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Article

Complete removal of phenolic contaminants from bismuth-modified TiO₂ single-crystal photocatalysts

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ABSTRACT

Exploring low-cost and highly active photocatalysts is very urgent to accomplish complete removal of phenolic contaminants and overcome the limitations of the existing photocatalysts. In this study, we designed and synthesized noble metal-free TiO₂ photocatalysts by introducing bismuth nanoparticles as modifiers of a TiO₂ single crystal (Bi-SCTiO₂). The Bi-SCTiO₂ can make full use of the synergistic effect of a small band overlap and low charge carrier density (Bi) with a high conductivity (single crystal), significantly boosting the separation and migration of the photogenerated charge pairs. Therefore, the Bi-SCTiO₂ photocatalyst exhibits a significantly enhanced degradation rate (12 times faster) of 4-nitrophenol than a TiO₂ single crystal under simulated sunlight irradiation. Notably, the complete removal of phenolic contaminants is achieved in various water matrices, which not only successfully overcomes the incomplete degradation in many reported photocatalytic systems, but also manifests a significant practical potential for sewage disposal. Therefore, this work presents a new insight in designing and constructing noble metal-free decorated semiconductor single-crystal photocatalysts with excellent activity and cyclability.

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1. Introduction

Phenols, or derivatives of phenols, are considered priority organic pollutants in toxic waste discharge [1–3]. The accumulation of these toxic pollutants from a large number of industrial sources is dangerous for living organisms because of their acute toxicity, endocrine disrupting abilities, and bio-recalcitrant nature [1,3]. Therefore, the complete removal of phenolic pollutants is important for human life and sustainable development.

Titanium dioxide (TiO₂), as an optimal semiconductor pho-

tocatalyst, has been extensively investigated due to its fantastic properties and widespread applications for the removal of phenolic compounds [1,4]. However, its wide bandgap and rapid recombination of photoinduced carriers lead to low efficiency for the degradation of organic pollutants [5]. Various methods, including metal doping [6,7], non-metal doping [8,9], and coupling with other semiconductors [10,11], were introduced to enhance photocatalytic performance of TiO₂-based photocatalysts. Guo et al. [11] prepared hollow mesoporous TiO₂@g-C₃N₄ and found that 73% of phenol could be removed under simulated sunlight irradiation. Nie et al. [12] reported a

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novel GQDs/Mn-N-TiO₂/g-C₃N₄ catalyst with a high removal rate (89%) of 4-nitrophenol under simulated sunlight irradiation. Cao et al. [13] found that the removal of phenol approached 91% over brookite/rutile TiO₂ nanocrystals under artificial UV light. However, the low photocatalytic efficiency makes it difficult to realize the high removal rate of phenolic compounds which have stable molecular structure.

Compared to its polycrystalline counterpart, single crystal TiO₂ usually shows an enhanced photocatalytic activity due to the continuous and orderly interior crystal structure of bulk TiO₂ [14–17], which exhibits a higher electronic conductivity of photoexcited carriers transferred from the bulk to the surface where redox reactions proceed. Zhou et al. [14] found that as-synthesized graphene-modified TiO₂ single crystals exhibited ~96% degradation rate of phenol under simulated sunlight irradiation. Xiong et al. [17] prepared Ag loaded single crystal TiO₂ manifesting a high degradation rate of phenol (~97%) under simulated sunlight irradiation, which showed much higher photocatalytic activity than P25. Unfortunately, the complete removal of phenolic compounds in wastewater still remains a great challenge for a large number of the reported photocatalytic systems under simulated sunlight irradiation, even under full spectrum light with UV light irradiation [1,11–14,17–19].

To address this challenge, we report the first example of a bismuth-modified TiO₂ single-crystal photocatalyst with excellent photocatalytic performance and cyclability. Coupling Bi nanoparticles (Bi NPs) with a TiO₂ single crystal can build a Schottky barrier at the interface between the metal Bi and TiO₂ single crystal, which can make full use of the respective advantages of Bi (low cost, small band overlap, large mean free path, and low charge carrier density [20–23]) and TiO₂ single crystal (high conductivity [14,17]), promoting the efficient separation and migration of the photogenerated charge pairs because the introduction of Bi can serve as an “electron reservoir and transfer channel” [6]. Therefore, Bi-decorated single-crystal TiO₂ (Bi-SCTiO₂) can completely remove phenolic contaminants (phenol, 4-nitrophenol, etc.) under simulated sunlight irradiation, effectively overcoming the incomplete removal of refractory contaminants for almost all of the reported photocatalytic systems.

2. Experimental

2.1. Materials

Methacryloxyethyltrimethyl ammonium chloride (DMC) was purchased from Sigma-Aldrich Company, Ltd. Tetrabutyltitanate (TBT) was obtained from J&K Chemical Technology. Bi(NO₃)₃, CH₃CH₂OH, phenol, and 4-nitrophenol were purchased from Sinopharm Chemical Reagent Co., Ltd. The inhibitor in styrene (St) was removed with an NaOH solution.

2.2. Synthesis of Bi-SCTiO₂ photocatalyst

2.2.1. Synthesis of single crystal TiO₂ nanorods (SCTiO₂)

Cationic polystyrene/titanium oxide core/shell spheres

(CPS@TiO₂) were prepared using previously published methods [24,25]. CPS@TiO₂ (480 mg) was dispersed in an aqueous solution with HCl (16 mL, 36%–38%). Then, the suspension was transferred into a Teflon-lined stainless-steel autoclave (100 mL), and the sealed autoclave was heated at 180 °C for 10 h. Finally, the product was washed, filtered, dried, and calcined at 450 °C, resulting in the SCTiO₂ nanorods.

2.2.2. Synthesis of Bi-SCTiO₂

Bi NPs were loaded onto the Bi-SCTiO₂ surface via the photoreduction method used in our previous work [26]. SCTiO₂ (100 mg) and Bi(NO₃)₃·5H₂O (20 mg) were dispersed in aqueous solution (60 mL) containing glycerinum (5 mL) and ethanol (5 mL), and then the solution was transferred into a 100 mL four neck flask. After purging with N₂ in the dark for 1 h, the system was irradiated by simulated sunlight with an AM 1.5G filter (XHA350W, 350 W) for 2 h. Subsequently, the photocatalyst was filtered, washed, and dried at 50 °C, resulting in the Bi-SCTiO₂ nanorods. The Bi loading (10, 20, and 30 mg of Bi(NO₃)₃·5H₂O) was adjusted to prepare various Bi-decorated TiO₂ single crystals, denoted as Bi(10)-SCTiO₂, Bi(20)-SCTiO₂, and Bi(30)-SCTiO₂, respectively.

2.3. Characterization

Transmission electron microscopy (TEM), scanning electron microscopy (SEM), high resolution TEM (HRTEM), and energy dispersive X-ray spectroscopy (EDX) elemental mapping analysis were employed to detect the morphology and structure of the SCTiO₂ and Bi-SCTiO₂ samples. EDX, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and UV-vis spectroscopy were used to characterize the crystal, bonding energy, and absorption spectrum of the samples. In addition, the electron spin resonance (ESR) was employed to characterize the photochemical properties.

2.4. Photocatalytic activity test

The catalytic activity was evaluated by degrading a solution containing phenolic pollutants (10 mg/L). The reaction system contained 50 mL of simulated wastewater and 10 mg of photocatalyst, which was used to measure the activity of the catalysts under simulated sunlight illumination (Perfectlight, PLS-SXE300, 300 W Xe lamp with an AM 1.5G filter). The photocatalytic system was stirred in the dark for 30 min to reach adsorption-desorption equilibrium before light irradiation. Finally, approximately 3 mL of solution was withdrawn from the reaction system, filtered, and detected via UV-vis spectroscopy ($\lambda_{\text{phenol}} \sim 270$ nm [27] and $\lambda_{4\text{-NP}} \sim 318$ nm [28]).

3. Results and discussion

3.1. Synthesis and characterization of Bi-SCTiO₂

Fig. 1(a) briefly introduces the preparation process of Bi-SCTiO₂. First, CPS@TiO₂ nanospheres were synthesized, which were then used as the precursor for the TiO₂ single crys-

Fig. 1. (a) Schematic of the preparation of Bi-SCTiO₂ nanorods; SEM (b), TEM (c), HRTEM (d), and SAED (e) images of Bi-SCTiO₂; STEM mapping of the Bi-SCTiO₂ photocatalyst ((g) Ti; (h) O; (i) Bi).

tal that was synthesized *via* a hydrothermal reaction at 180 °C for 10 h, forming SCTiO₂. Finally, Bi nanoparticles were loaded onto the surface of SCTiO₂ *via* a photoreduction method under simulated sunlight irradiation [26], resulting in the Bi-SCTiO₂ samples.

Compared to the smooth surface of the rod-shaped SCTiO₂ (Fig. S1(a)), there are many small white spots on the surface of the SCTiO₂ (Fig. 1(b)) after Bi loading, which is further confirmed by TEM analysis, as shown in Fig. 1(c). Moreover, HRTEM reveals that Bi-SCTiO₂ has a crystal lattice of 0.259 and 0.328 nm (Fig. 1(d)), which correspond to (101) crystal plane of rutile TiO₂ and (012) crystal plane of metal Bi, respectively [6,29], confirming the successful formation of Bi-decorated

single crystal TiO₂ *via* the photoreduction method. On the other hand, the SAED pattern of SCTiO₂ exhibits distinct and well-ordered fringe lattices without any impurity lattices (Fig. S1(b)), confirming the single-crystal nature. While new lattices from the Bi NPs can be found in the SAED pattern of Bi-SCTiO₂ (Fig. 1(e)). EDX mapping shows that the Ti and O signals both exhibit similar nanorod-shaped morphology, whereas the Bi signal (Fig. 1(i)) is mainly distributed on the surface of SCTiO₂ nanorods. All these characterizations confirm the successful preparation of the Bi-SCTiO₂ composite.

3.2. Crystal structure and surface chemical status of Bi-SCTiO₂ nanorods

XRD was conducted to analyze the crystal structure of the SCTiO₂ and Bi-SCTiO₂ samples. As shown in Fig. 2(a), the XRD pattern of SCTiO₂ exhibits five characteristic peaks at $2\theta = 27.4^\circ, 36.1^\circ, 41.2^\circ, 44.1^\circ$, and 56.6° that are well indexed to the (110), (101), (111), (210), and (220) crystal planes of rutile (JCPDS: 21-1276), respectively [30]. Interestingly, the as-synthesized Bi-SCTiO₂ presents three new peaks at $2\theta = 27.2^\circ, 37.9^\circ$, and 39.6° that are attributed to the characteristic peaks of metallic Bi (No. 44-1246) [6]. Additionally, XRD peaks are sharp and intense, indicating the high crystallinity of the SCTiO₂ and Bi-SCTiO₂ samples because of their single-crystal structure.

XPS was used to analyze the chemical structures and electronic states of the catalysts [31,32]. The XPS profile (Fig. 2(b)) shows that the Bi-SCTiO₂ sample contains Ti, O, C, and Bi, indicating the existence of Bi and TiO₂. In the case of Ti 2p (Fig. 2(c)), the peak located at 458.6 eV corresponds to the Ti 2p_{3/2} and the one located at 464.3 eV is indexed to Ti 2p_{1/2}. The posi-

Fig. 2. (a) XRD patterns of SCTiO₂ and Bi-SCTiO₂; XPS profiles in the full-scale (b), Ti 2p (c), O 1s (d), and C 1s (e) regions of the SCTiO₂ and Bi-SCTiO₂ samples; (f) the Bi 4f region for the Bi-SCTiO₂ sample.

tive shifts (0.2 eV for Ti $2p_{1/2}$ and 0.2 eV for Ti $2p_{3/2}$) for the Bi-SCTiO₂ sample are obtained than the corresponding binding energies of SCTiO₂, indicating the existence of a strong interaction between Bi and SCTiO₂. In addition, the two main peaks can be further divided into four Gaussian peaks at the binding energies of 457.5, 458.9, 463.6, and 465.8 eV, which are matched to Ti³⁺ $2p_{3/2}$, Ti⁴⁺ $2p_{3/2}$, Ti³⁺ $2p_{1/2}$, and Ti⁴⁺ $2p_{1/2}$, respectively. Moreover, a closer observation reveals that the O–H binding energy has a positive shift (0.1 eV) for Bi-SCTiO₂, indicating the existence of oxygen vacancies [24] because part of the Ti⁴⁺ in SCTiO₂ is reduced to Ti³⁺ during the photoreduction reaction. In addition, the peak of the O–Ti bond shows a slight shift to a lower binding energy, again confirming the strong interface coupling between Bi nanoparticles and SCTiO₂ [33]. The XPS profile of C 1s can be fitted to three peaks at 284.6, 285.5, and 288.6 eV, indicating the existence of three different chemical environments of the carbon species, in which the peak located at 284.6 eV can be ascribed to the residuary carbon species, which serves as a photo-adsorbent to improve the adsorption amount of phenolic pollutants. The XPS peak of Bi 4f (Fig. 2(f)) can be fitted to four Gaussian peaks. Two strong peaks located at 158.8 and 164.2 eV are ascribed to the characteristic orbital splitting of Bi $4f_{7/2}$ and Bi $4f_{5/2}$, respectively, while two peaks at 157.2 and 162.5 eV are attributed to metallic Bi⁰ [23]. All these results confirm that Bi-SCTiO₂ was successfully prepared *via* the photoreduction method.

3.3. Photocatalytic performance of Bi-SCTiO₂ photocatalyst

The photocatalytic activity of the as-synthesized Bi-SCTiO₂ was investigated by degrading 4-nitrophenol (4-NP) and phenol. Figure 3 displays that 4-NP and phenol themselves do not

efficiently decompose under simulated sunlight irradiation. In contrast, three Bi-SCTiO₂ photocatalysts exhibit good degradation of 4-NP and phenol (Fig. S2(a),(b)), especially for the Bi(20)-SCTiO₂ photocatalyst (afterward denoted as Bi-SCTiO₂), indicating that the suitable loading of Bi is very important to achieve optimal photocatalytic performance, although higher Bi loading may exhibit better light absorption (Fig. S2(c)). As shown in Fig. 3(a), after 150 min, the removal of 4-NP over SCTiO₂ is only 26.3%, while the degradation of 4-NP over Bi-SCTiO₂ is as high as 100%, indicating complete removal. The linear fitting of $\ln(C_0/C)$ - t curves shows the degradation constant k . Figure 3(b) shows that Bi-SCTiO₂ presents the highest degradation rate ($k = 0.0203 \text{ min}^{-1}$) obtained from the linear fitting of $\ln(C_0/C)$ - t curves, indicating that Bi-SCTiO₂ manifests 12 times faster towards the degradation of 4-NP than SCTiO₂ without Bi decorating ($k = 0.00165 \text{ min}^{-1}$). This result may be ascribed to the SPR effect of Bi NPs and the Schottky barrier constructed between Bi and SCTiO₂ that can synergistically accelerate the separation and migration of photoinduced charge pairs [6]. Even when the initial concentration of 4-NP is further increased to 15 or 20 mg/L, complete removal can be still obtained under simulated sunlight illumination, as demonstrated in Fig. 3(c).

The excellent photoactivity of Bi-SCTiO₂ was further investigated by evaluating the removal of phenol. Figure 3(d) shows that the Bi-SCTiO₂ achieves complete removal (100%) of phenol after 120 min, far beyond the value of phenol over SCTiO₂ without Bi decorating (58.7%) under the same conditions. In addition, the Bi-SCTiO₂ catalyst significantly enhances the photodegradation rate of phenol to $k = 0.0268 \text{ min}^{-1}$, which approaches four times than the value of SCTiO₂ without Bi decorating ($k = 0.0069 \text{ min}^{-1}$). The excellent activity of the Bi-SCTiO₂

Fig. 3. Photocatalytic degradation (a) and corresponding fitting curves (b) of 4-NP; (c) Effect of the initial concentration of 4-NP on the performance of Bi-SCTiO₂; photocatalytic degradation (d) and corresponding fitting curves (e) of phenol; (f) Effect of the initial concentration of phenol on the performance of Bi-SCTiO₂.

catalyst was further investigated by evaluating the effect of the initial concentration on the removal of phenol. Although a longer time is expected to degrade a higher initial concentration of phenol, complete removal is still obtained (Fig. 3(f)). These results significantly overcome the incomplete removal of phenolic compounds over almost all of the reported photocatalysts (Table. S1) [1,11–14,17–19]. Evidently, Bi decorating plays a key role in promoting the photocatalytic activity of the Bi-SCTiO₂ photocatalyst.

3.4. Role of environmental factors

3.4.1. pH value

The effect of pH on the degradation of phenol was investigated because changes in pH can affect the charges of Bi-SCTiO₂ and pollutants [34,35], leading to dissimilar degradation rates of phenol. Figure 4(a) indicates that the adsorption capacity remains unchanged whether under acidic or basic conditions, i.e. using HCl or NaOH, respectively, to adjust the pH value. When an acidic solution was used as the reaction medium (*e.g.*, pH = 3.7 and 5.1), the charge-charge repulsion between Bi-SCTiO₂ and phenol was enhanced, leading to a slight decrease in photocatalytic activity, and a similar result was achieved when a basic solution (*e.g.*, pH = 8.7) was used. When a neutral medium (*e.g.*, pH = 7) was used, the charge-charge repulsion was weakened because of the weakly acidic Bi-SCTiO₂ and phenol. Although more H⁺ or OH[−] ions in aqueous solutions evidently affect the surface charges of Bi-SCTiO₂ and phenol, only a 3%–4% decreased removal is observed when the irradiation time is prolonged to 150 min, indicating that pH value has little impact on the degradation of phenol.

3.4.2. Inorganic ions

It has been proven that the addition of inorganic ions has a

negative effect on the photocatalytic performance of TiO₂ for the removal of pollutants [34,35]. Under the presence of inorganic cations (*e.g.*, CaCl₂, NaCl, or KCl salts), the almost complete removal (> 98%) of phenol was still achieved over Bi-SCTiO₂ after 120 min under simulated sunlight irradiation, suggesting that the common inorganic cations have no evident impact on the degradation of phenol (Fig. 4(b)). In addition, the excellent removal of phenol over Bi-SCTiO₂ was further investigated by adding common inorganic anions (*e.g.*, Cl[−], HCO₃[−], and SO₄^{2−}), where the anions resulted from NaCl, NaHCO₃ and Na₂SO₄ dissolved in solution with three different concentrations (0.1, 0.2, and 0.4 mM). Figure 4(c) shows that only 1–2% degradation rate of phenol is decreased in the various concentrations of Cl[−], suggesting that it has little effect on the activity of Bi-SCTiO₂. In contrast, the addition of HCO₃[−] or SO₄^{2−} inhibits the photocatalytic activity of Bi-SCTiO₂, leading to a decreased degradation rates (96%–97%) of phenol, as shown in Fig. 4(d),(e). This can be ascribed to the fact that sulfates and carbonates are both good scavengers of reactive oxygen species [35]. The reactions that occurred during photocatalytic degradation are listed below:

Therefore, h^+ will be consumed by HCO₃[−] and SO₄^{2−} during the pollutant degradation process. As such, the as-synthesized Bi-SCTiO₂ still exhibits a stronger resistance to HCO₃[−] or SO₄^{2−} than previous works [34,35], indicating significant inorganic ions resistance.

3.4.3. Environmental waters

Water matrices (neat water, mineral water, tap water, and river water) were used as target matrices for the photodegra-

Fig. 4. The effects of pH (a), metal cations (b), Cl[−] (c), HCO₃[−] (d), SO₄^{2−} (e), and water matrix (f) on the degradation of phenol (initial concentration of phenol = 10 mg/L) under simulated sunlight irradiation.

dation of phenol, as shown in Fig. 4(f). Compared to neat water, other environmental waters show a negative effect for the degradation of phenol. When mineral water (Kang Master: SiO_3^{2-} , Ca^{2+} , Na^+ , K^+ , Mg^{2+} , etc.) is used as phenol solution, the degradation rate of phenol only decreases by $\sim 1.5\%$. Similar results ($\sim 1.4\%$) are obtained when using tap water (Cl^- , SO_4^{2-} , Ca^{2+} , K^+ , Mg^{2+} , Na^+ , organic substances including chlorinated disinfection byproducts) as the phenol solution [34]. Even when using river water (natural organic matters, bacteria, mineral substance, etc.) obtained from the Changjiang River as the phenol solution, the degradation of phenol is as high as 96% after 210 min under simulation irradiation. All results further confirm that the as-synthesized Bi-SCTiO₂ exhibits significant practical potential for sewage treatment.

3.5. Investigation of main reactive species

To measure active species during the photocatalytic process, trapping experiments were performed for degrading typical 4-NP using various scavengers, such as *t*-butanol (*t*-BuOH), triethanolamine (TEOA), and nitrogen (N_2). As shown in Fig. 5(a), when TEOA is used, a sharp decrease ($\sim 49.8\%$) in removal of 4-NP is observed, suggesting that h^+ plays a crucial role in the degradation of 4-NP during the photodegradation process. Furthermore, when N_2 is bubbled into the reactive system, the degradation of 4-NP decreases significantly. This result implies that $\bullet\text{O}_2^-$ is also a primary active species for the degradation of 4-NP. However, the removal rate of 4-NP remained almost unchanged when the *t*-BuOH is added, indicating that $\bullet\text{OH}$ is not a primary active species during the photocatalytic degradation of 4-NP.

To investigate the role of the active species, the ESR spin-trap with DMPO was performed under simulated sunlight illumination. As demonstrated in Figs. 5(b)–(d), neither DMPO- $\bullet\text{O}_2^-$ nor DMPO- $\bullet\text{OH}$ signals can be seen under dark

conditions. However, under simulated sunlight irradiation for 10 min, both Bi-SCTiO₂ and SCTiO₂ exhibit the DMPO- $\bullet\text{O}_2^-$ and DMPO- $\bullet\text{OH}$ signals. The DMPO- $\bullet\text{O}_2^-$ signal confirms that the former holds stronger intensities than the latter, implying that more $\bullet\text{O}_2^-$ are produced after light irradiation, which agrees with the free radical trapping experiments. As expected, the Bi-SCTiO₂ can produce more h^+ than SCTiO₂ after light irradiation, and the intensities of the signals decreased notably in simulated solar light, suggesting that this is the main contribution of h^+ for phenolic compounds degradation [36]. Therefore, the ESR measurements confirm that Bi-SCTiO₂ produces more main active species (superoxide radicals and h^+) to degrade refractory contaminants under simulated sunlight irradiation.

3.6. Degradation mechanism and pathway

The UV-vis absorption spectra and corresponding Kubelka-Munk plots provide evidences that Bi decorating can promote the photocatalytic activity of the SCTiO₂ photocatalyst. Fig. 6(a) shows that Bi-SCTiO₂ exhibits stronger visible light absorption than SCTiO₂ because of the SPR effect of Bi nanoparticles. Corresponding bandgaps of the SCTiO₂ and Bi-SCTiO₂ were calculated via the Kubelka-Munk method [17], as demonstrated in Fig. 6(b). Compared to the rutile SCTiO₂ (~ 3.0 eV) [37], Bi decorating narrows the bandgap energy of SCTiO₂ to ~ 2.8 eV, which can facilitate the excitation of electrons from the valence band to the conduction band under light irradiation. In addition, the measurement of transient photocurrent response and electrochemical impedance spectroscopy (EIS) Nyquist plots was performed to ascertain the separation efficiency of photoinduced charge carriers. Figures 6(c) and (d) show that Bi-SCTiO₂ manifests a stronger photocurrent and smaller Nyquist semicircle than SCTiO₂ without Bi decorating, suggesting that the separation and transfer ability of charge carriers in Bi-SCTiO₂ are more efficient than those in SCTiO₂ [38,39].

Fig. 5. (a) Photocatalytic performance of Bi-SCTiO₂ for degrading 4-NP; ESR spectra of DMPO- $\bullet\text{OH}$ (b), DMPO- $\bullet\text{O}_2^-$ (c), and TEMPO- h^+ (d) over SCTiO₂ and Bi-SCTiO₂.

Fig. 6. UV-vis spectra (a) and corresponding bandgap (b) of the SCTiO₂ and Bi-SCTiO₂; (c) transient photocurrent responses; (d) EIS of SCTiO₂ and Bi-SCTiO₂.

Based on experimental evidence, a photocatalytic mechanism for Bi-SCTiO₂ is proposed, as shown in Fig. 7. Under simulated sunlight irradiation, the electrons in the valence band (VB) of SCTiO₂ can be excited and transferred to the conduction band (CB) of SCTiO₂ via the sublevel states formed from the presence of Ti³⁺ [40], while photogenerated electrons will migrate to the surface of the Bi NPs, accelerating the charge separation. Meanwhile, hot electrons produced by the LSPR effect of Bi NPs can cross the Schottky barriers and inject into the CB of SCTiO₂ because hot electrons have much higher energy and exist much longer, leading to stronger photocatalytic activity [41]. Finally, electrons in the CB of SCTiO₂ and Bi NPs can capture O₂ molecules dissolved in water to form •O₂^{•−}. The h⁺ and •O₂^{•−} can oxidize 4-NP and phenol to form CO₂, H₂O, and other small molecules.

To obtain the degradation pathway of phenolic contaminants, intermediates produced in the photocatalytic process can be detected by MS [42]. Figure 8(a) shows the reasonable degradation pathway of 4-NP. First, the 4-NP molecule with

Fig. 7. Mechanism of photocatalytic degradation.

$m/z = 139$ is oxidized to anhaline ($m/z = 110$) [43]. Subsequently, the benzene ring in the anhaline is broken, generating product 2 ($m/z = 112$) [44], which is further oxidized into product 3 ($m/z = 90$). Eventually, these molecules decompose to CO₂ and H₂O. As a possible degradation pathway of phenol (Fig. 8(b)), the phenol molecule ($m/z = 94$) is attacked by •O₂^{•−}/h⁺ and oxidized to *p*-benzoquinone (product 1, $m/z = 108$) [45]. After that, the benzene ring of the *p*-benzoquinone is broken, producing product 2 ($m/z = 116$). Finally, these molecules are degraded into CO₂ and H₂O.

3.7. Recycling performance of Bi-SCTiO₂ photocatalyst

The stability of the photocatalyst during the photocatalytic reaction is an important factor for its potential application [10]. In order to investigate the cycling stability, phenol solution (10 mg/L) was employed to evaluate the photocatalytic activity of the Bi-SCTiO₂ sample, as shown in Fig. 9. The photocatalyst sample was collected by filtration and dried in an oven; then, the obtained sample was used for the next run. It can be seen that the phenol photodegradation efficiency is 100% for the first run. After the fourth use, the phenol photodegradation efficiency is still as high as 99.1%. In addition, the morphology, structure, and crystallization of Bi-SCTiO₂ do not change, indi-

Fig. 8. Possible degradation pathway of 4-NP (a) and phenol (b).

Fig. 9. Recycling performance of Bi-SCTiO₂ for degrading phenol under simulated sunlight irradiation.

catting the good chemical stability of the photocatalyst (Fig. S3).

4. Conclusions

In summary, we explore the Bi-TiO₂ photocatalyst by combining the respective advantages of Bi NPs and TiO₂ single crystals. The experimental results show that the Bi-SCTiO₂ photocatalyst displays excellent photocatalytic activity, far beyond the comparative values of both SCTiO₂ without Bi decorating and polycrystalline TiO₂ photocatalysts. This can be attributed to the synergistic effect of the SPR effect of Bi NPs, nature of single crystal, and Schottky barrier between Bi NPs and SCTiO₂. Accordingly, the complete removal of phenolic pollutants (4-NP, phenol, etc.) is obtained by employing Bi-SCTiO₂ as a photocatalyst under simulated sunlight irradiation, efficiently overcoming the disadvantage of incomplete removal that occurs in almost all other photocatalytic systems. Therefore, the as-synthesized Bi-SCTiO₂ provides a new insight in designing and constructing metal decorated semiconductor single-crystal photocatalysts with excellent catalytic activity.

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Graphical Abstract

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Complete removal of phenolic contaminants from bismuth-modified TiO₂ single-crystal photocatalysts

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The Bi-SCTiO₂ photocatalyst exhibits complete degradation of phenolic contaminants under simulated sunlight due to the synergistic effect of the small band overlap and the low charge carrier density (Bi) as well as high conductivity (single crystal).

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铋改性TiO₂单晶光催化剂的制备及其完全去除酚类污染物

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摘要: 伴随着人类社会生产生活需要, 工业污水中酚类物质的存在极易污染表面水、地下水甚至饮用水。然而, 传统污水处理工艺无法对其实现完全去除, 更因其稳定的化学结构和难降解特性, 对生态系统和人类健康构成了巨大威胁。因此, 寻求完全去除水体中酚类污染物是目前环境领域中重要的研究课题之一。

二氧化钛因具有优越的物理、化学和光学性能, 而被广泛应用于污染物降解研究, 然而, 传统TiO₂光催化剂由于可见光吸收弱和光生电荷复合率高, 导致污染物降解效率低, 尤其是针对难降解有机污染物如酚类难以实现高效的去除。为此, 本文通过引入铋纳米粒子作为TiO₂单晶的改性剂, 通过充分发挥铋纳米粒子的LSPR效应和TiO₂单晶结构的高传导率, 不仅有效地拓宽了TiO₂的光响应范围(~2.8 eV), 而且提高了光生电荷的分离效率, 导致其优越的光催化行为。酚类污染物的降解实验表明, 所合成的Bi-SCTiO₂光催化剂在模拟太阳光照射下, 能完全去除水体中的苯酚和对硝基酚, 克服了现有以TiO₂为基础的光催化剂无法实现酚类污染物完全去除的缺点。更重要的是, 当使用环境水如自来水或矿泉水配制苯酚溶液, 所制备的Bi-SCTiO₂光催化剂仍能实现苯酚的高效降解(>98%); 即使采用含有大量有机物质和微生物的长江水所配制的苯酚溶液, 在模拟太阳光照射下, Bi-SCTiO₂光催化剂对苯酚的降解率仍然高达96%。进一步研究发现, 在各种无机离子如Na⁺, K⁺, Ca²⁺, Cl⁻, HCO₃⁻或SO₄²⁻(0.1 mM)的干扰下, 制备的Bi-SCTiO₂对苯酚降解率仍然高达98%以上。光催化循环实验表明, 所制备的Bi-SCTiO₂循环四次后, 其对苯酚的降解率几乎保持不变, 说明Bi-SCTiO₂具有极好的循环稳定性。运用ESR和MS等分析手段, 确定了酚类污染物降解的中间体结构、形态和降解路径, 再结合Bi-SCTiO₂催化剂的光电性能和自由基捕获实验, 提出了酚类污染物完全降解的机理。

关键词: 铋改性; 二氧化钛单晶; 酚类污染物; 完全去除; 水体; 降解机理; 光催化作用

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