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Sonocatalytic activity of a heterostructured β-Bi_2O_3/$Bi_2O_2CO_3$ nanoplate in degradation of bisphenol A

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ABSTRACT

Novel heterostructured β-Bi_2O_3/$Bi_2O_2CO_3$ nanoplates (hBN) were synthesized to observe the sonocatalytic degradation of bisphenol A (BPA) (widely used as a model pollutant) under ultrasonic (US) irradiation. Prior to obtaining the hBN, the $Bi_2O_2CO_3$ micropowder precursor was prepared under hydrothermal conditions and then converted to hBN by increasing the calcination temperature to 300 °C. The synthesized hBN samples were characterized by field emission scanning electron microscope with energy dispersive X-ray analysis (FESEM/EDX), transmission electron microscopy (TEM), X-ray diffraction (XRD), ultraviolet–visible spectrophotometer diffuse reflection spectroscopy (UV–vis DRS), and X-ray photoelectron spectroscopy (XPS). The hBN/US system exhibited greater sonocatalytic activity for the degradation of BPA than the US treatment with the single element bismuth oxide, β-Bi_2O_3 prepared by annealing the $Bi_2O_2CO_3$ precursor at 400 °C for 1 h. The US frequency and US power intensity in the hBN/US system were the key operating parameters, which were responsible for the complete degradation of BPA during 6 h of reactions. The degradation efficiency of BPA under the US irradiation was positively correlated with the dose of hBN. Our findings indicate that heterostructured hBN can be used as an efficient sonocatalyst for the catalytic degradation of BPA in water and wastewater treatment.

1. Introduction

Over the last few decades, personal care products (PPCPs) and endocrine disrupting chemicals (EDCs) have been frequently detected at trace levels in common water resources (*i.e.*, lakes and rivers). It has been a serious issue since the early 1970s in that residual PPCPs and EDCs as water pollutants in surface water and sewage sludge may cause dyscrinism or cancers to living organisms [1,2]. However, not much attention has been paid so far to these potential problems due to their low concentration and lack of advanced detection technology. After several years of development of analytical techniques from the 2000s [3,4], a variety of undetectable micropollutants (*i.e.*, PPCPs and EDCs) was able to be detected and quantified down to ng L^{-1} levels. A total of 36 trace micropollutants (*e.g.*, atrazine, bisphenol A (BPA), carbamazepine, diclofenac, ibuprofen, naproxen, sulfamethoxazole, etc.) in water and wastewater associated with adverse health effects on human health has been detectable using ultra high performance Liquid Chromatography–Tandem Mass Spectrometry (LC/MS/MS) [5,6]. Thus, the populace needs to recognize the specific harmful effects of residual organic micropollutants in drinking water sources, while the scientists and policymakers are giving increasing regulatory attention to the sites contaminated with such micropollutants.

Among various EDCs, BPA has attracted considerable attention from researchers due to its wide applications (*e.g.*, manufacture of epoxy resins, paints, adhesives, polycarbonate, etc.) and harmful characteristics and was considered as a model pollutant. The wastewater discharged from manufacturing plants often contains high concentrations of BPA (> 100 mg L^{-1}) [7] which will highly contaminate the immediate environment. The BPA-contaminated sites may also cause serious health problems such as increasing breast cancer cells in the human body and/or decreasing estrogenic activity in living subjects [8,9]. Several physicochemical [10,11] or biological techniques [12–14] have been widely used to remediate waters contaminated by BPA. In general, biological treatment processes are economical, but they often require controlling suitable environmental conditions (*e.g.*, pH and temperature) for microbial activity [15,16]. The physicochemical remediation processes are advantageous because rapid BPA degradation can be achieved. However, those treatment processes generate large volumes of sludge [17] and produce undesirable intermediates which are more harmful than the parent organic compounds

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[18–20].

A variety of organic compounds have been rapidly removed by ultrasound-assisted adsorption process [21–23] or ultrasonic (US) irradiation via pyrolysis and oxidation within and around "hot spots" and inside collapsing cavitation bubbles without using toxic chemicals [24]. In US treatment, the reactive radicals ($^{\cdot}OH$, $^{\cdot}HO_2$, $^{\cdot}O_2$, etc.) generated by splitting water molecules promote an oxidizing redox environment in which complete mineralization of organic pollutants to non-toxic products occurs at the hot microbubble–liquid interface. In spite of many advantages over conventional physicochemical or biological techniques, the use of the US processes has been limited due to higher energy consumption and slow degradation kinetics for organic contaminants. For example, Inoue et al. [7] reported that BPA (0.50 mM) was completely degraded at US frequency of 404 kHz and high US intensities of 0.35, 0.90, and 1.3 W/cm^2 after 10, 3, and 2 h treatment, respectively. Guo and Feng [25] showed complete removal of BPA during 1 h US irradiation at higher US intensities of 60 W/cm^2 in the combined US/O_3 system with O_3 flow rate of 10–20 mL/min. The results of their study demonstrated that the increase in US intensity enhanced the degradation rate of BPA by enhancing the quantity of radicals that can be present in BPA solution, and non-volatile organic compounds were decomposed via the reaction with $^{\cdot}H$ and $^{\cdot}OH$ [7,25]. To overcome this limitation, various sonocatalysts including TiO_2 [26], magnetic mesoporous TiO_2 [27], stainless steel wire mesh [28], and perovskite oxide ($LaFeO_3$) [29] have been extensively studied for the catalytic removal of BPA. Those sonocatalysts may serve as additional nuclei in US processes to promote the rate of formation of cavitation bubbles. When the developing droplets reach a critical diameter, asymmetric bubble implosion can create high-speed microjets and high-pressure shock waves under US irradiation, which causes the increased local temperature and pressure (*e.g.*, temperature up to 15,000 K and pressure up to 1000 atm). This result enhances the pyrolysis of water molecules to form $^{\cdot}OH$ and thus the degradation rate of BPA [30,31].

Bismuth oxides have attracted relatively little attention over the past few decades [32]. In recent years, however, the interest in applications of bismuth is increasing due to its notable (photo)catalytic activity and lower toxicity. For example, Chen et al. [33] reported that β-Bi_2O_3 synthesized by the polyacrylamide sol-gel method could effectively degrade Rhodamine B (RhB) (98.7% degradation for 90 min) by producing a reactive oxygen species (ROS) (*i.e.*, $^{\cdot}OH$) under US irradiation. Kumar and Sahare [34] showed that nano-sized α-$Bi_4V_2O_{11}$ powders prepared using a combustion technique enhanced sonocatalytic degradation of RhB. He et al. [35] reported that Bi_2WO_6 synthesized by a hydrothermal method could generate ROS (*i.e.*, single molecular oxygen ($^{\cdot}O_2$) and $^{\cdot}OH$) under US irradiation, which played significant roles in sonocatalytic removal of methyl orange. More recently, the composite materials of bismuth oxide (*e.g.*, β-Bi_2O_3/$Bi_2O_2CO_3$ and α-Bi_2O_3/$(BiO)_2CO_3$ nanoplate heterojunctions) have been examined for enhanced photocatalytic activity due to their lower band gap [36–38]. Those heterostructured photocatalysts performed better than the single element bismuth oxides (α-Bi_2O_3 and β-Bi_2O_3) [39,40].

Although there have been research efforts to develop bismuth-based photocatalytic nanocomposites, no study has reported on the sonocatalytic activity of heterostructured bismuth oxide nanocomposites. Thus, in this study, we synthesized β-Bi_2O_3/$Bi_2O_2CO_3$ nanoplate (hBN) and characterized the nanocomposite materials using field emission scanning electron microscope with energy dispersive X-ray analysis (FESEM/EDX), transmission electron microscopy (TEM), X-ray diffraction (XRD), ultraviolet–visible spectrophotometer diffuse reflection spectroscopy (UV–vis DRS), and X-ray photoelectron spectroscopy (XPS). Then, we confirmed the enhancement of sonocatalytic activity in the hBN/US system compared to the US treatment in the presence of single element bismuth oxide (β-Bi_2O_3). Lastly, we evaluated the degradation performance of the hBN/US system at various US frequencies, US power intensity, and dose of the sonocatalyst to uncover the degradation mechanism of BPA.

2. Materials and methods

2.1. Material preparation

All chemicals were of analytical grades and used as-received without further purification. Bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$), nitric acid (HNO_3, 70%), sodium carbonate anhydrous (Na_2CO_3), BPA ($(CH_3)_2C(C_6H_4OH)_2$), potassium phthalate ($C_8H_4K_2O_4$), potassium iodide (KI), sodium hydroxide (NaOH), and ammonium molybdate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$) were purchased from Sigma-Aldrich (St. Louis, MO, USA). The physicochemical properties and chemical structures of BPA are presented in Table S1 in the Supporting Information. Stock solutions of BPA, hBN, and β-Bi_2O_3 were prepared in distilled (DI) water (Millipore Direct-Q3, Hach). The hBN was synthesized in-house, and its physicochemical characterization was inspected by FESEM (Quanta 450, FEI) with EDX (SU8010, Hitachi), TEM (Tecnai TF30, FEI), XRD (Empyrean, PANalytical) with Cu Ka radiation (k = 1.54443 Å) at 40 kV and 40 mA, UV–vis DRS (SolidSpec-3700, Shimadzu), Fourier transform-infrared (FT-IR) spectrometer (Thermo Scientific Nicolet 6700), and XPS (ULVAC-PHI Quantera II. PHI).

Briefly, the $Bi_2O_2CO_3$ precursor was synthesized by mixing 5.21 g of $Bi(NO_3)_3{\cdot}5H_2O$ with 27 mL of 1 M HNO_3. The Na_2CO_3 solution (dissolving 6.78 g of Na_2CO_3 powder into 107 mL of DI water) was slowly added dropwise to the prepared $Bi(NO_3)_3$ solution with continuous stirring (300 rpm for approximately 25 min) until the white precipitate formed. After another 15 min of stirring, the mixture was transferred into a 200 mL Teflon-lined autoclave reactor and treated at 180 °C for 12 h. After cooling to room temperature, the precipitate was collected by centrifugation, washed several times with ultrapure water and 70% ethanol, and oven-dried at 60 °C for 12 h to obtain the resultant $Bi_2O_2CO_3$ powder. The hBN was finally obtained by annealing the $Bi_2O_2CO_3$ powder at 300 °C for 1 h, while the β-Bi_2O_3 was produced by increasing the calcination temperature to 400 °C [39]. Those annealed products were left to cool to room temperature and stored in an oven at 60 °C.

2.2. Sonocatalytic degradation experiments

Experiments of sonocatalytic degradation of 10 mg L^{-1} BPA were carried out in triplicate in a cylindrical stainless steel US reactor (height 158 mm, inner dia. 110 mm) equipped with a circulating cooling system under controlled temperature conditions (20 ± 1 °C). The catalytic reactions were initiated by adding 0.01, 0.05, and 0.1 g L^{-1} of hBN or 0.01 and 0.05 g L^{-1} of β-Bi_2O_3 to 1.0 L BPA solution (US plate area = 0.046 m^{-2}) at different US frequencies (0, 35, 72, 100, and 170 kHz) and US power (0, 30, 50, 70, and 100 W) and kept under dark conditions to prevent unintended photocatalytic effects on the BPA. The US power intensity can be calculated to be 0, 0.066, 0.11, 0.15, and 0.22 W/cm^2. During the 6 h of reactions, 2 mL of aliquot samples were taken at predetermined times and filtered using 0.45 µm Whatman membrane filters for ultra-performance liquid chromatography (UPLC, ACQUITY UPLC H-Class System, Waters Co., Milford, MA) analysis using C18 column with a mobile phase reagent and acetonitrile (99.8%, Sigma-Aldrich, USA)/DI water (6:4, by vol.) at a fixed flow rate of 0.30 mL min^{-1}. The pseudo-first order rate constant (k_1) and synergistic index (SI) (Eq. (1)) were calculated in Table S2 [41].

$$SI = \frac{k_{(US+hBN)}}{k_{(US)} + k_{hBN}} \tag{1}$$

In addition, the concentrations of H_2O_2, which is an indicative of $^{\cdot}OH$ in solution were determined by the KI dosimetry method [42] using an ultraviolet–visible (UV–vis) spectrophotometer (G1103A, Agilent Technologies) at 350 nm in the hBN/US system. The two sample