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Article

Sulfur-doped g-C₃N₄/TiO₂ S-scheme heterojunction photocatalyst for Congo Red photodegradation

Juan Wang^a, Guohong Wang^{a,*}, Bei Cheng^{b,#}, Jiaguo Yu^b, Jiajie Fan^c^a Hubei Key Laboratory of Pollutant Analysis and Reuse Technology, College of Chemistry and Chemical Engineering, Institute for Advanced Materials, Hubei Normal University, Huangshi 435002, Hubei, China^b State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, Hubei, China^c Material Science and Engineering School, Zhengzhou University, Zhengzhou 450001, Henan, China

ARTICLE INFO

Article history:

Received 17 March 2020

Accepted 26 April 2020

Published 5 January 2021

Keywords:

TiO₂ nanofiberSulfur-doped g-C₃N₄

Step-scheme heterojunction

photocatalysis

In situ XPS

S-scheme mechanism

ABSTRACT

Constructing step-scheme (S-scheme) heterojunctions has been confirmed as a promising strategy for enhancing the photocatalytic activity of composite materials. In this work, a series of sulfur-doped g-C₃N₄ (SCN)/TiO₂ S-scheme photocatalysts were synthesized using electrospinning and calcination methods. The as-prepared SCN/TiO₂ composites showed superior photocatalytic performance than pure TiO₂ and SCN in the photocatalytic degradation of Congo Red (CR) aqueous solution. The significant enhancement in photocatalytic activity benefited not only from the 1D well-distributed nanostructure, but also from the S-scheme heterojunction. Furthermore, the XPS analyses and DFT calculations demonstrated that electrons were transferred from SCN to TiO₂ across the interface of the SCN/TiO₂ composites. The built-in electric field, band edge bending, and Coulomb interaction synergistically facilitated the recombination of relatively useless electrons and holes in hybrid when the interface was irradiated by simulated solar light. Therefore, the remaining electrons and holes with higher reducibility and oxidizability endowed the composite with supreme redox ability. These results were adequately verified by radical trapping experiments, ESR tests, and in situ XPS analyses, suggesting that the electron immigration in the photocatalyst followed the S-scheme heterojunction mechanism. This work can enrich our knowledge of the design and fabrication of novel S-scheme heterojunction photocatalysts and provide a promising strategy for solving environmental pollution in the future.

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1. Introduction

The treatment of industrial wastewater containing residual organics is still an immense challenge for humans in realizing sustainable development [1]. Congo Red (CR) is a widely used dye; however, its water-soluble and refractory characteristics

make it difficult to purify in its aqueous solution [2]. Although several traditional technologies (adsorption, coagulation, etc.) have been applied to solve this problem, these processes cannot completely detoxify the contaminants and simultaneously bear high operating costs [3]. Fortunately, as an advanced oxidation and eco-friendly technology, photocatalysis has attract-

* Corresponding author. Tel/Fax: +86-714-6515602; E-mail: wanggh2003@163.com

Corresponding author. Tel/Fax: +86-27-87871029; E-mail: chengbei2013@whut.edu.cn

This work was supported by the National Natural Science Foundation of China (51872220, 51932007, 51961135303, 21871217, U1905215, U1705251), National Key Research and Development Program of China (2018YFB1502001), and the Fundamental Research Funds for the Central Universities (WUT 2019VB050).

DOI: 10.1016/S1872-2067(20)63634-8 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 42, No. 1, January 2021

ed increasing attention in organic wastewater treatment because of its mild reaction conditions and relatively low energy consumption [4–6]. Recently, many photocatalysts with different structures and shapes have been designed and synthesized. In particular, the metal-oxide semiconductor has received intensive attention for the photocatalytic degradation of organic wastewater due to its suitable band structure, physicochemical stability, non-toxicity, and so on [7–9]. Moreover, the one-dimensional (1D) nanostructure has been confirmed as a favorable structure for the photocatalytic degradation process, profiting from the enlarged specific surface area, short immigrating path of the ion, and unique 1D electron transfer trajectory [10–12]. For example, TiO_2 nanofibers were applied to the treatment of water pollutants and exhibited excellent photocatalytic performances under ultraviolet (UV) irradiation as a result of its hydrophilia, special morphology, and proper band position [13–16]. However, the wide band gap of TiO_2 (~3.2 eV), instinctive recombination of photoinduced carriers, and other defects result in its low solar quantum efficiency and restrict its practical utility [17,18]. Therefore, several strategies have been proposed to improve the photocatalytic activity, such as doping metallic or non-metallic elements, loading noble metals, and constructing heterojunctions [19,20].

The heterojunction structure, which can efficiently facilitate the transfer and separation of photoinduced electrons, is commonly constructed by hybridizing two semiconductors with appropriate band alignments [21–23]. Presently, a novel step scheme (S-scheme) heterojunction has been proposed to elucidate the photocatalytic enhancement mechanism of heterojunction photocatalysts [24–26]. The S-scheme heterojunction not only efficiently separates photoinduced electrons and holes, but also reserves the promising redox abilities of semiconductors [27,28]. In a typical S-scheme heterojunction photocatalyst, the electrons flow from the conduction band (CB) of one semiconductor to the valence band (VB) of the other under the effect of the internal electric field (IEF), which usually exists at the interface of two semiconductors, exhibiting an S-scheme electron immigration route. Consequently, the electrons and holes with weak redox ability are transferred and consumed, whereas those electrons and holes with strong redox ability remain [29,30].

Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) is a type of polymeric semiconductor. With its desirable band structure and high chemical stability, $\text{g-C}_3\text{N}_4$ has been considered as a promising photocatalytic material for water splitting and degradation of organic pollution, especially under visible light illumination [31–33]. Like other semiconductors, the immanent properties of $\text{g-C}_3\text{N}_4$, such as low electronic conductivity, quick recombination of photoinduced charge carriers, small surface area (<10 m^2/g), and poor visible light absorption, inhibit its photocatalytic activity [34]. To overcome these flaws, numerous modification methods have been investigated, including doping metal or non-metal and hybridization with semiconductors [35–37]. In particular, the S-doped $\text{g-C}_3\text{N}_4$ (SCN), which was prepared through a sulfur doping process, was proven to have significantly stronger photocatalytic activity than pure $\text{g-C}_3\text{N}_4$ [38,39]. The introduction of the sulfur element to $\text{g-C}_3\text{N}_4$ can broaden

its light absorption range, resulting in more photogenerated charge carriers. Furthermore, the extra surface impurities contribute to the trapping and separation of e^- - h^+ pairs [39,40]. Based on the above introduction, it will be an interesting and practical task to integrate the advantages of the 1D nanostructure, S-doping, and S-scheme heterojunctions to fabricate SCN/ TiO_2 photocatalysts.

To the best of our knowledge, the preparation of SCN/ TiO_2 hybrid nanofibers and their application in photocatalytic degradation of organic pollutants have not been researched in detail. Herein, we report a facile method to prepare S-scheme SCN/ TiO_2 heterojunctions by a one-step calcination process. The obtained SCN/ TiO_2 nanofibers possessed remarkably enhanced photocatalytic performances. The results of in situ X-ray photoelectron spectroscopy (XPS) and electron paramagnetic resonance (EPR) demonstrated that the S-scheme heterojunction constructed between TiO_2 and SCN played a crucial role in enhancing photocatalytic activity for the decomposition of Congo Red.

2. Experimental

2.1. Preparation of SCN/ TiO_2 heterostructures

The TiO_2 nanofibers were fabricated following a similar process to the literature [14]. The formation process of SCN/ TiO_2 was described as follows. Firstly, 6 g of thiourea was dissolved in 50 mL of deionized water to form a transparent solution. Then, 0.2 g of TiO_2 nanofibers was added into the above solution and stirred to form the suspension. The suspensions were stirred for 2 h, followed by evaporation at 100 °C until dry. The resulting powders were annealed at 550 °C for 2 h at a heating rate of 2 °C/min to obtain the final SCN/ TiO_2 hybrids. The products were named SCNT6. In order to discuss the role of SCN content on the photocatalytic activity of SCN/ TiO_2 heterojunction photocatalysts, samples with different amounts of thiourea in the precursors (i.e., 5, 7, and 8 g) were prepared under the same conditions, and the obtained samples were denoted as SCNT x ($x = 5, 7$, and 8). Figure 1 schematically illustrates the preparation of SCN/ TiO_2 hybrid nanofibers.

2.2. Characterization

The crystal phases of the samples were determined by X-ray

Fig. 1. Schematic for the preparation of SCN/ TiO_2 hybrid nanofibers.

diffraction (XRD) with Cu $K\alpha$ radiation (D/max RB, Rigaku Co., Japan). The morphology was observed using a JSM 7500F field emission scanning electron microscope (FESEM). A Titan G2 60-300 electron microscope was used to take transmission electron microscopy (TEM) images and perform energy dispersive X-ray spectroscopy (EDX). The pore size distribution and specific surface area were obtained from nitrogen (N_2) adsorption-desorption isotherms on a Micromeritics ASAP 3020 instrument. The UV-vis diffuse reflectance spectra (DRS) were recorded on a Shimadzu UV-2600 UV-visible spectrophotometer (Japan) using $BaSO_4$ as a reference. XPS was recorded with an ESCALAB 250Xi system. In situ XPS measurements were conducted under UV-visible light irradiation. Photoluminescence (PL) spectra were recorded using an LS55 fluorescence spectrophotometer at an excitation wavelength of 320 nm.

2.3. Photocatalytic activity

The photocatalytic activities of the as-prepared SCN/TiO₂ composites (20 mg) were evaluated by degrading CR (100 mL, 50 mg/L) under 300 W xenon lamp irradiation. Before light illumination, the solution was stirred in the dark for 1 h to reach the adsorption equilibrium. The concentration of dye was analyzed every 10 min using a UV-visible spectrophotometer (Shimadzu UV/Vis 1240, Japan). The photodegradation cycling tests were performed using the procedure of typical photocatalytic activity experiments. In addition, the used photocata-

lyst in the cycling tests was separated through a centrifuge and washed with deionized water prior to the next cycling test.

2.4. Computational details

The density functional theory (DFT) calculations were carried out by using the CASTEP module in Materials Studio software. The exchange-correlation interaction was described by generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) function. The energy cutoff was set as 500 eV. The Monkhorst-Pack k-point mesh was set as $3 \times 3 \times 1$ and $3 \times 5 \times 1$ for SCN and TiO₂ (1 0 1) models, respectively. Vacuum spaces of 15 Å and 25 Å were used in SCN and TiO₂ (1 0 1) models, respectively. The SCN model was built by replacing a two-coordinated N atom in a 2×2 monolayer g-C₃N₄ model with an S atom. The TiO₂ (1 0 1) model was composed of 24 Ti and 48 O atoms. During the geometry optimization, the bottom third of Ti and O atoms were fixed, while other atoms were relaxed.

3. Results and discussion

3.1. Structure, surface chemical state, and morphology

Figure 2(a) shows the XRD spectra of the g-C₃N₄, SCN, SCNTx, and TiO₂. The characteristic peaks of g-C₃N₄ at 13.1° and 27.5° belong to its (1 0 0) and (0 0 2) planes (JCPDS 87-1526)

Fig. 2. (a) XRD patterns of g-C₃N₄, SCN, TiO₂, and SCN/TiO₂ composites; (b) FT-IR spectra of SCN, TiO₂, and SCN/TiO₂ composites; (c) Nitrogen adsorption-desorption isotherms and pore size distribution curves (inset) of SCN, TiO₂, and SCN/TiO₂ composites; (d) TG curves for SCN, TiO₂, and SCN/TiO₂ composites.

[41]. The peak at 13.1° can be ascribed to the in-planar structure of g-C₃N₄, but the peak at 27.5° is produced from the aromatic stacking structure. For the SCN sample, the location of the (0 0 2) peak negatively shifts to 27.3° , suggesting that the g-C₃N₄ lattice is influenced by the S element, which has a larger atomic radius than C or N. On the other hand, the distinctly decreased peak intensity of the SCN sample can be attributed to the changed lattice structure of g-C₃N₄, which is affected by the inserted S atoms [42,43]. Compared with g-C₃N₄, the above characteristic variations in the XRD spectra of SCN confirm that the S element has been successfully incorporated into g-C₃N₄. Additionally, the four typical diffraction peaks of TiO₂ located at 25.5° , 37.8° , 48.0° , and 53.8° demonstrate that only the anatase phase TiO₂ (JCPDS 21-1272) exists [44]. It is noteworthy that the peaks at 13.1° are not observed in the XRD spectra of the SCNTx samples. This can be ascribed to the inferior crystallization of SCN in the composites [45]. Interestingly, the intensities of the peaks at 27.3° for the SCNTx samples are enhanced monotonously with the increasing amount of SCN in the composites, and the intensities of the peaks at 25.5° are weakened accordingly. However, the intensities of the peaks (27.3°) belonging to SCN are always lower than those of the peaks (25.5°) belonging to TiO₂. This phenomenon results from the instinctive difference in crystallinity between TiO₂ and SCN. In addition, no peak shifts are observed comparing the XRD spectra of SCNTx samples with those of SCN and TiO₂, demonstrating that the lattice structures of TiO₂ and SCN have not been changed in the SCNTx samples.

Figure 2(b) shows the FT-IR spectra of SCNTx samples, SCN, and TiO₂. In the spectrum of pristine TiO₂, the absorption band at $\sim 475\text{ cm}^{-1}$ arises from the stretching vibration modes of Ti-O-Ti and Ti-O in anatase crystals. For the SCN sample, the absorption peak located at 808 cm^{-1} is induced by the breathing vibration of the g-C₃N₄ triazine structure. Meanwhile, the wide absorption band in the range of $1200\text{ to }1600\text{ cm}^{-1}$ is caused by the stretching vibration of C-N and C=N heterocycle unit of g-C₃N₄. The other obvious typical peaks at $\sim 3200\text{ cm}^{-1}$ belong to the amino and surface hydroxyl groups [46,47]. Clearly, all typical peaks of the two components, TiO₂ and SCN, are observed in the FT-IR spectra of the SCNTx samples, implying that the two materials have been successfully incorporated into composites. The results are in conformity with the above XRD analyses.

The N₂ adsorption isotherms and pore size distributions of the samples are displayed in Fig. 2(c) and its inset, respectively. All the isotherms can be identified as type IV, demonstrating the existence of mesopores [48]. Furthermore, the hysteresis loop of the TiO₂ and SCNT5 samples can be classified as type H2, suggesting the formation of ink-bottle pores caused by the particle aggregation. Notably, the hysteresis loops of the SCNTx samples gradually display the characteristic of type H3 with the increasing amount of SCN in SCNTx. This phenomenon can be ascribed to the existence of narrow slit-shaped mesopores, which are produced by the random distribution of SCN on the TiO₂ nanofibers [49]. As shown in the inset of Fig. 2(c), the pore sizes of pristine TiO₂ and SCN samples both show bimodal distributions. The peaks ($\sim 3.5\text{ nm}$ and $\sim 30\text{ nm}$) of TiO₂ and the

peaks ($\sim 3.8\text{ nm}$ and $\sim 5\text{ nm}$) of SCN further confirm their mesoporous structures. Particularly, the pore size of TiO₂ is mainly centered at $\sim 30\text{ nm}$, and that of SCN is mainly located at $\sim 3.8\text{ nm}$. The composites inherit the characteristics of the pores of TiO₂ and SCN. Moreover, the new $\sim 9\text{ nm}$ pores are produced in the SCNT6 sample after hybridizing, which is the result of homogeneous mixing of TiO₂ and SCN at the microscopic level. Therefore, the SCNT6 shows a tri-modal pore size distribution. Table 1 shows the Brunauer-Emmett-Teller (BET) surface area, pore volume, and pore size of all samples. Compared with pure TiO₂ and SCN, the SCNTx samples possess an enlarged specific surface area. The specific surface area of SCNTx gradually increases with increasing content of thiourea in the precursors (from 5 to 6 g), then gradually decreases with further addition of thiourea (from 6 to 8 g). The increased specific surface area of SCNTx could be attributed to the low content of thiourea in the precursor. Moreover, the highly scattered thiourea can produce lighter and smaller SCN particles, resulting in the increase in the specific surface area of the composite [39]. However, further increasing the content of thiourea may induce the self-aggregation of SCN in the hybridization process [50]. The composite with a larger specific surface area is believed to provide more sites for photocatalytic reaction and is thus considered to have enhanced photocatalytic activity.

The thermal stability and quantitative analysis were investigated through thermogravimetric analysis (TGA). The TG curves of the samples are shown in Fig. 2(d). The TiO₂ nanofibers exhibited an excellent thermal stability, and the slight weight loss could be ascribed to absorbed water on the TiO₂ surface. However, for pure SCN, there is weak thermal stability at higher temperatures in the oxygen atmosphere. The rapid decomposition of the SCN sample is observed from 500 to 640°C . When the temperature is further increased from 640 to 800°C , the residue of the SCN sample is close to zero, indicating the complete decomposition of SCN. As expected, the SCNTx samples have similar TG curves to those of the SCN sample. The rapid weight loss of the SCNTx samples can be detected, and finally the weight percentages of the residues achieve a constant value. However, the initial temperatures of the final plateaus in the TG curves of the SCNTx samples are different from that of the SCN sample. This is ascribed to the different amount of SCN in the as-prepared composites. Particularly, the TG curve of the SCNT5 sample displayed a very different characteristic, resulting from the relatively low content of SCN in the hybrid. In light of the above analyses, the final residues of the hybrids are a result of the TiO₂. Therefore, the content of SCN in the hybrids can be estimated based on the TG curves, and the results are shown in Fig. 2(d).

Table 1
Porosity and surface properties of the prepared samples.

Samples	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
TiO ₂	16	0.08	19.4
SCNT5	29	0.10	14.1
SCNT6	51	0.17	13.2
SCNT7	33	0.10	12.3
SCNT8	28	0.11	15.2
SCN	20	0.05	10.2

XPS analysis was conducted to investigate the surface chemical state of the as-prepared samples, and the results are shown in Fig. 3(a)–(f). In Fig. 3(a), all elements of the composing materials are detected in the corresponding samples. However, the extra element, O, is also observed in the pristine SCN, resulting from the adsorbed hydroxyl groups [51]. The element S was not detected in either the SCN or SCNT6 sample due to trace contents of sulfur. Moreover, the signal of C in the survey spectrum of pure TiO_2 is attributed to the adventitious contamination of hydrocarbons from the instrument.

Figure 3(b) shows the high-resolution Ti 2p XPS spectra of TiO_2 and SCNT6. The typical peaks belonging to Ti^{4+} in TiO_2 are observed at approximately 458.5 and 464.3 eV. Notably, compared with pure TiO_2 , the binding energies of Ti 2p for SCNT6 in the absence of light illumination exhibit slightly negative shifts. The changes in binding energies signify that the electrons transfer from SCN to TiO_2 on account of the hybridization [52]. This result is also further confirmed by the O 1s XPS spectra (Fig. 3(c)). The peaks located at approximately 529.7 and 532.1 eV are assigned to lattice O and –OH, respectively. Due to the immigration of electrons, the binding energy of lattice O for SCNT6 without light illumination also displays a slightly negative shift in comparison with pure TiO_2 . To further verify the above conclusion, the high-resolution C 1s and N 1s XPS spectra of SCN and SCNT6 were also analyzed. In Fig. 3(d), all binding energies were calibrated by the C 1s peaks located at 284.6 eV. The peaks at approximately 288.2 eV belong to sp^3 carbon in the N-C-N backbone of SCN and the precursors [53]. In Fig. 3(e), the characteristic peak at 398.6 eV is ascribed to sp^2 -hybridized

pyridine nitrogen ($\text{C}=\text{N}-\text{C}$), and the peak at approximately 400.0 eV is a typical signal for tertiary nitrogen ($\text{N}-\text{C}_3$) [54]. Compared to the C 1s and N 1s XPS spectra of SCN and SCNT6 without light illumination, the SCNT6 possesses slightly higher binding energies than SCN, confirming the electron transfer from SCN to TiO_2 and simultaneously agreeing with the opposite banding energy shifts of Ti and O.

The immigration of electrons between two different semiconductors after contact is commonly caused by the difference in Fermi level. As SCN has a higher Fermi level than TiO_2 (see DFT calculation), the different Fermi level will drive electrons to migrate from SCN to TiO_2 until their Fermi levels are equalized [55–57]. Sequentially, an internal electric field will be created at the interface of the two materials. It is interesting that all the binding energies of elements in the SCNT6 under light irradiation show reverse shifting directions compared with those of the SCNT6 without light irradiation. These phenomena can be attributed to the generation of photoinduced charge carriers, and the detailed analyses of this issue are performed in Section 3.5.

Figure 3(f) shows high-resolution S 2p XPS spectra of SCN and SCNT6. No distinct signal is probed in the S 2p XPS spectrum of SCNT6, due to its low content in the SCNT6 sample (< 0.35% w/w of S). However, a typical peak at 165.8 eV belonging to the C–S bond of SCN is detected, signifying that the sulfur is successfully substituted in the lattice nitrogen [40].

The morphologies and structures of bare TiO_2 nanofibers and SCN/ TiO_2 hybrid were characterized by SEM, TEM, and HRTEM. In Fig. 4(a), the as-prepared TiO_2 nanofibers with a

Fig. 3. (a) XPS survey spectra of TiO_2 , SCN, and SCNT6 samples; High-resolution XPS spectra of Ti 2p (b), O 1s (c) in TiO_2 and SCNT6, C 1s (d), N 1s (e), and S 2p (f) in SCN and SCNT6.

Fig. 4. FESEM images of TiO_2 (a) and SCNT6 (b); insets on left bottom are the corresponding low-magnification SEM images; TEM (c) and HRTEM (d) images of SCNT6; (e) EDX elemental mappings of O, Ti, N, C and S.

regular surface are constructed by uniform TiO_2 nanoparticles, and the mean diameters and lengths of the fibers are estimated to be ~ 150 nm and hundreds of micrometers, respectively. In Fig. 4(b), the SCN/ TiO_2 composite fibers, which were synthesized by calcining the mixture of thiourea and TiO_2 nanofibers,

still retain the morphologies of TiO_2 nanofibers. Interestingly, the thermal polymerization products of thiourea (SCN) appear in a veil-like fashion, closely and uniformly covered on the surface of the TiO_2 nanofibers. The unique structure benefits the immigration of charge carriers and the diffusion of species in aqueous solution. Figure 4(c) shows the typical TEM image of SCNT6. Clearly, SCN is still attached to the TiO_2 nanofibers in a veil-like fashion, even though the samples were treated by bath sonication for 5 min before the TEM test. This further confirms the structural stability of the SCN/ TiO_2 composite fibers. In addition, the crystalline structure of SCNT6 was probed by HRTEM (Fig. 4(d)), and the lattice spacing of 0.352 nm corresponds to the (1 0 1) plane of anatase phase TiO_2 . In Fig. 4(e), the elements of Ti, O, C, N, and S in SCNT6 are all confined to the same region, which is almost identical to the shape of the selected area of SCNT6. These results strongly demonstrate the even allocation of SCN and the successful hybridization of TiO_2 and SCN.

3.2. Optical absorption properties

The light absorption properties of the as-prepared samples were characterized by the UV-vis diffuse reflectance spectra (UV-vis DRS). As shown in Fig. 5(a), the typical absorption edges of SCN and $\text{g-C}_3\text{N}_4$ fall in the wavelength of approximately 510 and 460 nm, respectively, whereas the TiO_2 exhibits only UV light absorption characteristics, as previously reported. Interestingly, all the SCNT x samples present enhanced light absorption performances compared to TiO_2 . Even the SCNT5 sample with a low content of SCN displays an obviously enhanced light absorption property in the range of 400–600 nm. Moreover, all the hybrids except the SCNT5 sample show red shifts of the absorption edge in comparison with TiO_2 . Commonly, the band gap energy (E_g) of a semiconductor can be estimated based on the Kubelka-Munk function [58]. Therefore, the E_g values of TiO_2 , SCN, and $\text{g-C}_3\text{N}_4$ were estimated to be 3.28, 2.43, and 2.67 eV, respectively (Fig. 5(b)). Clearly, the E_g value of SCN is smaller than that of pure $\text{g-C}_3\text{N}_4$ due to the introduction of the S atom into $\text{g-C}_3\text{N}_4$. The SCN sample with a narrower band gap produces more photoinduced charge carriers in the photocatalytic process. Therefore, the SCNT x hybrids with better light absorption and a narrower band gap are expected to present an improved photocatalytic activity.

Fig. 5. (a) UV-vis diffused reflectance of SCN, $\text{g-C}_3\text{N}_4$, TiO_2 , and SCN/ TiO_2 composites; (b) Tauc plots of SCN, $\text{g-C}_3\text{N}_4$, and TiO_2 .

3.3. Photocatalytic activity

The photocatalytic performances of the as-prepared catalysts were evaluated by the photodegradation of CR under Xe lamp irradiation. Fig. 6(a) presents the concentration variation of CR during the photocatalytic degradation processes with different as-prepared samples. Clearly, the TiO_2 and SCN samples show slower degradation rates of CR in comparison with SCNTx heterojunction photocatalysts. Furthermore, the enhancements of photocatalytic activity of the SCNTx composites are highly relevant to the amount of SCN. According to Fig. 6(a), the apparent reaction rate constant (k) of all samples was calculated and shown in Fig. 6(b). The relatively low degradation rate ($28.6 \times 10^{-3} \text{ min}^{-1}$) of bare TiO_2 can be ascribed to the restriction of the light absorption range. Only the UV light could be absorbed by the bare TiO_2 . Owing to the inherent recombination of photoinduced charge carriers, the SCN also displays a fairly low degradation rate ($11.7 \times 10^{-3} \text{ min}^{-1}$) [34]. However, the composites of the two components present significantly enhanced photocatalytic activities. In particular, the SCNT6 sample with 36.5 wt% SCN exhibits the highest photocatalytic activity. Its apparent reaction rate constant is estimated to be $96.2 \times 10^{-3} \text{ min}^{-1}$, which exceeds that of bare TiO_2 and SCN by a factor of 3.4 and 8.2, respectively. The enhancement in photocatalytic activity of the hybrid can be explained by the following facts. First, the broadened photoabsorption range (Fig. 5) induces more photoinduced carriers. Second, the high-quality interface between TiO_2 and SCN (Figs. 3 and 4) provides vast electron immigration paths, resulting in fast charge carrier

separation and transportation [59]. Third, the large surface area plays a key role in the increment of the active site, resulting in an increasing degradation rate of SCNTx samples. It is noted that the content of SCN in the hybrid has an optimal value (36.5 wt%). When the amount of SCN is further increased, the photocatalytic performance of composites is deteriorated. This can be ascribed to the fact that most of the photoinduced e^-h^+ pairs from extra uncoupled SCN are recombined and do not participate in photocatalytic reactions due to the absence of heterojunction interfaces. These results further verify the effectiveness of the hybridization.

Figure 6(c) shows the absorbance of CR aqueous solutions with the SCNT6 sample versus the exposure time to the xenon lamp. Particularly, the concentration of the CR solution containing the SCNT6 photocatalyst quickly declined to below 5% of the initial value after 60 min of illumination. Furthermore, the stability of the composite was verified by the photodegradation cycling tests using the SCNT6 sample. The variations in concentration of CR in every cycle are shown in Fig. 6(d). The results revealed that the photocatalytic activity of the composite was not weakened after 5 cycles. Moreover, the FT-IR spectra (Fig. 6(e)) of the used and fresh SCNT6 samples displayed identical typical features, indicating its excellent chemical stability.

3.4. Charge separation and charge transfer

Photoluminescence spectroscopy was applied to analyze the separation efficiency of the photoinduced e^-h^+ pairs. Figure

Fig. 6. (a) Photocatalytic activity curves of SCN, TiO_2 , and SCN/ TiO_2 composites for the degradation of CR aqueous solution under xenon lamp irradiation; (b) Comparison of the apparent rate constants k (10^{-3} min^{-1}) of the SCN, TiO_2 , and SCN/ TiO_2 composites of the degradation of CR under xenon lamp irradiation; (c) Adsorption peaks of CR aqueous solution in the presence of the SCNT6 sample with increasing irradiation time under xenon lamp irradiation; (d) Circulating runs in the decomposition of CR for the SCNT6 sample under xenon lamp irradiation; (e) FT-IR patterns of the SCNT6 sample before and after 5 circulating runs.

Fig. 7. (a) PL spectra of TiO₂, SCN, and SCNT₆ under 320 nm excitation; (b) Time-resolved transient PL decay of SCN and SCNT₆; (c) Transient photocurrent responses of TiO₂, SCN, and SCNT₆ under xenon lamp irradiation; (d) EIS spectra of TiO₂, SCN, and SCNT₆ under xenon lamp irradiation; (e) MS plots for TiO₂ and SCN; (f) MS plot for g-C₃N₄.

7(a) shows the PL spectra of the as-prepared SCN, TiO₂, and SCNT_x samples under 320 nm light excitation. In accordance with the previous reports, no obvious emission peak was detected for pristine TiO₂ [60,61]. Although the SCN displayed the strongest PL intensity, the peak intensities of SCNT_x hybrids were remarkably weakened after the SCN coupled with TiO₂. The SCNT₅ sample did not exhibit any obvious emission peak because of the low content of SCN in the composite. However, the other composites presented remarkable PL signals. Among the SCNT_x ($x = 6, 7$, and 8) samples, the SCNT₆ sample showed the lowest PL intensity, suggesting that the recombination of charge carriers in the composite was greatly restrained due to the construction of the heterojunction at the interface between SCN and TiO₂. The extreme inhibition of the recombination of e⁻-h⁺ pairs could make the hybrid release more photoinduced carriers to activate the photocatalytic reaction. Thus, it can be inferred that the SCNT₆ sample possesses the highest photocatalytic activity (Fig. 6(b)). In addition, the TRPL spectra of SCN and SCNT₆ (Fig. 7(b)) further elucidate the difference in the recombination process of photoinduced carriers in intrinsic SCN and SCNT₆ samples. The fitting parameters and average lifetimes are summarized in Fig. 7(b). Evidently, the SCNT₆ sample presents an increased short ($\tau_1 = 3.04$ ns), long ($\tau_2 = 13.16$ ns), and average ($\tau_m = 10.93$ ns) emission lifetime in comparison with the intrinsic SCN ($\tau_1 = 3.13$ ns, $\tau_2 = 12.98$ ns, $\tau_m = 10.62$ ns). The lengthened fluorescence lifetime of the SCNT₆ sample further confirms the efficient separation of photoinduced e⁻-h⁺ pairs.

Moreover, the transient photocurrent response and electrochemical impedance were measured on a photoelectrochemical test device with a Xe lamp to further verify the differ-

ence in carrier separation efficiency under light irradiation. The cyclic photocurrent curves of pure TiO₂, SCN, and SCNT₆ are shown in Fig. 7(c). In these curves, the photocurrent intensities display sharp increases and drops when the light source was turned on and off, indicating the generation of photoinduced electrons under the light illumination. Particularly, the electrode coated with the SCNT₆ sample exhibits significantly higher current intensities than that of bare TiO₂ or SCN. In general, the photocurrent intensity is positively related to the separation efficiency of the photoinduced electron-hole pair in the material, and the high separation efficiency enhances the photocatalytic activity [62,63]. Therefore, it is not difficult to understand that the SCNT₆ sample with higher separation efficiency exhibits a higher photocatalytic activity than bare TiO₂ and SCN. Figure 7(d) shows the Nyquist plots of the pure TiO₂, SCN, and SCNT₆. The electron-transfer resistance in a sample is equivalent to the semicircle diameter on an EIS plot. The smaller arc radius of SCNT₆ suggests that the charge transfer resistance in the composite sample was lower than that of the TiO₂ and SCN samples. In other words, the migration and separation efficiencies of carriers in the SCNT₆ sample are obviously enhanced because of the formation of the heterojunction. All of these results demonstrate the superiority of the SCNT_x composites over the single component in the electron-hole transportation and separation.

It is critical to identify the band structures of the composite components to investigate the enhancement mechanism of photocatalytic activity. Figure 7(e) shows the Mott-Schottky curves of the TiO₂ nanofibers and SCN sample. Their positive slopes manifest that both TiO₂ nanofibers and SCN samples belong to the n-type semiconductor. Therefore, their CB posi-

tions can be estimated by the flat band potentials, which are ascertained according to the x -intercepts of the linear regions of their Mott-Schottky curves [64]. Consequently, the extrapolated CB positions of TiO₂ nanofibers and SCN samples are -0.88 and -1.36 V, respectively (vs Ag/AgCl, pH = 7). These values correspond to -0.25 and -0.73 V (vs NHE, pH = 0). According to the band gaps of TiO₂ (3.28 eV) and SCN (2.43 eV), their VB positions are calculated to be 3.03 and 1.7 V (vs NHE, pH = 0), respectively. Analogously, Fig. 7(f) shows that the CB position of pure g-C₃N₄ is -0.65 V (vs NHE, pH = 0). Clearly, the S-doped g-C₃N₄ with a stronger reductive performance than pure g-C₃N₄ will endow the composites with an enhanced photocatalytic activity [65,66].

3.5. Possible photocatalytic mechanism

In order to probe the exact active species and identify the electron transfer mechanism, radical trapping experiments were conducted for the degradation process of CR solution with SCNTx composites. Na₂C₂O₄, isopropanol (IPA), and benzoquinone (BQ) were adopted as the h^+ scavenger, $\bullet$ OH quencher, and $\bullet$ O₂⁻ scavenger in the trapping experiments, respectively. As shown in Fig. 8(a), the BQ had the strongest negative effects on the degradation rate for CR. The IPA played a relatively weaker role in photocatalytic activity than BQ. However, the Na₂C₂O₄ had no influence on the degradation process. These results clearly demonstrate that both $\bullet$ O₂⁻ and $\bullet$ OH species play an essential role in the CR photocatalytic degradation process, but the h^+ play a minor role. To further confirm the above conclusions, the ESR analyses were performed using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a spin-trapping agent. In Fig. 8(b), no signal of $\bullet$ O₂⁻ was detected in the absence of light irradiation, but the 1:1:1:1 quadruple signals were observed after the sample had been illuminated by the simulated solar light. Moreover, the signal intensities gradually increased with the increase in the illumination time. For $\bullet$ OH (Fig. 8(c)), a similar phenomenon was observed; the gradually enhanced 1:2:2:1 characteristic signals were detected when the light was on. The results of the trapping experiments and ESR tests revealed that the $\bullet$ O₂⁻ and $\bullet$ OH radicals, which were generated in the presence of the SCNT6 composite under the light irradiation, were the major active components in the

photocatalytic degradation process. It is noteworthy that the $\bullet$ O₂⁻ radical cannot be generated if the charge immigration in the composite follows the conventional type II heterojunction mechanism. Obviously, the previously introduced S-scheme heterojunction mechanism is a better candidate to explain the enhancement mechanism of photocatalytic degradation activity for SCNTx composite photocatalysts.

Figure 9(a) shows that TiO₂ with a larger work function (6.58 eV) is an oxidation-type photocatalyst. Conversely, pure g-C₃N₄ with a smaller work function (4.18 eV) is a reduction-type photocatalyst [67]. To clarify the influence of sulfur on the electrostatic potential of g-C₃N₄, the density functional theory (DFT) was used to calculate the work function of SCN. As shown in Fig. 9(b), the work function of SCN is 3.57 eV, which is smaller than that of pure g-C₃N₄ and in agreement with the previous reports [68,69]. In general, the work function of a material is negatively related to its Fermi level. Compared with TiO₂, the SCN with a smaller work function possessed a higher Fermi level (vs. vacuum level). Therefore, once the two materials were contacted together, the electrons spontaneously immigrated from SCN to TiO₂ across their interface until their Fermi levels achieved equilibrium (Fig. 9(c)). The electron output from SCN was equivalent to the positive charging process, resulting in the upward bent band edge of SCN due to the loss of electrons. Contrarily, the electron input to TiO₂ was equivalent to the negative charging process, resulting in the downward bent band edge of TiO₂ due to the accumulation of electrons. Simultaneously, an internal electric field was formed at the interface of TiO₂ and SCN. Under light irradiation, the photons absorbed by TiO₂ and SCN excited the electrons from their respective VB to CB. Benefiting from the internal electric field, band edge bending, and Coulomb interaction, some electrons (CB of TiO₂) were easily recombined with holes (VB of SCN), but the recombination of some SCN CB electrons and TiO₂ VB holes was restrained. Figure 9(c) shows the charge transfer mechanism of the S-scheme heterojunction between TiO₂ and SCN. The relatively useless TiO₂ CB electrons and SCN VB holes are quenched, but the SCN CB electrons and TiO₂ VB holes with the stronger redox abilities remain. Therefore, this electron transfer process endows the hybrid with a supreme redox capacity and has been confirmed by the radical trapping experiments and ESR tests. The in situ XPS spectra under light irradi-

Fig. 8. (a) Photocatalytic activities of the SCNT6 sample for CR degradation with disparate scavengers; ESR spectra of SCNT6 under dark and simulated solar light: DMPO $\bullet$ O₂⁻ (b) in methanol dispersions and DMPO $\bullet$ OH (c) in aqueous dispersions.

Fig. 9. (a) Calculated electrostatic potentials for the (101) face of TiO₂ and (b) SCN. The blue and red dashed lines denote the Fermi level and vacuum energy level, respectively. In the geometric structures of TiO₂ and SCN, the cyan, red, blue, orange, and yellow spheres stand for Ti, O, C, N, and S atoms respectively. (c) Proposed step-scheme heterojunction photocatalytic mechanism for SCN/TiO₂.

ation also provide strong evidence for the electron transfer route following the S-scheme heterojunction mechanism (Fig. 3). The binding energies of Ti 2p and O 1s for SCNT6 under light irradiation exhibit slightly positive shifts compared with the corresponding values without irradiation. Conversely, the binding energies of C 1s and N 1s under light irradiation showed negative shifts. The converse changes in binding energy with and without irradiation unequivocally validate that the photoinduced electrons in TiO₂ transfer to SCN under the light illumination. Consequently, the S-scheme heterojunction mechanism is more suitable to elucidate the reason for enhanced photocatalytic activity in the photodegradation of CR.

4. Conclusions

In summary, a series of SCN/TiO₂ S-scheme photocatalysts were prepared by electrospinning and calcination. The as-prepared SCN/TiO₂ composite exhibited a remarkably improved photocatalytic activity in degradation of CR compared

with the pure TiO₂ and SCN. The enhanced photocatalytic activity can be ascribed to the 1D structure, abundant reactive sites, and constructed heterojunction. The results of XPS, EPR, and DFT calculations prove that the S-scheme heterojunction mechanism is a rational theory to expound the electron migration process in composites, especially under light irradiation. This work can enrich our knowledge of the design and fabrication of novel S-scheme heterojunction photocatalysts, and also provides an effective strategy for solving environmental pollution in the future.

References

- [1] P. Senthilkumar, D. A. Jency, T. Kavinkumar, D. Dhayanithi, S. Dhanuskodi, M. Umadevi, S. Manivannan, N. V. Giridharan, V. Thiagarajan, M. Sriramkumar, K. Jothivenkatachalam, *ACS Sustainable Chem. Eng.*, **2019**, 7, 12032–12043.
- [2] H. Chen, S. Wageh, A. A. Al-Ghamdi, H. Y. Wang, J. G. Yu, C. J. Jiang, *J. Colloid Interface Sci.*, **2019**, 537, 736–745.
- [3] Y. Q. Zheng, B. Cheng, W. You, J. G. Yu, W. K. Ho, *J. Hazard. Mater.*,

Graphical Abstract

Chin. J. Catal., 2021, 42: 56–68 doi: 10.1016/S1872-2067(20)63634-8

Sulfur-doped g-C₃N₄/TiO₂ S-scheme heterojunction photocatalyst for Congo Red photodegradation

Juan Wang, Guohong Wang*, Bei Cheng*, Jiaguo Yu, Jiajie Fan
Hubei Normal University; Wuhan University of Technology;
Zhengzhou University

The S-doped g-C₃N₄ (SCN) possesses a stronger reductive performance than pure g-C₃N₄. The S-scheme heterojunction formed by SCN and TiO₂ can improve the separation efficiency of photoinduced electron-hole pairs as well as the photocatalytic activity.

- 2019**, 369, 214–225.
- [4] S. Y. Dong, L. F. Cui, W. Zhang, L. J. Xia, S. J. Zhou, C. K. Russell, M. Fand, J. L. Feng, J. H. Sun, *Chem. Eng. J.*, **2020**, 384, 123279.
 - [5] Y. Guo, W. X. Shi, Y. F. Zhu, Y. P. Xu, F. Y. Cui, *Appl. Catal. B*, **2020**, 262, 118262.
 - [6] Y. Y. Fan, W. G. Ma, D. X. Han, S. Y. Gan, X. D. Dong, L. Niu, *Adv. Mater.*, **2015**, 27, 3767–3773.
 - [7] J. Wang, G. H. Wang, X. H. Wei, G. Liu, J. Li, *Appl. Surf. Sci.*, **2018**, 456, 666–675.
 - [8] C. B. Bie, B. C. Zhu, F. Y. Xu, L. Y. Zhang, J. G. Yu, *Adv. Mater.*, **2019**, 31, 1902868.
 - [9] Q. L. Xu, L. Y. Zhang, J. G. Yu, S. Wageh, A. A. Al-Ghamdi, M. Jaroniec, *Mater. Today*, **2018**, 21, 1042–1063.
 - [10] C. Han, Y. D. Wang, Y. P. Lei, B. Wang, N. Wu, Q. Shi, Q. Li, *Nano Res.*, **2015**, 8, 1199–1209.
 - [11] P. Singh, K. Mondal, A. Sharma, *J. Colloid Interface Sci.*, **2013**, 394, 208–215.
 - [12] G. D. Lim, J. H. Yoo, Y. I. Lee, *J. Alloys Compd.*, **2019**, 806, 1060–1067.
 - [13] L. Wang, C. B. Zhang, F. Gao, G. Mailhot, G. Pan, *Chem. Eng. J.*, **2017**, 314, 622–630.
 - [14] G. Liu, G. H. Wang, Z. H. Hu, Y. R. Su, L. Zhao, *Appl. Surf. Sci.*, **2019**, 465, 902–910.
 - [15] R. Asahi, T. Morikawa, H. Irie, T. Ohwaki, *Chem. Rev.*, **2014**, 114, 9824–9852.
 - [16] M. Pelaez, N. T. Nolan, S. C. Pillai, M. K. Seery, P. Falaras, A. G. Kontos, P. S. M. Dunlop, J. W. J. Hamilton, J. A. Byrne, K. O'Shea, M. H. Entezari, D. D. Dionysiou, *Appl. Catal. B*, **2012**, 125, 331–349.
 - [17] W. K. Jo, S. Kumar, M. A. Isaacs, A. F. Lee, S. Karthikeyan, *Appl. Catal. B*, **2017**, 201, 159–168.
 - [18] A. Y. Meng, L. Y. Zhang, B. Cheng, J. G. Yu, *Adv. Mater.*, **2019**, 31, 1807660.
 - [19] J. Y. Park, K. I. Choi, J. H. Lee, C. H. Hwang, D. Y. Choi, J. W. Lee, *Mater. Lett.*, **2013**, 97, 64–66.
 - [20] F. Y. Xu, L. Y. Zhang, B. Cheng, J. G. Yu, *ACS Sustainable Chem. Eng.*, **2018**, 6, 12291–12298.
 - [21] Y. J. Sun, J. Z. Liao, F. Dong, S. J. Wu, L. D. Sun, *Chin. J. Catal.*, **2019**, 40, 362–370.
 - [22] W. L. Yu, S. Zhang, J. X. Chen, P. F. Xia, M. H. Richter, L. F. Chen, W. Xu, J. P. Jin, S. L. Chen, T. Y. Peng, *J. Mater. Chem. A*, **2018**, 6, 15668–15674.
 - [23] J. X. Low, B. Z. Dai, T. Tong, C. J. Jiang, J. G. Yu, *Adv. Mater.*, **2019**, 31, 1802981.
 - [24] C. Chen, J. L. Zhou, J. F. Geng, R. Y. Bao, Z. H. Wang, J. X. Xia, H. Li, *Appl. Surf. Sci.*, **2020**, 503, 144287.
 - [25] F. F. Mei, K. Dai, J. F. Zhang, W. Y. Li, C. H. Liang, *Appl. Surf. Sci.*, **2019**, 488, 151–160.
 - [26] J. Wang, Q. Zhang, F. Deng, X. B. Luo, D. D. Dionysiou, *Chem. Eng. J.*, **2020**, 379, 122264.
 - [27] H. X. Fan, H. L. Zhou, W. J. Li, S. N. Gu, G. W. Zhou, *Appl. Surf. Sci.*, **2020**, 504, 144351.
 - [28] X. B. Li, J. T. Huang, J. Xiong, Z. Chen, B. B. Kang, J. Y. Liu, H. Li, Z. J. Feng, X. M. Gao, J. Ma, *J. Hazard. Mater.*, **2020**, 387, 121690.
 - [29] X. M. Jia, Q. F. Han, M. Y. Zheng, H. P. Bi, *Appl. Surf. Sci.*, **2019**, 489, 409–419.
 - [30] H. N. Ge, F. Y. Xu, B. Cheng, J. G. Yu, W. K. Ho, *ChemCatChem*, **2019**, 11, 6301–6309.
 - [31] W. L. Yu, J. X. Chen, T. T. Shang, L. F. Chen, L. Gu, T. Y. Peng, *Appl. Catal. B*, **2017**, 219, 693–704.
 - [32] X. B. Li, J. Xiong, Y. Xu, Z. J. Feng, J. T. Huang, *Chin. J. Catal.*, **2019**, 40, 424–433.
 - [33] F. F. Mei, Z. Li, K. Dai, J. F. Zhang, C. H. Liang, *Chin. J. Catal.*, **2020**, 41, 41–49.
 - [34] Q. Xie, W. M. He, S. W. Liu, C. H. Li, J. F. Zhang, P. K. Wong, *Chin. J.*

- Catal.*, **2020**, 41, 140–153.
- [35] Q. Yan, G. F. Huang, D. F. Li, M. Zhang, A. L. Pan, W. Q. Huang, *J. Mater. Sci. Technol.*, **2018**, 34, 2515–2520.
- [36] E. X. Han, Y. Y. Li, Q. H. Wang, W. Q. Huang, L. Luo, W. Y. Hu, G. F. Huang, *J. Mater. Sci. Technol.*, **2019**, 35, 2288–2296.
- [37] J. Wang, G. H. Wang, X. Wang, Y. Wu, Y. R. Su, H. Tang, *Carbon*, **2019**, 149, 618–626.
- [38] L. Ke, P. F. Li, X. Wu, S. J. Jiang, M. B. Luo, Y. H. Liu, Z. G. Le, C. Z. Sun, S. Q. Song, *Appl. Catal. B*, **2017**, 205, 319–326.
- [39] M. Jourshabani, Z. Shariatnia, A. Badiei, *J. Mater. Sci. Technol.*, **2018**, 34, 1511–1525.
- [40] Y. J. Ren, D. Q. Zeng, W. J. Ong, *Chin. J. Catal.*, **2019**, 40, 289–319.
- [41] Y. Xia, Z. H. Tian, T. Heil, A. Y. Meng, B. Cheng, S. W. Cao, J. G. Yu, M. Antonietti, *Joule*, **2019**, 3, 2792–2805.
- [42] L. Tang, C. Y. Feng, Y. C. Deng, G. M. Zeng, J. J. Wang, Y. N. Liu, H. P. Feng, J. J. Wang, *Appl. Catal. B*, **2018**, 230, 102–114.
- [43] S. B. Yang, Y. J. Gong, J. S. Zhang, L. Zhan, L. L. Ma, Z. Y. Fang, R. Vajtai, X. C. Wang, P. M. Ajayan, *Adv. Mater.*, **2013**, 25, 2452–2456.
- [44] M. E. Aguirre, R. X. Zhou, A. J. Eugene, M. I. Guzman, M. A. Grela, *Appl. Catal. B*, **2017**, 217, 485–493.
- [45] R. R. Hao, G. H. Wang, H. Tang, L. L. Sun, C. Xu, D. Y. Han, *Appl. Catal. B*, **2016**, 187, 47–58.
- [46] H. F. Qin, W. H. Lv, J. R. Bai, Y. Zhou, Y. P. Wen, Q. T. He, J. H. Tang, L. B. Wang, Q. F. Zhou, *J. Mater. Sci.*, **2019**, 54, 4811–4820.
- [47] S. Y. Tan, Z. P. Xing, J. Q. Zhang, Z. Z. Li, X. Y. Wu, J. Y. Cui, J. Y. Kuang, J. W. Yin, W. Zhou, *Int. J. Hydrogen Energy*, **2017**, 42, 25969–25979.
- [48] K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, T. Siemieniewska, *Pure Appl. Chem.*, **1985**, 57, 603–619.
- [49] F. Y. Xu, B. C. Zhu, B. Cheng, J. G. Yu, J. S. Xu, *Adv. Optical Mater.*, **2018**, 1800911.
- [50] F. Chang, J. Zhang, Y. C. Xie, J. Chen, C. L. Li, J. Wang, J. R. Luo, B. Q. Deng, X. F. Hu, *Appl. Surf. Sci.*, **2014**, 311, 574–581.
- [51] T. P. Hu, K. Dai, J. F. Zhang, G. P. Zhu, C. H. Liang, *Mater. Lett.*, **2019**, 257, 126740.
- [52] A. Y. Meng, B. C. Zhu, B. Zhong, L. Y. Zhang, B. Cheng, *Appl. Surf. Sci.*, **2017**, 422, 518–527.
- [53] J. H. Luo, Z. X. Lin, Y. Zhao, S. J. Jiang, S. Q. Song, *Chin. J. Catal.*, **2020**, 41, 122–130.
- [54] J. W. Fu, B. C. Zhu, C. J. Jiang, B. Cheng, W. You, J. G. Yu, *Small*, **2017**, 13, 1603938.
- [55] H. P. Li, T. X. Hu, R. J. Zhang, J. Q. Liu, W. G. Hou, *Appl. Catal. B*, **2016**, 188, 313–323.
- [56] P. F. Xia, S. W. Cao, B. C. Zhu, M. J. Liu, M. S. Shi, J. G. Yu, Y. F. Zhang, *Angew. Chem. Int. Ed.*, **2020**, 59, 5218–5225.
- [57] X. C. Hu, G. H. Wang, J. Wang, Z. F. Hu, Y. R. Su, *Appl. Surf. Sci.*, **2020**, 511, 145499.
- [58] J. Wang, G. H. Wang, J. Jiang, Z. Wan, Y. R. Su, H. Tang, *J. Colloid Interface Sci.*, **2020**, 564, 322–332.
- [59] J. Li, M. Zhang, Q. Y. Li, J. J. Yang, *Appl. Surf. Sci.*, **2017**, 391, 184–193.
- [60] Y. G. Tan, Z. Shu, J. Zhou, T. T. Li, W. B. Wang, Z. L. Zhao, *Appl. Catal. B*, **2018**, 230, 260–268.
- [61] R. Wang, J. Shen, W. J. Zhang, Q. Q. Liu, M. Y. Zhang, Zulficar, H. Tang, *Ceram. Int.*, **2020**, 46, 23–30.
- [62] N. Nie, L. Y. Zhang, J. W. Fu, B. Cheng, J. G. Yu, *Appl. Surf. Sci.*, **2018**, 441, 12–22.
- [63] Y. P. Zhu, M. Li, Y. L. Liu, T. Z. Ren, Z. Y. Yuan, *J. Phys. Chem. C*, **2014**, 118, 10963–10971.
- [64] F. He, A. Y. Meng, B. Cheng, W. K. Ho, J. G. Yu, *Chin. J. Catal.*, **2020**, 41, 9–20.
- [65] C. Z. Sun, H. Zhang, H. Liu, X. X. Zheng, W. X. Zou, L. Dong, L. Qi, *Appl. Catal. B*, **2018**, 235, 66–74.
- [66] M. Jourshabani, Z. Shariatnia, A. Achari, C. H. Langford, A. Badiei, *J. Mater. Chem. A*, **2018**, 6, 13448–13466.
- [67] J. W. Fu, Q. L. Xu, J. X. Low, C. J. Jiang, J. G. Yu, *Appl. Catal. B*, **2019**, 243, 556–565.
- [68] Y. L. Wang, Y. Tian, L. K. Yan, Z. M. Su, *J. Phys. Chem. C*, **2018**, 122, 7712–7719.
- [69] L. M. Hu, J. T. Yan, C. L. Wang, B. Chai, J. F. Li, *Chin. J. Catal.*, **2019**, 40, 458–469.

光降解刚果红的S型硫掺杂g-C₃N₄/TiO₂异质结光催化剂

王娟^a, 王国宏^{a,*}, 程蓓^{b,#}, 余家国^b, 范佳杰^c

^a湖北师范大学化学化工学院, 湖北师范大学先进材料研究院, 污染物分析与资源化技术湖北省重点实验室, 湖北黄石435002

^b武汉理工大学材料复合新技术国家重点实验室, 湖北武汉430070

^c郑州大学材料科学与工程学院, 河南郑州450001

摘要:含有机物工业废水的处理仍然是人类实现可持续发展的重大挑战。而光催化作为一种先进的氧化环保技术, 以其反应条件温和、能耗相对较低的优点在有机废水处理中受到越来越多的关注。近年来, 人们设计和合成了许多不同结构和形状的光催化剂。特别是金属氧化物半导体以其适宜的能带结构、稳定的物化性质、无毒性等特点已成为光催化降解有机废水的研究热点。此外, 一维纳米结构(1D)已被证实有利于光催化降解过程, 其优势在于比表面积大, 离子的迁移路径短, 以及独特的一维电子转移轨道。尤其是TiO₂纳米纤维由于其亲水性、特殊的形貌和合适的能带位置, 在污染物水溶液的处理中表现出优异的光催化性能。然而, TiO₂(~3.2 eV)的宽禁带、光生载流子的易复合等缺陷导致其光利用率较低, 限制了其实际应用。因此, 人们提出了许多提高光催化活性的策略, 如掺杂金属或非金属元素、负载贵金属、构建异质结等。

构建梯形(S型)异质结已被证实是提高复合材料光催化活性的一种有前途的策略。S型异质结不仅能有效地分离光生电子和空穴, 而且还原能力低的半导体CB上的电子和氧化能力低的半导体VB上的空穴复合, 而氧化还原能力较强的空穴和电子分别被保留。因此, 这一电子转移过程赋予了复合物最大的氧化还原能力。同时, 在g-C₃N₄中引入硫元素可以拓宽其光吸收范围, 从而产生更多的光生载流子。此外, 额外的表面杂质将有助于e⁻-h⁺对的分离, 其光催化活性明显高于单纯的g-C₃N₄。

综合一维纳米结构、硫掺杂和S型异质结的优势,本文采用静电纺丝和煅烧法制备了一系列硫掺杂的g-C₃N₄(SCN)/TiO₂ S型光催化剂.制备的SCN/TiO₂复合材料在光催化降解刚果红(CR)水溶液中表现出比纯TiO₂和SCN更优越的光催化性能.光催化活性的显著增强是由于一维分布的纳米结构和S型异质结.此外,XPS分析和DFT计算表明,电子从SCN通过SCN/TiO₂复合材料的界面转移到TiO₂.在模拟太阳光照射下,界面内建电场、带边缘弯曲和库仑相互作用协同促进了复合物相对无用的电子和空穴的复合.因此,剩余的电子和空穴具有较高的还原性和氧化性,使复合材料具有最高的氧化还原能力.这些结果通过自由基捕获实验、ESR实验和XPS原位分析得到了充分的验证,说明光催化剂中的电子迁移遵循S型异质结机理.本文不仅可以丰富了新型S型异质结光催化剂的设计和制备方面的知识,并为未来解决环境污染问题提供一个有前景的策略.

关键词: TiO₂纳米纤维; 硫掺杂g-C₃N₄; 梯形异质结光催化剂; 原位XPS; S型机理

收稿日期: 2020-03-17. 接受日期: 2020-04-26. 出版日期: 2021-01-05.

*通讯联系人. 电话/传真: (0714)6515602; 电子邮箱: wanggh2003@163.com

#通讯联系人. 电话/传真: (027)87871029; 电子邮箱: chengbei2013@whut.edu.cn

基金来源: 国家自然科学基金(51872220, 51932007, 51961135303, 21871217, U1905215, U1705251); 国家重点研发计划项目(2018YFB1502001); 中央高校基本科研基金(WUT: 2019IVB050).

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