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Article

Br-doping of g-C₃N₄ towards enhanced photocatalytic performance in Cr(VI) reduction

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ABSTRACT

Semiconductor photocatalytic technology is widely recognized as one of the most promising technologies to solve current energy and environmental crisis, due to its ability to make effective use of solar energy. In recent years, graphite carbon nitride (g-C₃N₄), a new type of non-metallic polymer semiconductor photocatalyst, has rapidly become the focus of intense research in the field of photocatalysis because of its suitable bandgap energy, unique structure, and excellent chemical stability. In order to improve its intrinsic shortages of small specific surface area, narrow visible light response range, high electron-hole pair recombination rate, and low photon quantum efficiency, a simple method was utilized to synthesize Br-doped g-C₃N₄ (CN-BrX, X = 5, 10, 20, 30), where X is a percentage mole ratio of NH₄Br to melamine. Experimental results showed that Br atoms were doped into the g-C₃N₄ lattice by replacing the bonded N atoms in the form of C–N=C, while the derived material retained the original framework of g-C₃N₄. The interaction of Br element with the g-C₃N₄ skeleton not only broadened the visible-light response of g-C₃N₄ to 800 nm with an adjustable band gap, but also greatly promoted the separation efficiency of the photogenerated charge carrier and the surface area. The photocurrent intensity of bare CN and CN-BrX (X = 5, 10, 20, 30) catalysts is calculated to be 1.5, 2.0, 3.1, 6.5, and 1.9 μA, respectively. And their specific surface area is measured to be 9.086, 9.326, 15.137, 13.397, and 6.932 m²/g. As a result, this Br-doped g-C₃N₄ gives significantly enhanced photocatalytic reduction of Cr(VI), achieving a twice enhancement over g-C₃N₄, with high stability during prolonged photocatalytic operation compared to bare g-C₃N₄ under visible light irradiation. Furthermore, an underlying photocatalytic reduction mechanism was proposed based on control experiments using radical scavengers.

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1. Introduction

Hexavalent chromium (Cr(VI)), one of the most common heavy metal environmental contaminants, is widely found in wastewater from the dye production, electroplating, and leather

processing industries [1,2]. Demonstrated to be highly toxic, Cr(VI) has a strong carcinogenic effect on the human body. Methods for dealing with Cr(VI)-containing wastewater economically and effectively have attracted widespread attention. The most common solution at present is to convert Cr(VI) into

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lower toxicity Cr(III), which is then removed by precipitation under neutral or alkaline conditions. Yet repeated pollution with Cr(VI) is a big challenge caused by chromium-containing mud, which is difficult to handle and make use of [3–5].

Recently, the photocatalytic reduction of Cr(VI) using solar energy as the driving force in the reaction has become a research focus in the field by virtue of the low cost, high efficiency, and lack of collateral contamination. The semiconductor TiO_2 is the most extensively studied compound for this end, due to its excellent photochemical stability, strong reducibility, superhydrophilicity, and its non-toxic nature [6–8]. Despite this, TiO_2 has the inherent drawback of having low solar energy utilization efficiency due to its wide bandgap (3.2 eV) in photocatalytic reactions, which severely limits the practical application of TiO_2 as a photocatalyst. Accordingly, the development of new visible light driven catalytic materials to remove Cr(VI) effectively is highly desirable [9].

As a kind of non-metallic organic polymer n-type semiconductor, $\text{g-C}_3\text{N}_4$ with its unique electrical, optical, structural and physicochemical properties, and suitable forbidden band width (2.7 eV), conduction band (CB, -1.2 eV) and valence band (VB, 1.5 eV) locations also has the advantages of being a common raw material, with low cost, a simple synthesis reaction, and a visible light response. It has been applied in photocatalysis in many aspects owing to its more flexibility in structural modulation and stronger acid and alkali resistance compared with traditional metal oxide catalysts [10–15]. Theoretically, the reduction potential of Cr(VI)/Cr(III) is 1.33 eV. Thus, purification of highly toxic chromium-containing waste water could be achieved by photo-generated electrons. However, pure $\text{g-C}_3\text{N}_4$ itself has the shortages of small specific surface area, narrow visible light response range, high electron-hole pair recombination rate, and low photon quantum efficiency, which greatly restrict the practical applications of $\text{g-C}_3\text{N}_4$ [16–20].

Chemical element doping for the introduction of new elements into the structure of $\text{g-C}_3\text{N}_4$ by chemical or physical methods has been demonstrated to be the simplest and most effective method to modify the electronic structure of $\text{g-C}_3\text{N}_4$. Doping of $\text{g-C}_3\text{N}_4$ mainly includes metal elements, non-metal elements and self-doping [21–26]. Non-metallic element doping has proven to be an effective and commonly used method to enhance the catalytic performance of $\text{g-C}_3\text{N}_4$ [27–29]. The photocatalytic activity and reaction efficiency of $\text{g-C}_3\text{N}_4$ could also be enhanced by doping with halogen using carbon nitride precursors and ammonium halides as additives. These include precursors such as ammonium fluoride (NH_4F) [30], ammonium chloride (NH_4Cl) [31], ammonium bromine [32], and ammonium iodide (NH_4I) [33]. Inspired by these research and findings, we thought that valence electrons with lower electronegativity in iodine atoms were more likely to move and then interact with $\text{g-C}_3\text{N}_4$ in possession of π electron system. This extended conjugation system should make the light absorption range of $\text{g-C}_3\text{N}_4$ redshift and enhance the electron mobility. However, the large radius of the iodine atom leads to instability in the carbon nitride triazine ring structure.

In this work, we successfully obtained a Br-doped $\text{g-C}_3\text{N}_4$ photocatalyst via a simple thermal polymerization method with

melamine as the precursor and ammonium bromide as the dopant. X-ray powder diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and density functional theory (DFT) were employed to characterize the resulting structure and investigate the synthesis scheme of the materials. Then, photocatalytic reduction of hexavalent chromium was used to evaluate its photocatalytic performance and stability under visible light. The mechanism of the improved photocatalytic effect by afforded bromide doping is discussed at length and was studied by photocurrent analysis, UV diffuse reflectance spectroscopy (UV-DRS), and photoluminescence (PL). These results show that the CN-BrX samples retain the basic framework of $\text{g-C}_3\text{N}_4$, and the Br element are uniformly distributed in $\text{g-C}_3\text{N}_4$ structure by replacing the N atoms in carbon-nitrogen heterocycles. The introduction of Br element can obviously reduce the band gap, widen the range of visible light response, accelerate the separation efficiency of photogenerated carriers and increase its specific surface area, so that the modified samples have higher photocatalytic redox activity. In addition, photo-generated e^- , $\cdot\text{OH}$ and H_2O_2 play a certain role during the process of Cr(VI) photocatalytic reduction.

2. Experimental

2.1. Preparation of samples

Melamine (99.0%) and NH_4Br (99.0%) obtained, respectively, from Sinopharm Chemical Reagent Co., Ltd and Shanghai Macklin Biochemical Co., Ltd were of analytical grade and used without further treatment. Deionized water used during the experimental process was generated via an ultra-pure purification system.

The $\text{g-C}_3\text{N}_4$ (CN) was prepared by heating 4.0 g of melamine in an uncovered crucible to 520 °C at a heating rate of 10 °C/min and for a total incubation time of 4 h. The obtained product was collected and subsequently ground into a powder.

Br-doped $\text{g-C}_3\text{N}_4$ was synthesized by heating a mixture of melamine and ammonium bromide in a closed system. Typically, different weights of NH_4Br powder (15.55, 31.10, 62.20, and 93.30 g) and 4.0 g melamine were dissolved in 40 mL deionized water. After stirring for 24 h, the mixture was dried at 90 °C to evaporate the water, followed by a conventional thermal polymerization procedure sharing identical conditions to the synthesis of $\text{g-C}_3\text{N}_4$ described above. The product was then washed three times with water to remove residual impurities and is referred to as CN-BrX (X = 5, 10, 20, 30), in which X stands for the mole ratio of NH_4Br to melamine.

2.2. Characterization

The crystalline structure of $\text{g-C}_3\text{N}_4$ and the various CN-BrX photocatalysts were analyzed using XRD, recorded on a Bruker D8 diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Crystallite sizes of the catalysts were calculated using the Scherrer equation. The Fourier-transform infrared (FTIR) spectra were

recorded with a Vertex70 infrared spectrophotometer in the frequency range of 4000–400 cm^{-1} to get information about chemical bonds or functional groups in molecules. In order to analyze the chemical composition, the valence state of atoms, and the level structure in the surface, XPS (Thermo scientific escalab250Xi) were recorded with a monochromatic Mg K_{α} X-ray source ($h\nu = 1253.6$ eV), calibrated by carbon deposit C (1s) binding energy (BE) at 284.6 eV. UV-vis DRS was measured on a Solid Cary 5000 spectrophotometer and BaSO_4 was used as a reference material. PL were obtained using an FS5 spectrometer with an excitation wavelength of 355 nm, and the fluorescent lifetime was also obtained. The specific surface areas were deduced from N_2 adsorption-desorption isotherms at -196 °C (ASAP 2460, Micromeritics USA) on samples preheated to 200 °C for 4 h in a vacuum. S_{BET} values were calculated using the Brunauer-Emmett-Teller (BET) equation. To characterize the detailed morphology and surface structure of the samples, SEM (Verios 460) with an accelerating voltage of 2.00 kV and TEM with an accelerating voltage of 200 kV were used.

2.3. Theoretical calculations

To investigate the crystal structure of Br-doped CN, DFT calculations were carried out using the program package CASTEP. For the total and partial density of state (DOS) k-points were adopted in a $2 \times 2 \times 1$ grid, and the energy cut off chosen was 550 eV.

2.4. Photoelectrochemical experiments

Photoelectrochemical tests were carried out on a CHI 660 workstation with a three-electrode system, using a Pt plate ($1 \times 1 \text{ cm}^2$) as the counter electrode, a saturated calomel electrode as the reference electrode, and a photocatalyst-coated electrode as the working electrode. Typically, the working electrode was prepared as follows. A total of 3 mg of catalyst powder was dispersed in 0.15 mL of ethanol, followed by ultrasonication for 30 min. Then the above solution was dropped onto IFO ($1 \times 1.5 \text{ cm}^2$) conductive glass and dried at room temperature. Finally, a transient photocurrent was achieved in a 0.1 mol/L Na_2SO_4 aqueous electrolyte to study the surface charge transfer efficiency and carrier density. A 300 W Xe lamp with a filter ($\lambda > 420 \text{ nm}$) served as the simulated solar light source.

2.5. Photocatalytic testing

2.5.1. Photocatalytic reduction of Cr(VI)

The photocatalytic activities of obtained samples were evaluated by Cr(VI) reduction under visible light illumination. A 300 W Xe lamp with a filter ($\lambda > 420 \text{ nm}$) served as the simulated solar light source, and the irradiation distance is 30 cm.

Prior to irradiation, 50 mg of the sample was placed in a beaker containing 50 mL of 20 mg/L potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) solution acidulated by concentrated sulfuric acid and kept stirring in the dark for 1 h to reach an adsorption-desorption equilibrium. During the photoreaction process,

3 mL of suspension was withdrawn and centrifuged at 9000 rpm to remove the photocatalyst at certain time intervals for subsequent analysis. Finally, the concentration of Cr(VI) was analyzed using a UV-vis spectrophotometer, measuring the characteristic absorption peak at 350 nm.

The active species involved in the photocatalytic reduction of potassium dichromate was investigated by adding excess trapping agents to the solution. These generally included potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), which captures e^- , ammonium oxalate ($(\text{NH}_4)_2\text{C}_2\text{O}_4$), which captures H^+ , *tert*-butanol (TBA), which captures $\bullet\text{OH}$, and argon was used to reduce the production of superoxide anions ($\bullet\text{O}_2^-$).

Cycling experiments were conducted to explore the stability of prepared samples. Photocatalysts after the reaction were recovered by centrifugation and washed thoroughly with deionized water in order to completely remove residual materials. Subsequently, the recycled products were added into fresh Cr(VI) aqueous solution ($\text{K}_2\text{Cr}_2\text{O}_7$: 20 mg/L) for the next photocatalytic process.

2.5.2. Photocatalytic yield of H_2O_2

The production of hydrogen peroxide under visible light irradiation with a 300 W Xenon lamp ($\lambda > 420 \text{ nm}$) serving as the visible light source was analyzed by studying the resulting PL spectra from a photocatalytic reaction. Typically, 0.1 g of photocatalyst sample was dispersed in 100 mL of deionized water in a container with ice water around. Prior to visible light irradiation, the mixture was stirred in the dark for 10 min to reach an adsorption-desorption equilibrium among the photocatalyst, dissolved oxygen, and water. In the irradiation process, 3 mL of the suspension was taken out every 10 mins, and then filtered to remove the photocatalyst particles followed by a fluorescence measurement. Generally, 100 μL of fluorescence reagent (potassium hydrogen phthalate 8.2 g/L, *p*-hydroxyphenylacetic acid 270 mg/L, and horseradish peroxidase 100 mg/L) was added to the filtrate along with 1.0 mL of 1.0 mol/L NaOH after 10 min. Finally, the concentration of H_2O_2 was detected using a PL spectrophotometer with a characteristic emission peak of 409 nm and an excitation peak of 315 nm.

3. Results and discussion

3.1. Structure and morphology of CN-BrX

The obtained samples were characterized by XRD and FTIR to investigate the crystal structure, chemical bonds, and functional groups. It can be seen in Fig. 1a that all CN-BrX samples except for CN-Br30 exhibited a similar layered structure with two diffraction peaks at 2θ values of about 12.9° and 27.3° , which are well indexed into the tetragonal phase of CN. The (100) peak near 12.9° corresponded to the in-plane structural packing motif of aromatic segments in the CN crystal, which is a characteristic peak of a triazine species [34]. The lattice spacing calculated to be 0.688 nm was related to the hole-to-hole distance between nitrogen pores of the 3-s-triazine units. Another pronounced peak at 27.4° , which we ascribed to the (002) peak, represented the stacking of conjugated hexatomic rings of CN

Fig. 1. (a) XRD patterns, (b) FT-IR spectra, and (c) enlarged FT-IR spectra of CN and CN-BrX.

with an interlayer distance of 0.339 nm [35]. For comparison, the XRD patterns of CN-Br20m were also analyzed as shown in Fig. 1a. Three pronounced diffraction peaks at 2θ values of 22.0° , 31.7° , and 38.0° were observed for CN-Br20m, which we ascribed to characteristic reflections of NH_4Br . We failed to observe any peaks for NH_4Br in our prepared samples, demonstrating the complete washing away of raw materials. When the doping ratio of NH_4Br increased to 30, the diffraction peaks at 12.9° and 27.3° for CN-Br30 were somewhat offset and weakened along with the occurrence of new peaks, which are not attributable to the characteristic peak of NH_4Br and may have been due to defects arising from incomplete polymerization, indicating that the in-plane structure was destroyed or changed by large amounts of NH_4Br .

FTIR spectra of all the CN-BrX samples except for CN-Br30 (Fig. 1b) displayed the similar molecular skeletal vibration modes, confirming that the basic structure of CN was preserved after modification with Br. The sharp peak at 812 cm^{-1} was assigned to the bending vibration characteristic of a triazine unit, while the peak at $1200\text{--}1700\text{ cm}^{-1}$ was related to the stretching vibration characteristic peaks of $\text{C}=\text{N}$ and $\text{C}-\text{N}$ bonds in a carbon-nitrogen heterocycle structure. The region at $3000\text{--}3500\text{ cm}^{-1}$ corresponded to the stretching vibration of $-\text{NH}_2$ groups in the edge or a damaged position, or the $\text{O}-\text{H}$ bond from water molecules adsorbed on the surface [36–38]. However, when the doping ratio of NH_4Br increased to 30, the absorption peak of CN-Br30 at $1200\text{--}1700\text{ cm}^{-1}$ suffered from some attenuation and had deviations compared to bare CN (Fig. 1c), which was consistent with the assumption that the structure of CN was changed based on the XRD results.

To further study the morphology of the prepared CN and CN-Br20 semiconductors, SEM and TEM (Fig. 2) analyses were carried out. We found that SEM and TEM images (Fig. 2a and 2c) of CN exhibited a typical layered structure with no obvious surface damage or holes. Nevertheless, as shown in Fig. 2b and 2d, the introduction of Br had great influence on the morphology and structure of CN. CN-Br20 showed a curl-like porous structure with regular pores uniformly spread on the slice. Additionally, elemental mapping images of CN-Br20 were generated, which evidence that C, N, and Br atoms were detected and homogeneously distributed over the entire structure (Fig. 2e–2h). These results further confirmed the Br doping of the modified CN.

3.2. Formation mechanism of CN-Br

To rule out the existence of Br in the prepared samples, XPS was performed to test the chemical environment of C and N upon Br-doping. As shown in Fig. 3a, an obvious extra Br peak could be detected in CN-Br20 compared to bare CN, and the high resolution of Br $3d$ spectra (Fig. 3b) could be deconvoluted into two peaks at 67.6 and 68.5 eV, which are ascribed to Br $3d_{5/2}$ and Br $3d_{3/2}$, respectively, attesting to the successful introduction of Br into the g- C_3N_4 structure. The high resolution of C $1s$ spectra (Fig. 3c) of CN was divided into two peaks at 284.6 and 287.9 eV. The narrow peak at 284.6 eV was assigned to the sp^2 -hybridized carbon ($\text{C}-\text{C}$), which was determined to be standard carbon. The broad peak at 287.9 eV was ascribed to sp^2 -bonded carbon in the heterocycle ($\text{N}=\text{C}-\text{N}$) of an aromatic carbon nitride, which was related to the major skeleton carbon in the triazine-based heterocycle. In CN-Br20, extra peaks located at 286.0 and 290.3 eV, which corresponded to $\text{C}-\text{NH}_2$ and $\text{C}-\text{Br}$ bonds, could be observed. The former one could be attributed to the restrained polymerization rate of CN, due to the formation of NH_3 from the decomposition of NH_4Br in the calcining process. When excess amounts of NH_4Br were

Fig. 2. SEM images of (a) CN and (b) CN-Br20; TEM images of (c) CN and (d) CN-Br20; EDS image of (e) CN-Br20 and corresponding elemental mapping of (f) C atom, (g) N atom, and (h) Br atom.

Fig. 3. (a) XPS survey spectra and high-resolution XPS spectra of (b) Br 3d region, (c) C 1s region, and (d) N 1s region for CN and CN-Br20.

added to co-condensation with melamine (which involved the release of ammonia gas during the process), the produced NH_3 should impede the intrinsic deamination kinetics, and thus result in more $-\text{NH}_2$ bonded with C atoms. The latter may be due to the replacement of N atoms with Br, indicating that Br-doped graphitic carbon has been formed and introduced into the CN matrix. As for N 1s, the spectra (Fig. 3d) of two samples were separated into three peaks at 398.1, 399.4, and 400.5 eV, corresponding to the sp^2 hybridized aromatic N bonded with carbon atoms of $\text{C}=\text{N}=\text{C}$, the tertiary nitrogen in the form of $\text{N}-(\text{C})_3$ groups and the surface uncondensed amino groups bound to hydrogen ($\text{C}-\text{NH}_2$), respectively. Combined with the high-resolution spectra of C 1s, it can be demonstrated that CN-Br20 still retained the basic triazine ring structure of carbon nitride. Additionally, it was clear that the N1s band underwent an obvious binding-energy shift, implying that its chemical environment had been affected. Moreover, the peak area of $\text{C}=\text{N}=\text{C}$ decreased significantly, and that of $\text{C}-\text{NH}_2$ was increased compared to pure carbon nitride, which was in good agreement with the C 1s spectra and further gave evidence that Br had replaced the bonded N atoms in the form of $\text{C}=\text{N}=\text{C}$

[39,40].

To further analyze the presence of Br, CN-Br20 subjected to deep etching X-ray photoelectron spectroscopy (XPS). Fig. 4a shows the high-resolution energy spectrum of Br at the sample surface, etched at 30, 90, and 120 nm. As the etching depth increased, the peak strength remained consistent, indicating that Br existed in the internal structure of CN. Element analysis tests (EA) of the CN and CN-Br20 samples were performed to verify its structural composition (Fig. 4b). The results showed that the C/N ratio increased from 0.49 to 0.65, which attested to the previously stated reasoning that Br had replaced the bonded N. A possible formation mechanism is illustrated in Fig. 5.

3.3. Photocatalytic activity

The photocatalytic performance of CN and CN-BrX (X = 5, 10, 20, 30, 20 m) samples was analyzed using a time course of Cr(VI) (7 mg/L) reduction under visible light ($\lambda > 420 \text{ nm}$) at room temperature. Before light irradiation, the solution was kept in the dark for 1 h to ensure the establishment of an ad-

Fig. 4. XPS spectra (a) of CN-Br20 and EA analysis (b) of pure CN and CN-Br20.

Fig. 5. Schematic illustration of the formation of Br-doped g-C₃N₄.

sorption-desorption equilibrium between the photocatalyst and Cr(VI). It was clear from Fig. 6a that the adsorption removal ratio of Cr(VI) was negligible (about 5%) for the different catalyst systems. As presented in Fig. 6b, 25.1%, 35.9%, 55.2%, 61.6%, 35.2%, and 18.7% of Cr(VI) were removed over CN, CN-Br5, CN-Br10, CN-Br20, CN-Br30, and CN-Br20m, respectively. The concentration change of Cr(VI) was found to follow zero-order kinetics and the photoreduction rate of Cr(VI) for CN, CN-Br5, CN-Br10, CN-Br20, and CN-Br30 was calculated to be 0.082, 0.119, 0.119, 0.155, and 0.1 mg L⁻¹ h⁻¹, respectively, normalized with respect to the specific surface area (Fig. 6c and 6d). CN-BrX samples could dramatically improve the photoreduction activity, and CN-Br20 showed the best photocatalytic performance, as high as 0.155 mg L⁻¹ h⁻¹, displaying a twice enhancement compared to unmodified CN using the same illuminating conditions. Furthermore, the conclusion can be drawn that doping with Br in an internal structure was the primary cause for the improvement in photoreduction ability of Cr(VI) on the side of CN-Br20m.

In addition to testing the photocatalytic reduction of Cr(VI), the production of H₂O₂ in air using the prepared samples (Fig. 6e and 6f) was also tested. We found that all the modified samples exhibit strengthened activity, and CN-Br20 possessed the highest yield of H₂O₂, which was 10 times more active than CN, consistent with the above photoreduction results. Consequently, we concluded that the photoreduction capabilities of CN were greatly improved by Br modification.

3.4. The mechanism of activity enhancement

Density functional theory (DFT) calculations of pure and Br-doped CN were conducted to investigate the electronic properties of Br-doped g-C₃N₄. The structure diagrams of pure CN and doping system are shown in Fig. 7a and 7d, where a bonded N atom was substituted by a foreign Br atom. Calculation results of the energy band structure for CN (Fig. 7b) demonstrated that the top of the VB and the bottom of the CB were both at point G, indicating that CN is a direct band-gap semiconductor, which is consistent with previous reports. We found that a new energy band passing through the Fermi level was generated (Fig. 7e), close to the conduction band, implying that the substitution of a Br atom at an N site was an N-type doping. In addition, the top of the VB and the bottom of CB in the doped system were also seated at point G, demonstrating that modified CN was still a direct band gap semiconductor. Simultaneously, the energy density of Br-doped CN was much higher than that of pristine CN, illustrating that Br atoms may have reduced the symmetry of CN and caused electron delocalization, thus improving the photocatalytic activity. The value of E_g for CN was 0.81 eV and that of Br-doped CN was clearly narrowed to 0.46 eV (Fig. 7c and 7f), in addition to the decrease of both the CB and VB positions, which may have been due to the doped Br atom via influencing the distribution of C and N atoms in the lattice. The calculation results of energy band structure

Fig. 6. (a) C/C_0 , (b) removal rate, (c) zero-order kinetics fitting, and (d) the removal rate constant normalized with respect to the specific surface area for Cr(VI) reduction of the prepared photocatalysts, and (e, f) the mass concentration of generated H_2O_2 in different catalyst systems.

Fig. 7. Crystal structure (a, d), the energy band diagram (b, e), and DOS (c, f) of pure CN and Br-doped CN.

are consistent with the enhancement of photocatalytic activity under UV-vis light irradiation.

Photocatalytic activity is often related to the photo-absorption, photoexcitation and specific surface area of prepared samples. UV-vis DRS was utilized to monitor the alterations of the optical properties of CN and CN-BrX. It is important to note that the light responsive range of CN was expanded to cover the entire visible-light region due to Br modification, and the tail peak extending near the IR region was gradually enhanced with increasing NH_4Br concentration,

which is in good accordance with the sample color varying from pale yellow to gray (Fig. 8a and 8b). Consistent with this, CN-BrX should absorb more visible light than bulk CN, thereby generating more charges, which was expected to be beneficial for the enhancement of photocatalytic activity under visible light irradiation. Additionally, the CN-BrX samples may have advantages due to the exposure of active sites as they have its looser structures than pure CN. The intrinsic band edges of CN-Br5, CN-Br10, and CN-Br20 showed a slight redshift compared to CN, with the CN band gap of 2.80 eV decreasing to 2.79

Fig. 8. (a) Digital pictures, (b) UV-vis absorption spectra, (c) plots of transformed Kubelka–Munk function versus photon energy, (d) VB XPS spectra, and (e) band structure alignments for the CN and CN-BrX samples.

and 2.74 eV. While a blue shift was observed for CN-Br30, the band gap increased to 2.86 eV (Fig. 8c).

To further investigate the effect of the Br-doping on the position shifting of the CB and the VB of the synthesized samples, the VB X-ray photoelectron spectroscopy (VB XPS) was used to analyze the energy band structure. As shown in Fig. 8d, the VB of bare CN and CN-BrX (X = 5, 10, 20, 30) catalysts are calculated to be 1.53, 1.55, 1.68, 1.74, and 1.33 eV. Accordingly, the CB positions were derived to be -1.27, -1.24, -1.06, -1.00, and -1.53 eV based on their band gaps. This result indicated that Br element doping could lead to the down shift of CB and VB levels except in the case of CN-Br30, consistent with the DFT calculations. According to the above experimental results and mechanism calculation, a schematic of the band gap energy level of CN and a series of CN-BrX (X = 5, 10, 20, 30) are depicted in Fig. 8e.

After photoexcitation, the photogenerated electrons may undergo two ways: (1) they could be transferred to the surface of the photocatalyst for subsequent chemical reactions, or (2) they could recombine with photogenerated holes. Photoluminescence (PL) measurements were used to investigate the separation and recombination of photogenerated electrons and holes excited at 355 nm. The strong emission peak of CN at 465 nm was derived from the direct electron and hole recombination of the band transition. The PL intensity of CN-BrX was found to be greatly lowered in comparison to that of CN (Fig. 9a), implying that the photogenerated charge carrier recombination could be effectively suppressed by modification of Br. Moreover, apart from the intrinsic peak of CN at 465 nm, a new band at a shorter wavelength appeared in the PL spectrum of CN-Br30 samples, which may have been due to the recombination of electrons from a lower impurity level. Time-resolved PL spectra were captured to confirm the above results. As shown

in Fig. 9b, the fluorescent lifetime of CN-Br20 was obviously shorter than that of pristine CN, indicating that the doped Br could serve as a channel to efficiently transport the charge carriers to active sites and thus promote photochemical reactions.

Photoelectrochemical measurements were carried out in a typical three-electrode cell to analyze the CN and CN-BrX samples, and the results are displayed in Fig. 9c. CN-BrX samples exhibited a higher photocurrent intensity than pure CN, indicating the efficient utilization of solar-light resources after the modification. Distinctly, CN-Br20 exhibited the highest intensity among all the samples, which strongly illustrated that the mobility of the photoexcited charge carriers was greatly improved after modification. Furthermore, the laws governing our photocurrent response results agreed with the Cr(VI) photoreduction results.

N₂ adsorption-desorption isotherms of the prepared CN and CN-BrX materials are shown in Fig. 9d. All samples exhibited a type IV sorption isotherm with a pronounced hysteresis loop based on IUPAC classification, suggesting the existence of a porous structure. It was noteworthy that the calculated BET surface area of CN-BrX (except for the sample CN-Br30) was higher than that of CN, which may have been caused by NH₃ gas released during the calcining process. Materials with a larger specific surface area could provide more active sites on the surface and promote the adsorption and transportation capabilities of catalytic reactants, thereby leading to improved photocatalytic activity. However, the BET surface area decreased to 6.932 m²/g when the amount of NH₄Br was increased to 30, which could be due to the fact that the texture of the sample was changed.

3.5. Proposed mechanism of Cr(VI) removal

Fig. 9. (a) Photoluminescence spectra, (b) time-resolved PL spectra, (c) photocurrent response under visible light irradiation, and (d) N₂ adsorption-desorption isotherms of pristine CN and a series of CN-BrX samples.

Control experiments with different scavengers individually trapping the corresponding active species were employed to explore the possible mechanism of Cr(VI) reduction. The scavengers used in this study were potassium persulfate (K₂S₂O₈) for e⁻, ammonium oxalate (AO) for h⁺, and tertiary butanol (TBA) for •OH. The oxygen dissolved in the reaction solution may have helped to generate numerous oxidizing species, improving the oxidation reaction and suppressing the reduction activity. High purity Ar (> 99.99%) was used to purge the reaction system to get rid of the dissolved oxygen as much as possible before experiments began, and Ar was used throughout the photocatalytic process.

As shown in Fig. 10, the photoreduction efficiency of Cr(VI) increased in both the CN and CN-Br20 systems with the addition of AO. AO can serve as a hole scavenger, which can promote the separation of photogenerated electron-holes and exhibit a promoting effect on the reduction of Cr(VI). Meanwhile, the trapping of e⁻ by K₂S₂O₈ conversely restrained the removal rate of Cr(VI), implying that e⁻ was the main active species in the photocatalytic process, while h⁺ appeared to be negligible in the reaction. Moreover, when TBA was added to capture hydroxyl free radicals, the removal efficiency of Cr(VI) was signif-

icantly improved, and the effect of pure CN was much higher than that of Br-doped CN. This was because the Cr(III) in solution could be oxidized to Cr(VI) by hydroxyl free radicals, which are a kind of reactive oxygen species with strong oxidizing abilities. Thus, the reduction efficiency of Cr(VI) was greatly improved when it was removed. As shown in Fig. 10d, the hydroxyl free radicals produced in the CN-Br20 system were much higher than those produced in the bare CN system, while the inhibitory effect on the removal rate of Cr(VI) was exactly the opposite, which may have been due to the larger amounts of H₂O₂ generated by CN-Br20. Since H₂O₂ can show a strong reducibility to transfer Cr(VI) to Cr(III) when reacting with K₂Cr₂O₇ under acid condition. Nevertheless, when the reaction was operated under an Ar atmosphere, only a slight decrease in the Cr(VI) reduction activity could be observed, being attributed to the decreased electron transport of the O₂/•O₂⁻ mediated reduction in the absence of dissolved oxygen, which may have generated H₂O₂ to reduce Cr(VI) to Cr(III) and •OH to oxidize Cr(III) to Cr(VI) at the same time. In summary, the active species that played an important role in the Cr(VI) reduction of both the CN and CN-Br20 systems was photogenerated e⁻, •OH and H₂O₂, but •OH can inhibit the reduction of Cr(VI).

Fig. 10. Cr(VI) reduction with different scavengers and different ambient conditions under visible light irradiation in (a) CN and (b) CN-Br20 systems (c) Comparison of photocatalytic activities in different photocatalysis systems; (d) The concentration of generated $\bullet OH$ in CN and CN-Br20 systems.

Based on the above experimental results, a probable mechanism for the photocatalytic reduction of Cr(VI) over CN-Br20 was proposed. CN-Br20 has a porous structure, which means a higher specific surface area and numerous active sites for the reaction process. The visible light response region of a photocatalyst can be expanded by the doping of Br, thus promoting the solar energy utilization efficiency. The separation efficiency of photogenerated carriers can be greatly improved due to Br and its strong electronegativity. CN-Br20 could be motivated to generate electrons and holes under visible light irradiation. Subsequently, the photogenerated electrons in the conductor band could react with dissolved oxygen to produce $\bullet O_2^-$ and reduce Cr(VI) to Cr(III). Then the reaction between $\bullet O_2^-$ and H^+ could generate H_2O_2 as well as $\bullet OH$. According to the analysis mentioned above, the generation of the photogenerated electron-holes, radicals and reaction process can be described by the following equations:

Considering the practical application of photocatalysts, it is essential to investigate the repeatability and stability of a photocatalyst. As an example, recycling experiments of CN-Br20 were conducted. In these experiments, the recovered catalyst was washed with deionized water and then dried at 60 °C. Results in Fig. 11 revealed that the photocatalytic efficiency for

Fig. 11. The reusability of the CN-Br20 for the reduction of the Cr(VI) reaction system.

Fig. 12. (a) Power-XRD patterns and (b) FT-IR spectra of CN-Br20 before and after photoreaction.

the reduction of Cr(VI) could be maintained at approximately 50% even after five photocatalytic cycles, indicating the CN-Br20 was stable during these experiments. However, the removal efficiency of Cr(VI) dropped from 61.6% to 49.5% in the second cycle, which may have been due to the occupation of some active sites by Cr(VI) adsorbed on the material during the first reaction. To further confirm the physical and chemical stability of CN-Br20 after the photocatalytic reaction, the fresh and used photocatalysts were then subjected to characterizations by FT-IR and XRD, respectively. As shown in Fig. 12, no significant change could be observed in the structure of CN-Br20 after five successive cycles, further verifying the high stability and durability of the prepared CN-Br20.

4. Conclusions

A series of Br doped g-C₃N₄ composites were successfully synthesized via a thermo-induced copolymerization strategy by introducing large amount of NH₄Br into melamine. The experimental characterizations showed that Br was intercalated by replacing the lattice N atoms to form C-Br bonds. The doping of bromine into g-C₃N₄ could modulate the morphology and photocatalytic performance of g-C₃N₄, without destroying the major construction and architecture of the g-C₃N₄ polymer. Compared with bulk g-C₃N₄, the Br-doped g-C₃N₄ exhibited dramatically improved photocatalytic activity in Cr(VI) reduction under visible light irradiation. The photoreduction of Cr(VI) on a Br-incorporated g-C₃N₄ photocatalyst (CN-Br20) with high stability reached 0.155 mg L⁻¹ h⁻¹, which was almost 2.0 times higher than that of bare g-C₃N₄. We confirmed that the extended optical absorption, narrowed energy gap, high transfer rate of electron-hole pairs, and enlarged specific surface area attributed to the introduced Br atoms were responsible for the remarkably enhanced photoactivity, as demonstrated by both experimental and theoretical results. This work demonstrates a novel method for the synthesis of metal-free photocatalysts with high performance through a simple, low-cost, and environmentally friendly strategy.

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Graphical Abstract

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Br-doping of g-C₃N₄ towards enhanced photocatalytic performance in Cr(VI) reduction Mian Wang, Yubin Zeng*, Guohui Dong*, Chuanyi Wang*
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Br-doped g-C₃N₄ exhibits improved photocatalytic activity for Cr(VI) reduction under visible light irradiation. The Br element was intercalated into g-C₃N₄ to form C-Br bonds, and photogenerated e⁻, •OH, and H₂O₂ play important roles in Cr(VI) reduction.

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溴掺杂石墨相氮化碳对Cr(VI)光催化还原性能的提高汪 勉^a, 曾玉彬^{a,*}, 董国辉^{b,#}, 王传义^{b,\$}^a武汉大学动力与机械学院, 流体机械与动力工程装备技术湖北省重点实验室, 湖北武汉430072^b陕西科技大学环境科学与工程学院, 陕西西安710021

摘要: 半导体光催化技术不仅可将太阳能转化为化学能, 还能直接降解和矿化有机污染物, 在解决能源短缺和治理环境污染等方面具有广阔的应用前景。然而传统的TiO₂光催化剂具有较大的禁带宽度(3.2 eV), 使得材料只能吸收紫外光(仅占太阳光的4%)且量子产率较低。因此, 研究和开发新型的本身具有可见光响应的光催化材料在实际应用中具有重要的指导意义。g-C₃N₄作为一种非金属有机聚合物n型半导体, 因具有合适的禁带宽度、独特的电子结构和良好的化学稳定性, 迅速成为光催化领域的研究热点。但是, 由于g-C₃N₄本身存在比表面积小、可见光响应范围狭窄和光生电子-空穴对分离效率低等缺陷, 极大限制了其光催化实际应用。

为了解决该问题, 人们进行了很多尝试来改善石墨相氮化碳光催化材料的光催化活性。研究表明, 非金属元素掺杂是一种有效且常用的提高g-C₃N₄光催化性能的方法。例如, 通过高温煅烧三聚氰胺和氧化硼混合物可制备掺B的g-C₃N₄, g-C₃N₄结构中的H元素被B取代, B的掺杂大大提高了g-C₃N₄的光催化活性; 利用氟化铵和三聚氰胺合成F掺杂的g-C₃N₄, F原子与g-C₃N₄中心或边缘的C键合, 将部分sp²杂化的碳原子转化为sp³杂化, 降低了材料的平面性, 从而使材料的析氢性能

和催化苯氧化生成苯酚的能力有了明显提高;使用氯化铵和双氰胺作为前驱体制备Cl掺杂的g-C₃N₄, Cl元素的引入使g-C₃N₄晶格变形,带隙变窄,电荷迁移效率提高,光催化效率显著改善.

基于上述结果,并考虑到原子的电负性和大小等因素的影响,我们采用简单的一步法合成了系列Br掺杂的g-C₃N₄光催化剂CN-BrX.通过X射线衍射(XRD)、红外光谱(FTIR)和电子显微镜(SEM、TEM)等手段对材料的结构进行了表征,并结合元素分析(EA)和光电子能谱(XPS)研究了其形成机理.采用光催化还原Cr(VI)效率、光催化产双氧水浓度以及光催化氧化NO能力评价了CN-BrX的光催化活性,并进行了光催化反应过程动力学拟合和循环实验.通过理论计算(DFT)、紫外-可见漫反射光谱(UV-vis DRS)、荧光光谱(PL)、光电流(PC)和比表面积(BET)等测试分析了材料的光催化活性增强机理,并通过活性物种捕获实验深入探究了其光催化还原Cr(VI)的反应机理.结果表明,CN-BrX(CN-Br30除外)保留了g-C₃N₄的基本骨架,其中Br元素以取代碳氮杂环中N原子的形式均匀分布于g-C₃N₄结构中.引入的Br元素可以明显降低材料的禁带宽度,拓宽其可见光响应范围,加快光生载流子的分离效率,并增大其比表面积,从而使得改性材料具有更高的光催化氧化还原活性.此外,在Cr(VI)光催化还原过程中,光生e⁻, •OH和H₂O₂均起着重要作用.

关键词: 石墨相氮化碳; 溴; 掺杂; Cr(VI)还原; 可见光

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