In-situ growth of Ag₃VO₄ nanoparticles onto BiOCl nanosheet to form a heterojunction photocatalyst with enhanced performance under visible light irradiation

Peifang Wang, Hong Tang, Yanhui Ao *, Chao Wang, Jun Hou, Jin Qian, Yi Li

Key laboratory of Integrated Regulation and Resource Development on Shallow Lakes, Ministry of Education, College of Environment, Hohai University, Nanjing, 210098, China

Abstract: A series of BiOCl-Ag₃VO₄ heterojunction photocatalysts with high visible light photocatalytic activity were synthesized by a in-situ growth route. The obtained samples were characterized by X-ray diffraction spectroscopy, UV-vis diffuse reflectance spectra, field emission scanning electron microscopy and transmission electron microscopy. The azo dye reactive brilliant red X-3B was chosen as the target pollutant to investigate the photocatalytic activity of the as-prepared heterojunctions under visible light. The BiOCl-Ag₃VO₄ composite photocatalysts exhibited much higher photocatalytic efficiency than pure BiOCl. The photoluminescence spectra and photocurrent results **indicated** that the enhanced activity **was** ascribed to the efficient charge separation and transfer between BiOCl-Ag₃VO₄ heterojunction. Furthermore, it was found that the content of Ag₃VO₄ **affected** the photocatalytic activity apparently. The highest activity was obtained with mole ratio of 20% for Ag₃VO₄ in the present work. Besides, a possible mechanism of enhanced photocatalytic activity was proposed for the degradation of dye under visible light.

* Corresponding author. Tel./ fax: +86 25 83787330

E-mail address: andyao@hhu.edu.cn

In-situ growth of Ag_3VO_4 nanoparticles onto BiOCl nanosheet to form a heterojunction photocatalyst with enhanced performance under visible light irradiation

Peifang Wang, Hong Tang, Yanhui Ao *, Chao Wang, Jun Hou, Jin Qian, Yi Li

Key laboratory of Integrated Regulation and Resource Development on Shallow Lakes, Ministry of Education, College of Environment, Hohai University, Nanjing, 210098, China

Abstract: A series of $\text{BiOCl-Ag}_3\text{VO}_4$ heterojunction photocatalysts with high visible light photocatalytic activity were synthesized by a in-situ growth route. The obtained samples were characterized by X-ray diffraction spectroscopy, UV-vis diffuse reflectance spectra, field emission scanning electron microscopy and transmission electron microscopy. The azo dye reactive brilliant red X-3B was chosen as the target pollutant to investigate the photocatalytic activity of the as-prepared heterojunctions under visible light irradiation. The $\text{BiOCl-Ag}_3\text{VO}_4$ composite photocatalysts exhibited much higher photocatalytic efficiency than pure BiOCl . The photoluminescence spectra and photocurrent results **indicated** that the enhanced activity **was** ascribed to the efficient charge separation and transfer between $\text{BiOCl-Ag}_3\text{VO}_4$ heterojunction. Furthermore, it was found that the content of Ag_3VO_4 **affected** the photocatalytic activity apparently. The highest activity was obtained with mole ratio of 2% for Ag_3VO_4 in the present work. Besides, a possible mechanism of enhanced photocatalytic activity was proposed for the degradation of dye under visible light.

* Corresponding author. Tel./ fax: +86 25 83787330

E-mail address: andyao@hhu.edu.cn

Key words: Photocatalysis; Heterojunction; Ag_3VO_4 ; BiOCl ; Visible light

1. Introduction

Photocatalysis based on semiconductors has attracted wide attention for decades in the field of environmental purification, and a lot of achievements have been achieved [1-4]. Among all kinds of semiconductor photocatalysts, titanium dioxide (TiO_2) **has been one of the most famous** due to its good stability, high efficiency, nontoxicity and low cost [5-9]. However, TiO_2 **can only be excited** by the ultraviolet (UV) light (wavelength $\lambda \leq 380$ nm), while the UV light barely accounts for 4% of the solar spectrum. Therefore, TiO_2 exhibits poor utilization efficiency of solar light [10]. In order to utilize solar energy, **visible-light-driven photocatalysts must be exploited**. It has been demonstrated that coupling of TiO_2 with narrow band gap semiconductors can enhance the utilization efficiency of solar light. Furthermore, the coupling of two semiconductors can form heterojunctions which favor the separation of photoinduced electron and hole thus improves the photocatalytic activity. Therefore, it is an efficient way to improve the visible light activated activity of wide band gap semiconductors by coupling with narrow band gap semiconductors.

Nowadays, **bismuth (Bi) based semiconductors**, such as bismuth oxyhalides (BiOX , $\text{X}=\text{Cl}$, Br , I) [17-19], bismuth **tungstate** (Bi_2WO_6) and bismuth **molybdate** (Bi_2MoO_6) [20-22], **have become research hotspots of photocatalysis**. Among these photocatalysts, **BiOCl with a tetragonal layered structure can efficiently separate the photoexcited hole-electron pairs**. Furthermore, it exhibits high photocatalytic activity under UV light irradiation because of its open crystal structure and

indirect optical transitions [23]. However, BiOCl can not absorb visible light because of its wide band gap (3.4 eV). In order to extend its photoresponse to visible light region, great efforts have been made by coupling BiOCl with other semiconductors having narrow band gap [24-28].

Silver vanadate (Ag_3VO_4) is a typical n-type semiconductor with narrow band gap and monoclinic structure. It has attracted extensive attention in recent years [29-31]. Therefore, Ag_3VO_4 **can be used** as an efficient sensitizer to improve the visible light activity of one wide band gap semiconductor. For example, $\text{Ag}_3\text{VO}_4/\text{TiO}_2$ nanocomposite was prepared by Wang et al. successfully [32]. The composite photocatalyst showed higher efficiency in the oxidation of gaseous benzene under both visible and simulated solar light irradiation. **Aziz et al. investigated the effect of Ag_3VO_4 on the photocatalytic activity of ZnO under visible light irradiation extensively [33]. The results also illustrated that Ag_3VO_4 can improve the visible light activated activity of ZnO efficiently. Furthermore, other Ag based semiconductors can improve the activity of ZnO- Ag_3VO_4 further [34, 35].** However, to the best of our knowledge, the preparation and photocatalytic activity of BiOCl- Ag_3VO_4 heterojunctions have not been reported. The novel heterojunctions might show several advantages: expanded visible light absorption, enhanced interfacial charge transfer and improved photoinduced electron-hole separation efficiency.

In the present work, we successfully synthesized novel heterojunction photocatalysts: n type Ag_3VO_4 nanoparticles deposited p type BiOCl nanosheets.

The samples were characterized by a series of techniques. It was found that the heterojunctions exhibited expanded optical absorption and enhanced visible light photocatalytic activity.

2. Experimental section

2.1. Catalysts preparation

The chemical reagents involved in this work, such as $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and NH_3VO_3 etc, were all analytical grade and were used as received without further purification. Firstly, square-like 2D BiOCl nanoplates were synthesized via a mannitol-assisted hydrothermal method as reported by Xiong et al [33]. The BiOCl - Ag_3VO_4 nanocomposites with different Ag_3VO_4 mole ratio were prepared via a facile precipitation process at room temperature. In a typical process, 0.325 g as-prepared BiOCl powder was added into 60 mL AgNO_3 solution with an ultrasonic treatment for 1 h and a magnetic stirring for 1.5 h. Then 20 ml NH_4VO_3 solution with same concentration was added into the above suspension, followed by the adjustment of pH to 9 by NaOH aqueous solution (2 M). After be magnetically stirred for 24 h, the sample was separated by centrifugation, washed with ultrapure water, and dried at 60 °C. Then the final product, some greyish black powder was obtained and noted as B-A-1. Other samples (Ag_3VO_4 : BiOCl =0.10, 0.15, 0.20, 0.25) were synthesized by similar procedure just with the addition of different concentration of AgNO_3 and NH_4VO_3 solution, **which are successively defined as B-A-2, B-A-3, B-A-4 and B-A-5.**

2.2. Characterization methods

The crystal forms of the catalysts were obtained on an X-ray diffractometer (XRD, SHIMADAZU, XD-3A) using Cu K α radiation over the 2 θ range 10~80°. The accelerating voltage and the electric current were 40 kV and 100 mA, respectively. The UV-vis diffuse reflectance spectra (DRS, SHIMADZU, UV3600) from 200 nm to 800 nm were carried out to investigate the optical absorption property of each sample, and optically pure BaSO₄ was adopted as the reference material. The surface morphologies and microstructures were observed by field emission scanning electron micrograph (FESEM, HITACHI, S-4800) and transmission electron microscope (TEM, HITACHI, H-7650). The photoluminescence (PL) spectra in the wavelength range 200 nm to 600 nm were characterized using a fluorescence spectrophotometer (F-7000). Photocurrent responses were recorded using an electrochemical station (Chenhua Instruments, CHI660D) operated in a three-electrode configuration with the sample films as the working electrode, a Pt foil as the counter electrode and a Ag/AgCl electrode as the reference electrode.

2.3. Photocatalytic activity

Photocatalytic activity of the as-prepared samples was performed by the photodegradation of reactive brilliant red X-3B dye in aqueous solution under visible light irradiation. The pure BiOCl was also examined for comparison. In each experiment, 10 mg of the catalyst was added into 50 mL X-3B solution, whose initial concentration was *ca.* 25 mg.L⁻¹. An ultrasonic treatment of 2 min was carried out to make the catalyst dispersed evenly in the solution. Then, the suspension was stirred for more than 30 min in dark to reach the **adsorption-desorption equilibrium** prior

to illumination. A 300 W Xe lamp (CEAULIGHT, CEL-HXF300) was employed as the light source, equipped with a 400 nm cut-off optical filter. At given time intervals, 1.5 mL suspension was withdrawn and filtrated for further analysis on UV-vis spectrophotometer (SHIMADZU, UV3600). The characteristic absorbance band at 538 nm was recorded to determine the X-3B concentration.

What's more, the radical-trapping experiment was also conducted to determine the main active species in the photoreaction process. Tert-butanol (TBA), disodium ethylenediamine tetraacetate (EDTA- Na_2), and p-benzoquinone (BQ) were used as the scavenger of $\cdot\text{OH}$ radical, holes and $\cdot\text{O}_2^-$ radical, respectively.

3. Results and discussion

3.1 Characterization of the as-prepared samples

The obtained samples were firstly characterized by XRD to examine the crystal structure. As shown in Fig. 1, all the diffraction peaks of pure BiOCl can be indexed to tetragonal phase BiOCl (JCPDS, No. 06-0249) [24], **which indicates its** high purity. Some characteristic peaks for Ag_3VO_4 are detected in B-A-4 nanocomposite, and they match well with monoclinic Ag_3VO_4 (JCPDS, No. 43-0542) [31]. Compared with pure BiOCl , the main peaks of the nanocomposite are much weaker, probably because the Ag_3VO_4 nanoparticles deposited on the surface would shield BiOCl nanoplates thus induce weaker peak.

The DRS spectra of the as-prepared samples are displayed in Fig. 2 to investigate the optical absorption properties. It should be noted that $\text{BiOCl-Ag}_3\text{VO}_4$ hybrids all show absorption activity in the visible light range while BiOCl can only absorb UV

light. Furthermore, the absorption intensities of BiOCl-Ag₃VO₄ hybrids are all stronger than that of pure BiOCl **in both UV and visible light region**. The result may attribute to the nature of Ag₃VO₄ which can absorb visible light. Compared with pure BiOCl, an evident red shift can be observed in the hybrids. The results illustrate that BiOCl-Ag₃VO₄ hybrids may be served as visible light driven photocatalyst.

The BiOCl-Ag₃VO₄ hybrid has been synthesized via a facile precipitation procedure, and the formation mechanism is displayed in Fig. 3. **Firstly, BiOCl powder with square-like nanosheet morphology was synthesized by a hydrothermal method. Then, the nanosheets were uniformly dispersed in AgNO₃ solution by ultrasonic.** After the addition of NH₄VO₃ solution, NaOH solution was added into the above suspension drop by drop to adjust the pH of reaction system to 9. After full reaction, Ag₃VO₄ nanoparticles were generated under alkaline conditions (the reaction equation: $3\text{Ag}^+ + \text{VO}_3^- + 2\text{OH}^- \rightarrow \text{Ag}_3\text{VO}_4\downarrow + \text{H}_2\text{O}$). **At last, the resultant nanoparticles were uniformly anchored on BiOCl nanosheets and the BiOCl-Ag₃VO₄ hybrids were obtained.**

The morphologies and structures of the as-prepared products were detected by SEM and TEM. The obtained results are shown in Fig. 4. As seen in Fig. 4a, BiOCl **composites of square-like 2D nanosheets** whose thickness can be estimated to be 10~25 nm. Fig. 4 b~f show SEM of BiOCl-Ag₃VO₄ hybrids, in which BiOCl nanosheets with Ag₃VO₄ nanoparticles deposited on the surface can be observed clearly. The Ag₃VO₄ nanoparticles had an average size of around 15 nm. Furthermore, it can be found that the amount of Ag₃VO₄ nanoparticles deposited on the surface of

BiOCl increases with the increase of Ag_3VO_4 ratio. Moreover, the deposition of Ag_3VO_4 onto BiOCl nanosheets is more distinctly displayed in the typical TEM image shown in Fig. 4 g. Obviously, many Ag_3VO_4 nanoparticles are anchored on the square-like BiOCl nanosheet, further indicated the successful production of BiOCl- Ag_3VO_4 heterojunctions. **Furthermore, EDX spectra were characterized to show the purities of the as-prepared BiOCl- Ag_3VO_4 composites. The obtained typical EDX spectrum of B-A-4 is shown in Fig. 4 (h). It can be seen that elements Cu, C, Bi, O, Cl, Ag, V are obviously observed. Cu and C are come from the support for the TEM measurement. Therefore, the results illustrate that the as-prepared BiOCl- Ag_3VO_4 composites exhibit high purities in the present work.**

3.2 Photocatalytic activity

In order to investigate the photocatalytic activity of the obtained BiOCl- Ag_3VO_4 hybrids, the photocatalytic degradation experiments toward dye X-3B were carried out under visible light illumination and the results are shown in Fig. 5. The efficiency of pure BiOCl is relatively low, only about 23% of X-3B is degraded after 90 min irradiation. Compared with pure BiOCl, all BiOCl- Ag_3VO_4 hybrids display superior photocatalytic performance. **The highest one (B-A-4) can degrade about 74% X-3B within the same time.** It indicates the significant role of Ag_3VO_4 for the degradation of X-3B under visible light irradiation. Besides, the apparent rate constant was also calculated to compare the activity of each sample, and the results are shown in Fig. 5b. From the figure, the obtained values are 0.0024, 0.0040, 0.0052, 0.0081, 0.0128 and

0.0101 min⁻¹ for BiOCl, B-A-1, B-A-2, B-A-3, B-A-4 and B-A-5, respectively. **It can be seen that B-A-4 exhibits the highest degradation efficiency among all the BiOCl-Ag₃VO₄ hybrids. The apparent rate constant of B-A-4 is five times as that of pure BiOCl. Therefore, 0.20 is the optimum mole ratio of Ag₃VO₄/BiOCl to obtain the best photocatalytic performance in the present condition.** The recycle of BiOCl-Ag₃VO₄ hybrids is of great importance for **their** practical applications. Therefore, the typical cycling experiments of the B-A-4 were done to evaluate its long-term serving life, and the results are shown in Fig. 5 c. It can be clearly seen that the photocatalytic activity has no apparent decreasing after three cycles, indicating that BiOCl-Ag₃VO₄ composite photocatalysts have good stability.

Given the above experimental results, some efforts have been made to explain this phenomenon. As a wide band gap catalyst, BiOCl (3.5 eV) cannot response to visible light, but X-3B dye sensitization would make difference and cause some degradation under this condition. However, this efficiency is relatively limited, and the adsorption ability of BiOCl is not strong, lead to its poor photocatalytic performance. The Ag₃VO₄ (2.2 eV) [32] catalyst with narrow band gap can be excited to produce hole-electron pairs under visible light irradiation. Therefore, after the deposition of Ag₃VO₄ particles onto BiOCl nanosheets, except the photosensitization pathway induced by X-3B dye, there is an Ag₃VO₄ assisted photocatalytic process. The schematic of X-3B degradation by BiOCl-Ag₃VO₄ hybrids under visible light irradiation is illustrated in Fig. 6a. Under visible light irradiation, both X-3B molecules and Ag₃VO₄ can be excited. First of all, the X-3B dye molecules are

excited by **absorbed visible light photons** to produce an excited state (denoted as X-3B*). **And the subsequent electron injections from X-3B* into the conduction band (CB) of BiOCl occur. On the other hand, Ag₃VO₄ can also be excited by visible light to produce photo-generated electron-hole (e⁻-h⁺).** These electrons on CB of Ag₃VO₄ are subsequently transferred into the CB of BiOCl, thus inhibits the recombination of the generated e⁻-h⁺. Although holes on the valence band (VB) of Ag₃VO₄ don't have the potential to generate hydroxyl radical ($\cdot\text{OH}$) through the oxidation of OH⁻ [28], it can directly cause a decomposition on X-3B. Furthermore, because of the layered structure of BiOCl, sufficient space is provided for the polarization of related atoms and orbitals, and the induced dipole can also make e⁻-h⁺ separation more effectively [25]. Then, the electrons can be trapped by the surface-adsorbed O₂ molecule to yield reactive superoxide **radicals** ($\cdot\text{O}_2^-$). Ultimately, the X-3B can be photocatalytically degraded by the above formed different radicals.

In order to examine the effects and find out the key species, the radical-trapping experiment was carried out and the results are displayed in Fig. 6b. As known to all, *tert*-butanol (TBA), disodium ethylenediaminetetraacetate (EDTA-Na₂) and benzoquinone (BQ) can be used as the scavengers of $\cdot\text{OH}$, h⁺ and $\cdot\text{O}_2^-$ respectively. The processes are all the same as the photocatalytic degradation of X-3B just with the addition of different scavengers. It can be seen that when the hydroxyl radical scavenger (*t*-BuOH) is added, just a little decrease on the photocatalytic activity of BiOCl-Ag₃VO₄ is observed. When the $\text{O}_2^{\cdot-}$ radical scavenger (BQ) or hole scavenger (EDTA-Na₂) is added **into** the reaction system, an evident decreasing of

photocatalytic **activity** of the BiOCl-Ag₃VO₄ hybrid **is observed**. The above results illustrate that O₂^{•-} radicals and holes contribute mostly to the high photocatalytic performance of BiOCl-Ag₃VO₄ hybrid. **However, hydroxyl radicals show less importance to the degradation of X-3B by BiOCl-Ag₃VO₄ composite photocatalyst.**

3.3 Possible mechanism for the enhanced activity

The photocatalytic performance of semiconductors is influenced by the following factors: surface area (adsorption activity), crystal phase, and electronic properties (including band gap, band edge potential and charge carrier mobility) etc. **The data of surface area for different samples are shown in Table 1. It can be seen that the BiOCl-Ag₃VO₄ hybrids all exhibit higher surface area than that of pure BiOCl. Furthermore, the adsorption percents of X-3B are 8.4%, 10.1%, 16.1%, 18.5%, 23.4% and 23.8% for BiOCl, B-A-1, B-A-2, B-A-3, B-A-4 and B-A-5, respectively. Therefore, it indicates that higher surface area (enhanced adsorption activity) is the first factor for the photocatalytic activity enhancement of the hybrid photocatalysts.** From the DRS results, we can know that the deposition of Ag₃VO₄ onto BiOCl cause red shift of the band gap and increased absorption activity in visible light region for the BiOCl-Ag₃VO₄ hybrids. Therefore, we can conclude that the **second** factor for the photocatalytic activity enhancement of the hybrid photocatalyst is ascribed to the optical absorption properties. For seeking other reasons **for enhanced photocatalytic activity of BiOCl-Ag₃VO₄ hybrid photocatalyst, photocurrents were measured at open circuit potentials for all**

samples after be deposited on FTO, and the results are shown in Fig. 7. A uniform and apparent photocurrent response can be seen for all electrodes. Furthermore, it can also be seen that all BiOCl-Ag₃VO₄ hybrids exhibit higher photocurrent than pure BiOCl. It is well known that the photocurrent is determined by the speed of excited electrons transfer from the photocatalyst to FTO and the recombination at the electrolyte interface [34]. Therefore, the enhancement of photocurrent for BiOCl-Ag₃VO₄ hybrids can be ascribed to the higher separation efficiency of photo-generated electron-hole pairs. It results from the deposition of Ag₃VO₄ onto BiOCl nanosheets and forms heterojunctions between the two components. The formed heterojunctions help to transfer and separate the photo-generated electron-hole pairs, thus increase the photocatalytic activity.

Photoluminescence (PL) spectra reflect the transfer of photo-induced charges between two semiconductors, which is one of the most important factors for the photocatalytic activity [35]. **Lower PL intensity implies lower recombination rate of** photo-generated electron-hole pairs, thus the higher photocatalytic activity [36]. The PL spectra of pure BiOCl and BiOCl-Ag₃VO₄ composite samples were measured with an excitation wavelength of 260 nm, and the obtained results are shown in Fig. 8. The PL spectrum of pure BiOCl shows a strong emission peak at about 410 nm, which can be ascribed to the self-trapped excitations [43]. Furthermore, compared with pure BiOCl, the intensity of PL signal for the BiOCl-Ag₃VO₄ hybrids all decrease. The results indicate that BiOCl-Ag₃VO₄ hybrids have lower recombination rate of photo-generated electron-hole pairs.

Based on the above analysis, the enhanced photocatalytic activity for BiOCl-Ag₃VO₄ hybrids can be ascribed to three major factors. The first one is the enhanced surface area of BiOCl-Ag₃VO₄ hybrids induce to higher adsorption percent of X-3B molecules. Therefore, it would induce to higher photocatalytic activity because of the enhanced local concentration of X-3B on the surface of the hybrids. The second factor is the enhanced optical absorption property of BiOCl-Ag₃VO₄ hybrids. The enhanced absorption property in visible light region would induce more photo-generated electron-hole pairs, which would generate more radicals for the degradation of X-3B. The last one factor is the formation of heterojunctions between BiOCl and Ag₃VO₄. The photo-generated charges can transfer through the formed heterojunctions much more quickly. Therefore, recombination rate of photo-generated electron-hole pairs is depressed, and more radicals are formed to help the degradation of X-3B. All in all, higher surface area, good optical absorption property, faster transferring rate of charges and lower recombination rate of electron-hole pairs contribute to the high photocatalytic activity of BiOCl-Ag₃VO₄ hybrids.

4. Conclusions

In summary, a series of BiOCl-Ag₃VO₄ hybrids with different mole ratio were successfully prepared via a facile method. The results showed that Ag₃VO₄ nanoparticles anchored on square-like BiOCl nanosheets uniformly. Deposition of Ag₃VO₄ onto BiOCl induce visible-light-driven activity for the obtained Ag₃VO₄/BiOCl hybrids. In the photodegradation process towards X-3B dye

under visible light irradiation, BiOCl-Ag₃VO₄ hybrids exhibited higher efficiencies than pure BiOCl. The amount of Ag₃VO₄ affected the activity of BiOCl-Ag₃VO₄ hybrids apparently. It was found that 0.2 was the optimum mole ratio to obtain the best photocatalytic performance in this work. The enhanced activity could be attributed to the improved optical absorption, X-3B adsorption and fast transferring of photo-generated charges. Besides, the results indicated that h⁺ and ·O₂⁻ radicals were the key species in the reaction. The present work aims to develop new promising visible-light-driven photocatalysts with efficient activity for dye pollutants.

Acknowledgements

National Science Funds for Creative Research Groups of China (No.51421006), Program for Changjiang Scholars and Innovative Research Team in University (No. IRT13061), National Science Fund for Distinguished Young Scholars (No. 51225901), the Key Program of National Natural Science Foundation of China (No. 41430751), the National Science Foundation of China for Excellent Young Scholars (No. 51422902), the National Natural Science Foundation of China (No. 51579073), Natural Science Foundation of Jiangsu Province (BK20141417), Qinglan Project of Jiangsu Province, and PAPD.

References :

- [1] Han CC, Ge L, Chen CF, et al. Novel visible light induced Co₃O₄-gC₃N₄ heterojunction photocatalysts for efficient degradation of methyl orange. Applied Catalysis B: Environmental, 2014, 147: 546-553.

- [2] Xu JJ, Chen MD, Wang ZM. Preparation of CdWO₄-deposited reduced graphene oxide and its enhanced photocatalytic properties. Dalton Transactions, 2014, 43: 3537-3544.
- [3] Zhao H, Zhang GM, Zhang QL. MnO₂/CeO₂ for catalytic ultrasonic degradation of methyl orange. Ultrasonics Sonochemistry, 2014, 21(3): 991-996.
- [4] Qin L, Zhang G L, Fan Z, et al. Templated fabrication of hierarchically porous Fe-Ti bimetallic solid superacid for efficient photochemical oxidation of azo dyes under visible light. Chemical Engineering Journal, 2014, 244: 296-306.
- [5] Li Y F, Zhang W P, Li X, et al. TiO₂ nanoparticles with high ability for selective adsorption and photodegradation of textile dyes under visible light by feasible preparation. Journal of Physics and Chemistry of Solids, 2014, 75(1): 86-93.
- [6] Khan M M, Lee J, Cho M H. Au@TiO₂ nanocomposites for the catalytic degradation of methyl orange and methylene blue: an electron relay effect. Journal of Industrial and Engineering Chemistry, 2014, 20(4): 1584-1590.
- [7] Lin X X, Fu D G. Facile one-pot hydrothermal synthesis of B/N-codoped TiO₂ hollow spheres with enhanced visible-light photocatalytic activity and photoelectrochemical property. Solid State Sciences, 2014.
- [8] Linsebigler A L, Lu G, Yates Jr J T. Photocatalysis on TiO₂ surfaces: principles, mechanisms, and selected results. Chemical reviews, 1995, 95(3): 735-758.
- [9] Anandan S, Ikuma Y, Niwa K. An overview of semi-conductor photocatalysis: modification of TiO₂ nanomaterials. Solid State Phenomena, 2010, 162: 239-260.
- [10] Asahi R, Morikawa T, Ohwaki T, et al. Visible-light photocatalysis in

- nitrogen-doped titanium oxides. *Science*, 2001, 293(5528): 269-271.
- [11]Zhang X, Zhang L Z, Xie T F, et al. Low-temperature synthesis and high visible-light-induced photocatalytic activity of BiOI/TiO₂ heterostructures. *The Journal of Physical Chemistry C*, 2009, 113(17): 7371-7378.
- [12]Xu S H, Feng D L, Shangguan W F. Preparations and photocatalytic properties of visible-light-active zinc ferrite-doped TiO₂ photocatalyst. *The Journal of Physical Chemistry C*, 2009, 113(6): 2463-2467.
- [13]Chen C, Cai W M, Long M C, et al. Synthesis of visible-light responsive graphene oxide/TiO₂ composites with p/n heterojunction. *ACS nano*, 2010, 4(11): 6425-6432.
- [14]Zhao L, Chen X F, Wang X C, et al. One-step solvothermal synthesis of a carbon@TiO₂ dyade structure effectively promoting visible-light photocatalysis. *Advanced Materials*, 2010, 22(30): 3317-3321.
- [15]Kato R, Furube A, Yamanaka K, et al. Charge separation and trapping in N-doped TiO₂ photocatalysts: a time-resolved microwave conductivity study. *The Journal of Physical Chemistry Letters*, 2010, 1(22): 3261-3265.
- [16]Park H, Choi W, Hoffmann M R. Effects of the preparation method of the ternary CdS/TiO₂/Pt hybrid photocatalysts on visible light-induced hydrogen production. *Journal of Materials Chemistry*, 2008, 18(20): 2379-2385.
- [17]Choi YI, Jeon KH, Kim HS, Lee JH, Park SJ, Roh JE, et al. TiO₂/BiOX (X = Cl, Br, I) hybrid microspheres for artificial waste water and real sample treatment under visible light irradiation. *Separation and Purification Technology*, 2016, 160:

28-42.

- [18] Natarajan K, Bajaj HC, Tayade RJ, Photocatalytic efficiency of bismuth oxyhalide (Br, Cl and I) nanoplates for RhB dye degradation under LED irradiation. *Journal of Industrial and Engineering Chemistry*, 2016, 34: 146-156.
- [19] Sun D F, Li J P, Feng Z H, et al. Solvothermal synthesis of BiOCl flower-like hierarchical structures with high photocatalytic activity. *Catalysis Communications*, 2014, 51(5): 1-4.
- [20] Xu JJ, Ao YH, Chen MD. A simple method for the preparation of Bi₂WO₆-reduced graphene oxide with enhanced photocatalytic activity under visible light irradiation. *Materials Letters*, 2013, 92: 126-128.
- [21] Zhang G, Hu ZY, Sun M. Formation of Bi₂WO₆ bipyramids with vacancy pairs for enhanced solar-driven photoactivity. *Advanced Functional Materials*. 2015, 25: 3726-3734.
- [22] Wang PF, Ao YH, Wang C, Hou J, Qian J. A one-pot method for the preparation of graphene-Bi₂MoO₆ hybrid photocatalysts that are responsive to visible-light and have excellent photocatalytic activity in the degradation of organic pollutants. *Carbon*, 2012, 50: 5256-5264.
- [23] Zhang K L, Liu C M, Huang F Q, et al. Study of the electronic structure and photocatalytic activity of the BiOCl photocatalyst. *Applied Catalysis B: Environmental*, 2006, 68(3): 125-129.
- [24] Li N, Hua X, Wang K, Jin YJ, Xu JJ, Chen MD, et al. In situ synthesis of uniform Fe₂O₃/BiOCl p/n heterojunctions and improved photodegradation

- properties for mixture dyes. Dalton Transactions, 2014, 43: 13742-13750.
- [25] Tan C W, Zhu G Q, Hojamberdiev M, et al. Co_3O_4 nanoparticles-loaded BiOCl nanoplates with the dominant {001} facets: efficient photodegradation of organic dyes under visible light. Applied Catalysis B: Environmental, 2014, 152: 425-436.
- [26] Ao YH, Tang H, Wang PF, Wang C. Deposition of Ag@AgCl onto two dimensional square-like BiOCl nanoplates for high visible-light photocatalytic activity. Materials Letters, 2014, 131: 74-77.
- [27] Chang F, Xie YC, Zhang J, Chen J, Li CL, Wang J, et al. Construction of exfoliated g-C₃N₄ nanosheets-BiOCl hybrids with enhanced photocatalytic performance. RSC Advances, 2014, 4: 28519-28527.
- [28] He ZQ, Shi YQ, Gao C, Wen LN, Chen JM, Song S. BiOCl/BiVO₄ p-n heterojunction with enhanced photocatalytic activity under visible-light irradiation. Journal of Physical Chemistry C, 2014, 118: 389-398.
- [29] Konta R, Kato H, Kobayashi H, et al. Photophysical properties and photocatalytic activities under visible light irradiation of silver vanadates. Physical Chemistry Chemical Physics, 2003, 5(14): 3061-3065.
- [30] Wang SM, Li DL, Sun C, Yang SG, Guan Y, He Huan. Synthesis and characterization of g-C₃N₄/Ag₃VO₄ composites with significantly enhanced visible-light photocatalytic activity for triphenylmethane dye degradation. Applied Catalysis B: Environmental, 2014, 144: 885-892.
- [31] Zhu Q, Wang WS, Lin L, Gao GQ, Guo HL, Du H, et al. Facile synthesis of the

- novel $\text{Ag}_3\text{VO}_4/\text{AgBr}/\text{Ag}$ plasmonic photocatalyst with enhanced photocatalytic activity and stability. *Journal of Physical Chemistry C*, 2013, 117: 5894-5900.
- [32] Wang J X, Ruan H, Li W J, et al. Highly efficient oxidation of gaseous benzene on novel $\text{Ag}_3\text{VO}_4/\text{TiO}_2$ nanocomposite photocatalysts under visible and simulated solar light irradiation[J]. *The Journal of Physical Chemistry C*, 2012, 116(26): 13935-13943.
- [33] Fariba K, Aziz HY. **$\text{Ag}_3\text{VO}_4/\text{ZnO}$ nanocomposites with an n-n heterojunction as novel visible-light-driven photocatalysts with highly enhanced activity[J]. *Materials Science in Semiconductor Processing*, 2015, 39: 671-679.**
- [34] Mahsa P, Aziz HY. **Ultrasonic-assisted preparation of novel ternary $\text{ZnO}/\text{Ag}_3\text{VO}_4/\text{Ag}_2\text{CrO}_4$ nanocomposites and their enhanced visible-light activities in degradation of different pollutants. *Solid State Sciences*, 2016, 55: 58-68.**
- [35] Aziz HY, Maryam SG. **$\text{Fe}_3\text{O}_4/\text{ZnO}/\text{Ag}_3\text{VO}_4/\text{AgI}$ nanocomposites: Quaternary magnetic photocatalysts with excellent activity in degradation of water pollutants under visible light. *Separation and Purification Technology*, 2016, 166: 63-72.**
- [36] Xiong J Y, Cheng G, Li G F, et al. Well-crystallized square-like 2D BiOCl nanoplates: mannitol-assisted hydrothermal synthesis and improved visible-light-driven photocatalytic performance[J]. *RSC Advances*, 2011, 1(8): 1542-1553.
- [37] Duo FF, Wang YW, Mao XM, Zhang XC, Wang YF, Fan CM. A $\text{BiPO}_4/\text{BiOCl}$

heterojunction photocatalyst with enhanced electron-hole separation and excellent photocatalytic performance. *Applied Surface Science*, 2015, 340: 35-42.

Figure Captions

Fig. 1 XRD patterns of pure BiOCl and B-A-4

Fig. 2 DRS spectra of pure BiOCl and BiOCl-Ag₃VO₄ hybrids

Fig. 3 Formation procedure of BiOCl-Ag₃VO₄ hybrid

Fig. 4 SEM (a~f) and TEM (g) images of the samples: (a) BiOCl, (b) B-A-1, (c) B-A-2, (d) B-A-3, (e) B-A-4, (f) B-A-5, (g) B-A-4

Fig. 5 (a) Concentration variation of X-3B vs irradiation time, (b) apparent rate constant of each sample in the photocatalytic process under visible light irradiation, (C) recyclability of B-A-4 under visible light irradiation. (The initial concentration of X-3B was 25 mg.L⁻¹, the photocatalyst dose was 0.2 g.L⁻¹)

Fig. 6 (a) Photocatalytic mechanism of BiOCl-Ag₃VO₄ hybrid under visible light; (b) effects of a series of scavengers on the degradation towards X-3B dye

Fig. 7 Photocurrent responses of BiOCl-Ag₃VO₄ hybrid under visible light irradiation

Fig. 8 Fluorescence spectra of BiOCl and BiOCl-Ag₃VO₄ hybrids

Table 1 The BET surface area of the obtained samples

Sample	Pure BiOCl	B-A-1	B-A-2	B-A-3	B-A-4	B-A-5
$a_{s,BET}/[m^2\ g^{-1}]$	0.94	5.11	6.63	8.04	9.31	8.55

Fig. 1 XRD patterns of pure BiOCl and B-A-4

Fig. 2 DRS spectra of pure BiOCl and BiOCl-Ag₃VO₄ hybrids

Fig. 3 Formation procedure of $\text{BiOCl-Ag}_3\text{VO}_4$ hybrid

Fig. 4 SEM (a~f) and TEM (g) images of the samples: (a) BiOCl, (b) B-A-1, (c) B-A-2, (d) B-A-3, (e) B-A-4, (f) B-A-5, (g) B-A-4; (h) EDX spectrum of B-A-4

Fig. 5 (a) Concentration variation of X-3B vs irradiation time, (b) apparent rate constant of each sample in the photocatalytic process under visible light irradiation, (c) recyclability of B-A-4 under visible light irradiation. (The initial concentration of X-3B was 25 mg.L⁻¹, the photocatalyst dose was 0.2 g.L⁻¹)

Fig. 6 (a) Photocatalytic mechanism of BiOCl-Ag₃VO₄ hybrid under visible light; (b) effects of a series of scavengers on the degradation of dye X-3B

Fig. 7 Photocurrent responses of BiOCl-Ag₃VO₄ hybrid under visible light irradiation

Fig. 8 Fluorescence spectra of BiOCl and BiOCl-Ag₃VO₄ hybrids

Graphical abstract:

A novel Ag_3VO_4 nanoparticles deposited BiOCl nanosheets composite photocatalyst with heterojunctions was prepared for the first time. The as-obtained photocatalysts exhibit much higher activity than pure BiOCl under visible light irradiation.