Environmental Science Processes & Impacts

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

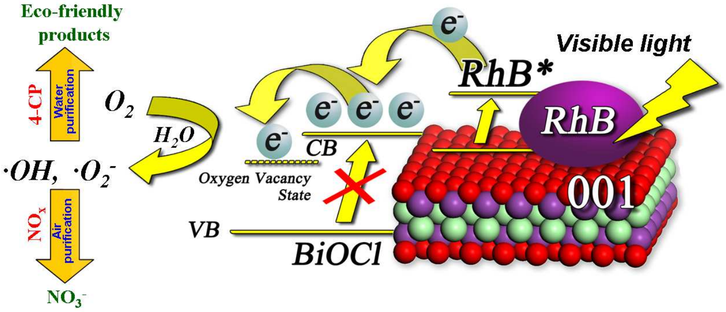
rsc.li/process-impacts

Table of Contents Entry

An Efficient Dye-sensitized BiOCl Photocatalyst for Air and Water Purification under Visible Light Irradiation

Guisheng Li[†], Bo Jiang[†], Shuning Xiao[†], Zichao Lian[†], Dieqing Zhang[†], Jimmy C. Yu*[‡], Hexing Li*[†]*

† Department of Chemistry, Key Laboratory of Resource Chemistry of Ministry of Education and Shanghai Key Laboratory of Rare Earth Functional Materials, Shanghai Normal University, Shanghai 200234, China. E-mail: Liguisheng@shnu.edu.cn; Hexing-Li@shnu.edu.cn, ‡ Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China). Fax: +(852)2603-5057; Tel: +(852)2609-6268; E-mail: jimyu@cuhk.edu.hk



An RhB/BiOCl system was proved effective for treating both air and water pollutants under visible light irradiation.

Environmental Impact Statement

Synthetic dyes are excellent light-harvesting materials but they are considered environmental hazards if discharged into water bodies. This is why dye-sensitization systems are not commonly used for pollution treatment. Interestingly, the same idea has gained popularity in dye-sensitized solar cells. This study describes the immobilization and integration of Rhodamine B to a BiOCl photocatalyst. The RhB-sensitized BiOCl system is highly effective for removing NO from air and 4-CP from water. More importantly, the dye molecules are well-retained in the treatment system. We believe the work provides immediate insight to solar-induced pollution treatment processes. We are also sure that this article will generate a lot of interest from researchers involved in environmental remediation and green catalysis.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

An Efficient Dye-sensitized BiOCl Photocatalyst for Air and Water Purification under Visible Light Irradiation

Guisheng Li,*† Bo Jiang,† Shuning Xiao,† Zichao Lian,† Dieqing Zhang,† Jimmy C. Yu,*‡ Hexing Li*†

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

A photosensitized BiOCl catalyst was found to be effective for photocatalytic water purification and air remediation under visible light irradiation (λ > 420 nm). Prepared by a solvothermal method, the BiOCl crystals possessed 3D hierarchical spherical structure with the highly active facets exposed. When sensitized by Rhodamine B (RhB), the photocatalyst system was more active than N-doped TiO_2 for breaking down 4-chlorophenol (4-CP, 200 ppm) and nitric monoxide (NO, 500 ppb). The high activity could be attributed to the hierarchical structure (supplying feasible reaction tunnels for adsorption and transition of reactants or products) and the efficient exposure of the {001} facets. The former provides an enriched oxygen atom density that promotes adsorption of cationic dye RhB, and creates an oxygen vacancy state. The HO· and $·O_2^-$ radicals produced from the injected electrons from the excited dye molecule (RhB*) into the conduction band of BiOCl were responsible for the excellent photocatalytic performance of the RhB/BiOCl system.

Introduction

Toxic chemical pollutants such as synthetic textile dyes, phenolic compounds and fluorescein dyes are often difficult to be decomposed by natural means.[1, 2] Degrading textile dyes by photocatalysis has been studied extensively.[3, 4] Due to its low cost, non-toxicity, and stability, titanium dioxide is an almost ideal photocatalyst. Its inherent UV photo-response region (λ < 387 nm) prohibits its solar-light utilization efficiency. Thus, many studies have focused on the utilization of visible light for treating pollutants with TiO_2 via doping hybrid atoms or coupling with other low band-gap semiconductors.[5-7] Nevertheless, doping or coupling routes still suffer from some disadvantages, such as the inhabitation of charge migration through the metal oxide8 and breaking of lattice symmetry.[9]

Photosensitization was explored as another effective approach to extend the photo-response of the large band-gap semiconductors into the visible light region.[10, 11] Dye-based photosensitized photo-degradation of organic pollutants undergoes the following steps: 1) Under visible-light irradiation, dye molecules adsorbed on semiconductors inject electrons into the conduction band (CB) of semiconductor particle,[12, 13] leading to the formation of dye cationic radicals. 2) The electrons trapped by the conduction band of semiconductor react with O_2 and H_2O adsorbed on the surface of semiconductors to produce HO· and $·O_2^-$.[14] In this process, the conduction band (CB) plays an important role in electron-transfer mediation, and the valence band (VB) remains unaffected.

BiOCl with a band gap of 3.4 eV exhibits high photocatalytic activity under ultraviolet light irradiation.[15-17] Much effort has been made to extend the response of BiOCl to the visible light range by chemical modification.[18-20] Recently, {001} facets exposure was proved to be effective for enhancing the photosensitization degradation of RhB.[21, 22] Xie et al.[23] utilized the vacancy associates for both enhancing the dye adsorption capability and narrowing the band gap of BiOCl. This allows both the improved photosensitization process and the increased photoinduced electron-hole pairs separation efficiency. More recently, Zhang et al.[24] found the surface structure dependent molecular oxygen activation properties of BiOCl single-crystalline nanosheets under UV light. The (001) surface of BiOCl prefers to reduce O_2 to $·O_2^-$ through one-electron transfer. Nevertheless, these BiOCl-based photocatalysts are still limited for self-sensitization degradation of dyes with low efficiency for solar-induced applications.

Herein, we report a simple but highly effective RhB/BiOCl system for treating pollutants, including highly concentrated 4-chlorophenol (4-CP) and indoor air pollutants (nitric oxide) under visible-light irradiation. 4-CP, an important intermediate for chemical industry, is widely used in the rubber, adhesive, plastic, cable, pesticide and dye productions.[25] However, the highly toxic 4-CP is difficult to be degraded due to the stability of the C-Cl bonds. The RhB photosensitized BiOCl was found to be effective for decomposing 4-CP (50-200 ppm) in water under visible-light irradiation. Besides, such system can also be used to oxidize NO (500 ppb, in a continuous flow reactor) in air with high efficiency under visible light irradiation.

Experimental

All chemicals were analytical grade and used without further purification. Bismuth nitrate ($Bi(NO_3)_3·5H_2O$) and alcohol were provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ethylene glycol (EG) and sodium chloride (NaCl) were obtained from Shanghai Chemical Company.

Photocatalyst preparation

In a typical process for BiOCl, 2.43 g $Bi(NO_3)_3{\cdot}5H_2O$ and 0.30 g NaCl were added into a mixture of alcohol containing 20.0 ml ethanol and 10.0 ml ethylene glycol under ultra-sonication. Then, the obtained mixture was autoclaved at a temperature 160 °C for 12 h. Subsequently, the autoclaved was cooled to room temperature naturally. The white sample was collected, washed with de-ionized water and alcohol three times and dried at 80 °C in vacuum for 12 h. Traditional BiOCl samples with no {001} facets exposed were prepared as a standard for comparison according to the reference. [26]

Photocatalytic activity test

The photocatalytic activities of the BiOCl samples were evaluated at 30 oC in a beaker with 50 mL aqueous suspensions of different organic pollutants (RhB: 100 mg/L; 4-CP: 50 mg/L) containing 50 mg of catalyst powder. The light source was a 300 W Xe lamp with a 420 nm cutoff filter. The dissolved oxygen in the reaction aqueous solution was utilized as molecular oxygen for producing oxidant radicals. The suspensions were stirred for 30 min in the dark in order to establish adsorption/desorption equilibrium between dye and the photocatalyst before illumination. At regular intervals, a 3 mL suspension was got into plastic tube and centrifuged to remove the photocatalyst particles. The concentration dyes were determined by colorimetry with the UV-vis spectroscopy (UV-7504PC). The 4-CP concentration was analyzed using Liquid chromatography-mass spectrometry (HPLC-MS, Agilent 1200). The reproducibility of the results was checked by repeating each reaction at least three times and was found to be within acceptable limits (± 5 %). The experimental process of NO oxidation is shown in supporting information.

Results and discussion

Fig. 1a shows a typical XRD pattern of as-prepared BiOCl, indicating its tetragonal lattice structure (JCPDS No Card No. 06-0249) No impurities were detected, suggesting that the single-phase products are of high purity. Compared to that of the traditional BiOCl samples (see Fig. S1), the broad and weak (001) diffraction peak indicates that the as-obtained sample possesses a high exposure percentage of {001} facets.

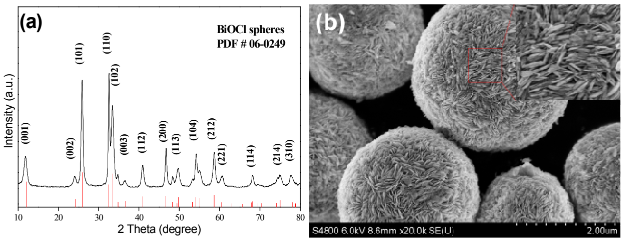


Figure 1. XRD pattern (a), FESEM images (b) of the as-prepared BiOCl spheres.

The morphology of the as-formed BiOCl samples was also examined by FESEM. From Fig. 1b, it can be seen that the BiOCl samples possess uniform hierarchical microspheres with BiOCl nanosheets assembly. The average size of the BiOCl microspheres is about 3 μm. The HRTEM was also utilized to analyze the crystal facets information of the as-prepared samples via using the traditional samples as a reference. As shown in Fig. 2, the traditional BiOCl crystals were exposed with {010} facets (see Fig. 2a and e). However, the as-prepared BiOCl crystals were dominated with {001} facets (see Fig. 2b and d).

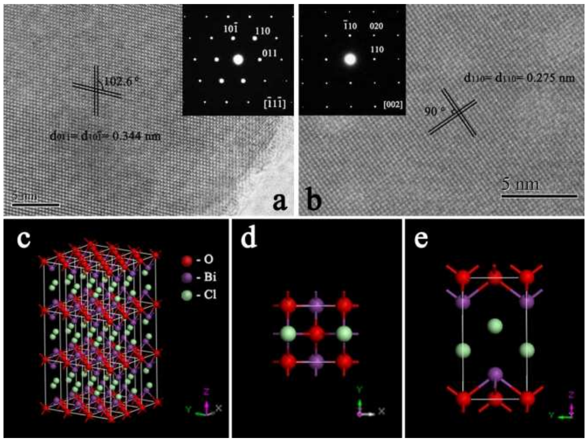


Figure 2. HRTEM comparison of traditional BiOCl (a) and as-prepared BiOCl (b) with SAED in the inset, (c) the structure model illustration of BiOCl crystals (3×3 lattices), side view of BiOCl crystal (d) {001} facets, and (e) {010} facets.

The as-formed hierarchical structure is confirmed by the corresponding nitrogen isotherm of the BiOCl spheres. As shown in Fig. 3a, the hysteresis loop ($0.45 < P/P_0 < 0.85$) suggests the filling of the framework confined smaller mesopores formed between intra-agglomerated primary particles, another hysteresis loop ($0.85 < P/P_0 < 1.0$) is caused by the filling of larger textural mesopores produced by inter-aggregated BiOCl secondary particles. The inset of Fig. 1c shows that the as-obtained BiOCl sample has a wide pore size distribution, ranging from 2 nm to 30 nm as calculated from the desorption branch of a nitrogen isotherm by the BJH method.

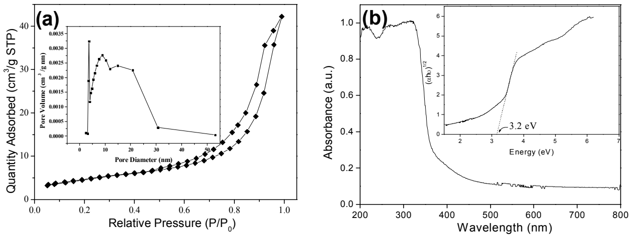


Figure 3. (a) N_2 adsorption-desorption isotherm and pore size distribution curve inset, and (b) UV-visible absorption spectum and determination of indirect inter-band transition energies (inset) of the as-prepared BiOCl spheres.

The average adsorption pore size is about 25 nm. The BET surface area of the hierarchical spherical BiOCl is 9.1 m^2/g. Though the BET surface area is not particularly large, such hierarchical structure with meso- and macro- pores can serve as efficient transport paths for reactants and products in photocatalytic reactions.[27] The optical properties of BiOCl were measured with the UV-vis diffuse reflectance spectra (Fig.3b). As a crystalline semiconductor, the optical absorption near the band edge follows the formula $(\alpha h\upsilon)n = k(h\upsilon\text{-}Eg)$,[28] where a, h, v, Eg, and B are the absorption coefficient, Planck constant, light frequency, band gap, and a constant, respectively. The intercept of the tangent to the plot gives a good approximation of the band gap energy of the sample (Fig.3b). The band gap of BiOCl is estimated to be about 3.2 eV. Pure BiOCl is obviously inactive in the visible-light range.

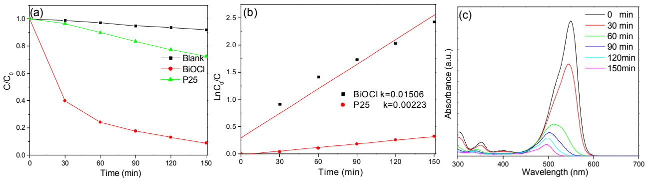


Figure 4 (a) The photo-sensitization induced degradation of RhB (100 mg/L) in the absence of catalysts (blank) and in the presence of the as-prepared BiOCl and P25 under visible light irradiation (λ > 420 nm); (b) corresponding dependence of Ln(C_0/C) on irradiation time for treating RhB solution by BiOCl and P25; (c) UV-visible spectral changes of RhB in an aqueous BiOCl dispersion as a function of irradiation time under visible light illumination.

As shown in Fig. 4a, the photo-induced degradation of RhB could be negligible under visible light irradiation (λ > 420 nm) in the absence of BiOCl. However, the removal rate of RhB owing to the photosensitization effect of RhB was greatly enhanced upon introducing the photocatalysts (BiOCl). After 150 min irradiation, about 90 % of RhB was removed in the presence of the BiOCl samples. On the contrary, only about 20 % RhB can be photo-degraded by using commercial photocatalyst (P25) as a standard. The photocatalytic reaction constants were also calculated to be as the following order: K_{BiOCl} (0.01506 min^{-1}) > K_{P25} (0.00223 min^{-1}) as shown in Fig. 4b. In Fig. 4c, it was found that the absorptive intensity of RhB at a wavelength of 553 nm gradually decreases and absorption band shifts to shorter wavelength (decrease in the absorbance at 498 nm). It may be the process of photochemical N-deethylation of RhB and turn to Rhodamine.[29] After 120 min of reaction, no new shifted peaks were observed, suggesting that the aromatic chromophore would continue to be attacked by the active species leading to the decomposition of RhB.[30] These results suggest that RhB/BiOCl is an excellent photosensitization system for treating pollutants.

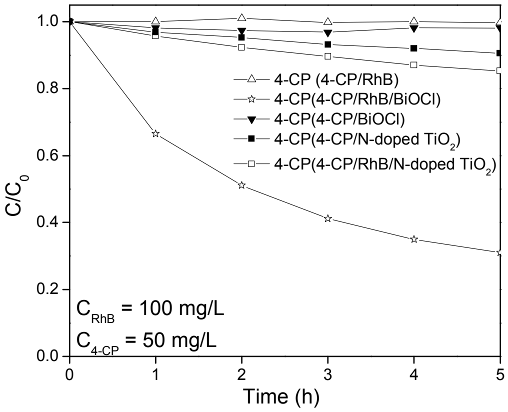


Figure 5 The comparison of photocatalytic decomposition of 4-CP in various reaction system: 4-CP/RhB (-△-), 4-CP/BiOCl (-▼-), 4-CP/RhB/BiOCl (-☆-), 4-CP/N-doped TiO_2 (-■-), and 4-CP /RhB/ N-doped TiO_2 (-□-) under visible light irradiation (λ > 420 nm). The concentrations of RhB and 4-CP are 100 and 50 mg/L, respectively.

As shown in Fig. 5, various controlled experiments were conducted to investigate the photocatalytic activity of the RhB/BiOCl system for degrading 4-CP. In the absence of catalysts, no 4-CP removal could be observed in the 4-CP/RhB system, suggesting RhB induced self-sensitization cannot lead to the oxidation of 4-CP. It was also observed that the visible-light induced degradation of 4-CP was negligible even after 5 h of reaction in the absence of RhB. It should be noted that a 4-CP removal rate of 69 % can be achieved upon introducing 100 mg/L of RhB. For comparison, an N-doped TiO_2 was utilized as a standard for treating the highly concentrated 4-CP (50 ppm). It is surprising that only about 9 % of 4-CP can be removed by the N-doped TiO_2. With the aid of RhB, N-doped TiO_2 obtained a 15 % removal rate of 4-CP.

As known, 4-CP is very difficult to be degraded due to the stability of the C-Cl bondsl.[31] Such greatly enhanced 4-CP degradation rate (about 7 times of that of the N-doped TiO_2) confirms the advantage of the RhB/BiOCl photosensitized system. Upon visible light irradiation, the dye (RhB) molecules adsorbed on the surface of BiOCl can be excited for the formation of electrons, which can further transfer to the conduction band (CB) of the BiOCl. The trapped electrons by the BiOCl crystals can react with hydroxyl groups and oxygen molecules to produce oxidative radicals, including HO· or $\cdot O_2^-$, for oxidizing organic pollutants, 4-CP. However, it should be noted that a 46 % removal rate of RhB was still obtained during the 4-CP degradation process. This may be ascribed to the competitive reaction of RhB and 4-CP with the oxidative radicals on the BiOCl surface.

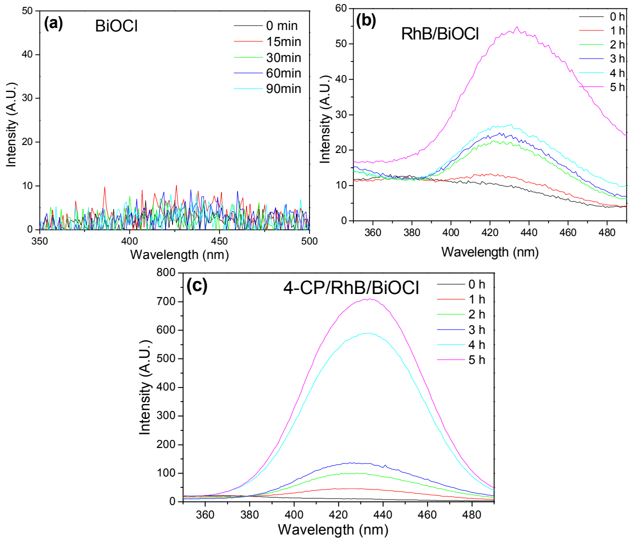


Figure 6 (a, b, c) Fluorescence spectra of the BiOCl in terephthalic acid (0.5 M) and NaOH (0.5 M) solution at different irradiation times (λ > 420 nm) (a: BiOCl-water system, b: RhB/BiOCl water system), c: 4-CP/RhB/BiOCl water system) (excitation wavelength = 312 nm; emission wavelength = 426 nm).

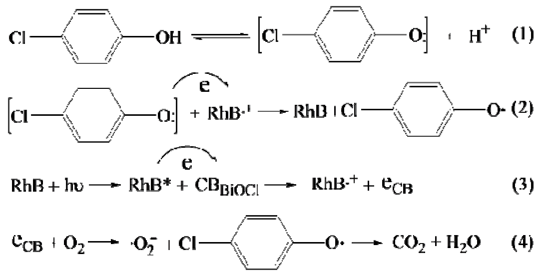
The PL-TA technique has been widely used in the detection of hydroxyl radicals.[32] As shown in Fig. 6a, no peak was detected in BiOCl-water system under visible light irradiation, while the intensity of the signal intensity was increased with prolonging the irradiation time from 0 to 5 hrs under visible light irradiation in BiOCl-RhB-water system (see Fig. 6b). These results indicate that the RhB dye molecules could be considered as a strong visible-light photo-sensitizer for BiOCl crystals. It should be pointed out that the PL intensity was greatly enhanced upon introducing 4-CP into the RhB/BiOCl system, as shown in Fig. 6c. This suggested that lots of hydroxyl radicals could be produced in the 4-

CP/RhB/BiOCl reaction system. It could explain why 4-CP was able to be degraded by the RhB/BiOCl system.

It is known that a dye photosensitization mechanism is closely related to the dye structural stability, the dye absorbance on the surface of photocatalyst and the adsorption capability of photocatalyst.[33] Owing to the high percentage of {001} facets exposed, the as-prepared BiOCl presents an enriched oxygen atom density, allowing a strong adsorption capability for the cationic dye RhB.[23] As shown in Fig. S2, the maximum adsorption capacity of the as-prepared BiOCl sample (115 μmol/g) is much larger that of the traditional BiOCl sample, though the BET surface area of the latter is about 9.8 m^2/g, larger than that of the former, as shown in Fig. S3. It should be pointed out that the maximum RhB adsorption on the as-prepared BiOCl is about 6 times of that (20 μmol/g) of the ultrafine BiOCl nanosheets reported by the Xie group.[23] Such high adsorption capability allowed the as-prepared BiOCl to have much higher photocatalytic activity for degrading 4-CP in the 4-CP/RhB/BiOCl system, as shown in Fig. S4.

In addition to the adsorption capability, the matching of energy levels between the excited dye and the semiconductor should also be considered. As known, the energy level of the excited Dye* (E(Dye*)) should be lower than the that of the CB of semiconductor. In the present system, the relative positions of the standard oxidation-redox potential of the RhB (E0(RhB*/RhB+)= -1.42 V vs NHE, pH= 7)[12] is lower than that of BiOCl (CB= -1.1 eV). Thus, electrons can transfer from the adsorbed dye in its singlet excited state to the CB of BiOCl. Based on the above discussion, such excellent RhB/BiOCl photosensitized system for degrading RhB may be attributed to the following factors: 1) strong RhB adsorption capability of the as-prepared BiOCl owing to its high {001} facets exposed percentage; 2) rapid electron transfer between the excited RhB molecules and the CB of BiOCl; 3) layered structure allowing a higher light utilization efficiency owing to light multi-reflection and a fast transition of reactants and products.[34] As shown in Fig. S4, the removal rate of 4-CP of the as-obtained {001} facets exposed BiOCl is much higher than that of the traditional BiOCl samples.

Though the RhB/BiOCl photosensitized system has been proven effective for treating highly concentrated 4-CP, it should be acknowledged that RhB acted as both sensitizer and sacrificial agents during the whole reaction process. Interestingly, RhB is regenerated during the photocatalytic process as shown in the following equations.[35]



4-CP is ionized to H+ and 4-CP- in an aqueous solution. The 4-CP- anions interact with the activated RhB radicals (RhB·+) by donating its electrons to form 4-CP radicals (4-CP·) and RhB molecules. It should be noted that the reactions are pH dependent. As shown in Fig. 7, a pH of 10 or higher should be maintained for effective removal of 4-CP while the process. At pH 12, about 80 % of 4-CP can be removed with a very small loss of RhB after 5 hours of reaction. Even improving the 4-CP concentration to 200 mg/L, an 80 % removal rate still can be obtained while keeping the RhB concentration nearly unchanged. This shows the potential for pollution treatment by such a photosensitized catalyst system.

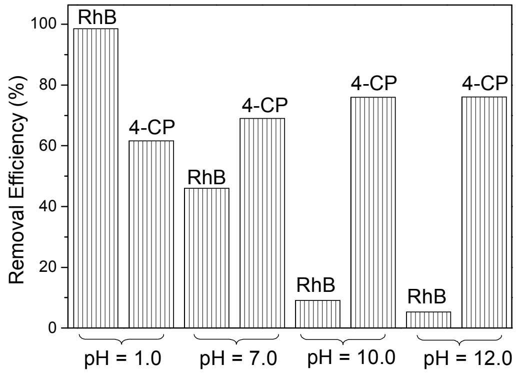
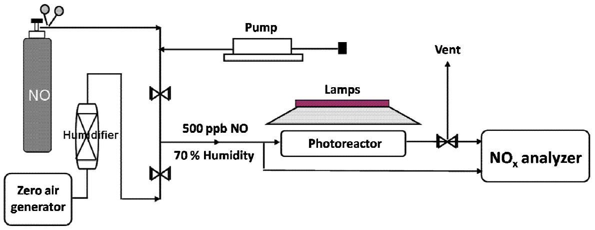


Figure 7. Removal rates of 4-CP and RhB in 4-CP/RhB/BiOCl system at various pH values under visible light irradiation. The concentrations of RhB and 4-CP are 100 and 50 mg/L, respectively. Reaction time = 5 h.

The RhB/BiOCl system also exhibits considerable activity for photocatalytic oxidation of NO gas-flow under visible light irradiation (see Scheme 1). As shown Fig. 8, pure BiOCl cannot oxidize NO gas under visible light irradiation owing to its large band gap. However, pre-adsorbing 10 mL of RhB (200 mg/L) on the surface of BiOCl would result in a 72% NO removal as shown in Fig. 8b. Meanwhile, it should be pointed out the stability of the photocatalytic performance can be well maintained to about 70 min. It indicates that RhB/BiOCl is a stable visible-light-driven photocatalytic system for treating NO.



Scheme 1. The scheme of the set-up for NO gas-flow oxidation

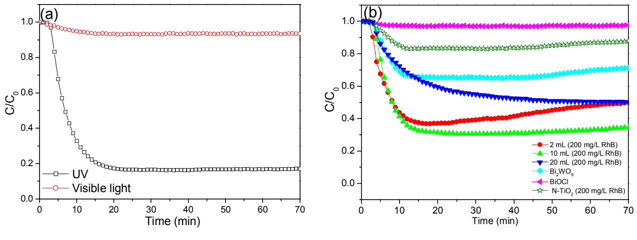


Figure 8. Photocatalytic oxidation of NO by pure BiOCl (a) under UV or visible-light irradiation and by the RhB/BiOCl system and Bi_2WO_6 [36] (b) under visible light irradiation.

Fig. 8b also shows the photocatalytic oxidation of NO on self-sensitized RhB/BiOCl system loaded with different amounts of RhB under visible light irradiation. As expected, pure BiOCl does not exhibit NO oxidation activity. A RhB/BiOCl system with 10 mL RhB pre-adsorbed is the best with a 72 % removal rate of NO under visible light irradiation, about two times of that of the standard photocatalyst (Bi_2WO_6) reported previously.[36] Under the same conditions an N-doped TiO_2 exhibited only a 20 % NO removal. The activity of the RhB/BiOCl system under visible-light (72 %) is very close to that under UV-light (80 %). This indicates the as-designed RhB/BiOCl system could be served as strong solar light driven photocatalytic tool for treating photochemical smog (NO). Overloading BiOCl with RhB (20 mL, 200 mg/L) would result in a greatly decreased activity. Such decrease may be ascribed to the light shielding effect of over loaded RhB. Only a low portion of light can penetrate into the RhB/BiOCl system for driving the photocatalytic reaction.

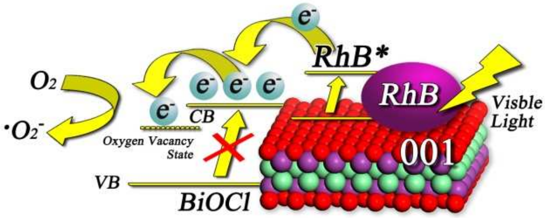


Figure 9. Possible mechanism of the RhB/BiOCl system.

Based on the above results, it could be recognized that RhB/BiOCl is an excellent photosensitized system for environmental remediation. Its high photocatalytic activity may be due to: 1) the 3D hierarchical spherical structure that provides channels for the transport of reactants or products; and 2) the high oxygen atom density on the {001} facets of BiOCl which allows a strong adsorption of cationic dye (RhB) on the surface of BiOCl samples. Such strong interaction could serve as the electron channels between RhB and BiOCl during the sensitization process. Therefore, more electrons can easily transfer from RhB to the conduction band of BiOCl. Meanwhile, such high {001} exposed oxygen atom density could also cause more oxygen vacancy concentration.[23] The EPR results (see Fig. S5) suggest that the {001} facets exposed BiOCl exhibits much stronger oxygen vacancy peaks as compared to the traditional samples. As shown in Fig. 9, the formation of an oxygen vacancy state could induce the second transfer of electron, promoting the photosensitization activity of the RhB/BiOCl system.

Conclusions

In summary, this work developed a highly efficient RhB/BiOCl system for both air and water remediation with the aid of the strong self-sensitization effect of RhB adsorbed on the {001} facets exposed hierarchical BiOCl spheres. Owing to the 3D hierarchical spherical structure, high oxygen atom density on the {001} facets, and high oxygen vacancy concentration, the as-formed BiOCl greatly enhanced the photosensitization effect of RhB for breaking down 4-chlorophenol (200 ppm) and nitric monoxide (500 ppb) under visible light irradiation with an excellent photocatalytic performance. At a basic condition (pH > 10), such RhB/BiOCl system could maintain the high photocatalytic activity for degrading 4-CP while keeping RhB nearly unchanged owing to the fast electron transfer from 4-CP- anions to RhB radicals (RhB·+) with the regeneration of RhB molecules. The present work may supply deep insight into the photosensitization induced photocatalytic mechanism, and also offer new opportunities for the practical applications of photocatalytic technology in environmental remediation.

Acknowledgments

This work was supported by the Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning, the National Natural Science Foundation of China (21207090, 21237003, and 21261140333), Shanghai Government (11SG42, 11ZR1426300, 12PJ1406800, 13YZ054), PCSIRT (IRT1269), a scheme administrated by Shanghai Normal University (DXL122, and S30406), and the Shenzhen Basic Research Program-JCYJ20120619151417947.

Notes and references

† Department of Chemistry, Key Laboratory of Resource Chemistry of Ministry of Education and Shanghai Key Laboratory of Rare Earth Functional Materials, Shanghai Normal University, Shanghai 200234, China. E-mail: Liguisheng@shnu.edu.cn; Hexing-Li@shnu.edu.cn
‡ Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China; and Shenzhen Research Institute, The Chinese University of Hong Kong, Shenzhen, China
Fax: +(852)2603-5057; Tel: +(852)3943-6268; E-mail: jimyu@cuhk.edu.hk

1. K. M. Wollin and B.D. Goerlitz, *J. Environ. Pathol. Tox.,* 2004, **23**, 267.
2. M. A. Brown and S. C. De-Vito, *Crit. Rev. Environ. Sci. Technol.,* 1993**, 23**, 249.
3. O. Legrini, E. Oliveros and A. M. Braun, *Chem. Rev.,* 1993**, 93**, 671.
4. M. R. Hoffmann, S. T. Martin, W. Y. Choi and D. W. Bahnemann, *Chem. Rev.,* 1995**, 95**, 69.
5. J. C. Yu, W. K. Ho, J. G. Yu, H. Yip, P. K. Wong and J. C. Zhao, *Environ. Sci. Technol.,* 2005**, 39**, 1175.
6. G. S. Li, D. Q. Zhang and J. C. Yu, *Environ. Sci. Technol.,* 2009**, 43**, 7079.
7. H. Choi, M. G. Antoniou, M. Pelaez, A. A. De la Cruz, J. A. Shoemaker and D. D. Dionysiou, *Environ. Sci. Technol.,* 2007**, 41**, 7530.
8. W. Y. Choi, A. Termin and M. R. Hoffmann, *J. Phys. Chem.,* 1994**, 98**, 13669.
9. J. H. Clark, M. S. Dyer, R. G. Palgrave, C. P. Ireland, J. R. Darwent, J. B. Claridge and M. J. Rosseinsky, *J. Am. Chem. Soc.,* 2011, **133**, 1016.
10. T. X. Wu, G. M. Liu, J. C. Zhao, H. Hidaka and N. Serpone, Photoassisted degradation of dye pollutants. V. *J. Phys. Chem: B,* 1998, **102**, 5845.
11. M. Q. Hu, Y. M. Xu and J. C. Zhao, *Langmuir,* 2004, **20**, 6302.
12. H. Meier, *Photochem. Photobiol.,* 1972, **16**, 219.
13. H. Gerischer, *Photochem. Photobiol.,* 1972, **16**, 243.
14. D. Zhao, C. Chen, Y. Wang, W. Ma, J. Zhao, T. Rajh and L. Zang, *Environ. Sci. Technol.,* 2008, **42**, 308.
15. L. P. Zhu, G. H. Liao, N. C. Bing, L. L. Wang, Y. Yang and H. Y. Xie, *CrystEngComm,* 2010, **12**, 3791.
16. F. Chen, H. Q. Liu, S. Bagwasi, X. X. Shen and J. L. Zhang, *J. Photochem. Photobio. A-Chem.,* 2010, **215**, 76.
17. Y. Lei, G. Wang, S. Song, W. Fan and H. Zhang, *CrystEngComm,* 2009**, 11**, 1857.
18. S. Y. Chai, Y. J. Kim, M. H. Jung, A. K. Chakraborty, D. Jung and W. I. Lee, *J. Catal.,* 2009, **262**, 144.
19. L. Ye, L. Zan, L. Tian, T. Peng, J. Zhang, *Chem. Commun.,* 2011**, 47**, 6951.
20. L. Q. Ye, K. J. Deng, F. Xu, L. H. Tian, T. Y. Peng, L. Zan, *Phys. Chem. Chem. Phys.,* 2012, **14**, 82.
21. D. H. Wang, G. Q. Cao, Y. W. Zhang, L. S. Zhou, A. W. Xu and W. Chen, *Nanoscale,* 2012, **4**, 7780.

22. J. Jiang, K. Zhao, X. Y. Xiao and L. Z. Zhang, *J. Am. Chem. Soc.,* 2012, **134**, 4473.
23. M. L. Guan, C. Xiao, J. Zhang, S. J. Fan, R. An, Q. M. Cheng, J. F. Xie, M. Zhou, B. J. Ye and Y. Xie, *J. Am. Chem. Soc.,* 2013, **135**, 10411.
24. K. Zhao, L. Z. Zhang, J. J. Wang, Q. X. Li, W. W. He and J. J. Yin, *J. Am. Chem. Soc.,* 2013, **135**, 15750.
25. S. Babel and T. A. Kurniawan, *J. Hazard. Mater.,* 2003, **97**, 219.
26. J. Xiong, G. Cheng, G. Li, F. Qin and R. Chen, *Rsc Adv.,* 2011, **1**, 1542.
27. J. C. Yu, G. S. Li, X. C. Wang, X. L. Hu, C. W. Leung and Z. D. Zhang, *Chem. Commun.,* 2006, **25**, 2717.
28. Butler, M. A., *J. Appl. Phys.,* 1977, **48**, 1914.
29. T. Watanabe, T. Takizawa and K. Honda, *J. Phys. Chem.,* 1977, **81**, 1845.
30. W. Li, D. Li, S. Meng, W. Chen, X. Fu, Y. Shao, *Environ. Sci. Technol.,* 2011, **45**, 2987.
31. T. A. Kurniawan, W. H. Lo, E. Repo and M. E. T. Sillanpaa, *J. Chem. Technol. Biotechnol.,* 2010, **85**, 1616.
32. J. C. Barreto, G. S. Smith, N. H. Strobel, P. A. McQuillin and T. A. Miller, *Life Sci.* 1995, **56**, 89.
33. X. Lin, T. Huang, F. Huang, W. Wang and J. Shi, *J. Phys. Chem. B,* 2006, **110**, 24629.
34. L. S. Zhang, W. Z. Wang, Z. G. Chen, L. Zhou, H. L. Xu and W. Zhu, *J. Mater. Chem.,* 2007, **17**, 2526.
35. G. S. Li, Y. Zhang, L. Wu, F. Wu, R. Wang, D. Q. Zhang, J. Zhu and H. X. Li, *Rsc Adv.,* 2012, **2**, 4822.
36. G. S. Li, D. Q. Zhang and J. C. Yu, *Environ. Sci. Technol.,* 2010, **44**, 4276.