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Ternary Ag/AgCl/BiOIO₃ composites for enhanced visible-light-driven photocatalysis

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ABSTRACT

Ternary Ag/AgCl/BiOIO₃ composite photocatalysts are prepared by a facile method. Enhanced visible-light absorption and charge carrier separation are achieved after the introduction of Ag/AgCl particles into BiOIO₃ systems, as revealed by ultraviolet-visible diffuse-reflectance spectrometry, photocurrent response and electrochemical impedance spectroscopy. The Ag/AgCl/BiOIO₃ composites are applied to the visible-light photocatalytic oxidization of NO in air and exhibit an enhanced activity for NO removal in comparison with Ag/AgCl and pure BiOIO₃. A possible photocatalytic mechanism for Ag/AgCl/BiOIO₃ is proposed, which is related to the surface plasmon resonance effects of Ag metal and the effective carrier separation ability of BiOIO₃. This work provides insight into the design and preparation of BiOIO₃-based materials with enhanced visible-light photocatalysis ability.

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1. Introduction

Semiconductor photocatalysts, used for solar-energy conversion with application in environment and energy, have attracted extensive interest [1–3]. The search for highly efficient photocatalysts is the key to practical applications. The photocatalysis efficiency is mainly associated with the optical absorption, charge separation, and interfacial transfer [4–7]. Generally, a single component photocatalyst suffers from poor visible-light absorption or/and a high charge recombination rate. To address these major problems, much effort has been devoted to investigating strategies such as doping, deposition, grafting, surface sensitization, and heterostructure construction [8–12].

Constructing heterostructures is not only appealing in en-

hancing the performance of the individual photocatalysts but also for introducing some novel and unique properties [13–16]. Recently, Ag/AgX (X = Cl, I, Br) have been suggested as efficient cocatalysts to construct ternary photocatalysts and improve the photocatalytic performance [17–19]. Especially, Ag/AgCl has been successfully applied to boost the photocatalytic activity of semiconductors with narrow or wide bandgaps. For instance, Yu et al. [20] prepared Ag/AgCl/TiO₂ nanotube array and found that it exhibited a high visible-light photocatalytic activity for the degradation of methyl orange. Zhang et al. [21] reported Ag/AgCl/Bi₂MoO₆ composites with superior visible-light photocatalytic activities in the decomposition of rhodamine B solution. Xu et al. [22] found that Ag/AgCl/WO₃ hollow spheres displayed excellent visible-light-response photocatalytic activity and recycling ability for the degradation of

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4-chlorophenol.

Various types of semiconductor photocatalysts have been developed, including monometal oxides, metal sulfides, and composite oxides [23–26]. Much attention has been given to Bi-based photocatalysts, such as Bi_2O_3 , Bi_2WO_6 , BiOCl , $\text{Bi}_2\text{O}_2\text{CO}_3$, BiVO_4 , and NaBiO_3 , for hydrogen production and environmental remediation [27–31]. Recently, nanostructured BiOIO_3 possessing two lone-pair cations and displaying an Aurivillius-type $(\text{BiO})_{2^{2+}}$ layer has been reported to exhibit high photocatalytic activity [32–34]. Unfortunately, owing to its large bandgap, it can be only activated by ultraviolet light, which impedes its application. Some efforts have been made for the enhancement of the photocatalytic ability of BiOIO_3 through heterojunction construction, including the synthesis of $\text{BiOIO}_3/\text{Bi}_2\text{WO}_6$, $\text{BiOIO}_3/\text{g-C}_3\text{N}_4$, $\text{BiOIO}_3/\text{RGO}$, and $\text{BiOIO}_3/\text{BiOI}$ [35–38]. Nonetheless, the photocatalytic activity of BiOIO_3 is far from efficient for practical applications, and it is highly desirable to improve the photocatalysis efficiency. To our knowledge, using Ag/AgCl as co-catalyst to create ternary BiOIO_3 -based composites with enhanced photocatalytic performance is not reported yet.

Herein, we prepared ternary $\text{Ag}/\text{AgCl}/\text{BiOIO}_3$ composites by a two-step method. The as-prepared composites showed enhanced visible-light absorption owing to the surface plasmon resonance of metallic Ag. Strong interfacial interactions existed in these components, and the significantly improved charge separation and migration in $\text{Ag}/\text{AgCl}/\text{BiOIO}_3$ composites were demonstrated by the photocurrent response and electrochemical impedance spectroscopy. The $\text{Ag}/\text{AgCl}/\text{BiOIO}_3$ composites showed higher visible-light photocatalytic performance than the Ag/AgCl and BiOIO_3 for the removal of NO. The possible photocatalytic mechanism responsible for the improved photocatalytic performance was also proposed. The outstanding properties associated with the novel $\text{Ag}/\text{AgCl}/\text{BiOIO}_3$ composite materials suggest that they can be used as visible-light harvesting photocatalysts for air purification applications.

2. Experimental

2.1. Materials and synthesis

All the chemicals were of analytical reagent grade and were used without further purification. BiOIO_3 was obtained by a simple hydrothermal method [37]. In a typical synthesis, 0.485 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was added to 70 mL distilled water and stirred vigorously for 30 min. Then, 0.214 g of KIO_3 was added into the above aqueous solution and stirred continuously for 10 min. The resulting suspension was then hydrothermally treated at 150 °C for 6 h. Finally, the BiOIO_3 product was collected and dried at 60 °C for 12 h.

$\text{Ag}/\text{AgCl}/\text{BiOIO}_3$ nanocomposites were synthesized by a chemical precipitation method at room temperature. A certain amount of NaCl was dissolved in 80 mL H_2O , and 0.48 g of BiOIO_3 (1.2 mmol) was added into the above aqueous solution and stirred for 30 min. Then, 30 mL aqueous solution containing AgNO_3 (equal molar amount to NaCl) was added dropwise into the above solution and stirred for 2 h. After the stirring was completed, the resulting suspension was aged for 1 h. Fi-

nally, the resulting products were collected by filtration, washed with water and ethanol four times and dried at 60 °C to obtain the final products. Depending on the molar ratio of BiOIO_3 to NaCl (6:1, 3:1, 1:1, 1:3, and 1:6), different composites can be synthesized. Ag/AgCl was synthesized by a chemical precipitation method at room temperature without adding BiOIO_3 , and Ag metal was produced by photoreduction from the surrounding light.

2.2. Characterization

The crystal phases of the samples were analyzed by X-ray diffraction (XRD) with Cu K_α radiation (model D/max RA, Rigaku Co., Japan). Scanning electron microscopy (SEM; model JSM-6490, JEOL, Japan) was used to characterize the morphology of the obtained products. The morphology and structure of the samples were examined by transmission electron microscopy (TEM; JEM-2010, JEOL, Japan). X-ray photoelectron spectroscopy (XPS) with Al K_α X-rays ($h\nu = 1486.6$ eV) radiation operated at 150 W (Thermo ESCALAB 250, USA) was used to investigate the surface properties. The UV-vis diffuse-reflectance spectrometry (DRS) spectra were obtained for the dry-pressed disk samples using a scanning UV-vis spectrophotometer (TU-1901, China) equipped with an integrating sphere assembly, using 100% BaSO_4 as the reflectance sample. N_2 adsorption-desorption isotherms were obtained on N_2 adsorption apparatus (ASAP 2020, Micromeritics, USA). All the samples were degassed at 100 °C prior to measurements. The photocurrent response and electrochemical impedance spectra measurements were performed in three-electrode quartz cells with a 0.1 mol/L Na_2SO_4 electrolyte solution. Platinum wire was used as the counter electrode, and saturated calomel electrodes were used as the reference electrodes. The as-prepared samples film electrodes on ITO served as the working electrode. The photoelectrochemical experiment results were recorded using an electrochemical system (CHI-660B, China). All the photoelectrochemical measurements were performed under visible light of a 500 W Xe lamp coupled with 420 nm cutoff filters with average light power of 45 mW/cm².

2.3. Evaluation of photocatalytic activity

The photocatalytic activity was investigated by removal of NO at ppb levels in a continuous flow reactor at ambient temperature. The volume of the rectangular reactor, made of polymeric glass and covered with Saint-Glass, was 4.5 L (30 cm × 15 cm × 10 cm). For the visible-light photocatalytic activity test, a 150-W commercial tungsten halogen lamp was vertically placed outside the reactor, and a UV cut-off filter (420 nm) was adopted. The as-prepared sample (0.20 g) was dispersed in distilled water (50 mL) in a beaker by ultrasonic treatment for 10 min, coated onto two glass dishes (12.0 cm in diameter) and then pre-treated at 70 °C to remove the water. The NO gas was acquired from a compressed gas cylinder at a concentration of 100 ppm of NO (N_2 balance). The initial concentration of NO was diluted to about 550 ppb by the air stream supplied by a zero air generator. The desired relative humidity (RH) level of

the NO flow was controlled at 50% by passing the zero air stream through a humidification chamber. The flow rates of the air stream and NO were controlled at 2.4 L/min and 15 mL/min, respectively. After the adsorption-desorption equilibrium was achieved in the dark, the lamp was turned on. The concentration of NO was continuously measured by a chemiluminescence NO analyzer (Thermo Environmental Instruments Inc., model 42c-TL), which monitors NO, NO₂, and NO_x (NO_x represents NO + NO₂) with a sampling rate of 1.0 L/min. The removal ratio (η) of NO was calculated as $\eta = (1 - c/c_0) \times 100\%$, where c and c_0 are the concentrations of NO in the outlet stream and the feeding stream, respectively.

3. Results and discussion

3.1. Structure and composition

The crystallographic structures of BiOIO₃, Ag/AgCl, and the Ag/AgCl/BiOIO₃ ternary composites were characterized by XRD, as shown in Fig. 1(a). All the peaks for the as-prepared BiOIO₃ and Ag/AgCl are indexed to the orthorhombic phase of BiOIO₃ (ICSD #262019) and cubic phase of AgCl (JCPDS 31-1238), respectively. In the composites, the peaks at $2\theta = 27.82^\circ$, 32.24° , and 46.25° , which are assigned to the (111), (200), and (220) planes of AgCl, are detected, and the intensity of these peaks becomes stronger with the increased molar ratio of NaCl to BiOIO₃. In contrast, the diffraction peaks attributed to BiOIO₃ gradually decrease as the amount of BiOIO₃ is reduced in the composites. Notably, there are no XRD peaks about Ag⁰ observed in the as-prepared Ag/AgCl and ternary composites mainly because of the low content and high dispersity of Ag⁰. Moreover, from the enlarged view (Fig. 1(b)), the diffraction peak positions of BiOIO₃ in the composites experience shifts,

demonstrating that strong interactions exist between the introduced Ag/AgCl and BiOIO₃.

XPS was further used to investigate the composition of Ag/AgCl and the ternary composites photocatalyst (1:3). As shown in Fig. 2(a), all peaks can be indexed to Ag, Cl, O, and C elements, and no peaks of other elements are observed for Ag/AgCl. The C peak is mainly derived from the adventitious carbon from the XPS instrument, and the O peak is attributed to the surface adsorbed H₂O. For the ternary composite (1:3), besides the C peak, peaks arising from Bi, O, I, Cl, and Ag elements are observed. Fig. 2(b) shows the high-resolution XPS spectra of Bi 4f, and the peaks located at 159.0 and 164.4 eV are ascribed to Bi 4f_{7/2} and Bi 4f_{5/2} of Bi³⁺, respectively [33]. The O 1s peaks at 530.1 and 532.2 eV in Fig. 2(c) are attributed to the Bi–O bonds and the O–H bonds of the surface adsorbed water, respectively. The binding energies of I 3d_{5/2} and I 3d_{3/2} of I⁵⁺ are 623.8 and 635.3 eV (Fig. 2(d)) [33]. In the Ag/AgCl sample (Fig. 2(e)), the Ag 3d spectrum consists of two peaks at about 367.80 and 373.8 eV, which can be assigned to Ag 3d_{5/2} and Ag 3d_{3/2} of Ag⁺, respectively. Moreover, the two peaks at 368.5 and 374.7 eV, corresponding to metallic Ag, are observed, suggesting that partial Ag⁺ ions are reduced to Ag⁰ [39]. Thus, the as-prepared Ag/AgCl does contain some metallic Ag, which mainly results from the photoreduction by the surrounding light. For the ternary composite (1:3), peaks of both Ag⁺ and Ag⁰ can be detected. In terms of Cl 2p (Fig. 2f), the binding energies of Cl 2p_{3/2} and Cl 2p_{1/2} are approximately 198.3 and 199.9 eV, respectively, which are detected in Ag/AgCl and the composite (1:3). It can be seen that the peaks of Ag⁰, Ag⁺, and Cl[–] undergo chemical shifts in the composite (1:3) relative to those of Ag/AgCl, indicating the presence of strong interactions among the three components, which is consistent with the XRD result. The XPS results suggest the successful coupling of

Fig. 1. XRD patterns (a) and enlarged view of $2\theta = 26^\circ$ – 34° diffraction region (b) of BiOIO₃, Ag/AgCl, and the Ag/AgCl/BiOIO₃ ternary composites prepared using different BiOIO₃ to NaCl molar ratios.

Fig. 2. XPS spectra of Ag/AgCl and the Ag/AgCl/BiOIO₃ ternary composite (1:3). (a) Survey spectra; (b) Bi 4f; (c) O 1s; (d) I 3d; (e) Ag 3d; (f) Cl 2p.

Ag/AgCl with BiOIO₃.

3.2. Morphology

The morphology of Ag/AgCl, BiOIO₃, and the composite (1:3) were investigated by SEM and TEM. As shown in Fig. 3(a) and (b), particle-like AgCl can be observed, while pure BiOIO₃ is mainly composed of nanosheets, as revealed by Fig. 3(c) and (d). In the composite (1:3), particle-like AgCl and nanosheet-shaped BiOIO₃ can be observed (Fig. 3(e) and (f)), implying that the shapes of BiOIO₃ and Ag/AgCl do not show significant changes after compositing. The TEM image further confirms that the composites have two morphologies, as particles and

nanosheets (Fig. 3(g)). From the HRTEM image (Fig. 3(h)), the distance between the two adjacent planes is 0.37 nm, corresponding to the (111) plane of BiOIO₃, and the distance of 0.32 nm belongs to the (111) plane of AgCl. As can be seen, the intimate interfacial contact exists in these components, which is beneficial for charge separation and transfer.

3.3. Optical properties

The optical properties of the as-obtained samples were characterized by UV-vis DRS spectra and the results are shown in Fig. 4. BiOIO₃ has a clear edge around 390 nm, and no significant absorption in the visible-light region is observed. The

Fig. 3. SEM images of Ag/AgCl (a, b), BiOIO₃ (c, d), and the ternary composite (1:3) (e, f); TEM and HRTEM images of the ternary composite (1:3) (g, h).

Fig. 4. UV-vis DRS spectra of the as-prepared samples.

bandgap of BiOIO_3 is 3.1 eV [37]. The Ag/AgCl sample exhibits a wide and strong light absorption centered at 545 nm, and this strong visible-light absorption can be attributed to the strong plasmon resonance absorption of Ag particles [40–42]. After construction of the ternary composites, none of the composites show an obvious enhanced absorption in the ultraviolet-light region in contrast to the pure BiOIO_3 , but display a boost in the visible-light absorption. The absorption intensity in the visible-light region continually increases as the molar ratio of BiOIO_3 to NaCl is increased. The enhanced visible-light absorption can be ascribed to the plasmon resonance absorption of Ag particles. It can be concluded that the introduction of Ag/AgCl into BiOIO_3 benefits the optical absorption property and the usage efficiency of visible light. Similar phenomena are also observed in the cases of $\text{Ag}/\text{AgCl}/\text{TiO}_2$ and $\text{Ag}/\text{AgCl}/\text{WO}_3$ [20,22]. The remarkable absorption enhancement in the visible region is beneficial to improve the photocatalytic performance.

3.4. Charge separation

Photoelectrochemical measurements were performed to investigate the excitation, separation, transfer, and recombina-

tion of photoinduced charge carriers [43]. Fig. 5(a) shows the photocurrent of the samples irradiated under visible light. Obviously, the enhanced photocurrent is observed in the ternary composites, implying an enhanced separation efficiency of photoinduced electrons and holes [44]. The typical electrochemical impedance spectra (EIS) were adopted to investigate the photogenerated charge separation process, as shown in Fig. 5(b). It is observed that with the addition of Ag/AgCl , although in a small amount, the diameters of the arc radius on the EIS Nyquist plot of the ternary composites are smaller than those of pure BiOIO_3 , which reveals a decrease in the interface layer resistance and the charge transfer resistance on the surface. Among these composites, the composite (1:6) shows the strongest photocurrent and the most efficient separation ability of charge carriers. Overall, charge transfer is accelerated and charge recombination is suppressed owing to the interfacial interaction between the Ag/AgCl and BiOIO_3 . Thereby, a high efficiency in photocatalysis over the ternary composites would be achieved.

3.5. Pore structures

The N_2 adsorption-desorption isotherms of all the prepared photocatalysts are shown in Fig. 6(a). From the isotherms, the Ag/AgCl sample displays the type III (Brunauer-Deming-Deming-Teller classification) isotherm, which characteristically indicates a weak interaction existing between N_2 and the sample. However, it is observed that the other samples show type IV isotherms with H3 hysteresis loops [45]. In view of the morphological structure, the H3 hysteresis loops might arise from the aggregation of nanosheet-like particles possessing slit-shaped pores. Fig. 6(b) displays the corresponding pore-size distributions. No pores exist in Ag/AgCl . The composites, as well as pure BiOIO_3 , contain macropores and large mesopores over a broad range with the peaks centered at approximately 50 nm. These results demonstrate the formation of hierarchically nanoporous structures. The BET surface areas of Ag/AgCl , BiOIO_3 , and the composites (6:1), (3:1), (1:1), (1:3), and (1:6) are calculated to be 1, 14, 10, 10, 8.5, 4.8, and 5 m^2/g , respectively. It is clear that the specific surface areas of these photocatalysts are relatively low.

Fig. 5. Transient photocurrent response (a) and electrochemical impedance spectroscopy Nyquist plots (b) of BiOIO_3 and the ternary composites.

Fig. 6. N_2 adsorption-desorption isotherms curves (a) and pore-size distribution (b) of the as-prepared samples.

3.6. Photocatalytic activity and mechanism

The as-synthesized ternary samples show high visible absorption and efficient charge transfer, so they are expected to show high visible-light photocatalytic activity. NO, which is chemically stable and hard to remove, was chosen as the representative air pollutant to evaluate the photocatalytic performance of the as-synthesized photocatalysts. Fig. 7(a) shows the photocatalytic activity of the seven photocatalysts. $BiOIO_3$ exhibits poor photocatalytic activity with a removal ratio of 13.0% owing to its large bandgap. The as-prepared Ag/AgCl

sample shows a certain photocatalytic performance (removal ratio of ca. 30%) because of the existence of Ag^0 . Metal Ag with plasmon resonance effects can be excited by visible light to generate carriers, and electrons can react with the species at the interfaces while holes inject into the nearby AgCl to oxidize Cl^- ions to yield Cl atoms, which are reactive for oxidizing species in the surrounding environment. Meanwhile, Cl atoms would be reduced back to Cl^- after redox reactions [40,41]. With the assistance of composite photocatalysts, the high visible-light photocatalytic activity is obviously superior to those observed from the $BiOIO_3$ and Ag/AgCl. Adding a small amount of Ag/AgCl can result in significantly increased photocatalytic

Fig. 7. Photocatalytic oxidation of NO over the as-prepared samples (a), cycling runs of the composite (1:3) in air under visible-light irradiation (b), and XRD pattern (c) and UV-vis DRS spectrum (d) of the composite (1:3) after cycling testing.

Fig. 8. Proposed photocatalytic mechanism of the as-prepared ternary composites.

activity. The composite (6:1) displays a high removal ratio of 56.0%. With an increased Ag/AgCl content in the composites, the NO removal ratio gradually increases and finally reaches a stable value. The composites (1:3) and (1:6) show a comparable and high removal ratio of approximately 64.0% for the removal of NO. To evaluate the stability of the photocatalytic performance of the composite (1:3), circulating runs were carried out. As shown in Fig. 7(b), the composite (1:3) shows a slight decrease in activity after four recycles, which can be attributed to the products or intermediates blocking the active sites. Furthermore, XRD, combined with the UV-vis DRS spectra, reflects the good stability in the phase structure and light absorption properties of the composite (1:3) (Fig. 7(c) and (d)).

Based on the previously reported photocatalyst systems, such as Ag/AgCl/TiO₂, Ag@AgCl, and the above experimental results [20,40], the photocatalytic mechanism of the Ag/AgCl/BiOI₃ system is proposed, as depicted in Fig. 8. Under visible-light irradiation, photogenerated electron-hole pairs are created in Ag particles owing to surface plasmon resonance. A Schottky barrier is formed at the Ag/BiOI₃ interface owing to the different work functions. As the plasmon-induced electrons of Ag particles can transfer to the conduction band (−0.2 V vs NHE) of TiO₂ under visible-light irradiation [46], it is believed that the photo-induced electrons of Ag particles can easily transfer to the conduction band (+0.99 V vs NHE) of BiOI₃ [37]. The potential of the electrons on the conduction band of BiOI₃ are not negative enough to induce the generation of •O₂[−]. Alternatively, electrons can be consumed by multi-electrons reactions to yield H₂O [47]. Meanwhile, the holes left on the surface of Ag particles can transfer to the surface of AgCl to oxidize Cl[−] to Cl⁰. The light irradiation induces reduction of partial Ag⁺ ions and leaves Cl[−] ions, so that the surface of AgCl particles is negatively charged and terminated by Cl[−] ions. Cl⁰ atoms are reactive radical species, which are able to oxidize NO and then be reduced to Cl[−] again. In this case, BiOI₃ contributes to the rapid transfer of photogenerated electrons, leading to a lower recombination rate and enhanced photocatalytic activity.

4. Conclusions

Ag/AgCl/BiOI₃ was constructed through a two-step synthesis route. The generation of AgCl was accompanied with the in situ formation of metallic Ag by photoreduction of Ag⁺ ions by the surrounding light. Remarkable improvement of NO removal capability for Ag/AgCl/BiOI₃ was a result of the enhanced visible-light harvesting and decreased recombination of photogenerated electron-hole pairs owing to the strong interfacial interaction of Ag/AgCl and BiOI₃. This originated from the surface plasmon resonance absorption of Ag particles under visible-light irradiation and the charge separation at Ag/BiOI₃ surface, which included electrons transferring from the photo-excited Ag to BiOI₃ and holes transferred to AgCl to oxidize Cl[−]. The present work provides fundamental insights into the role of BiOI₃ in tuning interfacial charge transfer processes. The highly efficient Ag/AgCl/BiOI₃ composites are widely applicable in various fields, such as air purification and waste water treatment.

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Graphical Abstract

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Ternary Ag/AgCl/BiOIO₃ composite photocatalysts show improved activity for NO removal compared with Ag/AgCl and pure BiOIO₃. This arises from the surface plasmon resonance effects of Ag metal and the effective carrier separation ability of BiOIO₃.

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Ag/AgCl/BiOIO₃三元复合物光催化剂的性能增强机制

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摘要: 半导体光催化技术是一种环境友好技术,它既能在温和条件下应用于环境领域——利用光能降解有机和无机污染物,又可应用于能源领域——将低密度的太阳能转化为高密度的洁净能源,因而在解决环境污染和能源匮乏问题方面展现出巨大的应用潜力。最近,一种新型Bi基光催化剂,BiOIO₃,表现出优异的紫外光催化性能。它由层状[Bi₂O₂]²⁺和[IO₃]⁻组装而成,带隙为3.1 eV左右。然而,其较大的带隙限制了其对太阳光的利用。近年来,多种方法如金属掺杂、非金属掺杂、半导体复合、光敏化改性和加氢处理被用来提高半导体的光催化效率。其中,以Ag/AgX (X = Cl, I和Br)作为助催化剂可提高体系的可见光吸收和载流子的分离能力,从而增强光催化性能。基于此,我们设计并合成了一种新型的三元光催化剂。首先采用水热法合成了BiOIO₃纳米片,然后在室温条件下原位引进Ag/AgCl,制备了Ag/AgCl/BiOIO₃三元异质结构。与Ag/AgCl和纯的BiOIO₃相比,该三元Ag/AgCl/BiOIO₃复合物光催化剂对NO表现出优异的可见光光催化去除性能。

本文采用X射线衍射(XRD)、X射线光电子能谱(XPS)、扫描式电子显微镜(SEM)、电化学测试(光电流和阻抗谱)和紫外-可见漫反射光谱(UV-Vis)等表征手段研究了Ag/AgCl/BiOIO₃光催化性能增强的机制。SEM结果表明,制备的Ag/AgCl/BiOIO₃三元复合物为纳米颗粒和纳米片形貌,Ag/AgCl的引入对BiOIO₃形貌影响不大。XRD和XPS测试结果表明,与纯的BiOIO₃相比,随着Ag/AgCl

的加入,复合物的峰位置发生了明显位移,表明Ag,AgCl和BiOIO₃三组分间存在强的相互作用.光电流响应图谱表明,随着Ag/AgCl的加入,Ag/AgCl/BiOIO₃的光电流强度明显增强,同时阻抗谱的圆弧直径明显减小,表明电子和空穴的分离能力增强. UV-Vis图谱中,BiOIO₃在可见光区几乎没有吸收,而三元复合物表现出明显的可见光吸收,且随着Ag/AgCl量的增加,复合物的可见光吸收增强,该吸收归结于复合物中Ag的表面等离子体吸收.结合之前报道的光催化剂体系如Ag/AgCl和Ag/AgCl/TiO₂,我们提出了Ag/AgCl/BiOIO₃复合物光催化剂性能增强的机制.

在可见光照射下,Ag⁰因其表面等离子体吸收而产生电子空穴对.由于功函数不同,Ag和BiOIO₃之间形成肖特基势垒.电子从Ag⁰表面转移到BiOIO₃的导带上,BiOIO₃导带上电子的电势不足以把O₂氧化成[•]O₂⁻,但电子能以多电子的形式与O₂和H⁺生成水.同时,Ag⁰表面的空穴能将AgCl表面的Cl⁻氧化成Cl⁰.光照诱导AgCl表面的部分Ag⁺离子被还原,所以AgCl粒子的表面带负电荷.Cl⁰是活性自由基,能够氧化去除NO,反应之后自身被还原成Cl⁻.由此可见,在三元复合光催化剂中,Ag⁰在可见光照射下因其表面等离子体效应产生电子空穴对,随后BiOIO₃有效地分离了光生载流子,使得复合材料能有效地利用光生电子和空穴.故三元Ag/AgCl/BiOIO₃复合物光催化剂增强的光催化性能可归结于Ag的表面等离子体吸收和BiOIO₃的载流子分离能力.该结果有助于设计和制备具有优异的光催化性能的BiOIO₃基材料.

关键词: 银/氯化银/碘酸氧铋;三元复合物;可见光催化;一氧化氮去除;载流子分离

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