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Enhancement of the photocatalytic activity of g-C_3N_4 via treatment in dilute NaOH aqueous solution

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ABSTRACT

A simple, effective and environmental-friendly method was adopted for enhancing the photocatalytic activity of g-C_3N_4 (which was synthesized by thermal condensation of melamine) in the reduction of aqueous Cr^{6+} under visible-light irradiation. The enhancement was achieved via treatment of g-C_3N_4 in 0.2 mol/L NaOH aqueous solution at 80 °C for 6 h. The photocatalytic experiments demonstrated that the treated g-C_3N_4 exhibited much higher photocatalytic activity than pristine g-C_3N_4 in the reduction of aqueous Cr^{6+} under visible-light ($\lambda > 420$ nm) irradiation (for example, the reduced ratios of Cr^{6+} in the presence of the treated g-C_3N_4 and pristine g-C_3N_4 were 100% and 29.4%, respectively, when irradiated for 120 min). Based on the characterization results of the structures and other physiochemical properties of the treated g-C_3N_4 and pristine g-C_3N_4 by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, N_2 adsorption/desorption isotherms, photocurrent measurement and electrochemical impedance spectroscopy, the possible reasons responsible for the enhanced photocatalytic activity of the treated g-C_3N_4 were proposed.

1. Introduction

Graphite-like carbon nitride (g-C_3N_4) is a metal-free polymer semiconductor with a band gap of about 2.7 eV [1]. It is nontoxic, stable, and easy to synthesize from abundant and cheap CN-containing precursors [1]. Furthermore, it has been proved to have visible-light-driven photocatalytic activity for many chemical reactions [2–8]. Hence, g-C_3N_4 has been widely considered as a promising visible-light-driven photocatalyst for industrial applications. Nonetheless, the g-C_3N_4 synthesized via the traditional thermal condensation methods exhibited relatively low photocatalytic activity, due to its large particles size, small surface area and high recombination rate of photogenerated charges [9], etc. Hence, it is necessary to explore a simple, effective and environmental-friendly modification method to enhance the photocatalytic activity of g-C_3N_4.

Among the many modification methods developed so far, acid treatment is a simple and effective way for enhancing the photocatalytic activity of g-C_3N_4 [7–9]. The acid treatment not only enabled the protonation of g-C_3N_4, but also increased the specific surface area of g-C_3N_4 through etching or exfoliation, which result in higher photocatalytic activity [7–9]. However, the concentrations of the acids used were rather large (> 5 mol/L) in all reports [7–9], which can cause pollution to the environment and lead to high cost. Besides, the yields of the acid-treated g-C_3N_4 were quite low because of the dissolution of g-C_3N_4 in large concentration of the oxidizing acids, such as HNO_3 [9]. Therefore, the acid treatment method may have some limits for practical applications. In order to develop an environmental-friendly and high yield way to improve the photocatalytic activity of g-C_3N_4, we conducted the treatment of g-C_3N_4 in 0.2 mol/L NaOH aqueous solution at 80 °C for 6 h. The photocatalytic activities of g-C_3N_4 and the treated g-C_3N_4 were compared in the reduction of aqueous Cr^{6+} under visible-light ($\lambda > 420$ nm) irradiation. Moreover, the possible reasons responsible for the enhanced photocatalytic activity of the treated g-C_3N_4 were proposed, based on the characterization results of the structures and other physiochemical properties of g-C_3N_4 and the treated g-C_3N_4.

2. Experimental

First, g-C_3N_4 was synthesized via heating 5000 mg of melamine in air at 580 °C for 2 h, by adopting the procedure reported

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previously [9]. Then, 500 mg of g-C_3N_4 was put into a 50 mL Teflon jar, and 40 mL of 0.1, 0.2 or 0.3 mol/L NaOH aqueous solution was added and stirred for 10 min. The Teflon jar containing the reactant mixture was sealed into stainless steel autoclave and heated at 80 °C for 6 h. After the autoclave cooled down to room temperature naturally, the resulting powder was centrifuged, washed with water and absolute ethanol, and dried in air at 100 °C for 6 h. *For the convenience of description*, the products obtained in 0.1, 0.2 and 0.3 mol/L NaOH aqueous solution were named as g-$C_3N_4-0.1$, g-$C_3N_4-0.2$ and g-$C_3N_4-0.3$, respectively. The yields of g-$C_3N_4-0.1$, g-$C_3N_4-0.2$ and g-$C_3N_4-0.3$ were 90.6%, 85.6% and 80.7%, respectively, with reference to the amount of g-C_3N_4.

The samples were characterized by XRD (Bruker AXS D8 ADVANCE X-ray diffractometer), SEM (Hitachi S−4800 Field Emission SEM), TEM (Philips Tecnai 12 Electron Microscope), N_2 adsorption/desorption isotherms (Micromeritics Instrument Corporation TriStar II 3020 surface area and porosity analyzer), electrochemical impedance spectroscopy (Autolab PGSTAT30 Electrochemical Workstation), and photocurrent response (Beijing Chinese Science Days Technology Co., Ltd. CHI−660D electrochemical workstation). Photocatalytic activities of the samples (300 mg) were tested in the reduction of Cr^{6+} in 300 mL of 50 mg/L $K_2Cr_2O_7$ aqueous solution under visible-light ($\lambda > 420$ nm) irradiation, with the addition of 1.0 mL of 100 mg/mL citric acid solution as sacrificing reagent.

3. Results and discussion

Fig. 1 shows the photocatalytic reduction of aqueous Cr^{6+} over g-C_3N_4, g-$C_3N_4-0.1$, g-$C_3N_4-0.2$ or g-$C_3N_4-0.3$ under visible-light ($\lambda > 420$ nm) irradiation, together with the results from the blank experiments (no photocatalyst) and dark adsorption experiments. Without the presence of photocatalyst, the Cr^{6+} concentration remained constant no matter in the dark or under visible-light ($\lambda > 420$ nm) irradiation. In the dark adsorption experiments, the adsorption of Cr^{6+} by each sample can reach equilibrium when the sample and Cr^{6+} aqueous solution were mixed and magnetically stirred for 60 min. After the dark adsorption equilibrium, the Cr^{6+} concentration further decreased continuously in the presence of g-C_3N_4, g-$C_3N_4-0.1$, g-$C_3N_4-0.2$ or g-$C_3N_4-0.3$ under visible-light ($\lambda > 420$ nm) irradiation, suggesting that g-C_3N_4, g-$C_3N_4-0.1$, g-$C_3N_4-0.2$ and g-$C_3N_4-0.3$ all had visible-light-driven photocatalytic activity in the reduction of aqueous Cr^{6+}. However, the photocatalytic activities followed the order of g-$C_3N_4-0.2 >$ g-$C_3N_4-0.3 >$ g-$C_3N_4-0.1 >$ g-C_3N_4, for example, when irradiated by visible-light ($\lambda > 420$ nm) for 120 min, the reduced ratios of Cr^{6+} in the presence of g-$C_3N_4-0.2$, g-$C_3N_4-0.3$, g-$C_3N_4-0.1$ and g-C_3N_4 were 100%, 96.5%, 93.1% and 29.4%, respectively. This suggested that the treatment in $0.1-0.3$ mol/L NaOH aqueous solution can enhance greatly the photocatalytic activity of g-C_3N_4, but 0.2 mol/L is the optimum concentration of NaOH aqueous solution to obtain the most efficient g-C_3N_4. Nevertheless, it can be seen from Fig. S1, Fig. S2 and Table S1 in The Supplementary Materials that the BET specific surface areas and BJH adsorption pore volumes of g-C_3N_4, g-$C_3N_4-0.1$, g-$C_3N_4-0.2$ and g-$C_3N_4-0.3$ were in ascending order, whereas their BJH adsorption average pore diameters were in descending order. This suggested that although the specific surface area and pore structure of g-C_3N_4 played key roles in its photocatalytic activity, but the specific surface area and pore structure were not the whole factors to affect the photocatalytic activity of g-C_3N_4. It was likely that the treatment in excessively large concentration (0.3 mol/L) of NaOH aqueous solution may cause more defects in g-C_3N_4 that decreased the photocatalytic activity [6].

To clarify the reasons accounting for the enhanced photocatalytic activity of the dilute alkali-treated g-C_3N_4, the structures and other physiochemical properties of g-$C_3N_4-0.2$ and g-C_3N_4 were further characterized. Fig. 2 shows the XRD patterns of g-C_3N_4 and g-$C_3N_4-0.2$. Both samples displayed two obvious XRD peaks at about 13.0° and 27.3°, which can be indexed as the (100) and (002) crystal planes of graphite-like carbon nitride [9], respectively. The nearly same XRD patterns of g-$C_3N_4-0.2$ and g-C_3N_4 suggested that the intrinsic crystal structure of g-C_3N_4 had been maintained after the treatment in 0.2 mol/L NaOH aqueous solution at 80 °C for 6 h.

Fig. 3(a) and (b) shows the SEM images of g-C_3N_4 and g-$C_3N_4-0.2$, respectively. Both samples comprised mainly nanoplates, but g-$C_3N_4-0.2$ nanoplates seemed to be smaller/thinner and more porous than g-C_3N_4 nanoplates. Furthermore, the TEM image in Fig. S3 indicated that g-$C_3N_4-0.2$ consisted of porous nanosheets. The smaller size and more pores of g-$C_3N_4-0.2$ implied the shorter distance for its photogenerated electrons and holes to migrate from the generated sites to the solid–liquid interface, thus reducing the recombination of its photogenerated electrons and holes [9]. Besides, the BET specific surface areas of

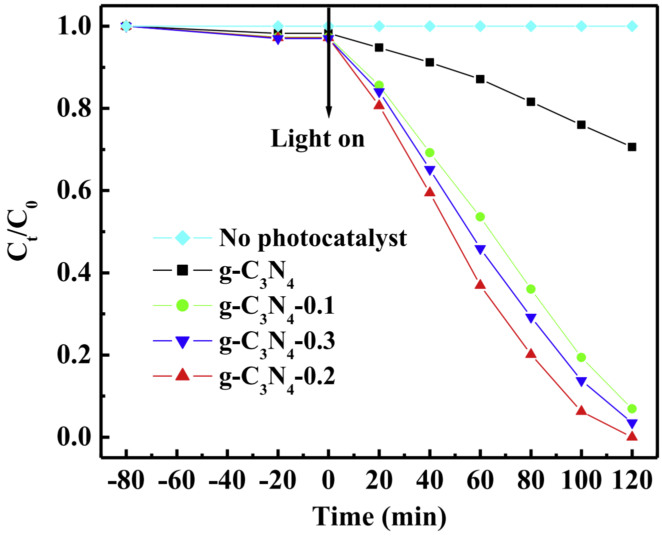

Fig. 1. Photocatalytic reduction of aqueous Cr^{6+} over g-C_3N_4, g-$C_3N_4-0.1$, g-$C_3N_4-0.2$ or g-$C_3N_4-0.3$ under visible-light ($\lambda > 420$ nm) irradiation.

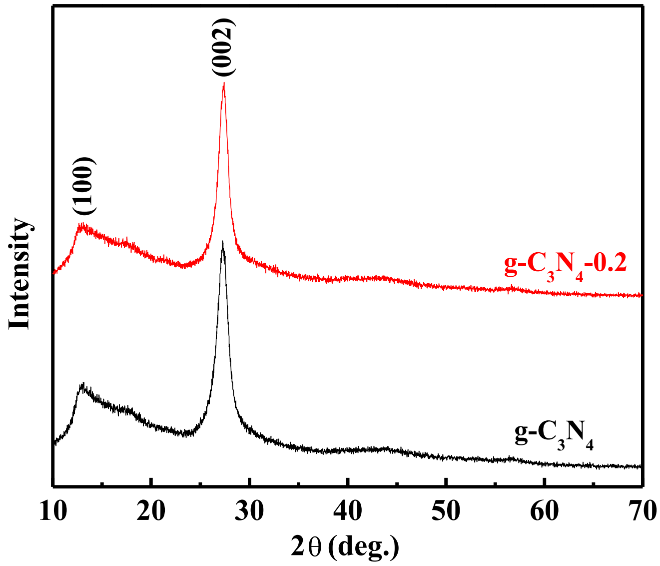

Fig. 2. XRD patterns of g-C_3N_4 and g-$C_3N_4-0.2$.