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BiVO₄/Cobalt Phthalocyanine (CoPc) Nanofiber Heterostructures: Synthesis, Characterization and Application in Photodegradation of Methylene Blue

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BiVO₄/cobalt phthalocyanine (CoPc) hierarchical nanostructures_{OI:} Were^{warticle Online} prepared. The structural and photo-chemical properties were characterized with X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), UV-vis Diffuse reflectance spectroscopy (DRS) and Brunauer-Emmett-Teller (BET) surface area test. The samples are well-defined hierarchical nanostructures, and its absorption was extended to the near-infrared region. The photocatalytic activities of the BiVO₄/CoPc photocatalysts were evaluated by the decomposition of methylene blue (MB) under visible light irradiation and showed excellent visible light photocatalytic performances than the BiVO₄ nanofiber.

1. Introduction

TiO₂ is the most investigated photocatalyst because of it owned properties including nontoxicity, easy availability, low cost etc.^{1,2}.Nevertheless, the energy band gap of TiO₂ (ca. 3.2 eV) limits its application because the electron-hole pairs can only be exited by UV light with wavelength shorter than 380 nm^{3,4}. Therefore, in view of solar energy utilization, the search for semiconductor photocatalysts that can harvest the wide spectrum of solar light, from ultraviolet to visible light wavelength, and achieve efficient solar energy conversion remains one of the most meaningful missions. Developing the new non titania types of photocatalysts considered to be active under visible light is an attractive research area⁵. Bismuth vanadate species are such promising kinds of materials and recently are being used as active visible-light driven photocatalysts⁶⁻⁹. Its monoclinic phase has shown high photocatalytic activity and it is also non-toxic and chemically stable in aqueous solution under irradiation. However, monoclinic BiVO₄ usually shows low photocatalytic activity due to the poor charge-transport properties¹⁰. Phthalocyanine complexes are also known as a

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new type of visible light active materials¹¹. These organometallic compounds are appealing and have attracted many interests in various fields including homogeneous and heterogeneous catalysis¹². Metal phthalocyanines have been used as the sensitizers for TiO_2 and enhanced the photocatalytic activity¹³.

In this study, we prepared BiVO₄ nanofiber by electrospinning and followed by immobilized of cobalt phthalocyanine (CoPc) molecules onto the surface of the fiber. Photochemical activity of the final products was studied from the degradation of MB and compared with the unmodified catalysts. We found that the BiVO4/CoPc samples enhanced the photocatalytic activity apparently compared pure BiVO₄ fiber.

2. EXPERIMENTAL SECTION

2.1 Preparation of the BiVO₄ nanofibers

All reagents were of the analytical purity and used without further treatment. In a typical experimental procedure, 0.195 g Bi(NO₃)₃·5H₂O (0.4 mmol) and 0.5 g citrate acid were added into 1.4 mL deionized water with magnetic stirring to form a suspension, and then 0.0468 g (0.4 mmol) NH₄VO₃ were dissolved in 2 mL deionized water to form a solution. The above suspension and the solution were mixed, and subsequently nitric acid was added to adjust the pH value to 1 form a solution. Finally, it was mixed with 10 mL polyvinylpyrrolidone (PVP, Mw=1300 000) ethanol solution (0.1 g/mL) to form the spinnable precursor sol. The precursor sol were drawn into the needle tube, and the inner diameter of the needle is 0.5 mm. The electrospinning voltage was set as 25 kV with a pumping speed of 0.0015 mm/s while the distance between needle and collector is 30 cm. After electrospinning, the mat-like gel fibers

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were obtained. Then it was heated to 500 °C in a furnace with a heating rate $2^{D_{\Theta}C_{1}^{10}1039/C4RA08759C}$ and kept for 1 h and finally cooled to room temperature naturally to obtain the BiVO₄ nanofibers.

2.2 Synthesis of CoPc

6.67 g C₆H₄(CO)₂O, 1.79 g CoCl₃, 13.64 g CO(NH₂)₂ and 0.47 g $H_{24}Mo_7N_6O_{24}\cdot 4H_2O$ were mixed in a 100 mL beaker, and the beaker was heated to 140 °C in a furnace for 5 h. Taken out of the beaker, grinding the sample to granular and then heated to 200 °C in furnace for 2 h. After cooling, 20 mL ammonia added into the beaker, cover with plastic wrap, heated to ammonia boiling for 15 minutes, cooling and filtering. The products were washed with deionized water, ethanol and toluene for several times and then dried at 150 °C for 10 h, the CoPc was obtained. The UV-vis spectrum of the CoPc as shown in Fig. 3b.

2.3 Fabrication of the CoPc/BiVO₄ hierarchical nanostructures

0.5 g CoPc dissolved in 15 mL glycol was added into a 20 mL Teflon-lined autoclave, then 0.15 g BiVO₄ nanofibers were added into the system. The autoclave was heated to 180 °C for 18 h. The sample was washed with deionized water and ethanol for several times, then dried at 70 °C for 10 h for further characterization.

2.4 Characterization

Fourier transform infrared spectroscopy (FT-IR) spectrum was tested on Infrared Spectrometer (IR Prestige-21). X-ray diffraction (XRD) patterns of the samples were measured on a D8 ADVANCE X-ray diffractometer (Bruker, Germany), using monochromatized Cu Ka ($\lambda = 0.15418$ nm) radiation with a scan range from 10 to 90°.

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The accelerating voltage and the applied current were 40 kV and 40 mA. The morphologies and microstructures of as-prepared samples were analyzed by a FESEM-4800 field emission scanning electron microscope (SEM, Hitachi). The Brunauer-Emmett-Teller (BET) surface area was determined by nitrogen sorption using a Micromeritics ASAP 2020 analyzer. The UV-vis diffuse reflectance spectroscopy (DRS) of the sample was recorded on a UV-2550 spectrophotometer (Shimadzu) in the wavelength range of 200-800 nm.

2.5 Photocatalytic activity measurement

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The photocatalytic activities of the samples were evaluated by the degradation of MB under irradiation by using a 500 W Xe lamp with cutoff filter ($\lambda \ge 400$ nm), which was set about 12 cm from the liquid surface of the MB suspension, and the irradiation area was approximately 25 cm². The initial concentration of MB solution was 20 mg/L. 0.06 g photocatalysts were put into 40 mL MB solution. Before the photodegradation experiment was initiated, the suspension was magnetically stirred in the dark for 30 min. Once the photodegradation experiment started, at given time intervals, 4 mL solution was sampled and centrifuged to remove the photocatalysts. The filtrates were analyzed by the variations of the maximum absorbance (664 nm) in the UV-vis spectrum of MB with a UV-2550 spectrophotometer. The ratio (C/C_0) of MB concentrations was adopted to evaluate the photocatalytic performance. The concentration is proportional to the absorbance of the MB, so we calculated the C/C_0 by the ratio of the variations of the maximum absorbance of the MB, C_0 represents the concentration when the adsorption-desorption equilibrium. A radical trapping

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experiment was performed in the same condition of degradation for MB. The trapping molecule concentration was 1 mM L⁻¹, and the stabilization time was 30 minutes. The dye mineralization degree was monitored by analyzing the total organic carbon content (TOC) in the solutions at different irradiation times. The samples were analyzed in a Shimadzu VSCN8 TOC analyzer.

3. RESULTS AND DISCUSSION

X-ray diffraction patterns of the prepared samples are shown in Fig. 1. The characteristic diffraction peaks for the monoclinic BiVO₄ phase are confirmed by comparing the XRD data with those reported in literature¹⁴. It is obvious that monoclinic phase is the dominant phase. The main XRD peaks for the monoclinic phase appear at around 18.7, 19, 28.9 and 30.6° (attributed to [101], [011], [112] and [004] crystal planes, respectively). As for the BiVO₄/CoPc samples, the diffraction peaks of the CoPc were not observed, which might be due to the low mass of the CoPc.



Fig. 1 The X-ray diffraction patterns of BiVO₄ and BiVO₄/CoPc samples.

The FT-IR spectra of the prepared samples are shown in Fig. 2. The pure BiVO₄ has a broad band between 650 and 850 cm⁻¹, which is attributed to Bi-O and V-O vibrations¹⁵. From the curve of the BiVO₄/CoPc samples, the sample appeared several

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absorption peaks at around 1090, 1165, 1280, 1420, 1460, and 1605 cm^{-pOL10,1030/C4RA08759C} might be assigned to phthalocyanine skeletal and metal-ligand vibrations, respectively^{16,17}. And, the other absorption peaks at 1502 and 1605 cm⁻¹ may be assigned to the C=N stretching and symmetric C=C stretching on the aromatic ring structure of the CoPc molecule. And, these peaks were also observed in the FT-IR spectrum of pure CoPc.



Fig. 2 The FT-IR spectra of BiVO₄, CoPc and BiVO₄/CoPc samples.

The DRS of the prepared BiVO₄, BiVO₄/CoPc and CoPc samples are shown in Fig. 3. The BiVO₄ sample exhibit the absorption in the visible light range and we can ascertain the band gap of BiVO₄ fiber in this paper by the equation⁹: Eg=1240/ λ , λ is the value of the target line to the X-axis, the band gap of BiVO₄ fiber and BiVO₄/CoPc samples prepared in this paper were about 2.4 eV and 2.39 eV, respectively. The CoPc sample is present mainly as monomers, characterized by the sharp absorption bands in the Soret (350 nm) and in the Q-band region (around 680 nm)¹³. Furthermore, for the BiVO₄/CoPc samples, the adsorb edge shifted slightly toward higher wavelengths compared with BiVO₄ and the composite exhibits remarkable absorbance in near-IR region. the distinguished bands around 650 and 600 nm are attributed to the monomeric and dimeric forms of cobalt phthalocyanine

species, respectively^{18,19}.





Fig. 3 UV-vis Diffuse reflectance spectra of BiVO₄, BiVO₄/CoPc (a) and CoPc (b) samples.

The SEM micrographs of the samples are shown in Fig. 4. Gel fiber (a) showed well defined fiber morphologies, the lengths of these randomly oriented gel fibers can reach several micrometers, and the diameters of those nanofibers are around 250 nm. The BiVO₄ fiber (b) almost the same morphologies with gel fibers but the diameter reduced to around 200 nm caused by the removal of the PVP in the calcined procedure, and the surface is smooth. As for the BiVO₄/CoPc samples (c), the CoPc nanoparticles with a diameter of ca. 4 nm were grew twining on the surface of BiVO₄ nanofibers and formed the BiVO₄/CoPc nanofiber heterostructures. The EDS analysis (d) of the BiVO₄/CoPc samples, revealing that the samples are composed of Bi, V, O, Co, C and O elements. The results of FT-IR, DRS, SEM and EDS analysis indicate that the BiVO₄/CoPc nanofiber heterostructures samples were successfully synthesized.



Fig. 4 SEM images of the gel fibers (a), the BiVO₄ nanofibers (b), the BiVO₄/CoPc sample (C)

and the EDS analysis (d) of the BiVO₄/CoPc sample.

The possible formation mechanismof the BiVO₄/CoPc hierarchical nanostructure: at the early stage, the CoPc in the form of molecules uniformly distribute in the ethylene glycol solution, grew into the primary seeds on the surface of the BiVO₄ nanofibers through the hydrogen bonds, which formed by the nitro groups of CoPc and the surface hydroxyl groups of BiVO₄ nanofibers, Finally, after further growth, the BiVO₄/CoPc hierarchical nanostructured was prepared.

The Brunauer-Emmett-Teller (BET) specific surface areas of the BiVO₄ and BiVO₄/CoPc samples were investigated by using nitrogen adsorption and desorption isotherms. As shown in Figure 5, the BET specific surface area of BiVO₄/CoPc sample was calculated to be $32.51m^2/g$, which was much larger than the BiVO₄ sample ($16.63m^2/g$). The BiVO₄/CoPc samples exhibit larger specific surface than the BiVO₄ fiber samples for the immobilization of cobalt phthalocyanine on the BiVO₄ surface.

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Fig. 5 Nitrogen absorption-desorption isotherms of BiVO₄ (a) and BiVO₄/CoPc (b) samples.

To prove the photocatalytic activity of the BiVO₄/CoPc nanofiber heterostructures, the decomposition of MB in water under visible light irradiation as a function of irradiation time were investigated (Figure 6 a). For comparison, decomposition abilities of BiVO₄ nanofibers and MB solution with out photocatalysts were measured under the same experimental conditions. As figure 6 a shows, when assembling CoPc

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particles on the surface of BiVO₄ nanofibers, the visible photocatalytic performance^{CARAO8759C} of the BiVO₄/CoPc nanofiber heterostructures is dramatically improved. The corresponding decomposition rate increases to 85% under 120 min irradiation, which is much higher than that of BiVO₄ nanofibers (65%). The MB solution exhibited little photolysis, indicating the photolysis of MB could be ignored in the photocatalysis. The BiVO₄/CoPc nanofiber heterostructures possess enhanced visible photocatalytic activities compared with BiVO₄ fiber samples.



Fig. 6 The photodegradation MB of the BiVO₄/CoPc under visible light irradiation (a), UV-vis

spectra of MB solution degraded by the BiVO₄/CoPc sample(b).

To further make the reaction mechanism clear, the effects of various additives on the photodegradation processes of the BiVO₄/CoPc nanofiber heterostructures for MB are examined. It is well known that EDTA is a very effective trap for holes and tert-butanol (TBA) is widely used for ·OH scavenger¹⁴. From Fig. 7, we can see that EDTA and TBA all lead to a marked suppression of the degradation rate of MB. The results confirm that ·OH and holes play important roles in the mineralization of MB.

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Fig. 7 Various additives on the photodegradation processes of the BiVO₄/CoPc nanofiber heterostructures for MB.

The conduction band of the investigated phthalocyanine complexes is estimated to be -0.9 V and the band gap is about 2 eV²⁰. As calculated in the DRS analysis, the E_g of BiVO₄ is about 2.4 eV, we can calculate the conduction and valence band positions theoretically through the following equation: $E_{VB} = X - E_e + 0.5E_g$, where E_e is the energy of free electrons on the hydrogen scale (\approx 4.5 eV), and X is the Mulliken's electronegativities. For BiVO₄, the value of X is 6.035 and E_g is the band gap¹⁴. The E_{cb} of BiVO₄ prepared in this paper is estimated to be 0.38 eV.

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On the basis of the above results and the earlier reports on the dye-sensitized photocatalytic oxidation of pollutants^{21,22}, a proposed mechanism of visible light-induced photodegradation of MB with the BiVO₄/CoPc hierarchical nanostructures was elucidated schematically in Fig. 8. Upon irradiation with visible light ($\lambda > 400$ nm), the phthalocyanine particles and the BiVO₄ nanofibers are excited and generated the excited charge (e⁻) and the hole (h⁺), the excited charge of CoPc then injected from the excited state of the CoPc particle into the conduction band of the BiVO₄. The hole (h⁺) of BiVO₄ then injected from the valence band of BiVO₄ nanofibers into the valence band of CoPc. Dissolved oxygen molecules reacted with

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conduction band electrons (e⁻) in the BiVO₄ to yield superoxide radical anions (O_2^{-1}), and then protonated to generate the hydroxyl radicals (OH) which has strong oxidization ability to decompose the MB. The hole (h⁺) in the valence band of CoPc reacted with MB directly and decompose the MB to products. Because the interior charge recombination is avoided in the BiVO₄/CoPc hierarchical nanostructures, and the BiVO₄/CoPc samples owned larger specific surface than the BiVO₄ fiber samples can absorb more active species and reactants on their surface, so the visible photocatalytic activity of BiVO₄/CoPc hierarchical nanostructures enhance apparently than the BiVO₄ fiber samples.



Fig.8 Postulate Mechanism of the Visible-Light-Induced Photodegradation of MB with the

BiVO₄/CoPc Heterostructures sample.

In practical applications, the efficient mineralization of organic dyes and pollutants is very important for preventing secondary pollution¹⁴. In order to study the mineralization of the dyes, TOC (Total Organic Carbon) for the MB solution with different irradiation times in the photocatalytic procedure by the BiVO₄/CoPc sample was also investigated. As shown in Fig. 9a, the TOC content decreased to ca. 47% after the irradiation of 120 min. Compared to the degradation in photocatalytic experiment, the value was higher, which is because the bleaching of the dye solution

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goes beyond the inactivation of the chromophore groups in the molecular structure. The complete inactivation of the chromophore groups of MB leads to bleaching of the solution, but not necessarily to mineralization of the dye. The stability of the BiVO₄/CoPc was also evaluated by recycling the catalyst experiment and the photocatalytic activity was examined in each cycle. As shown in Fig. 9b, the photocatalytic activity of the BiVO₄/CoPc does not exhibit obvious loss. After four recycles, the degradation ration for the BiVO₄/CoPc sample is still 79.2%. The decrease of its activity may be due to the slight weight loss in the cycle experiment. The BiVO₄/CoPc sample exhibits high stability and excellent reusability in catalytic process, which facilitates in practical application.



Fig.9 Variation of TOC removal versus time for the MB dye solution (a) and . cycling degradation of MB mediated by BiVO₄/CoPc (b).

4. Conclusions

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The BiVO₄/CoPc heterostructured nanofibers were prepared. The heterostructured BiVO₄/CoPc nanofibers extend the light adsorption to near IR region, owned large specific surface area and possess enhanced visible light photocatalytic activities compared with BiVO₄. This study demonstrate that BiVO₄/CoPc nanocomposite is a very promising candidate for development of high photocatalysis performance for

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environmental and energy applications.

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Notes and references

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Electronic Supplementary Information (ESI) available: The UV-vis spectrum of the CoPc. Various additives on the photodegradation processes of the BiVO₄/CoPc nanofiber heterostructures for MB. Variation of TOC removal versus time for the MB dye solution. Cycling degradation of MB mediated by BiVO₄/CoPc.

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