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Article

S-scheme $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ photocatalysts with enhanced visible-light-induced photocatalytic NO oxidation performance

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ABSTRACT

Normal photocatalysts cannot effectively remove low-concentration NO because of the high recombination rate of the photogenerated carriers. To overcome this problem, S-scheme composites have been developed to fabricate photocatalysts. Herein, a novel S-scheme $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ nanocomposite was fabricated by an ultrasound-assisted method, which exhibited excellent performance for photocatalytic ppb-level NO removal. Compared with the pure constituents of the nanocomposite, the as-prepared 15% $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ photocatalyst could remove more than 68% continuous-flowing NO (initial concentration: 400 ppb) under visible-light irradiation in 30 min. The findings of the trapping experiments confirmed that $\bullet\text{O}_2^-$ and h^+ were the important active species in the NO oxidation reaction. Meanwhile, the transient photocurrent response and PL spectroscopy analyses proved that the unique S-scheme structure of the samples could enhance the charge separation efficiency. In situ DRIFTS revealed that the photocatalytic reaction pathway of NO removal over the $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ nanocomposite occurred via an oxygen-induced route. The present work proposes a new concept for fabricating efficient photocatalysts for photocatalytic ppb-level NO oxidation and provides deeper insights into the mechanism of photocatalytic NO oxidation.

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1. Introduction

Most air pollution incidents involve the over-emission of NO_x from vehicles and plants [1,2]. Hence, it is urgently necessary to effectively decompose the NO_x in the atmosphere [3,4]. The photocatalytic technology, which can effectively convert NO_x to NO_3^- , has been developed for a few years for NO_x removal [5–7]. However, most photocatalysts can only oxidize a high concentration of NO_x in the stable atmosphere, and only a few works have investigated the photocatalytic ppb-level NO_x oxidation in continuous-flowing air [8–10]. Hence, it is necessary to develop highly efficient photocatalysts for

low-concentration NO_x removal.

The graphite-like carbon nitride ($\text{g-C}_3\text{N}_4$), which is thermally stable, inexpensive, visible-light responsive, and has a large specific surface area [11–16], has attracted wide attention for photocatalytic low-concentration NO_x removal. Lin et al. [17] developed a novel ball-in-ball-structured $\text{g-C}_3\text{N}_4/\text{SiO}_2$ photocatalyst with outstanding photocatalytic ability for hydrogen evolution and pollutant removal. Wang et al. [18] developed a porous $\text{g-C}_3\text{N}_4$ catalyst that exhibits better photocatalytic ability than original $\text{g-C}_3\text{N}_4$. However, $\text{g-C}_3\text{N}_4$ can hardly be applied in the field of photocatalysis because of the high rate of recombination of photoexcited carriers. The fabrication of a composite

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photocatalyst is an effective way to overcome the above-mentioned shortcoming [19–25]. For example, Wang et al. [26] fabricated a Bi_3TaO_7 QDs/ $\text{g-C}_3\text{N}_4$ photocatalyst that demonstrated enhanced photocatalytic ability than the single-phase photocatalyst for the photocatalytic degradation of antibiotics. Jiang et al. [27] developed $\text{N-TiO}_2/\text{g-C}_3\text{N}_4$, which demonstrated excellent photocatalytic performance for photocatalytic NO oxidation.

Nevertheless, despite the enhanced separation efficiency for the photoexcited charges, normal composite photocatalysts exhibit low oxidation and reduction properties than each of the components because of the electron migration pathway. Yu et al. [28–33] developed a S-scheme structured composite photocatalyst that exhibited an excellent charge separation property and enhanced photooxidation or photoreduction ability simultaneously. Ge et al. [34] fabricated a S-scheme TiO_2/CdS nanofiber photocatalyst for hydrogen evaluation and studied the S-scheme charge transfer pathway in some detail. Jia et al. [35] synthesized a S-scheme heterojunction AgI/I-BiOAc by the one-pot milling method. The photocatalyst exhibited better performance than BiOAc and AgI for the degradation of organic pollutants. Thus, the coupling of unique S-scheme structured photocatalysts can evidently enhance the photocatalytic ability [36–40].

Over the years, Sb_2WO_6 has attracted considerable interest in the photocatalytic field because of its strong visible-light-harvesting capability [41–44]. Chen et al. [45] reported a Ag-loaded Sb_2WO_6 semiconductor that can effectively decompose organic pollutants such as rhodamine, methyl blue, and methyl orange. Ding et al. [44] synthesized 3D graphene aerogel Sb_2WO_6 hybrid by a facile hydrothermal process. Importantly, the band structure of such a photocatalyst matches that of $\text{g-C}_3\text{N}_4$, thus allowing the building of a S-scheme heterogeneous photocatalyst.

In this work, a series of S-scheme $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ nanocomposites were synthesized by an ultrasound-assisted method and were used for photocatalytic NO (400 ppb) oxidation under visible-light irradiation to assess their photocatalytic abilities. The $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ nanocomposite exhibited a higher NO removal efficiency than pure Sb_2WO_6 and $\text{g-C}_3\text{N}_4$. Furthermore, the band structure, reaction pathway, and photocatalytic mechanism of the $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ photocatalyst were analyzed by DRS, in situ DRIFTS, and trapping experiments, respectively. The photocatalytic mechanism investigation results confirmed that the enhanced photocatalytic activities are because of the S-scheme structure of the $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ photocatalyst.

2. Experimental

2.1. Photocatalyst preparation

All the chemical reagents were of analytical-grade purity and used without further purification.

Synthesis of Sb_2WO_6 . First, 1.37 g of SbCl_3 and 0.76 g of $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}$ were dissolved in 65 mL of deionized water with stirring for 30 min. Then, the pH of above-mentioned mixed solution was adjusted to 2 with a 4

mol/L NaOH solution. The adjusted solution was added to a 100 mL PPL-lined stainless steel autoclave and heated at 180 °C for 48 h in an oven [46]. The resulting precipitate was centrifuged, washed with water and ethanol several times, and dried at 60 °C overnight.

Synthesis of $\text{g-C}_3\text{N}_4$. The $\text{g-C}_3\text{N}_4$ powder was synthesized by heating melamine at 550 °C for 4 h at a 5 °C/min heating rate [47,48]. The prepared light-yellow samples were ground, washed with water and ethanol several times, and dried at 60 °C overnight.

Preparation of $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ nanocomposite. Different amounts of Sb_2WO_6 particles (5%, 10%, 15%, and 20% to the weight of $\text{g-C}_3\text{N}_4$, respectively) were dissolved in absolute ethanol under ultrasonication for 30 min. Then, 0.5 g of the as-obtained $\text{g-C}_3\text{N}_4$ sample was mixed with the Sb_2WO_6 solution under ultrasonication for 2 h and stirred for another 20 h. The resulting nanocomposite was washed with deionized water and ethanol several times and dried at 60 °C overnight.

2.2. Characterization

The lattice structures of the as-obtained samples were analyzed by X-ray diffraction (XRD) analysis using a Rigaku D/MAX-RB diffractometer with $\text{Cu K}\alpha$ radiation under the operation conditions of 40 kV and 50 mA. A Thermo Fisher VG Multilab 2000 spectrometer (UK) with a monochromatic $\text{Al K}\alpha$ source was used to analyze the surface compositions and chemical states of the samples. Besides, the binding energies were revised based on the C 1s peak of surface adventitious carbon at 284.5 eV. Scanning electron microscopy (SEM, JSM-5610LV, JEOL) and transmission electron microscopy (TEM, JEOL 2100, JEOL) were performed to investigate the morphologies and microstructures of the samples. Fourier transform infrared (FT-IR, Nicolet, Thermo Fisher) spectroscopy and Raman spectroscopy were performed to identify the functional groups and molecular structures of the samples. The light absorption edges of the samples were recorded by UV-vis spectrophotometry (UV-2450, Shimadzu). The photoelectrochemical measurements were recorded using a CHI660C electrochemical analyzer. Photoluminescence (PL) emission spectra were recorded using a spectrofluorometer.

2.3. Photocatalytic experiments

The photocatalytic tests of the as-obtained samples were performed on a continuous-flow gas monitoring system (Fig. S1). Firstly, 50 mg of photocatalyst was pasted onto a piece of glass, which was placed in the center of the sealed reactor (35×20×12 cm) with a quartz cover. Secondly, a Xe lamp was switched on after the reactant gas (400 ppb NO, in air balance) was pumped into the reactor continuously to reach the adsorption-desorption equilibrium. Then, the concentrations of NO and NO_2 in the reactor were continually recorded by a FT-IR spectrometer.

The removal ratio of NO was determined as:

$$\eta (\%) = (1 - C/C_0) \times 100\%,$$

where C_0 and C denote the NO concentration in the inlet stream

Fig. 1. XRD patterns (a), Raman spectra (b) and FT-IR spectra (c) of the Sb_2WO_6 , $\text{g-C}_3\text{N}_4$, and 15- $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ samples.

and outlet stream, respectively.

3. Results and discussion

3.1. Characterization and analysis

The XRD patterns of the series of $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ nanocomposites are displayed in Fig. 1(a). The diffraction peaks of pure $\text{g-C}_3\text{N}_4$ at 27.51° and 13.50° are indexed to the (002) and (100) planes, respectively. The diffraction peaks of Sb_2WO_6 at 20.4° , 26.90° , 32.83° , 36.37° , 40.25° , 47.49° , 49.69° , and 53.07° correspond to the (01-1), (1-11), (003), (20-1), (020), (202), (023), (2-2-1), and (3-10) planes, respectively. Furthermore, the characteristic diffraction peaks of Sb_2WO_6 and $\text{g-C}_3\text{N}_4$ appeared in the XRD patterns of the $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ nanocomposite without any other impurities. More importantly, the changes in the peak intensities of the constituents are consistent with the change in the proportions of the constituents in the $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ photocatalyst.

The Raman spectra of the Sb_2WO_6 , $\text{g-C}_3\text{N}_4$, and $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ samples are presented in Fig. 1(b). The Raman spectrum of pure Sb_2WO_6 shows characteristic peaks at around 245, 300, 423, 500, 760, and 880 cm^{-1} , which are in agreement with that in reference [49]. The tiny peaks at 471, 707, and 1232 cm^{-1} are consistent with those reported for pure $\text{g-C}_3\text{N}_4$ [50]. However, some characteristic peaks of Sb_2WO_6 cannot be observed clearly in the Raman spectrum of the 15- $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ nanocomposite because of the low content of Sb_2WO_6 in the nanocomposite. The functional groups and surface chemical bonds of the Sb_2WO_6 , $\text{g-C}_3\text{N}_4$, and 15- $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ samples were investigated by FT-IR spectroscopy. As shown in Fig. 1(c), the FT-IR spectrum of pure Sb_2WO_6 has three obvious bands: the two broad bands at 1631 and 3403 cm^{-1} are ascribed to physically adsorbed H_2O , while the narrow bands at $500\text{--}727\text{ cm}^{-1}$ result from the stretching vibrations of Sb-O, W-O, and W-O-W bonds [49]. In the case of $\text{g-C}_3\text{N}_4$, the absorption peak at 807 cm^{-1} is ascribed to the triazine ring modes [50]. The peaks at 1240, 1319, 1408, 1454, and 1572 cm^{-1} are assigned to the aromatic C-N stretching, while the peak at 1638 cm^{-1} can be attributed to the C=N stretching vibration modes [51]. Meanwhile, the peak at 3244 cm^{-1} corresponds to the N-H stretching vibrations [52]. Besides, in agreement with the Raman analysis results, the main characteristic peaks of Sb_2WO_6 were not observed clearly in the FT-IR

spectrum of the nanocomposite.

The morphology and microstructure of the photocatalysts were investigated by SEM, TEM, and HRTEM. Flower-like Sb_2WO_6 hierarchical microspheres are observed in Fig. S2(a). Moreover, the layered structure $\text{g-C}_3\text{N}_4$ nanosheets can be seen in Fig. S2(b). Fig. S2(c) and (d) show that Sb_2WO_6 is composed of spherical particles that are bonded to the $\text{g-C}_3\text{N}_4$ nanoflakes. Fig. 2(a) shows that the Sb_2WO_6 nanocrystals are adsorbed on the flake-like $\text{g-C}_3\text{N}_4$. From Fig. 2(b), the interplanar distances of the lattice fringes were determined as 0.345 and 0.310 nm corresponding to the (1-11) and (022) crystal planes of Sb_2WO_6 particles, respectively. Additionally, the SAED pattern (Fig. 2(c)) confirms that the Sb_2WO_6 particles in the nanocomposite have a favorable crystallinity, and proves that $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ nanocomposites were successful prepared. HAADF-STEM analysis was performed to examine the microstructure and composition of $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$. Fig. 2(d)-(k) reveal the uniform distribution of C, N, O, Sb, and W elements in

Fig. 2. TEM (a), HRTEM (b), and HAADF-STEM (c) images and the corresponding EDS elemental mapping images (d-k) of the 15- $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ nanocomposite.

the 15-Sb₂WO₆/g-C₃N₄ sample. These results strongly suggest the successful construction of a Sb₂WO₆/g-C₃N₄ heterojunction.

XPS analysis was performed to confirm the surface compositions and chemical states of the pure Sb₂WO₆, pure g-C₃N₄, and 15-Sb₂WO₆/g-C₃N₄ samples. Fig. 3(a) shows the XPS survey spectrum of each sample. The C 1s spectra of the samples show similar peaks at 284.8 and 288.2 eV (Fig. 3(b)), which correspond to adsorbed carbon and the C–N₃ group, respectively [53,54]. The N 1s spectra of the samples are fitted to four peaks at 404.6, 400.4, and 398.7 eV (Fig. 3(c)). The peak at the highest binding energy of 398.7 eV is ascribed to the *sp*²-bonded nitrogen (C–N–C), the one at 399.9 eV corresponds to the tertiary nitrogen bonded to carbon (N–(C)3), the one at 401.1 eV corresponds to the amino groups (C–N–H), the peak at the lowest binding energy of 404.5 eV resulted from positive charge localization in the heterocycles [55,56]. As shown in Fig. 3(d), the peaks at 530.1 and 530.3 eV in the O 1s spectra of the Sb₂WO₆ and 15-Sb₂WO₆/g-C₃N₄ samples are ascribed to W–O. In addition, compared with the O 1s spectrum of Sb₂WO₆, a new peak appeared in the O 1s spectrum of the Sb₂WO₆/g-C₃N₄ nanocomposite at 531.9 eV, which is attributed to the oxygen-containing intermediates derived from the incomplete thermal condensation of melamine [57]. The Sb 3d spectrum of the nanocomposite deconvoluted into two peaks at 529.8 and 539.3 eV (Fig. 3(e)), which are attributed to Sb 3d_{5/2} and Sb 3d_{3/2} of Sb³⁺, respectively [58]. As shown in Fig. 3(f), the peaks at 35.1 eV and 37.1 eV in the W 4f spectra of the nanocomposites resulted from W⁶⁺, while the peaks at 33.6 and 35.3 eV resulted from W⁵⁺ [59,60]. As shown in Fig. 3, compared with the pure constituents, the binding energies of C 1s, O 1s, Sb 3d, and W 4f slight shifted for the 15-Sb₂WO₆/g-C₃N₄ nanocomposite because of the electron screening effect resulting from the change in electron density [61]. The above phenomena imply

the presence of a strong interface effect between Sb₂WO₆ and g-C₃N₄ in the nanocomposite [62].

The light absorption range of a photocatalyst is the key factor for evaluating its photocatalytic activity. As can be seen in Fig. 4(a), compared with the absorption edges of g-C₃N₄, the absorption edges of the Sb₂WO₆/g-C₃N₄ nanocomposite are slightly red shifted, and the shift gradually increased with an increase in the amount of Sb₂WO₆ from 5% to 15% in the nanocomposite (Fig. 4(b)). Besides, the band gaps of the samples can be calculated using the following formula:

$$ah\nu = A(h\nu - E_g)^{n/2},$$

where α , ν , h , A , and E_g represent the coefficients of absorption, light frequency, Planck constant, constant number, and band gap, respectively. For Sb₂WO₆ and g-C₃N₄, n is 4. Thus, as shown in Fig. 4(c), the E_g values of Sb₂WO₆ and g-C₃N₄ were estimated as 2.25 and 2.65 eV, respectively. The Mott-Schottky plots of the Sb₂WO₆, g-C₃N₄, and 15-Sb₂WO₆/g-C₃N₄ samples were evaluated to study the effect on charge carrier concentration. As shown in Fig. 4(d), the flat potentials (E_{FB}) are –0.45, –1.14, and –0.60 V vs. Ag/AgCl (pH = 6.8) for Sb₂WO₆, g-C₃N₄, and 15-Sb₂WO₆/g-C₃N₄, respectively. The E_{FB} , which was measured using a Ag/AgCl reference electrode, could be converted into the normal hydrogen electrode (NHE) potentials using the following equation [63]:

$$E_{FB} = E_{Ag/AgCl} + 0.059 \times \text{pH} + E^0_{Ag/AgCl},$$

where the pH of the electrolyte is 6.8 and $E^0_{Ag/AgCl}$ is 0.197 eV. Hence, the E_{FB} values of Sb₂WO₆ and g-C₃N₄ are calculated as 0.15 and –0.54 V vs. NHE, respectively. In addition, the E_{CB} is very close to (–0.3 V more negative) the E_{FB} for an n-type semiconductor. Therefore, the E_{CB} values of Sb₂WO₆ and g-C₃N₄ are equivalent to –0.15 and –0.84 V vs. NHE, respectively. Combined with the UV-vis DRS findings, the corresponding E_{VB} values of Sb₂WO₆ and g-C₃N₄ were calculated as 2.10 and 1.81 eV

Fig. 3. XPS spectra of Sb₂WO₆, g-C₃N₄, and 15-Sb₂WO₆/g-C₃N₄. (a) Survey spectra; (b) C 1s; (c) N 1s; (d) O 1s; (e) Sb 3d; (f) W 4f spectra.

Fig. 4. UV-vis diffuse reflection spectra of the as-prepared samples (a) and enlarged image (b) of the zone marked in (a); $(\alpha h\nu)^{1/2}$ versus $h\nu$ plots (c) and Mott-Schottky plots (d) of pure Sb_2WO_6 and $\text{g-C}_3\text{N}_4$.

vs. NHE, respectively.

3.2. Photocatalytic performance

The photocatalytic abilities of all the photocatalysts were assessed by the visible-light-driven photocatalytic continuous-flow low-concentration NO removal experiments. Fig. 5(a) displays the NO removal ratio of the Sb_2WO_6 , $\text{g-C}_3\text{N}_4$, and $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ samples. The pure Sb_2WO_6 sample could hardly remove NO under visible-light irradiation, while pure $\text{g-C}_3\text{N}_4$ could degrade approximately 55% NO after 30 min under the

same conditions. Compared with the as-obtained Sb_2WO_6 and $\text{g-C}_3\text{N}_4$ samples, the $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ nanocomposite exhibited higher activities for photocatalytic NO oxidation. More importantly, among the as-synthesized samples, the 15- $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ sample exhibited the best visible-light-driven photocatalytic activity with the removal of 68% NO after 30 min. Fig. 5(b) displays the reusability and stability of the 15- $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ nanocomposite. The ratio of photocatalytic NO removal of the 15- $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ photocatalyst decreased by only 5% after five cycles. Moreover, as shown in Fig. 5(c) and 5(d), the XRD and FT-IR spectra of the

Fig. 5. (a) Photocatalytic NO oxidation of the as-prepared samples; (b) Five consecutive runs of NO removal over the 15- $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ nanocomposite; XRD patterns (c) and FT-IR spectra (d) of 15- $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ nanocomposite before and after photocatalytic reaction.

Fig. 6. (a) PL spectra of g-C₃N₄ and Sb₂WO₆/g-C₃N₄ nanocomposites; Photocurrent responses (b) and EIS spectra (c) of Sb₂WO₆, g-C₃N₄, and 15-Sb₂WO₆/g-C₃N₄ samples; (d) Results of radical species trapping experiments of the 15-Sb₂WO₆/g-C₃N₄ sample and the removal of NO with different scavengers.

fresh and used 15-Sb₂WO₆/g-C₃N₄ samples do not show obvious changes, which indicates that the 15-Sb₂WO₆/g-C₃N₄ sample was stable during the removal of NO.

3.3. Photocatalytic mechanism

As shown in the Fig. 6(a), the recombination rate of the photoexcited carriers in the photocatalysts was tested by PL spectroscopy performed with an excitation wavelength of 365 nm. Compared with the emission intensity of g-C₃N₄, the emission intensity of the Sb₂WO₆/g-C₃N₄ photocatalysts decreased significantly. Particularly, the 15-Sb₂WO₆/g-C₃N₄ sample shows the weakest intensity, which indicates the effective separation of photogenerated charge carriers by the heterojunction structure of the nanocomposite.

Further, the separation efficiency for the photoinduced carriers of the photocatalysts was assessed by photocurrent analysis performed under visible-light irradiation. Among the as-obtained photocatalysts, the 15-Sb₂WO₆/g-C₃N₄ nanocomposite showed the highest photogenerated current (Fig. 6(b)), which suggests that 15-Sb₂WO₆/g-C₃N₄ can more effectively separate the photogenerated carriers during the photocatalytic reaction. Moreover, EIS was performed to assess the charge-transfer efficiency of the semiconductor. The 15-Sb₂WO₆/g-C₃N₄ nanocomposite exhibited the smallest arc radius of the Nyquist circle compared with pure Sb₂WO₆ and g-C₃N₄ (Fig. 6(c)), which indicates that the 15-Sb₂WO₆/g-C₃N₄ nanocomposite can more effectively transport the charges.

Moreover, the photocatalytic mechanism of the 15-Sb₂WO₆/g-C₃N₄ nanocomposite for the removal of NO was investigated by radical species trapping experiments. Benzoquinone (BQ), salicylic acid (C₇H₆O₃), and sodium oxalate (Na₂C₂O₄) were used as the scavengers of •O₂⁻, •OH, and h⁺,

respectively. Fig. 6(d) shows the removal ratio of NO over the 15-Sb₂WO₆/g-C₃N₄ sample in the presence of different scavengers. Compared with the blank group, the addition of BQ significantly affected the performance of photocatalytic NO removal, which indicates that •O₂⁻ plays the main role in the NO removal reaction. Besides, the addition of C₇H₆O₃ slightly affected the photocatalytic activity, which implies that •OH partly participates in the photocatalytic reaction. Meanwhile, the decrease in NO in the case of Na₂C₂O₄ is similar to that in the case of blank group, which suggests that h⁺ was not efficiently involved in the photocatalytic NO removal reaction. The oxygen and vapor contents in the photocatalytic reaction can explain the above findings. We designed an oxygen-enriched and water-deficient environment in the photocatalytic experiment. Hence, the photoinduced electrons preferably reacted with oxygen, while the photoinduced holes could not obtain enough vapor to form •OH.

The reaction pathways of NO removal were studied by in situ DRIFTS (Fig. 7). After irradiation under visible light for 5 min, some new absorption bands and significant changes appeared in the regions of 850–1000, 1050–1200, and 2800–3600 cm⁻¹, which are attributed to some reaction intermediates (NO₂⁻, N₂O₃, NO⁻, and NO₂) and the final products (NO₂⁻ and NO₃⁻) [64]. As displayed in Table S1, the absorption bands at 858, 880, 891, 928, 948, and 1128 cm⁻¹ can be attributed to NO₂⁻ [65]. The peaks at 961 and 976 cm⁻¹ belong to the oxidized N₂O₃ [66]. The bands at 1063, 1080, 1100, and 1285 cm⁻¹ can be indexed to nitrates (NO₃⁻) [17,67], and the bands at 1090 and 1124 cm⁻¹ can be assigned to N₂O. The peaks at 1170 and 1178 cm⁻¹ belong to oxidized NO⁻. Moreover, a peak corresponding to N₂O⁻ appeared at 1144 cm⁻¹ [68]. The bands at 2823, 2855, 2950, 3460, 3601, and 3795 cm⁻¹ can be assigned to NO₂ [69]. The bands at 1320–1390 and

Fig. 7. In situ DRIFT spectra of the photocatalytic reaction of NO over 15-Sb₂WO₆/g-C₃N₄ nanocomposite under visible-light irradiation.

1510–1615 cm⁻¹ can be assigned to the double bond stretching vibrations of -NO₂ [70]. Besides, g-C₃N₄ slightly decomposes under strong light irradiation, and the band at 1620–1680 cm⁻¹ can be attributed to -C=C- from g-C₃N₄.

Combined with the above findings of the trapping experiments, the main radical species in the photocatalytic NO removal reaction was found to be •O₂⁻, while the secondary species was found to be •OH. Nitrite and nitrate are the final oxidation products of photocatalytic NO removal. Hence, the photocatalytic process of NO removal over the Sb₂WO₆/g-C₃N₄ nanocomposite is identified to occur via an oxygen-induced route. The detailed NO removal reactions are as follows (NO_x = NO₂⁻, N₂O₃, NO⁻, and N₂O):

Based on the above analyses and references, the entire process of electron migration and photocatalytic mechanism for NO removal over the Sb₂WO₆/g-C₃N₄ nanocomposite can be divided to three parts (Fig. 8). As shown in Fig. 8, the first step is before the contact of the components. In this step, Sb₂WO₆ and g-C₃N₄ are in their original states, and the E_{FB} of Sb₂WO₆ is lower than that of g-C₃N₄. The second step is after the contact of the components in the dark. The electrons can migrate from g-C₃N₄ to Sb₂WO₆ to build a new Fermi level (F_{B}^* in the Fig. 8). Simultaneously, a built-in electric field (IEF) is generated be-

Fig. 8. S-scheme photocatalytic mechanism for Sb₂WO₆/g-C₃N₄ nanocomposite under visible-light irradiation.

tween the components in the direction from the higher original Fermi level to a lower level. The last step is the photocatalytic reaction. The photogenerated electrons in the CB of Sb₂WO₆ combine with the photoinduced holes in the VB of g-C₃N₄ under the built-in electric field. Meanwhile, •O₂⁻ radicals are formed by the photoexcited electrons and O₂ in the CB of g-C₃N₄, and •OH radicals are generated via the reaction of the photogenerated holes and water in the VB of Sb₂WO₆. Lastly, the absorbed NO is oxidized by the formed radicals.

4. Conclusions

Sb₂WO₆/g-C₃N₄ nanocomposites were successfully fabricated by an ultrasound-assisted method. Among the as-synthesized samples, the 15-Sb₂WO₆/g-C₃N₄ nanocomposite demonstrated the best photocatalytic performance for the complete conversion of ppb-level NO to nitrate under visible-light irradiation. Meanwhile, PL spectroscopy, transient photocurrent response analysis, and EIS confirmed that the 15-Sb₂WO₆/g-C₃N₄ nanocomposite could effectively separate the photoexcited charges in the visible-light-driven photocatalytic reaction. Hence, the outstanding photocatalytic performance of the nanocomposite resulted from its excellent separation efficiency for the photogenerated carriers. The PL spectra, photocurrent response, and EIS spectra of the as-obtained samples indicated that the S-scheme structure of the Sb₂WO₆/g-C₃N₄ photocatalyst effectively enhanced the separation efficiency for the photogenerated carriers. More importantly, the results of in situ DRIFTS indicated that the main photocatalytic process of NO removal over the Sb₂WO₆/g-C₃N₄ nanocomposite occurred via an oxygen-induced route. This study demonstrated that the S-scheme Sb₂WO₆/g-C₃N₄ semiconductor is a promising photocatalyst for NO removal.

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Graphical Abstract

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S-scheme $\text{Sb}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ photocatalysts with enhanced visible-light-induced photocatalytic NO oxidation performance

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The S-scheme heterojunctions between Sb_2WO_6 and $\text{g-C}_3\text{N}_4$ enhanced both the utilization of visible light and the separation of photoinduced electron-hole pairs.

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S型Sb₂WO₆/g-C₃N₄复合光催化剂及其增强的可见光诱导的光催化氧化NO性能

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摘要: 近年来, 随着工业化和城镇化的飞速发展, 作为一种典型的空气污染物, NO_x已经造成严重的环境问题, 甚至威胁到人类的身体健康. 为了解决这个问题, 科研工作者研发了许多NO_x去除技术, 其中光催化技术被认为是一种能有效地去除空气中NO_x的技术. 作为一种廉价、无毒、热稳定性强、能带结构合适的光催化材料, 石墨相氮化碳(g-C₃N₄)能够有效的利用可见光, 将NO光催化氧化为NO₃⁻. 但是由于自身的光生载流子复合率较高, 光谱响应范围较窄等缺点, g-C₃N₄不能有效的光催化去除空气中持续流动的低浓度NO, 限制了其在光催化领域中的实际应用. 因此, 有必要合成出高催化活性、高光响应范围的S型复合光催化剂来克服以上光催化材料的不足. 为此, 我们利用超声辅助法制备了一系列的S型Sb₂WO₆/g-C₃N₄复合光催化剂, 呈现出优异的光催化活性: 与其纯组分相比, 所制备的15-Sb₂WO₆/g-C₃N₄复合光催化剂在可见光下照射30 min, 可去除68%以上的持续流动的NO(初始浓度400 ppb), 且五次循环实验后, Sb₂WO₆/g-C₃N₄复合光催化剂仍然具备良好的光催化活性和稳定性. 透射电子显微镜结果清楚地表明, Sb₂WO₆颗粒已成功均匀地负载到g-C₃N₄纳米片表面. 紫外可见漫反射光谱的结果表明, Sb₂WO₆和g-C₃N₄的复合可以有效地提高对可见光的吸收能力. 与纯g-C₃N₄样品相比, 复合样的吸收带边具有明显的红移. 光致发光光谱结果表明, 在Sb₂WO₆/g-C₃N₄复合半导体中, 光生载流子的复合受到抑制. 光电流与电阻抗分析可知, 与纯Sb₂WO₆和g-C₃N₄相比较, 在15-Sb₂WO₆/g-C₃N₄复合光催化剂中的光生载流子的迁移速率和分离效率较高. 通过对样品的能带结构分析并已有参考文献, 我们认为Sb₂WO₆和g-C₃N₄的接触边界形成了S型异质结, 使光生载流子的转移速率更快, 改善了光生电子-空穴对分离, 而且增强可见光的利用效率, 从而提高了光催化性能. 自由基捕获实验结果证实, •O₂⁻主导了Sb₂WO₆/g-C₃N₄复合光催化剂去除NO反应, h⁺也在一定程度上参与了光催化氧化NO的反应. 通过原位红外光谱技术研究了Sb₂WO₆/g-C₃N₄光催化NO氧化的反应机理, 研究发现, Sb₂WO₆/g-C₃N₄复合光催化剂光催化去除是氧诱导的反应. 具体反应机理是在可见光的驱动下, 光催化剂表面的光生电子会与吸附的O₂反应生成•O₂⁻, 并与光生h⁺一起, 共同将低浓度的NO光催化氧化为亚硝酸盐或硝酸盐. 该研究有助于深入研究光催化氧化NO机理, 并为设计高效光催化剂用于光催化氧化ppb级NO提供了一种极具前景的策略.

关键词: 钨酸锑; 石墨相C₃N₄; S型光催化剂; 光催化去除氮氧化物; 原位红外测试

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