Sonochemical Synthesis of Copper-doped BiVO₄/g-C₃N₄ Nanocomposite Materials for Photocatalytic Degradation of Bisphenol A under Simulated Sunlight Irradiation

Gang-Juan Lee 1, Xin-Yu Lee 1, Cong Lyu 2, Na Liu 2, Sambandam Andandan 3 and Jerry J. Wu 1,*

1 Department of Environmental Engineering and Science, Feng Chia University, Taichung 407, Taiwan; leeganjiuan@gmail.com (G.-J.L.); chatter850603@gmail.com (X.-Y.L.)
2 College of New Energy and Environment, Jilin University, Changchun 130021, China; lvcong@jlu.edu.cn (C.L.); liuna@jlu.edu.cn (N.L.)
3 Nanomaterials & Solar Energy Conversion Lab, Department of Chemistry, National Institute of Technology, Trichy 620015, India; sanand@nitt.edu
* Correspondence: jjwu@mai.fcu.edu.tw; Tel.: +886-4-24517250 (ext. 5206); Fax: +886-4-24517686

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Abstract: Copper-doped bismuth vanadate/graphitic carbon nitride (BiVO₄/g-C₃N₄) nanocomposite materials were successfully fabricated using a sonochemical approach. Cu-doped BiVO₄/g-C₃N₄ nanocomposite photocatalysts could improve electron/hole (e⁻/h⁺) pair separation, stability, and light-harvesting efficiency compared to pristine BiVO₄ or g-C₃N₄, resulting in the enhancement of photocatalytic activity. The optimal parameters, such as pH value at 10, photocatalyst dosage of 0.4 g L⁻¹, and 10 mol% Cu-doped BiVO₄/g-C₃N₄ photocatalyst, were determined to degrade initial concentration of 20 ppm Bisphenol A, which could be completely removed after 90 min. Furthermore, the excessive doping of copper (> 10 mol%) could not synthesize the pure monoclinic scheelite phase, which substantially resulted in the reduction of the photocatalytic activity.

Keywords: sonochemical synthesis; composite nanomaterials; photocatalytic degradation

1. Introduction

Bismuth vanadate (BiVO₄) has three crystal phases, such as tetragonal-scheelite, monoclinic scheelite, and zircon. Among those, the monoclinic phase, in particular, exhibits outstanding visible-light photocatalytic properties because monoclinic scheelite BiVO₄ possesses the small bandgap 2.4 eV [1–5]. Dong et al. (2016) [6] prepared monoclinic scheelite BiVO₄ semiconductors with porous structures using a two-step method. The porous BiVO₄ material prepared at hydrothermal temperatures of 200 °C displays enhanced photocatalytic efficiency by degrading methylene blue (MB). Sun et al. (2019) revealed that the two-dimensional BiVO₄ nanosheets/reduced graphene oxide (RGO) exhibited higher photocatalytic activity [7]. In addition, the heterojunction of semiconductor composite has been reported to be an effective strategy to fabricate efficient photocatalysts [6]. Xie et al. (2018) exhibited that the BiVO₄/Mn-Zn ferrite (Mn₁₋ₓZnxFe₂O₄)/RGO photocatalyst could degrade rhodamine B (Rhb) about 96% [8]. Thus, in this article, we chose graphitic carbon nitride (g-C₃N₄) to modify BiVO₄ to enhance photocatalytic efficiency due to graphene-like structure, good thermal and chemical stability, good visible light absorption, and photocatalytic properties of g-C₃N₄ [6]. In addition, g-C₃N₄ nanosheets could enhance an easier electron transfer during the reaction [9]. Smykalova et al. (2019) indicated that g-C₃N₄ nanosheets possessed a large specific surface area, which
resulted in the higher degradation ratio of medicines in water [10]. Zhang et al. (2017) indicated that the composite with 7 wt% g-C3N4 had better photocatalytic efficiency than bare BiVO4 [11]. The stable core/shell structure of the BiVO4/g-C3N4 composite material not only enlarges the surface area but also enhances the photo-generated charge separation. Therefore, a new composite photocatalyst is expected to improve the stability, solar light utilization, charge separation, and transfer by combining with the two semiconductors.

BPA (bisphenol A) is not only a synthetic organic chemical with various applications in the polymer industry used as intermediate for the production of epoxy resins and plastics but also an endocrine disruptor, which would lead to serious ecology exacerbation [12,13]. Some researchers have shown that exposure to very low BPA levels may result in reduced fertility and increased incidence of breast, ovarian, and testicular cancers [13]. Therefore, BPA should be completely removed from the water for safety consideration to human beings. In this research, we prepared the BiVO4 nanocomposite photocatalysts at 60 °C, 1 atm, and 1.5 h via a sonochemical synthesis way. The advantage of sonochemistry in fabricating nanostructured samples occurs mostly from acoustic cavitation [14]. In addition, we also introduced the synthesis of copper and g-C3N4-modified BiVO4 and removal of BPA using photocatalytic reaction under simulated sunlight irradiation. Some parameters that affect the efficiency of BPA removal via the photocatalytic degradation process, including the pH values in solution, the dosages of BiVO4 nanocomposite material, and the various BiVO4 nanocomposite materials, were studied.

2. Methods

2.1. Sonochemical Synthesis of BiVO4 Nanocomposite Photocatalysts

A total of 5 g urea (NH2CONH2, NIHON SHIYAKU REAGENT) was added into an aluminum crucible, and subsequent thermal treatment at 550 °C for 2 h with 5 °C min−1 of heating rate in argon atmosphere could obtain a light-yellow powder composed of g-C3N4 nanoparticles. A total of 3.38 g bismuth (III) nitrate pentahydrate (Bi(NO3)3·5H2O, Alfa Aesar) was placed in 40 mL of 2 M nitric acid solution (solution A). Then, 0–40 wt% g-C3N4 was put into solution A to be stirred for 1 h. The 0.81 g ammonium metavanadate (NH4VO3, Acros) was dissolved in 40 mL of deionized (DI) water (solution B). The 1 wt% surfactant, such as citric acid monohydrate (CIT, C6H8O7·H2O, fw: 192.12, SHOWA), (1-hexadecyl)trimethylammonium bromide (CTAB, CH3(CH2)15N(CH3)3Br, fw: 364.42, Alfa Aesar), and polyethylene glycol (PEG, C2nH4n+2O)n+1, fw: 4,000, SHOWA), was added into the solution B. The 0–20 mol% copper (II) acetate monohydrate (Cu(CH3COO)2·H2O, Merck) was also added in 20 mL of DI water (solution C). Subsequently, solution A and solution C were added into solution B. Then, the reaction mixture was treated with a sonochemical instrument (700 W, 20 kHz, Q700 SONICATOR) for 0.5 h–2 h at 60 °C [4]. Finally, the copper-doped BiVO4/g-C3N4 samples were collected.

2.2. Characterization of BiVO4 Nanocomposite Photocatalysts

The morphologies were examined by the JEOL JSM-7800F model and the JEOL JEM-2010 model. The XRD patterns were examined by the Rigaku Ultima III diffractometer (Rigaku Japan Sales Division, Tokyo, Japan). Particle size distribution, bandgap, and photoluminescence (PL) properties were measured using the Shimadzu SALD-2300 model, Shimadzu UV-2600 and Shimadzu RF-3501 spectrometer (Shimadzu Corporation, Tokyo, Japan), respectively. The flat-band potential of the sample was recorded using potentiostat/galvanostat PGSTAT302N, Metrohm Autolab (Metrohm AG, Herisau, Switzerland). The surface area, pore size, and pore volume were measured by using a Micrometrics ASAP-2020 nitrogen adsorption instrument (Micrometrics Headquarters, Norcross, GA, USA).

2.3. Photocatalytic Reaction

Typically, an appropriate amount of BiVO4 nanocomposite material was put into 100 mL of BPA solution (4,4’-dihydroxy-2,2-diphenylpropane, Bisphenol A, C15H16O2, ECHO) with a concentration
of 20 ppm. The reactor was irradiated with a 350 W Xenon light (KIT-XENON-ADJ350W) for 6 h. During the experiment, about 1.5 mL sample was withdrawn at predetermined time intervals, and the sample was immediately filtered through the 0.22 µm polyvinylidene difluoride (PVDF) syringe filter to remove the powders, and the clarified solution was analyzed by High-performance liquid chromatography (HPLC, LC-20A, Shimadzu Corporation, Tokyo, Japan).

3. Results

3.1. Characterization of BiVO₄ Nanocomposite Photocatalysts

Reaction conditions could effectively affect the morphology of photocatalysts. Figure 1a–d show when irradiation time was extended, the particle size of BiVO₄ nanoparticles could gradually enlarge. As time was irradiated for 1.5 h, BiVO₄ samples had the uniform particle size and the rough surface. The phase and crystallographic nanostructures of the BiVO₄ particles are shown in Figure 1e. The major diffraction peaks at 18.83°, 28.84°, 30.56°, 34.51°, 35.22°, 39.96°, 42.40°, 45.84°, 46.74°, 47.25°, 50.28°, and 53.22° belonged to the (011), (121), (040), (200), (002), (211), (051), (132), (240), (042), (202), and (161) planes of BiVO₄ nanostructures and matched well with the crystal phase of monoclinic BiVO₄ (JCPDS Card No. 14-0688, cell parameter a = 5.195 Å, b = 11.70 Å, and c = 5.092 Å). No other impurities could be detected. This also indicated that the ultrasonic time did not influence the crystal structure.

According to our previous study, surfactant would affect the formation of various morphological structures [15]. Therefore, we used three types of surfactants to control the particle size of BiVO₄, such as CIT (chelating agent), CTAB (cationic surfactant), and PEG (non-ionic surfactant). Figure 1f–h show FE-SEM images and particle size distribution of BiVO₄ with various surfactants. The particle size distribution (D₅₀) of BiVO₄ with surfactants significantly decreased from 11.971 µm to 0.330 µm, which could be attributed to better dispersibility by adding the surfactants with long molecular chain and hydrophilic end during the synthetic process [16–18]. Therefore, the smaller particle size could be formed than that of pristine BiVO₄.

The BiVO₄ photocatalyst was further modified by g-C₃N₄ and copper in order to promote the photocatalytic activity. The results were confirmed by HR-TEM measurement on the 10Cu/BiVO₄/g-C₃N₄ powders (Figure 2). The corresponding selected area electron diffraction (SAED) pattern indicated rings; the as-synthesized BiVO₄ nanocomposite photocatalysts was the polycrystalline structure (Figure 2b). Furthermore, the element of Bi, V, O, C, N, and Cu substantially existed in the sample from the EDX image and TEM-EDX element mapping (Figure 2c–i). The bandgap of g-C₃N₄ and copper-modified BiVO₄ slightly reduced from 2.47 eV to 2.28 eV (Figure 3a). The PL spectra of the BiVO₄ samples are exhibited in Figure 3b. BiVO₄ photocatalyst displayed two peaks at 530.7 nm and 357.7 nm [19]. The g-C₃N₄ had its characteristic peak around at 450.4 nm [20]. In addition, the pristine BiVO₄ sample had higher PL intensity than that of g-C₃N₄ and copper-modified BiVO₄ samples. In other words, the e⁻/h⁺ recombination rate could be efficiently restrained in the g-C₃N₄ and Cu-modified BiVO₄ samples. In the high concentration of copper (> 10 mol%), the PL peak of BiVO₄ nanocomposite photocatalysts shifted from 530.7 nm to 492.7–469.4 nm due to the fabrication of the tetragonal-scheelite structure BiVO₄, as shown in Figure 4. Therefore, the excessive doping of copper (> 10 mol%) could not synthesize the pure monoclinic scheelite phase, which might result in the reduction of the photocatalytic activity.
Figure 1. FESEM images (a–d), and XRD patterns (e) of BiVO$_4$ photocatalysts with different ultrasound irradiation time (without surfactant). FESEM images (f–h) of BiVO$_4$ materials via various surfactants at 1 wt%. Insets reveal the particle size distribution for the corresponding samples.
3.2. Photocatalytic Degradation Activity

The photocatalytic degradation activities of the BiVO$_4$ nanocomposite photocatalysts were performed for the degradation of wastewater pollutants containing BPA under simulated sunlight irradiation. Photocatalytic parameters of degrading BPA were investigated as below, including the pH values of BPA solution, the dosages of BiVO$_4$ nanocomposite photocatalyst, and the content of copper.
Figure 3. (a) UV-Vis absorption spectra, and (b) photoluminescence spectra of BiVO$_4$/g-C$_3$N$_4$ nanocomposite materials with various amounts of copper.
Figure 4. XRD patterns of BiVO$_4$/g-C$_3$N$_4$ nanocomposite materials with various amounts of copper.

3.2.1. Initial pH of the BPA Solution

Figure 5a plots the photo-degradation of BPA at various pH values. The results could be well fitted by pseudo-first-order kinetics model with a rate constant of $0.0036 \text{ min}^{-1}$, $0.0034 \text{ min}^{-1}$, $0.0072 \text{ min}^{-1}$, $0.0426 \text{ min}^{-1}$, and $0.0053 \text{ min}^{-1}$ for pH value of 4, 7, 9, 10, and 12, respectively. With the increase of the pH value to 10, the BPA could be completely removed to 100% for 120 min. This result could be illustrated by the net signs of the surface charge of the BPA species and BiVO$_4$ nanocomposite photocatalysts at different pH values. Because the dissociation constants ($pK_{a1}$ and $pK_{a2}$) of BPA are 9.6 and 10.2 [21–23], the surface charge of the BPA species is negatively charged under alkaline conditions. In addition, the pH changes also could affect the surface properties of 10Cu/BiVO$_4$/g-C$_3$N$_4$ photocatalyst. Meanwhile, we measured the point of zero charge of 10Cu/BiVO$_4$/g-C$_3$N$_4$ photocatalyst ($pH_{pzc} = 11.3$). Therefore, BPA molecules were adsorbed onto the surface of 10Cu/BiVO$_4$/g-C$_3$N$_4$ photocatalyst via electrostatic interaction (pH smaller than 11.3), which is an important step in the process of photocatalytic degradation. Conversely, BPA was adsorbed weakly onto the negatively charged 10Cu/BiVO$_4$/g-C$_3$N$_4$ surfaces due to the coulombic repulsion (pH greater than 11.3). Based on the above results, the best pH value of the BPA solution for the photocatalytic degradation of BPA was at 10.
Figure 5. (a) Effect of bisphenol A (BPA) photodegradation at the different initial solution pH values on 10Cu/BiVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> photocatalyst. ((BPA): 20 mg L<sup>-1</sup>; catalyst concentration of 0.4 g L<sup>-1</sup>), (b) The zeta potential values of 10Cu/BiVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> photocatalyst, (c) Changes of the apparent BPA photodegradation reaction kinetics at a different dosage of 10Cu/BiVO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> photocatalyst. ((BPA): 20 mg L<sup>-1</sup>; pH = 10).
3.2.2. Photocatalyst Dosage

The photocatalytic efficiency by using metal oxides can be determined by their physical and chemical properties. Physical properties, such as pore size, surface area, and surface charge, could affect the photocatalytic activity [24]. Therefore, the function of the photocatalysts is able to provide effective surface area and play the role of the active center. The effect of photocatalyst dosage on the degradation efficiency was evaluated by various amounts of 10Cu/BiVO$_4$/g-C$_3$N$_4$ from 0.2 g to 0.6 g in a 1000 mL BPA solution. The result of the photo-degradation performance has been depicted in Figure 5c, which exhibits that the rate of degradation increased linearly with an increase in the amount of photocatalyst up to 0.4 g and then decreased. The presence of 10Cu/BiVO$_4$/g-C$_3$N$_4$ photocatalyst could provide more active centers, which led to increased photocatalytic activity. As the amount of photocatalyst increased, the number of BPA molecules adsorbed were increased, leading to an increase in BPA degradation. At higher concentrations of photocatalyst, more surface areas were available for constant BPA molecules. However, more photocatalyst would also induce greater aggregation of the photocatalyst, and the specific surface area decreased, leading to a reduction in the reaction rate. In addition, the inactivation of activated molecules by collision with ground-state molecules might also hinder the photocatalytic efficiency. Hence, above a certain level, additional catalyst amounts were not involved in catalysis reaction, and thus the rate might level off. Hence, the appropriate photocatalyst dosage showed an outstanding performance of photocatalytic degradation.

3.2.3. Cu Doping Content

In view of the above results, we conducted the experiments of the photocatalytic degradation of BPA by BiVO$_4$ nanocomposite photocatalyst equal to 0.4 g L$^{-1}$ at pH 10. Figure 6a exhibits the photocatalytic activity of BiVO$_4$ nanocomposite photocatalysts with various Cu contents. It could be seen that the Cu content in the BiVO$_4$ presented an excellent influence on the photocatalytic activity of BiVO$_4$ nanocomposite materials. The conduction band (CB) edge position and valence band (VB) edge position of bare BiVO$_4$ were about 0.75 eV and 3.22 eV, respectively, leading to a weak reduction ability, as shown in Figure 6b. The 10 mol% Cu-doped BiVO$_4$ photocatalyst could not only shift the CB edge position more negative than the others but also decrease the intensity of PL emission (Figure 3b). Therefore, 10Cu/BiVO$_4$/g-C$_3$N$_4$ photocatalyst had the highest activity ($k = 0.0426$ min$^{-1}$) for photocatalytic degradation. Moreover, the addition of excess Cu contents (> 10 mol%) to synthesize BiVO$_4$ nanocomposite photocatalysts resulted in a reduction in the photocatalytic activity because BiVO$_4$ formed the tetragonal-scheelite phase, as shown in Figure 4. According to the references, we know that the crystal structure of monoclinic type BiVO$_4$ exhibits excellent photocatalytic properties [2–4]. In addition, copper-doped photocatalyst can fabricate the trap energy levels (TEL), and the activated electrons could transfer to TEL$_{Cu}$, which leads to the useful e$^-$/h$^+$ separation [15,16,25–27]. Therefore, the appropriate addition of Cu contents displayed an excellent photocatalytic degradation performance. Furthermore, the 10Cu/BiVO$_4$/g-C$_3$N$_4$ was assigned to the type IV isotherm, displaying with a type H3 hysteresis loop, which indicated the presence of mesopores (2–50 nm), as shown in Figure 7. The BiVO$_4$/g-C$_3$N$_4$ nanocomposite materials with various amounts of copper addition are compared in Table 1, revealing a slight decrease in the surface areas with copper doping. However, the slight loss of specific surface area did not compete with the enhanced activity of doping copper as reaction centers for photocatalytic degradation of BPA.
Figure 6. (a) Changes of the apparent BPA photodegradation reaction kinetics at different photocatalysts. ([BPA]: 20 mg L\(^{-1}\); pH = 10; catalyst concentration of 0.4 g L\(^{-1}\)). (b) Mott–Schottky plots for BiVO\(_4\). (c) Energy-level diagram displaying the conduction band and valence band edge positions of BiVO\(_4/g\)-C\(_3\)N\(_4\) nanocomposite photocatalysts with different amounts of copper.
Figure 7. Nitrogen adsorption-desorption and Brunauer-Emmett-Teller (BJH) pore diameter distribution of 10Cu/BiVO$_4$/g-C$_3$N$_4$.

Table 1. The surface area of BiVO$_4$/g-C$_3$N$_4$ nanocomposite materials with various amounts of copper.

| Cu (mol%) | 0  | 1  | 2  | 3  | 4  | 5  | 10 | 15 | 20 |
|-----------|----|----|----|----|----|----|----|----|----|
| Surface area (m$^2$/g) | 23.1 | 22.6 | 22.1 | 21.5 | 20.6 | 20.0 | 19.4 | 17.0 | 15.6 |

4. Conclusions

BiVO$_4$ nanocomposite photocatalysts were prepared using the sonochemical approach. Cu-doped BiVO$_4$/g-C$_3$N$_4$ nanocomposite photocatalysts exhibited a remarkable improvement in degradation performance. The pH values of BPA solution, the dosages of 10Cu/BiVO$_4$/g-C$_3$N$_4$, and the various types of BiVO$_4$ nanocomposite material had a great influence on the removal efficiency of BPA. The optimal parameters, such as pH value at 10, photocatalyst dosage of 0.4 g L$^{-1}$, and 10 mol% Cu-doped BiVO$_4$/g-C$_3$N$_4$ photocatalyst, were determined to degrade the initial concentration of 20 ppm bisphenol A, which could be completely removed after 90 min.

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