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Sono-synthesis of nanocrystallized $BiFeO_3$/reduced graphene oxide composites for visible photocatalytic degradation improvement of bisphenol A

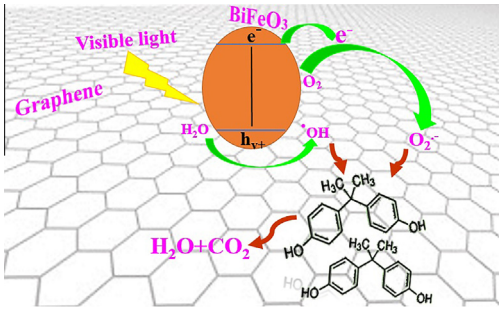
Tayyebeh Soltani, Byeong-Kyu Lee *

Department of Civil and Environmental Engineering, University of Ulsan, Nam-gu, Daehak-ro 93, Ulsan 680-749, Republic of Korea

HIGHLIGHTS

- $BiFeO_3$ magnetic nanoparticle/rGO composite was obtained from a simple sono synthesis.
- BFO MNP/rGO had reduced band gap energy, particle size, and recombination rate.
- BFO MNP/rGO showed greatly improved photocatalytic degradation of aqueous BPA.
- Complete mineralization of BPA was obtained after 120 min visible light irradiation.

GRAPHICAL ABSTRACT



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ABSTRACT

This study sustainably developed bismuth ferrite/reduced graphene oxide ($BiFeO_3$/rGO) nanocomposites by introduction of graphene oxide (GO) in the structure of $BiFeO_3$ magnetic nanoparticles (BFO MNPs) in a short term ultrasonic treatment. Successful reduction of GO into rGO took place during ultrasonic nanocomposite (BFO/rGO) preparation. The synthesized BFO MNP/rGO composites were used to improve the photocatalytic degradation of aqueous bisphenol A (BPA) under visible irradiation. BFO MNPs with sphere-like shapes and an average size of 10–15 nm, smaller than pure BFO MNPs, were homogeneously distributed on the surface of rGO. d spacing values of 3.6 Å and 1.2 Å, corresponding to the (1 0 1) and (0 1 2) lattice planes of BFO MNPs in BFO/rGO nanocomposites, indicate well developed nanocrystallites of BFO MNPs in the nanocomposites. The lower band gap energies of 1.9–2.0 eV were identified for BFO MNP/rGO composites as compared to 2.1 eV for BFO MNP. BFO MNP/rGO composites with 4 wt% of GO exhibited almost complete photocatalytic degradation (>99%) of the BPA under visible light irradiation and the significant reduction of the total organic carbon (TOC) after irradiation for 70 min (78%) and 120 min (100%). Such high photocatalytic degradation for the BFO MNP/rGO composite was mainly attributed to the increased interaction between BPA and rGO due to the very large π-conjugation plane of graphene, decrease in particle size and band gap energy and the lower recombination rate of electron–hole pairs due to the strong electron transfer ability of rGO in the nanocomposites.

1. Introduction

Bisphenol A (2,2-bis (4-hydroxyphenyl) propane, BPA), an organic synthetic compound, is commonly used as an important industrial chemical to manufacture various products such as

* Corresponding author.
E-mail address: bklee@ulsan.ac.kr (B.-K. Lee).

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bottles, packaging, plastics, paper and epoxy resins. During the manufacturing and application processes, most of the BPA used ends up directly or indirectly in the aquatic environment via municipal and industrial wastewater effluent discharge [1]. However, the concentration of BPA varies greatly from the ng L^{-1} to the μg L^{-1} level in different surface water systems, and BPA has become one of the most common organic pollutants in wastewater. Based on current research BPA carries adverse environmental and health risk even at the low dose of 0.05 mg per kg body weight because it can pose potential estrogenic and toxicological risks [2]. BPA in the blood of both men and women has been affected so seriously by disorders of the reproductive system such as endometrial hyperplasia, unnatural genetics, repeated abortion and poly-cystic ovarian syndrome. It was also reported that BPA is associated with diabetes, obesity, and an increased risk of developing miscarriages and cardiovascular disease [3]. Therefore, numerous efforts have been dedicated to develop new efficient and sustainable treatment technologies for the purpose of removing BPA from aqueous solutions [4,5].

Heterogeneous photocatalytic materials have been found to show excited attention in the past decade due to world-wide environmental issues, especially pollution of air and water [6,7].

Perovskite bismuth ferrite ($BiFeO_3$), currently known as one of the most well-known single-phase materials, has a ferroelectric Curie temperature T_C = 830 °C and an antiferromagnetic Neel temperature T_N = 370 °C [8]. $BiFeO_3$ magnetic nanoparticles (BFO MNPs) have recently drawn much attention for both water splitting and the degradation of organic pollutants due to their narrow band gap energy of 2.2 eV. The photocatalytic performance of BFO MNPs can be improved by controlling its size and shape, doping it with metal ions for band engineering [9], and designing relevant nanocomposites, as well as by preparing BFO samples, i.e., nanoparticles[10], nanowires [11], micro cubes [12] and porous thin films [13] with a large surface area.

Graphene, a new two-dimensional allotrope of crystallinecarbon, has become a rapidly rising star in materials science and condensed-matter physics because of its high surface area, good electrical conductivity and strong mechanical stability. Thus, graphene has undergone a great deal of promising research for a wide range of applications in various areas such as nanoelectronics, sensors, catalysts and energy conversion since its discovery in 2004 [14]. The introduction of graphene in the structure of semiconductor oxides as the nanoscale substrates for the formation of nonocomposites with metal oxides can significantly enhance the photocatalytic activity of metal oxide under visible light irradiation [15,16] and affect the morphology, particle size, band structure and band gap energy of the modified semiconductor oxide due to an idea to obtain a hybrid which can be combined both properties of graphene oxide (GO) as fascinating paper-shape material and the features of single nano-sized metal oxide particles. Because of the importance of understanding the mechanism of the coupling between GO and semiconductor oxides, the product is currently being intensively investigated as a photocatalyst. However, little attention has been directed toward BFO-GO nanocomposites.

Today, ultrasound has been proposed to be an effective method for the synthesis of inorganic nanoparticles/graphene composites [17]. When liquids are treated with ultrasonic irradiation, sonic cavitation make an extremely high temperature about 5000 K, very high cooling rate around 1010 K/s and high pressure about 20 MPa. Such unusual chemical environments from asymmetric cavitation lead to promote or accelerate chemical reaction and also for the synthesis and modification of nanosized inorganic materials with functionality, which are not generally accessible in conventional synthesis methods [18,19].

The main aim of this study is to sustainably introduce GO into BFO MNPs via a short term ultrasonic mixing of BFO MNPs and GO to create a BFO MNPs/rGO composite with exceptional properties, which can greatly contribute to improving the photocatalytic degradation of BPA from aqueous solutions under visible light irradiation.

2. Materials and methods

2.1. Chemical and materials

Pure grade graphite powder, 98% sulfuric acid (H_2SO_4), 85% phosphoric acid (H_3PO_4), potassium permanganate (KMnO4), hydrochloric acid (HCl) and ethylene glycol (EG) were purchased from Merck. Iron nitrate (Fe $(NO_3)_3{\cdot}9H_2O$), bismuth nitrate (Bi $(NO_3)_3{\cdot}5H_2O$) and bisphenol A (BPA) purchased from Aldrich and Hydrogen peroxide (30%, H_2O_2) purchased from Fluka were used without further purification. Ethanol without further purification and de-ionized water were used for the sample preparation.

2.2. Preparation of nanoparticles

Typical experimental procedures for the synthesis of BFO/rGO nanocomposite were as follows.

2.2.1. Preparation of graphene oxide (GO)

Graphene oxide (GO) was obtained using the ultrasonic modified Hummers method. 1 g of graphite and 6 g of $KMnO_4$ were added to 120 mL H_2SO_4 (98%) and 13.3 mL H_3PO_4 (85%). The mixture was then irradiated for 50 min in an ultrasonic bath at 30 °C to obtain a dark brown suspension. 1 mL H_2O_2 (30%) was gradually added to 266 mL of deionized (DI) water to reduce residual permanganate into soluble manganese ions. The color of the mixture changed from dark brown to dark yellow. The mixture was filtered and washed with HCl aqueous solution to remove metal ions and then centrifuged at 6000 rpm. The filtered materials were washed with distilled water to remove residual acids and other impurities and the centrifugation step was repeated. Finally, the resulting solid was dried in an oven at 70 °C for 24 h to obtain GO.

2.2.2. Preparation of BFO MNPs

First, 0.0016 mol of Bi$(NO_3)_3{\cdot}5H_2O$ in ethylene glycol (EG) was placed in an ultrasonic bath and irradiated for 2 min to form a clear, homogenous solution at a temperature of 25 °C. Then, a stoichiometric proportion of Fe $(NO_3)_3{\cdot}9H_2O$ was added to the solution and irradiated for another 10 min at the same temperature to get a brownish red sol. The sample was kept in the oven at a temperature of 60 °C for 24 h to form a xerogel. BFO MNPs powders were subsequently obtained by calcination of the xerogel powder with a heating rate of 6 °C/min for 0.5 h at 500 °C.

2.2.3. Preparation of BFO/ reduced graphene oxide (rGO) nano composite

In order to introduce GO sheets into BFO MNPs, a number of BFO MNPs and GO were dispersed into absolute ethanol solution and irradiated ultrasonically in an ultrasonic bath for 10 min at a temperature of 40 °C. The obtained mixture was dried in the oven at 60 °C for 8 h. By changing the graphene content, several BFO/rGO nanocomposite samples with GO weight fractions of 2% and 4% were successfully prepared. Finally, the powders was washed with distilled water and absolute alcohol several times and dried at room temperature.

2.3. Characterization and equipment

Structural analysis of the nanocrystalline powders are studied using XRD (BrukerD8Advance) with monochromatic Cu Kα radia-