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Pt/Bi₂₄O₃₁Cl₁₀ composite nanosheets with significantly enhanced photocatalytic activity under visible light irradiationBoran Xu ^{a,b}, Juan Li ^a, Lu Liu ^b, Yandong Li ^b, Shaohui Guo ^b, Yangqin Gao ^b, Ning Li ^b, Lei Ge ^{a,b,*}^a State Key Laboratory of Heavy Oil Processing, College of Science, China University of Petroleum Beijing, Beijing 102249^b Department of Materials Science and Engineering, College of Science, China University of Petroleum Beijing, Beijing 102249

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ABSTRACT

Efficient composite semiconductor photocatalysts are highly desirable for the visible-light-driven degradation of organic pollutants. In this study, Bi₂₄O₃₁Cl₁₀ photocatalyst was prepared via a hydrothermal method and modified with Pt nanoparticles (NPs) through a facile deposition procedure. The composite photocatalyst was characterized by X-ray diffraction, transmission electronic microscopy, X-ray photoelectron spectroscopy, UV-vis diffuse reflectance spectroscopy, photoluminescence spectroscopy, and electron spin resonance. The 1.0 wt% Pt/Bi₂₄O₃₁Cl₁₀ photocatalyst showed the highest activity for the degradation of methyl orange under visible light (source: 300 W Xe lamp coupled with a UV-cutoff filter), and the photocatalytic degradation efficiency improved about 2.2 times compared to that of pure Bi₂₄O₃₁Cl₁₀. The composite photocatalyst could maintain most of its activity after four runs of the photocatalytic experimental cycle. This study could provide a novel insight for the modification of other desirable semiconductor materials to achieve high photocatalytic activities.

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1. Introduction

In addition to continuously improving the quality of life, the rapid development of technology and industry has also led to serious water pollution globally. Solving this environmental problem has already been considered as one of the most urgent tasks of this century [1–3]. As an environmentally friendly technology for the remediation of the organic pollutants present in water, the semiconductor photocatalyst TiO₂ has attracted considerable attention [4–6]. However, its wide bandgap (3.2 eV) limits its optical absorption in the UV range, hence the application of TiO₂ for the photodegradation of the organic pollutants contained in water under visible light is extremely impractical [7]. In order to utilize the solar energy cor-

responding to the visible range, various novel visible-light-driven photocatalysts have been developed [8]. Among these photocatalysts, Bi-based compounds have attracted a lot of attention owing to their suitable gap widths, high electron mobilities, and large absorption coefficients for visible light absorption [9].

Bi_xO_yX_z (X = Cl, Br, I) is a series of semiconductor photocatalysts with a unique layered stacking structure [10–14] that permits a high separation efficiency of photogenerated carriers, thus resulting in good photocatalytic activities [15]. Recently, Huang's group [16] found that the open crystal structure of BiOCl plays an important role in determining its photocatalytic activity. Li and his colleagues [17] prepared Bi₃O₄Cl nanocrystals with a high exposure rate of the (001) crystal surface,

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therefore, the separation and transmission of photoelectric charge was enhanced, leading to improved photocatalytic performance. Besides that, many other types of $\text{Bi}_x\text{O}_y\text{X}_z$ have also attracted widespread attention [18–22]. In order to further improve the photocatalytic performance of $\text{Bi}_x\text{O}_y\text{X}_z$, various strategies have been proposed, such as constructing heterostructures [23–25] and loading with co-catalysts [26–28]. On the basis of a comprehensive literature search, we noticed that the $\text{Bi}_x\text{O}_y\text{X}_z$ photocatalysts still exhibit limited photocatalytic performance under visible light irradiation. Therefore, further functional modifications are highly desired for this type of photocatalyst [29].

Precious metal particles usually act as a sink for electrons, and facilitate charge migration at the heterogeneous interface, resulting in a better photocatalytic performance [9,30,31]. In this regard, we are interested in studying the activity of $\text{Bi}_x\text{O}_y\text{X}_z$ photocatalysts with surface decoration of noble metal nanoparticles. Among them, $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ is visible-light-driven and has the most appropriate bandgap, but, based on our knowledge, there are few reports on its photocatalytic performance.

In this work, different weight fraction of the noble metal Pt was first introduced onto the surface of $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ nanosheets and the effect of Pt loading amount on the photocatalytic performance of $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ was investigated in detail. Photoluminescence (PL) and electron spin resonance (ESR), as well as first-principle modeling, were performed, and the results were combined to discuss the mechanism of the photocatalytic degradation of methyl orange (MO) by Pt-modified $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$. Based on our study, better photocatalytic activity is expected from the synergetic effect of Pt and $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$, which results in a highly enhanced charge separation efficiency. As a result, the Pt/ $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ nanosheets exhibit significantly enhanced activity for the photodegradation of MO, and the composite sample also retained its stability after the catalytic cycling experiments.

2. Experimental

2.1. Synthesis of $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ nanosheets

In a typical procedure, 4 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 2 mmol of NaCl were added to 24 mL of distilled water at room temperature with continuous stirring, and then, 25 wt% ammonia was added to adjust the pH of the solution to 10. The solution was then stirred vigorously for 30 min and transferred into a 100 mL Teflon-lined stainless autoclave, which was heated up to 160 °C for 18 h and then air cooled to room temperature. The resulting precipitates were collected, washed with ethanol and deionized water thoroughly, and finally dried at 50 °C in air. The precipitate was then collected by using a centrifuge tube and rinsed with distilled water and absolute alcohol and then dried at 50 °C in air.

2.2. Synthesis of Pt/ $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$

Pt nanoparticles were obtained on the surface of $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ nanosheets by the photoreduction technique. $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ (0.1 g) was dispersed in 100 mL of deionized water by ultrasonication

for 0.5 h. Afterwards, 0.25 mL of H_2PtCl_6 solution was added with continuous magnetic stirring for 0.5 h. The product was then reduced by Xe arc lamp irradiation for 0.5 h and dried at 50 °C for 12 h. Finally, $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ nanosheets with 0.5 wt% loading fraction of Pt nanoparticles were obtained. Similarly, other loading samples were prepared by the same procedure.

2.3. Characterization

The crystal structure of the sample was analyzed by X-ray diffraction with Cu K_α radiation (XRD; Bruker D8 Advance) by using a scanning step of 3°. The morphology of the sample was examined by high-resolution transmission electron microscopy (HRTEM). X-ray photoelectron spectroscopy (XPS) was carried out on a PHI 5300 ESCA system with the beam voltage of 3.0 eV and Ar ion beam energy of 1.0 keV to determine the composition of the final product. The binding energy was normalized to an indefinite carbon signal at 284.8 eV. The PL spectrum was recorded by a Varian Cary Eclipse spectrometer. The total organic carbon (TOC) was analyzed by a TOC measuring instrument (Shimadzu TOC-5000). The ESR signals of spin-captured oxidized radicals were obtained on a Bruker-type ESR JES-FA200 spectrometer equipped with a quantum ray Nd: YAG laser as the light source by using an UV cut-off filter (≥ 400 nm).

Electronic structure calculations were carried out by using density functional theory (DFT) combined with the projector augmented wave (PAW) method, as implemented in the Vienna ab initio simulation package. The exchange-correlation energy is in the Perdew-Burke-Ernzerh of the generalized gradient approximation. A $3 \times 3 \times 1$ Monkhorst-Pack k mesh was used to optimize the crystal structure and a $6 \times 6 \times 2$ Monkhorst-Pack k mesh was applied to calculate the electronic structure of Mg_3Sb_2 . The plane-wave cutoff energy was set at 400 eV, and the energy convergence criterion was set at 10^{-4} eV.

2.4. Photocatalytic activity

The photocatalytic activities of the as-prepared samples were investigated for the degradation of MO under visible-light irradiation. A 30 mg photocatalyst powder was suspended in 100 mL of aqueous MO solution (20 mg/L). The suspension was stirred for 30 min in the dark to establish the adsorption-desorption equilibrium. Subsequently, a 300 W Xe lamp coupled with a UV-cut-off filter (≥ 400 nm) was used as the visible light source to irradiate the suspensions under vigorous stirring. The light intensity employed was 72 mW cm^{-2} . After irradiation, 4 mL of the sample solution was collected at certain time intervals, and the photocatalysts were removed by centrifugation; the remaining solution was analyzed using the UV-vis spectrometer.

3. Results and discussion

3.1. Characterization of the Pt/ $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ nanosheets

The composition and phase structure of the sample were investigated by XRD, and the obtained patterns are shown in

Fig. 1. XRD patterns of $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$.

Fig. 1. All the peaks could be indexed to $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ (JCPDS file no. 70-4761). The main peaks at the 2θ values of 11.97° , 18.82° , 24.19° , 29.05° , 30.16° , 31.97° , 41.71° , and 43.46° could be readily indexed to the (002), (202), (218), (311), (218), (127), (406) and (413) planes of $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$.

To confirm the successful loading of Pt onto the surface of $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$, characterizations of the crystallography and microstructural morphology were performed by TEM (Fig. 2(a) and (b)) and HRTEM (Fig. 2(c)). It can be seen that the $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ sample is composed of layer stacked nanosheets and that the Pt nanoparticles are dispersed on the surface of these nanosheets. In addition, the lattice spacings of $\text{Pt}/\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ were measured to be 0.2265 and 0.2963 nm based on the HRTEM image, which can be correlated to the (111) crystal plane of Pt and (313) crystal plane of $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$, respectively.

The surface elemental composition and atomic valence states of the $\text{Pt}/\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ sample with 3.0 wt% Pt were examined by XPS, which confirmed that the sample only comprised the four elements Bi, O, Cl, and Pt (Fig. 3). In Fig. 3(a), the peaks at 529.94 and 531.82 eV correspond to $\text{Bi } 4f_{7/2}$ and $\text{Bi } 4f_{5/2}$, which are related to the Bi^{3+} in the Bi–O bond of the $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ nanosheets [32]. Fig. 3(b) illustrates two types of O species corresponding to O 1s signals at 529.94 and 531.82 eV that indicate that O exists in the form of O^{2-} [33]. Fig. 3(c) reveals the binding energies of the Cl $2p_{3/2}$ and Cl $2p_{1/2}$ peaks of the samples as 198.44 and 199.77 eV [34], respectively. In ad-

dition, in Fig. 3(d), the binding energies 71.00 and 74.84 eV are assigned to Pt $4f_{7/2}$ and Pt $4f_{5/2}$, respectively, which indicates that the valence state of Pt is 0 (metallic) [35].

3.2. Visible light photocatalytic activity of $\text{Pt}/\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ nanosheets

The photocatalytic activity of the synthesized samples was studied based on the efficiency of degradation of MO under visible light irradiation (≥ 400 nm). Compared to as-prepared $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ nanosheets, all the Pt co-catalyzed samples exhibit significantly enhanced photocatalytic activities (Fig. 4(a)). This superior photocatalytic activity can be attributed to the formation of intimate interfaces between the Pt NPs and the $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ nanosheets in the $\text{Pt}/\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ sample, which in turn effectively promotes the efficiency of separation of the photoexcited charge carriers. By increasing the weight fraction of the Pt nanoparticles, the photocatalytic activity of the $\text{Pt}/\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ sample increased at the initial stage, reaching the highest point for 1.0 wt% loading of Pt nanoparticles, and then started to decline with further loading of the nanoparticles. This decline in photocatalytic activity may be caused by the light-shielding effect of the excess surface-loaded Pt nanoparticles. Furthermore, higher loading amounts of the Pt nanoparticles would also lead to screening of the active sites on the surface of the $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ nanosheets, which hinders the migration of charge carriers at the semiconductor/co-catalyst interface. These results indicate that an appropriate loading fraction of Pt nanoparticles is crucial for achieving the highest photocatalytic activity of $\text{Pt}/\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ nanosheets for the photodegradation of organic dyes under visible light. For a quantitative investigation of the kinetics of the MO photodegradation process, the result was fitted by applying a first-order model [36] (Fig. 4(b)). It can be seen that $\ln(C_0/C)$ and the duration of irradiation can be fitted to a linear law, which provides a preliminary proof for the stability of the photocatalyst. The TOC in the solution was examined after each photocatalytic test and provided additional information on the degradation of MO. The inset of Fig. 4(a) shows the TOC removal of MO with respect to irradiation time for the sample containing 1.0 wt% $\text{Pt}/\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ nanosheets. It can be seen that the degree of mineralization (obtained from the TOC result) of MO was 39% after visible light irradiation for 180 min. However, decolorization of the

Fig. 2. TEM images of (a) $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ and (b) $\text{Pt}/\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$. (c) HRTEM image of $\text{Pt}/\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ nanosheets.

Fig. 3. XPS spectra of the Pt/Bi₂₄O₃₁Cl₁₀ sample. (a) Bi 4f; (b) O 1s; (c) Cl 2p; (d) Pt 4f; (e) Survey.

Fig. 4. Time course of the decrease in (a) the concentration and (b) $\ln(C_0/C)$ for the photodegradation of MO under visible light irradiation.

MO solution characterized by UV-vis spectroscopy indicates that 48% of MO is removed. This mismatch between the TOC and the UV-vis characterization result indicates that a certain fraction of MO is not fully degraded into volatile products, but rather is converted into a colorless compound.

Stability is critical to the practical application of photocatalysts. Therefore, cycle runs of the photooxidation of MO were performed by using the 1.0 wt% Pt/Bi₂₄O₃₁Cl₁₀ nanosheets. After every cycle of 3 h of the photodegradation process, the sample was recovered by centrifugation and reused in the subsequent run of the photocatalytic degradation test. Fig. 5 reveals that the photocatalytic activity of 1.0 wt% Pt/Bi₂₄O₃₁Cl₁₀ retained after four cycle runs was 94% of its original value, indicating reliable photocatalytic stability. If not for the unavoidable loss of the photocatalyst during the centrifugation recycling step, the photocatalytic stability of the 1.0 wt%

Pt/Bi₂₄O₃₁Cl₁₀ nanosheets could be even higher.

3.3. Discussion of the photocatalytic mechanism

The optical absorptions of the as-prepared pure Bi₂₄O₃₁Cl₁₀ and Pt/Bi₂₄O₃₁Cl₁₀ nanosheets were characterized by UV-vis spectroscopy (Fig. 6). Bi₂₄O₃₁Cl₁₀ exhibits photoabsorption from the UV to the visible range, and the absorption edge is estimated to be 506 nm. These results are consistent with the light yellow color of the Bi₂₄O₃₁Cl₁₀ nanosheets. The optical band gap of Bi₂₄O₃₁Cl₁₀ is derived to be 2.45 eV (inset of Fig. 6) according to Tauc formula [37]. With increasing amount of Pt loading, the color of the powder changed from yellowish to light grey, and the absorption in the visible light region significantly improved. Hence, the enhanced light absorption is expected to lead to an improved photocatalytic degradation per-

Fig. 5. Cycling runs for the photocatalytic degradation of MO in the presence of 1.0 wt% Pt/Bi₂₄O₃₁Cl₁₀ composite under visible light irradiation.

Fig. 6. UV-vis diffuse reflectance spectra of pure Bi₂₄O₃₁Cl₁₀ nanosheets and Pt/Bi₂₄O₃₁Cl₁₀ composites with different weight fraction of Pt nanoparticles.

formance.

The energy gap of Bi₂₄O₃₁Cl₁₀ was also derived from DFT modeling. The Bi₂₄O₃₁Cl₁₀ unit cell corresponding to the monoclinic phase (space group *P2/c*), shown in Fig. 7, was used for the modeling. The arrangement of Bi, Cl, and O atoms follows the layered superposition model, with each layer stacked perpendicular to the internal electrostatic field. Fig. 8 displays the band structure and projected density of states (DOS) of Bi₂₄O₃₁Cl₁₀. The position of the conduction band (CB) edge is dominantly determined by the Bi *p* orbitals, whereas that of the valence band (VB) is mainly influenced by the O *p* orbitals. The bottom of the CB and the top of the VB in Bi₂₄O₃₁Cl₁₀ are scattered (Fig. 8(b)). This suggests that the effective mass of the light-excited carrier is relatively small, rendering the transportation of charge carriers easier. From the calculation results, Bi₂₄O₃₁Cl₁₀ is determined to be a direct-gap semiconductor with an energy gap of 2.1 eV. There is an acceptable difference between this value and the optical bandgap derived from the DRS characterization (2.45 eV). It is worth noting that first-principle calculations usually underestimate the value of the energy gap [38].

The PL spectra of the Bi₂₄O₃₁Cl₁₀ nanosheets and 1.0 wt%

Fig. 7. Simulated crystal structure of Bi₂₄O₃₁Cl₁₀.

Fig. 8. (a) Band structure and (b) density of states (DOS) of Bi₂₄O₃₁Cl₁₀ nanosheets.

Pt/Bi₂₄O₃₁Cl₁₀ are shown in Fig. 9. From the PL spectra, a qualitative comparison of the charge separation efficiencies of the photocatalysts could be performed. The relatively lower PL intensity of the Pt/Bi₂₄O₃₁Cl₁₀ sample indicates enhanced charge carrier separation compared to the pure Bi₂₄O₃₁Cl₁₀ nanosheets. In addition, the charge carrier lifetime was evaluated by time-resolved PL spectroscopy, and the result shows an increased lifetime for the Pt/Bi₂₄O₃₁Cl₁₀ sample (2.84 ns, Fig. 9(b)). Therefore, the Pt/Bi₂₄O₃₁Cl₁₀ sample is expected to show higher photocatalytic activity for MO degradation compared to pure Bi₂₄O₃₁Cl₁₀.

To explore the mechanism of enhancement of the photocatalytic activity through noble metal decoration, the CB and VB potentials of Bi₂₄O₃₁Cl₁₀ were calculated by using the following empirical equations [39]:

$$E_{VB} = \chi - E^e + 0.5E_g \quad (1)$$

Fig. 9. (a) PL spectra and (b) time-resolved PL spectra of $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ and 1.0 wt% Pt/ $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ nanosheets.

$$E_{\text{CB}} = E_{\text{VB}} - E_{\text{g}} \quad (2)$$

where χ denotes the absolute electronegativity, defined as the geometric mean of the absolute electronegativity of the constituent atoms; E° is the energy of free electrons on the hydrogen scale (ca. 4.5 eV); E_{CB} and E_{VB} are the conduction band and valence band edge potentials, respectively; and E_{g} is the bandgap energy of the semiconductor obtained from the previous DRS test. In order to calculate the VB and CB positions of $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$, the χ and E_{g} of $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ were determined to be 6.12 and 2.45 eV, respectively [40]. Using Eqs. (1) and (2), the top of the VB and the bottom of the CB of $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ were calculated to be 2.845 and 0.395 eV, respectively. The work function of Pt is 5.36 eV (relative to vacuum level), and its Fermi energy level could be determined as 0.8 eV, which implies that electrons can easily transfer from $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ to Pt, thereby achieving effective separation of the photoinduced charges [38]. This conjecture is also consistent with the PL characterization results. On this basis, the mechanism of enhancement of the photocatalytic MO degradation activity of Pt/ $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ is proposed to be as follows (Fig. 10). The electrons in the VB of $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ are excited to the CB under visible light irradiation, leaving behind holes in the VB, as depicted in Fig. 10(a). When noble metals are deposited onto the $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ surface, the photogenerated electrons will transfer from $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ to Pt

due to the strong internal field developed at the interface, and then, further reaction takes place via the active sites on the surface of the Pt.

Both ESR and steady-state fluorescence techniques were employed to investigate the active groups in the degradation process when the Pt/ $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ nanosheets are illuminated by visible light. It is generally accepted that photocatalytic oxidation is the main reaction occurring during the photodegradation of organic pollutants. In this process, a series of photoinduced reactive species like e^- , h^+ , $\cdot\text{OH}$, and $\cdot\text{O}_2^-$ are suspected to be involved in the photocatalytic degradation reaction. In the ESR test, TEMP is often used as the radical scavenger of electrons. The signal of TEMP could be detected in the dark (Fig. 11(a)). When the system is positioned under light irradiation, no signal of TEMP was revealed, which indicates that light irradiation results in the generation of large numbers of electrons and converts TEMP into TEMPO. As for $\cdot\text{OH}$ and $\cdot\text{O}_2^-$, no ESR signal can be seen in the dark condition, but both their ESR peaks can be observed in the illuminated condition, which suggests that e^- , $\cdot\text{OH}$, and $\cdot\text{O}_2^-$ are all involved as the main active species in the photodegradation process. However, because of the standard redox potential of $\text{Bi}^{5+}/\text{Bi}^{3+}$ (+1.59 eV) being more negative than that of $\cdot\text{OH}/-\text{OH}$ (+1.99 eV), it is impossible in theory to generate the $\cdot\text{OH}$ species in the Bi-based photocata-

Fig. 10. Proposed mechanism of the photocatalytic degradation of MO under visible light irradiation.

Fig. 11. ESR spectra of (a) e^- , (b) $\cdot\text{OH}$, and (c) $\cdot\text{O}_2^-$ at ambient temperature for 1.0 wt% Pt/Bi₂₄O₃₁Cl₁₀ photocatalyst.

lyst system via the catalytic oxidation of H₂O. Therefore, the $\cdot\text{OH}$ species observed in the ESR test should be produced via a two-electron reduction process with the assistance of active molecular oxygen (Eqs. (3) and (4)) [32].

Fig. 10(b) reveals the possible mechanisms of improvement of the photocatalytic activity in the case of the noble-metal-deposited Bi₂₄O₃₁Cl₁₀. Bi₂₄O₃₁Cl₁₀ generates photoexcited electrons and holes upon visible light irradiation, which can also recombine with each other during their migration to the surface. When noble metals are deposited onto the Bi₂₄O₃₁Cl₁₀ surface, the noble metal particles can act as electron traps to promote electron-hole separation. Subsequently, the electrons trapped are captured by the surface-adsorbed O₂ to form active oxygen molecules. The generated $\cdot\text{O}_2^-$ further reacts with MO to complete the photodegradation process.

4. Conclusions

Pt-nanoparticle-decorated Bi₂₄O₃₁Cl₁₀ nanosheets were successfully synthesized through a facile solution-based process. After the introduction of the nanoparticles on the surface of the nanosheets by the photoreduction technique, the Pt/Bi₂₄O₃₁Cl₁₀ photocatalyst exhibits enhanced photocatalytic performance. The amount of Pt loaded onto the surface of Bi₂₄O₃₁Cl₁₀ significantly impacts its photocatalytic activity. The optimized loading of 1.0 wt% Pt yields the best photocatalytic performance. The enhancement in the photocatalytic performance of the Pt-loaded Bi₂₄O₃₁Cl₁₀ nanosheets is mainly due to efficient interfacial charge transfer in the composite sample. In conclusion, the Pt/Bi₂₄O₃₁Cl₁₀ nanosheets are promising photocatalysts for the degradation of organic pollutants. Our work may provide valuable information for modifying O-enriched Bi oxyhalide semiconductors to obtain improved photocatalytic performances.

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Graphical Abstract

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Pt/Bi₂₄O₃₁Cl₁₀ composite nanosheets with significantly enhanced photocatalytic activity under visible light irradiation

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Bi₂₄O₃₁Cl₁₀ photocatalyst was prepared and modified with Pt nanoparticles. The Pt/Bi₂₄O₃₁Cl₁₀ composite with 1 wt% Pt showed the highest methyl orange photocatalytic degradation efficiency and great stability.

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具有高可见光催化活性的Pt/Bi₂₄O₃₁Cl₁₀复合纳米片的合成

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摘要: 卤氧铋是一类具有独特层状堆叠结构的半导体光催化剂, 但单一的卤氧铋存在着光生电子与空穴易复合等缺陷。而贵金属颗粒通常可以充当电子“陷阱”, 促进电荷转移, 延长载流子寿命, 从而产生更好的光催化性能。

本文成功合成了Bi₂₄O₃₁Cl₁₀光催化剂, 并对其进行Pt纳米颗粒修饰, 从而获得了具有高光催化性能的光催化剂Pt/Bi₂₄O₃₁Cl₁₀。其中, Bi₂₄O₃₁Cl₁₀是以Bi(NO₃)₃·5H₂O和NaCl作为前驱体并用氨水调节pH后水热制得, 而Pt的负载使用光还原法。对获得的样品进行XRD测试并将结果与Bi₂₄O₃₁Cl₁₀的标准卡片进行对比, 发现各峰的位置都有较好的对应, 证明Bi₂₄O₃₁Cl₁₀合成成功。采用TEM观测Pt/Bi₂₄O₃₁Cl₁₀的形貌, 发现Bi₂₄O₃₁Cl₁₀呈片状, 其表面存在Pt颗粒。XPS测试发现, 该样品只含有Pt, Bi, O, Cl四种元素, 且它们的价态符合预期。这进一步说明成功合成了Pt/Bi₂₄O₃₁Cl₁₀。

考察了可见光照射下Bi₂₄O₃₁Cl₁₀和Pt负载量分别为0.5%, 1%, 2%和3%的Pt/Bi₂₄O₃₁Cl₁₀对甲基橙溶液的降解的光催化性能。结果表明, 相比于载体, Pt/Bi₂₄O₃₁Cl₁₀的光催化性能有了显著提高, 其中1% Pt/Bi₂₄O₃₁Cl₁₀的光催化活性最佳, 并且在循环降解实验中表现出稳定的光催化活性。

DRS测试结果表明, Bi₂₄O₃₁Cl₁₀的带隙宽度为2.45 eV, 而Pt的负载有效减小了禁带宽度, 从而提高了催化剂对光的利用率。对Bi₂₄O₃₁Cl₁₀进行了DFT建模, 结果显示, Bi, Cl和O原子的排列遵循分层叠加模型, 且每层垂直于内部静电场堆叠。而

从它的能带结构和状态密度(DOS)可知,其导、价带边沿较为分散,这意味着光生载流子的有效质量较小,从而使载流子的运输更为容易.利用DRS以及对 $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ 能带结构的计算结果,根据半经验公式可知, $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ 的导、价带位置分别为0.395和2.845 eV.而Pt的费米能级为0.8 eV.结合ESR测试结果,可对Pt/ $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ 催化降解甲基橙的过程提出合理猜想: $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ 被光激发后,其表面的Pt充当电子"陷阱"以促进电子和空穴分离,被Pt捕获的电子与表面吸附的 O_2 形成 O_2^- ,并进一步与甲基橙反应,完成光降解过程.

关键词: 卤氧铋; 光催化; $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$; 甲基橙降解

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