Pt nanoparticles decorated heterostructured g-C$_3$N$_4$/Bi$_2$MoO$_6$ microplates with highly enhanced photocatalytic activities under visible light

Z. Jia$^{1,2}$, F. Lyu$^{1,2}$, L. C. Zhang$^3$, S. Zeng$^{4,5}$, S. X. Liang$^3$, Y. Y. Li$^{4,5,6}$ & J. Lu$^{1,2,6}$

Exploring an efficient and photostable heterostructured photocatalyst is a pivotal scientific topic for worldwide energy and environmental concerns. Herein, we reported that Pt decorated g-C$_3$N$_4$/Bi$_2$MoO$_6$ heterostructured composites with enhanced photocatalytic performance under visible light were simply synthesized by one-step hydrothermal method for methylene blue (MB) dye degradation. Results revealed that the synthetic Pt decorated g-C$_3$N$_4$/Bi$_2$MoO$_6$ composites with Bi$_2$MoO$_6$ contents of 20 wt.% (Pt@CN/20%BMO) presented the highest photocatalytic activity, exhibiting 7 and 18 times higher reactivity than the pure g-C$_3$N$_4$ and Bi$_2$MoO$_6$, respectively. Structural analyses showed that Bi$_2$MoO$_6$ microplates were anchored on the wrinkled flower-like g-C$_3$N$_4$ matrix with Pt decoration, leading to a large expansion of specific surface area from 10.79 m$^2$/g for pure Bi$_2$MoO$_6$ to 46.09 m$^2$/g for Pt@CN/20%BMO. In addition, the Pt@CN/20%BMO composites exhibited an improved absorption ability in the visible light region, presenting a promoted photocatalytic MB degradation. Quenching experiments were also conducted to provide solid evidences for the production of hydroxyl radicals (•OH), electrons (e$^-$), holes (h$^+$) and superoxide radicals (•O$_2^-$) during dye degradation. The findings in this critical work provide insights into the synthesis of heterostructured photocatalysts with the optimization of band gaps, light response and photocatalytic performance in wastewater remediation.

Advanced oxidation processes (AOPs) with their superior purification efficiency of toxic organic compounds have been recently attracted large attentions in industrial wastewater treatment$^{1–6}$. Compared to alternatives, such as Fenon/Fenton-like process$^{7–9}$ and ozone oxidation$^{10–12}$, semiconductor photocatalysts have received tremendous attentions to address the worldwide environmental and energy concerns$^{13}$. Since Fujishima and Honda discovered the photoelectrochemical effects of TiO$_2$$^{14}$, the research of various single component semiconductors, such as oxides$^{15,16}$ and sulfide semiconductors$^{17,18}$, has caught much attentions in the last decades. However, many reports have demonstrated that these single component semiconductors are photo-instability, fast recombination rate of electron hole pairs and wide band gaps$^{19}$, exhibiting a significant limitation in achieving practical industrialization. To date, attempts have been made to overcome these disadvantages. For example, doping agents with non-metal ions, metalloids or ionic groups on the photocatalysts could effectively alter energy band structure and carrier separation$^{20}$. It was found that N-doped CeO$_x$ nanoparticles on g-C$_3$N$_4$ matrix presented a promoted photocatalytic activity due to formation of intimate interfacial contact$^{21}$. B-doped BiOBr nanosheets could enhance the charge carrier separation efficiency, thereby enhancing the ability of accepting electrons from the valence

1Hong Kong Branch of National Precious Metals Material Engineering Research Center, Department of Material Science and Engineering, City University of Hong Kong, Hong Kong, China. 2Department of Mechanical Engineering, City University of Hong Kong, Hong Kong, China. 3School of Engineering, Edith Cowan University, 270 Joondalup Drive, Joondalup, Perth, WA, 6027, Australia. 4Center of Super-Diamond and Advanced Films (COSDAF), City University of Hong Kong, Kowloon, Hong Kong, China. 5Department of Physics and Materials Science, City University of Hong Kong, Shenzhen Research Institute, 8 Yuxing 1st Road, Shenzhen Hi-Tech Industrial Park, Nanshan District, Shenzhen, China. Correspondence and requests for materials should be addressed to J.L. (email: jianlu@cityu.edu.hk)
band of BiOBr.\(^{22}\) \(\text{PO}_4\) ionic group doped Bi\(_2\)WO\(_6\) nanoplates demonstrated a significant regulation of their band structure, charge carrier separation efficiency and light absorbance for improving photocatalytic activity\(^{20}\). In addition, synthesis of heterojunction structure\(^{23}\) and decoration of noble metals\(^{29}\) in photocatalysts with enhanced visible light response and easy separation of electron-hole pairs have also induced extensive interests in recent years. For example, the formation of heterojunction structure on TiO\(_2\),\(^{23}\) ZnO\(^{36}\) and some carbon matrix such as g-C\(_3\)N\(_4\),\(^{22}\) r-GO\(^{38}\) and carbon nanotubes\(^{39}\) presents an efficient separation of electrons and holes to facilitate photocatalytic activity. The decoration of noble metals, such as Au,\(^{40}\) Ag,\(^{41}\) Pt\(^{42}\) and Pd\(^{43}\) exhibits an improved light response to extend the light absorbance range.

Bi\(_2\)MoO\(_6\) as one of the most important members in Aurivillius oxide family, is always at the cutting edge of research in photocatalytic degradation of organic pollutants\(^{44}\) and energy evolution\(^{45}\). The pure Bi\(_2\)MoO\(_6\) with a relatively lower band gap (2.5–2.8 eV)\(^{46}\) presents an enhanced light response compared to some photocatalytic sy\(_\text{stem}s\), such as TiO\(_2\) and ZnO with the band gaps of 3.2–3.3 eV\(^{37}\). However, due to their fast recombination efficiency of charge carriers, Bi\(_2\)MoO\(_6\) usually presents a poor quantum yield that would greatly restrain their practical applications. So far, many attempts have been exploited to improve the photocatalytic performance of Bi\(_2\)MoO\(_6\) such as doping lanthanide ions\(^{48}\) or noble metals\(^{49}\) to act as redox centers, the formation of heterojunction structures containing metal oxides\(^{50}\), metal sulfates\(^{51}\) or carbon materials\(^{52,53}\), etc.

Recently, g-C\(_3\)N\(_4\) with its superior optical properties (band gap \(\approx 2.7\) eV) and photostability has been widely employed as a matrix to synthesize heterostructured photocatalysts\(^{54}\). The unique structure of covalently-linked sp\(^2\) bonded carbon network with the decoration of nitrogen atoms in g-C\(_3\)N\(_4\) presents an excellent thermal and chemical stability. Moreover, the large scaffold structure could undoubtedly provide a large specific surface area for being anchored by other semiconductors and also could effectively prevent the particle aggregation. Nevertheless, the most important drawback of high–low–hole pairs still largely inhibits their extensive applications. As such, the formation of heterojunctions by two semiconductors or anchoring noble metallic nanoparticles is rapid development in recent years, for example, the synthesis of g-C\(_3\)N\(_4\) with semiconductors of TiO\(_2\),\(^{44}\) ZnO\(^{45}\), NaNB\(_2\)O\(_6\),\(^{46}\) Bi\(_2\)WO\(_6\)\(^{47}\) or TaO\(_2\)\(^{48}\) and the decoration of noble metals on g-C\(_3\)N\(_4\) by Au,\(^{49}\) Pt,\(^{50}\) Ag,\(^{51}\) or Pd\(^{52}\). However, the current studies have been focusing on synthesizing photocatalysts with two components. There are few attempts to investigate the noble metals being anchored on the heterojunctions, in which the optical structure is regulated by the synthesis of two semiconductors with a similar band gap and the electron-hole recombination efficiency is effectively suppressed by the noble metals doping.

In this work, Pt decorated g-C\(_3\)N\(_4\)/Bi\(_2\)MoO\(_6\) heterostructured semiconductors are synthesized by one-step hydrothermal method to investigate their photocatalytic activity of MB degradation under visible light. Various amounts of Bi\(_2\)MoO\(_6\) loading (10%, 20% and 50%) on g-C\(_3\)N\(_4\) matrix are initially examined to demonstrate the optimal combination of the two semiconductors followed by Pt decoration. The structures of the synthetic composites are systematically characterized. The MB degradation and mineralization as well as the corresponding reaction kinetics (\(k_{\text{obs}}\)) using the synthetic photocatalysts are comparatively investigated in detail. Quenching experiments by adding radical scavengers are also conducted to study the photocatalytic mechanisms.

**Results**

**Structures and morphologies.** Figure 1 shows scanning electron microscope (SEM) images of the as-prepared g-C\(_3\)N\(_4\) (CN), Bi\(_2\)MoO\(_6\) (BMO), g-C\(_3\)N\(_4\)/Bi\(_2\)MoO\(_6\) composites with Bi\(_2\)MoO\(_6\) contents of 10 wt. % (CN/10%BMO), of 20 wt. % (CN/20%BMO), of 50 wt. % (CN/50%BMO) and Pt decoration (Pt@CN/20%BMO), providing a direct view of surface morphologies of the photocatalysts. As shown in Fig. 1a, the obtained pure CN presents a flower-like structure with multiple wrinkled-layers, exhibiting a large surface area for further BMO and Pt nanoparticles decoration. Fig. 1b presents the pure BMO microplates with a laminar and irregular sheet-like microstructure. Notably, the BMO microplates have much smaller particle size than the CN, demonstrating great potential for them to anchor on the CN matrix. Fig. 1c–e show the morphologies of BMO and CN composites with a certain amount of BMO loading of 10%, 20% and 50%, respectively. Apparently, a denser BMO laminar sheet (Fig. 1d,e) is decorated on the wrinkled CN matrix compared to the CN/10%BMO loading in Fig. 1c. In addition, the size of the anchored BMO (Fig. 1c–e) is much smaller than that of the pure BMO (Fig. 1b) without altering the sheets-like morphology, providing more active sites for dye degradation. The smaller size of the anchored BMO is primarily ascribed to the initial adsorption of Bi\(^{1+}\) onto the CN according to the benefit of facile one-step hydrothermal synthetic method. The morphology of Pt@CN/20%BMO composites and atomic mapping images, e.g., Bi, Mo, C for CN/20%BMO and Pt, Bi, C for Pt@CN/20%BMO, are shown in Fig. 1f–h, providing a solid indication for the formation of Pt@CN/20%BMO heterojunctions.

Figure 2 shows transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images of CN, CN/10%BMO, CN/20%BMO, CN/50%BMO and Pt@CN/20%BMO. The pure CN presents a wrinkled and layered morphology, as shown in Fig. 2a, which agrees with the SEM image (Fig. 1a) and other reports\(^{55}\). Fig. 2b–d imply the formation of CN and BMO heterojunctions and further reveal that the anchored BMO is in a sheet-like microplate. HRTEM images of CN/20%BMO and Pt@CN/20%BMO are presented in Fig. 2e,f. A lattice fringe with a space of 0.32 nm (Fig. 2e) corresponds to (131) plane of BMO, while the spacing of 0.22 nm (Fig. 2f) is ascribed to (111) plane of Pt with a particle size of \(-5\) nm. The fast fourier transform (FFT) images in the insets of Fig. 2e,f show that the single-crystalline structure of BMO is converted to poly-crystalline structure of Pt and BMO composites. Combining the elemental mapping images in Fig. 2g, this result further confirms the successful formation of Pt@CN/20%BMO heterojunctions.

The crystalline structures of the as-prepared samples are also investigated by X-ray diffraction (XRD) (Fig. 3). Two distinct peaks at 13.1° and 27.3° are observed on the CN curve, indicating (100) plane of tri-s-triazine group and (002) plane of aromatic laminar sheets, respectively\(^{54}\). XRD patterns are clearly characterized to confirm the orthorhombic crystalline structure of \(\gamma\)-BMO (JCPDS No. 21–0102)\(^{40}\). The strongest intensity at (131) plane is in accordance with the result of HRTEM image (Fig. 2e). For the CN/BMO composites, all the characterized
diffraction peaks of BMO are remained, demonstrating the successful formation of heterojunctions. However, the peaks at (100) and (002) plane of CN are detected to be invisible and be overlapped with the peak at (131) plane of BMO, which is similar to other report55. For the Pt@CN/20%BMO composites, characterized diffraction peaks of Pt at 40.1, 46.9 and 67.9° indicate the (111), (100) and (220) planes while all the peaks of BMO are clearly observed, demonstrating Pt nanoparticles are decorated on the CN/BMO heterojunctions.

**Chemical states.** X-ray photoelectron spectroscopy (XPS) and fourier-transform infrared spectroscopy (FTIR) analyses have been conducted to confirm the surface chemical and valence states of the as-prepared

---

**Figure 1.** SEM images of (a) CN, (b) BMO, (c) CN/10%BMO, (d) CN/20%BMO, (e) CN/50%BMO, (f) Pt@CN/20%BMO and corresponding elemental mapping results of (g) CN/20%BMO and (h) Pt@CN/20%BMO.
samples. As shown in Figure S1, the elements including Pt, Bi, Mo, O, C and N with strong intensities are observed in the composites. No other impurity peaks are obtained. Fig. 4a shows the high-resolution spectra of Bi 4f for BMO, CN/20%BMO and Pt@CN/20%BMO. The bonding energies at 159.1 and 164.4 eV correspond to Bi 4f7/2 and Bi 4f5/2 of Bi3+, respectively. For the Mo 3d spectra in Fig. 4b, the peaks located at 232.3 and 235.5 eV are attributed to Mo 3d5/2 and Mo 3d3/2 of Mo6+, respectively. In the O 1 s spectra (Fig. 4c), it is noted that the peak at 530.0 eV of pure BMO presents slight shifts to 529.9 eV and 530.1 eV for CN/20%BMO and Pt@CN/20%BMO samples, respectively. The shifted peaks in Bi 4f and Mo 3d (Fig. 4a,b) indicate formation of the groups of Bi-O and Mo-O. Such results further imply the formation of CN/BMO heterojunctions with Pt decoration. Fig. 4d shows the high-resolution of Pt 4f spectra. The characterized peaks at 70.9 and 74.2 eV of Pt0 are clearly observed on 4f7/2 and 4f5/2, respectively. The peaks at 72.0 and 75.6 eV are attributed to Pt2+, indicating the formation of Pt-O and further demonstrating the partial pre-adsorption of Pt2+ onto the CN matrix during the facile one-step hydrothermal synthetic method. Fig. 5 shows the FTIR results of the as-prepared composites. For the pure CN, a group of characterized peaks are clearly observed in the range from 1241 to 1639 cm⁻¹. In detail,
the peaks located at 1241, 1325 and 1408 cm$^{-1}$ are attributed to the stretching vibration mode of C-N bonds with the aromatic structure, while the peak at 1639 cm$^{-1}$ can be ascribed to the stretching vibration mode of C≡N$^{59}$. For the pure BMO, the characterized peaks located at 570 and 734 cm$^{-1}$ indicate the bending vibration of the octahedral structure and the asymmetric stretching mode in MoO$_6$, respectively, while the wavenumbers at 796 and 842 cm$^{-1}$ correspond to the Mo-O symmetric and asymmetric stretching vibration modes in the MoO$_6$ octahedral structure$^{59}$. Clearly, all the characterized peaks in pure CN and BMO are presented in the CN/20%BMO and Pt@CN/20%BMO composites, demonstrating the successful formation of the photocatalysts. Such a result is in great agreement with the aforementioned SEM, TEM and XRD analyses.
Optical property. The optical property plays a significant role in revealing the band gap structures of heterojunction photocatalysts. Fig. 6a shows the ultraviolet photoelectron spectroscopy (UPS) spectra of the as-prepared CN and BMO composites to indicate the Fermi ($E_{\text{Fermi}}$) and cut-off ($E_{\text{cut-off}}$) energy states by estimating the intersection values. Notably, the valence band energy ($E_{\text{VB}}$), which is equivalent to the ionization potential ($\varphi$), is calculated by the equation below (Equation 1)\(^{54}\):

$$\varphi = hv - E_{\text{cut-off}} + E_{\text{Fermi}}$$

whereas $hv$ is the photon energy from He I source as 21.22 eV.

The values of $\varphi$ are then calculated as 6.24 and 6.78 eV for the as-prepared CN and BMO, respectively, suggesting the electrons would transfer from CN to BMO ($\varphi_{\text{CN}} < \varphi_{\text{BMO}}$) after the formation of heterojunction structure\(^{40}\).
In order to find out the position of conduction band \((E_{CB})\), the band gap energy \((E_g)\) is estimated by UV-Vis diffuse reflectance spectrum (UV-DRS) spectra as shown in Fig. 6b using the equation below (Equation 2)\(^60\),

\[
E_g (eV) = \frac{1240}{\lambda_g}
\]

whereas the absorption edge \((\lambda_g)\) is observed by the intersection values of the tangent and the wavelength axis.

The values of \(E_g\) and \(E_{CB}\) of the as-prepared CN and BMO samples can be subsequently calculated as 2.66, 2.77 eV \((E_g)\) and 3.58, 4.01 eV \((E_{CB} = E_{VB} - E_g)\), respectively. In the expression of reversible hydrogen electrode (RHE) vs. volts (V) (0 V in RHE is equivalent to \(-4.44\) eV in energy potential\(^61\)), the \(E_{CB}\) can be positioned at \(-0.86\) and \(-0.43\) V of the CN and BMO composites, respectively. Fig. 6c presents the estimated band structures of the prepared CN and BMO samples according to the above calculation. Due to the similar band structures of CN and BMO, the electrons in the CB and the holes in the VB would be promoted from the CN to BMO and BMO to CN, respectively. The electronic motion in the modified band structure of CN/BMO heterostructures would be improved, and more importantly, the inclusion of Pt nanoparticles as electron mediators anchoring on the CN/BMO heterostructures would further promote the electron transfer. In addition, the observation of the improved absorption intensity in the visible light region for the Pt@CN/20%BMO photocatalyst indicates that the band structure could be effectively altered to enhance the visible light response and charge transformation. The improved absorption intensity and slight red shift of Pt@CN/20%BMO photocatalyst can be ascribed to the localized surface plasmon resonances (LSPRs) of Pt nanoparticles\(^24\), which would enhance the photocatalytic activity for dye degradation.

The heterogeneous photocatalytic activity is also significantly influenced by the specific surface area of photocatalysts due to the provision of surface-reactive sites. Figure S2 presents the nitrogen adsorption/desorption isotherms of the as-prepared samples. Clearly, strong N\(_2\) adsorption/desorption curves are observed in the pressure range of 0.1–0.9, indicating the capillary condensation in large mesopores exists in all the samples\(^35\). As shown in Figure S2 inset, the Brunauer-Emmett-Teller (BET) specific surface area of Pt@CN/20%BMO with 46.09 m\(^2\)/g presents significant improvement compared to the pure BMO with 10.79 m\(^2\)/g and CN/20%BMO with 39.92 m\(^2\)/g, respectively. In addition, the Pt@CN/20%BMO with a total pore volume of 1.092 cm\(^3\)/g (Barrett-Joyner-Halenda (BJH) process) would provide much more active sites compared to the other samples. Such results are in accordance with the above SEM analysis. The Pt nanoparticles and BMO laminar sheets are densely distributed on the wrinkled CN matrix that would lead to a higher photocatalytic activity for the following dye degradation. Figure S3 shows the thermogravimetric analysis (TGA) results of the as-prepared samples. It is noted that the TGA curve of the pure CN presents a sharp weight loss in the temperature range from 500 to 680 °C and nearly no CN remaining after 680 °C, while there is only 1.1% weight loss for the pure BMO samples due to the slight adsorption and activation of atmospheric oxygen\(^55\). However, the significant weight loss of CN/20%BMO and Pt@CN/20%BMO is shifted to the temperature range from 400 to 580 °C and 380 to 570 °C, respectively. Surprisingly, the obtained ratio between BMO and CN from TGA result is higher than the theoretical value of 20%, which is mainly attributed to the existence of BMO and Pt would promote the oxidation of CN and the adsorption of atmospheric oxygen. Similar performance has been reported in g-C\(_3\)N\(_4\)/Bi\(_2\)MoO\(_6\) as-prepared samples. Clearly, the Pt decorated photocatalysts present a significant enhancement for the MB degradation compared to all the others, whereas nearly 100% dye degradation is achieved at 120 min, indicating that its heterojunction structure is successfully regulated by the facile hydrothermal synthesis. The corresponding kinetic rates \((k_{obs})\) of the as-prepared samples for MB degradation are calculated by the pseudo-first-order kinetics model (Equation 3) as shown in Fig. 7b.

\[
\ln(C_0/C) = k_{obs}t
\]

whereas \(k_{obs}\) is the kinetic rate constant; \(C_0\) is the original concentration of dye; \(C\) is the dye concentration at time \(t\).

Notably, the Pt@CN/20%BMO composites with the \(k_{obs} = 0.036\) min\(^{-1}\) presents 7 times and 18 times higher photocatalytic activity than the pure CN with \(k_{obs} = 0.005\) min\(^{-1}\) and BMO with \(k_{obs} = 0.002\) min\(^{-1}\), respectively. In addition, the photoactivity of the synthetic Pt@CN/20%BMO composites is much promoted than the commercial p-25 with \(k_{obs} = 0.002\) min\(^{-1}\) and also other state-of-the-art ternary photocatalysts under visible light (Table 1), demonstrating their excellent catalytic property in wastewater remediation. Fig. 7c presents the UV-Vis spectra
of MB degradation using 0.5 g/L of Pt@CN/20%BMO photocatalyst at different time intervals. It can be observed that the characterized peaks at $\lambda = 292$ nm (triazine group) and $\lambda = 664$ nm (heteropoly aromatic linkage) of MB gradually decrease to be invisible from 0 min to 120 min, indicating the organic components in the dye are decomposed to nontoxic NO$_3^-$, SO$_4^{2-}$, H$_2$O and CO$_2$. The slight blue shift (towards blue end in the spectrum) of the absorbance in MB dye from 664 nm to 634 nm is likely ascribed to the initial degradation of auxochrome (-CH$_3$), resulting in a slight color change during photocatalytic activity. The inset of Fig. 7c presents a solid evidence of the visible color change during MB degradation.

Figure 7. (a) photocatalytic MB degradation and (b) corresponding kinetic rates ($k_{\text{obs}}$) of the as-prepared samples, (c) UV-Vis spectra of color removals for Pt@CN/20%BMO photocatalysts and (d) COD removals at 150 min of as-prepared samples under visible light.

| SC 1 | SC 2 | Metallic mediators | Light source (Power, W) | Organic pollutants | Degradation (%) and Time (h) | Ref. |
|------|------|-------------------|------------------------|-------------------|-----------------------------|------|
| CdS | TiO$_2$ | Au | LP Hg lamp (20) | MB | 72 and 2 | 76 |
| g-C$_3$N$_4$ | BiPO$_4$ | Au | Xe lamp (300) | MO | 88 and 2.6 | 71 |
| Mo$_2$ | Ag,PO$_4$ | Ag | Solar Xe arc lamp (35) | PhOH | 95 and 2 | 72 |
| g-C$_3$N$_4$ | WO$_3$ | Cu, Ag, Au | Xe arc lamp (500) | 4-NPPhOH | 100 and 2 | 73 |
| In$_2$S$_3$ | Ag, CrO$_4$ | Ag | Xe arc lamp (300) | MO | 65.3 and 2 | 74 |
| ZnS | Ag,PO$_4$ | Ag | Xe lamp (350) | MB | 82 and 2 | 75 |
| g-C$_3$N$_4$ | Ag, CrO$_4$ | Ag | HP Xe Lamp (500 W) | 2,4-DCP | 94 and 2 | 76 |
| CdS | BiOCl | Au | Xe lamp (300) | SD | 100 and 4 | 77 |
| g-C$_3$N$_4$ | Bi$_2$MoO$_6$ | CNT | Xe lamp (500) | 2,4-DBP | 68.8 and 2 | 78 |
| g-C$_3$N$_4$ | Bi$_2$MoO$_6$ | Pt | Xe lamp (300) | MB | 100 and 2 | This work |

Table 1. Comparison of ternary photocatalysts for degradation of organic pollutants under visible light.
It is well accepted that the progress of dye molecule decomposition is mainly due to the generation of the active species during photocatalysis. To identify these dominant active species, various radical scavengers including IPA, CrO3, SO and BQ are employed to prove the generation of $\bullet$OH, $e^-$, $h^+$ and $\bullet$O2$^-$, respectively. As shown in Figure S4, the addition of IPA causes a decrease in MB degradation compared to the only addition of Pt@CN/20%BMO photocatalysts, suggesting the $\bullet$OH radicals are gradually formed during this photocatalytic activity. In comparison, the MB degradation efficiency is more affected by the addition of CrO3, SO and BQ, leading to the efficiency sharply decreases to nearly 50% at 150 min. Such performance indicates that the generated $e^-$, $h^+$ and $\bullet$O2$^-$ are the dominant oxidants for MB degradation in this work.

Discussion

Fig. 8 shows the proposed photocatalytic mechanism of the synthetic heterojunctions. Considering the above band gap analysis in Fig. 6, the photo-induced $h^+$ with an energy of 2.34 V at VB presents lower energy state than the $\bullet$OH of 2.70 V, leading to the $\bullet$OH cannot be directly activated from H2O during the photocatalysis. The existing $\bullet$OH is produced by the reaction of $e^-$ and the gradually generated H2O2. This is the reason why sole $\bullet$OH plays partially synergistic dye degradation in this work. Therefore, the $h^+$ with strong oxidation ability is directly employed for decomposing the MB molecule. In comparison, the potential of $e^-$ with the value of -0.86 V at CB is much negative than the $\bullet$O2$^-$ with the value of 1.23 V, resulting in easy reduction of dissolved O2 to $\bullet$O2$^-$ thereby degrading the organic matters.

More importantly, the decorated Pt nanoparticles in this work play a significant role to serve as a solid-state electron mediator. The generated $e^-$ on the CB of g-C3N4 in the heterojunctions is easily transferred to the Pt particles and Bi2MoO6 microplates that would effectively promote electron transfer and suppress the electron-hole recombination efficiency. In addition, the produced $h^+$ also could migrate from Bi2MoO6 to g-C3N4 in the heterojunctions, which also provides significant reduction of recombination efficiency. Therefore, the photocatalytic dye degradation efficiency of Pt@CN/20%BMO is more enhanced than those of the pure BMO, CN and even for the CN/BMO composites.

Methods

Materials. Bismuth nitrate pentahydrate (Bi(NO3)3·5H2O), ammonium molybdate tetrahydrate ((NH4)6Mo7O24·4H2O), potassium tetrachloroplatinate (K2PtCl4) and melamine were purchased from Strem Chemicals, INC (USA). Chromium trioxide (CrO3), sodium oxalate (SO, Na2C2O4), 1,4-benzoquinone (BQ) and isopropanol (IPA) supplied from J&K Scientific Ltd., (China) were used throughout this work as electron ($e^-$), hole ($h^+$),
visible light. Afterwards, 4 ml of the MB solution were taken at different predetermined time intervals and separated, and the analytical grades.

weights of g-C3N4 (i.e. 2.7 g, 1.2 g and 0.3 g) were gradually added into the mixed solvent and stirred for another 90 min. XRD (Rigaku SmartLab) using Cu Kα radiation. XPS measurements were performed on a VG ESCALAB 220i-XL surface analysis system to record the surface atomic distribution of the as-prepared powders. The structural characterization of the as-prepared samples was collected using FTIR (Thermo Scientific Nicolet iS50) and UV-Vis DRS (PerkinElmer Lambda 750) using BaSO4 as the reference to characterize the electronic levels and band structures of the as-prepared samples. The specific surface area was recorded by BET on a Micromeritics, ASAP2020 gas sorption analyzer at 77 K. TGA was carried out on a TGA Q50 instrument by heating from 30 to 800 °C at a heating rate of 10 °C/min under nitrogen protection. The UV-Vis spectrometer (PerkinElmer Lambda2S) was employed for measuring the dye absorbance.

Characterizations. The SEM (JEOL JSM-820) and TEM (JEOL TEM 2100F FEG) as well as HRTEM equipped with energy-dispersive X-ray spectroscopy (EDS) were employed for characterizing the surface morphology and inner structure of the as-prepared samples. The crystalline phases of the samples were examined by XRD (Rigaku SmartLab) using Cu Kα radiation. XPS measurements were performed on a VG ESCALAB 220i-XL surface analysis system to record the surface atomic distribution of the as-prepared powders. The structural characterization of the as-prepared samples was collected using FTIR (Thermo Scientific Nicolet iS50) and UV-Vis DRS (PerkinElmer Lambda 750) using BaSO4 as the reference to characterize the electronic levels and band structures of the as-prepared samples. The specific surface area was recorded by BET on a Micromeritics, ASAP2020 gas sorption analyzer at 77 K. TGA was carried out on a TGA Q50 instrument by heating from 30 to 800 °C at a heating rate of 10 °C/min under nitrogen protection. The UV-Vis spectrometer (PerkinElmer Lambda2S) was employed for measuring the dye absorbance.

Photocatalytic activity. In the photocatalytic experiments, a specific mass of the as-prepared photocatalysts was dispersed in 100 ml of MB solution with 10 ppm concentration (10 mg/L). The MB solution with catalysts was initially stirred for 60 min in darkness to achieve equilibrium adsorption, followed by a direct irradiation under a source of 300 W Xeon simulated solar light lamp with an ultraviolet cut off filter (λ ≤ 420 nm) to provide visible light. Afterwards, 4 ml of the MB solution were taken at different predetermined time intervals and separated, and the analytical grades.

The as-prepared photocatalysts were investigated using a specific mass of the as-prepared photocatalysts was dispersed in 100 ml of MB solution with 10 ppm concentration (10 mg/L). The MB solution with catalysts was initially stirred for 60 min in darkness to achieve equilibrium adsorption, followed by a direct irradiation under a source of 300 W Xeon simulated solar light lamp with an ultraviolet cut off filter (≥ 420 nm) to provide visible light. Afterwards, 4 ml of the MB solution were taken at different predetermined time intervals and separated, and the analytical grades.

References
1. Ribeiro, A. R., Nunes, O. C., Pereira, M. F. R. & Silva, A. M. T. An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched Directive 2013/39/EU. Environ. Int. 75, 33–51 (2015).
2. Jia, Z. et al. Attractive In Situ Self-Reconstructed Hierarchical Gradient Structure of Metallic Glass for High Efficiency and Remarkable Stability in Catalytic Performance. Adv. Funct. Mater. 29, 1807857 (2019).
3. Liang, S. X. et al. Compelling Rejuvenated Catalytic Performance in Metallic Glasses. Adv. Mater. 30, 1802764 (2018).
4. Wang, J. C. et al. Chemically dealloyed Fe-based metallic glass with void channels-like architecture for highly enhanced peroxymonosulfate activation in catalysis. J. Alloys Compd. 785, 642–650 (2019).
5. Jia, Z. et al. Activation of peroxymonosulfate by Fe78Si9B13 metallic glass: the influence of crystallization. J. Alloys Compd. 728, 525–533 (2017).
6. Miao, J., Lin, H. C., Wang, W. M. & Zhang, L. C. Amphoteric composite membranes for nanofiltration prepared from sulfated chitosan crosslinked with hexamethylene disiocyanate. Chem. Eng. J. 234, 132–139 (2013).
7. Jia, Z. et al. Heterogeneous photo Fenton-like degradation of the cibacron brilliant red 3B-A dye using amorphous Fe78Si9B13 and Fe73.5Si13.5B9Cu1Nb3 alloys: the influence of adsorption. J. Taiwan Inst. Chem. Eng. 71, 128–136 (2017).
8. Liang, S. X., Jia, Z., Zhang, W. C., Wang, W. M. & Zhang, L. C. Rapid malachite green degradation using Fe73.5Si13.5B9Cu1Nb3 metallic glass for activation of persulfate under UV-Vis light. Mater. Des. 119, 244–253 (2017).
9. Li, X.-F. et al. Excellent Performance of Fe78Si9B13 Metallic Glass for Activating Peroxymonosulfate in Degradation of Naphtol Green B. Metals 7, 273 (2017).
49. Samanta, S., Martha, S. & Parida, K. Facile Synthesis of Au/g-C3N4 Nanocomposites: An Inorganic/Organic Hybrid Plasmonic...

48. Yan, S. C., Lv, S. B., Li, Z. S. & Zou, Z. G. Organic-inorganic composite photocatalyst of g-C3N4 and TaON with improved visible...

51. Li, Z., Wang, J., Zhu, K., Ma, F. & Meng, A. Ag/g-C3N4 composite nanosheets: Synthesis and enhanced visible photocatalytic activities. *Mater. Lett.* **145**, 167–170 (2015).
Ma, D., Wu, J., Gao, M., Xin, Y. & Chai, C. Enhanced debromination and degradation of 2,4-dibromophenol by an Z-scheme
Jia, Z.
Luo, J.
Li, Q.
Wei, N.
Zhu, C.
Li, J., Yuan, H. & Zhu, Z. Photoelectrochemical performance of g-C3N4/Au/BiPO4 Z-scheme composites to improve the
Li, H., Yu, H., Quan, X., Chen, S. & Zhang, Y. Uncovering the Key Role of the Fermi Level of the Electron Mediator in a Z-Scheme
Li, H., Hao, P., Wei, N., Cui, H. & Liu, H. 3D Bi2MoO6 Nanosheet/TiO2 Nanobelt Heterostructure: Enhanced Photocatalytic
Activities and Photoelectrochemistry Performance. ACS Catal. 5, 4530–4536 (2015).
Liu, J., et al. Metal-free efficient photocatalyst for stable visible water splitting via a two-electron pathway. Science 347, 970–974
(2015).
Li, T., et al. Synthesis of g-C3N4/SmVO4 composite photocatalyst with improved visible light photocatalytic activities in RhB
degradation. Appl. Catal. B: Environ. 129, 255–263 (2013).
Di, L., Yang, H., Xian, T. & Chen, X. Enhanced Photocatalytic Degradation Activity of BiFeO3 Microspheres by Decoration with
g-C3N4 Nanoparticles. Mater. Res. 21 (2018).
Jia, Z., et al. Disordered Atomic Packing Structure of Metallic Glass: Toward Ultrafast Hydroxyl Radicals Production Rate and Strong
Electron Transfer Ability in Catalytic Performance. Adv. Funct. Mater. 27, 1702258 (2017).
Zhang, T. et al. Photooxidative N-demethylation of methylene blue in aqueous TiO2 dispersions under UV irradiation. J. Photochem.
Photobiol. A 140, 163–172 (2001).
Zhu, H. et al. Construction of Z-scheme type CdS–Au–TiO2 hollow nanorods with enhanced organic pollutant degradation. Appl.
Catal. B: Environ. 90, 463–469 (2009).
Li, J., Yuan, H. & Zhu, Z. Photoelectrochemical performance of g-C3N4/Au/BiPO4 Z-scheme composites to improve the
mineralization property under solar light. RSC Adv. 6, 70563–70572 (2016).
Zhu, C. et al. Fabrication of Z-scheme Ag3PO4/MoS2 composites with enhanced photocatalytic activity and stability for organic
pollutant degradation. Appl. Surf. Sci. 377, 99–108 (2016).
Li, H., Yu, H., Quan, X., Chen, S. & Zhang, Y. Uncovering the Key Role of the Fermi Level of the Electron Mediator in a Z-Scheme
Photocatalyst by Detecting the Charge Transfer Process of WO3-metal-gC3N4 (Metal = Cu, Ag, Au). ACS Appl. Mater. Interfaces 8,
2111–2119 (2016).
Wei, N. et al. Highly efficient photocatalytic activity of Ag3PO4/Au/ZnS(10−15%) photocatalysts through Z-scheme photocatalytic
mechanism. RSC Adv. 7, 18392–18399 (2017).
Gong, Y., Quan, X., Yu, H. & Chen, S. Synthesis of Z-scheme Ag2CrO4/Ag–g-C3N4 composite with enhanced visible-light
photocatalytic activity for 2,4-dichlorophenol degradation. Appl. Catal. B: Environ. 219, 439–449 (2017).
Li, Q. et al. Z-Scheme BiOCl-Au-CdS Heterostructure with Enhanced Sunlight-Driven Photocatalytic Activity in Degrading Water
Dyes and Antibiotics. ACS Sustain. Chem. Eng. 5, 6958–6968 (2017).
Ma, D., Wu, J., Gao, M., Xin, Y. & Chai, C. Enhanced degradation and mineralization of 2,4-dibromophenol by an Z-scheme
Bi2MoO6/CNTs/g-C3N4 visible light photocatalyst. Chem. Eng. J. 316, 461–470 (2017).
Li, Q. et al. Ultra-sustainable Fe78Si9B13 metallic glass as a catalyst for activation of persulfate on methylene blue degradation under
UV-Vis light. Sci. Rep. 6, 38520 (2016).
Li, Z., Zhang, W. C., Wang, W. M., Habibi, D. & Zhang, L. C. Amorphous Fe78%SB13 alloy: An efficient and reusable photo-
enhanced Fenton-like catalyst in degradation of cibacron brilliant red 3B-A dye under UV–vis light. Appl. Catal. B: Environ. 192,
46–56 (2016).
Luo, J. et al. Synthesis and characterization of Z-scheme In2S3/Ag2CrO4 composites with an enhanced visible-light photocatalytic
performance. New J. Chem. 41, 845–856 (2017).

Acknowledgements
This work was supported by the National Key R&D Program of China (Project No. 2017YFA0204403), the Major Program of National Natural Science Foundation of China: NSFC 51590892, the RGC Hong Kong General
Research Fund (grant number CityU 11247516), and Hong Kong Innovation and Technology Commission via the
Hong Kong Branch of National Precious Metals Material Engineering Research Center (Grant No. 9448003).

Author Contributions
Z.J., F.L., L.C.Z., S.X.L., Y.Y.L. and J.L. analyzed the data. All authors reviewed the manuscript.

Additional Information
Supplementary information accompanies this paper at https://doi.org/10.1038/s41598-019-42973-6.

Competing Interests: The authors declare no competing interests.

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.
