Fabrication and Photocatalytic Performance of CQDs/Co-g-C\textsubscript{3}N\textsubscript{4} Heterojunction

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Abstract. A novel heterojunction photocatalyst by loading CQDs on Co-g-C\textsubscript{3}N\textsubscript{4} was synthesized by simple hydrothermal process successfully. The crystal phase, surface chemical component and optical properties of CQDs/Co-g-C\textsubscript{3}N\textsubscript{4}, Co-g-C\textsubscript{3}N\textsubscript{4} and g-C\textsubscript{3}N\textsubscript{4} were analyzed based on characterizations such as XRD, FT-IR, DRS and PL. The effect of CQDs loading ratio on the properties and photocatalytic performance of the composites was investigated in detail. The optimized CQDs/Co-g-C\textsubscript{3}N\textsubscript{4} (mass ratio of CQDs and Co-g-C\textsubscript{3}N\textsubscript{4} was 0.12%) showed wide visible light adsorption within the wavelength of 800 nm. Moreover, it showed an improved RhB photodegradation efficiency which was 40.9% and 68.3% higher than the value of Co-g-C\textsubscript{3}N\textsubscript{4} and g-C\textsubscript{3}N\textsubscript{4}, respectively. The higher photocatalytic activity of CQDs/Co-g-C\textsubscript{3}N\textsubscript{4} should be ascribed to the effective separation of photo-induced carriers.

1. Introduction
Environmental pollution, especially water contamination, is becoming a serious issue in the world. With the rapid development of dyeing industry, dye wastewater has become one of vital original sources causing water pollution. Thus, it is urgent to find an eco-friendly and efficient way to remove high-concentration organic dyes [1]. In recent years, it is popular to degrade organic pollutants by utilizing photocatalysts with advantages such as solar utilization, thorough degradation, low cost, safe and so on. Particularly, visible-light responded photocatalysts have attracted much attention of researches.

As a novel metal-free photocatalyst, graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4}) shows visible-light response because of the narrow band gap of ~2.7 eV [2]. It has many advantages, such as high chemical and thermal stability, recycling performance, unique electronic structure and so on. However, the high recombination rate of photo-generated carriers in g-C\textsubscript{3}N\textsubscript{4} limits the practical application of g-C\textsubscript{3}N\textsubscript{4} in photocatalytic field. A number of attempts have been made to settle the question, including designing specific morphologies, doping with hetero elements, loading noble metal on its surface and designing heterogeneous structures.

Transition metal doping can broaden the light response of photocatalysts and the energy band of photocatalysts, which makes the photocatalysts behave much higher photocatalytic activity. It has been reported that after introducing transition metals of Cr\textsuperscript{3+}, Mn\textsuperscript{3+}, Fe\textsuperscript{3+}, Co\textsuperscript{2+}, Ni\textsuperscript{2+} and Cu\textsuperscript{2+} into the structure of TiO\textsubscript{2}, the light adsorption edge shifted to 450 nm, which made the optical property of TiO\textsubscript{2} quite different [3]. Moreover, after introducing Co to the structure of g-C\textsubscript{3}N\textsubscript{4}, the heterojunction of
TiO$_2$/Co-g-C$_3$N$_4$ showed much higher degradation efficiency of phenol in the presence of Cr$^{6+}$. On the other hand, carbon quantum dots (CQDs) also has attracted much attention because of its superior conductivity and strong visible-light adsorption. CQDs has been widely applied to constructing heterojunctions, and the corresponding photocatalytic activities of photocatalysts improved significantly [4]. Therefore, in this work, we designed a g-C$_3$N$_4$-based composite by co-modification with Co ions and CQDs. The obtained CQDs/Co-g-C$_3$N$_4$ heterojunction, Co-g-C$_3$N$_4$ and pure g-C$_3$N$_4$ were analyzed by a series of characterizations. Photodegradation for RhB was chosen as the model to evaluate the photocatalytic activity of CQDs/Co-g-C$_3$N$_4$ heterojunction.

2. Experimental

2.1. Synthesis of Co-g-C$_3$N$_4$

In this work, Co-g-C$_3$N$_4$ (CoCN) was prepared by a process as reported [5]. Typically, cobalt acetate (0.05 g) and dicyandiamide (2 g) were added into ultrapure water (50 mL) separately under vigorous stirring. After stirring for 60 min, the mixture was transferred to a culture dish and put in a temperature-constant oven at 60 °C for 24 h. The dried mixture then became magenta. To obtain Co-g-C$_3$N$_4$, the magenta sample was calcined at 520 °C for 2 h in a muffle, and the heating rate and cooling rate are both set as 2 °C/min. To make a comparison, pure g-C$_3$N$_4$ (CN) was also prepared. 2 g of dicyandiamide was directly calcined as procedure described above.

2.2. Synthesis of CQDs/Co-g-C$_3$N$_4$

CQDs sample was prepared as the process described in our previous publication [6]. CQDs with a concentration of 5 mg/mL was prepared and used in subsequent experiments. To obtain CQDs/ Co-g-C$_3$N$_4$ with different mass ratios of the two components, 0.2 g Co-g-C$_3$N$_4$ and specific volumes of prepared CQDs suspension were separately added into 40 mL of anhydrous alcohol. After stirring for 2 h, the four mixtures were separately transferred into four autoclaves, and then put in an oven for 2 h at 120 °C. After natural cooling, final solids were gained by centrifugation and dried at 60 °C. The CQDs/ Co-g-C$_3$N$_4$ composites were marked as CQDs-CoCN-X (CQDs-CN-X) (X=0.05%, 0.12% and 0.15%).

2.3. Characterizations

All the samples were characterized by X-ray diffraction (XRD, Shimadzu XRD-6100, Japan) instrument for crystal phase confirmation, FT-IR for analyzing the chemical components (Spectrometer PerkinElmer Spectrum Two, USA), diffuse reflection spectrum (DRS, lambda 750, China) for analyzing the visible-light response ability and photoluminescence (PL, Zolix LSP-X500A, China) for evaluating the recombination rate of photo-induced carries.

2.4. Photocatalytic Experiment

The photocatalytic experiments for RhB degradation (10 mg/L) were carried out in an optical reaction apparatus. 50 mg of one sample was added to a specialized quartz tube containing 50 mL of initial RhB solution. After physical adsorption equilibrium, first sample (4mL) was taken and the concentration of RhB solution was marked as C$_0$. Then Xeon lamp ($\lambda$> 420 nm) was turned on to provide visible light illumination. Samples will be taken every 20 min, the corresponding RhB concentration was marked as C.

3. Results and Discussion

Figure 1 showed the XRD results of the samples. Pattern of CN shows typical peaks located at 2θ= 13.1°and 27.4°, which are ascribed to the in-plane structural packing motif of tri-s-triazine units (100) and the characteristic interlayer stacking of aromatic system (002) of graphitic carbon nitride (JCPDS No. 87-1526), respectively [5, 7]. For the pattern of CoCN, it is obviously that the crystal phase of
graphitic carbon nitride hardly changed. However, the intensities of the two typical peaks decreased significant and the peak located at $2\theta = 27.4^\circ$ became a little broader, which should be ascribed to the incorporation of Co ions into the structure of CN [5]. After introducing CQDs to the surface of CoCN, the XRD patterns showed no significant change. Typical characteristic peak of CQDs did not appear in the patterns, which may be due to the small loading amount of CQDs. In addition, the structure of CoCN kept well after the hydrothermal treatment for composites.

FT-IR curves of the samples were shown in figure 2. Typical peaks of graphitic carbon nitride are exhibited in the FT-IR curve of CN. The peak located at the wave number between 3600-3000 cm$^{-1}$ stands for the N-H stretching and few hydrogenated N of graphitic carbon nitride. The peak at 1700-1200 cm$^{-1}$ means the C=N and C-N stretching vibration modes of graphitic carbon nitride. The sharp peak appearing at 810 cm$^{-1}$ indicated the triazine rings of graphitic carbon nitride [8]. The FT-IR curve of CoCN shows no significant difference from these typical peaks of CN, which indicated that the structure of CN kept well after introducing Co. Besides, after loading CQDs on CoCN, the peak at 3600-3000 cm$^{-1}$ showed a blue shift and located at 3400-2800 cm$^{-1}$, which should be ascribe to the incorporation of CQDs. As reported in literature, CQDs had typical peaks at 2940 cm$^{-1}$ and 2870 cm$^{-1}$ standing for the skeletal vibration of sp$^2$ and sp$^3$ C-H, respectively [9]. In general, the surface components of CN did not change after introducing Co and CQDs.

Figure 1. XRD patterns of CN, CoCN and CQDs/CoCN-0.05%, CQDs/CoCN-0.12%, CQDs/CoCN-0.15%, respectively.

Figure 2. FT-IR curves of CN, CoCN and CQDs/CoCN-0.05%, CQDs/CoCN-0.12%, CQDs/CoCN-0.15%, respectively.

UV-vis diffuse reflectance spectra were applied to evaluating the visible light response of the samples, and the results were shown in figure 3. It is obviously that after introducing Co into the structure of CN, the visible light absorption edge of the sample was broadened from 460 nm to 650 nm. In addition, after loading CQDs on the surface of CoCN, the visible light absorption edge was further extended to longer than 700 nm. When the CQDs loading ratio is 0.12%, CQDs/CoCN shows the most promising visible-light response. Besides, PL spectra of the samples illuminated by laser with a wavelength of 325 nm were shown in figure 4. The separation rate of photo-induced carriers can be identified by the intensity of PL spectrum. It was clearly that CoCN showed much lower separation rate of photo-induced carriers than that of CN. After loading CQDs, the separation rate of photo-induced carriers decreased sharply again. CQDs/CoCN-0.12% behaved the most effective separation of photo-induced carriers, which was in accordance with the result of DRS and also will facilitate the photocatalytic performance of the sample.
Figure 3. DRS spectra of CN, CoCN and CQDs/CoCN-0.05%, CQDs/CoCN-0.12%, CQDs/CoCN-0.15%, respectively.

Figure 4. PL spectra of CN, CoCN and CQDs/CoCN-0.05%, CQDs/CoCN-0.12%, CQDs/CoCN-0.15%, respectively.

As indicated in figure 5a, the pristine RhB dye hardly showed photodegradation performance under visible-light illumination while all the photocatalysts showed photocatalytic activity to varying degree. For CN, RhB degradation efficiency is 33.4%. After introducing Co, the degradation efficiency increased to 39.9%, which was 19.5% higher than that of CN. In addition, after loading CQDs, the photocatalytic activity improved much more remarkably. Particularly, when the mass ratio of CQDs and CoCN was 0.12%, the photodegradation efficiency was 56.2%, which was 40.9% and 68.3% higher than the value of CoCN and CN, respectively. The reaction kinetics of the samples for RhB degradation were also discussed (figure 5b). The relevant data was fitted by pseudo-first-order kinetic model $\ln C/C_0 = kt$, and the slope rate ($k$) of the fitting lines was the corresponding kinetic rate. The degradation rate constant was 0.0044 min$^{-1}$, which was 5.5% and 46.8% higher than that of CoCN and CN, respectively. In short, it was evident that promoted photocatalytic activity of CQDs/CoCN should be attributed to the corresponding highly improved separation rate of photo-induced carriers as described above.

Figure 5. Photodegradation performance (a) and kinetic plots (b) for RhB of pristine RhB dye, CN, CoCN and CQDs/CoCN-0.05%, CQDs/CoCN-0.12%, CQDs/CoCN-0.15%, respectively.

A series of scavengers were used for investigating the active species during RhB degradation process using CQDs/CoCN-0.12%. Benzoquinone (BQ), triethanolamine (TEOA) and tertiary butanol (t-BuOH) were used as scavengers for active species of $\bullet OH$, $h^+$ (hole), $\bullet O_2^-$, respectively. The effectiveness was distinct as shown in figure 6. $\bullet OH$ and $\bullet O_2^-$ were the main active species during the
degradation process. h⁺ (hole) has less impact on the photocatalytic activity of CQDs/CoCN-0.12%. Finally, photodegradation stability of CQDs/CoCN-0.12% was evaluated by five-time recycling experiment. As shown in figure 7, the degradation efficiency kept well and decreased less than 10% after 5th experiment, which indicated that CQDs/CoCN-0.12% behaved relatively good photodegradation stability.

| Figure 6. Effect of a series of scavengers on the photodegradation efficiency for RhB for CQDs/CoCN-0.12%.

| Figure 7. Recycle experiment of CQDs/CoCN-0.12% for RhB degradation.

4. Conclusions

Broad visible-light responded CQDs/Co-g-C₃N₄ composites have been prepared by hydrothermal method successfully. After the co-modification of Co ion and CQDs, the separation efficiency of photo-induced carriers of g-C₃N₄ was improved by a large extent. When the mass ratio of CQDs and Co-g-C₃N₄ was 0.12%, the photodegradation efficiency for RhB of optimized CQDs/Co-g-C₃N₄ was the best, and it was 40.9% and 68.3% higher than the value of Co-g-C₃N₄ and g-C₃N₄, respectively. Moreover, the optimized CQDs/Co-g-C₃N₄ behaved good photodegradation stability. This work can provide a novel insight for designing g-C₃N₄-based composite with higher visible-light photocatalytic performance.

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