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# Photocatalytic reduction of aqueous chromium(vi) by RuO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> composite under visible light irradiation†

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Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) 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-C<sub>3</sub>N<sub>4</sub> composite (RuO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>) was prepared by forced oxidative hydrolysis of ruthenium(III) chloride on the surface of g-C<sub>3</sub>N<sub>4</sub> 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 RuO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> than in pure g-C<sub>3</sub>N<sub>4</sub>. 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-C<sub>3</sub>N<sub>4</sub> and 0.1 RuO<sub>2</sub> (1.0 wt%)/g-C<sub>3</sub>N<sub>4</sub>, 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 RuO<sub>2</sub> not only boosts the charge separation but also protects the g-C<sub>3</sub>N<sub>4</sub> from decomposition by its extraordinary catalytic action for OER. The used RuO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> was separated from the solution by microfiltration, with little leaching and residue remaining in the filtrate. The reclaimed RuO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> 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.<sup>1</sup> 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.<sup>2,3</sup> Therefore, developing atom-economic processes for Cr(vi) reduction is in great need.

Recently, graphite carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) 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.<sup>4</sup> In theory, g-C<sub>3</sub>N<sub>4</sub> 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-C<sub>3</sub>N<sub>4</sub> exhibits low photocatalytic activity due to its high recombination speed of photo-generated charge carriers and its low conductivity. Constructing g-C<sub>3</sub>N<sub>4</sub>-based composites is considered as a promising strategy in promoting photocatalytic reductions. Wang *et al.*<sup>5</sup> found that the 1D black phosphorus-tubular g-C<sub>3</sub>N<sub>4</sub> can remove 94.1% of Cr(vi) with a rate constant of 0.0404 min<sup>-1</sup>. Ren *et al.*<sup>6</sup> constructed a g-C<sub>3</sub>N<sub>4</sub>/NH<sub>2</sub>-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 NH<sub>2</sub>-UiO-66(Zr) under visible light irradiation. Eslamlu *et al.*<sup>7</sup> reported that Sb<sub>2</sub>MoO<sub>6</sub> coupled with g-C<sub>3</sub>N<sub>4</sub> nano-tubes showed Cr(vi) reduction efficiency of 22 times higher than the bare g-C<sub>3</sub>N<sub>4</sub>. When MoS<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> was grafted with cyclodextrins, Cr(vi) reduction in the simulated agricultural wastewater was remarkably enhanced.<sup>8</sup> Mohamed *et al.*<sup>9</sup> synthesized mesoporous BiVO<sub>4</sub>/2D-g-C<sub>3</sub>N<sub>4</sub> 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-C<sub>3</sub>N<sub>4</sub> 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 ( $\text{O}_2$ ), ( $2\text{H}_2\text{O} - 4e^- \rightarrow \text{O}_2 + 4\text{H}^+$ ,  $\phi_{\text{O}_2/\text{H}_2\text{O}} = 1.23 \text{ V}$ ), it is not positive enough to oxidize water to  $\text{O}_2$  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.<sup>10</sup> Although  $g\text{-C}_3\text{N}_4$  can be protected by using sacrificial electron donor (usually organic additives such as alcohols<sup>10</sup>), 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 ( $\text{RuO}_2$ ) is with no doubt an appealing material for forming heterostructures due to its superior chemical stability,<sup>11,12</sup> metallic conductivity [ $2.0\text{--}2.5 \times 10^4 \text{ S cm}^{-1}$ ], and high catalytic activity for the OER<sup>13</sup> for its optimal oxygen binding energy. In addition, the precursor of  $\text{RuO}_2$  is relatively lower cost as compared to other precious metals.  $\text{RuO}_2$  nanoparticles-accommodated  $g\text{-C}_3\text{N}_4$  for photocatalytic oxidation of trichloroethylene has been reported.<sup>14</sup> However, its action in promoting photocatalytic reductions is rarely reported. In this report, effect and mechanism of  $\text{RuO}_2$  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  $\text{RuO}_2$  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  $\text{RuO}_2$  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 ( $\text{CH}_3\text{OH}$ ), 1,5-diphenylcarbazine, acetone ( $\text{CH}_3\text{COCH}_3$ ) 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.<sup>15</sup> 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.<sup>11</sup> 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  $\text{RuO}_2$  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<sup>+</sup> diffractometer equipped with  $K\alpha$  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  $K\alpha$  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  $\text{BaSO}_4$  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  $4000 \text{ cm}^{-1}$ ). 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  $25 \text{ mW cm}^{-2}$ , 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-



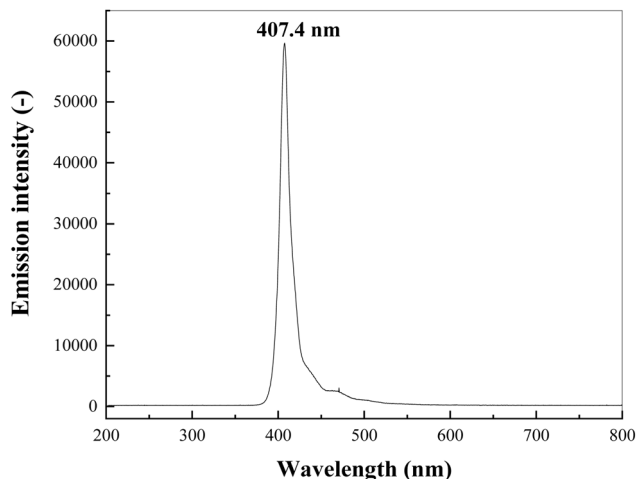


Fig. 1 Emission spectra of the LED lamp used for the photocatalytic reduction of Cr(VI).

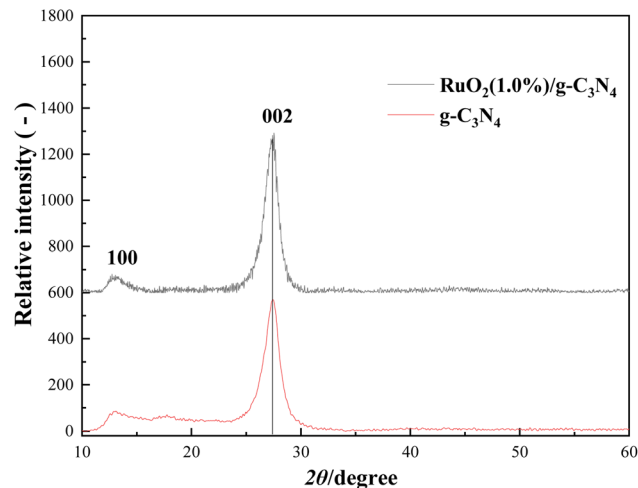


Fig. 2 XRD patterns of bare g-C<sub>3</sub>N<sub>4</sub> and RuO<sub>2</sub> (1.0%)/g-C<sub>3</sub>N<sub>4</sub> composite.

diphenylcarbazine was used as the coloration developer. The photocatalytic reduction efficiency ( $\eta$ ) 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).

### 3. Results and discussions

#### 3.1. Catalyst characterizations

Fig. 2 shows the XRD patterns of the prepared bare g-C<sub>3</sub>N<sub>4</sub> and RuO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> composite, respectively.

As shown in Fig. 2, two distinct diffraction peaks were observed for pure g-C<sub>3</sub>N<sub>4</sub>. The weak low-angle reflection peak at 12.74° ( $d_{100} = 0.694$  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 ( $d_{002} = 0.325$  nm) of the polymeric melon, implying successful condensation of melamine and the distinctive graphitic structure of C<sub>3</sub>N<sub>4</sub> formed.<sup>4</sup> XRD pattern of RuO<sub>2</sub> (1.0%)/g-C<sub>3</sub>N<sub>4</sub> composite was quite similar to that of bare g-C<sub>3</sub>N<sub>4</sub>, indicating that the composition and structure of g-C<sub>3</sub>N<sub>4</sub> was not altered appreciably with deposition of the RuO<sub>2</sub>. In addition, no peaks for RuO<sub>2</sub> were observed, possibly because of its low contents.<sup>14</sup>

According to the Scherrer's formula, the thickness ( $D_{002}$ , nm) of bare g-C<sub>3</sub>N<sub>4</sub> and RuO<sub>2</sub> (1.0%)/g-C<sub>3</sub>N<sub>4</sub> composite can be estimated by:

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

where  $\lambda$  is wavelength of the X-ray used for diffraction (nm),  $B_{002}$  is the FWHM of the diffraction peak at 27.42° (rad) and  $\theta$  is the Bragg angle (°). It can be calculated that the thicknesses of g-C<sub>3</sub>N<sub>4</sub> and RuO<sub>2</sub> (1.0%)/g-C<sub>3</sub>N<sub>4</sub> were about 5.9 nm and 5.7 nm, respectively. As the interlayer-stacking of g-C<sub>3</sub>N<sub>4</sub> is *ca.* 0.325 nm, the sheet of the above catalysts consists of 18–19 layers of polymeric melons.<sup>15</sup> Nanosheets usually possess high conductivity, which is beneficial to the charge transfer.<sup>16</sup>

FTIR spectra of bare g-C<sub>3</sub>N<sub>4</sub> and RuO<sub>2</sub> (1.0%)/g-C<sub>3</sub>N<sub>4</sub> composite were determined as shown in Fig. 3.

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

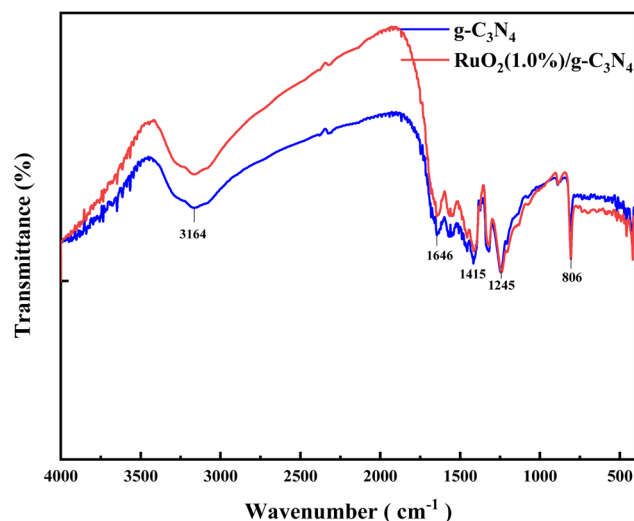


Fig. 3 FTIR spectra of bare g-C<sub>3</sub>N<sub>4</sub> and RuO<sub>2</sub> (1.0%)/g-C<sub>3</sub>N<sub>4</sub> composite.



peak at  $3164\text{ cm}^{-1}$  was due to the stretching of the terminal N–H from the uncondensed amine.<sup>14</sup> 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  $\text{g-C}_3\text{N}_4$ ,<sup>15</sup> 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  $\text{RuO}_2$  (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  $\text{RuO}_2$  (1.0%)/ $\text{g-C}_3\text{N}_4$  composite revealed that small  $\text{RuO}_2$  particles are evenly dispersed on the  $\text{g-C}_3\text{N}_4$  surface. The size of  $\text{RuO}_2$  particles is in the range 10–20 nm. HRTEM images and STEM-EDS mapping of  $\text{RuO}_2$  (1.0%)/ $\text{g-C}_3\text{N}_4$  composite were presented in Fig. S1 and S2,<sup>†</sup> respectively. It can be clearly observed from Fig. S1<sup>†</sup> that the lattice fringe of  $\text{RuO}_2$  was present in the sample. Fig. S2<sup>†</sup> 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  $\text{RuO}_2$  but also from  $\text{g-C}_3\text{N}_4$  (Fig. 5). These results verified that  $\text{RuO}_2$  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  $\text{NH}$  groups. The peaks located at 280.62 eV and 282.53 eV belong to  $3d_{5/2}$  of  $\text{RuO}_2$ .<sup>14</sup> The theoretical peaks of  $\text{Ru } 3d_{3/2}$  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.*<sup>17</sup>  $\text{RuO}_2$  exists in  $\text{Ru}^{4+}$  state in  $\text{RuO}_2$  (1.0%)/ $\text{g-C}_3\text{N}_4$ ,

indicating the successful deposition of  $\text{RuO}_2$  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.<sup>14</sup> Outside the wavelength range, the absorption decreases with increasing  $\text{RuO}_2$  loading.<sup>15,16</sup>

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

Variations in  $\text{Cr}(\text{VI})$  concentration with illumination time in the presence of 0.1 g of pure  $\text{g-C}_3\text{N}_4$ , pure  $\text{RuO}_2$  and  $\text{RuO}_2$  (1.0%)/ $\text{g-C}_3\text{N}_4$  composite were shown in Fig. 7, respectively.

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

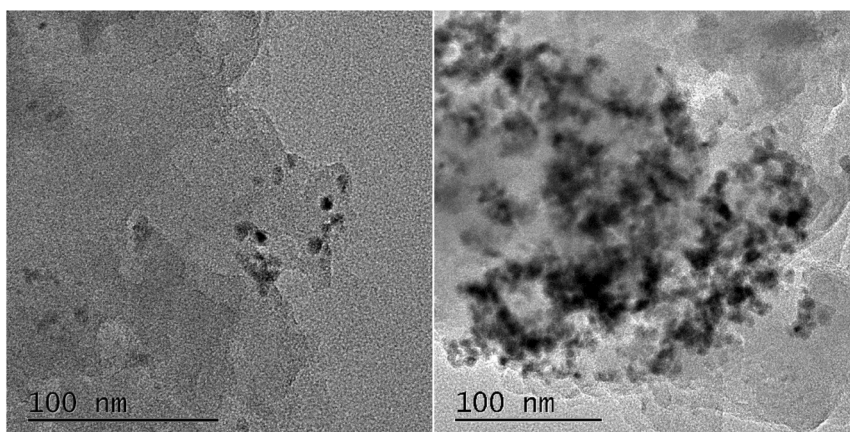


Fig. 4 TEM images of pure  $\text{g-C}_3\text{N}_4$  (left) and  $\text{RuO}_2$  (1.0%)/ $\text{g-C}_3\text{N}_4$  composite (right).



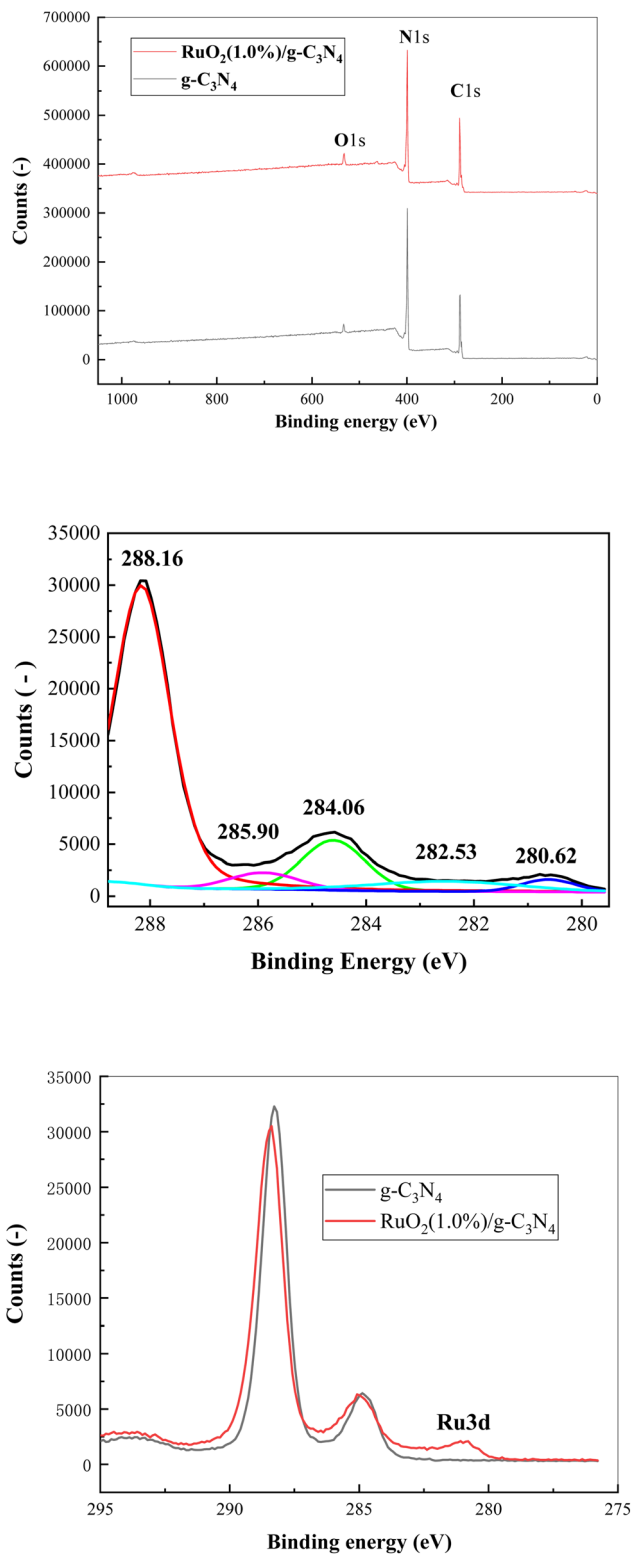


Fig. 5 XPS survey spectra of  $g\text{-C}_3\text{N}_4$  and  $\text{RuO}_2$  (1.0%)/ $g\text{-C}_3\text{N}_4$  (upper), high resolution XPS of  $\text{RuO}_2$  (1.0%)/ $g\text{-C}_3\text{N}_4$  (278–294 eV, middle) and Ru 3d scan of  $\text{RuO}_2$  (1.0%)/ $g\text{-C}_3\text{N}_4$  (lower).

### 3.3. Effect of initial pH on $\text{Cr}(\text{vi})$ photocatalytic reduction

The natural pH of the  $\text{Cr}(\text{vi})$  solution prepared by dissolving  $\text{K}_2\text{Cr}_2\text{O}_7$  in ultrapure water is about 5.5, at which little  $\text{Cr}(\text{vi})$

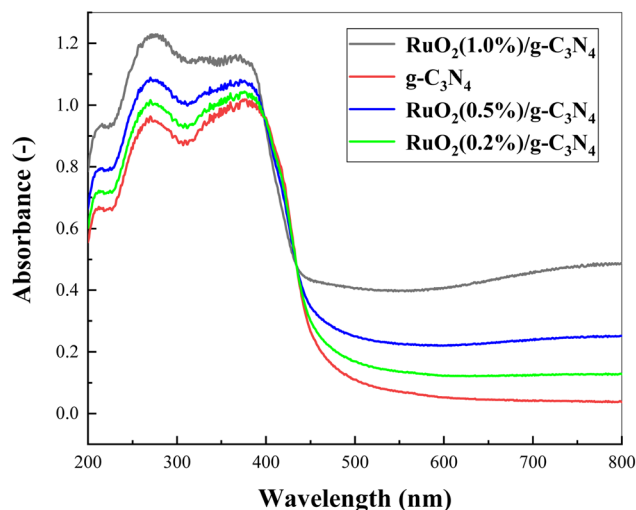


Fig. 6 UV-Vis absorption spectra of pure  $g\text{-C}_3\text{N}_4$  and  $\text{RuO}_2/g\text{-C}_3\text{N}_4$  composite.

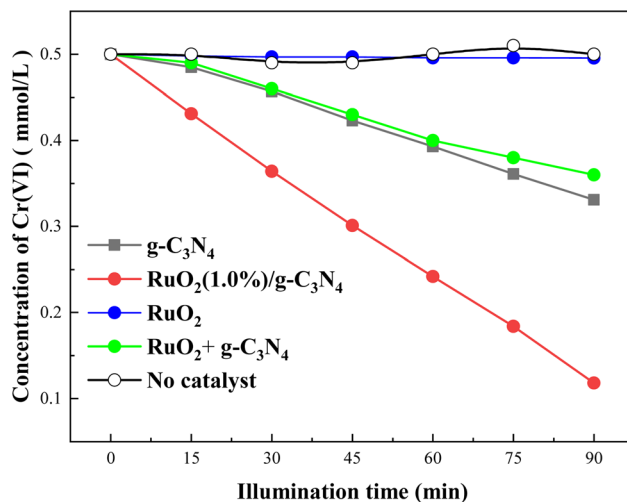


Fig. 7 Photocatalytic reductions of  $\text{Cr}(\text{vi})$  by pure  $g\text{-C}_3\text{N}_4$ , pure  $\text{RuO}_2$  and  $\text{RuO}_2$  (1.0%)/ $g\text{-C}_3\text{N}_4$  composite (solution volume, 200 mL; catalyst, 0.1 g; initial  $\text{Cr}(\text{vi})$  concentration, 0.5 mM; initial pH, 2.3; light source, LED (410 nm, 40 W)).

reduction was observed under photocatalytic conditions. Therefore, we studied  $\text{Cr}(\text{vi})$  reduction in acidic medium. Fig. 8 shows  $\text{Cr}(\text{vi})$  photocatalytic reductions in the presence of 0.1 g  $\text{RuO}_2$  (1.0%)/ $g\text{-C}_3\text{N}_4$  composite under different initial pH ( $\text{pH}_0$ ) values.

It is demonstrated from Fig. 8 that the  $\text{Cr}(\text{vi})$  reduction proceeds more rapidly in lower  $\text{pH}_0$ . However, the trend is reversed at  $\text{pH}_0$  2.4. After 90 min of illumination, the  $\text{Cr}(\text{vi})$  removal is 40% at  $\text{pH}_0$  3.0 and increases to 95% at  $\text{pH}_0$  2.4 and drops to 88% at  $\text{pH}_0$  2.2. The above phenomena can be explained as follows.

In the present experimental conditions,  $\text{Cr}(\text{vi})$  exists mainly in the form of dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) and hydrogen chromate ( $\text{HCrO}_4^-$ ). Their mutual relations can be described by reactions (3) and (4).<sup>20,21</sup>



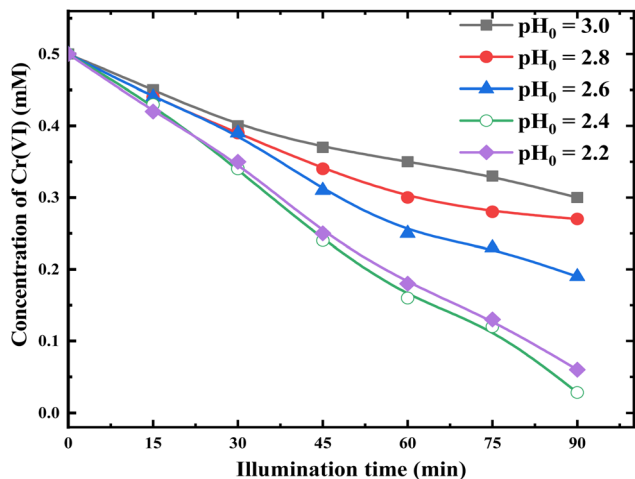
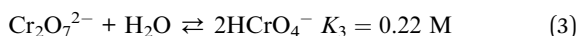
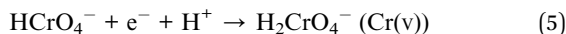


Fig. 8 Photocatalytic reduction of Cr(vi) with RuO<sub>2</sub> (1.0%)/g-C<sub>3</sub>N<sub>4</sub> under different pH<sub>0</sub> values (solution volume, 200 mL; catalyst, 0.1 g; initial Cr(vi) concentration, 0.5 mM; light source, LED (410 nm, 40 W)).



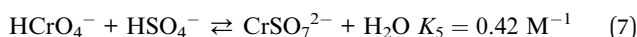
Over 96% of Cr(vi) is present in the form HCrO<sub>4</sub><sup>-</sup> and ca. 4% is in the form Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> within pH range 2.0–5.0 at 0.5 mM Cr(vi). As the reaction between HCrO<sub>4</sub><sup>-</sup> and e<sup>-</sup> is promoted by H<sup>+</sup> (reaction (5)), the Cr(vi) reduction rate increases as the solution pH decreases.<sup>21</sup>



At high concentrations of H<sup>+</sup>, completing reaction between H<sup>+</sup> and e<sup>-</sup> (reaction (6)) prevails, which leads to less e<sup>-</sup> available for Cr(vi) reduction. As a result, the Cr(vi) reduction rate decreased with further decreasing pH<sub>0</sub>:<sup>8</sup>



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 HCrO<sub>4</sub><sup>-</sup> to form CrSO<sub>7</sub><sup>2-</sup>, which decreased the effective HCrO<sub>4</sub><sup>-</sup> concentration and the Cr(vi) reduction would slow down in highly acidic condition (eqn (7)):<sup>21</sup>



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<sup>+</sup>, as the overall Cr(vi) reduction stoichiometry can be represented by reactions (8) and (9):

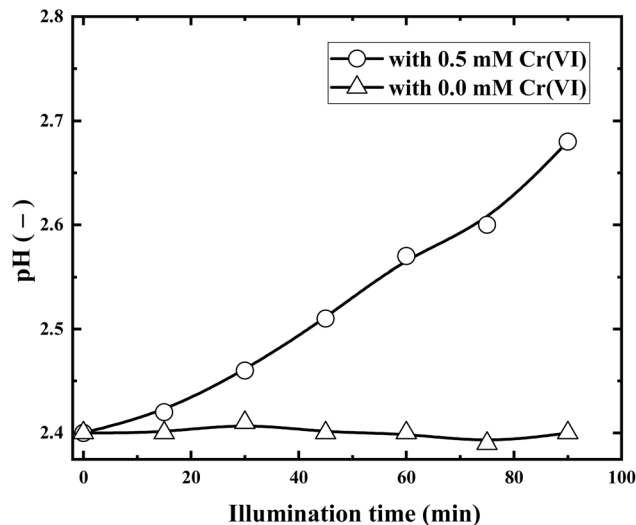
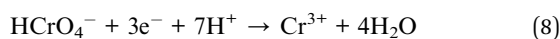
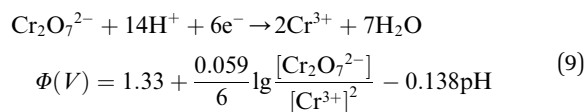


Fig. 9 Variations of pH during illumination with and without Cr(vi) (solution volume, 200 mL; RuO<sub>2</sub> (1.0%)/g-C<sub>3</sub>N<sub>4</sub> composite, 0.1 g; initial Cr(vi) concentration, 0.5 mM; pH<sub>0</sub>, 2.4; light source, LED (410 nm, 40 W)).



Reactions (8) and (9) need the involvement of H<sup>+</sup> from the dynamic aspect. As shown in Fig. 8, Cr(vi) reduction proceeded fastest at pH<sub>0</sub> 2.4, and pH<sub>0</sub> 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<sup>-</sup> and h<sup>+</sup> were simultaneously produced. The h<sup>+</sup> can re-oxidize the Cr(III) back to Cr(vi) as the oxidation potential of h<sup>+</sup> (ca. 1.5 V) is 0.2 V higher than that of Cr(vi) (ca. 1.3 V, reaction (9)). In addition, the h<sup>+</sup> can recombine with e<sup>-</sup> to decrease the number of e<sup>-</sup> available for Cr(vi) reduction. The most desirable way is to convert the h<sup>+</sup> 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<sup>-</sup>, but also converts the oxidizing h<sup>+</sup> to the reducing ones:<sup>22</sup>



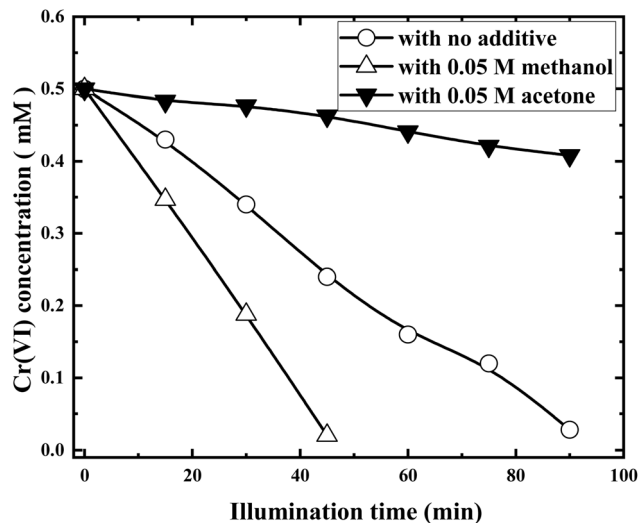


Fig. 10 Photocatalytic reductions of Cr(vi) with RuO<sub>2</sub> (1.0%)/g-C<sub>3</sub>N<sub>4</sub> in the presence of methanol and acetone (solution volume, 200 mL; RuO<sub>2</sub> (1.0%)/g-C<sub>3</sub>N<sub>4</sub> composite, 0.1 g; initial Cr(vi) concentration, 0.5 mM; pH<sub>0</sub>, 2.4; light source, LED (410 nm, 40 W)).

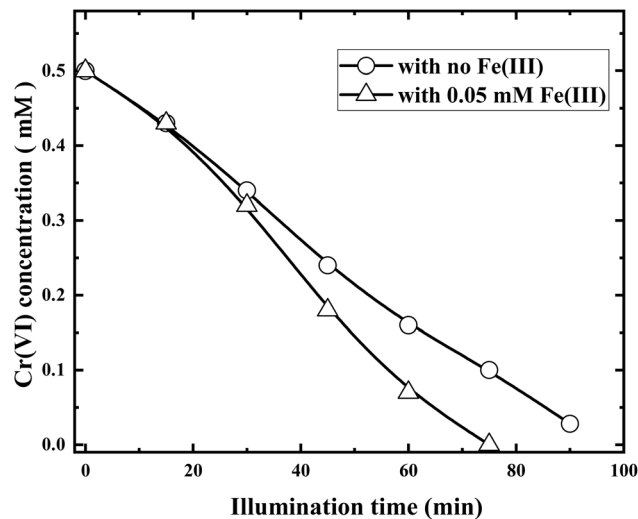
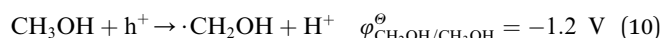


Fig. 11 Photocatalytic reductions of Cr(vi) with RuO<sub>2</sub> (1.0%)/g-C<sub>3</sub>N<sub>4</sub> in the presence and absence of 0.05 mM Fe(III) (solution volume, 200 mL; RuO<sub>2</sub> (1.0%)/g-C<sub>3</sub>N<sub>4</sub> composite, 0.1 g; initial Cr(vi) concentration, 0.5 mM; pH<sub>0</sub>, 2.4; light source, LED (410 nm, 40 W)).



As reaction (10) goes, more e<sup>-</sup> 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<sup>+</sup> but can react with e<sup>-</sup> as the following:<sup>23-25</sup>

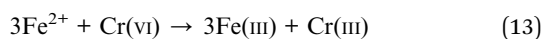


As reaction (11) involved in the process, less e<sup>-</sup> is available for Cr(vi) reduction and the Cr(vi) reduction rate decreased in the presence of acetone.

### 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 Fe<sup>2+</sup> by the e<sup>-</sup>, and then the resulting Fe<sup>2+</sup> reduces Cr(vi) to Cr(III) and next circle begins, which means that Fe(III) can be used as a co-catalyzer.<sup>3</sup>



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 RuO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>

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,<sup>21</sup> 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.<sup>26,27</sup> 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-C<sub>3</sub>N<sub>4</sub> and RuO<sub>2</sub> are both n-type semiconductors. The values of E<sub>CB</sub> and E<sub>VB</sub> for pure g-C<sub>3</sub>N<sub>4</sub> are -1.125 eV and +1.585 eV,<sup>28</sup> respectively. E<sub>CB</sub> and E<sub>VB</sub> of RuO<sub>2</sub> can be calculated according to the formula (14) and (15):<sup>29</sup>

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

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

where X is the absolute electronegativity of RuO<sub>2</sub> (6.35 eV),<sup>27</sup> E<sub>e</sub> is the vacuum electron level corresponding to the standard hydrogen (4.5 eV). E<sub>g</sub> of RuO<sub>2</sub> was determined to be 2.32 eV.<sup>14</sup> It can be calculated that E<sub>CB</sub> and E<sub>CB</sub> of RuO<sub>2</sub> are 3.01 eV and



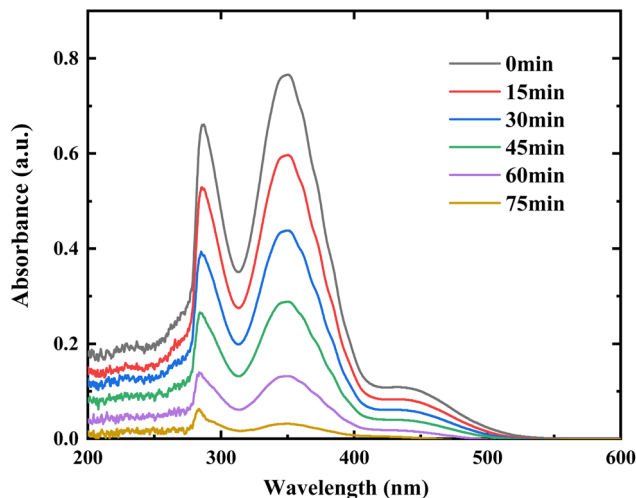


Fig. 12 Evolution of UV-Vis absorption spectra of the solution during photocatalytic reduction of Cr(vi) (solution volume, 200 mL; RuO<sub>2</sub> (1.0%)/g-C<sub>3</sub>N<sub>4</sub> composite, 0.1 g; initial Cr(vi) concentration, 0.5 mM; pH<sub>0</sub>, 2.4; light source, LED (410 nm, 40 W)).

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-C<sub>3</sub>N<sub>4</sub> and RuO<sub>2</sub> are about  $-1.125$  eV and  $-0.69$  eV. As the  $E_F$  of g-C<sub>3</sub>N<sub>4</sub> is lower than that of RuO<sub>2</sub>, when g-C<sub>3</sub>N<sub>4</sub> and RuO<sub>2</sub> contact each other, the electrons on g-C<sub>3</sub>N<sub>4</sub> automatically flow to the conduction band of RuO<sub>2</sub>, leaving positive charges, thus forming a built-in electric field between RuO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> (g-C<sub>3</sub>N<sub>4</sub> pointing to RuO<sub>2</sub>). When g-C<sub>3</sub>N<sub>4</sub> 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 RuO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> was much lower than g-C<sub>3</sub>N<sub>4</sub>, showing the suppressed recombination of photo-carriers.

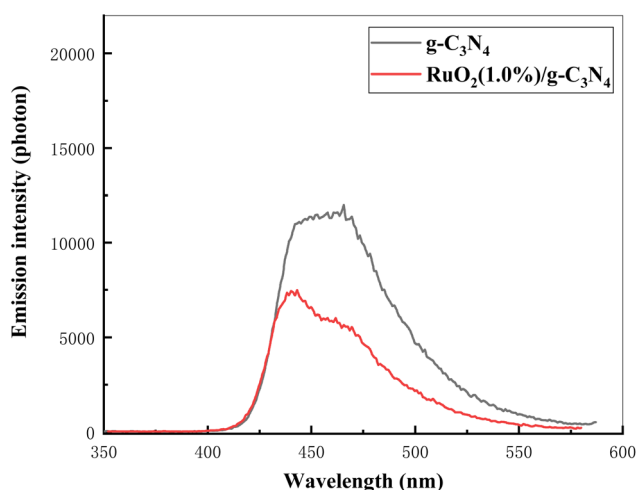


Fig. 13 Fluorescence emission spectra of g-C<sub>3</sub>N<sub>4</sub> and RuO<sub>2</sub> (1.0%)/g-C<sub>3</sub>N<sub>4</sub>.

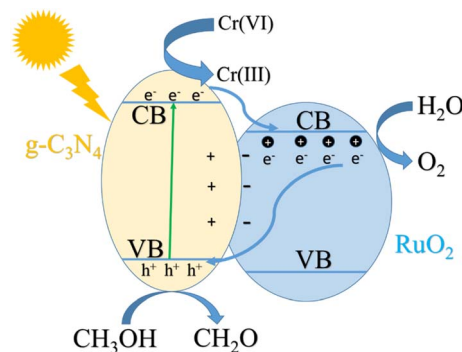
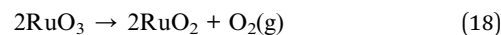
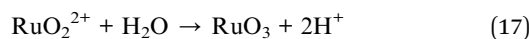
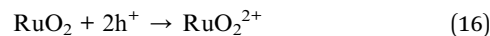


Fig. 14 Mechanism of photocatalytic reduction of Cr(vi) by RuO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>.

In addition, the absorption of RuO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> is slightly weaker than pure g-C<sub>3</sub>N<sub>4</sub> near 410 nm as shown in Fig. 6, indicating that the role of RuO<sub>2</sub> 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 RuO<sub>2</sub> is able to take up the  $h^+$  from g-C<sub>3</sub>N<sub>4</sub>, exhibiting functionality as efficient O<sub>2</sub> evolution sites. The reaction sequence for O<sub>2</sub> evolution can be expressed as follows:<sup>30</sup>



In order to confirm the above assumptions, time courses of O<sub>2</sub> and N<sub>2</sub> evolution during the illumination were examined and the results are presented in Fig. 15.

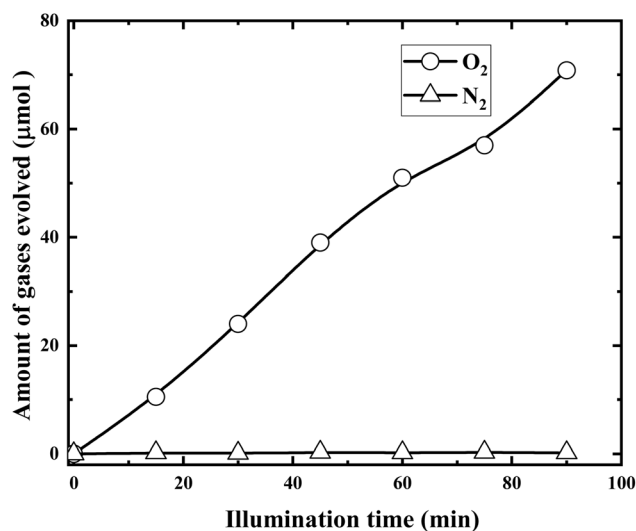
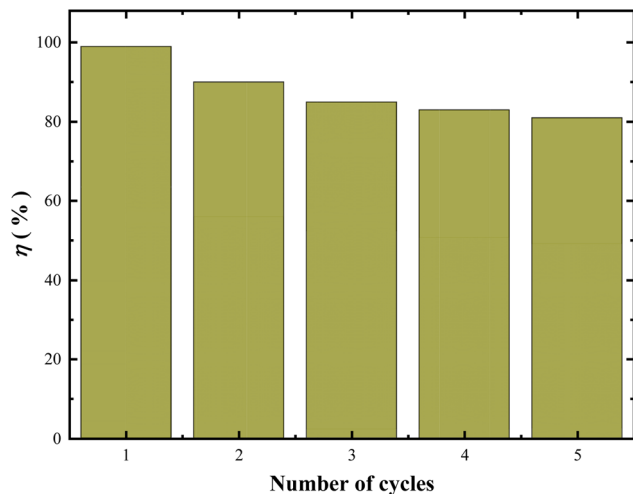


Fig. 15 Time courses of O<sub>2</sub> and N<sub>2</sub> evolution during the illumination (solution volume, 200 mL; RuO<sub>2</sub> (1.0%)/g-C<sub>3</sub>N<sub>4</sub> composite, 0.1 g; initial Cr(vi) concentration, 0.5 mM; pH<sub>0</sub>, 2.4; light source, LED (410 nm, 40 W)).



**Fig. 16** Cycle stability test of RuO<sub>2</sub> (1.0%)/g-C<sub>3</sub>N<sub>4</sub> composite (solution volume, 200 mL; RuO<sub>2</sub> (1.0%)/g-C<sub>3</sub>N<sub>4</sub> composite, 0.1 g; initial Cr(VI) concentration, 0.5 mM; pH<sub>0</sub>, 2.4; light source, LED (410 nm, 40 W)).

It is demonstrated from Fig. 15 that RuO<sub>2</sub> (1.0%)/g-C<sub>3</sub>N<sub>4</sub> composite exhibited high activity for O<sub>2</sub> evolution with no N<sub>2</sub> evolution. This further indicated that RuO<sub>2</sub> loading not only boost the separation of the charge carriers but also protects the decomposition of g-C<sub>3</sub>N<sub>4</sub>.

### 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 RuO<sub>2</sub> (1.0%)/g-C<sub>3</sub>N<sub>4</sub> still maintains more than 80% after five repeated experiments, indicating that the photocatalytic stability of RuO<sub>2</sub> (1.0%)/g-C<sub>3</sub>N<sub>4</sub> is still very good and can be reused. ICP-AES test showed no leaching of Ru from RuO<sub>2</sub> (1.0%)/g-C<sub>3</sub>N<sub>4</sub>. In addition, TOC analysis also showed no apparent carbon and nitrogen increase in the solution, indicating that RuO<sub>2</sub> (1.0%)/g-C<sub>3</sub>N<sub>4</sub> is very stable during the photocatalysis.

## 4. Conclusions

RuO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> 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 RuO<sub>2</sub> particles not only functionalized as an effective charge separator for Cr(VI) reduction, but also protects the g-C<sub>3</sub>N<sub>4</sub> from self-decomposition through catalyzing O<sub>2</sub> 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.

## Acknowledgements

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