Research Article

Synthesis, Characterization, and Photocatalytic Activity of g-C₃N₄/KTaO₃ Composites under Visible Light Irradiation

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Novel graphitic carbon nitride/KTaO₃ (g-C₃N₄/KTaO₃) nanocomposite photocatalysts have been successfully synthesized via a facile and simple ultrasonic dispersion method. Compared to either g-C₃N₄ or KTaO₃, the composite photocatalysts show significantly increased photocatalytic activity for degradation of Rhodamine B (RhB) under visible light irradiation. The increased photocatalytic performance of the composite could be attributed to the enhanced photogenerated charge carrier separation capacity. Moreover, it is observed that $\bullet\text{O}_2^-$ is the main active species in the photocatalytic degradation of RhB using the g-C₃N₄/KTaO₃ composite photocatalysts.

1. Introduction

Semiconductor photocatalysis has been regarded as an ideal green chemistry technology in dealing with the globally concerned energy shortage and environment pollution issues. In view of practical application, developing highly active photocatalysts has drawn great attention in recent years. Among the various photocatalytic materials, KTaO₃ has been reported as a unique photocatalyst for hydrogen generation as well as organic pollutant degradation [1, 2]. However, its large band gap (3.6 eV) limits the photoactivity only to the UV light, which covers less than 4% of the solar spectrum.

Recently, Wang and coworkers discovered that the graphitic carbon nitride (g-C₃N₄), a conjugative π structure material, is a metal-free visible-light-driven semiconductor [3]. Due to its narrow band gap (2.7 eV) and high thermal and chemical stability, g-C₃N₄ has attracted extensive interest. However, the photocatalytic efficiency of bare g-C₃N₄ is

greatly limited by the high recombination of photogenerated electron-hole pairs. It has been proved that the composite can promote the generation and separation of photoinduced electron-holes pairs. So far Bi₂WO₆/g-C₃N₄ [4], CdS/g-C₃N₄ [5, 6], DyVO₄/g-C₃N₄ [7], WO₃/g-C₃N₄ [8], TaON/g-C₃N₄ [9], SrTiO₃/g-C₃N₄ [10], C₆₀/g-C₃N₄ [11], Ag₂O/g-C₃N₄ [12], NiS/g-C₃N₄ [13], and rGO/g-C₃N₄ [14] have been demonstrated to exhibit better photocatalytic performance compared with pure g-C₃N₄.

Since the conduction band bottom of g-C₃N₄ (−1.13 eV) [15] is more negative than that of KTaO₃ (−0.96 eV) [1, 2, 16]; g-C₃N₄ (CN) and KTaO₃ (KTO) might be suitable candidates to form an ideal composite photocatalyst to show a high visible light activity. In this paper, we report for the first time that the g-C₃N₄/KTaO₃ composite photocatalyst synthesized by a facile ultrasonic dispersion method has demonstrated a significantly improved photocatalytic performance for Rhodamine B degradation.

2. Experiment Section

2.1. Sample Preparation. The g-C₃N₄ powder sample was synthesized by directly heating melamine under 550°C according to the previously reported procedure [17]. KTaO₃ (KTO) was prepared by an improved polymerized complex (PC) method [15]. In a typical run, 1 g TaCl₅ was added into 15 mL 2-methoxyethanol and the solution was stirred for 30 min. Then, 0.20 g K₂CO₃, 12.0 g critic acid, 30 mL 2-methoxyethanol, and 2.0 mL of ethylene glycol were added. After it was stirred for 30 min, the mixture was heated to 120°C for 20 h in air and, finally, the polymer was oxidized in air at 600°C for 2 h.

The typical process for preparation of g-C₃N₄/KTaO₃ (CN/KTO) composites was as follows: an appropriate amount of g-C₃N₄ was added into methanol and then ultrasonically treated in an ultrasonic bath for 30 min. After KTaO₃ powder was added, the solution was stirred in the fume hood for 24 h. Finally the mixture was dried at 100°C overnight and then heated to 300°C for 2 h. The CN/KTO composites with different ratios of g-C₃N₄ to KTO were prepared and denoted as gcn30, gcn50, and gcn70, respectively, in which the number indicates percentage (mass%) of g-C₃N₄ in the composite.

2.2. Characterization. Crystal structures of the synthesized samples were examined by a powder X-ray diffractometer (XRD, Rigaku D/MAX 2500 with Cu Kα1 radiation, λ = 0.154 nm). UV-Vis diffuse reflectance spectra (DRS) of the samples were measured in the range of 200–800 nm using a spectrophotometer (UV-2700, Shimadzu). Transmission electron microscopy (TEM) images were recorded on a Tecnai G2 F20 with an accelerating voltage of 200 kV. The photoluminescence (PL) emission spectra were measured on a spectrofluorometer (Fluorolog-3 system, Horiba Jobin Yvon) using the Xenon lamp with a 325 nm as a source of excitation.

2.3. Photocatalytic Activity Evaluation. Photocatalytic activities of CN/KTO samples were evaluated by Rhodamine B (RhB) degradation in aqueous solution under visible light irradiation. 100 mL aqueous solution of RhB (4 mg/L) was put in a glass beaker, and 0.1 g photocatalyst was then added. In order to establish the adsorption-desorption equilibrium, the suspension was ultrasonically treated and stirred in the dark for 60 min, respectively. Photocatalytic activity was evaluated under irradiation from a 300 W Xenon lamp with a UV cutoff filter, which provides the visible light ranging from 420 to 700 nm. At each given irradiation time interval, 3 mL of the mixture was collected and then the slurry sample was centrifuged to separate the photocatalyst particles. The concentration of RhB was analyzed by measuring the maximum absorption at 553 nm using Shimadzu UV2700 spectrophotometer.

3. Results and Discussion

3.1. Characterization of the CN/KTO. The XRD patterns of KTO, g-C₃N₄, and their composites are shown in Figure 1.

FIGURE 1: XRD patterns of KTO, g-C₃N₄, and their composites.

We can see that the pattern of KTO matches the standard data for a cubic structure (JCPDS Card number 38-1470). The formation of g-C₃N₄ can be confirmed by the strong characteristic peak at $2\theta = 27.4^\circ$ in its XRD pattern. For the composites, the XRD patterns can be indexed by two corresponding phases, that is, KTO and g-C₃N₄ (featured by the peak at $2\theta = 27.4^\circ$), respectively.

From the UV-Vis diffuse reflectance spectra of KTO, g-C₃N₄, and their composites as shown in Figure 2, we can see clearly that KTO and g-C₃N₄ show absorption edges of 360 nm and 460 nm, respectively. For the composites, two absorption edges corresponding to KTO and g-C₃N₄ are observed. With the increase of g-C₃N₄ amount, the absorbance of the composite to visible light also increases.

The microstructures of KTO, g-C₃N₄, and their composites were observed on a transmission electron microscope (TEM). As shown in Figure 3(a), KTO is like small and irregular cube and the mean size is about 30 nm. The TEM image of g-C₃N₄ (Figure 3(b)) shows typical layered platelet-like morphology. From Figure 3(c) we can see clearly that the KTO nanoparticles are deposited on the surface of g-C₃N₄. In other words, KTO nanoparticles are wrapped well by g-C₃N₄.

3.2. Photocatalytic Activity. As shown in Figure 4, no noticeable degradation of RhB was observed with pure KTO photocatalyst or without photocatalyst. Pure g-C₃N₄ photocatalyst could degrade RhB by 65% in 90 min. All of the CN/KTO composites exhibit photocatalytic activities under visible light irradiation, indicating the success of hybrid. When the g-C₃N₄ amount was less than 50% of the total catalyst weight (such as gcn30, gcn50), the photocatalytic activities of gcn30 and gcn50 are inferior compared with g-C₃N₄. When the g-C₃N₄ amount was 70% of the total catalyst weight, the CN/KTO composite exhibited the best activity and nearly 90% RhB was photodegraded. The reason why gcn70 sample showed the best performance could be a result of competition between the following two facts, that is, the absorbance of CN/KTO composite to incident visible light and the effectiveness of photoexcited charge transfer from CN to

FIGURE 2: UV-Vis DRS of KTO, g-C₃N₄, and their composites.

FIGURE 3: TEM images of (a) KTO, (b) g-C₃N₄, and (c) gcn70. The scale bar for (a) and (b) is 100 nm; the scale bar for (c) is 200 nm.

KTO. When the g-C₃N₄ amount was small in the CN/KTO composite (such as gcn30 and gcn50), while the charge transfer from photoexcited CN to KTO could be secured, less visible light could be absorbed by CN because its surface was largely covered by the KTO nanocrystals. Therefore, the CN/KTO composite with too small amount of g-C₃N₄ did not show a higher activity than pure g-C₃N₄. On the contrary, when the amount of g-C₃N₄ was too high in the CN/KTO composite, although the absorbance of CN/KTO to visible light was sufficient, the charge transfer from photoexcited

CN to KTO could not be secured due to the less amount of KTO. Thus, the CN/KTO composite with too large amount of g-C₃N₄ did not show a higher activity than pure g-C₃N₄. The competition and compromise between the absorbance to visible light and effectiveness of charge transfer give rise to the best performance of CN/KTO composite with an appropriate ratio of CN to KTO (such as the gcn70).

It is known that *tert*-butyl alcohol (TBA) can easily react with hydroxyl radicals (OH•) for a dehydrogenation reaction [18, 19]: $\bullet\text{OH} + (\text{CH}_3)_3\text{COH} \rightarrow \text{H}_2\text{O} + \bullet\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$.

FIGURE 4: Photocatalytic degradation of RhB over g-C₃N₄, KTO, and their composites under visible light irradiation.

FIGURE 5: Photocatalytic degradation of RhB with different scavengers under visible light irradiation.

As an effective electron donor, triethanolamine (TEOA) can supply electrons to combine with photogenerated holes [20]. As for p-benzoquinone (p-benz), it can react with $\bullet\text{O}_2^-$ and possibly form phenol, implying that p-benz is an effective $\bullet\text{O}_2^-$ trapper [21, 22]. Considering the above-mentioned facts, TBA, TEOA, and p-benz could be employed as the scavengers for hydroxyl radicals ($\text{OH}\bullet$), photogenerated holes (h^+), and superoxide radicals ($\bullet\text{O}_2^-$), respectively. Corresponding control reactions were carried out with the purpose of clarifying the main active species in the photocatalytic process of RhB degradation.

As shown in Figure 5, when TBA was added, the photocatalytic degradation of RhB was decreased slightly. With the introduction of TEOA, the photocatalytic activity also decreased with the addition of hole-scavenger. At last, the introduction of scavenger for $\bullet\text{O}_2^-$ (p-benz, 0.5 mM) resulted

in a remarkable deactivation. These results clearly indicate that superoxide radical $\bullet\text{O}_2^-$ plays the main role in the photocatalytic performance.

Repeatability of the photocatalytic activity was tested by running several cycles of photocatalytic degradation for RhB over gcn70. Each cycle ran for the same time of 90 min, and the photocatalyst was filtered to use for next cycle. As shown in Figure 6(a), gcn70 could still degrade RhB by nearly 90% after running 5 cycles, indicating quite good stability for photocatalytic degradation for RhB. Moreover, the XRD patterns spectra (Figure 6(b)) of gcn70 sample are almost the same before and after running for 5 cycles of photocatalytic degradation for RhB, which further proved the stability of the composite photocatalyst.

Figure 7 presents the PL spectra of the samples. Obviously, a KTO modification leads to a significant fluorescence

FIGURE 6: (a) Cycling test for the degradation of RhB by gcn70 sample and (b) XRD patterns of gcn70 before and after the cycling test.

FIGURE 7: Photoluminescence (PL) spectra of g-C₃N₄ and gcn70.

quenching of the gcn70 composite because it prevents the recombination of photogenerated charge pairs. In order to rule out the possibility that the PL intensity decreased when the g-C₃N₄ was diluted with KTO in the composite, the intensity was normalized to the mass of g-C₃N₄.

As mentioned above, the composites CN/KTO have shown much better photocatalytic activity than either KTO or g-C₃N₄ under visible light irradiation. It is known that under visible light irradiation, g-C₃N₄ can be excited due to the appropriate band gap (2.7 eV), whereas KTO is inert owing to its wide band gap. Since the conduction band bottom of g-C₃N₄ (−1.13 eV) [15] is more negative than that of KTO (−0.96 eV) [1, 2, 16], the photoexcited electrons on g-C₃N₄ could be directly injected into the CB of KTO through the well-developed interfaces. The charge transfer from g-C₃N₄ to KTO was also confirmed by the significantly decreased photoluminescence intensity of gcn70 in comparison with

that of g-C₃N₄ (see Figure 7). It is believed that the effective charge transfer can inhibit the recombination of photogenerated electrons and holes and thus enhance the photocatalytic activity. The photoinduced electrons diffuse to the surface and reacted with the oxygen molecule (electron acceptor), generating superoxide radicals $\bullet\text{O}_2^-$. The active superoxide radicals are highly oxidative to decompose RhB effectively. On the basis of experimental results and theoretical analysis, a possible synergistic mechanism for the charge transfer between g-C₃N₄ and KTO and for the enhanced photocatalytic activity of RhB degradation was proposed as illustrated in Figure 8.

4. Conclusions

The novel g-C₃N₄/KTaO₃ composites were successfully prepared by a facile and simple ultrasonic dispersion

FIGURE 8: Proposed mechanism for the photodegradation of RhB on CN/KTO composite.

method. The resulting $g\text{-C}_3\text{N}_4/\text{KTaO}_3$ composites showed an enhanced photocatalytic activity for degradation of RhB under visible light irradiation, and the optimal mass ratio of $g\text{-C}_3\text{N}_4/\text{KTaO}_3$ was 70/30. Owing to the well-aligned energy band edges and interface between $g\text{-C}_3\text{N}_4$ and KTaO_3 , effective photogenerated charge carrier transfer and separation was evidenced by photoluminescence, which suppressed the recombination of electrons and holes. As a consequence, the photocatalytic activity of the $g\text{-C}_3\text{N}_4/\text{KTaO}_3$ composite was significantly improved.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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