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Photocatalytic reduction of aqueous chromium(vi) by RuO₂/g-C₃N₄ composite under visible light irradiation†

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Graphitic carbon nitride (g-C₃N₄) has been extensively investigated as a novel nonmetallic visible-light response photocatalyst. However, its uses in photocatalytic reductions were limited because of the sluggish oxygen evolution reaction (OER) and the resulting self-decomposition. In this paper, a ruthenium dioxide loaded g-C₃N₄ composite (RuO₂/g-C₃N₄) was prepared by forced oxidative hydrolysis of ruthenium(III) chloride on the surface of g-C₃N₄ that was obtained by direct condensation polymerization of melamine. Photocatalytic reduction of aqueous Cr(vi) by it under illumination from a 400–410 nm light-emitting diode was examined. It was shown that the Cr(vi) reduction rate was much higher in RuO₂/g-C₃N₄ than in pure g-C₃N₄. Without any sacrificial electron donor and at initial solution pH 2.3, Cr(vi) removal (200 mL and 0.5 mM) was 34% and 76.4% with 0.1 g pure g-C₃N₄ and 0.1 RuO₂ (1.0 wt%)/g-C₃N₄, respectively. The optimum initial solution pH was 2.4. Methanol accelerates while acetone suppresses the Cr(vi) reduction significantly. Ferric ions catalyze the reduction, especially in the later stage. UV-Vis diffusion reflectance spectroscopy and theoretical analysis showed that RuO₂ not only boosts the charge separation but also protects the g-C₃N₄ from decomposition by its extraordinary catalytic action for OER. The used RuO₂/g-C₃N₄ was separated from the solution by microfiltration, with little leaching and residue remaining in the filtrate. The reclaimed RuO₂/g-C₃N₄ was recycled for 5 cycles and no obvious decrease in catalytic activity was observed, indicating its superior potential in industrial applications.

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1. Introduction

Chromium is a common pollutant in water, where it usually exists in the extremely toxic and carcinogenic hexavalent [Cr(vi)] form.¹ Converting Cr(vi) to much less toxic and precipitable trivalent form [Cr(III)] *via* chemical reduction is a key step to treat the Cr(vi) contaminated wastewater. However, the chemical reduction needs excess reducing agents and acids to drive the reaction, adding tremendous amounts of neutralizing reagents in the subsequent precipitation.^{2,3} Therefore, developing atom-economic processes for Cr(vi) reduction is in great need.

Recently, graphite carbon nitride (g-C₃N₄) has emerged as a novel nonmetallic photocatalyst due to its narrow band gap (2.7 eV), visible light response capability, rich sources of precursors and simple preparation method.⁴ In theory, g-C₃N₄ can be applied for reduction of heavy metal ions because of its highly active conduction band electrons ($E_{cb} = -1.1$ eV vs. NHE,

slightly dependent on fabrication method and reaction procedure). However, pure g-C₃N₄ exhibits low photocatalytic activity due to its high recombination speed of photo-generated charge carriers and its low conductivity. Constructing g-C₃N₄-based composites is considered as a promising strategy in promoting photocatalytic reductions. Wang *et al.*⁵ found that the 1D black phosphorus-tubular g-C₃N₄ can remove 94.1% of Cr(vi) with a rate constant of 0.0404 min⁻¹. Ren *et al.*⁶ constructed a g-C₃N₄/NH₂-UiO-66(Zr) heterojunction by solvothermal and *in situ* deposition to effect both Cr(vi) reduction and tetracycline hydrochloride oxidation in aqueous solution, where the photocatalytic removal of Cr(vi) by CU-20 wt% forming heterojunction was 1.86 times that of pure NH₂-UiO-66(Zr) under visible light irradiation. Eslamlu *et al.*⁷ reported that Sb₂MoO₆ coupled with g-C₃N₄ nano-tubes showed Cr(vi) reduction efficiency of 22 times higher than the bare g-C₃N₄. When MoS₂/g-C₃N₄ was grafted with cyclodextrins, Cr(vi) reduction in the simulated agricultural wastewater was remarkably enhanced.⁸ Mohamed *et al.*⁹ synthesized mesoporous BiVO₄/2D-g-C₃N₄ heterostructures for superior visible light-driven photocatalytic reduction of Hg(II) in the presence of HCOOH.

Metal oxides or metal sulfides were usually employed to couple with g-C₃N₄ to improve the photocatalytic efficiency. However, most of the metal oxides or metal sulfides are, due to

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their chemical nature, not durable enough in corrosive media, such as acidic, alkaline, reducing, oxidizing or chelating conditions which are frequently encountered in real wastewater samples. Stability of the applied catalysts is pivotal in real wastewater treatment, as the decomposition or leaching not only results in cost rising but also polluting the water for treatment. At present, little work concerning the catalyst leaching was reported. When the photogenerated electrons (e^-) are captured by the heavy metal ions, the holes (h^+) will inevitably accumulate in the valence band. Although the band potential of $g\text{-C}_3\text{N}_4$ ($E_{\text{VB}} \sim 1.5 \text{ V}$) is higher than that of oxygen (O_2), ($2\text{H}_2\text{O} - 4e^- \rightarrow \text{O}_2 + 4\text{H}^+$, $\phi_{\text{O}_2/\text{H}_2\text{O}} = 1.23 \text{ V}$), it is not positive enough to oxidize water to O_2 due to the large kinetic barrier in the four-electron oxygen evolution reaction (OER), which makes OER in conventional $g\text{-C}_3\text{N}_4$ -metal oxide heterojunctions particularly sluggish. If the accumulated h^+ were not effectively removed by water molecule, they would oxidize the catalyst itself, leading to the $g\text{-C}_3\text{N}_4$ break down.¹⁰ Although $g\text{-C}_3\text{N}_4$ can be protected by using sacrificial electron donor (usually organic additives such as alcohols¹⁰), such a strategy works well only when the real wastewater contains both $\text{Cr}(\text{vi})$ and organic pollutants. As some $\text{Cr}(\text{vi})$ wastewater contains organic pollutants and some not, searching efficient and stable heterostructure-forming units that can not only enhance the separation of photogenerated charge carriers but also promote OER during $g\text{-C}_3\text{N}_4$ photocatalytic reduction is of paramount importance. In this regard, ruthenium oxide (RuO_2) is with no doubt an appealing material for forming heterostructures due to its superior chemical stability,^{11,12} metallic conductivity [$2.0\text{--}2.5 \times 10^4 \text{ S cm}^{-1}$], and high catalytic activity for the OER¹³ for its optimal oxygen binding energy. In addition, the precursor of RuO_2 is relatively lower cost as compared to other precious metals. RuO_2 nanoparticles-accommodated $g\text{-C}_3\text{N}_4$ for photocatalytic oxidation of trichloroethylene has been reported.¹⁴ However, its action in promoting photocatalytic reductions is rarely reported. In this report, effect and mechanism of RuO_2 on promoting the $g\text{-C}_3\text{N}_4$ photocatalytic $\text{Cr}(\text{vi})$ reduction was examined and explored. It was found that small amount of RuO_2 deposition on $g\text{-C}_3\text{N}_4$ can improve its photocatalytic reduction activity greatly, even without the addition of extra organic additives. The composite is stable in the reaction but also protects the $g\text{-C}_3\text{N}_4$ from decomposition, which means that the RuO_2 has multiple effect on the photocatalytic ability and greatly broaden the application of $\text{RuO}_2/g\text{-C}_3\text{N}_4$ composite in wastewater treatment.

2. Experimental

2.1. Materials

Ruthenium chloride ($\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$) and melamine ($\text{C}_3\text{H}_6\text{N}_6$, 99%) were purchased from Tianjin Meiske Chemical Co., Ltd and Tianjin Zhiyuan Chemical Reagent Co., Ltd respectively. Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), methanol (CH_3OH), 1,5-diphenylcarbazine, acetone (CH_3COCH_3) and *tert*-butanol ($(\text{CH}_3)_3\text{COH}$) were all of analytical reagent grade and used as received. Ultra-pure water for preparation of any solution was obtained from the Milli-Q® system.

2.2. Syntheses of $g\text{-C}_3\text{N}_4$ and $\text{RuO}_2/g\text{-C}_3\text{N}_4$ composite

$g\text{-C}_3\text{N}_4$ was prepared by calcining melamine in a muffle furnace.¹⁵ Typically, 10 g of melamine was placed into an alumina crucible with a cover and heated from room temperature with a ramp rate of $10 \text{ }^\circ\text{C min}^{-1}$ to $520 \text{ }^\circ\text{C}$ and then sustained for 4 h in a muffle furnace. After natural cooling, product in the crucible was transferred into a mortar to be grinded into yellow $g\text{-C}_3\text{N}_4$ powder (20 min) for later use.

For the synthesis of $\text{RuO}_2/g\text{-C}_3\text{N}_4$ composite, *in situ* deposition by forced hydrolysis and oxidation of ruthenium chloride was adopted.¹¹ Briefly, 0.02 g of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was dissolved in 30 mL of $60 \text{ }^\circ\text{C}$ aqueous $g\text{-C}_3\text{N}_4$ suspension with stirring for 60 min. The obtained mixture was evaporated to get the gel. The resulting gel was dried in an electrothermal drier at $105 \text{ }^\circ\text{C}$ for 24 h and then was added into an alumina crucible with a cover and heated from room temperature with a ramp rate of $10 \text{ }^\circ\text{C min}^{-1}$ and then sustained at $520 \text{ }^\circ\text{C}$ for 30 min. Finally, $\text{RuO}_2/g\text{-C}_3\text{N}_4$ composite was obtained and labeled as $\text{RuO}_2 (x\%)/g\text{-C}_3\text{N}_4$, where “x%” denoted the mass fraction of RuO_2 in the composite.

2.3. Characterization

X-ray diffraction (XRD) patterns of the pure $g\text{-C}_3\text{N}_4$ and $\text{RuO}_2/g\text{-C}_3\text{N}_4$ composite were examined by a Rigaku D/Max-Ultima⁺ diffractometer equipped with $\text{K}\alpha$ radiation of Cu ($\lambda = 0.15418 \text{ nm}$). Transmission electron microscopy (TEM) of $g\text{-C}_3\text{N}_4$ and $\text{RuO}_2/g\text{-C}_3\text{N}_4$ were investigated operating at 200 kV through a JEOL JEM-2100 electron microscope. X-ray photoemission spectroscopy (XPS) analysis was evaluated in a Kratos-AXIS ULTRA DLD equipped with a monochromatic Al $\text{K}\alpha$ X-ray source. UV-Vis diffuse reflectance spectra of $g\text{-C}_3\text{N}_4$ and $\text{RuO}_2/g\text{-C}_3\text{N}_4$ were analyzed on a TU-1901 UV/Vis spectrophotometer with an IS19-1 integrating sphere to collect the diffusing light with BaSO_4 as the reference. FTIR spectra of the $\text{RuO}_2/g\text{-C}_3\text{N}_4$ KBr mixed disks, were recorded utilizing a Thermo Nicolet is5 (400 to 4000 cm^{-1}). PL spectra were recorded by RF-5301 PC spectrophotometer using a 150 W xenon lamp at $\lambda \sim 365 \text{ nm}$.

2.4. Photocatalytic reduction of aqueous $\text{Cr}(\text{vi})$

The photocatalytic reduction activity of $g\text{-C}_3\text{N}_4$ and $\text{RuO}_2/g\text{-C}_3\text{N}_4$ composite was tested for $\text{Cr}(\text{vi})$ reduction in an aqueous solution. In each typical run, 0.1 g of the prepared photocatalyst was added to 200 mL of 0.5 mM $\text{Cr}(\text{vi})$ solution. The mixture was magnetically stirred without illumination for 30 min to attain the adsorption-desorption equilibrium. The suspension was then illuminated by an LED lamp (40 W) surrounded outside the reactor with wavelength centered at 407.4 nm with full-width at half-maximum (FWHM) of 24.7 nm for 2 h with intensity of 25 mW cm^{-2} , where the emission spectra of the LED lamp was presented in Fig. 1.

During the illumination, 4.0 mL of the suspension was taken out from the reactor every 15 min, followed by filtration with $0.22 \text{ }\mu\text{m}$ membrane and then the filtrate was subjected to chemical analyses. $\text{Cr}(\text{vi})$ concentration in the filtrate was determined spectrophotometrically at 520 nm where 1,5-

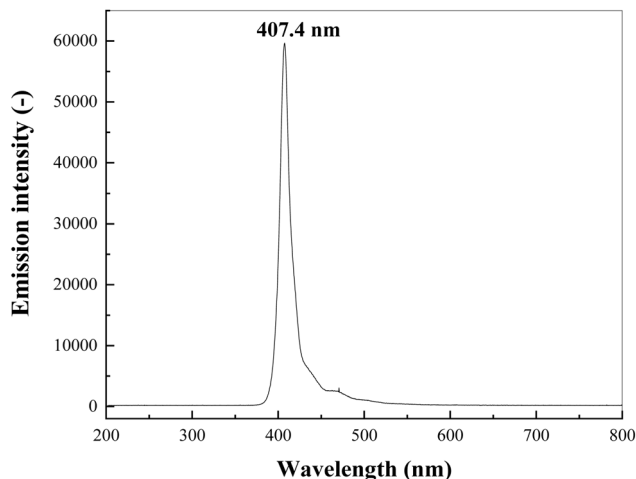


Fig. 1 Emission spectra of the LED lamp used for the photocatalytic reduction of Cr(vi).

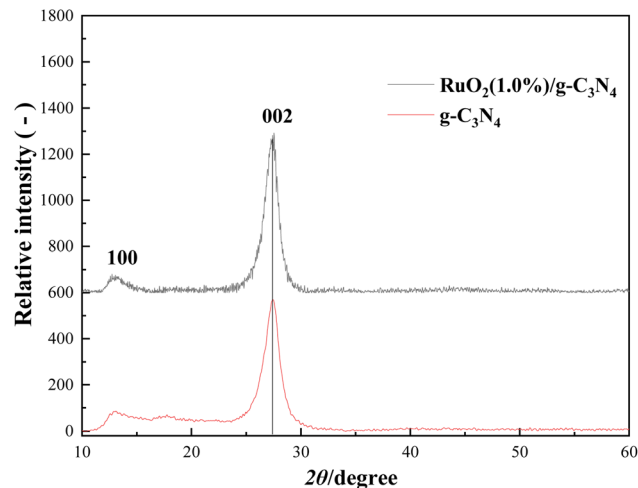


Fig. 2 XRD patterns of bare g-C₃N₄ and RuO₂ (1.0%)/g-C₃N₄ composite.

diphenylcarbazine was used as the coloration developer. The photocatalytic reduction efficiency (η) of the prepared catalysts was determined as:

$$\eta (\%) = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (1)$$

where C_0 and C_t is the Cr(vi) concentration at the beginning of illumination and illumination time t (min), respectively. Possible ruthenium leaching from the catalyst was analyzed by an inductively coupled plasma atomic emission spectrometer (ICPAES, Prodigy, Leeman Laboratories). The residue catalysts were evaluated by TOC analysis of the filtrate. Oxygen and nitrogen evolved during the photocatalytic reactions were collected by an air bag and analyzed with a gas analyzer (ST8100A, Smart Sensor Co. Ltd, China).

$$D_{002} = \frac{0.9\lambda}{B_{002} \cos \theta} \quad (2)$$

where λ is wavelength of the X-ray used for diffraction (nm), B_{002} is the FWHM of the diffraction peak at 27.42° (rad) and θ is the Bragg angle ($^\circ$). It can be calculated that the thicknesses of g-C₃N₄ and RuO₂ (1.0%)/g-C₃N₄ were about 5.9 nm and 5.7 nm, respectively. As the interlayer-stacking of g-C₃N₄ is *ca.* 0.325 nm, the sheet of the above catalysts consists of 18–19 layers of polymeric melons.¹⁵ Nanosheets usually possess high conductivity, which is beneficial to the charge transfer.¹⁶

FTIR spectra of bare g-C₃N₄ and RuO₂ (1.0%)/g-C₃N₄ composite were determined as shown in Fig. 3.

The peak at 806 cm^{-1} is originated to the breathing of the heptazine ring system. The absorption bands between 1200 and 1700 cm^{-1} indicate the presence of C–N heterocycles. The broad

3. Results and discussions

3.1. Catalyst characterizations

Fig. 2 shows the XRD patterns of the prepared bare g-C₃N₄ and RuO₂/g-C₃N₄ composite, respectively.

As shown in Fig. 2, two distinct diffraction peaks were observed for pure g-C₃N₄. The weak low-angle reflection peak at 12.74° ($d_{100} = 0.694 \text{ nm}$) was originated from in-planar repeating of tri-s-triazine (melem) unit and the peak centered at 27.42° was attributed to the periodic interlayer-stacking ($d_{002} = 0.325 \text{ nm}$) of the polymeric melon, implying successful condensation of melamine and the distinctive graphitic structure of C₃N₄ formed.⁴ XRD pattern of RuO₂ (1.0%)/g-C₃N₄ composite was quite similar to that of bare g-C₃N₄, indicating that the composition and structure of g-C₃N₄ was not altered appreciably with deposition of the RuO₂. In addition, no peaks for RuO₂ were observed, possibly because of its low contents.¹⁴

According to the Scherrer's formula, the thickness (D_{002} , nm) of bare g-C₃N₄ and RuO₂ (1.0%)/g-C₃N₄ composite can be estimated by:

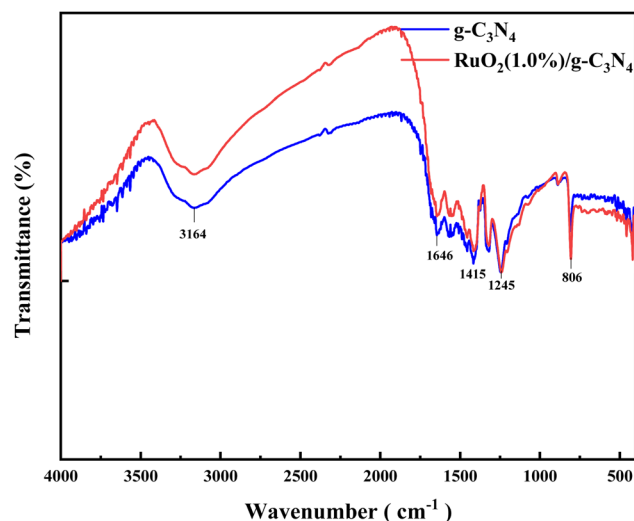


Fig. 3 FTIR spectra of bare g-C₃N₄ and RuO₂ (1.0%)/g-C₃N₄ composite.



peak at 3164 cm^{-1} was due to the stretching of the terminal N–H from the uncondensed amine.¹⁴ FTIR spectra of $\text{RuO}_2/\text{g-C}_3\text{N}_4$ composite are comparable to those of bare $\text{g-C}_3\text{N}_4$ in the lower wavenumber range. However, the peak intensities of $\text{RuO}_2/\text{g-C}_3\text{N}_4$ composite were a little weaker than those of bare $\text{g-C}_3\text{N}_4$,¹⁵ indicating loss of N–H bond during the preparation of $\text{RuO}_2/\text{g-C}_3\text{N}_4$ composite.

Representative TEM images of bare $\text{g-C}_3\text{N}_4$ and RuO_2 (1.0%)/ $\text{g-C}_3\text{N}_4$ composite were presented in Fig. 4a and b respectively.

The TEM image of pure $\text{g-C}_3\text{N}_4$ indicated a wrinkled-layer structure along with some stacking layers that have a thin sheet and a typical lamellar morphology. The TEM image of RuO_2 (1.0%)/ $\text{g-C}_3\text{N}_4$ composite revealed that small RuO_2 particles are evenly dispersed on the $\text{g-C}_3\text{N}_4$ surface. The size of RuO_2 particles is in the range 10–20 nm. HRTEM images and STEM-EDS mapping of RuO_2 (1.0%)/ $\text{g-C}_3\text{N}_4$ composite were presented in Fig. S1 and S2,[†] respectively. It can be clearly observed from Fig. S1[†] that the lattice fringe of RuO_2 was present in the sample. Fig. S2[†] indicated the distribution of Ru agrees well with those of both dark field and bright field mapping but differs slightly from that of oxygen, meaning that the oxygen not only comes from RuO_2 but also from $\text{g-C}_3\text{N}_4$ (Fig. 5). These results verified that RuO_2 is tightly contacted with $\text{g-C}_3\text{N}_4$, forming the $\text{RuO}_2/\text{g-C}_3\text{N}_4$ heterojunctions.

To further identify the chemical structure of $\text{g-C}_3\text{N}_4$ and $\text{RuO}_2/\text{g-C}_3\text{N}_4$, XPS analyses were performed and given in Fig. 5. The XPS survey spectra of $\text{g-C}_3\text{N}_4$ confirm that $\text{g-C}_3\text{N}_4$ is mainly composed of carbon and nitrogen, with a small amount of oxygen. The existence of oxygen in $\text{g-C}_3\text{N}_4$ is likely due to oxidation during the condensation polymerization. It is noteworthy that the relative intensity of nitrogen peak in $\text{g-C}_3\text{N}_4$ is higher than that in $\text{RuO}_2/\text{g-C}_3\text{N}_4$. The higher nitrogen content in $\text{g-C}_3\text{N}_4$ can be attributed to the preservation of $-\text{NH}_2$ and NH groups. The peaks located at 280.62 eV and 282.53 eV belong to $3\text{d}_{5/2}$ of RuO_2 .¹⁴ The theoretical peaks of $\text{Ru } 3\text{d}_{3/2}$ should be observed at 284.88 eV and 286.78 eV, however as they are partially overlapped with those from C 1s, making it difficult to differentiate them, which is consistent with the results of Hwang *et al.*¹⁷ RuO_2 exists in Ru^{4+} state in RuO_2 (1.0%)/ $\text{g-C}_3\text{N}_4$,

indicating the successful deposition of RuO_2 on the $\text{g-C}_3\text{N}_4$ surface.

UV-Vis absorption spectra of the pure $\text{g-C}_3\text{N}_4$ and the $\text{RuO}_2/\text{g-C}_3\text{N}_4$ composite at various concentrations were illustrated in Fig. 6. It can be observed from Fig. 6 that all of them were capable of visible light absorption. In general, absorption of the $\text{RuO}_2/\text{g-C}_3\text{N}_4$ composite was stronger than the bare $\text{g-C}_3\text{N}_4$, especially in the visible range. However, the absorption of $\text{RuO}_2/\text{g-C}_3\text{N}_4$ composite was weaker than bare $\text{g-C}_3\text{N}_4$ in the range 397–434 nm, which is different from those reported earlier.¹⁴ Outside the wavelength range, the absorption decreases with increasing RuO_2 loading.^{15,16}

3.2. Photocatalytic reduction of Cr(VI) by $\text{g-C}_3\text{N}_4$ and $\text{RuO}_2/\text{g-C}_3\text{N}_4$

Variations in Cr(VI) concentration with illumination time in the presence of 0.1 g of pure $\text{g-C}_3\text{N}_4$, pure RuO_2 and RuO_2 (1.0%)/ $\text{g-C}_3\text{N}_4$ composite were shown in Fig. 7, respectively.

As seen in Fig. 7, Cr(VI) concentration decreased smoothly with the illumination time. However, the Cr(VI) concentration decreased much more rapidly in the case of $\text{RuO}_2/\text{g-C}_3\text{N}_4$ composite than pure $\text{g-C}_3\text{N}_4$ or RuO_2 . After 90 min of illumination, the Cr(VI) removal is *ca.* 76.4% for RuO_2 (1.0%)/ $\text{g-C}_3\text{N}_4$ and 33.8% for pure $\text{g-C}_3\text{N}_4$, while it is negligible for pure RuO_2 (<5%). The Cr(VI) reduction rate (calculated at the initial stage) with RuO_2 (1.0%)/ $\text{g-C}_3\text{N}_4$ composite is 4.6 times that of the $\text{g-C}_3\text{N}_4$, which obviously confirms the promoting effect of RuO_2 in photocatalytic reduction activity of $\text{g-C}_3\text{N}_4$. It is noted that the Cr(VI) removal is much less when the combination of RuO_2 and $\text{g-C}_3\text{N}_4$ was used to reduce Cr(VI) , illustrating the successful preparation of heterojunction. In addition, Fig. 7 also showed that the Cr(VI) removal due to adsorption and the direct photolysis were both negligible.^{18,19} Therefore, the present experiments do not consider the direct photolysis of Cr(VI) in the subsequent experiments. When the illumination time is increased to 150 min, the Cr(VI) is below the detection limit (not shown in the figure) in the case of RuO_2 (1.0%)/ $\text{g-C}_3\text{N}_4$, which means that Cr(VI) can be totally reduced without any sacrificial electron donor.

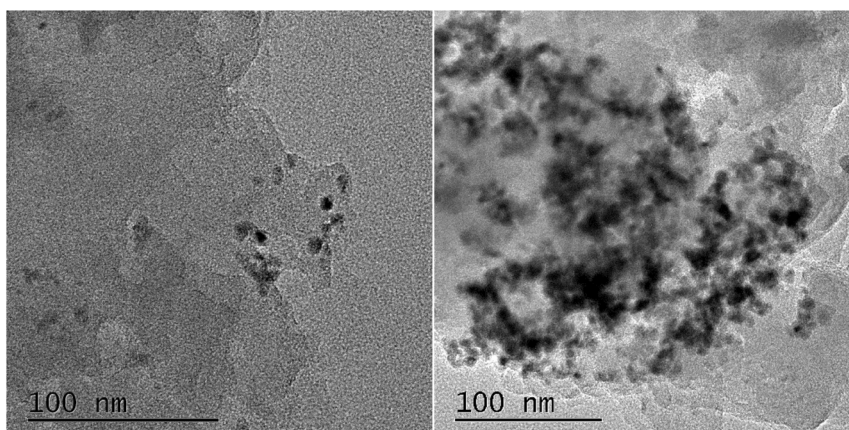


Fig. 4 TEM images of pure $\text{g-C}_3\text{N}_4$ (left) and RuO_2 (1.0%)/ $\text{g-C}_3\text{N}_4$ composite (right).

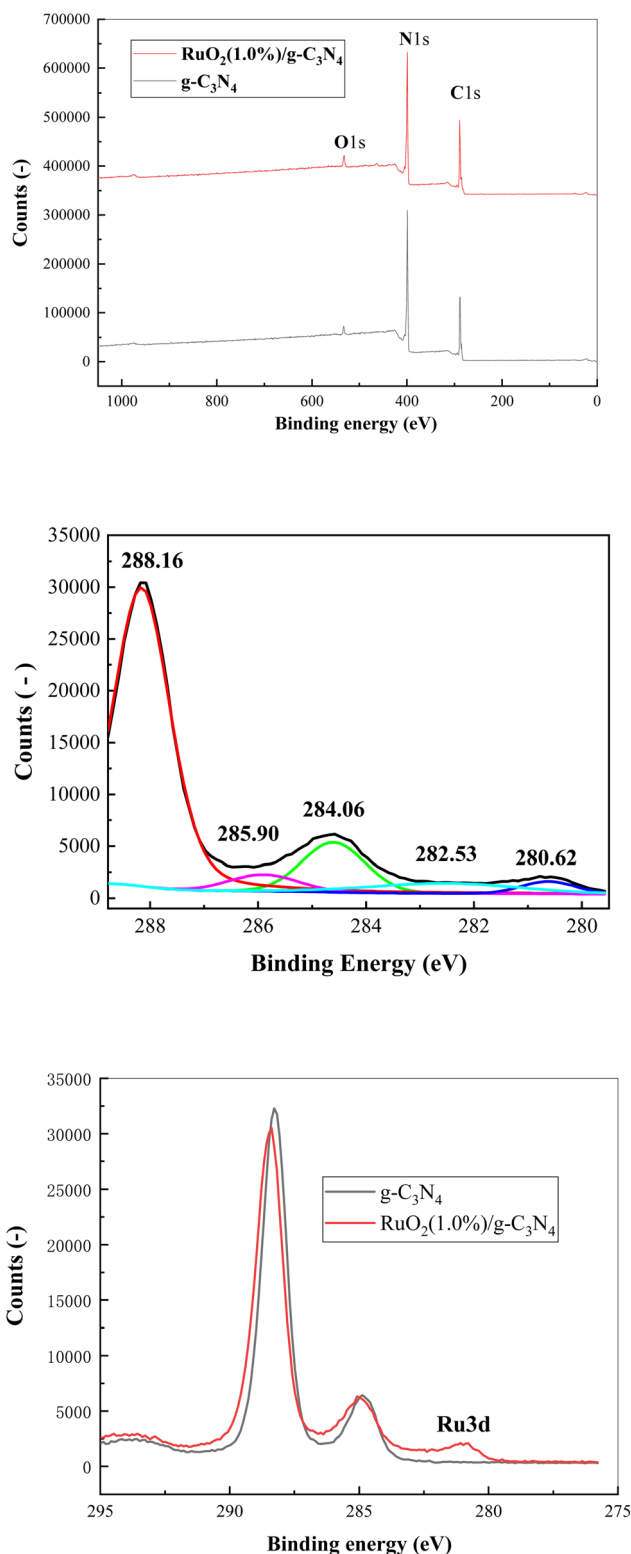


Fig. 5 XPS survey spectra of g-C₃N₄ and RuO₂ (1.0%)/g-C₃N₄ (upper), high resolution XPS of RuO₂ (1.0%)/g-C₃N₄ (278–294 eV, middle) and Ru 3d scan of RuO₂ (1.0%)/g-C₃N₄ (lower).

3.3. Effect of initial pH on Cr(vi) photocatalytic reduction

The natural pH of the Cr(vi) solution prepared by dissolving K₂Cr₂O₇ in ultrapure water is about 5.5, at which little Cr(vi)

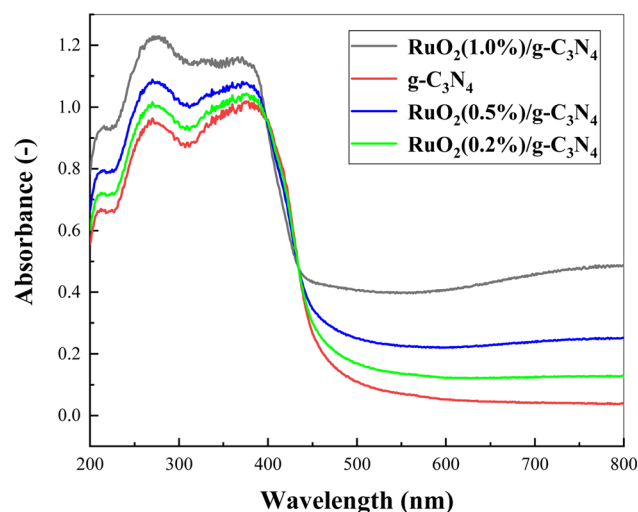


Fig. 6 UV-Vis absorption spectra of pure g-C₃N₄ and RuO₂/g-C₃N₄ composite.

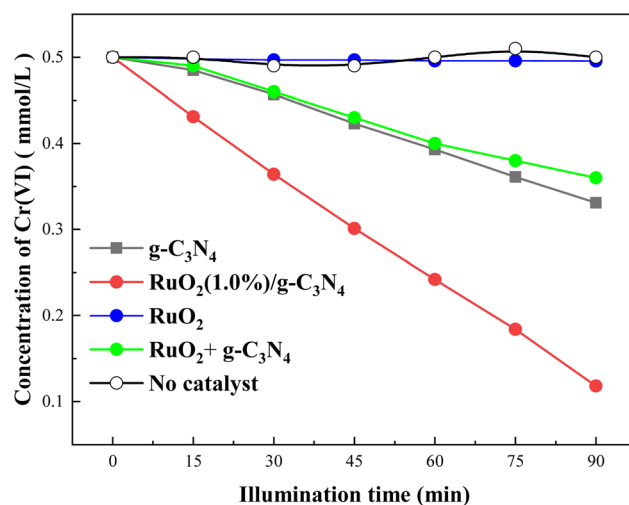


Fig. 7 Photocatalytic reductions of Cr(vi) by pure g-C₃N₄, pure RuO₂ and RuO₂ (1.0%)/g-C₃N₄ composite (solution volume, 200 mL; catalyst, 0.1 g; initial Cr(vi) concentration, 0.5 mM; initial pH, 2.3; light source, LED (410 nm, 40 W)).

reduction was observed under photocatalytic conditions. Therefore, we studied Cr(vi) reduction in acidic medium. Fig. 8 shows Cr(vi) photocatalytic reductions in the presence of 0.1 g RuO₂ (1.0%)/g-C₃N₄ composite under different initial pH (pH₀) values.

It is demonstrated from Fig. 8 that the Cr(vi) reduction proceeds more rapidly in lower pH₀. However, the trend is reversed at pH₀ 2.4. After 90 min of illumination, the Cr(vi) removal is 40% at pH₀ 3.0 and increases to 95% at pH₀ 2.4 and drops to 88% at pH₀ 2.2. The above phenomena can be explained as follows.

In the present experimental conditions, Cr(vi) exists mainly in the form of dichromate (Cr₂O₇²⁻) and hydrogen chromate (HCrO₄⁻). Their mutual relations can be described by reactions (3) and (4).^{20,21}

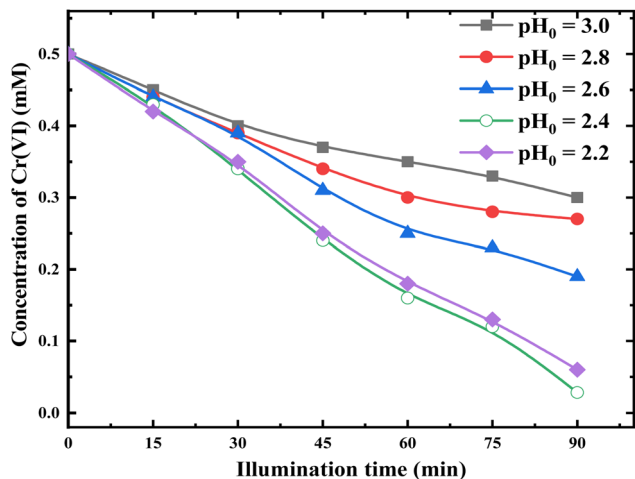
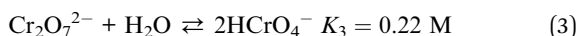
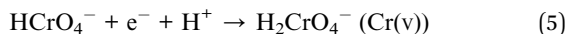


Fig. 8 Photocatalytic reduction of Cr(vi) with RuO₂ (1.0%)/g-C₃N₄ under different pH₀ values (solution volume, 200 mL; catalyst, 0.1 g; initial Cr(vi) concentration, 0.5 mM; light source, LED (410 nm, 40 W)).



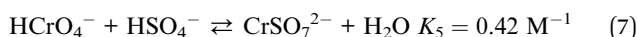
Over 96% of Cr(vi) is present in the form HCrO₄[−] and ca. 4% is in the form Cr₂O₇^{2−} within pH range 2.0–5.0 at 0.5 mM Cr(vi). As the reaction between HCrO₄[−] and e[−] is promoted by H⁺ (reaction (5)), the Cr(vi) reduction rate increases as the solution pH decreases.²¹



At high concentrations of H⁺, completing reaction between H⁺ and e[−] (reaction (6)) prevails, which leads to less e[−] available for Cr(vi) reduction. As a result, the Cr(vi) reduction rate decreased with further decreasing pH₀:⁸



On the other hand, when using sulfuric acid to lower the solution pH, hydrogen sulfate ion will be inevitably formed, and it will react with HCrO₄[−] to form CrSO₇^{2−}, which decreased the effective HCrO₄[−] concentration and the Cr(vi) reduction would slow down in highly acidic condition (eqn (7)):²¹



To further elucidate the pH role in Cr(vi) reduction, variations of solution pH during illumination in the presence and absence of Cr(vi) are presented in Fig. 9.

It can be seen from Fig. 9 that the pH of solution containing Cr(vi) increases apparently with illumination time. However, without Cr(vi), pH of the solution changes little. This can be explained by the fact that the Cr(vi) reduction consumes H⁺, as the overall Cr(vi) reduction stoichiometry can be represented by reactions (8) and (9):

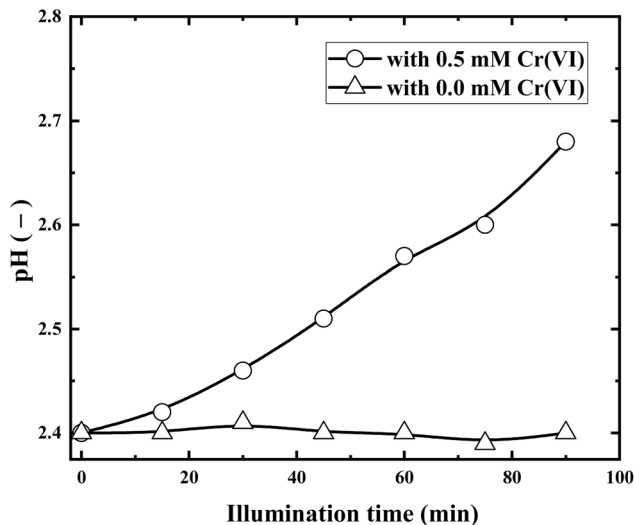
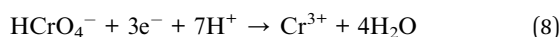
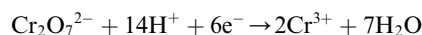


Fig. 9 Variations of pH during illumination with and without Cr(vi) (solution volume, 200 mL; RuO₂ (1.0%)/g-C₃N₄ composite, 0.1 g; initial Cr(vi) concentration, 0.5 mM; pH₀, 2.4; light source, LED (410 nm, 40 W)).



$$\Phi(V) = 1.33 + \frac{0.059}{6} \lg \frac{[\text{Cr}_2\text{O}_7^{2-}]}{[\text{Cr}^{3+}]^2} - 0.138\text{pH} \quad (9)$$

Reactions (8) and (9) need the involvement of H⁺ from the dynamic aspect. As shown in Fig. 8, Cr(vi) reduction proceeded fastest at pH₀ 2.4, and pH₀ 2.4 is chosen as the optimum pH in the following investigations.

3.4. Effect of electron and hole scavengers on Cr(vi) reduction

In order to further improve the reduction efficiency of Cr(vi), small amount of organic additives was added to the solution to explore whether the organic solvent will inhibit or promote the reduction of Cr(vi). Fig. 10 shows the Cr(vi) concentration variations in the presence of methanol and acetone, respectively.

It is clearly shown from Fig. 10 that acetone suppresses while methanol promotes the Cr(vi) reduction dramatically. Cr(vi) removal rate was more than doubled and three quarters decreased in the presences of 0.05 M methanol and acetone, respectively. The above phenomena can be explained as follows.

Upon illumination, e[−] and h⁺ were simultaneously produced. The h⁺ can re-oxidize the Cr(III) back to Cr(vi) as the oxidation potential of h⁺ (ca. 1.5 V) is 0.2 V higher than that of Cr(vi) (ca. 1.3 V, reaction (9)). In addition, the h⁺ can recombine with e[−] to decrease the number of e[−] available for Cr(vi) reduction. The most desirable way is to convert the h⁺ into organic radicals possessing reduction potentials in the range of −1 to −2 V and are thus capable of reducing Cr(vi) to lower oxidation states, which not only inhibits the re-oxidation of Cr(III) and increases the concentration of e[−], but also converts the oxidizing h⁺ to the reducing ones:²²



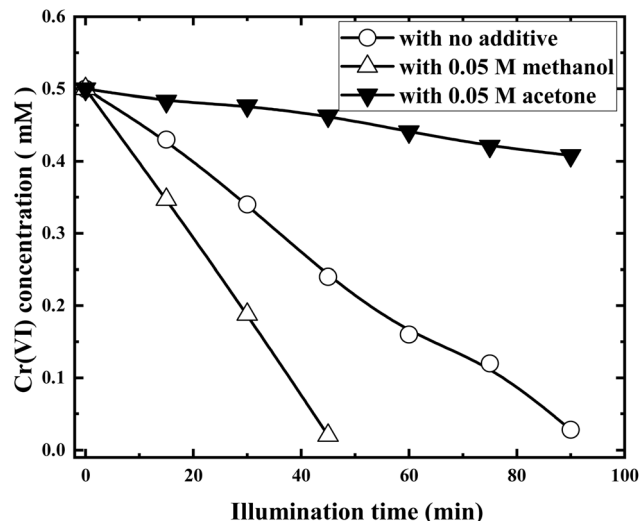


Fig. 10 Photocatalytic reductions of Cr(vi) with RuO₂ (1.0%)/g-C₃N₄ in the presence of methanol and acetone (solution volume, 200 mL; RuO₂ (1.0%)/g-C₃N₄ composite, 0.1 g; initial Cr(vi) concentration, 0.5 mM; pH₀, 2.4; light source, LED (410 nm, 40 W)).

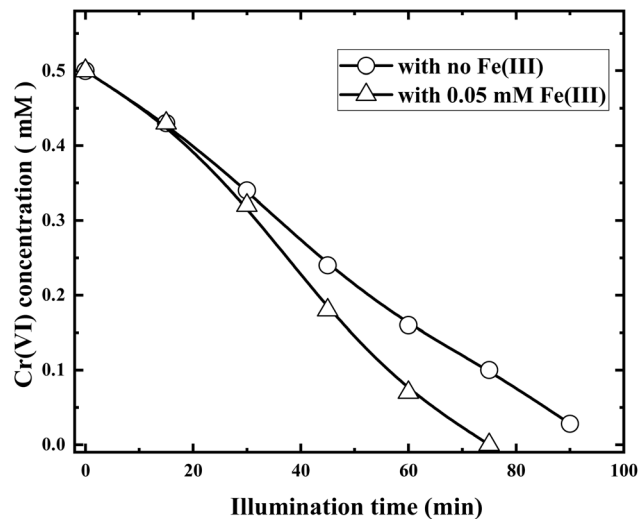


Fig. 11 Photocatalytic reductions of Cr(vi) with RuO₂ (1.0%)/g-C₃N₄ in the presence and absence of 0.05 mM Fe(III) (solution volume, 200 mL; RuO₂ (1.0%)/g-C₃N₄ composite, 0.1 g; initial Cr(vi) concentration, 0.5 mM; pH₀, 2.4; light source, LED (410 nm, 40 W)).



As reaction (10) goes, more e[−] are available for Cr(vi) reduction. Consequently, the Cr(vi) reduction rate increased in the presence of methanol. On the other hand, as acetone is very stable and cannot be oxidized by the h⁺ but can react with e[−] as the following:^{23–25}

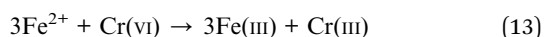


As reaction (11) involved in the process, less e[−] is available for Cr(vi) reduction and the Cr(vi) reduction rate decreased in the presence of acetone.

3.5. Effect of Fe(III) on Cr(vi) photocatalytic reduction

Fe(III) is an ubiquitous and nontoxic elements in earth, and investigate its action on photocatalytic reduction of Cr(vi) is of great significance. Fig. 11 compares the Cr(vi) concentration variations in the presence and absence of 0.05 mM Fe(III), respectively.

It can be clearly observed from Fig. 11 that at the initial stage (<20 min), Fe(III) displayed little effect on the reduction of Cr(vi). However, the effect becomes apparent at the later stage. The Cr(vi) removal of Cr(vi) at 75 min can reach 100% with 0.05 mM Fe(III), where it is only 80% without it. When Fe(III) was added, it was reduced to Fe²⁺ by the e[−], and then the resulting Fe²⁺ reduces Cr(vi) to Cr(III) and next circle begins, which means that Fe(III) can be used as a co-catalyzer.³



It is noted that as isopropanol ultimately generated by the reaction (11) cannot reduce Cr(vi), the reduction of Cr(vi) is suppressed. Therefore, although both Fe(III) and acetone belong to electron scavengers, they showed opposing effects on Cr(vi) reductions.

3.6. Mechanism of photocatalytic reduction of Cr(vi) by RuO₂/g-C₃N₄

To elucidate the mechanism in Cr(vi) reduction, evolution of UV-Vis absorption spectra of the solution during photocatalytic reduction are presented in Fig. 12.

As shown in Fig. 12, the peak height at about 350 nm, which is characteristic of the absorption band of Cr(vi) species,²¹ together with that at 285 nm, gradually decreases with the illumination time. In general, Cr(vi) would undergo a series of intermediate processes before being finally converted to Cr(III). As shown in Fig. 12, no new bands appeared during the reduction, indicating that the possible Cr(IV) and Cr(IV) were too short-lived to be detected by the present technique.^{26,27} In the experiment, color of the solution changed from orange to light yellow and finally to colorless, which was verified by the decrease in absorption band from 400 to 450 nm.

According to ref. 14, g-C₃N₄ and RuO₂ are both n-type semiconductors. The values of *E*_{CB} and *E*_{VB} for pure g-C₃N₄ are −1.125 eV and +1.585 eV,²⁸ respectively. *E*_{CB} and *E*_{VB} of RuO₂ can be calculated according to the formula (14) and (15):²⁹

$$E_{\text{CB}} = E_{\text{VB}} - E_{\text{g}} \quad (14)$$

$$E_{\text{VB}} = X - E_{\text{e}} + 0.5E_{\text{g}} \quad (15)$$

where *X* is the absolute electronegativity of RuO₂ (6.35 eV),²⁷ *E*_e is the vacuum electron level corresponding to the standard hydrogen (4.5 eV). *E*_g of RuO₂ was determined to be 2.32 eV.¹⁴ It can be calculated that *E*_{CB} and *E*_{CB} of RuO₂ are 3.01 eV and



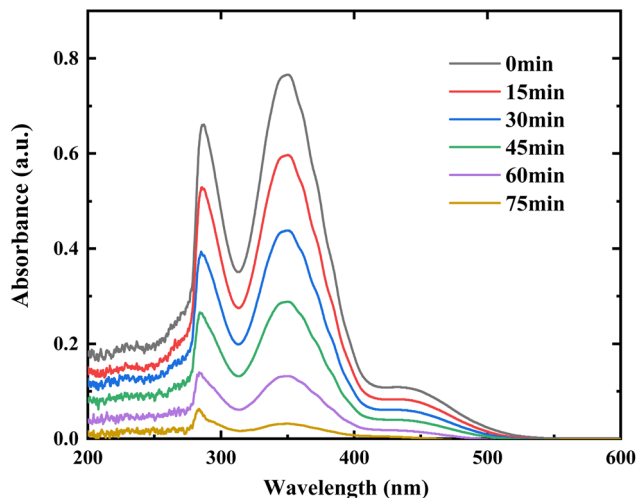


Fig. 12 Evolution of UV-Vis absorption spectra of the solution during photocatalytic reduction of Cr(vi) (solution volume, 200 mL; RuO₂ (1.0%)/g-C₃N₄ composite, 0.1 g; initial Cr(vi) concentration, 0.5 mM; pH₀, 2.4; light source, LED (410 nm, 40 W)).

0.69 eV respectively. Because the Fermi level (E_F) of n-type semiconductor is very close to its E_{CB} , the Fermi levels of g-C₃N₄ and RuO₂ are about -1.125 eV and -0.69 eV. As the E_F of g-C₃N₄ is lower than that of RuO₂, when g-C₃N₄ and RuO₂ contact each other, the electrons on g-C₃N₄ automatically flow to the conduction band of RuO₂, leaving positive charges, thus forming a built-in electric field between RuO₂ and g-C₃N₄ (g-C₃N₄ pointing to RuO₂). When g-C₃N₄ absorbs visible light, electron hole pairs ($e^- + h^+$) were generated. Under the action of built-in electric field, the e^- move towards the solution and are captured by Cr(vi) in the solution, resulting in the reduction of Cr(vi) and suppress the electron hole recombination. Such explanation was documented by Fig. 13.

It can be shown in Fig. 13 that the emission intensity of RuO₂/g-C₃N₄ was much lower than g-C₃N₄, showing the suppressed recombination of photo-carriers.

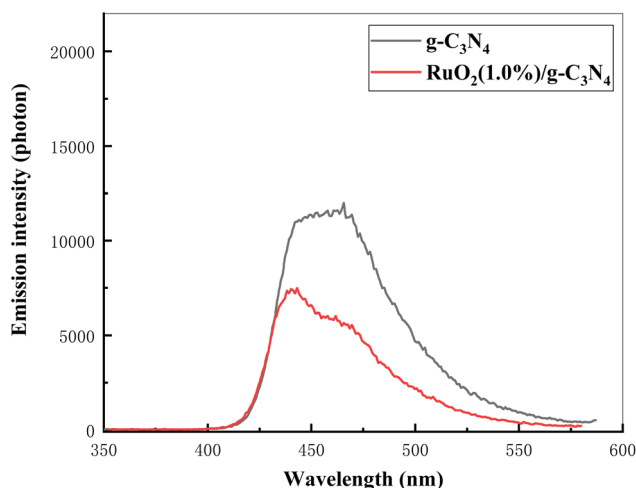


Fig. 13 Fluorescence emission spectra of g-C₃N₄ and RuO₂ (1.0%)/g-C₃N₄.

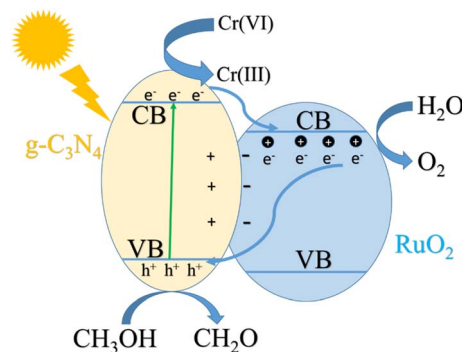
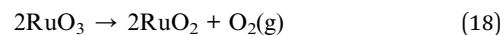
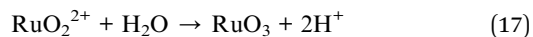
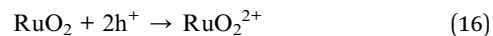


Fig. 14 Mechanism of photocatalytic reduction of Cr(vi) by RuO₂/g-C₃N₄.

In addition, the absorption of RuO₂/g-C₃N₄ is slightly weaker than pure g-C₃N₄ near 410 nm as shown in Fig. 6, indicating that the role of RuO₂ belongs to the enhancement of charge separation rather than the enhancement of light absorption, which also indicates that the mechanism speculation is reasonable. The process can be demonstrated in Fig. 14:

On the other hand, the loaded RuO₂ is able to take up the h^+ from g-C₃N₄, exhibiting functionality as efficient O₂ evolution sites. The reaction sequence for O₂ evolution can be expressed as follows:³⁰



In order to confirm the above assumptions, time courses of O₂ and N₂ evolution during the illumination were examined and the results are presented in Fig. 15.

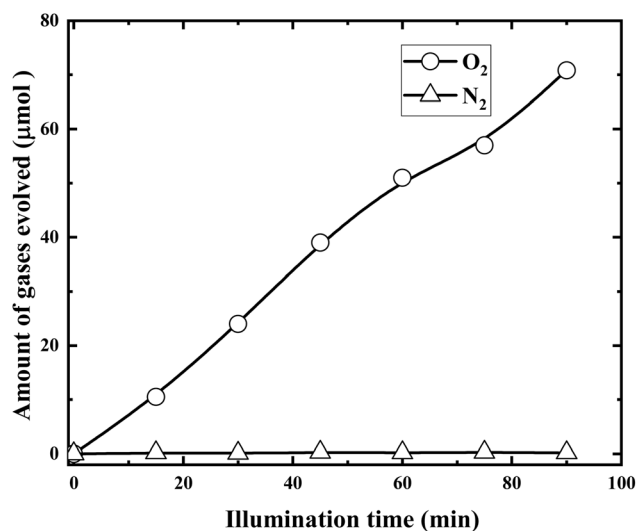


Fig. 15 Time courses of O₂ and N₂ evolution during the illumination (solution volume, 200 mL; RuO₂ (1.0%)/g-C₃N₄ composite, 0.1 g; initial Cr(vi) concentration, 0.5 mM; pH₀, 2.4; light source, LED (410 nm, 40 W)).

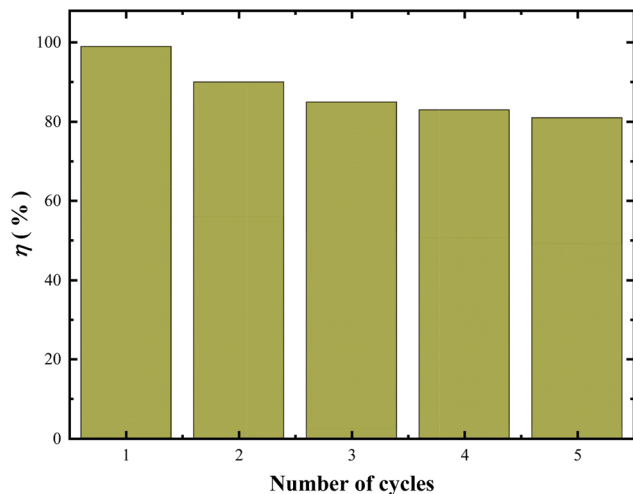


Fig. 16 Cycle stability test of RuO₂ (1.0%)/g-C₃N₄ composite (solution volume, 200 mL; RuO₂ (1.0%)/g-C₃N₄ composite, 0.1 g; initial Cr(vi) concentration, 0.5 mM; pH₀, 2.4; light source, LED (410 nm, 40 W)).

It is demonstrated from Fig. 15 that RuO₂ (1.0%)/g-C₃N₄ composite exhibited high activity for O₂ evolution with no N₂ evolution. This further indicated that RuO₂ loading not only boost the separation of the charge carriers but also protects the decomposition of g-C₃N₄.

3.7. Recyclability and stability test

To evaluate the reusability and stability of the samples, five successive cycles of experiments were performed for Cr(vi) reduction. After completion of each reduction reaction (90 min), the catalyst in the solution was filtered with 0.22 μm filter membrane, washed with ethanol and water for 3 times respectively, put it into the oven, and bake at 60 °C for 24 hours for the next experiment. Namely, the used sample after each cycle was collected through centrifugation and rinsed three times with ethanol and ultrapure water. Subsequently, the washed powder was dried for 8 h (60 °C) to conduct next photocatalytic cycle. Moreover, the XRD of the samples after six cycles was characterized and compared to that of the fresh samples. A total of 5 cycles were carried out. The reduction ratio of Cr(vi) at each final cycle is shown in Fig. 16.

It can be seen from Fig. 16 that the Cr(vi) reduction ratio with recycled RuO₂ (1.0%)/g-C₃N₄ still maintains more than 80% after five repeated experiments, indicating that the photocatalytic stability of RuO₂ (1.0%)/g-C₃N₄ is still very good and can be reused. ICP-AES test showed no leaching of Ru from RuO₂ (1.0%)/g-C₃N₄. In addition, TOC analysis also showed no apparent carbon and nitrogen increase in the solution, indicating that RuO₂ (1.0%)/g-C₃N₄ is very stable during the photocatalysis.

4. Conclusions

RuO₂/g-C₃N₄ composite can be easily prepared by *in situ* forced hydrolysis and oxidation and is able to catalytically photo-

reduce Cr(vi) effectively even in the absence of sacrificial electron donor. The optimum initial pH for the reduction is 2.4. Acetone inhibits the reduction and methanol promotes the reduction. In addition, a small amount of Fe(III) catalyzes the reduction of Cr(vi), especially in the later stage.

The deposited RuO₂ particles not only functionalized as an effective charge separator for Cr(vi) reduction, but also protects the g-C₃N₄ from self-decomposition through catalyzing O₂ evolution, which is indispensable for the reduction without presence of electron donors. Little leaching and residue remained in the solution further proves its potential application in real wastewater treatment process.

Data availability

The authors confirm that the data supporting the findings of this study are available within the article.

Author contributions

Conceptualization, Y. Liu; methodology, Y. Liu; software, Y. Liu; validation, Y. Liu; formal analysis, Y. Liu; investigation, X. Du and Z. Huang; resources, Y. Liu; data curation, Y. Liu; writing—original draft preparation, Y. Liu; writing—review and editing, Y. Liu; visualization, Y. Liu; supervision, Y. Liu; project administration, Y. Liu; funding acquisition, Y. Liu. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

The authors declare no conflict of interest.

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