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Article

Sulfur promoted $n\text{-}\pi^*$ electron transitions in thiophene-doped $\text{g-C}_3\text{N}_4$ for enhanced photocatalytic activity

Feiyue Ge^a, Shuquan Huang^a, Jia Yan^b, Liquan Jing^a, Feng Chen^a, Meng Xie^c, Yuanguo Xu^{a,*}, Hui Xu^b, Huaming Li^{b,#}

^a School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, Jiangsu, China

^b Institute for Energy Research, Jiangsu University, Zhenjiang 212013, Jiangsu, China

^c School of Pharmacy, Jiangsu University, Zhenjiang 212013, Jiangsu, China

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ABSTRACT

Expanding the optical absorption range of photocatalysts is still a key endeavor in graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) studies. Here, we report on a novel thiophene group extending the optical property, which is assigned to $n\text{-}\pi^*$ electronic transitions involving the two lone pairs on sulfur (TLPS). The as-prepared samples, denoted as CN-ThA_x (where x indicates the amount of ThA added, mg), showed an additional absorption above 500 nm as compared to pristine $\text{g-C}_3\text{N}_4$. Further, the thiophene group enhanced charge carrier separation to suppress e^-/h^+ pair recombination. The experimental results suggest that the thiophene group can obstruct the polymerization of melem to generate a large plane, thus exposing the lone electron pairs on the sulfur. The photocatalytic activity was evaluated in the decomposition of bisphenol A and H_2 evolution. Compared with $\text{g-C}_3\text{N}_4$, the optimized CN-ThA_{30} sample led to a 6.6- and 2-fold enhancement of the degradation and H_2 generation rates, respectively. The CN-ThA_{30} sample allowed for synchronous H_2 production and BPA decomposition.

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1. Introduction

Photocatalysis is regarded as a potentially “green” chemistry technique that can exploit inexhaustible solar energy to decompose toxic pollutants and generate hydrogen from water [1,2]. In this regard, numerous researchers are drawn to this technology [3–7]. Admittedly, the core of this technology is semiconductor photocatalysis, where solar energy is used to induce the generation of electron-hole pairs in semiconductors, which then participate in redox reactions [8–10]. However, the poor visible-light utilization and rapid recombination of elec-

tron-holes hinder the practical application of semiconductor photocatalysts [11,12]. Therefore, solving these problems and realizing effective and economical applications have been the focus of many researchers.

As a new type of polymer semiconductor, graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) has attracted research interest due to its earth-abundant source, facile synthesis, and high chemical-physical stability, as well as fascinating its band structure [13–16]. Therefore, researchers have adjusted the intrinsic electronic structure, band structure, and light absorption capability of pristine $\text{g-C}_3\text{N}_4$ through various methods. For instance,

* Corresponding author. Tel/Fax: +86-511-88791108; E-mail: xuyg@ujs.edu.cn

Corresponding author. Tel/Fax: +86-511-88791108; E-mail: lhm@ujs.edu.cn

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synthesizing a two-dimensional thin-layer structure maximized the exposure of the surface active sites for catalytic reactions, which essentially regulated the electronic properties of pure g-C₃N₄ and improved the efficiency of utilization of light-induced electrons [17–20]. Doping with other elements (including metal and non-metal elements [21–25]) and the construction of a heterojunction (such as quantum dots/g-C₃N₄ [26–28], metal oxide/g-C₃N₄ [29–31], metal sulfide/g-C₃N₄ [32–34], etc. [35,36]) have also been employed, where all of the developed photocatalytic systems facilitated electron transfer and allowed for efficient photocatalytic degradation of pollutants and hydrogen evolution. Improving the specific activity of photocatalysts can in principle be achieved by changing the band structure, accelerating the photoinduced electron transport, and separating photogenerated electrons and holes from the intrinsic skeleton structure of g-C₃N₄. In a clever approach, small molecular organic compounds containing aromatic rings were copolymerized with the precursor to construct an electron donor and acceptor structure [37,38], which not only led to enhanced optical absorption by the structure, but also accelerated the characteristic π -electron delocalization due to the structural advantages of the copolymer, realizing the effective use of electron-hole pairs. Through copolymerization with monomers possessing specific conjugated structures, synthesized g-C₃N₄-based materials with extended visible absorption could be obtained to achieve tailored band structures [38]. Polymer g-C₃N₄-based catalysts were thus optimized for optical absorption in the visible region (beyond 500 nm), and the photocatalytic performance was improved to a certain extent [39]. In the skeleton structure of g-C₃N₄, π -electron transfer dominates the photocatalytic activity, where this process requires excitation with blue light below 420 nm to generate the photoexcited electrons. By changing the polymerization temperature, researchers designed distorted plane structures exposing the lone pairs of electrons on N to the outside of the plane and causing the visible light to induce an n - π^* transition [40]. Zhang et al. [41] also constructed carbon nitride nanotubes by self-assembly, where the n - π^* electron transition involving the lone pairs of the N atoms was operative, and obtained clear optical absorption of visible light. However, the study focused only on the n - π^* transition of the lone pair electrons on the N atoms, but did not explore whether the lone pairs electrons on other heteroatoms had similar effects. Therefore, our objective is to find appropriate strategies to induce modified π -electron transfer and enhance the ability of g-C₃N₄ to capture photogenerated electrons at long wavelengths, so as to effectively promote the photoactivity.

To this end, 3-thiophenemalonic acid (ThA), a five-membered sulfur-containing heterocycle, is selected for modifying the triazine skeleton structure via copolymerization with urea. Because of the suitable monomer and highly π -conjugated structure, ThA readily undergoes parallel π - π stacking. More importantly, the effect of sulfur as a heavy atom and the n - π^* transition of the two lone pairs on sulfur (TLPS), resulting in intersystem crossing, may be another non-ignorable and nonradiative pathway for achieving the optical effect [42–44]. It is thus desirable to develop novel and

promising polymer g-C₃N₄-based materials with beneficial long-wavelength optical properties to improve visible light photocatalytic activity.

2. Experimental

2.1. Synthesis of g-C₃N₄ and CN-PhA_x

Urea (10 g, Sinopharm Chemical Reagent Co., Ltd., China) and a designed amount of 3-thiophenemalonic acid (ThA, Aladdin Chemistry Co., Ltd. China) were homogenized in the solid state. The mixture was heated in a crucible at 550 °C for 1 h at a rate of 3 °C min⁻¹. The cooled polymer sample is denoted as CN-ThA_x (where *x* indicates the amount of ThA added, mg). As a control, pristine g-C₃N₄ was prepared by heating urea and was maintained under the same conditions.

2.2. Structural characterization

The X-ray diffraction (XRD) patterns of the samples were acquired with a Bruker D8 (Cu-*K*_α, λ = 1.514 Å) diffractometer. The Fourier-transform infrared (FTIR) spectra were acquired with a Nicolet Nexus 470 instrument. The micromorphology of the samples was observed by scanning electron microscopy (SEM, JEOL JSM-7800F) and transmission electron microscopy (TEM, JEM-2100F). UV/Vis diffuse reflectance absorbance spectra (UV/Vis DRS) were acquired with a UV-3600Plus UV-Vis-NIR spectrophotometer (Shimadzu Corporation, Japan) by using BaSO₄ as a reflectance standard. Photoluminescence (PL) spectra were collected at room temperature on a QuantaMaster&TimeMaster Spectrofluorometer. An ESCALab MKII X-ray photoelectron spectrometer using a Mg-*K*_α source was employed to conduct X-ray photoelectron spectroscopy (XPS) measurements. Electron spin resonance (ESR) spectra were acquired on a Bruker model ESR JES-FA200 spectrometer. Dimethyl pyridine *N*-oxide (DMPO, Sigma Chemical Co.) was used as a spin-trapping reagent. The photocatalytic degradation of BPA was determined by high-performance liquid chromatography (HPLC) with an Agilent TC-C 18 column. The mobile phase was methanol and water (3:1) at a flow rate of 1 mL min⁻¹. The electrochemical performance was analyzed by using a CHI 660E electrochemical workstation (Chenhua Instrument). The detailed electrochemical operation is described in the Supplementary Information.

2.3. Theoretical calculation method

The calculations were based on density functional theory (DFT) using the generalized gradient approximation (GGA) and Perdew-Burke-Ernzerhof (PBE) functional, as implemented in the Vienna Ab Initio Simulation Package (VASP). All-electron plane-wave basis sets with an energy cut-off of 400 eV and a projector augmented wave (PAW) method were adopted. The convergence threshold was set at 10⁻⁴ eV for the total energy, and 0.05 eV Å⁻¹. The conjugate gradient algorithm was used in the optimization.

Fig. 1. (a) DRS data for CN-ThA_x; (b) Photoluminescence spectra of the samples.

2.4. Evaluation of photocatalytic activity

Photocatalytic degradation of the endocrine disruptor BPA in water (10 mg L⁻¹) was performed under visible light (300 W Xe arc lamp with cut-off filter ($\lambda \geq 420$ nm)) excitation. A suspension of a BPA solution mixed with the catalyst was placed in the photocatalytic reaction equipment. After stirring the suspension for 30 min to achieve saturation adsorption, the light was turned on. The temperature was maintained at 30 °C during the reaction. The concentration of BPA was determined by HPLC with UV-Vis detection at 230 nm. The H₂ evolution performance and synchronous H₂ production with BPA decomposition were evaluated. The details are provided in the Supplementary Information.

3. Results and discussion

3.1. Optical properties

To optimize the optical properties of the samples, the light absorption of synthesized g-C₃N₄ and the CN-ThA_x samples was recorded by UV/Vis DRS (Fig. 1(a)). Pure g-C₃N₄ showed negligible light response above 500 nm and an intrinsic absorption edge at 450 nm in the blue region, corresponding to the π - π^* transition of photoinduced electrons in the π -conjugated network [45,46]. In stark contrast, a significant change in the light response occurred in the long wavelength region for the CN-ThA_x samples, where an absorption appeared around 520 nm, attributed to the n - π^* transitions of the TLPS of the thio-phenene group [42–44]. This is different from other studies in which a distortion of the polymeric unit is realized through calcining to induce the n - π^* electronic transition [47]. The PL spectra of the samples after excitation by a UV laser (337 nm) showed that the ThA-modified semiconductor could effectively suppress e^-/h^+ recombination in the photocatalyst [48]. As shown in Fig. 1(b), the fluorescence emission spectrum of g-C₃N₄ exhibited an intense peak at 460 nm, corresponding to the typical π - π^* electron transmission fluorescence signal [47]. With the introduction of ThA, the fluorescence intensity decreased for the composites and another fluorescence quench-

ing peak appeared at longer wavelength (around 520 nm), where the emission peak is attributed to the n - π^* overlap [47]. The reduced fluorescence intensity demonstrates that the thio-phenene group effectively suppresses recombination of the photogenerated electron-hole pairs [39], and the n - π^* overlap associated with transitions involving the S lone pair electrons allowed more electronic transition [43,44]. Theoretical calculations are expected to explain the unique optical-absorption properties resulting from the n - π^* transition of CN-ThA₃₀. The absorption spectrum in Fig. 2 was simulated (Fig. S1) by calculating the dielectric functions. The optical-response signals (at 500 nm) can be seen in the absorption spectrum of CN-ThA₃₀. These results indicate the possibility that the two lone pairs of electrons on S extend the visible light absorption. In other words, the TLPS of the incorporated thio-phenene group is beneficial for charge separation and optical absorption in the tri-s-triazine structure, which may be of key importance in improving the photocatalytic performance.

3.2. Morphology and structure analysis

The micromorphology of CN-ThA₃₀ and g-C₃N₄ was observed via the SEM technique (Fig. S2), where slight differences between the samples could be observed. Microstructural

Fig. 2. Theoretical optical-absorption from the calculated dielectric functions.

Fig. 3. TEM images of g-C₃N₄ (a, b) and CN-ThA₃₀ (c, d).

changes in CN-ThA₃₀ versus g-C₃N₄ were observed by TEM (Fig. 3). Typical sheet and stacked structures are seen clearly in the image of pristine g-C₃N₄ (Figs. 3(a) and (b)). Compared to the big sheet of g-C₃N₄, the typical layered platelet-like surface morphology was shredded into smaller structures when ThA was incorporated (Figs. 3(c) and (d)), which suggests that the connectivity and packing of the tri-s-triazine units changed significantly. It is concluded that ThA sterically hinders copolymerization between the urea molecules. The specific surface area of pure g-C₃N₄ and CN-ThA₃₀ were measured to be 68.4 and 58.9 m² g⁻¹, respectively. As the content of ThA increased from 0 to 90 mg, the BET surface area of the CN-PhA_x samples decreased from 64.0 to 51.9 m² g⁻¹ (Fig. S3). Therefore, it can be deduced that the thiophene groups become involved in the polymerization, and are thought to change the surface area [49].

The typical XRD patterns of g-C₃N₄ and CN-ThA_x, with a dominant interlayer-stacking peak (002) around 27° and an in-planar peak (100) around 13° [30,50], are presented in Fig. 4(a). The two distinct diffraction peaks retained the shape and corresponding position after thiophene functionalization. The changes in the FTIR patterns are shown in Fig. 4(b), reflecting

that all the samples also possess the same basic skeleton structure as bulk g-C₃N₄. The strong characteristic peaks at 808 and 1200–1600 cm⁻¹ are attributed to the typical aromatic C–N heterocycle stretches and the breathing mode of the tri-s-triazine units, respectively [51–53], which confirm that the original C–N network of g-C₃N₄ was retained. The terminal amino group and hydroxyl groups without polycondensation with peaks at 3000–3500 cm⁻¹ are linked to the residual N–H and O–H bands [54,55]. This suggests that the skeleton structure of g-C₃N₄ is mostly unaltered. Unfortunately, no peaks of the thiophene groups were detected in the FTIR spectra because of the low content. However, by conjugation with a small amount of aromatic heterocycles, these groups are sufficient to alter the properties of the semiconductor, which will be investigated in the next section.

To prove the presence of the thiophene groups, the resulting CN-ThA₃₀ was further investigated by XPS. The XPS survey spectra of synthesized g-C₃N₄ and CN-ThA₃₀ indicate the presence of C, N, and O (Fig. 5(a)). The corresponding high-resolution spectra are presented in Fig. 5. Owing to the introduction of ThA, the O 1s peak of CN-ThA₃₀ became slightly more intense compared to that of pure g-C₃N₄ (Fig. S4), which is attributed to partial condensation by O-bonding and the surface absorbed H₂O [56,57]. The C 1s high-resolution spectrum (Fig. 5(b)) was deconvoluted into peaks of the *sp*²-hybridized carbon (N=C=N) in an N-containing aromatic ring and *sp*² carbon (C=C) in CN-ThA₃₀ and g-C₃N₄ [58]. The broad peak in the N 1s high-resolution spectrum (Fig. 5(c)) was separated into three peaks, including that of the *sp*² hybridized aromatic N bonded to carbon atoms (C–N=C) and triply coordinated nitrogen atoms (N–C₃), as well as that of the amino functional groups with hydrogen (C–N–H) [59,60]. However, the C=C signal for CN-ThA₃₀ was distinctly stronger. This apparent *sp*² carbon bond is formed by the introduction of carbon (C=C) in the aromatic thiophene ring [61,62]. Apart from that, it is worth noting that the binding energy of the N=C=N and C–N=C groups in CN-ThA₃₀ is lower than that of pure g-C₃N₄, which indicates that the aromatic thiophene ring is connected to the tri-s-triazine (heptazine) structures of g-C₃N₄. Previous studies have demonstrated that thiophene rings can be grafted into the heptazine rings of carbon nitride [39,63]. Deconvolution of the

Fig. 4. XRD pattern (a) and FTIR spectra (b) of CN-PhA_x and g-C₃N₄.

Fig. 5. Survey (a), C 1s (b), N 1s (c), and S 2p (d) XPS spectra of CN-PhA₃₀ and g-C₃N₄.

S 2p spectra in Fig. 5(d) showed two peaks corresponding to the S 2p_{3/2} and S 2p_{1/2} states at 163.8 and 164.9 eV, which is attributed to the presence of sulfur in thiophene, similar to previous reports for thiophene-modified g-C₃N₄ [39]. Therefore, combined with the above results, it can be concluded that the aromatic thiophene ring was grafted onto the structure of carbon nitride.

3.3. Photoelectrochemical properties

The intrinsic electronic structures of the semiconductor

photocatalysts were characterized by analyzing the room-temperature EPR spectra (Fig. 6(a)). Obvious EPR signals were observed for g-C₃N₄ and CN-ThA₃₀, attributed to the unpaired electrons in the poly(tri-s-triazine) skeleton [57,64,65]. When thiophene was incorporated into the poly skeleton, the intensity of the EPR signal originating from the unpaired electrons increased, proving that the thiophene component promotes electron delocalization due to the rich π -electrons and TLPS of the thiophene group [39,44]. Upon irradiation with visible light, this thiophene group containing TLPS can efficiently facilitate the generation and separation of photochemi-

Fig. 6. (a) Room-temperature EPR spectra of CN-ThA₃₀ and g-C₃N₄ recorded in the dark and under visible light; (b) Transient photocurrent responses of the as-prepared photocatalysts.

cal radical pairs to give an enhanced EPR signal. Furthermore, the excellent photochemical-carrier separation was demonstrated by the transient photocurrent responses and electrochemical impedance spectra (EIS). As shown in Fig. 6(b), the photocurrent signals of CN-ThA_x became significantly stronger than those of g-C₃N₄ with on-off cycles of intermittent visible light irradiation, which indicates that the CN-ThA_x samples produce more photogenerated electrons, thereby generating a strong photocurrent. This proves that CN-ThA_x has higher efficiency for electron-hole separation. Simultaneously, compared to pure g-C₃N₄, the EIS (Fig. S5) Nyquist plot of CN-ThA_x exhibits a smaller arc radius, where CN-ThA₃₀ has the smallest radius, suggesting that the CN-ThA_x semiconductor possesses higher electrical conductivity. Based on these results, it is also proved that grafting the thiophene groups of TLPS into the tri-s-triazine structure can rapidly transport electrons to the surface/interface with efficient transfer of the photogenerated e⁻/h⁺, which may improve the catalytic activity.

The bandgap energy was further calculated from the DRS data by applying the formula: $(\alpha h\nu)^{1/2} = A(h\nu - E_g)$ [66]. As shown in Fig. 7(a), the bandgaps of CN-PhA₃₀ and g-C₃N₄ were 2.35 and 2.61 eV, respectively. In addition, the XPS valence band (XPS-VB) and Mott-Schottky plots were evaluated to understand the influence of the TLPS of the thiophene group on the structure of the photocatalysts. The XPS-VB of CN-PhA₃₀ and g-C₃N₄ was determined to be 1.78 and 1.96 eV, respectively

(Fig. 7(b)). The flat band positions of CN-PhA₃₀ and g-C₃N₄ are estimated to be at -1.16 V and -1.33 V (vs. Ag/AgCl, pH = 6.8. Figs. 7(c) and S6), corresponding to -0.56 and -0.73 V (vs. normal hydrogen electrode, NHE, pH = 0), respectively, which is approximately equal to the Fermi level [67]. Combined with the bandgap data, the band structure was calculated. As shown in Fig. 7(d), the band energy of CN-ThA₃₀ decreased, indicating that the TLPS of the thiophene group improved the band structure, thereby boosting photoelectron transport and resulting in effective photocatalytic activity.

3.4. Photocatalytic activity

The photocatalytic action of CN-ThA_x and pristine g-C₃N₄ was evaluated by degrading BPA in aqueous solution (Fig. 8(a)). The photocatalysts were first kept in the dark for 30 min, after which the reactor was irradiated with visible light. Self-degradation of BPA was negligible based on the blank experiment, and only 37% photodegradation was achieved in the presence of pristine g-C₃N₄. Within 100 min, however, the CN-ThA_x photocatalysts could efficiently catalyze the conversion of BPA with boosted degradation activities in the order of CN-ThA₃₀ (98.8%) > CN-ThA₆₀ (96.8%) > CN-ThA₁₀ (87.2%) > CN-ThA₉₀ (83.3%). Distinctly, the experimental results show that the introduction of thiophene groups has a great influence on the catalytic performance of the g-C₃N₄ system. Figs. 8(b)

Fig. 7. (a) Plots of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$); (b) Valence band XPS spectra of CN-ThA₃₀ and g-C₃N₄; (c) Electrochemical Mott-Schottky plots of CN-ThA₃₀ at selected frequencies; (d) Band structure of the samples.

Fig. 8. (a, b) Photocatalytic activity and corresponding rate constants of the as-prepared photocatalysts for BPA degradation; (c, d) H₂ production and rates with various catalysts; (e) Synchronous photocatalytic H₂ evolution and BPA decomposition; (f) Recycling of CN-ThA₃₀ for BPA degradation.

and S7 display the first-order kinetics of BPA degradation with all photocatalysts. The rate constants (k) were computed, where the best was 0.0249 min^{-1} , indicating nearly 6.6-fold greater efficiency compared to that of pure g-C₃N₄ (0.0038 min^{-1}). Excitingly, better H₂ evolution (Fig. 8(c) and (d)) was achieved with CN-ThA₃₀ ($60.3 \text{ } \mu\text{mol h}^{-1}$), where the hydrogen generation is 2.3 times higher than that achieved with pristine g-C₃N₄ ($26.0 \text{ } \mu\text{mol h}^{-1}$). The photocatalytic activity of CN-ThA₃₀ at 475 nm is $922 \text{ } \mu\text{mol g}^{-1} \text{ h}^{-1}$ (Fig. S8), which is 3.5 times higher than that of g-C₃N₄. These experimental observations illustrate that the two lone pairs of electrons on the sulfur of the thiophene groups improve the optical absorption and efficiency of the photoinduced electrons, thereby boosting the light activity and improving the reaction kinetics. Furthermore, BPA was used as a sacrificial agent for consuming h^+ during photocatalytic H₂ production. After 4 h, the BPA degradation in the presence of CN-PhA₃₀ exceeded 30%, with a H₂ evolution rate of $38.7 \text{ } \mu\text{mol g}^{-1} \text{ h}^{-1}$ (Fig. 8(e)), which is higher than that of g-C₃N₄. Thus, it could be speculated that BPA, like TEOA, could consume light-induced holes, leaving sufficient photogenerated electrons for the generation of H₂.

The universality of the photocatalysts for the degradation of other water pollutants was investigated. The photocatalytic degradation of antibiotics (CIP (10 mg L^{-1}) and TC (20 mg L^{-1})) under visible-light was assessed for evaluating the catalytic activity. As shown in Figs. S9(a) and (b), photodegradation of CIP and TC by the CN-ThA₃₀ composites was more efficient than degradation by pure g-C₃N₄, and the degradation rate of CIP and TC in the presence of CN-ThA₃₀ was 1.3 and 2 times that achieved with g-C₃N₄ based on kinetic fitting calculation (Figs. S9(c) and (d)). Therefore, these results also indicate that the synthesized photocatalyst shows good photocatalytic performance in removing environmental pollutants from water,

and can be regarded as a candidate for environmental remediation. The reusability of the catalyst is also an indicator of the practical applicability of the catalyst. The stability of the photocatalysts was evaluated by using the photocatalysts repeatedly to degrade BPA in aqueous medium. As shown in Fig. 8(f), the degradation of BPA by CN-ThA₃₀ remained at the optimum value for four cycles, suggesting that the catalyst is stable during the photoreaction process. The CN-ThA₃₀ catalyst was then recovered and further characterized to determine the stability of its physical structure. The basic structure of the catalyst was studied by XRD and FTIR. The results show that the structure of CN-ThA₃₀ remained unchanged after recycling, as shown in Fig. S10.

3.5. Mechanism of photocatalytic activity enhancement

The mechanism of photodegradation using the CN-ThA₃₀ system was investigated by the trapping of active species in the photocatalytic process. 1,4-Benzoquinone (BQ; 1 mmol) as a superoxide radical ($\bullet\text{O}_2^-$) scavenger, 1 mmol of isopropanol (IPA) as a hydroxyl radical ($\bullet\text{OH}$) scavenger, and 1 mmol of triethanolamine (TEOA) as a hole (h^+) scavenger were added to the reaction system, respectively [68]. Blank tests without any scavenger were also performed under the same conditions. As shown in Fig. 9(a), the photodegradation performance of BPA decreased only slightly with the addition of IPA, indicating that $\bullet\text{OH}$ is not the main active species for BPA degradation. After the addition of BQ and TEOA, drastic inhibition of the degradation of BPA was observed, which proves that both h^+ and $\bullet\text{O}_2^-$ play an undeniable role in the photocatalytic decomposition of BPA. The ESR spectra with DMPO as the trapping agent were acquired for CN-ThA₃₀ and g-C₃N₄ (Fig. 9(b)), indicating the existence of $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ under light excitation [69,70]. No

Fig. 9. (a) Trapping of active species during the degradation of BPA over CN-ThA₃₀; (b) ESR spectrum of samples for detecting DMPO- $\bullet O_2^-$ and DMPO- $\bullet OH$; (c) Plausible reaction mechanism of CN-ThA₃₀.

obvious signal was observed for CN-ThA₃₀ and g-C₃N₄ under dark conditions, indicating that neither $\bullet O_2^-$ nor $\bullet OH$ is formed under dark conditions. After 4 min of exposure to visible light, $\bullet O_2^-$ and $\bullet OH$ radical signals were observed for both CN-ThA₃₀ and g-C₃N₄, and the change in the intensity of the $\bullet OH$ radical signal was more pronounced than in the case of pure g-C₃N₄. Combined with the experimental results of hydroxyl group capture by IPA, the formation of $\bullet OH$ radicals enhances the photocatalytic activity. Therefore, more electrons are transferred to the conduction band to reduce O_2 into $\bullet O_2^-$ radicals, which can then participate in the generation of $\bullet OH$ radicals and be used for the decomposition of BPA and intermediates. In addition, the holes in the valence band reacted with BPA or other intermediates, thus undergoing further decomposition to small molecular products. Consequently, the n- π^* transition of TLPS in the tri-s-triazine structure enhances the light absorption of the thiophene group to improve the visible light utilization efficiency and promote carrier separation. For the photodecomposition of water into hydrogen, the n- π^* transmission can enhance the utilization rate of visible light and promote photoelectron transmission to Pt to react with H⁺ to form H₂. The holes oxidized TEOA or BPA and were thus consumed. Thus, a possible photocatalytic mechanism for the decomposition of BPA and H₂ generation via the TLPS in thiophene-doped carbon nitride was proposed (Fig. 9(c)).

4. Conclusions

Lone pair electrons on sulfur were utilized for the first time to support the activity of g-C₃N₄ photocatalysts. Sulfur-containing thiophene-grafted g-C₃N₄ was synthesized by polymerization of ThA and urea. Evaluation of the optical properties proved that the TLPS of the thiophene group can undergo n- π^* electronic transitions to extend the absorption region from 450 to 550 nm, which improves the visible light capture and utilization efficiency of the catalysts. DFT analysis also indicates that CN-ThA₃₀ exhibits enhanced optical absorption. The thiophene group accelerates the efficient transmission and separation of photoexcited e^-/h^+ , thus boosting the photocatalytic activity. The optimal CN-ThA₃₀ samples exhibit better photocatalytic performance for BPA decomposition and H₂ production. Notably, the optimal sample affords higher H₂ production synchronously with BPA decomposition. We be-

lieve that this report provides significant insight for extending the absorption of g-C₃N₄ to boost the photocatalytic activity.

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Graphical Abstract

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Sulfur promoted n- π^* electron transitions in thiophene-doped g-C₃N₄ for enhanced photocatalytic activity

Feiyue Ge, Shuquan Huang, Jia Yan, Liquan Jing, Feng Chen, Meng Xie, Yuanguo Xu*, Hui Xu, Huaming Li*
Jiangsu University

Lone pairs on sulfur were first exploited to support the activity of g-C₃N₄-photocatalysts. The sulfur in the thiophene group extends the optical absorption range due to n- π^* electronic transitions involving the two lone pairs on sulfur.

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噻吩硫掺杂氮化碳促进 $n-\pi^*$ 电子跃迁增强光催化活性

葛飞跃^a, 黄树全^a, 颜佳^b, 景立权^a, 陈烽^a, 谢萌^c, 徐远国^{a,*}, 许晖^b, 李华明^{b,#}

^a江苏大学化学化工学院, 江苏镇江212013

^b江苏大学能源研究院, 江苏镇江212013

^c江苏大学药学院, 江苏镇江212013

摘要: 光催化技术是一种绿色的化学技术, 它可以利用取之不尽的太阳能来降解有毒污染物或者分解水产生氢气等。毋庸置疑, 这项技术的核心是半导体光催化剂, 在太阳光的照射下, 半导体产生电子-空穴对, 分别迁移至表面参与氧化还原反应。然而, 半导体光催化剂中电子和空穴易快速复合以及其对太阳能中占主导的可见光利用率较低阻碍了其在实际中的应用。因此, 解决这些问题, 实现光催化技术的产业化应用, 成为更多研究者关注的焦点。

石墨相碳氮化物(g-C₃N₄)作为一种新型的聚合物半导体, 因其来源丰富、合成简便、化学和物理性质稳定以及能带结构可调而吸引了研究人员的兴趣, 但是它仍然存在上述问题。目前, 提高g-C₃N₄光催化性能的方法大致有以下三种: 改变形貌或进行元素掺杂以调节能带结构, 与其他半导体复合构建异质结构来加速光生载流子的迁移, 拓展可见光吸收范围。g-C₃N₄的光催化活性主要受自身骨架结构中的 π 电子传输影响, 但 π 电子只能在波长<420 nm的高能量光下才能被激发。研究可知, 设计N原子上孤对电子暴露于平面外部的氮化碳结构, 在可见光激发下即可产生 $n-\pi^*$ 电子跃迁, 获得显著增强的光吸收能力, 从而提升光催化活性。然而, 这些研究仅关注了g-C₃N₄中N原子上孤对电子形成的 $n-\pi^*$ 跃迁, 并未研究外来材料杂原子上的孤对电子是否具有相似的作用。因此, 利用合适的、含孤对电子的材料来修饰g-C₃N₄, 也有可能获得类似的 $n-\pi^*$ 电子跃迁。

本工作以含芳香环结构的噻吩基丙二酸(ThA)与尿素作为前驱体, 通过热聚合方法合成了具有高效 $n-\pi^*$ 电子跃迁的CN-ThA_x材料, 并在可见光条件下, 通过降解双酚A以及分解水实验测试其光催化性能。采用漫反射光谱(DRS)、光致发光光谱(PL)、理论计算、扫描电镜(SEM)、透射电镜(TEM)和X射线光电子能谱(XPS)等表征手段分析了催化剂的光学性质、微观形貌和结构特征。通过DRS、PL和理论计算分析可知, $n-\pi^*$ 电子跃迁可提升CN-ThA_x在450–550 nm区域的光学吸收, 增强材料对可见光利用效率。SEM和TEM结果显示, ThA修饰并未改变g-C₃N₄的形貌, 结合XPS结果可知, $n-\pi^*$ 电子跃迁不是由g-C₃N₄中N原子的孤对电子引起的, 而是由ThA中S元素的孤对电子引起的。光催化性能测试结果也表明, ThA修饰后的CN-ThA_x在可见光下具有更优的光催化性能。因此, 本研究为设计具有较高可见光利用率的氮化碳材料提供了新思路。

关键词: 噻吩; 碳氮化物; 硫元素的孤对电子; $n-\pi^*$ 电子跃迁; 可见光催化

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*通讯联系人. 电话/传真: (0511)88791108; 电子信箱: xuyg@ujs.edu.cn

#通讯联系人. 电话/传真: (0511)88791108; 电子信箱: lhm@ujs.edu.cn

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