Fig. 2c, the surface and top of the uniform porous  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> NWs with the width of ca. 80–90 nm and the length of ca. 1.5–1.8  $\mu$ m (Fig. 2b) are totally covered by the GO nanosheets with a crumpled morphology (Fig. 2a). With the increasing magnification of the TEM images (from Fig. 2d and e), more light-colored pores are apparently identified and the surface of the nanowires covered by the thin and light-gray GO nanosheets can be clearly observed. The GO bundling on the lattice fringes of a single  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> nanowire exhibited on the HRTEM image (Fig. 2f) further demonstrates that the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> NWs are entirely wrapped by the rGO nanosheets.

More information about the formation of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>-rGO composite can be supplied by the Raman spectroscopy (Fig. 3a). It is obvious that  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> exhibits strong Raman characteristic peaks (Fig. 3aSa) at 198, 342, 413, 649 and 760 cm<sup>-1</sup>, respectively. However, the intensities of these characteristic peaks indicate a significant enhancement after coupling with rGO (Fig. 3aSd). The reason is attributed to the charge transfer between rGO and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> [33]. It is well known that Raman characteristic peaks of graphene is a powerful and diffusely used data to distinguish the order and disorder/defect structures of sp<sup>2</sup> and sp<sup>3</sup> hybridized carbon [34]. The Raman characteristic peaks of GO, rGO and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>-rGO are shown in Fig. 3B. The D band is connected with the defects and disorder in the hexagonal graphitic layers, while the G band is associated with the Raman-active E<sub>2g</sub> mode induced by the presence of sp<sup>2</sup> carbon-type structures [24]. Moreover, the disorders/defects in graphene are usually measured by the intensity ratio of the D band to G band and a smaller intensity ratio of I<sub>D</sub>/I<sub>G</sub> results from the less sp<sup>3</sup> defects/disorder and larger average size (or less amount) of the in-plane graphitic crystallite sp<sup>2</sup> domains [35]. The I<sub>D</sub>/I<sub>G</sub> ratio of rGO (1.038) was higher than GO (0.914), which

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