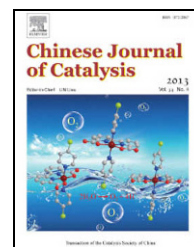


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Article

Photocatalytic decomposition of perfluorooctanoic acid in pure water and wastewater by needle-like nanostructured gallium oxide

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ABSTRACT

Nanostructured β -Ga₂O₃ with a needle-like structure was synthesized by a polyvinyl alcohol (PVA)-assisted hydrothermal method and subsequent heat treatment. It has a high specific surface area (25.95 m²/g) and large number of nanopores (4–25 nm), and it exhibited good photocatalytic activity for perfluorooctanoic acid (PFOA) decomposition in pure water under UV irradiation ($\lambda = 254$ nm). PFOA had a half-life of 18.2 min, and the first order rate constant (2.28 h⁻¹) for PFOA decomposition with the needle-like β -Ga₂O₃ was 7.5 and 16.8 times higher, respectively, than with commercial Ga₂O₃ and TiO₂ (P25). In addition, in combination with vacuum UV (VUV) irradiation ($\lambda = 185$ nm), the needle-like β -Ga₂O₃ showed high activity for the removal of trace PFOA in both pure water and wastewater, with first order rate constants of 4.03 and 3.51 h⁻¹, respectively. The adverse effect that coexisting natural organic matters in wastewater have on the decomposition of PFOA was mostly eliminated with VUV irradiation, and the energy consumption in this method was much less than the values reported for other methods in the literature.

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1. Introduction

Perfluorooctanoic acid (PFOA, C₇F₁₅COOH) is an emerging persistent organic pollutant that belongs to a class of fully fluorinated hydrocarbons known as perfluorocarboxylic acids (PFCAs, C_nF_{2n+1}COOH). Due to the strong carbon-fluorine bonds, PFOA is extraordinarily stable thermally and chemically. As a result, it is widely used as a surfactant and fire retardant in various industrial fields. Owing to its environmental persistence and bioaccumulation, it has been extensively reported that PFOA is now globally distributed in world waters, animals and humans [1–5]. Toxicological studies have demonstrated that exposure to PFOA can lead to developmental and reproductive toxicity problems, liver damage, and possibly cancer [6–8]. The potential hazard that PFOA poses to human health

and wild life has increasingly attracted worldwide concerns.

Due to its wide application in consumer products and industrial manufacture [9], PFOA and its precursors have been widely released into nature, particularly from wastewater treatment plants [10,11]. PFOA resists most conventional treatment processes including biological degradation, and oxidation and reduction methods [12]. Recent studies showed that special techniques such as thermolysis [13], ultrasonication [14,15], and photochemistry approaches [16–19] can decompose PFOA in aqueous solution, but these also have serious drawbacks, such as severe operation conditions and high energy consumption. Among the potential methods for PFOA decomposition, heterogeneous photocatalysis is attractive for its low energy consumption and high efficiency for completely degrading various kinds of organic contaminants. However,

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TiO₂, which is the most widely investigated photocatalyst, showed very low activity for PFOA decomposition under mild conditions [20]. Fortunately, our previous research has shown that other semiconductors, such as β-Ga₂O₃ and In₂O₃, can decompose PFOA, and their activity can be further enhanced by a proper synthesis strategy to give nanostructure materials [21–23].

Here, we synthesized Ga₂O₃ with a needle-like nanostructure. The needle-like β-Ga₂O₃ was prepared by a polyvinyl alcohol (PVA)-assisted hydrothermal method followed by calcination. The prepared materials exhibited remarkable photocatalytic activity for PFOA decomposition in pure water as well as municipal wastewater.

2. Experimental

2.1. Preparation of needle-like Ga₂O₃

All reagents were analytical grade and were used as received. Ga₂O₃ was synthesized by a hydrothermal method followed by calcination. In a typical procedure, 2 g (5 mmol) of Ga(NO₃)₃·xH₂O and 0.1173 g of PVA (*M_w* = 22000) were dissolved in 20 ml pure water, and the pH was adjusted to 6.4 using NaOH solution. After heating at 90 °C for 10 min, the mixture was transferred into a 25 ml Teflon-lined stainless steel autoclave and maintained at 200 °C for 8 h. After the autoclave was naturally cooled to room temperature, the white precipitate (precursor of Ga₂O₃) was collected by centrifugation and washed with ultra-pure water and ethanol three times. Then the white precipitate was dried at room temperature for 12 h. Ga₂O₃ powder was obtained from the precursor by calcination at 700 °C for 2 h in nitrogen (heating rate 1 °C/min).

2.2. Characterization

X-ray powder diffraction (XRD) patterns were obtained on a PANalytical X'Pert pro diffractometer at 40 kV voltage and 200 mA current. The morphologies of the samples were observed using a Hitachi S-5500 ultra-high resolution field emission scanning electron microscope (FESEM) performed at an accelerating voltage of 5.0 kV. Transmission electron microscopy (TEM) images were taken on a JEOL JEM 2010F microscope at an accelerating voltage of 200 kV. The diffuse reflectance absorption spectra (DRS) of the samples were recorded by a Shimadzu UV2700 UV-Vis spectrophotometer. Nitrogen adsorption isotherms were obtained on a Quantachrome Autosorb-1MP instrument.

2.3. Photocatalytic decomposition of PFOA

The photocatalytic decomposition of PFOA was conducted in a tubular quartz reactor under ultraviolet irradiation. Two kinds of low pressure mercury lamps (14 W, Cnlight Co. Ltd., China) with the same electric power, appearance, and size were alternatively used. One only emits 254 nm UV light (hereafter referred as UV), and the other emits 254 nm UV and 185 nm vacuum UV light (hereafter referred as VUV). The UV or VUV

lamp was placed in the center of the reactor with a two-layer quartz tube protection. In a typical experiment, 150 ml of PFOA aqueous solution (*C*₀ ≈ 500 μg/L) was prepared by diluting the stock solution in a beaker. Photocatalyst (0.075 g, 0.5 g/L) was added in the PFOA solution and stirred for 1 h. Then, the suspension was added into the reactor, and oxygen gas was continuously bubbled in at a flow rate of 60 ml/min for 10 min before the lamp was turned on. The reaction temperature was maintained at 25 °C with a cooling water jacket around the reactor. At regular time intervals, aliquots of solution were taken and filtered with 0.22 μm ultrafiltration membrane to remove the photocatalyst powder. The filtered samples were kept at 4 °C for analysis.

The concentrations of PFOA and its decomposition products were measured with a Waters Acquity UPLC system coupled with a Waters Micromass Quattro Premier tandem quadrupole mass spectrometer. The multiple reaction monitoring mode (MRM) was used for the quantitative analysis of PFOA and other shorter chain PFCAs. The separation column was a Waters Acquity UPLC BEH C₁₈ column (2.1 mm i.d. × 50 mm, 1.7 μm particles), and the column temperature was set at 50 °C. The concentration of fluoride ion (F⁻) was determined by an ICS-2000 Dionex ion chromatography. The sample was injected into an IonPac AS11-HC column (4 mm × 250 mm) with an IonPac AG11-HC guard column (4 mm × 50 mm). A mixture solution containing 3.2 mmol/L Na₂CO₃ and 1 mmol/L NaHCO₃ was used as the mobile phase at a flow rate of 1.0 ml/min.

3. Results and discussion

3.1. Crystal phase of Ga₂O₃

The XRD pattern of the final product synthesized by the PVA-assisted hydrothermal process and subsequent heat treatment is shown in Fig. 1. All the peaks can be indexed to β-Ga₂O₃ (*a* = 12.2270, *b* = 3.0389, *c* = 5.8079, JCPDS 41-1103) with no observation of other crystal phases. The peaks were sharp and narrow, indicating a high crystallinity for the samples.

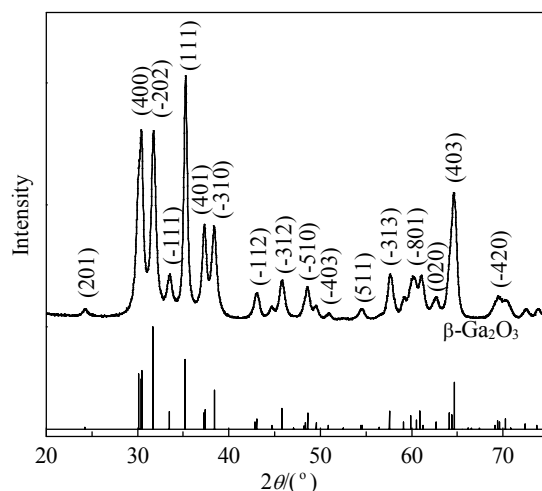


Fig. 1. XRD pattern of the Ga₂O₃ sample.

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