Research Article

Properties and Photocatalytic Activity of β -Ga₂O₃ Nanorods under Simulated Solar Irradiation

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β -Ga₂O₃ nanorods are prepared by hydrothermal method and characterized by X-ray diffraction, high-resolution transmission electron microscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, and photoluminescence spectra. The results reveal that high crystallinity, monoclinic phase of β -Ga₂O₃ nanorods were prepared with a diameter of about 60 nm and length of 500 nm. Photoluminescence study indicates that the β -Ga₂O₃ nanorods exhibit a broad blue light emission at room temperature. The β -Ga₂O₃ nanorods displayed high photocatalytic activity under simulated solar irradiation; after 2 h irradiation, over 95% of methylene blue solution and over 90% of methyl orange solution were decolorized. Since this process does not require additional hydrogen peroxide and uses solar light, it can be developed as an economically feasible and environmentally friendly method to treat dye effluent.

1. Introduction

Organic dyes are common pollutants in industrial wastewaters which cannot be degraded and thus result in potentially severe environmental problems. Various physical, chemical, and biological techniques have been developed to degrade them. Heterogeneous photocatalysis using semiconductors has attracted much attention due to its ability to decolorize dye-containing wastewater [1, 2], which has proven to be a green technology for the degradation of organic pollutants. This process can mineralize organic dyes completely into H₂O, CO₂, and other nontoxic inorganic compounds without producing secondary pollution. One of such commonly used semiconductors is β -Ga₂O₃, which has a wide bandgap ($E_g = 4.9$ eV). In particular, its one-dimensional (1D) nanostructures, such as nanowires [3, 4], nanoribbons [5], and nanorods [6–10], have attracted much attention due to their unique nanostructures and photocatalytic properties. To be more specific, due to the strong redox ability of photogenerated electron-hole pairs [7, 8, 11], β -Ga₂O₃ exhibits high and stable photocatalytic activity over commercial TiO₂. When exposed to light irradiation, different phases of Ga₂O₃ possess extraordinary photocatalytic ability of dye and volatile

organic compounds [7–14]. Moreover, β -Ga₂O₃ is also an environmentally friendly material according to WorkSafe Australia criteria.

In this study, β -Ga₂O₃ nanorods are synthesized by the hydrothermal method and subsequent heat treatments. The physical properties of the products are characterized by powder X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and photoluminescence (PL) spectra. Photocatalytic activity of as-prepared nanorods is evaluated by degrading methylene blue (MB) and methyl orange (MO) in aqueous suspensions under simulated solar light irradiation. The performance of this degrading method is found to be very good. In particular, it requires no hydrogen peroxide, and thus it is economically feasible and environmentally friendly.

2. Experimental

The β -Ga₂O₃ nanorods are prepared by hydrothermal method. Ga(NO₃)₃·9H₂O, urea, and polyethylene glycol-200 (PEG) are used as starting materials, all of which are of

FIGURE 1: XRD patterns of β -Ga₂O₃ nanorods.

FIGURE 2: (a) TEM images of β -Ga₂O₃ nanorods, (b) TEM image of a single β -Ga₂O₃, (c) SAED patterns, and (d) EDS spectrum of the β -Ga₂O₃ nanorods.

analytical pure grade (99.9%). Our experiment goes as follows. First, 0.01 mol Ga(NO₃)₃·9H₂O, 0.1 mol urea, and PEG are dissolved in deionized water and then stirred vigorously using a magnetic stirrer for 1 h at room temperature. Second, the solution is transferred into a Teflon-lined stainless steel autoclave (400 mL in capacity) and hydrothermally reacted at 160°C for 8 h. Third, the obtained product is separated by centrifugation and washed repeatedly with alcohol and distilled water to remove the unreacted ions, by-products, organic impurities, and so forth. Then, the material is dried

under 100°C for 24 h. Finally, the obtained product is calcined at 800°C for 10 h in muffle furnace to obtain desired β -Ga₂O₃ nanorods.

3. Results and Discussion

Figure 1 shows XRD pattern of β -Ga₂O₃ nanorods. All of the diffraction peaks of the XRD patterns are in agreement with those of monoclinic phase of β -Ga₂O₃ (JCPDS: 41-1103). Moreover, no other diffraction peaks are found, indicating

FIGURE 3: Raman spectra of β -Ga₂O₃ nanorods.

that the product is predominantly in single β -Ga₂O₃ phase with high purity. The sharp diffraction peaks also reveal that the prepared sample has a high crystalline quality.

Figure 2 shows the TEM images of the β -Ga₂O₃ nanorods. It can be observed from Figures 2(a) and 2(b) that the prepared nanorods have a diameter of about 60 nm and length of 500 nm with dense hole on their surface. The pores might be formed during the recrystallization process or elimination of water from constitutional OH⁻ groups [15]. The porous nature of this semiconductor material should be useful to improve the photocatalytic activity. Figure 2(c) presents the corresponding selected area electron diffraction (SAED) pattern, which reveals the crystalline monoclinic structure of β -Ga₂O₃ and is consistent with the XRD result. The corresponding EDX data shown in Figure 2(d) indicates that they are composed of Ga and O. The C peaks are due to the contamination from the carbon coated copper grids when preparing HRTEM specimens. The molecular ratio of Ga and O of the nanorods was found to be 2:3, which is close to that of the β -Ga₂O₃ crystal.

Figure 3 shows the Raman spectra of β -Ga₂O₃ nanorods using a 514.5 nm Ar ion laser as the excitation source. The peaks are very sharp and narrow indicating the high crystalline quality of the prepared sample. Raman spectrum can be divided into three groups named low frequency mode (below 200 cm⁻¹), mid frequency mode (500–300 cm⁻¹), and high frequency mode (770–500 cm⁻¹), all of which are related to different vibrational modes [16]. The eight Raman vibration peaks 169, 199, 345, 415, 474, 562, 651, and 765 cm⁻¹ are visible, as shown in Figure 3. The Raman bands observed at 169 and 199 cm⁻¹ are due to libration of Ga-O chains; the Raman bands at 345, 415, and 474 cm⁻¹ belong to deformation of Ga₇(O₁)₂ octahedra; the Raman bands observed at 562, 651, and 765 cm⁻¹ are related to symmetric stretching bands of GaO₄ tetrahedra. No peak corresponding to organic impurities is found as in the XRD pattern.

FIGURE 4: XPS spectra of β -Ga₂O₃ nanorods.

Figure 4 shows the XPS spectra of β -Ga₂O₃ nanorods. The XPS spectrum indicates that the chemical composition of the particles mainly includes O, Ga, and C. The C peaks come mainly from the atmospheric contamination due to the sample exposure to the air. The XPS spectra of O 1s and Ga 3d are shown in Figures 5(a) and 5(b), respectively. The binding energies of the Ga 3d and O 1s are 531.5 eV and 20.8 eV.

Figure 6 shows the excitation and emission spectra of the as-prepared β -Ga₂O₃ nanorods at room temperature. The excitation peaks are located at 281 nm and 376 nm under the emission of 441 nm. The emission spectrum shows a broad emission band under a 281 nm or 376 nm excitation, which has been observed with PL spectra in Ga₂O₃ [17–19], due to the oxygen vacancy (V_O) and gallium-oxygen vacancy pairs (V_{Ga} , V_O) in the Ga₂O₃ [20]. Besides, the asymmetric emission band shape can be explained by the electron-phonon interaction in the substances [21]. The major emission band can be separated into three Gaussian bands centered at about 419, 442, and 470 nm, respectively.

The photocatalytic activity of β -Ga₂O₃ nanorods is evaluated by the photocatalytic degradation of dye under simulated solar irradiation. The degradation trend of 10 mgL⁻¹ MB and MO solution as a function of irradiation time is shown in Figure 7. The degradation rate increases as the irradiation time increases. After 4 h of simulated solar irradiation, the degradation rate of MB and MO reaches 95.32% and 90.47%, respectively. The photocatalytic properties in the degradation of the dye of the Ga₂O₃ nanorods suggest that the samples should have valuable application in water treatment.

4. Conclusions

The β -Ga₂O₃ nanorods are prepared by hydrothermal method. Results of the XRD, TEM, Raman, and XPS analysis indicate that the high crystallinity, monoclinic phase, and purity of β -Ga₂O₃ nanorods were achieved. PL shows that the intense blue emission at room temperature can be attributed to oxygen vacancy (V_O) and gallium-oxygen vacancy pairs (V_{Ga} , V_O). The photocatalytic degradation ability of β -Ga₂O₃ nanostructures toward photodegradation of MB and MO

FIGURE 5: XPS spectra of Ga 3d (a) and O 1s (b).

FIGURE 6: Excitation (a) and emission (b) spectra of β -Ga₂O₃ nanorods.

FIGURE 7: Degradation trend of MB (a) and MO (b) as a function of irradiation time.

under simulated solar irradiation showed that nanorods have superior degradation efficiency. The results suggest that β -Ga₂O₃ nanorods are very promising photocatalysts for degrading dye wastewater treatment under simulated solar irradiation.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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