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Pd-nanoparticle-decorated peanut-shaped $BiVO_4$ with improved visible light-driven photocatalytic activity comparable to that of TiO_2 under UV light

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ABSTRACT

Porous, peanut-shaped $BiVO_4$ was prepared and further decorated with palladium nanoparticles on its surface using a photodeposition approach. The well-dispersed palladium nanoparticles were found to suppress photogenerated charge carriers, and may also improve the capacity of $BiVO_4$ to harvest visible light photons due to a local surface plasmon resonance effect. The prepared Pd–$BiVO_4$ composites exhibited excellent photocatalytic activity in the degradation of phenol under visible light irradiation. This performance rivaled that of TiO_2 under UV light. However, the active oxidants in Pd–$BiVO_4$ and TiO_2 processes are different, with photogenerated holes in $BiVO_4$ photocatalysis and OH radicals in TiO_2 photocatalysis. Furthermore, different mechanisms and different pathways for the degradation of phenol under the effects of different oxidants were proposed. This work not only opens up new possibilities for the efficient removal of phenolic compounds in wastewater via visible-light-driven photocatalysis in the presence of a Pd–$BiVO_4$ composite, but also suggests that OH radicals may not be the most important oxidants in all photocatalysis processes.

1. Introduction

Photocatalysis, as one of the advanced oxidation processes (AOPs), has been extensively studied and implemented in various areas, mainly including hydrogen generation and environmental remediation. Recently developed bismuth-based photocatalysts, compared with the traditional and most widely studied photocatalyst, TiO_2, possess advantages such as a suitable bandgap for a visible light response. This property makes it possible to utilize solar irradiation for photocatalysis, which is economically favorable for the implementation of this advanced technology. In addition, a variety of bismuth-based photocatalysts with high activities have been fabricated, increasing the possibility of their being applied in practice [1].

$BiVO_4$ is a ferroelastic and ion-conductive material, whose properties significantly depend on its crystal form [2]. There are three primary forms, zircon with a tetragonal structure (ZT) and scheelite with monoclinic (SM) and tetragonal (ST) structures [3]. It has been reported that the bandgaps of $BiVO_4$ (SM) and $BiVO_4$ (ZT) are 2.4 and 2.9 eV, respectively [4], and that $BiVO_4$ (SM) powder exhibits higher photocatalytic activity for O_2 evolution than $BiVO_4$ (ZT) powder. Zhang et al. have compared $BiVO_4$ (SM) and $BiVO_4$ (ST) for photocatalytic degradation of organic pollutants in water [5]. $BiVO_4$ (SM) showed higher photocatalytic activity than $BiVO_4$ (ST). However, the photocatalytic activity of pure $BiVO_4$ in these three crystal forms is relatively low, most likely resulting from the difficult migration of its photogenerated charge carriers and its poor adsorptive capacity [6]. It should be noted that the above-mentioned problems are not merely those of $BiVO_4$, but also arise for most bismuth-based photocatalysts [1,7–11]. Approaches to overcome these challenges mainly include metal/nonmetal doping [12,13], the formation of heterostructures [14], and morphology adjustments [15].

Interest in the photodeposition of metal nanoparticles has expanded significantly since 1978 [16], and it has increasingly become an effective approach to improving photocatalytic performance under visible light irradiation. Well-dispersed metallic nanoparticles on the surface of a support facilitate the separation of photogenerated electron/hole pairs [17], as well as improving the capacity to harvest photons in the visible light range via the local surface plasmon resonance (SPR) effect [18]. The deposition of silver (Ag) nanoparticles on $BiVO_4$ has been reported to enhance visible-light-induced photocatalytic activity in the degradation of organics [19]. Palladium oxide (PdO)-modified $BiVO_4$ is reported to have enhanced visible-light-driven photocatalytic activity for

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the degradation of methyl orange (MO) [20,21]. In this case, palladium plays an important role in suppressing the recombination of photogenerated e^-/h^+ pairs. However, it took 9 h to completely remove MO, which is still too slow to be used in practice.

As reported, the SPR peaks for palladium (Pd) nanoparticles can be tuned from 410 to 870 nm [22,23]. It can be deduced that depositing palladium nanoparticles on the surface of $BiVO_4$ may be a promising way to significantly improve photocatalytic activity. We recently reported Bi_2MoO_6 hybrid photocatalysts decorated with Pd nanoparticles, which exhibited significantly improved photocatalytic activity in the oxidation of phenol in water [7,24]. This suggests that surface photodeposition of palladium nanoparticles may be a promising approach to facilitating the uptake of photogenerated electrons in order to improve photocatalytic activity. In the context of the morphology of a photocatalyst, it has been demonstrated that porous materials with tailored pore structures are capable of enhancing light harvesting via multiple scattering and facilitating the transfer of organic molecules [25,26]. Among various morphologies of $BiVO_4$, peanut-shaped porous $BiVO_4$ was successfully prepared by a controlled one-step template-free method [27].

In this work, peanut-shaped $BiVO_4$ constructs decorated with palladium nanoparticles were fabricated via a solvothermal method following photodeposition. The photocatalytic activity of as-prepared composites was evaluated with regard to the degradation of a colorless organic model compound, phenol. Phenol is a common pollutant in wastewater from many industrial processes and is refractory to decomposition using traditional approaches due to its high chemical stability [28,29]. A mechanism for photocatalysis in the presence of $BiVO_4$ was proposed and compared with that for TiO_2. This work has shed light on the possibility of applying photodeposited Pd nanoparticles to improve visible-light-driven photocatalysis for the treatment of phenolic compounds in water.

2. Experimental

2.1. Preparation of peanut-shaped $BiVO_4$

Peanut-shaped $BiVO_4$ was prepared as reported [27]. In a typical process, 2 mmol of $Bi(NO_3)_3{\cdot}5H_2O$ (Fisher Scientific, Certified ACS) was first dissolved in 30 mL of ethylene glycol (EG) (Fisher Scientific, Certified ACS), and 2 mmol of NH_4VO_3 (Fisher Scientific, Certified ACS) was dissolved in 20 mL of hot deionized distilled water (DDW). Next, the NH_4VO_3 solution was added dropwise into the $Bi(NO_3)_3$ solution under magnetic stirring for 30 min. After that, the yellow solution was transferred into a 50 mL Teflon-lined autoclave and heated at 100 °C for 15 h. The yellowish precipitates were filtered out and washed twice with DDW and once with ethanol. The precipitates were then dried at 60 °C for 12 h before being collected for further use.

2.2. Preparation of palladium-modified $BiVO_4$ composites

Palladium (Pd)-modified $BiVO_4$ composites were prepared using a photodeposition method as previously reported [7,24]. Specifically, 0.3 g of prepared $BiVO_4$ was dispersed into 40 mL of DDW with magnetic stirring for 10 min. Then a designated amount of $PdCl_2$ (Fisher Scientific Canada, ACS certified) suspension was added under magnetic stirring for another 10 min. After that, the combined suspension was illuminated under a 300 W halogen tungsten projector lamp (Ushio, USA) for 1 h. The resultant products were filtered out, washed twice with DDW, and dried at 60 °C for 12 h. Samples of 1, 2, 4, 8, and 10% Pd–$BiVO_4$ were prepared following the above procedures and labeled as 1, 2, 4, 8, and 10% Pd–Bi.

2.3. Characterization

A Rigaku Ultima IV diffractometer with CuKα radiation ($\lambda = 0.15418$ nm) at 40 kV and 44 mA was used for X-ray diffraction (XRD). Surface composition and chemical states were measured using a XSAM-800 X-ray photoelectron spectroscope (XPS). Morphologies of prepared samples were investigated using a field-emission scanning electron microscope (FE-SEM, JEOL JSM-7500F) and a transmission electron microscope (TEM, JEM-2100F). A Thermo Evolution 300 spectrophotometer was used to study the optical properties of samples through ultraviolet–visible diffuse reflectance spectroscopy (UV–vis DRS). The specific surface area was obtained from N_2 sorption isotherms at 77 K, using an automatic adsorption apparatus and measurement system (ASAP 2020, Micromeritics and Nova 4200E, Quantachrome). The Brunauer–Emmett–Teller (BET) surface area of the samples was calculated using multipoint estimation. Electrochemical properties of prepared samples were performed on a CHI 604E electrochemical analyzer (CH Instruments Inc., USA) with a platinum wire as a counter electrode, a calomel reference electrode, and a working electrode. The working electrode was composed of indium tin oxide (ITO) glass ($75 \times 25 \times 1.1$ mm, 15–25 Ω, Sigma-Aldrich Canada Co.) coated with the prepared samples. The electrolyte was a Na_2SO_4 solution with a concentration of 0.1 mol/L.

2.4. Photocatalytic activity tests

Photocatalytic activity of as-prepared samples was evaluated through the degradation of a colorless organic pollutant, phenol, in water under visible light irradiation. The photoreactor consisted of a 500 mL beaker with a cooling jacket to maintain the system temperature at around 20 °C and a 300-W halogen tungsten projector lamp (wavelength mainly in the range 310–800 nm) with a UV cutoff (Kenko Zeta, transmittance >90%) to filter out irradiation with wavelengths below 410 nm. The irradiation intensity at the surface of the solution was measured by a quantum meter (Biospherical QSL-2100, $400 < \lambda < 700$ nm) to be 1.1×10^{-2} einstein $m^{-2}\,s^{-1}$. For each test, 100 mL of phenol solution with an initial concentration of 10 mg/L was mixed with 0.1 g of photocatalysts. This suspension was first magnetically stirred in the dark for 60 min to ensure that adsorption–desorption equilibrium was reached between the organics and photocatalysts. Photocatalysis started when the light was turned on and lasted for 6 h. During the process, aliquots were drawn and centrifuged at 13,000 rpm for 5 min. The supernatant was analyzed using a high-performance liquid chromatograph (HPLC, Agilent 1100 series) equipped with a UV–vis detector. A ZORBAX Eclipse Plus C18 column (4.6×250 mm) was used at a temperature of 60 °C. The detecting wavelength was fixed at 270 nm for the detection of phenol and possible intermediates. The flow phase was composed of methanol (55%, V/V) and water (45%, V/V) at a flow rate of 0.6 mL/min. The injection volume was set to 25 μL.

In the quenching experiments, ethylenediaminetetraacetic acid disodium (EDTA-2Na) and isopropanol at concentrations of 1 mol/L were added to the reaction system as scavengers for holes and oxidative free radicals, respectively. The concentration of OH radicals produced during photocatalysis was determined using *p*-chlorobenzoic acid (pCBA) as a probe. The initial concentration of pCBA was set to 10 mg/L, the catalyst dosage amount was equal to 1 g/L, and the solution volume was 100 mL. Photocatalytic degradation of pCBA was carried out for 90 min. Aliquots were taken and centrifuged and the supernatant was analyzed using the HPLC with detecting wavelength at 254 nm. All other parame-