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Cite this: *RSC Adv.*, 2017, 7, 2163

# Novel $\beta$ - $\text{Ag}_2\text{MoO}_4/\text{g-C}_3\text{N}_4$ heterojunction catalysts with highly enhanced visible-light-driven photocatalytic activity†

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The kernel of photocatalysis research is the development of catalysts with remarkable photocatalytic activity.  $\text{g-C}_3\text{N}_4$  has attracted much interest as a new and promising photocatalyst, but further modification and improvement of  $\text{g-C}_3\text{N}_4$  is urgently needed. Herein, we report a novel  $\beta$ - $\text{Ag}_2\text{MoO}_4/\text{g-C}_3\text{N}_4$  heterojunction system with highly enhanced visible-light-driven photocatalytic activity.  $\beta$ - $\text{Ag}_2\text{MoO}_4$  nanoparticles were *in situ* loaded onto thin  $\text{g-C}_3\text{N}_4$  nanosheets to make these heterojunction photocatalysts. The photocatalytic activities of these heterojunctions and the relevant samples were investigated by degrading Rhodamine B (RhB), methylene blue (MB), and methyl orange (MO) under visible light irradiation ( $\lambda > 400$  nm).  $\beta$ - $\text{Ag}_2\text{MoO}_4/\text{g-C}_3\text{N}_4$  heterojunctions were found to be much more active than pristine  $\beta$ - $\text{Ag}_2\text{MoO}_4$ ,  $\text{g-C}_3\text{N}_4$ , or a mechanical mixture of both in the degradation of organic pollutants. The optimal catalyst had a  $\beta$ - $\text{Ag}_2\text{MoO}_4/\text{g-C}_3\text{N}_4$  mass ratio of 37.5%. Through relevant characterization, the upgraded photocatalytic activities of the  $\beta$ - $\text{Ag}_2\text{MoO}_4/\text{g-C}_3\text{N}_4$  heterojunctions were mainly attributed to the efficient separation of photogenerated charge carriers. Superoxide radical anions ( $^{\cdot}\text{O}_2^-$ ) and photogenerated holes ( $\text{h}^+$ ) were found to be the main active species.

Received 5th November 2016

Accepted 1st December 2016

DOI: 10.1039/c6ra26352f

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## 1. Introduction

Photocatalysis, an attractive technology that involves photocatalysts and light irradiation, has been widely studied for the degradation of pollutants, the splitting of water, the reduction of  $\text{CO}_2$ , and antibacterial applications.<sup>1–4</sup> However, a bottleneck for its practical applications is that many catalysts such as  $\text{TiO}_2$  (ref. 5) and  $\text{Ag}_2\text{MoO}_4$  (ref. 6) only respond to UV light ( $\sim 5\%$  of the solar spectrum).

$\text{Ag}_2\text{MoO}_4$  has been used as high-temperature lubricants,<sup>7</sup> ion-conducting glasses,<sup>8</sup> photoluminescent materials,<sup>9</sup> and photo-switch devices.<sup>10</sup> However, the wide band gap ( $\sim 3.2$  eV) still limits its applications in visible-light-driven photocatalysis. Various methods, such as doping ions (*e.g.*,  $\text{Eu}^{3+}$ ),<sup>11</sup> depositing noble metals (*e.g.*, Ag),<sup>12</sup> and forming heterojunctions (*e.g.*,  $\text{Ag}@\text{Ag}_2\text{MoO}_4\text{-AgBr}$ ,  $\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4$ ,  $\text{Ag}_2\text{MoO}_4/\text{Ag}/\text{AgBr}/\text{GO}$ ),<sup>13–15</sup> have been used to enhance the visible-light absorption, thus enhancing the visible-light-driven photocatalytic performance. However, reports on  $\text{Ag}_2\text{MoO}_4$ -based photocatalysts are still rare.

Graphitic carbon nitride ( $\text{g-C}_3\text{N}_4$ ), due to its suitable band gap of  $\sim 2.7$  eV and excellent structural stability, has attracted much attention for the applications in visible-light-driven

photocatalytic water splitting,<sup>16–19</sup> degradation of pollutants,<sup>20–24</sup> and removal of  $\text{NO}_x$ .<sup>25–27</sup>  $\text{g-C}_3\text{N}_4$  is abundant, of low cost, and can be easily prepared by thermal polycondensation of nitrogen-rich organic precursors such as cyanamide,<sup>28,29</sup> dicyandiamide,<sup>22</sup> melamine,<sup>23</sup> and urea.<sup>30</sup> However, the photocatalytic activity of pure  $\text{g-C}_3\text{N}_4$  is still unsatisfactory due to the rapid recombination of photogenerated charge carriers. Generally, the construction of semiconductor heterojunctions is an efficient strategy to upgrade the separation efficiency of photo-induced electrons.  $\text{g-C}_3\text{N}_4$  has been coupled with other compounds, such as  $\text{Al}_2\text{O}_3$ ,<sup>31,32</sup>  $\text{V}_2\text{O}_5$ ,<sup>33</sup>  $\text{W}_{18}\text{O}_{49}$ ,<sup>34</sup>  $\beta\text{-Ni}(\text{OH})_2$ ,<sup>35</sup>  $\text{Bi}_{12}\text{TiO}_{20}$ ,<sup>36</sup>  $\text{CdV}_2\text{O}_6$ ,<sup>37</sup>  $\text{BiPO}_4$ ,<sup>38</sup>  $\text{SnS}_2$ ,<sup>39</sup>  $\text{Bi}_4\text{O}_5\text{I}_2$ ,<sup>40</sup>  $\text{Nb}_2\text{O}_5$ ,<sup>41</sup>  $\text{FeO}_x$ ,<sup>42</sup> and  $\text{ZnMoCdS}$ .<sup>43</sup> In particular,  $\text{g-C}_3\text{N}_4$  can be coupled with silver-containing compounds such as  $\text{Ag}_2\text{O}$ ,<sup>44</sup>  $\text{Ag}_2\text{CO}_3$ ,<sup>45</sup>  $\text{Ag}_3\text{PO}_4$ ,<sup>46</sup>  $\text{Ag}/\text{AgX}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ),<sup>47</sup>  $\text{Ag}_3\text{VO}_4$ ,<sup>48</sup>  $\text{Ag}_2\text{CrO}_4$ ,<sup>49</sup> and  $\text{Ag}_2\text{WO}_4$  (ref. 50) to form heterojunctions with improved photocatalytic performance. However, to the best of our knowledge, there is no report on photocatalysis over  $\beta$ - $\text{Ag}_2\text{MoO}_4/\text{g-C}_3\text{N}_4$  heterojunctions.

Considering that the band edges of  $\text{g-C}_3\text{N}_4$  ( $E_{\text{CB}} = -1.12$  eV,  $E_{\text{VB}} = 1.58$  eV) match well with those of  $\beta$ - $\text{Ag}_2\text{MoO}_4$  ( $E_{\text{CB}} = -0.27$  eV,  $E_{\text{VB}} = 3.11$  eV),<sup>13,51</sup> we suppose that this feature is beneficial for constructing a staggered band-gap type (type II) heterojunction system. Such a catalyst system may promote the separation and migration of photogenerated carriers efficiently. Thus, in the present work, we developed a novel  $\beta$ - $\text{Ag}_2\text{MoO}_4/\text{g-C}_3\text{N}_4$  heterojunction catalyst system and found that the heterojunction catalysts exhibited much higher photocatalytic

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ra26352f



activity than pristine  $\beta\text{-Ag}_2\text{MoO}_4$  or  $\text{g-C}_3\text{N}_4$  in the degradation of dyes under visible-light irradiation. Possible reasons for the enhanced photocatalytic activity of  $\beta\text{-Ag}_2\text{MoO}_4/\text{g-C}_3\text{N}_4$  heterojunction were investigated. This work not only furnishes a new photocatalyst system with improved photocatalytic activity, but also provides some mechanistic information.

## 2. Experimental

### 2.1. Materials

Melamine,  $\text{CH}_3\text{OH}$ ,  $\text{AgNO}_3$ ,  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ , absolute ethanol, Rhodamine B (RhB), methylene blue (MB), and methyl orange (MO) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were of analytical grade and used as received.

### 2.2. Preparation of $\text{g-C}_3\text{N}_4$

Bulk  $\text{g-C}_3\text{N}_4$  (B-CN) was prepared by thermal polymerization.<sup>52</sup> Typically, 10.0 g melamine powders were put into an  $\text{Al}_2\text{O}_3$  crucible with a cover. The crucible was heated to 550 °C at a ramping rate of 3 °C  $\text{min}^{-1}$ , kept at 550 °C for 4 h, and then cooled down to room temperature. After that, 1.0 g bulk  $\text{g-C}_3\text{N}_4$  was ground into powders, and ultrasonically crashed in 15 mL methanol for 5 h to obtain thin  $\text{g-C}_3\text{N}_4$  nanosheets (T-CN).

### 2.3. Preparation of $\beta\text{-Ag}_2\text{MoO}_4/\text{g-C}_3\text{N}_4$

$\beta\text{-Ag}_2\text{MoO}_4/\text{g-C}_3\text{N}_4$  heterojunctions were prepared by deposition-precipitation at room temperature. Briefly, 0.50 g T-CN powders were dispersed with 50 mL deionized water (in a 100 mL beaker) by ultrasonication for 30 min. 10.0 mL  $\text{AgNO}_3$  solution (0.1 M) was then added dropwise into the breaker, and the mixture was magnetically stirred for 30 min to obtain  $\text{Ag}^+$ -T-CN suspension. After that, 5.0 mL  $\text{Na}_2\text{MoO}_4$  solution (0.1 M) was added in the above suspension, and the mixture was continuously stirred for 2 h. The solid (with a theoretical  $\beta\text{-Ag}_2\text{MoO}_4/\text{g-C}_3\text{N}_4$  mass ratio of 37.5%) collected by filtration was washed with water-ethanol for three times, and dried at 60 °C for 24 h. A series of samples with different  $\beta\text{-Ag}_2\text{MoO}_4/\text{g-C}_3\text{N}_4$  mass ratios (9.3%, 18.9%, 37.5%, 75.1%, and 150.2%) were prepared that way, and were named as AMOCNX ( $X = 1, 2, 3, 4, \text{ and } 5$ ). For comparison,  $\beta\text{-Ag}_2\text{MoO}_4$  (denoted as AMO) was prepared *via* a similar process without adding T-CN.

### 2.4. Characterization

Powder X-ray diffraction (XRD) data were collected using a MSAL XD2 X-ray diffractometer with  $\text{CuK}\alpha$  radiation at 40 kV and 30 mA at a scanning speed of 8°  $\text{min}^{-1}$ . The oxidation states of elements were analyzed by using X-ray photoelectron spectroscopy (Axis Ultra Dld, Kratos). Scanning electron microscope (SEM) experiments were conducted on a Shimadzu SUPERSCAN SSX-550 field emission scanning electron microscope. Transmission electron microscopy (TEM) data were obtained by a JEOL JEM-2100F high-resolution transmission electron microscope.  $\text{N}_2$  adsorption-desorption isotherms at liquid  $\text{N}_2$  temperature were obtained on a Micrometrics ASAP 2020M + C adsorption apparatus. Optical diffuse reflectance spectra were

recorded on a UV-VIS-NIR scanning spectrophotometer (Lambda 35, Perkin-Elmer) using an integrating sphere accessory.

### 2.5. Evaluation of photocatalytic performance

Photocatalytic performance in the degradation of RhB, MO, or MB dye was investigated under visible light irradiation ( $\lambda > 420$  nm) at room temperature. The distance between the Xe lamp and the beaker mouth was 15 cm (Fig. S1 in the ESI†).<sup>53</sup> In a typical procedure, 30.0 mg photocatalyst was suspended in 50 mL RhB (5.0  $\text{mg L}^{-1}$ ), MO (6.0  $\text{mg L}^{-1}$ ), or MB (5.0  $\text{mg L}^{-1}$ ) solution in a 100 mL beaker. The beaker was placed in a water bath placed on top of an electromagnetic stirrer. The solution was stirred (854 rpm) for 30 min in the dark before the Xe lamp (300 W, HSX-F300, Beijing NBeT Technology Co., Ltd.) coupled with a UV-cutoff filter (420 nm) was turned on. During the experiment,  $\sim 4.0$  mL of suspension was sampled in certain intervals, centrifuged to separate the catalyst and the liquid, and the clear liquid was then monitored by a UV-5200PC spectrometer.

Experiments involving radicals capture were conducted by adding 1 mmol ammonium oxalate (AO), 1 mmol isopropanol (IPA), 1 mmol  $\text{AgNO}_3$ , or 0.02 mmol benzoquinone (BQ) into RhB (5.0  $\text{mg L}^{-1}$ ) solution before the standard photocatalytic tests.

## 3. Results and discussion

### 3.1. Preparation and characterization of $\beta\text{-Ag}_2\text{MoO}_4/\text{g-C}_3\text{N}_4$ heterojunctions

Thin  $\text{g-C}_3\text{N}_4$  nanosheets (T-CN) were first prepared *via* thermal polymerization and subsequent ultrasonication.  $\beta\text{-Ag}_2\text{MoO}_4$  (0.125, 0.250, 0.500, 1.00, and 2.00 mmol) was then *in situ* deposited onto T-CN (0.50 g) through the reaction of  $\text{AgNO}_3$  and  $\text{Na}_2\text{MoO}_4$  in the aqueous solution at room temperature. The resulting catalysts are named as AMOCN1, AMOCN2, AMOCN3, AMOCN4, AMOCN5, respectively. The theoretical  $\beta\text{-Ag}_2\text{MoO}_4/\text{g-C}_3\text{N}_4$  mass ratios of these composite samples are 9.3%, 18.9%, 37.5%, 75.1%, and 150.2%, respectively.

Fig. S2† shows the XRD patterns of bulk  $\text{g-C}_3\text{N}_4$  (B-CN), thin  $\text{g-C}_3\text{N}_4$  nanosheets (T-CN), and  $\text{Ag}_2\text{MoO}_4$  (AMO). Both B-CN and T-CN show a characteristic peak at 27.4°, indexed as the (002) peak of  $\text{g-C}_3\text{N}_4$ .<sup>22</sup> For  $\text{Ag}_2\text{MoO}_4$ , the peaks at  $2\theta = 16.5^\circ, 27.1^\circ, 31.8^\circ, 33.3^\circ, 38.6^\circ, 42.2^\circ, 47.8^\circ, 50.9^\circ, 55.8^\circ, 65.7^\circ, \text{ and } 66.6^\circ$  are assigned to the (111), (220), (311), (222), (400), (331), (422), (511), (440), (533), and (622) planes of cubic  $\beta\text{-Ag}_2\text{MoO}_4$ , respectively (JCPDS 08-0473).<sup>13</sup> The XRD patterns of AMOCN1, AMOCN2, AMOCN3, AMOCN4, and AMOCN5 can be indexed to a combination of  $\text{g-C}_3\text{N}_4$  and  $\beta\text{-Ag}_2\text{MoO}_4$  (Fig. 1). The intensities of the  $\beta\text{-Ag}_2\text{MoO}_4$  peaks enhance gradually when the  $\beta\text{-Ag}_2\text{MoO}_4/\text{g-C}_3\text{N}_4$  mass ratio increases. No impurity phase is identified.

Representative catalysts were subjected to XPS analysis. The survey XPS spectra in Fig. 2A show that  $\text{g-C}_3\text{N}_4$  contains C and N, and  $\beta\text{-Ag}_2\text{MoO}_4$  contains Ag, Mo, O, and adventitious C. AMOCN3 comprises C, N, Ag, Mo, and O. For AMOCN3, the peaks at 284.70 and 287.87 eV can be ascribed to  $\text{sp}^2$  C-C bonds of graphitic carbon and  $\text{sp}^2$ -bonded carbon (N-C=N) of the s-





Fig. 1 XRD patterns of T-CN (thin  $g$ - $C_3N_4$  nanosheets), AMOCN1, AMOCN2, AMOCN3, AMOCN4, AMOCN5, and AMO ( $\beta$ - $Ag_2MoO_4$ ).

triazine rings, respectively (Fig. 2B).<sup>50,52</sup> The binding energy for the C 1s peak at 284.70 eV can be attributed to adventitious carbon species on the sample (normally used as the reference

for XPS calibration). The N 1s signal also shows two feature peaks at 398.22 and 399.90 eV (Fig. 2C), ascribed to the  $sp^2$ -bonded N ( $C-N=C$ ) and tertiary nitrogen  $N-(C)_3$  groups.<sup>50,52</sup> The binding energies of 367.85 eV for Ag  $3d_{5/2}$  and 373.84 eV for Ag  $3d_{3/2}$  (Fig. 2D) confirm the existence of  $Ag^+$ .<sup>49</sup> Fig. 2E shows two peaks at 232.70 and 235.85 eV, corresponding to the Mo  $3d_{5/2}$  and Mo  $3d_{3/2}$  binding energies of  $Mo^{6+}$ .<sup>54</sup> There are three main signals in O 1s spectra (Fig. 2F). The peaks at 532.92 and 530.54 eV are assigned to chemisorbed  $H_2O$  (532.92 eV) and hydroxyls ( $OH^-$ , 530.54 eV), respectively.<sup>42</sup> Another peak at 532.31 eV is ascribed to oxygen in  $\beta$ - $Ag_2MoO_4$ . Overall, the XPS results confirm that AMOCN3 is composed of  $g$ - $C_3N_4$  and  $\beta$ - $Ag_2MoO_4$ .

Fig. 3 shows the morphology and microstructure of B-CN, T-CN, and AMOCN3. The TEM (Fig. 3A) and SEM (Fig. S3A†) images indicate that B-CN exhibits a stratified structure built from numerous nanosheets with smooth surfaces. After ultrasonic dispersion, some B-CN is exfoliated to form T-CN (Fig. 3B and S3B†). Upon loading  $\beta$ - $Ag_2MoO_4$  onto T-CN, some  $\beta$ - $Ag_2MoO_4$  nanoparticles with sizes from nanometers to decades of nanometers are well dispersed on the surface of



Fig. 2 (A) Survey XPS spectra of T-CN, AMOCN3, and AMO; high-resolution XPS spectra of C 1s (B), N 1s (C), Ag 3d (D), Mo 3d (E), and O 1s (F) from AMOCN3.





Fig. 3 TEM images of (A) B-CN, (B) T-CN and (C) AMOCN3; (D) EDS pattern of AMOCN3.

nanosheets (Fig. 3C). The EDS result exhibits the existence of C, N, Ag, Mo, and O elements in AMOCN3 (Fig. 3D). The calculated C/N and Ag/Mo atom ratios, shown in the inset of Fig. 3D, are very close to the theoretical values (3/4 for  $g\text{-C}_3\text{N}_4$ , 2/1 for  $\beta\text{-Ag}_2\text{MoO}_4$ ). Furthermore, HAADF-FSEM coupled with EDS mapping indicate the uniform distribution of C, N, Ag, Mo, and O on the catalyst (Fig. S4†).

With the increase of the  $\beta\text{-Ag}_2\text{MoO}_4/g\text{-C}_3\text{N}_4$  mass ratio, more  $\beta\text{-Ag}_2\text{MoO}_4$  nanoparticles are observed on the surface of T-CN (Fig. S5†). Occasionally, some particles with sizes ranging from 0.5 to 5  $\mu\text{m}$  are also found on the surface of T-CN (Fig. S6†). The TEM results are consistent with the XRD results (Fig. 1) that the  $\beta\text{-Ag}_2\text{MoO}_4$  peaks become sharper as the  $\beta\text{-Ag}_2\text{MoO}_4/g\text{-C}_3\text{N}_4$  mass ratio increases.

Representative samples were characterized by  $\text{N}_2$  adsorption-desorption (Fig. S7†). The pore size distributions calculated from the adsorption branches reveal the existence of nanopores (diameter: 29.9, 29.5, and 31.0 nm) in B-CN, T-CN, and AMOCN3. The BET surface areas of B-CN, T-CN, and AMOCN3 are 9.2, 9.8, and 8.2  $\text{m}^2 \text{g}^{-1}$ , respectively.

The optical property of catalysts was investigated by UV-Vis-NIR DRS (Fig. 4A). Pure  $\beta\text{-Ag}_2\text{MoO}_4$  exhibits a strong absorption in the UV region with an absorption edge around 388 nm, indicating that  $\beta\text{-Ag}_2\text{MoO}_4$  can only be excited by UV light.<sup>6,13,55</sup> Both B-CN and T-CN exhibit strong absorption from the UV to visible-light region with an absorption edge around 460 nm, consistent with previous results.<sup>51,56</sup>  $\beta\text{-Ag}_2\text{MoO}_4/g\text{-C}_3\text{N}_4$ -heterojunctions can absorb visible light, and their wavelength thresholds are estimated to be 450–460 nm.

The optical absorption near the band edge follows the Tauc equation:

$$\alpha h\nu = A(h\nu - E_g)^{n/2}, \quad (1)$$



Fig. 4 (A) UV-Vis diffuse reflectance spectra of AMO, B-CN, T-CN, and  $\text{Ag}_2\text{MoO}_4/g\text{-C}_3\text{N}_4$  heterojunctions (AMOCN1, AMOCN2, AMOCN3, AMOCN4, and AMOCN5); (B) a plot of  $(\alpha h\nu)^{1/2}$  versus the bandgap (eV) for T-CN and AMO.



where  $A$  is constant,  $\alpha$ ,  $h$ ,  $\nu$ , and  $E_g$  are the absorption coefficient, Planck's constant, light frequency, and band gap, respectively. The power index  $n$  depends on the type of electronic transition, *i.e.*,  $n$  equals to 1 for a direct band-gap material and 4 for an indirect band-gap material. For semiconductors, the square of absorption coefficient is usually linearly proportional to the energy ( $h\nu$ ) in the absorption edge region during the direct optical transition process. Fig. 4B shows the plots of  $(\alpha h\nu)^{1/2}$  versus energy ( $h\nu$ ). The  $E_g$  values of  $\beta\text{-Ag}_2\text{MoO}_4$  (AMO) and  $g\text{-C}_3\text{N}_4$  (T-CN) are calculated to be 3.20 and 2.69 eV, respectively.

The band edge positions of  $\beta\text{-Ag}_2\text{MoO}_4$  (band gap: 3.20 eV) and  $g\text{-C}_3\text{N}_4$  (band gap: 2.69 eV) were further evaluated using the following empirical equations:<sup>57</sup>

$$E_{\text{VB}} = X - E_0 + 0.5E_g; \quad (2)$$

$$E_{\text{CB}} = E_{\text{VB}} - E_g, \quad (3)$$

where  $E_{\text{VB}}$  is the VB edge potential and  $X$  is the electronegativity of the semiconductor (*i.e.*, the geometric mean of the electronegativity of the constituent atoms). The  $X$  values for  $\beta\text{-Ag}_2\text{MoO}_4$  and  $g\text{-C}_3\text{N}_4$  are calculated to be 5.92<sup>13</sup> and 4.73 eV.<sup>58</sup>  $E_0$  is the energy of free electrons on the hydrogen scale ( $\sim 4.5$  eV) and  $E_g$  is the band gap energy of the semiconductor. According to eqn (2) and (3), the  $E_{\text{VB}}$  and  $E_{\text{CB}}$  values of  $\beta\text{-Ag}_2\text{MoO}_4$  are determined to be 3.02 and  $-0.18$  eV, respectively. Those of  $g\text{-C}_3\text{N}_4$  are 1.57 and  $-1.12$  eV, respectively.

### 3.2. Photocatalytic performance under visible light irradiation

The photocatalytic performance of  $\beta\text{-Ag}_2\text{MoO}_4/g\text{-C}_3\text{N}_4$  heterojunctions was evaluated in the degradation of organic dyes (RhB, MO, and MB) in aqueous systems under visible light irradiation. Prior to irradiation, the mixture containing dye solution and a catalyst (30.0 mg) was kept in the dark for 30 min to ensure the adsorption-desorption equilibrium.

The degradation of RhB under visible light irradiation is extremely slow without adding a catalyst (Fig. 5A). The degradation efficiencies achieved by using AMOCN1, AMOCN2, AMOCN3, AMOCN3, AMOCN4, and AMOCN5 after 60 min of reaction are 98.3%, 99.3%, 99.4%, 90.1%, and 69.4%, respectively, all higher than those achieved by using pristine  $\beta\text{-Ag}_2\text{MoO}_4$  (21.3%), B-CN (40.8%), or T-CN (53.7%) with the same mass (30.0 mg). Especially, AMOCN3 with a  $\beta\text{-Ag}_2\text{MoO}_4/g\text{-C}_3\text{N}_4$  ratio of 37.5% exhibits the highest activity among these catalysts. The degradation efficiency achieved using AMOCN3 (99.4%) is even much higher than the degradation efficiency (54%) achieved using a mechanical mixture of  $\beta\text{-Ag}_2\text{MoO}_4$  (8.20 mg) and  $g\text{-C}_3\text{N}_4$  (21.8 mg) with a  $\beta\text{-Ag}_2\text{MoO}_4/g\text{-C}_3\text{N}_4$  ratio of 37.5%, indicating the advantageous role of nanojunction in the  $\beta\text{-Ag}_2\text{MoO}_4/g\text{-C}_3\text{N}_4$  system.

The degradation data were fit using the pseudo-first-order model (Fig. 5B):  $-\ln(C/C_0) = Kt$ ,<sup>59,60</sup> where  $C$  is the concentration of RhB at time  $t$ ,  $C_0$  is the original concentration of RhB, and  $K$  is the reaction rate constant. As shown in Fig. 5C, the photocatalytic degradation rates using AMOCN1 (0.0854

$\text{min}^{-1}$ ), AMOCN2 (0.105  $\text{min}^{-1}$ ), AMOCN3 (0.111  $\text{min}^{-1}$ ), AMOCN4 (0.0730  $\text{min}^{-1}$ ), and AMOCN5 (0.0332  $\text{min}^{-1}$ ) are much higher than those obtained by using  $\beta\text{-Ag}_2\text{MoO}_4$  (0.00449  $\text{min}^{-1}$ ), B-CN (0.0120  $\text{min}^{-1}$ ), T-CN (0.0193  $\text{min}^{-1}$ ), or a mixture of  $\beta\text{-Ag}_2\text{MoO}_4$  and T-CN (0.0173  $\text{min}^{-1}$ ). Clearly, AMOCN3 exhibits the highest photocatalytic activity.

Fig. 5D shows the temporal evolution of the absorption spectrum of RhB solution in the presence of AMOCN3 under visible-light irradiation. The absorption peak at 553 nm decreases gradually as the irradiation time increases and completely disappears after 45 min, indicating the destruction of the conjugated structure. The stepwise blue shift of the main peak can be attributed to the de-ethylation of RhB, accompanied by slight concomitant blue-shifts from 553 to 492 nm of the maximum absorption.<sup>61,62</sup> This phenomenon is due to the incomplete mineralization of RhB in 45 min. However, the absorption peak at 492 nm also completely disappears after additional 15 min of reaction. In addition, the color of RhB solution gradually changes from red to pale yellow as the reaction proceeds, and even becomes colorless and transparent at the end of reaction, confirming that RhB can be decomposed into small molecules, *e.g.*,  $\text{H}_2\text{O}$  and  $\text{CO}_2$ .<sup>60,63</sup>

The photocatalytic degradation of MO and MB under visible-light irradiation was also studied using AMOCN3 (Fig. 6). A rapid decrease of MO absorption at 464 nm is observed as the reaction proceeds (Fig. 6A). The color of MO solution gradually changes from dark yellow to pale yellow. During 30 min in the dark, AMOCN3 exhibits a higher adsorption efficiency for anionic MO (16.7%) than cationic RhB (9.8%), consistent with previous studies.<sup>64,65</sup> After 60 min of reaction, the MO photodegradation efficiency reaches 84.4%, much higher than that by using B-CN (12.9%), T-CN (20.4%), AMO (2.7%), or a mixture of T-CN and AMO (54.7%, Fig. 6B). Moreover, the photodegradation rate (0.0264  $\text{min}^{-1}$ ) of MO is about 11.7, 7.7, 5.1, or 2.4 times as that by using B-CN (0.00226  $\text{min}^{-1}$ ), T-CN (0.00343  $\text{min}^{-1}$ ), AMO (0.00520  $\text{min}^{-1}$ ), or the mixture (0.0111  $\text{min}^{-1}$ ) as the catalyst (Fig. S8A†). In another reaction, the MB degradation efficiency achieved by using AMOCN3 reaches 100% after 60 min of reaction, higher than that by using B-CN (88.7%), T-CN (95.9%), AMO (73.4%), or the mixture (82.1%) as the catalyst (Fig. 6C and D). The photodegradation rate (0.0762  $\text{min}^{-1}$ ) of MB is about 2.2, 1.5, 3.5, or 2.8 times as that by using B-CN (0.0355  $\text{min}^{-1}$ ), T-CN (0.0519  $\text{min}^{-1}$ ), AMO (0.0218  $\text{min}^{-1}$ ), or the mixture (0.0276  $\text{min}^{-1}$ ) as the catalyst (Fig. S8B†).

The effect of initial concentration of RhB, MO, or MB on the catalytic activity of AMOCN3 was further studied. The degradation efficiency (Fig. 7) and rate (Fig. S9†) decrease with the increase of initial dye concentration. One possible reason is that, when the concentration of dye is too high, a significant portion of visible light may be absorbed by the dye molecules rather than by AMOCN3, which may inhibit the photoactivity. Another reason is that the intermediates formed during the photocatalytic reaction may compete with the dye molecules, further limiting the adsorption and catalytic sites on the catalyst.



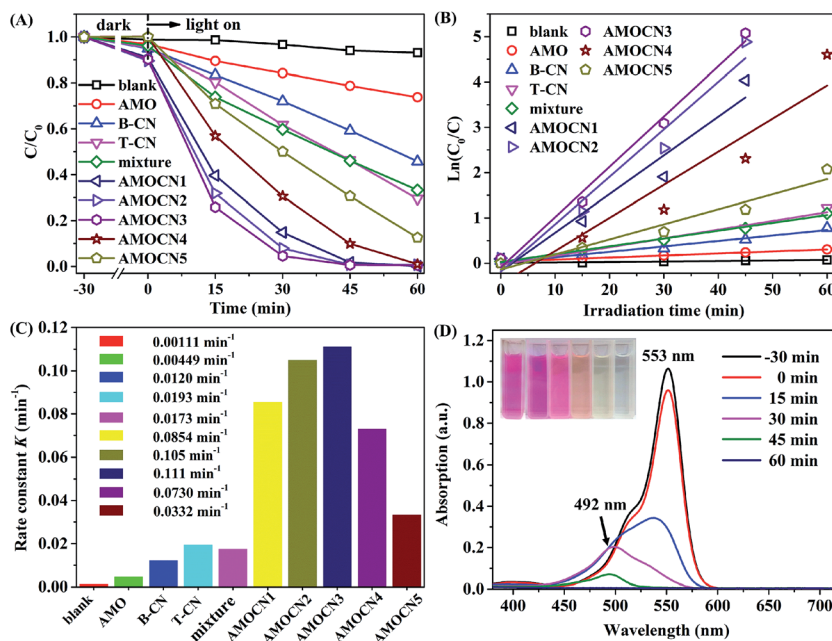


Fig. 5 (A) The adsorption and degradation curves of RhB without photocatalyst and in the presence of the as-prepared catalysts under visible light irradiation; (B) first-order kinetics and (C) rate constants of photocatalytic degradation of RhB over the catalysts; (D) absorption spectra of RhB with reaction time in the presence of AMOCN3 (30.0 mg).

The recyclability of AMOCN3 in photocatalytic degradation of RhB, MO, or MB was studied (Fig. 8A). After the first run, AMOCN3 does not lose activity in the subsequent four runs. The used catalyst exhibits the similar XRD peaks (Fig. 8B) and survey XPS spectrum (Fig. S10A†) as the fresh one. Usually, the transformation of  $\text{Ag}^+$  into  $\text{Ag}^0$  takes place in silver-containing compounds and the resulting photocorrosion may decrease

the catalytic activity.<sup>50,66</sup> However, the formation of  $\text{Ag}^0$  does not happen after five recycling runs in the current work, as seen from high-resolution XPS spectra of Ag 3d from the used AMOCN3 (Fig. S10B–D†), consistent with the result of XRD pattern (Fig. 8B). This is mainly attributed to the fact that the N–H groups or conjugated  $\pi$  structures in g- $\text{C}_3\text{N}_4$  can bond with  $\text{Ag}^+$  (in  $\beta\text{-Ag}_2\text{MoO}_4$ ) tightly due to the chemical adsorption,

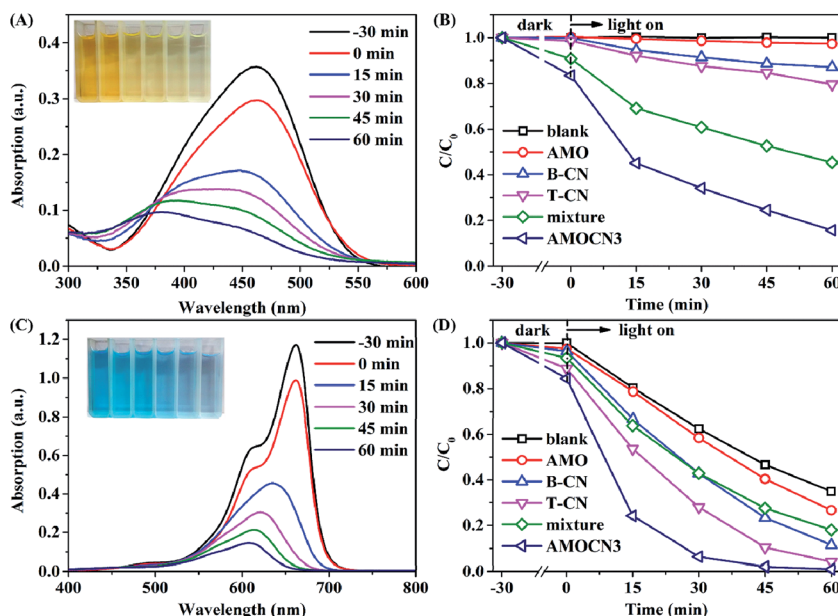


Fig. 6 Absorption spectra of MO (A) or MB (C) with reaction time in the presence of AMOCN3 (30.0 mg); the adsorption and degradation curves of MO (B) or MB (D) without catalyst and in the presence of relevant catalysts under visible light irradiation.





Fig. 7 The effect of initial concentration of (A) RhB, (B) MO or (C) MB on the catalytic performance of AMOCN3 (30.0 mg) under visible light irradiation.

which may protect  $\beta\text{-Ag}_2\text{MoO}_4$  from photo-reduction ( $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}^0$ ) during the photocatalytic process.<sup>46,50</sup>

To analyze the reaction mechanism, it is essential to identify the main active species. Trapping agents such as benzoquinone (BQ), ammonium oxalate (AO),  $\text{AgNO}_3$ , and isopropyl alcohol (IPA) have been used to capture superoxide radical anions ( $\text{O}_2^-$ ), photogenerated holes ( $\text{h}^+$ ), photogenerated electrons ( $\text{e}^-$ ), and hydroxyl free radicals ( $\text{OH}$ ), respectively.<sup>53,60,67</sup> As shown in Fig. 9, the addition of IPA or  $\text{AgNO}_3$  has no obvious effect on the photocatalytic activity of AMOCN3, suggesting that  $\text{OH}$  and  $\text{e}^-$  are not the primary active species. However, when AO or BQ is added into the system, the RhB degradation efficiency decreases from 100% to 9.9% or 31.4% after 45 min of reaction, and the



Fig. 8 (A) Cycling runs in photocatalytic degradation of RhB, MO or MB over AMOCN3 (30 mg) under visible light irradiation; (B) XRD patterns of AMOCN3 before and after respective photocatalytic reactions.

photodegradation rate also decreases from 0.111 to 0.00073 and 0.00693  $\text{min}^{-1}$ , respectively (Fig. 9). Thus,  $\text{O}_2^-$  and  $\text{h}^+$  play a critical role in the photodegradation of RhB over AMOCN3.

Based on the band edge positions, the transfer path of the photogenerated charge carriers in  $\beta\text{-Ag}_2\text{MoO}_4/\text{g-C}_3\text{N}_4$  under visible light is drawn in Fig. 10. Under visible light irradiation, the electrons ( $\text{e}^-$ ) in  $\beta\text{-Ag}_2\text{MoO}_4$  cannot be excited from the VB to CB but the electrons photoexcited in the CB of  $\text{g-C}_3\text{N}_4$  still drift to the CB of  $\beta\text{-Ag}_2\text{MoO}_4$  because of the more negative potential of the CB for  $\text{g-C}_3\text{N}_4$ . Because the CB potential of  $\beta\text{-Ag}_2\text{MoO}_4$  is higher than that of  $\text{O}_2/\text{O}_2^-$  ( $-0.33$  eV),<sup>50</sup> the electrons on the CB of  $\beta\text{-Ag}_2\text{MoO}_4$  cannot reduce  $\text{O}_2$  to generate  $\text{O}_2^-$ . Thus,  $\text{O}_2^-$  may be firstly generated by the electrons excited on the CB of  $\text{g-C}_3\text{N}_4$ . The excessive electrons will then transfer from the CB of  $\text{g-C}_3\text{N}_4$  to that of  $\beta\text{-Ag}_2\text{MoO}_4$ . The photogenerated holes left in the CB of  $\text{g-C}_3\text{N}_4$  could not oxidize  $\text{H}_2\text{O}$  to generate  $\text{OH}$  owing to the more positive potential of  $\text{OH}/\text{H}_2\text{O}$  (2.68 eV).<sup>50</sup> Hence, the photogenerated holes will react with the target pollutants (RhB, MO, and MB) directly due to their strong oxidative capacity. These main active species ( $\text{O}_2^-$  and  $\text{h}^+$ ) can break down the chromophores of the organic dyes (RhB, MO, and MB) into small molecules, e.g.,  $\text{H}_2\text{O}$  and  $\text{CO}_2$ .<sup>60,63</sup>





Fig. 9 Comparison of the photocatalytic performances of AMOCN3 for the degradation of RhB without adding or with the addition of ammonium oxalate (AO), benzoquinone (BQ), isopropyl alcohol (IPA), or  $AgNO_3$  under visible light irradiation.

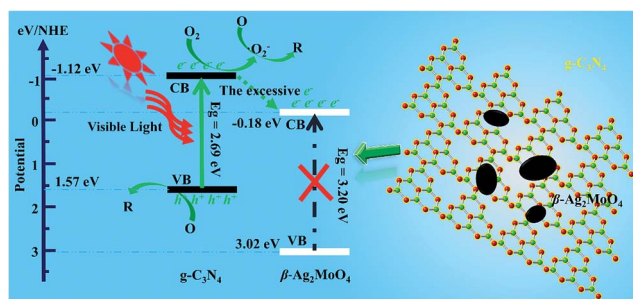


Fig. 10 The proposed mechanism for the improvement of photocatalytic activity.

## 4. Conclusions

$\beta\text{-Ag}_2\text{MoO}_4/\text{g-C}_3\text{N}_4$  heterojunctions were synthesized by the *in situ* deposition of  $\beta\text{-Ag}_2\text{MoO}_4$  nanoparticles on the surface of thin  $\text{g-C}_3\text{N}_4$  nanosheets. They were much more active than pristine  $\beta\text{-Ag}_2\text{MoO}_4$  or  $\text{g-C}_3\text{N}_4$  in photocatalytic degradation of several organic dyes (Rhodamine B, methyl orange, and methylene blue) under visible light irradiation. The optimal  $\beta\text{-Ag}_2\text{MoO}_4/\text{g-C}_3\text{N}_4$  mass ratio is 37.5%. Superoxide radical anions ( $\text{O}_2^-$ ) and photogenerated holes ( $h^+$ ) are the primary active species in the photocatalytic degradation of RhB. There are two

main reasons for the high photocatalytic activity of the  $\beta\text{-Ag}_2\text{MoO}_4/\text{g-C}_3\text{N}_4$  heterojunctions. First,  $\text{g-C}_3\text{N}_4$  has an appropriate band gap for the visible light absorption. Second, the nanojunction between  $\beta\text{-Ag}_2\text{MoO}_4$  and  $\text{g-C}_3\text{N}_4$  can promote the separation efficiency of photogenerated electrons ( $e^-$ ) and holes ( $h^+$ ). This work provides a new example on the development of  $\text{g-C}_3\text{N}_4$ -based or  $\beta\text{-Ag}_2\text{MoO}_4$ -based photocatalysts with excellent photocatalytic activity under visible-light irradiation, and it provides new opportunities for us to expand the application of this type of catalysts in other reactions such as photocatalytic bacterial/virus inactivation and removal of air pollutants in the future.

## Acknowledgements

Zhen Ma acknowledges the financial support by National Natural Science Foundation of China (Grant No. 21477022).

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