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# Facile synthesis of g-C<sub>3</sub>N<sub>4</sub> nanosheets loaded with WO<sub>3</sub> nanoparticles with enhanced photocatalytic performance under visible light irradiation†

Jie Meng,  Jingyuan Pei, Zefang He, Shiyuan Wu, Qingyun Lin, Xiao Wei,\* Jixue Li and Ze Zhang

Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) nanosheets loaded with WO<sub>3</sub> nanoparticles were prepared *via* heat treatment of g-C<sub>3</sub>N<sub>4</sub> together with WO<sub>x</sub>-EDA nanobelts. The thermal treatment temperature and WO<sub>x</sub>-EDA precursor play the key role in enhancing the interaction between WO<sub>3</sub> nanoparticles and g-C<sub>3</sub>N<sub>4</sub> nanosheets, because the temperature of thermal decomposition of WO<sub>x</sub>-EDA (~400 °C) is close to the thermal exfoliation temperature of g-C<sub>3</sub>N<sub>4</sub>. The structure evolution and promotion effect of the nanocomposites in photocatalytic performance were well studied. It is found that WO<sub>3</sub> nanoparticles uniformly dispersed on the surface of the g-C<sub>3</sub>N<sub>4</sub> nanosheets, and the close integration of WO<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> lead to the high photocatalytic activity in the degradation of RhB under visible light irradiation. Meanwhile, a larger specific area and increase of visible light absorption are also of benefit to speed up the degradation of organic dye. Also, the mechanism of the photocatalytic reaction and its reutilization properties were investigated.

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## Introduction

Photocatalysts have been receiving much attention as a promising material in recent years due to their applications in alleviating global environmental pollution and the energy crisis, such as waste pollutant degradation,<sup>1,2</sup> water splitting<sup>3</sup> and CO<sub>2</sub> reduction.<sup>4</sup> However, there are some major challenges that hamper the requirements of their practical applications, for instance, a high recombination rate of photo-excited charge carriers, low solar energy conversion efficiency resulting from a wide band gap, and other restrictions.<sup>5,6</sup> Accordingly, it is essential to develop a high performance photocatalyst that could not only enhance the separation and transportation efficiency of electron-hole pairs but also improve the light absorption properties under solar radiation.

Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>), a great potential material for photocatalytic reaction first reported by Wang *et al.* in early 2009,<sup>7</sup> has received intensive attention on account of its unique electronic and optical properties, such as visible light response, good reduction ability, easy synthesis, and high stabilities. What's more, the band gap of g-C<sub>3</sub>N<sub>4</sub> is around 2.7 eV, which could absorb visible light up to 460 nm correspondingly.<sup>8,9</sup> The

conduction band edge potential of g-C<sub>3</sub>N<sub>4</sub> is more negative (about -1.12 eV *vs.* NHE), therefore, photo-induced electrons would have high reduction capacity.<sup>10,11</sup> Nevertheless, it has been concluded that the low photocatalytic activities of g-C<sub>3</sub>N<sub>4</sub> are mainly attributed to high recombination of photo-generated charge carriers and low specific surface area.<sup>12-14</sup> Many efforts have been made to overcome these bottlenecks. It was reported that ultrasonic vibration,<sup>15</sup> thermal exfoliation<sup>16</sup> and hydro-thermal treatment<sup>17</sup> could be used to change the BET surface area. Meanwhile, doping,<sup>18</sup> noble metal loading<sup>19</sup> and coupling with other semiconductors<sup>8</sup> are also effective methods to achieve the separation of carriers and then further increase the photocatalytic performance under visible light illumination. Among all the strategies, coupling with other semiconductors is an efficient attempt to solve above two questions due to the suitable band position and enhanced hole-electron pairs transfer between the two semiconductors by appropriate combination style. Especially, g-C<sub>3</sub>N<sub>4</sub> nanosheets which show distinct physical and chemical features with larger specific area and outstanding electronic mobility,<sup>20,21</sup> are considered to be an appropriate candidate to couple with other semiconductors to form high-performance photocatalysts. As a matter of fact, many progresses have been made on g-C<sub>3</sub>N<sub>4</sub> nanosheets based composites,<sup>22</sup> such as TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>,<sup>23</sup> ZnO/g-C<sub>3</sub>N<sub>4</sub>,<sup>24</sup> Bi<sub>2</sub>WO<sub>6</sub>/g-C<sub>3</sub>N<sub>4</sub>,<sup>25</sup> MoS<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>,<sup>26</sup> *etc.* These composite systems have deservedly achieved enhanced photocatalytic performance which is generally ascribed to the improved reaction sites, charge separation and migration processes. Nevertheless, it is necessary for a practical photocatalyst to be provided with

Center of Electron Microscopy, State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou, 310027, P. R. China. E-mail: [mseweixiao@zju.edu.cn](mailto:mseweixiao@zju.edu.cn); Fax: +86 571 87952797; Tel: +86 571 87952797

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stable crystal structure, narrow band gap, low material cost, and easy preparation. So there is still a long way to seek a proper material coupling with  $g\text{-C}_3\text{N}_4$  nanosheets to form highly active composite photocatalysts.

Alternatively, tungsten(vi) oxide ( $\text{WO}_3$ ) which is deemed as a promising material of photocatalysts<sup>27</sup> with a narrow band gap of about 2.7 eV, is a potential candidate to form composites with  $g\text{-C}_3\text{N}_4$  nanosheets to get excellent photocatalytic performance. Meanwhile, its stable crystal structure, resistance to photo-corrosion, and inexpensiveness are all important issues for the practical application.<sup>28</sup> The VB edge potential of  $\text{WO}_3$  is more positive, implying that it has a better oxidation capability in photocatalytic activities. However, the CB position of  $\text{WO}_3$  limits its photocatalytic reaction under visible light illumination since this CB level is not beneficial to the single-electron reaction of  $\text{O}_2$ .<sup>29,30</sup> It could decrease the recombination of hole–electron pairs and make up the defects of the conduction band by synergistic effect of two semiconductors when  $\text{WO}_3$  coupling with  $g\text{-C}_3\text{N}_4$ .<sup>30</sup> Therefore,  $\text{WO}_3$  is a proper candidate to form composites with  $g\text{-C}_3\text{N}_4$  to achieve excellent photocatalytic performance under visible light irradiation. However, for photocatalytic composites, the separation efficiency of photo-induced carriers is not only related to appropriate electronic structures, but most importantly determined by effective combination with better contact, that is still a challenge for most semiconductor composites. Many attempts have been applied to form  $\text{WO}_3/g\text{-C}_3\text{N}_4$  composites to achieve the above goals, but there are no reports about using the  $\text{WO}_x\text{-EDA}$  nanobelts, as the precursor of  $\text{WO}_3$  to synthesize  $\text{WO}_3/g\text{-C}_3\text{N}_4$  composites with a suitable combination method which could not only enlarge the specific surface area but also restrain the recombination of photo-excited carriers.<sup>29–33</sup> The  $\text{WO}_x\text{-EDA}$  nanobelts was synthesized by solvothermally treating  $\text{WO}_3$  in ethanediamine (EDA) following a so-called solvent-coordination molecular template (SCMT) mechanism.<sup>34</sup>

In this paper, we prepared the  $\text{WO}_3/g\text{-C}_3\text{N}_4$  composites through heat treatment of  $\text{WO}_x\text{-EDA}$  and  $g\text{-C}_3\text{N}_4$ . Since the decomposition temperature (around 400 °C) of  $\text{WO}_x\text{-EDA}$  is close to thermal exfoliation temperature of  $g\text{-C}_3\text{N}_4$ , both of two reaction processes conduct simultaneous, which was found to facilitate  $\text{WO}_3$  nanoparticles to uniformly disperse on  $g\text{-C}_3\text{N}_4$  nanosheets. The photocatalytic performance of the  $\text{WO}_3/g\text{-C}_3\text{N}_4$  composites was evaluated by the degradation of Rhodamine B under visible light illumination. The decrease of recombination of photo-generated hole–electron pairs evaluated by photoluminescence (PL) spectra, larger specific surface area calculated by BET method and enhanced visible light absorption characterized by diffuse reflectance spectrum (DRS) are main reasons to increase photocatalytic activity. Based on the systematically characterizations of the photocatalysts, a possible mechanism for the enhanced photocatalytic performance of  $\text{WO}_3/g\text{-C}_3\text{N}_4$  composites is proposed.

## Experimental section

### Materials and synthesis

All of the chemical reagents used in this experiment were of analytical stage without further purification.

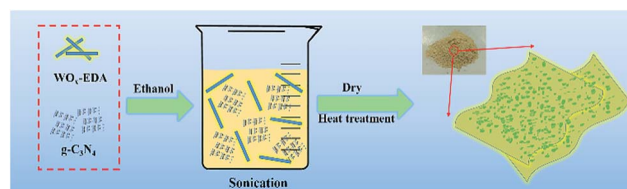
**Pristine  $g\text{-C}_3\text{N}_4$  synthesis.** Pristine  $g\text{-C}_3\text{N}_4$  was prepared by directly heating melamine in muffle furnace.<sup>35</sup> In a typical procedure, melamine powder was put into alumina crucible with a cover, then heated to 550 °C for 4 h at a heating rate of 3.5 °C  $\text{min}^{-1}$ ; after cooling to room temperature in the way of furnace cooling, the yellow powder was ground and collected for subsequent use.

**$\text{WO}_x\text{-EDA}$  synthesis.** The  $\text{WO}_x\text{-EDA}$  was synthesized by solvothermal treatment of  $m\text{-WO}_3$  (monoclinic  $\text{WO}_3$ ), and  $m\text{-WO}_3$  was prepared by hydrothermal route. Firstly, 10 mmol  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  was dissolved in distilled water (40 mL), then 5 mL of  $\text{HNO}_3$  was added into aqueous solution under stirring at room temperature. After stirring for about 1 h, the mixture was transferred into a 50 mL Teflon-lined stainless-steel autoclave, heated to 200 °C for 48 h and then cooled to room temperature naturally. The yellow product, named  $m\text{-WO}_3$ , was washed, dried, ground and collected for next use. Secondly,  $\text{WO}_x\text{-EDA}$  was prepared according to previous report similarly.<sup>34</sup> Typically, 1 g of as-prepared  $m\text{-WO}_3$  powder and 40 mL of ethanediamine (EDA) were mixed under stirring for 60 min. The mixture was heated to 200 °C for 12 h by solvothermal treatment. After cooling to room temperature, the product was collected after washed, dried and ground for subsequent use, namely  $\text{WO}_x\text{-EDA}$  (Fig. S1†).

**$\text{WO}_3/g\text{-C}_3\text{N}_4$  composites synthesis.** Typically, 0.4 g  $\text{WO}_x\text{-EDA}$  and 1 g pristine  $g\text{-C}_3\text{N}_4$  were mixed in ethanol solution under ultrasonication for 1 h, and then dried at 80 °C for about 12 h (Fig. S2†). The obtained mixture was annealed to 400 °C for 2 h, and the final sample is called WECN40. According to different mass ratio between  $\text{WO}_x\text{-EDA}$  and  $g\text{-C}_3\text{N}_4$ , the samples are named CN or  $g\text{-C}_3\text{N}_4$ , WECN20, WECN40, WECN60, WECN80 and  $\text{WO}_3$  (Scheme 1). All above six samples were prepared using the same treating process as same as WECN40.

### Characterization

The crystalline phases of the as-synthesized samples were characterized by X-ray diffraction (XRD, PANalytical X'Pert PRO) with  $\text{Cu K}\alpha$  radiation with  $2\theta$  from 10–80°. The morphology and composition of the as-obtained samples were investigated by field emission scanning electron microscopy (SEM, Hitachi SU-70) and transmission electron microscopy (TEM, FEI Tecnai G<sup>2</sup> F20 S-TWIN) equipped with an energy dispersive X-ray spectrometer (EDX). Specific surface area ( $S_{\text{BET}}$ ) was determined with a surface area analyser (Quantachrome AUTOSORB-IQ2-MP) by the BET method. Diffuse reflectance spectra (DRS) was measured by a UV-vis spectrophotometer (Persee TU-1900)



Scheme 1 Schematic presentation of the synthesis process of  $\text{WO}_3/g\text{-C}_3\text{N}_4$  composites.



equipped with an integrating sphere unit using BaSO<sub>4</sub> as the reflectance standard. Photoluminescence (PL) spectra was obtained by fluorescence spectrometer (Edinburgh instruments FLS920). Fourier transform infrared (FTIR) spectra of samples was recorded using a Nicolet Avatar-370 spectrometer at room temperature. The surface electronic states of the samples were measured by X-ray photoelectron spectroscopy (XPS, Escalab 250Xi). The concentration of phenol was characterized by liquid chromatograph (C18-ODS column).

### Photocatalytic measurement

The photocatalytic performances of the WO<sub>3</sub>/CN samples were characterization by the degradation of Rhodamine B (RhB) under visible light. A 300 W xenon lamp acts as a visible light source equipped with a UV cutoff filter ( $\lambda > 420$  nm) during the experiment. For photocatalytic test, 0.05 g of the photocatalyst was dissolved in 100 mL of 10 mg L<sup>-1</sup> RhB solution in a glass beaker. Before irradiation, the solution was magnetically stirred in the dark for 30 minutes to achieve adsorption-desorption equilibrium between photocatalyst and dye. After the illumination, 5 mL of solution was taken from the reaction suspension and centrifuged to remove the particles every time before measuring the absorption spectra. The UV-vis spectrophotometer (Persee TU-1900) was used to study the concentration of RhB in solution. The characteristic absorption peak of RhB at 554 nm was used to determine the extent of its degradation.

### Electrochemical analysis

Electrochemical measurements were conducted on a CHI 760 electrochemical workstation in a standard three-electrode cell, using a Pt plate as counter electrode and an Ag/AgCl electrode as reference electrode and photocatalyst-coated FTO conductive glass slides (*ca.* 2 cm<sup>2</sup>) as working electrode, respectively. Na<sub>2</sub>SO<sub>4</sub> aqueous solution was selected as the electrolyte. The working electrode was prepared by follow deposition method: 20 mg sample powder was mixed in 40 mL PEG10000 solution, sonicated for 30 min and as-prepared solution was drop onto FTO. Then, parallel FTO glasses were placed in the drying oven for at 100 °C for 6 h. Finally, as-prepared FTO glasses with sample film were annealed at 300 °C for 3 h in muffle furnace. The bias voltage was set at -0.5 V *vs.* Ag/AgCl. 300 W Xe lamp with a UV filter ( $\lambda > 420$  nm) served as light source in the photocurrent tests obtained at 0.5 V *vs.* Ag/AgCl.

## Results and discussion

### Characterization of WO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composites

Fig. 1 shows the XRD patterns of g-C<sub>3</sub>N<sub>4</sub>, WO<sub>3</sub> and serials WO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composite photocatalysts. It is observed that two diffraction peaks areas around 27.7° and 12.9° for g-C<sub>3</sub>N<sub>4</sub> (JCPDS 87-1526), are corresponding to the (002) and (100) diffraction planes, respectively. According to the reported results,<sup>36</sup> the stronger peak at 27.7° corresponds to the interlayer stacking of the aromatic systems with the interlayer distance of 0.322 nm. The weaker one at 12.9° which attributes to a distance around  $d = 0.686$  nm is related to in-plane tris-

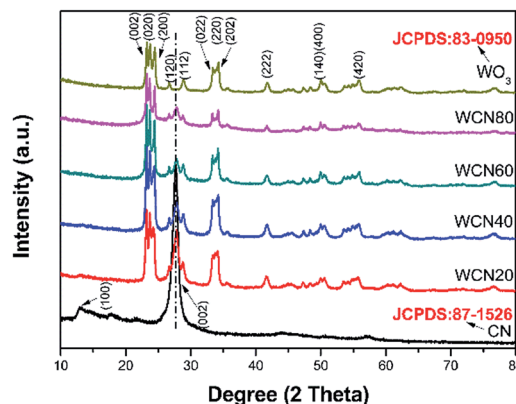


Fig. 1 XRD patterns of g-C<sub>3</sub>N<sub>4</sub>, WO<sub>3</sub> and WO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composite photocatalysts.

triazine structural packing. For WO<sub>3</sub>, it can be index to the monoclinic structure (JCPDS card no. 83-0950 with lattice parameters of  $a = 7.301$  Å,  $b = 7.539$  Å,  $c = 7.690$  Å and  $\alpha = \gamma = 90^\circ$ ,  $\beta = 90.892^\circ$ ) and the main diffraction peaks at 23.3°, 23.7°, 24.5°, 26.7°, 28.8°, 34.3°, 41.7°, 50.0°, and 55.94° are corresponding to (002), (020), (200), (120), (112), (202), (222), (400), and (420) planes, respectively. For WO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composites, the XRD patterns reveal a coexistence of WO<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>. The intensity of characteristic (002) peak assigned to g-C<sub>3</sub>N<sub>4</sub> becomes weaker with the increasing WO<sub>3</sub> content in the composites gradually. The (100) peak ascribed to g-C<sub>3</sub>N<sub>4</sub> is not observed in the composites which may be due to the relative low intensity compared to WO<sub>3</sub>. The main peak changes slightly compared to original 27.7° for g-C<sub>3</sub>N<sub>4</sub> resulted from the introduction of WO<sub>3</sub> indicate that a small shift of interlayers for the interaction between WO<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>.

The morphologies and microstructures of the as-obtained samples are shown in Fig. 2 and S3.† As seen in Fig. 2(a), g-C<sub>3</sub>N<sub>4</sub> displays a sheet-like structure with different thickness through high or low contrast in the picture. This microstructure

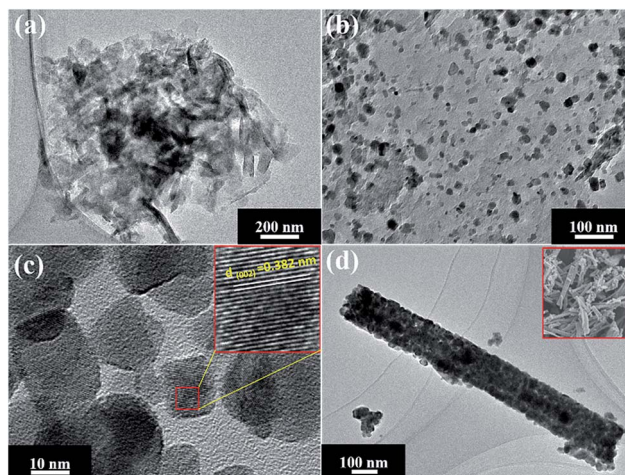


Fig. 2 TEM images of (a) CN; (b) WE/CN40; (c) high resolution TEM of WE/CN40; (d) WO<sub>3</sub> (the SEM images could be observed by the inset).



of  $g\text{-C}_3\text{N}_4$  is consistent with our assumption after the process of ultrasonic and thermal exfoliation. As can be seen in Fig. 2(b),  $\text{WO}_3$  particles are deposited on the surface of  $g\text{-C}_3\text{N}_4$  in the  $\text{WO}_3/g\text{-C}_3\text{N}_4$  composite (WECN40) morphology. The crystal phase of particles is attributed to monoclinic  $\text{WO}_3$  which could be demonstrated by high resolution transmission electron microscopy (HRTEM) in Fig. 2(c). The fringes of particles match the crystallographic plane of  $\text{WO}_3$  described in Fig. 2(c) and the interfaces in  $\text{WO}_3/g\text{-C}_3\text{N}_4$  composites are thought to be beneficial to suppress the recombination of hole and electron under photo-excited environment. The Fig. 2(d) presents the morphology of pure  $\text{WO}_3$  nanobelts prepared without the  $g\text{-C}_3\text{N}_4$ . From the SEM images, it is clearly found that  $\text{WO}_3$  nanobelts are mainly composed of nanoparticles due to the thermal decomposition of EDA.<sup>37</sup> These results are according with the XRD results. As shown in Fig. S4,<sup>†</sup> the peaks of EDS spectrum for  $\text{WO}_3/g\text{-C}_3\text{N}_4$  composites are ascribed to C, N, O and W, the presence of Cu and partly high intensity of C are due to the influence of the micro grid, implying that the composites are composed of  $\text{WO}_3$  and  $g\text{-C}_3\text{N}_4$  without any kind of impurity. The FT-IR spectra of  $g\text{-C}_3\text{N}_4$ ,  $\text{WO}_3$  and  $\text{WO}_3/g\text{-C}_3\text{N}_4$  composite (WECN40) are presented in Fig. 3. For pure  $g\text{-C}_3\text{N}_4$ , several strong bands in the  $1000\text{--}1650\text{ cm}^{-1}$  region and the peak at  $810\text{ cm}^{-1}$  were observed, which belong to the *s*-triazine ring modes.<sup>38,39</sup> The absorption peaks at  $1638\text{ cm}^{-1}$  and  $1238\text{ cm}^{-1}$  are attributed to the C=N and C-N stretching modes respectively.<sup>40–43</sup> The sharp peak at  $1638\text{ cm}^{-1}$  is an indication of good crystallinity of  $g\text{-C}_3\text{N}_4$  crystals. Also, broad bands of stretching and deformation modes of the  $\text{NH}_2$  (as well as an overlapping band of O-H stretching possibly) groups at  $3414\text{ cm}^{-1}$ .<sup>44</sup> The broad absorption peak at  $817\text{ cm}^{-1}$  is assigned to O-W-O stretching vibrations for  $\text{WO}_3$ . Obviously, the characteristic peaks of  $g\text{-C}_3\text{N}_4$  between  $800$  and  $1600\text{ cm}^{-1}$  weakened to some extent when combined with  $\text{WO}_3$ . The peak at  $3414\text{ cm}^{-1}$  for all samples is attributed to O-H stretching vibration and the bending vibration of adsorbed water molecules is located at  $1620\text{ cm}^{-1}$  for samples.<sup>45</sup>

XPS spectra are shown in Fig. 4 to analyse the surface chemical composition and chemical state. It is observed that as-

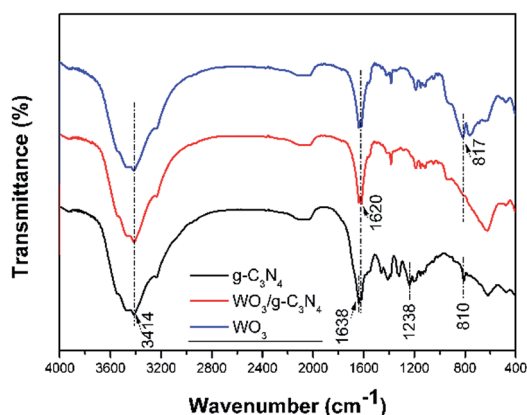


Fig. 3 FT-IR spectra of  $g\text{-C}_3\text{N}_4$ ,  $\text{WO}_3$  and  $\text{WO}_3/g\text{-C}_3\text{N}_4$  composite (WECN40).

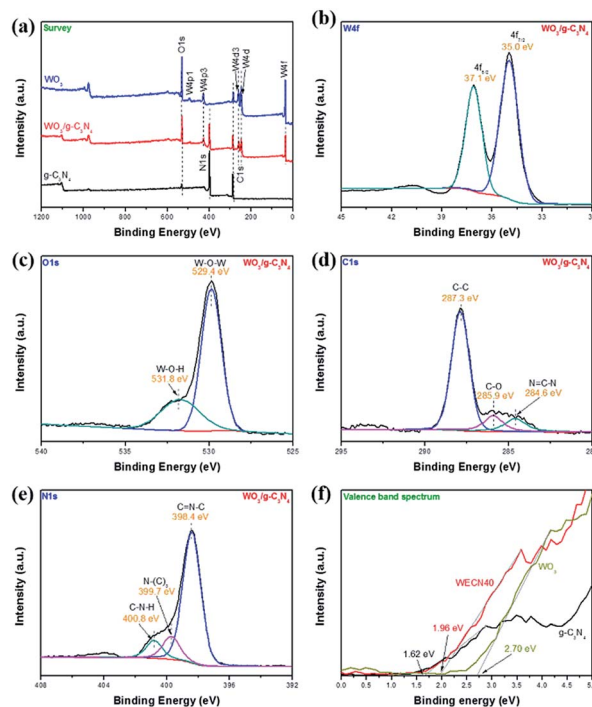
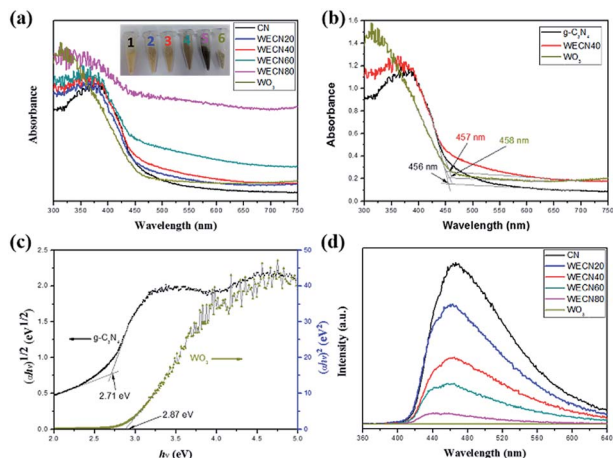


Fig. 4 (a) XPS survey spectra of  $g\text{-C}_3\text{N}_4$ ,  $\text{WO}_3$  and  $\text{WO}_3/g\text{-C}_3\text{N}_4$  composite (WECN40); high resolution XPS spectra of (b) W4f, (c) O1s, (d) C1s, (e) N1s; (f) valence band spectra of  $g\text{-C}_3\text{N}_4$  and  $\text{WO}_3$ .

synthesized  $\text{WO}_3/g\text{-C}_3\text{N}_4$  composites are primarily composed of the elements like W, O, C and N from the XPS survey spectrum in Fig. 4(a). It is clearly seen that  $g\text{-C}_3\text{N}_4$  and  $\text{WO}_3$  are coexist in composite and slight shift of peaks indicates the interaction between  $g\text{-C}_3\text{N}_4$  and  $\text{WO}_3$  is exist indeed. The W4f spectrum (Fig. 4(b)) centred at  $35.0\text{ eV}$  is ascribed to  $4f_{7/2}$  and the other peak at  $37.1\text{ eV}$  is ascribed to  $4f_{5/2}$ , which indicate that they are the typical valence state peaks of  $\text{W}^{6+}$ .<sup>46–48</sup> Two peaks (Fig. 4(c)) are showed at about  $529.4\text{ eV}$  and  $531.8\text{ eV}$  for O1s XPS spectra, which could be associated with W-O-W and W-O-H, respectively.<sup>49</sup> The C1s peaks (Fig. 4(d)) could be separated into three characterization parts: the peak located at  $287.3\text{ eV}$  is typically related to the  $\text{sp}^2$ -bonded  $\text{N}=\text{C}-\text{N}$ , the peak centred at  $285.9\text{ eV}$  is attributed to the C-O species on the  $g\text{-C}_3\text{N}_4$  surface and the peak at  $284.6\text{ eV}$  can be assigned to C-C may due to the surface adventitious carbon or defect in the  $g\text{-C}_3\text{N}_4$ .<sup>50,51</sup> Additionally, the N1s peaks (Fig. 4(e)) can be deconvoluted into three peaks at  $398.4\text{ eV}$ ,  $399.7\text{ eV}$ , and  $400.8\text{ eV}$  which refer to triazine rings (C=N-C), tertiary nitrogen (N-(C)<sub>3</sub>), and amino functions (C-N-H).<sup>52</sup> Fig. 4(f) shows valence band spectra of samples and valence band potentials of  $g\text{-C}_3\text{N}_4$  and  $\text{WO}_3$  are  $1.62$  and  $2.70\text{ eV}$  respectively. The changes of electronic structure for  $\text{WO}_3/g\text{-C}_3\text{N}_4$  (WECN40) indicate that the existence of interaction between  $g\text{-C}_3\text{N}_4$  and  $\text{WO}_3$  compared to pure  $\text{WO}_3$  and  $g\text{-C}_3\text{N}_4$  (Fig. S5 and S6<sup>†</sup>) and that would be beneficial to photocatalytic performance.

As can be seen in Fig. 5(a), the UV-vis diffuse reflectance spectra of  $g\text{-C}_3\text{N}_4$ ,  $\text{WO}_3$ ,  $\text{WO}_3/g\text{-C}_3\text{N}_4$  composites are exhibited. For  $\text{WO}_3/g\text{-C}_3\text{N}_4$  composites, they are red-shifted in the region





**Fig. 5** (a) UV-vis diffuse reflectance spectra of g-C<sub>3</sub>N<sub>4</sub>, WO<sub>3</sub> and WO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composites (the different number colors marked in samples are consistent with the nomination of samples); (b) the band gap determination of g-C<sub>3</sub>N<sub>4</sub>, WO<sub>3</sub> and WECN40 by Tauc's approach; (c) the optical transition type determination of g-C<sub>3</sub>N<sub>4</sub> and WO<sub>3</sub>; (d) PL spectra of g-C<sub>3</sub>N<sub>4</sub>, WO<sub>3</sub> and WO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composites.

of 300–750 nm and the absorption ability increases with the increasing amount of WO<sub>3</sub>, which is consistent with gradually darkening colour of samples (inset of Fig. 5(a)). It is observed that the composite sample WECN40 shows stronger absorption in the visible region at wavelengths more than around 400 nm compared with g-C<sub>3</sub>N<sub>4</sub> and WO<sub>3</sub>. The band gap of samples can be estimated by the following equation:

$$(ah\nu)^{n/2} = A(h\nu - E_g)$$

where  $a$ ,  $h$ ,  $\nu$ ,  $A$ ,  $E_g$  are absorption coefficient, Planck constant, light frequency, proportionality constant and band gap, respectively. The factor  $n$  is related to the optical transition of a semiconductor that  $n = 1$  for direct transition and  $n = 4$  for indirect transition. The values of  $n = 1$  and 4 are corresponding to g-C<sub>3</sub>N<sub>4</sub> and WO<sub>3</sub> respectively.<sup>53,54</sup> From Fig. 5(b), the values of the absorption bands located at 456 and 458 nm are ascribed to g-C<sub>3</sub>N<sub>4</sub> and WO<sub>3</sub>, exhibiting good absorption ability in the visible region, and the corresponding band gaps are 2.71 and 2.87 eV respectively (Fig. 5(c)). Meanwhile, the value at 457 nm of the WO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composite for WECN40 is between 456 and 458 nm and red shift which occurs among all WO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composites in absorption curves may be attributed to the interaction between g-C<sub>3</sub>N<sub>4</sub> and WO<sub>3</sub> shown in Fig. 5(a and b). The positions of valence band (VB) and conduction band (CB) could be estimated by the following equation:

$$E_{VB} = X - E^c + 0.5E_g$$

$$E_{CB} = E_{VB} - E_g$$

In this equation,  $E_{VB}$ ,  $X$ ,  $E^c$ ,  $E_{CB}$ , and  $E_g$  are defined as the VB edge potential, the electronegativity of the semiconductor, the energy of free electrons on the hydrogen scale (around 4.5 eV), the CB edge potential and the band gap energy of the semiconductor respectively.<sup>55</sup> The valence band edge potential of

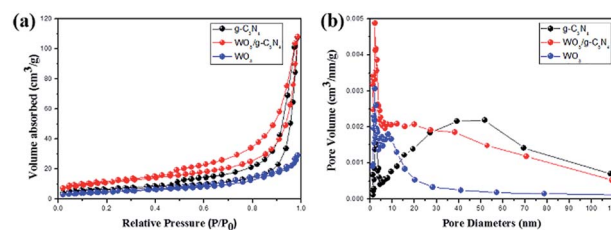
g-C<sub>3</sub>N<sub>4</sub> and WO<sub>3</sub> are 1.62 and 2.70 eV respectively from above XPS analysis (Fig. 5(f)). And the conduction band potentials of g-C<sub>3</sub>N<sub>4</sub> and WO<sub>3</sub> are calculated to be  $-1.09$  eV and  $-0.17$  eV, respectively.

Fig. 5(d) shows the PL spectra of g-C<sub>3</sub>N<sub>4</sub>, WO<sub>3</sub> and WO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composites under the excitation wavelength of 325 nm. For g-C<sub>3</sub>N<sub>4</sub>, a strong emission band centred at about 465 nm could be attributed to the band-band PL phenomenon of photo-excited electron-hole.<sup>56</sup> While a weak emission peak of WO<sub>3</sub> could be related to localized state in the band gap with the existence of defects or oxygen vacancies.<sup>57</sup> It is clear that the peak intensities for WO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composites decrease with the increase of WO<sub>3</sub>. This means that an increasing number of charge carriers take part in photocatalytic reactions since the lower PL intensities implied a slower recombination rate of the photo-generated electron-hole pairs. Meanwhile, this result also indicates that the interfaces between g-C<sub>3</sub>N<sub>4</sub> and WO<sub>3</sub> do promote the separation and migration of photo-induced charge carriers.

As shown in Fig. 6(a), the BET surface area of samples is determined by nitrogen adsorption and desorption isotherms. The  $S_{BET}$  of WECN40 composites (Table S1†) increased by 1.81 and 1.96 times compared to pure g-C<sub>3</sub>N<sub>4</sub> and WO<sub>3</sub> photocatalysts, indicating that the interaction between g-C<sub>3</sub>N<sub>4</sub> nanosheets and WO<sub>3</sub> nanoparticles (about 19.8 nm calculated by Scherrer equation) enlarges the BET surface area and corresponding composite materials provide more reaction sites for photodegradation. From Fig. 6(b) and Table S1,† average pore diameters of g-C<sub>3</sub>N<sub>4</sub>, WO<sub>3</sub> and WO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composite (WECN40) are distributed at about 51.796, 2.105, 19.844 nm, which corresponds to the pore volume of 0.166, 0.167, 0.046 cm<sup>3</sup> g<sup>-1</sup>. It means that WECN40 is a photocatalyst with smaller pore diameter and larger pore volume. The pore volume of WO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composite is almost the same as pure g-C<sub>3</sub>N<sub>4</sub> but it has smaller pore diameter, which can be related to the presence of WO<sub>3</sub> particles dispersing on g-C<sub>3</sub>N<sub>4</sub> nanosheets.

### Photocatalytic performance and stability of the WO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composites

The photocatalytic performance of samples was investigated by the degradation of RhB under visible light illumination. As depicted in Fig. 7(a), for WO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composite (WECN40), the absorption peak of the RhB solution decreased with the increase of time which indicates the photodegradation of RhB



**Fig. 6** (a) N<sub>2</sub> adsorption-desorption isotherm and (b) pore size distribution curves of g-C<sub>3</sub>N<sub>4</sub>, WO<sub>3</sub> and WO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composite (WECN40).



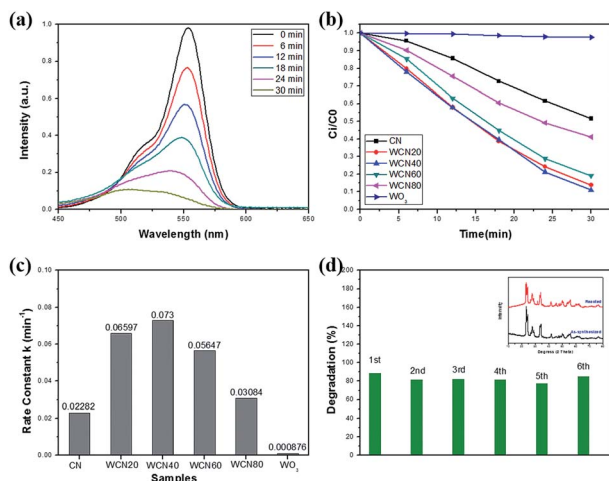


Fig. 7 (a) Photodegradation of RhB with WECN40; (b)  $C_t/C_0$  of all the samples; (c) rate constants  $k$  values of all the photocatalysts; (d) recyclability of WECN40.

under visible light. And the blue shift from 554 to 503 nm for the wavelength of maximum characteristic peak could be attributed to *N*-deethylation mechanism in photocatalytic reaction.<sup>58</sup> The  $(C_t/C_0)$  of all the samples are shown in Fig. 7(b), it is obvious that  $WO_3/g-C_3N_4$  composites display much higher photocatalytic capability compared with pure  $g-C_3N_4$  and  $WO_3$ . The photocatalyst of WECN40 exhibits best degradation rate of contamination. In order to further estimate the photocatalytic reactions of pollutants in aqueous solutions, the first order equation of the Langmuir–Hinshelwood model is used as follows:<sup>59</sup>

$$\ln(C_t/C_0) = kt$$

where  $C_t$  is the concentration of the organic dye at time  $t$  and  $C_0$  is the initial concentration of dye in solution. Fig. 7(c) depicts the Plot of  $\ln(C_t/C_0)$  versus irradiation time  $t$  for the catalysts. The rate constant  $k$  of all  $WO_3/g-C_3N_4$  composites show higher photocatalytic performance than pure  $g-C_3N_4$  and  $WO_3$ . Furthermore, the highest  $k$  value, corresponding to the WECN40 sample ( $k = 0.073 \text{ min}^{-1}$ ), is 3.2 and 83.3 times as high as that of  $g-C_3N_4$  ( $k = 0.0228 \text{ min}^{-1}$ ) and  $WO_3$  ( $k = 0.00088 \text{ min}^{-1}$ ), respectively. The improved photocatalytic performance could be ascribed to a synergistic effect of  $g-C_3N_4$  and  $WO_3$  from their effective coupling which gives rise to suitable band gap, lower recombination rate of charge carriers, larger specific surface area and increased light absorption. Meanwhile, when the amount of  $WO_x$ -EDA exceeds 40 wt%, the photocatalytic capability decreases gradually which could be attributed to the poor catalytic performance of  $WO_3$ . It is well known that the dye sensitization could contribute to dye degradation and we choose a colorless pollutant phenol to evaluate the performance of  $WO_3/g-C_3N_4$  photocatalysts in order to exclude the dye sensitization effect. According to Fig. S7,† all samples show the degradation of phenol and  $WO_3/g-C_3N_4$  composites show higher photocatalytic performance than pure  $g-C_3N_4$  and  $WO_3$ . The above phenol degradation results, which are consistent

with RhB degradation, well exclude the disturbing of dye sensitization.

To demonstrate the advantages of  $WO_x$ -EDA precursor, commercial  $WO_3$  (bought from Aladdin) was selected instead of  $WO_x$ -EDA as precursor to prepare  $WO_3/g-C_3N_4$  composites. According to different mass ratio between commercial  $WO_3$  and CN, the samples were named CN, WCN20, WCN40, WCN60, WCN80, and  $WO_3(C)$ . The above samples were prepared by the same process according to the  $g-C_3N_4$  nanosheets loading with  $WO_3$  nanoparticles using  $WO_x$ -EDA as precursor and its photocatalytic performance was tested with the same conditions under visible light illumination (Fig. S8†). Among the above six samples, WCN60 shows the highest photocatalytic activity with the 68% degradation of RhB after 30 min visible light irradiation, but it is still lower than WECN20 (89%) which was prepared using  $WO_3$ -EDA nanobelts as precursor. The poor photocatalytic performance could be attributed to its large particles size of commercial  $WO_3$ , which can be seen in Fig. S7.†

Recycling tests of the  $WO_3/g-C_3N_4$  composites are carried out to assess photostability and recyclability as shown in Fig. 7(d). The degradation of RhB for WECN40 sample, from 89% to 85% in the first and sixth cycle respectively, remains relative stable without distinct fluctuation throughout six runs under visible light irradiation. Furthermore, the main diffraction peaks of XRD of the catalyst, before and after reaction, retain almost the same which implies the structural stability. Only the  $2\theta$  at around  $31^\circ$  may ascribe to catalyst contamination or reaction between sample and aqueous solution. The stability of photocatalytic performance and crystal phase implies the interaction between  $g-C_3N_4$  and  $WO_3$  is relative strong.

### Electrochemical characterization

To further support the restrained recombination of photo-induced electron–hole pairs for the  $WO_3/g-C_3N_4$  composites, the transient photocurrent response tests were carried out for several on–off cycles under visible light irradiation (Fig. S9†). The WECN40 exhibits higher photocurrent intensity than that of CN, which is in accordance with its enhanced photocatalytic degradation rate under visible light irradiation. The fact indicates that the  $WO_3/g-C_3N_4$  composites show better separation or transfer of photo-induced electrons and holes, which is also in accordance with the PL spectra results. For  $WO_3$  sample, it holds high photocurrent intensity, nevertheless, the inappropriate CB position limits its photocatalytic activity under visible light illumination.<sup>24,25</sup>

### Possible photocatalytic mechanism

To investigate the photocatalytic mechanism of the  $WO_3/g-C_3N_4$  composites, several scavengers were applied to check the active species during the photodegradation process under visible light irradiation (Fig. 8). Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), *tert* butyl alcohol (TBA) and 1,4-benzoquinone (BQ) were employed as the hole ( $h^+$ ) scavenger, hydroxyl radical ( $\cdot OH$ ) scavenger and superoxide radical ( $\cdot O_2^-$ ) scavenger. It is clear that the degradation of organic pollutants decreases by the addition of scavengers compared with catalyst without any



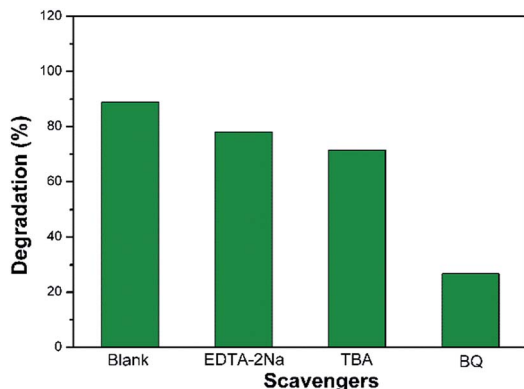


Fig. 8 The effects of various scavengers on the photodegradation of  $\text{WO}_3/\text{g-C}_3\text{N}_4$  composite (WECN40) under visible light.

scavengers, implying that reactive species are significant for the RhB degradation in aqueous solution under visible light. What's more, the effect of the scavengers of TBA and BQ based on suppression of RhB degradation is much bigger than that of EDTA-2Na, indicating that the species of hydroxyl radical ( $\cdot\text{OH}$ ) and superoxide radical ( $\cdot\text{O}_2^-$ ) are the major active species in this photocatalytic system.

Based on the above analysis, a proposed mechanism for the improved photocatalytic activity is briefly described in Fig. 9. For  $\text{g-C}_3\text{N}_4$ , the CB and VB potentials are 1.62 and  $-1.09$  eV respectively, whereas these values of  $\text{WO}_3$  are 2.70 and  $-0.17$  eV respectively. The  $\text{g-C}_3\text{N}_4$  and  $\text{WO}_3$  would be excited and the transition of electrons from VB to CB will happen in both semiconductor under visible light irradiation. Because the VB level of  $\text{g-C}_3\text{N}_4$  is more negative than that of  $\text{WO}_3$  and the CB potential of  $\text{WO}_3$  is more positive than that of  $\text{g-C}_3\text{N}_4$ , the photo-generated holes can transfer from the VB of  $\text{WO}_3$  to that of  $\text{g-C}_3\text{N}_4$ . Meanwhile, the photo-excited electrons in the CB of  $\text{g-C}_3\text{N}_4$  could move to the CB of  $\text{WO}_3$ . These electrons can react with  $\text{W}^{6+}$  species in the  $\text{WO}_3$  and then  $\text{W}^{6+}$  be reduced into  $\text{W}^{5+}$ . The  $\text{W}^{5+}$  ions in the surface of  $\text{WO}_3$  can be re-oxidized into  $\text{W}^{6+}$  through the reaction with oxygen to generate superoxide radical ( $\cdot\text{O}_2^-$ ). Superoxide radical ( $\cdot\text{O}_2^-$ ) can also react with  $\text{H}_2\text{O}$  molecules to form  $\cdot\text{OH}$ .<sup>30</sup> Hydroxyl radical ( $\cdot\text{OH}$ ) and superoxide

radical ( $\cdot\text{O}_2^-$ ) are the main species to degrade RhB into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  under visible light irradiation. Hence, it is concluded that  $\text{g-C}_3\text{N}_4$  coupling with  $\text{WO}_3$  increases the separation efficiency of the photo-induced holes and electrons through reduction or oxidation reaction in the surface of composites under visible light illumination.

## Conclusions

The  $\text{WO}_3/\text{g-C}_3\text{N}_4$  composites were facile prepared through heat treatment of  $\text{WO}_x$ -EDA nanobelts and  $\text{g-C}_3\text{N}_4$  powder. The heat treatment temperature of  $400^\circ\text{C}$  is the key factor to obtain  $\text{g-C}_3\text{N}_4$  nanosheets with uniformly dispersed  $\text{WO}_3$  nanoparticles. The enhanced photocatalytic performance is considered to arise from the increased reaction sites, enhanced visible light absorption and the restrained recombination of photo-induced electron-hole pairs under visible light irradiation. The  $\text{WO}_3/\text{g-C}_3\text{N}_4$  composite exhibits best activity for the degradation of RhB when the amount of  $\text{WO}_x$ -EDA reached 40 wt% in the mixture with  $\text{g-C}_3\text{N}_4$ . Meanwhile, it is concluded that the species of hydroxyl radical ( $\cdot\text{OH}$ ) and superoxide radical ( $\cdot\text{O}_2^-$ ) are the major active species in the photocatalytic system. Therefore, this work demonstrates a method using  $\text{WO}_x$ -EDA as precursor, which could improve the photocatalytic degradation under visible light illumination. And it also provides the reference for other composites synthesis.

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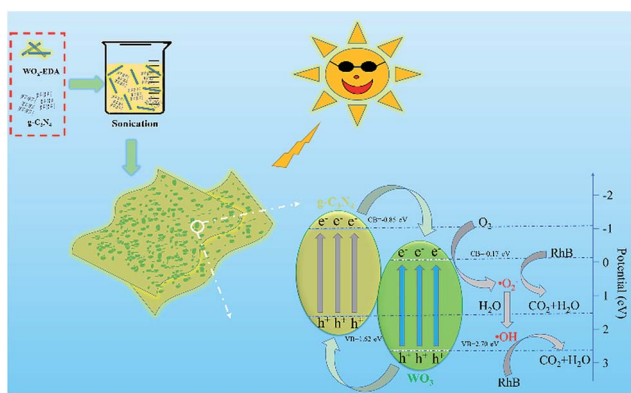


Fig. 9 Possible degradation mechanism of RhB for photocatalysts under visible light illumination.



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