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$Cu_2O/BiVO_4$ heterostructures: synthesis and application in simultaneous photocatalytic oxidation of organic dyes and reduction of Cr(VI) under visible light

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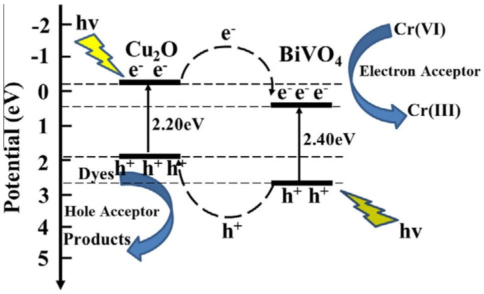
HIGHLIGHTS

- $Cu_2O/BiVO_4$ photocatalyst was synthesized under mild conditions.
- It shows high catalytic activity for the simultaneous removal of dyes and Cr(VI).
- The degradations of cationic and/or anionic dyes operate under neutral condition.
- A synergistic photoreduction–oxidation mechanism is proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

We synthesized $Cu_2O/BiVO_4$ composites by growing Cu_2O nanoparticles on $BiVO_4$ under mild condition. The optimized composite shows high photocatalytic efficiency in the simultaneous oxidation of organic dyes and reduction of Cr(VI) in neutral media. The XPS results confirm that the Cr(VI) adsorbed on $Cu_2O/BiVO_4$ was completely reduced to Cr(III). The photocatalyst can be used for the degradation of cationic or anionic dyes as well as a mixture of them under visible light irradiation. The photocatalytic activity of the composite can be ascribed to the heterojunctions between Cu_2O and $BiVO_4$, which facilitate the separation of photogenerated electrons and holes. The work demonstrates that the as-synthesized $Cu_2O/BiVO_4$ composite is a promising photocatalyst for the treatment of wastewater that contains organic dyes and Cr(VI) ions.

1. Introduction

Arising from industrial processes, toxic (carcinogenic and mutagenic) hexavalent chromium (Cr(VI)) is commonly found in wastewater [1,2]. The reduction of Cr(VI) to less mobile and less toxic Cr(III) is a key procedure in wastewater treatment [3]. Recently, the photocatalytic reduction of Cr(VI) to Cr(III) is considered to be efficient [4–7]. However, the photocatalysts only work under acidic condition, making the processes difficult to handle. To avoid problems such as secondary pollution and catalyst corrosion, it is necessary to develop photocatalysts that can efficiently reduce Cr(VI) under neutral condition.

For the treatment of wastewater, the degradation of organic dyes by a photocatalytic approach is found to be applicable [8]. In photooxidation, dyes are oxidized by photogenerated holes [9,10]. In wastewater treatment, the presence of different kinds of pollutants is common [11]. In a case such as the coexistence of Cr(VI) and organic dyes, it is highly desirable to reduce Cr(VI)

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and to oxidize dyes simultaneously using a single photocatalyst. Such an idea was investigated over TiO_2-based photocatalysts in the past years [10,12–14]. Yu et al. [10] reported simultaneous oxidation of RY15 and reduction of Cr(VI) at TiO_2-BDD heterojunctions under UV illumination. Kyung et al. [15] and Sun et al. [16] investigated the photoinduced dye oxidation and Cr(VI) reduction in acidic suspension using TiO_2 under visible-light illumination. Nonetheless, TiO_2 can only be excited under UV irradiation and the quantum yield is low. Furthermore, the photocatalysts developed so far function only in an acidic medium and the use of a sacrificial agent is a necessity. To be practical for the simultaneous reduction of Cr(VI) and oxidation of organic dyes, it is imperative to design photocatalysts that work in neutral media under visible light without the need of a sacrificial agent.

Bismuth-based compounds are cheap and nontoxic. Due to their unique electronic structures, they are efficient photocatalysts [17–19]. With a valence band edge of ca. +2.4 V (vs. NHE) and excellent ability for visible light absorption (E_g = 2.4 eV), the n-type monoclinic bismuth vanadate (m-$BiVO_4$) is used for the oxidation of organic dyes under visible-light irradiation. Furthermore, the conduction band edge of m-$BiVO_4$ (ca. 0 V vs. NHE) is more negative than that of Cr(VI)/Cr(III) (E^0 = 1.33 vs. NHE) [20]. It is envisaged that one can achieve simultaneous photocatalytic reduction of Cr(VI) and oxidation of organic dyes over m-$BiVO_4$. However, it is known that the activity of $BiVO_4$ is usually not satisfactory due to the high recombination rate of photogenerated electrons and holes. One of the ways to improve the separation of charge carriers is to combine $BiVO_4$ with a semiconductor of appropriate band position [21,22]. With successful cases such as Ag/$BiVO_4$ [19], Bi_2O_3/$BiVO_4$ [21], and $Bi_2O_2CO_3$/BiOI [22] in mind, we turn our attention to composites that can be used for simultaneous photoredox reactions. Cu_2O is a p-type semiconductor with a direct band gap of 2.0 eV [23,24]. The conduction band edge of Cu_2O is much higher than that of $BiVO_4$. At Cu_2O/$BiVO_4$ heterojunctions, there is easy transfer of photoelectrons from the conduction band of Cu_2O to that of $BiVO_4$, consequently enhancing the separation of charge carriers and promoting the photocatalytic activity of $BiVO_4$.

In this study, Cu_2O/$BiVO_4$ composites were fabricated by a two-step method. Their photocatalytic efficiency towards the simultaneous reduction of Cr(VI) and oxidation of organic dyes in a neutral medium under visible light irradiation was evaluated. The Cu_2O/$BiVO_4$ composites were tested for the photodegradation of cationic and anionic dyes, individually as well as in the form of a mixture. Through the determination of major active species during the photocatalytic process, we establish the mechanism of the synchronized actions of photoreduction/oxidation. To the best of our knowledge, investigation of this kind over Cu_2O/$BiVO_4$ composites has never been reported.

2. Experimental

2.1. Synthesis

All reagents were of analytical grade and commercially available. They were used without further purification. The Cu_2O/$BiVO_4$ composites were prepared by a two-step method. First, $BiVO_4$ was prepared through a homogeneous co-precipitation process (HCP) reported elsewhere [25]. Second, with constant low-speed stirring, a designated amount of as-prepared $BiVO_4$ was added into a mixed solution (80 mL) of 0.5 g PVP and 0.1 mmol (17 mg) $CuCl_2 \cdot H_2O$, while the pH was maintained at 8.5 (by adding 0.01 M sodium hydroxide dropwise). Finally, 8 mL of 0.1 M hydrazine hydrate ($N_2H_4 \cdot H_2O$) was added with constant stirring to the above solution. The resulting solution was heated to 45 °C and kept at this temperature for 1 h with constant stirring. The precipitate was recovered by centrifugation, washed with water and absolute ethyl alcohol, and dried at 60 °C. The harvested composites with Cu_2O mole percentage of 2.5%, 5% and 7.5% are denoted hereinafter as 2.5%-Cu_2O/$BiVO_4$, 5%-Cu_2O/$BiVO_4$ and 7.5%-Cu_2O/$BiVO_4$, accordingly.

2.2. Characterization

The Cu_2O, $BiVO_4$, and Cu_2O/$BiVO_4$ samples in the form of powder were collected and characterized by powder X-ray diffraction (XRD) on a Brüker Automatic Diffractometer (Bruker D8 Advance) with mono-chromatized Cu-Kα radiation (λ = 0.15406 nm) at a setting of 40 kV and 80 mA. The scanning rate was 0.02° s^{-1} and the scanning range was 10–80° (2θ). The micro- and nano-structures as well as the morphology of as-prepared samples were examined using a field emission scanning electron microscope (FE-SEM) (Hitachi S-4800). Images of transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were taken over a JEM-3010F transmission electron microscope at an accelerating voltage of 200 kV. UV–vis diffuse reflectance spectra (UV–vis DRS) of samples were obtained over a UV–vis spectrophotometer (Cary 100) using $BaSO_4$ as reference. X-ray photoelectron spectroscopy (XPS) was used to determine the Bi4f, V2p, Cu2p, Cr2p and O1s binding energies (BEs) of surface bismuth, vanadium, copper, chromium and oxygen species, using Mg-Kα ($h\nu$ = 1253.6 eV) as excitation source (XPS, SSX-100, Mg-Kα). The pH of solutions was measured using OHAUS STARTER 2100/3C. The element analysis was carried out by ICP-AES (IRIS1000). The photoluminescence (PL) spectra were recorded using a Hitachi F-7000 fluorescence spectrophotometer.

2.3. Catalyst evaluation

The photoreduction of Cr(VI) and the photocatalytic degradation of methylene blue (MB), rhodamine B (RhB), crystal violet (CV), methyl orange (MO) as well as their mixtures were adopted to evaluate the photocatalytic activities of the as-synthesized Cu_2O/$BiVO_4$ samples. The molecular formulae and the lambda maxima of dyes are given in Table 1. Typically, 50 mg photocatalyst was added to a 100 mL aqueous solution of MB, RhB, CV or MO (2×10^{-5} mol/L) in a homemade Pyrex glass vessel. When it was the simultaneous degradation of organic dyes and reduction of Cr(VI), 100 mg photocatalyst was added into a homemade Pyrex glass vessel containing 50 mL aqueous solution of organic dye (2×10^{-5} mol/L) and Cr(VI) (3×10^{-5} mol/L). Before illumination, the suspension was stirred (using a magnetic stirrer) for 30 min in the dark to establish adsorption–desorption equilibrium. Afterwards, the contents were exposed to visible light ($\lambda \geqslant$ 400 nm) originated from a 300 W Xe lamp with a 400 nm cutoff-filter. The distance between the light and the liquid surface was 25 cm. The content was sampled (about 4 mL) at selected intervals. With the catalyst removed by centrifugation (10000 r/min for 3 min), the concentration of residual dye in the solution was determined over a Cary-100 UV–vis spectrophotometer.

Cr(VI) concentrations were measured using the 1,5-diphenylcarbazide (DPC) colorimetric method [16,26] by monitoring the

Table 1
Description of dyes.

Name	The molecular formulae	The maximum absorption wavelength (λ_{max}) (nm)
Methylene blue (MB)	$C_{16}H_{18}ClN_3S \cdot 3H_2O$	664
Rhodamine B (RhB)	$C_{28}H_{31}ClN_2O_3$	552
Crystal violet (CV)	$C_{25}H_{30}N_3Cl \cdot 9H_2O$	590
Methyl orange (MO)	$C_{14}H_{14}N_3SO_3Na$	463