Enhancement of photocatalytic activity of Bi$_2$WO$_6$ hybridized with graphite-like C$_3$N$_4$†

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Bi$_2$WO$_6$ photocatalyst was hybridized by graphite-like C$_3$N$_4$ via facile chemisorption. After hybridization with C$_3$N$_4$, the photocatalytic activity of Bi$_2$WO$_6$ was obviously enhanced. A C$_3$N$_4$/Bi$_2$WO$_6$ photocatalyst hybridized with monolayer C$_3$N$_4$ exhibited the highest photocatalytic activity which was 68.9% higher than that of pure Bi$_2$WO$_6$. The enhanced photocatalytic activity of the C$_3$N$_4$/Bi$_2$WO$_6$ photocatalysts could be attributed to the synergetic effect between C$_3$N$_4$ and Bi$_2$WO$_6$. The photogenerated holes on the valence band of Bi$_2$WO$_6$ could transfer to the highest occupied molecular orbital of C$_3$N$_4$ via the well developed interface, causing rapid photoinduced charge separation and enhancing the photocatalytic activity.

1. Introduction
Heterogeneous photocatalytic oxidation technologies are promising methods to deal with water pollutants.$^{1,2}$ To date, TiO$_2$ is still the most investigated and promising semiconductor material in photocatalytic oxidation.$^{3,4}$ However, very poor response to visible light has obstructed the application of TiO$_2$ photocatalysis in water treatment. To reduce this drawback, some efforts have been devoted to modifying the surface or bulk properties of TiO$_2$, such as doping,$^5$ combining TiO$_2$ with another semiconductor$^6$ and dye sensitization.$^7$ Though the above methods could partly enhance the visible light photocatalytic activity of TiO$_2$, some key problems are still unresolved. So from the viewpoint of using solar energy, it is very urgent to develop efficient visible-light-active photocatalysts.

Recently, many new visible-light-active photocatalysts have been reported, such as Bi$_2$WO$_6$,$^8-10$ BiVO$_4$,$^{11,12}$ CaBi$_2$O$_4$,$^{13}$ and InVO$_4$.$^{14,15}$ Nanosized Bi$_2$WO$_6$ is an excellent visible-light-active photocatalyst which has attracted a great deal of scientific interest.$^{16-18}$ The materials with delocalized conjugated π structures have been proven to efficiently arouse a rapid photoinduced charge separation and a relatively slow charge recombination in electron-transfer processes.$^{19}$ Our group has developed some efficient photocatalysts via conjugative π structured material hybridization, such as a C$_{60}$/TiO$_2$ photocatalyst,$^{18}$ a PANI/TiO$_2$ photocatalyst,$^{19}$ and a graphene-like carbon/TiO$_2$ photocatalyst.$^{20}$ Recently, Wang and co-workers reported that graphite-like C$_3$N$_4$ could absorb visible light to split water to generate hydrogen or oxygen in the presence of a sacrificial donor.$^{21}$ Graphite-like C$_3$N$_4$ (denoted as C$_3$N$_4$) possesses a very high thermal and chemical stability and has attracted extensive attention due to its outstanding mechanical, electrical, thermal, and optical properties.$^{22}$ Our group has already carried out research on a C$_3$N$_4$-hybridized ZnO photocatalyst fabricated by a chemisorption method.$^{23}$ After hybridization with C$_3$N$_4$, the photocatalytic activity of ZnO was greatly enhanced and the photocorrosion phenomenon was successfully suppressed. Moreover, surface coating is a promising way to fabricate functional materials.$^{24}$ The introduction of C$_3$N$_4$ into Bi$_2$WO$_6$ may cause a more effective charge separation of Bi$_2$WO$_6$. To the best of our knowledge, no report has been done on this topic. In this work, we present the first example of a C$_3$N$_4$-hybridized Bi$_2$WO$_6$ photocatalyst fabricated by a chemisorption method. Compared with pure Bi$_2$WO$_6$, C$_3$N$_4$-hybridized Bi$_2$WO$_6$ exhibited a higher photocatalytic activity and photocurrent. It is postulated that the enhanced photocatalytic activity of the C$_3$N$_4$/Bi$_2$WO$_6$ photocatalyst results from the high separation efficiency of photoinduced electron–hole pairs. The structure between Bi$_2$WO$_6$ and C$_3$N$_4$ as well as the mechanism of enhanced photocatalytic activity were systematically investigated.

2. Experimental section

2.1 Preparation of the C$_3$N$_4$/Bi$_2$WO$_6$ photocatalyst
Bi$_2$WO$_6$ nanosheets were prepared by the hydrothermal method according to the literature.$^9$ Melamine (C$_6$H$_6$N$_6$) was purchased from Sinopharm Chemical Reagent Corp, P.R. China. All other reagents were of analytical grade and were used without further purification. The C$_3$N$_4$ used in this study was prepared by
heating melamine to 550 °C for 2 h in N₂ atmosphere according to the literature. In a typical synthesis of C₃N₄/Bi₂WO₆ photocatalysts, an appropriate amount of C₃N₄ was added into methanol and was totally dispersed by ultrasonication. The as-prepared Bi₂WO₆ powder was added into the above solution and stirred in a fume hood for 24 h. After volatilization of the methanol, opaque powder was obtained after drying at 100 °C in air. C₃N₄/Bi₂WO₆ photocatalysts with other different mass ratios from 1% to 8% were prepared according to this method. Bi₂WO₆ and C₃N₄/Bi₂WO₆ electrodes were prepared as follows: 2 mg of as-prepared photocatalyst was suspended in 2 mL ethanol to produce a slurry, which was then dip-coated onto a 2 cm × 4 cm indium–tin oxide (ITO) glass electrode. Electrodes were exposed to UV light for 12 h to eliminate ethanol and subsequently calcined at 200 °C for 30 min under N₂ flow (rate = 60 mL min⁻¹). All investigated electrodes were of similar thickness (0.8–1.0 µm).

2.2 Characterization

Morphologies and microstructures of the as-prepared photocatalysts were analyzed by transmission electron microscopy (TEM) (JEM 1010, accelerating voltage 100 kV). The high-resolution transmission electron microscopy (HRTEM) images were obtained using a Tecnai TF20 transmission electron microscope operated at an accelerating voltage of 200 kV. Fourier transform infrared (FT-IR) spectra were acquired by using a Perkin Elmer System 2000 infrared spectrometer with microscope operated at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy using a Perkin Elmer System 2000 infrared spectrometer with KBr as the reference sample. X-ray photoelectron spectroscopy (XPS) was performed in a PHI 5300 ESCA system. The beam voltage was 3.0 kV, and the energy of the Ar ion beam was 1.0 keV. The binding energies were normalized to the signal for adventitious carbon at 284.8 eV. UV-vis diffuse reflectance spectra (DRS) were obtained on a UV-vis spectrophotometer (Hitachi U-3010), using BaSO₄ as the reference sample. The X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8-advance diffractometer using Cu-Kα radiation (λ = 1.5418 Å). Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were performed on a Dupont 1090 thermal analyzer. The atmosphere was air and the heating rate was 10 °C min⁻¹. The photoelectrochemical measurements were measured on an electrochemical system (CHI-660B, China), using a conventional three-electrode cell. Bi₂WO₆ and C₃N₄/Bi₂WO₆ electrodes served as the working electrode. The counter and the reference electrodes were a platinum wire and a saturated calomel electrode (SCE), respectively, and 0.1 M Na₂SO₄ was used as electrolyte solution. Potentials are given with reference to the SCE. The photoresponses of the photocatalysts as UV light was switched on and off were measured at 0.0 V. Electrochemical impedance spectra (EIS) were measured at 0.0 V. A sinusoidal ac perturbation of 5 mV was applied to the electrode over the frequency range of 0.05–10⁴ Hz.

2.3 Photocatalytic experiments

The photocatalytic activities were evaluated by the decomposition of methylene blue (MB) under visible light and simulated solar irradiation. Visible irradiation was obtained from a 500 W xenon lamp (Institute for Electric Light Sources, Beijing) with a 450 nm cutoff filter, and the average visible light intensity was 40 mW cm⁻². Simulated solar irradiation was obtained from the xenon lamp without the cutoff filter. 25 mg of photocatalyst was totally dispersed in an aqueous solution of MB (100 mL, 10⁻⁵ mol L⁻¹). Before irradiation, the suspensions were magnetically stirred in the dark for 30 min to get an absorption–desorption equilibrium between the photocatalyst and MB. At certain time intervals, 5 mL aliquots were sampled and centrifuged to remove the particles. The concentration of MB was analyzed by recording the absorbance at the characteristic band of 633 nm using a Hitachi U-3010 UV-Vis spectrophotometer. The oxidative species in the photocatalytic system could be detected through the trapping experiments of hydroxyl radicals by using tert-butyl alcohol (tBuOH, hydroxyl radical scavenger).

3. Results and discussion

3.1 Enhancement of photocatalytic activity and photocurrent

The degradation of MB (λ > 450 nm) were carried out to investigate the photocatalytic performances of Bi₂WO₆ before and after C₃N₄ hybridization. The photocatalytic degradation of organic pollutants follows pseudo-first-order kinetics, and the values of apparent reaction rate constants k were calculated and are shown in Fig. 1a. Compared with pure Bi₂WO₆, all C₃N₄/Bi₂WO₆ photocatalysts had enhanced photocatalytic activity. When the proportion of C₃N₄ reached 2%, the C₃N₄/Bi₂WO₆ photocatalyst exhibited the optimum photocatalytic activity. The apparent rate constant k was 0.1522 h⁻¹, which was 68.9% higher than that of pure Bi₂WO₆ (0.0901 h⁻¹). When the loading amount of C₃N₄ was higher than 2%, the degradation rate decreased gradually though it remained higher than that of pure Bi₂WO₆. The loading amount of C₃N₄ had a great influence on the photocatalytic activity of the C₃N₄/Bi₂WO₆ photocatalysts. The optimal C₃N₄ loading amount of C₃N₄/Bi₂WO₆ was 2%. Moreover, pure Bi₂WO₆ and mechanically blended C₃N₄ and Bi₂WO₆ (2%) were used as references. Compared with pure Bi₂WO₆, the photocatalytic activity of mechanically blended C₃N₄ and Bi₂WO₆ (2%) was not increased. These results indicated that there may be some interaction between C₃N₄ and Bi₂WO₆, which may be of significance to enhance the photocatalytic activity.

The photocatalytic activity of C₃N₄/Bi₂WO₆-2%, C₃N₄ and Bi₂WO₆ under simulated solar irradiation was also studied (Fig. 1b), a xenon lamp was used to simulate the solar irradiation. As can be seen from Fig. 1b, the apparent rate constant k of C₃N₄/Bi₂WO₆-2% was 1.0291 h⁻¹, which was 69.8% higher than that of pure Bi₂WO₆ (0.6606 h⁻¹). The C₃N₄ hybridization can effectively enhance the photocatalytic performance of Bi₂WO₆ under simulated solar irradiation, which was similar to the result under visible light irradiation (λ > 450 nm).

The photocurrent of C₃N₄/Bi₂WO₆-2%, C₃N₄ and Bi₂WO₆ electrodes were studied and the results are shown in Fig. 2. Fast and uniform photocurrent responses of C₃N₄/Bi₂WO₆-2%, C₃N₄ and Bi₂WO₆ electrodes can be observed in Fig. 2. After hybridization with C₃N₄, the photocurrent of Bi₂WO₆ was enhanced by 2 times under visible light irradiation. The photocurrent enhancement of C₃N₄/Bi₂WO₆ originated from an enhanced photoinduced charge separation.
3.2 Structure and morphology of C$_3$N$_4$/Bi$_2$WO$_6$ photocatalysts

Fig. 3 showed the TEM and HRTEM images of Bi$_2$WO$_6$ and various C$_3$N$_4$/Bi$_2$WO$_6$ photocatalysts. As can be seen from Fig. 3(a), the Bi$_2$WO$_6$ crystals prepared by the hydrothermal process are sheet-shaped and the average size of a Bi$_2$WO$_6$ nanosheet was about 60 nm. Fig. 3(b) shows the TEM image of C$_3$N$_4$/Bi$_2$WO$_6$ photocatalyst, the Bi$_2$WO$_6$ nanosheets were surrounded by C$_3$N$_4$ shells. Fig. 3(c) shows the HRTEM image of C$_3$N$_4$/Bi$_2$WO$_6$-2% photocatalyst, there was no change of lattice structure of Bi$_2$WO$_6$ after C$_3$N$_4$ was adsorbed on the surface and the outer boundary was obviously different from the Bi$_2$WO$_6$ core. The thickness of the C$_3$N$_4$ layer coated on the C$_3$N$_4$/Bi$_2$WO$_6$-2% sample was estimated to be 0.372 nm, which was close to the scale of monolayer C$_3$N$_4$ (about 0.325 nm). Therefore, it can be estimated that the absorbed C$_3$N$_4$ layer on the surface of C$_3$N$_4$/Bi$_2$WO$_6$-2% was an approximately monolayer structure. The thickness of the C$_3$N$_4$ layer increased with increasing of the C$_3$N$_4$/Bi$_2$WO$_6$ mass ratio (Fig. 3(d)). The thickness of the C$_3$N$_4$ layer of the C$_3$N$_4$/Bi$_2$WO$_6$-8% photocatalyst was about 2 nm, indicating the C$_3$N$_4$ layer was a multilayer structure.
The absorption states of C\textsubscript{3}N\textsubscript{4} on the surface of C\textsubscript{3}N\textsubscript{4}/Bi\textsubscript{2}WO\textsubscript{6} could be revealed by the TG-DTA analyses (Fig. 4). As can be seen from Fig. 4, a weight loss region occurring from 200 °C to 500 °C could be observed in the TG curve of pure Bi\textsubscript{2}WO\textsubscript{6}, which originated from desorption of surface bound water. For pure C\textsubscript{3}N\textsubscript{4}, another weight loss region occurring from 500 °C to 720 °C could be found, which could be assigned to the burning of C\textsubscript{3}N\textsubscript{4}. These two weight loss regions could be seen in all C\textsubscript{3}N\textsubscript{4}/Bi\textsubscript{2}WO\textsubscript{6} samples. The amount of C\textsubscript{3}N\textsubscript{4} on the surface of Bi\textsubscript{2}WO\textsubscript{6} could be obtained from the second weight loss, and is shown in the insert of Fig. 4. In the DTA curve of pure C\textsubscript{3}N\textsubscript{4} (Fig. S1†), the endothermic peak occurring from 550 to 720 °C might be attributed to the burning of C\textsubscript{3}N\textsubscript{4}. For C\textsubscript{3}N\textsubscript{4}/Bi\textsubscript{2}WO\textsubscript{6} photocatalysts, the endothermic peak occurring from 500 to 600 °C was attributed to the burning of C\textsubscript{3}N\textsubscript{4}.

FT-IR spectra were determined to reveal the interface interaction between C\textsubscript{3}N\textsubscript{4} and Bi\textsubscript{2}WO\textsubscript{6} (Fig. 5). It could be clearly seen that the main characteristic peaks of C\textsubscript{3}N\textsubscript{4} and Bi\textsubscript{2}WO\textsubscript{6} all appear in the FT-IR spectra of C\textsubscript{3}N\textsubscript{4}/Bi\textsubscript{2}WO\textsubscript{6} photocatalysts. In the FT-IR spectrum of C\textsubscript{3}N\textsubscript{4}, the peak at 1639 cm\textsuperscript{-1} and 1237 cm\textsuperscript{-1} was attributable to the C≡N and C–N stretching vibrations.\textsuperscript{26,27} Compared with that of pure C\textsubscript{3}N\textsubscript{4}, these main characteristic peaks all moved to lower wavenumber in the FT-IR spectra of C\textsubscript{3}N\textsubscript{4}/Bi\textsubscript{2}WO\textsubscript{6} photocatalysts, indicating that the conjugated system of C\textsubscript{3}N\textsubscript{4} was weakened and an intense interface interaction between C\textsubscript{3}N\textsubscript{4} and Bi\textsubscript{2}WO\textsubscript{6} occurred. To further investigate the interaction between C\textsubscript{3}N\textsubscript{4} and Bi\textsubscript{2}WO\textsubscript{6}, XPS spectra were recorded and are shown in Fig. S2.† Compared with pure C\textsubscript{3}N\textsubscript{4}, the binding energy of N 1s of C\textsubscript{3}N\textsubscript{4}/Bi\textsubscript{2}WO\textsubscript{6} showed a negative shift. Due to the low loading concentration of C\textsubscript{3}N\textsubscript{4}, the peak of N 1s of C\textsubscript{3}N\textsubscript{4}/Bi\textsubscript{2}WO\textsubscript{6}-2% was weak. In contrast, the binding energy of Bi 4f of C\textsubscript{3}N\textsubscript{4}/Bi\textsubscript{2}WO\textsubscript{6}-2% exhibited a positive shift as compared to pure Bi\textsubscript{2}WO\textsubscript{6}. These results showed that there was an intense interface interaction between Bi and N atoms, not a simply physical adsorption. This interaction was essential to transfer carriers and enhance photocatalytic activity.

A comparison of the UV-vis DRS spectra of Bi\textsubscript{2}WO\textsubscript{6} and different mass ratios of C\textsubscript{3}N\textsubscript{4}/Bi\textsubscript{2}WO\textsubscript{6} photocatalysts is displayed in Fig. S3.† The Bi\textsubscript{2}WO\textsubscript{6} photocatalyst showed a fundamental absorption edge at 470 nm, which corresponds to the visible light photocatalytic activity. After hybridization with C\textsubscript{3}N\textsubscript{4}, the C\textsubscript{3}N\textsubscript{4}/Bi\textsubscript{2}WO\textsubscript{6} photocatalysts showed the same absorption edge as Bi\textsubscript{2}WO\textsubscript{6}, indicating identical band gap energies. With the increasing amount of C\textsubscript{3}N\textsubscript{4}, the absorption intensity of C\textsubscript{3}N\textsubscript{4}/Bi\textsubscript{2}WO\textsubscript{6} photocatalysts did not obviously change.

The XRD patterns of Bi\textsubscript{2}WO\textsubscript{6}, C\textsubscript{3}N\textsubscript{4} and various C\textsubscript{3}N\textsubscript{4}/Bi\textsubscript{2}WO\textsubscript{6} photocatalysts are shown in Fig. S4.† All the diffraction peaks of Bi\textsubscript{2}WO\textsubscript{6} can be exactly indexed as the square Bi\textsubscript{2}WO\textsubscript{6} structure (JCPDS 73-1126). The XRD patterns of Bi\textsubscript{2}WO\textsubscript{6} showed no change when Bi\textsubscript{2}WO\textsubscript{6} was hybridized with C\textsubscript{3}N\textsubscript{4}, indicating the hybridization of C\textsubscript{3}N\textsubscript{4} did not influence the lattice structure of Bi\textsubscript{2}WO\textsubscript{6}. No XRD diffraction peaks indexed to C\textsubscript{3}N\textsubscript{4} were observed because the C\textsubscript{3}N\textsubscript{4} layer was too thin.
3.3 Stability of the C$_3$N$_4$/Bi$_2$WO$_6$ photocatalysts

To evaluate the stability of the as-prepared C$_3$N$_4$/Bi$_2$WO$_6$ photocatalysts, 4 recycling experiments for the photodegradation of MB were performed (Fig. 6). After being used 4 times for MB degradation, the rate constants of MB degradation of C$_3$N$_4$/Bi$_2$WO$_6$ declined from 0.1522 h$^{-1}$ to 0.1501 h$^{-1}$. This result indicated the as-prepared C$_3$N$_4$/Bi$_2$WO$_6$ photocatalysts were photostable during the photocatalytic degradation.

3.4 Mechanism of enhancement of photocatalytic activity

Photocatalytic activity was governed by some crucial factors, such as phase structure, adsorption ability, and separation efficiency of photogenerated electrons and holes. XRD patterns of C$_3$N$_4$/Bi$_2$WO$_6$ exhibited similar diffraction peaks as those of Bi$_2$WO$_6$, indicating the as-prepared C$_3$N$_4$/Bi$_2$WO$_6$ photocatalysts were such as phase structure, adsorption ability, and separation efficiency of photogenerated electron–hole pairs and a faster interfacial charge transfer had occurred. The separation efficiency of photogenerated electron–hole pairs and a faster interfacial charge transfer had occurred. This result indicated the as-prepared C$_3$N$_4$/Bi$_2$WO$_6$ photocatalysts were photostable during the photocatalytic degradation.

The smaller arc radius on the EIS Nyquist plot of C$_3$N$_4$/Bi$_2$WO$_6$ indicates that the introduction of C$_3$N$_4$ changed the charge distribution of Bi$_2$WO$_6$ and made charge transfer easier. This result indicated that the introduction of C$_3$N$_4$ into Bi$_2$WO$_6$ can effectively enhance the separation efficiency of photogenerated electron–hole pairs. To reveal the photocatalytic mechanism, the main oxidative species in the photocatalytic process were detected through the trapping experiments of hydroxyl radicals by using tBuOH (hydroxyl radical scavenger). As shown in Fig. 8, the photocatalytic activity of C$_3$N$_4$/Bi$_2$WO$_6$ was not changed by the addition of the scavenger for hydroxyl radicals, indicating that the hydroxyl radicals were not the main oxidative species of the C$_3$N$_4$/Bi$_2$WO$_6$ system. Therefore, the main oxidative species of the C$_3$N$_4$/Bi$_2$WO$_6$ system would be holes.

As discussed above, the phase structure of Bi$_2$WO$_6$ remained unchanged and the adsorptivity of Bi$_2$WO$_6$ increased a little, so we may conclude that the enhancement of the photocatalytic activity of the C$_3$N$_4$/Bi$_2$WO$_6$ photocatalysts was attributed mainly to the effective separation of the photogenerated electron–hole pairs. The smaller arc radius on the EIS Nyquist plot of C$_3$N$_4$/Bi$_2$WO$_6$ indicates that the introduction of C$_3$N$_4$ changed the charge distribution of Bi$_2$WO$_6$ and made charge transfer easier. This result indicated that the introduction of C$_3$N$_4$ into Bi$_2$WO$_6$ can effectively enhance the separation efficiency of photogenerated electron–hole pairs. To reveal the photocatalytic mechanism, the main oxidative species in the photocatalytic process were detected through the trapping experiments of hydroxyl radicals by using tBuOH (hydroxyl radical scavenger). As shown in Fig. 8, the photocatalytic activity of C$_3$N$_4$/Bi$_2$WO$_6$ was not changed by the addition of the scavenger for hydroxyl radicals, indicating that the hydroxyl radicals were not the main oxidative species of the C$_3$N$_4$/Bi$_2$WO$_6$ system. Therefore, the main oxidative species of the C$_3$N$_4$/Bi$_2$WO$_6$ system would be holes.

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4. Conclusion

In summary, C$_3$N$_4$/Bi$_2$WO$_6$ photocatalysts were prepared via facile chemisorption. The photocatalytic activity of C$_3$N$_4$/Bi$_2$WO$_6$ was obviously enhanced compared to pure Bi$_2$WO$_6$. A C$_3$N$_4$/Bi$_2$WO$_6$ photocatalyst hybridized with monolayer C$_3$N$_4$ (0.372 nm) showed the highest photocatalytic activity which was 68.9% higher than that of pure Bi$_2$WO$_6$. The enhanced photocatalytic activity of the C$_3$N$_4$/Bi$_2$WO$_6$ photocatalysts could be attributed to the rapid photoinduced charge separation caused by the hybridization of C$_3$N$_4$. This work demonstrated that C$_3$N$_4$ is a very promising candidate for development of highly active photocatalysts, and C$_3$N$_4$ hybridization could be a new possibility to design new photocatalysts with high performance for environmental applications.

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References and Notes