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Enhanced photochemical oxidation ability of carbon nitride by π - π stacking interactions with graphene

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ABSTRACT

A one-pot method for the preparation of g-C₃N₄/reduced graphene oxide (rGO) composite photocatalysts with controllable band structures is presented. The photocatalysts are characterized by Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscope, transmission electron microscope, and Mott-Schottky analysis. The valance band (VB) of g-C₃N₄ exhibits a noticeable positive shift upon hybridizing with rGO, and thus results in a strong photo-oxidation ability. The g-C₃N₄/rGO composites show a higher photodegradation activity for 2,4-dichlorophenol (2,4-DCP) and rhodamine B (RhB) under visible light irradiation ($\lambda \geq 420$ nm). The g-C₃N₄/rGO-1 sample exhibits the highest photocatalytic activity, which is 1.49 and 1.52 times higher than that of bulk g-C₃N₄ for 2,4-DCP and 1.52 times degradation, respectively. The enhanced photocatalytic activity for g-C₃N₄ originates from the improved visible light usage, enhanced electronic conductivity and photo-oxidation ability by the formed strong π - π stacking interactions with rGO.

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1. Introduction

The synthesis of advanced photocatalysts has attracted much attention since their potential applications in environmental purification and hydrogen production [1,2]. Among the semiconductors, TiO₂ has been studied the most widely owing to its excellent photocatalytic activity, good stability and non-toxicity [3–5]. However, owing to the limitation of the wide band gap (3.2 eV), TiO₂ cannot use visible light. To effectively use solar energy, investigations of visible-light photocatalysts have attracted a great deal of attention. A large number of photocatalysts with a high efficiency under the irradiation of visible

light, such as modified TiO₂ [6,7], sulfides [8,9], oxynitrides [10,11] and Bi-based composite oxides [12–14], have successfully been designed and exploited.

As a metal-free polymeric photocatalyst, graphitic carbon nitride (g-C₃N₄) has recently been intensively investigated for its potential practical applications, considering its high stability, good biocompatibility, nontoxicity and controllable band structures [15]. This material can be applied for the conversion of solar energy into electrical energy or chemical energy. Compared with the traditional inorganic photocatalytic materials, such as TiO₂ [16–18] and ZnO [19–21], g-C₃N₄ has a narrower band gap (2.7 eV). This is a key property for its ability to absorb

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visible light to realize a visible light response range of the photocatalyst. Nevertheless, g-C₃N₄ still has some shortcomings, for instance, its redox ability is weak, its spectral response range is not sufficiently wide and the transport efficiency of its photo-generated charge carriers is low [12,20]. Therefore, it is difficult for g-C₃N₄ to be used for practical application. To address these problems, a number of methods have been determined for the modification of pure g-C₃N₄, such as post-functionalization, semiconductor coupling, texture tuning by templates and band gap modification by heteroatom doping [22–25].

Graphene has a perfect two-dimensional (2D) crystal structure. It is composed of hexagonal carbon rings in a single atomic layer [26]. Graphene exhibits many interesting electronic and optoelectronic properties, which have recently attracted much interest in a wide range of fields. Particularly, it can be used as an electron mediator for shuttling electrons, leading to the effective separation of photogenerated charge carriers at the junction interface. Owing to its outstanding performance, graphene has already been used in combination with semiconductors for an enhancement of the photocatalytic performance [27,28]. Coupling graphene with g-C₃N₄ is regarded as an effective method for improving the conductivity and electrocatalytic performance of g-C₃N₄ [29,30]. Especially, both graphene and g-C₃N₄ have the 2D nanosheet structure, which can be constructed into a layered junction, consequently increasing the contact area for efficient charge transfer at the interface. However, the bottom of the conduction band (CB) of g-C₃N₄ is located at approximately –1.3 V, normal hydrogen electrode (NHE) (pH = 7), which is sufficient for hydrogen photogeneration. Therefore, graphene in the g-C₃N₄/reduced graphene oxide (rGO) junction has generally been used as an electron mediator for increasing the reactivity of g-C₃N₄. The valance band (VB) of g-C₃N₄ is located at approximately 1.4 V, hence, its efficiency for the oxidation and mineralization of organic pollutants is not high. An urgent requirement is to improve the photo-oxidation ability of g-C₃N₄ for environmental application. More importantly, both g-C₃N₄ and graphene have a natural π – π conjugated structure [31,32] and can easily be hybridized owing to the strong π – π stacking interactions. Thus, the introduction of graphene could obviously shift the highest occupied molecular orbital (HOMO) of g-C₃N₄ to lower energies through π – π or charge-transfer interactions [25], resulting in the enhancement of the photo-oxidation ability. Therefore, it is expected that the introduction of graphene can not only improve the electron transfer efficiency, but also lower the VB location of g-C₃N₄. However, in most reports, graphene has generally been used to improve the electron transfer of the catalysts. The modification of the band gap of the semiconductor through π – π stacking interactions has seldom been studied.

Herein, we report a one-pot synthesis of g-C₃N₄/rGO composites using melamine and GO as the precursors. rGO can readily hybridize with g-C₃N₄ through strong π – π stacking interactions. The introduction of rGO is obviously able to shift the HOMO of g-C₃N₄ to lower energies through π – π interactions, resulting in the enhancement of the photo-oxidation ability of g-C₃N₄. The photocatalytic activities of g-C₃N₄/rGO composites

were evaluated by the degradation of aqueous 2,4-DCP and RhB solutions under visible light irradiation.

2. Experimental

2.1. Synthesis of g-C₃N₄/rGO samples

All chemicals used were reagent grade and used without further purification. The graphene oxide (GO) was prepared by Hummers' method [33]. The typical g-C₃N₄/rGO composite was prepared as follows. Suspensions of GO (0.01 g/mL) were made by dispersing 2.5 g of GO in 250 mL of ultra-pure water. A certain amount of GO suspension was mixed with 10 mL of melamine aqueous suspension (0.2 g/mL) under ultrasonication for 2 h. The resultant suspension was dried at 90 °C for 12 h. Finally, the obtained powder was heated to 540 °C within 135 min and kept at this temperature for 4 h under air. The mass ratios of GO to melamine were controlled at 0.5%, 1.0%, 3.0% and 5.0%, and the resulting samples were referred to as g-C₃N₄/rGO-0.5, g-C₃N₄/rGO-1, g-C₃N₄/rGO-3 and g-C₃N₄/rGO-5, respectively.

2.2. Characterization

The crystallinity of the g-C₃N₄/rGO samples was tested by X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer at 25 °C. Morphologies and structures of the prepared samples were examined with a Hitachi HT770 transmission electron microscope (TEM) operated at an accelerating voltage of 100 kV and a Hitachi SU-8010 field emission scanning electron microscope (SEM) at 10 kV and 5 μ A. BaSO₄ was used as the reference to test the ultraviolet-visible (UV-vis) diffuse reflectance spectra (DRS) of the samples on a Hitachi U-3010 UV-vis spectrophotometer. A Bruker spectrometer was used to obtain the Fourier transform infrared (FTIR) spectra in the wavenumber range of 4000–600 cm^{–1} with a resolution of 1 cm^{–1}. The N₂ adsorption-desorption analysis was performed on a Micromeritics ASAP2010 V5.02H automatic physical and chemical adsorption instrument. Electrochemical and photoelectrochemical measurements were performed in three-electrode quartz cells with a Na₂SO₄ electrolyte solution (0.1 mol/L). Saturated calomel electrodes (SCE) were used as the reference electrodes, and platinum wire was used as the counter electrode. The as-prepared photocatalyst film electrodes on ITO served as the working electrode. The photocurrents were measured on an electrochemical system (CHI-660B, China). Photoluminescence (PL) spectra of the prepared samples in aqueous suspensions were obtained at 25 °C under excitation by incident light of 375 nm using a Hitachi F-4600 fluorescence spectrometer. X-ray photoelectron spectroscopy (XPS) of the as-prepared samples was obtained after vacuum deoxidation from a PHI Quantera XPS microprobe. Raman spectroscopy was obtained from a Horiba HR 800 laser confocal micro Raman spectrometer using a laser at 514 nm. The suspensions of the samples were prepared by dispersing 5 mg of the as-prepared samples in 500 μ L of ultra-pure water under sonication for 1 h. The electron paramagnetic resonance (ESR)

spectra were recorded on a Bruker ESR 300E, using the radical scavenger dimethyl pyridine N-oxide (DMPO).

2.3. Photocatalytic activity

The photocatalytic activities of the as-prepared samples were evaluated by the decomposition of 2,4-dichlorophenol and RhB under visible light irradiation. The visible light source was obtained by a 500-W Xe lamp with a cutoff filter (420 nm) and the average light intensity was 35 mW/cm².

50 mg of photocatalyst was well-dispersed in an aqueous solution of 2,4-dichlorophenol (50 mL, 5 ppm) or RhB (50 mL, 5 ppm). Prior to light irradiation, the suspensions were first ultrasonically dispersed in the dark for 15 min, then magnetically stirred for 120 min to reach adsorption-desorption equilibrium. Then, the Xe lamp was turned on, and 3.0 mL aliquots were sampled at given time intervals and filtered with a micropore membrane (diameter of 0.45 μm, Jin Teng company). High-performance liquid chromatography (HPLC) (Shimadzu LC-20AT) was adopted to detect 2,4-dichlorophenol concentration. The mobile phase was methanol and water (volume ratio: 75/25), the elution time was 7 min, the flow rate was 1 mL/min, detection wavelength was 270 nm and the chromatographic column was a Venusil XBP-C18 (3.9 × 200, Agela Technologies Inc.) column. The concentration of RhB was analyzed by recording the absorbance at the characteristic band of 553 nm using a UV-vis spectrophotometer (HITACHI U-3100). The degradation efficiency (%) was calculated as follows:

$$\text{Degradation (\%)} = (C_0 - C)/C_0 \times 100\%$$

where C_0 is the initial concentration of RhB, and C is the RhB concentration at time t .

3. Results and discussion

3.1. Morphology and structure of g-C₃N₄/rGO samples

Fig. 1 shows the XRD patterns of as-prepared g-C₃N₄/rGO samples. Two distinct diffraction peaks ascribed to g-C₃N₄ (JCPDS 87-1526) can be observed in all these samples. The stronger peak at 27.1° can be attributed to the (002) crystal plane diffraction peak and represents interplanar graphitic

Fig. 1. XRD patterns of g-C₃N₄ and g-C₃N₄/rGO samples.

stacking with an interlayer distance of 0.33 nm. The small peak at approximately 13.1° corresponds to the (100) diffraction peak and represents an interplanar separation of 0.68 nm [34,35]. This means that the rGO modification did not transform the structure of g-C₃N₄. However, with an increasing amount of rGO, the two peaks gradually became weaker, which means the introduction of rGO decreases the crystallinity of g-C₃N₄. Furthermore, the peaks of rGO cannot be observed in the XRD patterns and the crystallization disappeared, suggesting that rGO might be uniformly combined with g-C₃N₄.

Fig. 2 shows the FT-IR spectra of g-C₃N₄, GO and the g-C₃N₄/rGO samples. For all the tested samples, the peak at 1629 cm⁻¹ is attributed to the C=N stretching vibration modes, while the peaks at 1228, 1318 and 1403 cm⁻¹ are assigned to the aromatic C-N stretching [36–38]. The peak at 808 cm⁻¹ is the typical bending vibration of s-triazine units [39]. The stretching mode of -OH and the physically adsorbed H₂O cause a broad peak at 3000–3700 cm⁻¹ in the spectra of GO. The C-O stretching mode of COOH groups and deformation vibration of intercalated water cause two peaks at 1732 and 1622 cm⁻¹, respectively. For the rGO/g-C₃N₄ composites, only the characteristic peaks of CN heterocycles in g-C₃N₄ appeared, while those of rGO were not observed, because of the low quantity of GO in the composites. After calcination, the characteristic functional groups of GO all disappeared, indicating that GO had been transformed to rGO.

Fig. 2. FT-IR spectra of g-C₃N₄, GO and g-C₃N₄/rGO samples.

Fig. 3. Raman spectra of the g-C₃N₄ and g-C₃N₄/rGO-1.

The Raman spectra is used to further confirm the presence of graphene in g-C₃N₄/rGO composites. Fig. 3 shows the Raman spectra of g-C₃N₄ and g-C₃N₄/rGO-1. Several characteristic peaks of g-C₃N₄ at 475, 705, 748, 975, 1231 and 1301 cm⁻¹ were observed. For g-C₃N₄/rGO-1, all the Raman bands for g-C₃N₄ can be found, moreover, two new peaks at 1351 and 1556 cm⁻¹ can be observed, which are ascribed to the presence of graphene [30].

Fig. 4 shows the survey data of the samples and the higher resolution spectra of the C1s, N1s and O1s peaks. In Fig. 4(a), the XPS survey spectra of pure g-C₃N₄ shows only carbon and nitrogen elements. However, that of the g-C₃N₄/rGO composite obviously shows the presence of C, N and O elements, indicating the incorporation of elemental oxygen into the framework of the g-C₃N₄/rGO composite [40,41]. Fig. 4(b) shows the high resolution C1s XPS spectra of pure g-C₃N₄ and g-C₃N₄/rGO. Both samples exhibit three peaks at 288.8, 288.2 and 284.8 eV. The peaks at 288.8 and 288.2 eV could be assigned to the sp² C atoms bonded to N in the sample. The smaller peak at 284.8 eV is related to the C–C bonds of graphitic or adventitious carbons. Different from bulk g-C₃N₄, the C1s XPS spectrum of

g-C₃N₄/rGO-1 shows a new peak at 287.8 eV, which is attributed to the formation of C–O–C bonding configurations during thermal treatment [42]. Three peaks were observed at 404.3, 400.58 and 398.8 eV in the N1s XPS spectra of both g-C₃N₄ and g-C₃N₄/rGO-1 (Fig. 4(c)), implying the presence of three types of N bonding in the samples. The dominant N1s peak at 398.8 eV is associated with sp² hybridized nitrogen involved in triazine rings, while the peak at a binding energy of approximately 400.58 eV is assigned to the bridging N atoms in N(C)₃ or N bonded with H atoms. The weak peak located at 404.3 eV can be attributed to the charging effects arising from the π -excitation [40]. More importantly, for g-C₃N₄/rGO-1, the peak area at 404.3 eV is larger than that of pure g-C₃N₄ indicating a stronger π - π conjugate interaction. The above results show that most oxygen functional groups in GO can be removed after 540 °C thermal treatment, but the remaining –OH groups can act as the cross-linker for forming C–O–C bonds responsible for the narrowed bandgap of the composites.

The morphologies of the g-C₃N₄/rGO samples were examined by SEM and TEM. As can be seen in Fig. 5, rGO displays a two-dimensional structure crumpled into thin multilayer

Fig. 4. (a) XPS survey spectra of the synthesized g-C₃N₄ and g-C₃N₄/rGO-1 samples. High resolution C1s (b), N1s (c) and O1s (d) spectra of pure g-C₃N₄ and g-C₃N₄/rGO-1 samples.

Fig. 5. SEM (a, c, e) and TEM (b, d, f) micrographs of g-C₃N₄/rGO samples. (a, b) g-C₃N₄; (c) graphene oxide, (d) reduced graphene oxide, (e, f) g-C₃N₄/rGO-1.

sheets, and pure g-C₃N₄ shows the agglomeration of the lamellar structure. In comparison to rGO, the g-C₃N₄/rGO sample exhibits a more compact structure because g-C₃N₄ was sandwiched between rGO sheets through polymerization of melamine molecules preadsorbed on the GO sheets. This sandwiched structure can facilitate the formation of π - π conjugated structure between g-C₃N₄ and rGO.

Fig. 6 shows the UV-vis diffuse reflectance spectra of g-C₃N₄ and g-C₃N₄/rGO samples. Pure g-C₃N₄ exhibited an absorption edge at 460 nm, corresponding to an optical band gap of 2.70 eV. With an increasing rGO content, the absorption edge of the g-C₃N₄/rGO composites showed an obvious redshift, which was attributed to the π - π stacking and the assembly of g-C₃N₄ and rGO. Furthermore, the g-C₃N₄/rGO composites show a broad

Fig. 6. UV-vis diffuse reflectance spectra of g-C₃N₄ and g-C₃N₄/rGO samples.

visible light wave-band absorption because of the presence of rGO. The band gap of g-C₃N₄ and g-C₃N₄/rGO samples were estimated with the Kubelka-Munk function, which decreased from 2.70 to 2.42 eV, as the designed GO content increased from 0% to 5%. The high light harvesting efficiency of the g-C₃N₄/rGO hybrid results from rGO possessing a strong absorption in the visible light region and the π - π stacking by the assembly of g-C₃N₄ and rGO.

The specific surface area of the samples was measured by the N₂ adsorption-desorption analysis (Fig. 7) and calculated using the Brunauer-Emmett-Teller (BET) model. The specific surface area of bulk g-C₃N₄ was 6.6 m²/g, and increased from 7.2 to 14.7 m²/g for the g-C₃N₄/rGO samples as the designed GO content increased from 0.5% to 5%. The higher specific surface area of the g-C₃N₄/rGO sample indicates more adsorption sites for reactants, which is beneficial for the photocatalytic reaction.

Fig. 8 shows Mott-Schottky (MS) plots, $1/C^2$ versus potential, for the g-C₃N₄ and g-C₃N₄/rGO-1. The intersection point of the potential and linear potential curves provides a flat band potential, which, in this case, is approximately -1.12 and -0.85 V versus SCE for g-C₃N₄ and g-C₃N₄/rGO-1, respectively. g-C₃N₄/rGO-1 exhibits a positive shift of the flat-band potential

Fig. 7. N₂ adsorption-desorption isotherms of g-C₃N₄ and g-C₃N₄/rGO samples.

Fig. 8. Mott-Schottky (MS) plots of the different catalyst film electrodes. The MS plots were obtained at a frequency of 1 kHz in an aqueous solution of Na₂SO₄ (0.1 mol/L).

when compared with g-C₃N₄. According to the value of the band gap (Fig. 6), the estimated positions of the valence band maximum (VBM) are 1.58 and 1.74 V versus SCE for g-C₃N₄ and g-C₃N₄/rGO-1, respectively. The VBM of g-C₃N₄/rGO-1 is 0.16 V lower than that of g-C₃N₄. The lowering of the VBM theoretically indicates that g-C₃N₄/rGO-1 has a stronger oxidation ability. In addition, it is noteworthy that the slope of the linear region for the g-C₃N₄/rGO-1 electrode is lower in value, which suggests a higher donor density. This has been proved by the fact that the photocurrent of the g-C₃N₄/rGO-1 sample is higher than that of the g-C₃N₄ sample. Therefore, the higher separation efficiency of electron-hole pairs and the stronger oxidation ability are of key importance for the enhanced photocatalytic activity.

3.2. Photocatalytic activity and photocurrent response

The photocatalytic activities of the as-prepared samples were evaluated from the degradation of 2,4-DCP and RhB solutions under visible light irradiation ($\lambda > 420$ nm), as shown in Fig. 8(a) and (b). In the control experiment, no degradation of RhB or 2,4-DCP was observed in the absence of photocatalyst. Fig. 9 shows that all the g-C₃N₄/rGO composites exhibited a higher visible light photocatalytic activity than pure g-C₃N₄, suggesting that the introduction of rGO can improve the photo-oxidation ability of g-C₃N₄. The photocatalytic activities of the g-C₃N₄/rGO composites increased gradually with the increase of rGO content and reached the optimum activity when the content of rGO was 1.0%. The photocatalytic activity of g-C₃N₄/rGO-1 was 1.49 times higher than pure g-C₃N₄ for 2,4-DCP degradation, and for RhB, the photocatalytic activity increased by a factor of 1.52. When the rGO content increased to than 1.0%, a further increased to 3.0% or 5.0%, it caused a rapid decrease in the photocatalytic activity. This decrease can be attributed to the increase in the opacity and light scattering, leading to a decrease in the amount of irradiation passing through the reaction suspension solution.

Fig. 10 shows the transient photocurrent density responses of bulk g-C₃N₄ and g-C₃N₄/rGO-1 electrodes with light on/off cycles under visible light irradiation ($\lambda > 420$ nm). The recombination efficiency of the photogenerated charge carriers is directly correlated with the transient photocurrent responses

Fig. 10. The transient photocurrent density responses of pure g-C₃N₄ and g-C₃N₄/rGO-1 sample electrodes with light on/off cycles under visible light irradiation ($\lambda > 420$ nm).

of the photocatalyst [43–46]. Compared with pure g-C₃N₄, it is clear that the photocurrent over g-C₃N₄/rGO-1 was greatly improved. The enhanced photocurrent over the g-C₃N₄/rGO-1 sample suggests a higher separation efficiency of the photo-generated electron-hole pairs and longer lifetime of the photo-generated charge carriers than that of pure g-C₃N₄, which can help to enhance the photocatalytic activity.

3.3. Proposed mechanism for photocatalytic activity enhancement

The PL technique is often used to study the recombination of electrons and holes in the process of photocatalytic reaction in semiconductors [47]. The photoluminescence spectra of pure g-C₃N₄, g-C₃N₄/rGO-0.5, g-C₃N₄/rGO-1, g-C₃N₄/rGO-3 and g-C₃N₄/rGO-5 photocatalysts are shown in Fig. 10. Pure g-C₃N₄ showed a strong peak in the PL spectrum, while with the introduction of rGO, the composites exhibited a lower peak than pure g-C₃N₄. The g-C₃N₄/rGO-1 sample showed the lowest peak, which means it had the highest electronic transmission efficiency, and the electron-hole recombination was effectively suppressed. Hence, we can conclude that rGO successfully hybridizes with g-C₃N₄ and the higher separation efficiency of the photogenerated charges is the direct reason for the enhanced photocatalytic activities of the g-C₃N₄ and rGO composites.

Fig. 9. Photodegradation of 2,4-DCP (a) and RhB (b) using different catalysts under visible light irradiation.

Fig. 11. ESR spectra of radical adducts trapped by DMPO. (a) DMPO- $\text{O}_2^{\bullet-}$ radical species detected for the samples dispersed in methanol; (b) DMPO- $\bullet\text{OH}$ radical species detected for the samples dispersed in water.

As is known, all the reactive oxygen species (ROS), such as superoxide radicals ($\text{O}_2^{\bullet-}$) and hydroxyl radicals ($\bullet\text{OH}$), are mainly involved in the photocatalytic degradation of dyes in water [48]. To probe the nature of the ROS generated over $\text{g-C}_3\text{N}_4$ and the $\text{g-C}_3\text{N}_4/\text{rGO-1}$ composite during visible light irradiation, the ESR spectra of DMPO-trapped $\bullet\text{OH}$ in an aqueous medium and DMPO-trapped $\text{O}_2^{\bullet-}$ in a methanol medium were investigated. As shown in Fig. 11, in a dark environment, neither $\text{g-C}_3\text{N}_4$ nor $\text{g-C}_3\text{N}_4/\text{rGO-1}$ shows a signal. Under irradiation with visible light, $\text{g-C}_3\text{N}_4$ shows a stronger response signal of $\text{O}_2^{\bullet-}$ (Fig. 12(a)) than $\text{g-C}_3\text{N}_4/\text{rGO-1}$, while the signal of $\bullet\text{OH}$ for $\text{g-C}_3\text{N}_4/\text{rGO-1}$ (Fig. 12(b)) is stronger than that of $\text{g-C}_3\text{N}_4$. This fact is directly related to the change of the band gap structure of $\text{g-C}_3\text{N}_4$. The $\text{g-C}_3\text{N}_4/\text{rGO}$ has a more positive VB position compared with the bulk $\text{g-C}_3\text{N}_4$, suggesting that the holes on the VB of $\text{g-C}_3\text{N}_4/\text{rGO}$ might possess a stronger oxidation ability to react with H_2O to produce more $\bullet\text{OH}$. The VB of $\text{g-C}_3\text{N}_4$ is not sufficiently positive to oxidize water and generate $\bullet\text{OH}$, but an obvious $\bullet\text{OH}$ signal can be observed, which is generated by $\text{O}_2^{\bullet-}$.

Based on the above results, a mechanism for the separation and transportation of electron-hole pairs at the interface of $\text{g-C}_3\text{N}_4/\text{rGO}$ photocatalysts is proposed in Scheme 1. Under visible light irradiation, electrons (e^-) are excited from the VB populated by $\text{N}2\text{p}$ orbitals to the CB formed by $\text{C}2\text{p}$ orbitals of

$\text{g-C}_3\text{N}_4$, creating holes (h^+) in the VB. Usually, these charge carriers can quickly recombine and only a small number of electrons can participate in the photocatalytic reaction. However, when rGO was hybridized on the surface of $\text{g-C}_3\text{N}_4$ and formed a conjugated structure, these photogenerated electrons on the CB of $\text{g-C}_3\text{N}_4$ tend to transfer to rGO owing to its excellent electronic conductivity, leading to hole-electron separation. The transferred electrons will accumulate on the surface of rGO and presumably as interface bound exciton pairs to capture the adsorbed O_2 on $\text{g-C}_3\text{N}_4$ surface to form superoxide radical ($\text{O}_2^{\bullet-}$), and then participate in photocatalytic oxidation reaction. Meanwhile, on the VB of $\text{g-C}_3\text{N}_4$, the high separation efficiency of photoinduced electron-hole pairs could result in the increase of the number of holes, which could directly improve the photocatalytic activity. Furthermore, the introduction of rGO could lower the VB position of $\text{g-C}_3\text{N}_4$ and improve the photo-oxidation ability in the degradation of organic pollutants.

4. Conclusions

A simple one-pot method is used to prepare a $\text{g-C}_3\text{N}_4/\text{rGO}$ nanohybrid photocatalyst. rGO can easily hybridize with $\text{g-C}_3\text{N}_4$

Fig. 12. PL spectra of pure $\text{g-C}_3\text{N}_4$ and the $\text{g-C}_3\text{N}_4/\text{rGO}$ photocatalysts.

Scheme 1. Schematic drawing illustrating the mechanism of charge separation and the photocatalytic process over $\text{g-C}_3\text{N}_4$ and $\text{g-C}_3\text{N}_4/\text{rGO}$ photocatalysts under visible light irradiation.

through strong π - π stacking interactions. The introduction of rGO can not only improve the electron transfer, but also lowers the VB location of g-C₃N₄, resulting in the enhancement of the photo-oxidation ability. The g-C₃N₄/rGO composites exhibit a higher photocatalytic activity than pure g-C₃N₄ for 2,4-DCP and RhB degradation under visible light irradiation. When the weight ratio of rGO in the g-C₃N₄/rGO composites is 1%, the maximum photocatalytic activity is achieved.

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Graphical Abstract

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Enhanced photochemical oxidation ability of carbon nitride by π - π stacking interactions with graphene

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rGO can easily hybridized with g-C₃N₄ through π - π stacking interactions, as a result, the VB became more positive and the photooxidation ability was enhanced.

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通过rGO与g-C₃N₄的 π - π 堆积作用提高氮化碳光化学氧化能力

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摘要: 石墨相氮化碳(g-C₃N₄)具有较高的催化活性、良好的生物相容性、廉价易得、低毒性等特点, 因而受到了广泛的关注。g-C₃N₄的禁带宽度为2.7 eV, 可被可见光激发, 相对于二氧化钛和氧化锌, 它对可见光具有更高的太阳光利用率。尽管理论上g-C₃N₄是类似于石墨烯结构的二维材料, 但通常情况下g-C₃N₄却是层层堆积起来的三维体相结构。从而导致了其比表面积降低, 催化反应过程中与反应物接触面积小。同时又使光照下生成的载流子不能迅速传递到材料表面参与反应, 大大降低了g-C₃N₄光生载流子的分离和传递效率。另外, 作为一种可见光催化剂, g-C₃N₄的禁带宽度比一般的无机半导体光催化剂窄, 仅能够吸收部分可见光。本文利用原位煅烧法制备了g-C₃N₄/rGO复合光催化剂, 以罗丹明B和2,4-二氯酚为目标探针分子, 考察了其可见光催化活性。这对于设计开发其他具有共轭大 π 键的光催化体系, 具有一定的借鉴意义。

X射线衍射(XRD), 傅里叶变换红外光谱(FTIR), X射线光电子能谱(XPS)和激光共聚焦拉曼光谱(Raman)结果表明, 氧化石墨烯成功地被还原为石墨烯, 并成功地引入到了g-C₃N₄中去。在三聚氰胺聚合的过程中, 石墨烯被夹杂在氮化碳的片层中间, 有利于形成 π - π 共轭作用。

复合光催化剂C₃N₄/rGO的带边发生明显的红移, 在可见光区域内的吸收强度也有所增加, 因而有利于其可见光催化活性的提高。通过外推法算得g-C₃N₄和C₃N₄/rGO-1复合光催化剂的带隙宽度分别为2.70和2.42 eV。为了更好地考察复合光催化剂C₃N₄/rGO的能带结构的变化, 通过光电化学的手段对其进行进一步的研究。莫特-肖特基结果表明该半导体是n型。计算得出g-C₃N₄和C₃N₄/rGO复合光催化剂的平带电势分别为-1.12和-0.85 V对甘汞标准电极, C₃N₄/rGO复合光催化剂的平带电位发生明显的正移。由此分别确定g-C₃N₄和C₃N₄/rGO复合光催化剂的价带底则位于1.58和1.74 V对甘汞标准电极。相比g-C₃N₄, g-C₃N₄/rGO复合光催化剂的价带位置的降低意味着其具有更强光氧化的能力, 且比表面积的增大也有利于光催化反应。结果发现, 石墨烯与g-C₃N₄的比例为1%时, 复合样品的光催化性能最佳, 对罗丹明B和2,4-二氯酚的降解性能均有提高。

关键词: 石墨相氮化碳; 还原氧化石墨烯; π - π 堆积; 光催化; 相互作用

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