NJC

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/njc

NJC

ARTICLE

Efficient Visible-Light Photocatalytic Heterojunctions Coupled by Plasmonic $Cu_{2-x}Se$ and Graphitic Carbon Nitride

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Jing Han,[ab] Hong Yan Zou, [ab] Ze Xi Liu,[a] Tong Yang,[b] Ming Xuan Gao[b] and Cheng Zhi Huang[ab]

Photocatalytic semiconductors have attracted considerable attention due to applications in the degradation of organic polluants. However, the low solar-light harvesting and high electron-hole recombination rate limits the efficiency of photocatalysts. The newly developed localized surface plasmon resonance (LSPR) can offer a new opportunity to overcome the limited efficiency to some extent. In this study, the heterojunctions ($Cu_{2-x}Se/g\text{-}C_3N_4$) incorporating plasmonic semiconductor $Cu_{2-x}Se$ with graphitic carbon nitride ($g\text{-}C_3N_4$) are proposed as visible light photocatalysts. Their photocatalytic performance is tested and proven via the degradation of methyl blue (MB) in aqueous solution. When the mass percentage composition of $Cu_{2-x}Se$ reached 60%, the as-prepared composite exhibited the highest photocatalytic activity, which was almost 6.1 and 2.8 times as high as that of individual $Cu_{2-x}Se$ and $g\text{-}C_3N_4$, respectively. The remarkable photocatalytic efficiency of such $Cu_{2-x}Se/g\text{-}C_3N_4$ heterojunction under visible light illumination due to both plasmonic enhancement of the catalyst and synergetic effect of the co-catalyst is shown. This work can provide a new methodology to develop stable and high efficient heterojunctions photocatalysts.

Introduction

Photocatalysis has proved to be a green and potential technology to solve environmental issues such as air and water pollution.[1] Much efforts have been made to focus on semiconductor-based photo-catalysts and photocatalytic processes using titanium dioxide (TiO_2) since the pioneering work of Honda in 1972,[2] wherein TiO_2 can only absorbs ultraviolet (UV) light gap because of its large band. In nature, visible-light energy (about 48% of the solar spectrum) within solar spectra is far more abundant than UV energy (about 4% of the solar spectrum). Therefore, it has stimulated researchers to develop novel materials to enhance the response to the more abundant visible light to NIR photons.

It has reported that the localized surface plasmon resonance (LSPR) in the semiconductor can enhance the absorption of solar light throughout the visible to near-infrared light range by concentrating the incident photon energy in plasmon oscillations, and it can usually amplify the electromagnetic field of the surface inducing carrier separation in the semiconductor.[3] The cation-deficient copper chalcogenides nanocrystals, with the high density of holes in the valence band often, show exciting plasmonic photo-properties over UV to NIR region.[4] $Cu_{2-x}Se$ nanocrystals, as a *p*-type semiconductor with electron–hole pair which can be excited on absorption of a photon with energy as low as 1.0-2.2 eV, can absorb the long wavelengths of solar light for the upward energy transition, and thus have promising potential for photocatalytic activity. Even though, the photocatalytic performance of $Cu_{2-x}Se$ nanocrystals is limited by the high recombination rate of the photogenerated free carriers. The pollution degradation by the copper chalcogenides nanostructures must be in the presence of H_2O_2, which can cause the second pollution and the cost push.[5] To minimize electron–hole recombination, Lee et al designed photocatalysts with heterojunctions because the band level differences and inner electrostatic field in the heterojunction could provide the driving force for the separation of photogenerated electrons and holes.[6]

Graphitic carbon nitride ($g\text{-}C_3N_4$), as a *n*-type semiconductor, is one of promising candidate photocatalysts due to its electron-rich properties, suitable bandgap and high chemical stability.[7] However, the photocatalytic performance of $g\text{-}C_3N_4$ is far from satisfactory due to the large optical band gap (2.7 eV, corresponds to a utilization of solar energy at $\lambda < 460$ nm). Design of heterojunctions with other semicoductors can supply an opportunity to yield an elevated visible light response.[8] This methodology could significantly expand light response range to visible light region and could effectively promote photogenerated charge separation and transfer. However, the design strategy is limited to band matching of the semiconductors, most of which are not easily synthesized under mild conditions.

Herein, we developed a simple solvent-thermal route to synthesize plasmonic $Cu_{2-x}Se/g\text{-}C_3N_4$ heterojunctions composites with enhanced absorption throughout the visible to near-infrared light range. The promising photocatalytic activity was screened via the photocatalytic degradation of an

[a]*Key Laboratory of Luminescence and Real-Time Analytical Chemistry (Southwest University), Ministry of Education, College of Pharmaceutical Science, Southwest University, Southwest University, Chongqing, 400715, P. R. China. E-mail: chengzhi@swu.edu.cn, Tel: (+86) 23 68254659, Fax: (+86) 23 68367257.*
[b]*College of Chemistry and Chemical Engineering, Southwest University C, Chongqing 400716, China.*
†Electronic Supplementary Information (ESI) available: experiment detals and characterization of $Cu_{2-x}Se/g\text{-}C_3N_4$ heterojunction. See DOI: 10.1039/x0xx00000x

organic dye (MB) in an aqueous solution under visible light illumination. This strategy might provide a new methodology to develop stable and high efficient photocatalysts.

Experimental

Preparation of g-C_3N_4

The g-C_3N_4 was synthesized by directly heating melamine according to a reported procedure.[9] In detail, melamine was heated at 600 °C for 2 h under air condition with a ramp rate of about 3 °C min^{-1} for both of the heating and cooling processes. The obtained yellow product was the g-C_3N_4 powder.

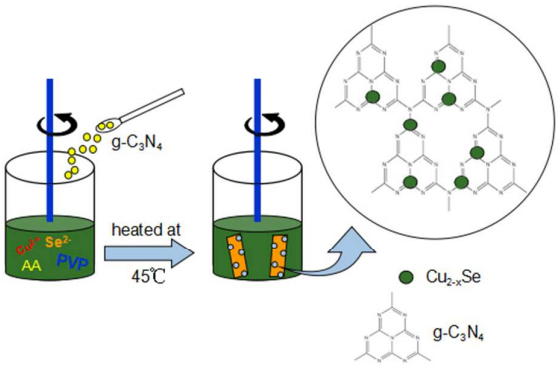
Preparation of $Cu_{2-x}Se/g-C_3N_4$

A certain amount of the as-prepared g-C_3N_4 was dispersed in 8 mL of deionized water and sonicated for 30 min. Then 0.2 mL 0.05 M SeO_2 and 0.4 mL 15 μg/mL Vc was added, successively. After 10 min, a mixed solution of 0.4 mL 0.1M $CuSO_4·5H_2O$ and 0.8 mL 15μg/mL Vc were added under vigorous stirring at 30 °C for 0.5 h, then heated up to 45 °C. The resulting mixture was allowed to proceed under vigorous stirring at room temperature in 10 h until a green solution was obtained. The solution was centrifuged at 10000 rpm for 10 min and purified through a 10 kDa dialysis membrane for 24 hours with distilled water.

A series of $Cu_{2-x}Se/g-C_3N_4$ composites with different mass amounts of $Cu_{2-x}Se$ were prepared marked as 20 wt%, 40 wt%, and 60 wt%. As a reference, the pure $Cu_{2-x}Se$ was prepared without adding g-C_3N_4 under the same conditions. Moreover, a mechanically mixed sample (the mass ratio of g-C_3N_4 and $Cu_{2-x}Se$ was 2:3) was obtained by grinding 4.8 mg of g-C_3N_4 with 7.2 mg of $Cu_{2-x}Se$.

Photocatalytic test

As a common organic pollutant, MB was employed to evaluate the photocatalytic activities of the as-prepared photocatalysts under visible-light (λ > 420 nm) degradation illuminated by a 500W xenon lamp. 12 mg of the powder photocatalysts were dropped into quartz tubes which were containing 50 mL MB solution ($2×10^{-5}$ mol L^{-1}), respectively. Then, the above solution was ultrasonic dispersion for 10 min and stirred for 30 min in dark to achieve an adsorption-desorption equilibrium between the photocatalyst powder and MB. Turn on the light and the photocatalytic reaction systems were exposed to visible light irradiation. At the same intervals, 0.5 mL of the mixture were taken out to centrifuge tubes, and the catalysts were removed out of the suspensions (10000 r/min, 5 min). The centrifuged solution was analysed by recording the maximum absorption band (664 nm) and UV-vis spectra were recorded by Hitachi U-3600.



Scheme 1. Schematic illustration of the formation process of $Cu_{2-x}Se/g-C_3N_4$ heterojunctions.

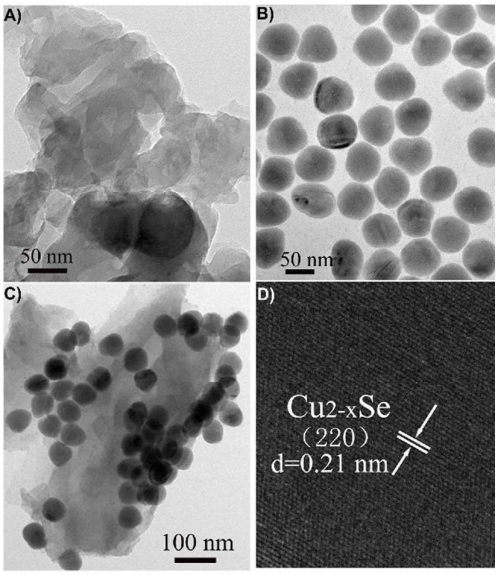


Fig. 1 Structure characterization of the photocatalysts. TEM images of g-C_3N_4 (A), $Cu_{2-x}Se$ (B), 60 wt% $Cu_{2-x}Se/g-C_3N_4$ (C) and the HRTEM image of the $Cu_{2-x}Se$ nanoparticle of the $Cu_{2-x}Se/g-C_3N$ heterojunctions (D).

Results and discussion

Structure and property analysis

The $Cu_{2-x}Se/g-C_3N_4$ heterojunction materials were fabricated by a simple solvent-thermal route as shown in Scheme 1. $CuSO_4·5H_2O$, SeO_2 and VC solutions were mixed with dispersed g-C_3N_4. With water-thermal reaction, small distributed uniform spherical $Cu_{2-x}Se$ nanoparticles were successfully deposited on the surface of g-C_3N_4. Typical morphologies of the as-prepared heterojunctions (SEM, Fig.S1; TEM images, Fig. 1 and Fig. S2, ESI†) showed that the bulk g-C_3N_4 was quite rough, ranging from hundreds of nanometers to several micrometers (Fig. 1A). Small spherical $Cu_{2-x}Se$ nanoparticles with 50 nm in diameter (Fig. 1B) were successfully deposited on the surface of g-C_3N_4 as nanoislands (Fig. 1C). Fringes with an inter-planar spacing of 0.21 nm were identified (Fig. 1D), which were attributed to the (220) diffraction plane of $Cu_{2-x}Se$ nanoparticles.[10] Elemental analysis was determined by SEM-EDS (Fig. S3, ESI†) showed an average Cu/Se atomic ratio of 1.69/1 with averaging among several particles. The $Cu_{2-x}Se$

nanoparticles were distributed separately on g-C_3N_4 as nanoislands, which could not only improve the dispersion property of layered materials but also offer more photocatalytic reaction sites, and the heterojunction structure was formed.

The XRD patterns of the $Cu_{2-x}Se$/g-C_3N_4 photocatalysts were measured (shown in Fig. 2). For g-C_3N_4, the strong peak located at 27.42° was ascribing to the (002) plane of the stacking of the conjugated aromatic system. The other peak at 12.74°as the (100) plane corresponded to the in-plane structural packing motif of tristriazine units.[11] New peaks at 44.85° and 53.41° were observed for $Cu_{2-x}Se$/g-C_3N_4 which matched well with the (220) and (311) crystal planes of the standard XRD data for the cubic berzelianite phase of $Cu_{2-x}Se$ (PDF card 06-0680),[12] and the intensity of peak at 53.41° increased as the increasing content of the $Cu_{2-x}Se$.

The FT-IR spectra of $Cu_{2-x}Se$/g-C_3N_4 heterojunctions were shown in Fig. 3. In the FT-IR spectrum of g-C_3N_4, the bands at 1648, 1562,

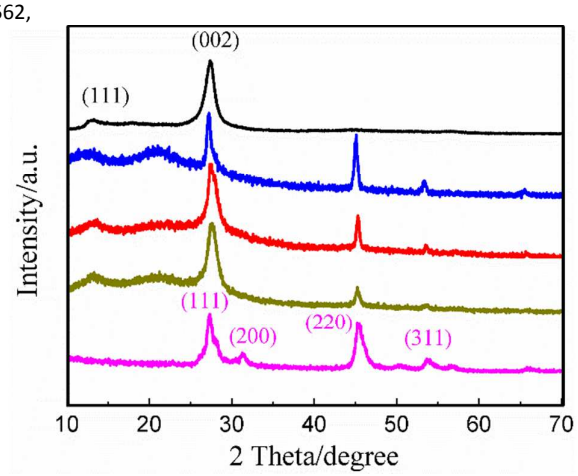


Fig. 2 XRD patterns of g-C_3N_4, $Cu_{2-x}Se$ and $Cu_{2-x}Se$/g-C_3N_4 samples.

1456, and 1402 cm^{-1} should be assigned to typical stretching vibration modes of the heptazine-derived repeating units, while the intense band at 804 cm^{-1} represented the out-of-plane bending vibration characteristic of heptazine rings,[13] and the bands at 1237 cm^{-1} corresponded to stretching vibration of connected units of C–N(–C)–C or C–NH–C.[14] For $Cu_{2-x}Se$/g-C_3N_4, the broad band at 3000–3700 cm belonged to the N–H vibration due to partial condensation of the capping agent and the adsorbed water molecules,[8d] and the band (652 cm^{-1}) corresponded to the vibration of –Se for $Cu_{2-x}Se$.[15] All the characteristic peaks of g-C_3N_4 and $Cu_{2-x}Se$

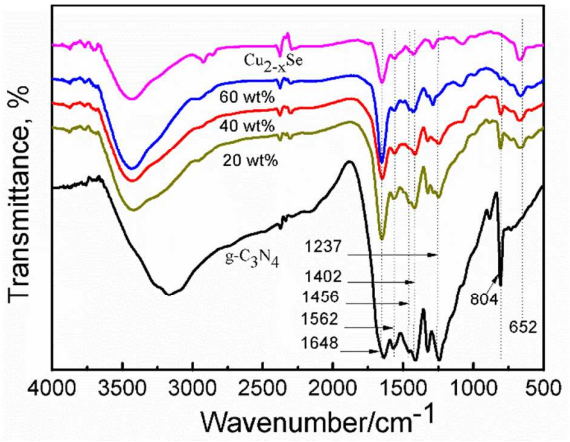


Fig.3 FT-IR spectra of g-C_3N_4, $Cu_{2-x}Se$ and $Cu_{2-x}Se$/g-C_3N_4 samples.

were observed in the $Cu_{2-x}Se$/g-C_3N_4 heterojunctions composition

The chemical compositions of the as-prepared heterojunctions were further characterized by XPS spectra (Fig. 4). As for $Cu_{2-x}Se$/g-C_3N_4, new Cu and Se peaks were observed, confirming the decoration of $Cu_{2-x}Se$ nanoparticles on the g-C_3N_4 surface (Fig. 4A, B). The evolution of the Cu 2p XPS spectra contained in Fig. 4C showed a clear indication of monovalent copper. The peaks of 932.4 and 952.8 eV were ascribed to Cu 2p 3/2 and Cu 2p 1/2 which was mainly in the form of Cu (I). In addition, the Cu2p peak had a satellite line at 940–945 eV, which resulted from a little Cu (II) (Fig. 4C).[10, 16] Since XPS is

NJC

ARTICLE

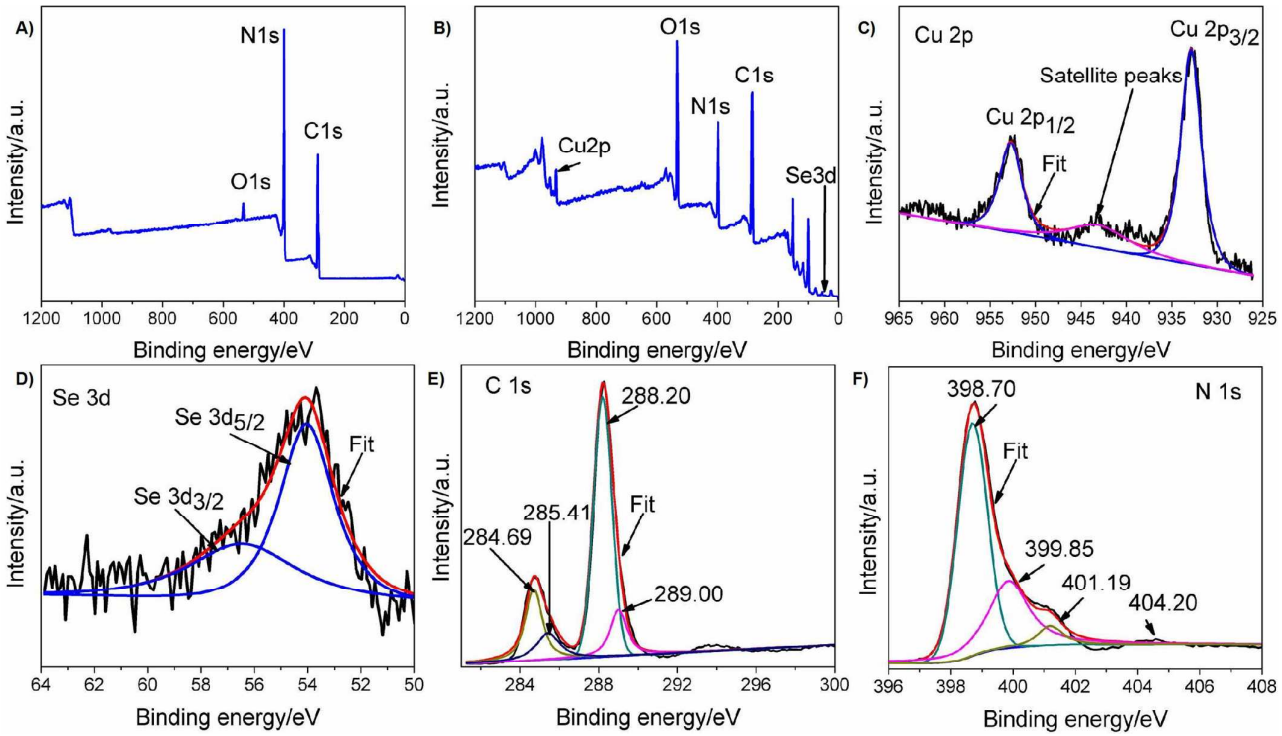


Fig. 4 (A) XPS spectra of the $Cu_{2-x}Se$ (B) XPS spectra of the $Cu_{2-x}Se/g\text{-}C_3N_4$ heterojunctions. (C) XPS spectra of Cu $2p_{1/2}$and Cu $2p_{3/2}$. (D) XPS spectra of Se 3d. (E) XPS spectra of C 1s, and (E) XPS spectra of N 1s.

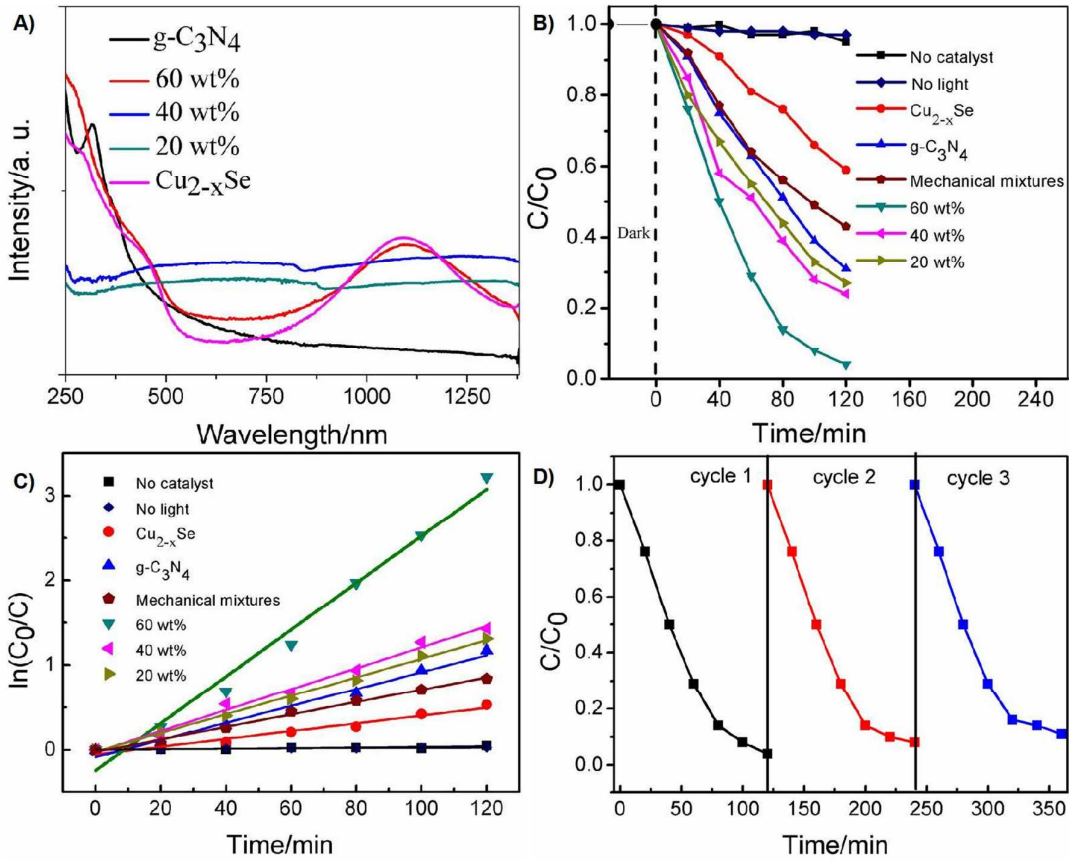


Fig.5 Photocatalytic activity of catalysts estimated by the degradation of MB under visible light irradiation (A) UV–vis-NIR spectra of the photocatalysts. (B) Photocatalytic degradation of MB in aqueous solution under different conditions. (C) ln (c_0/c) versus irradiation time for degradation of MB under different conditions. (D) Recyclability of the $Cu_{2-x}Se/g\text{-}C_3N_4$ heterojunctions in three successive experiments for the degradation of MB under visible-light irradiation.

primarily a surface characterization technique, the non-stoichiometric $Cu_{2-x}Se$ in the 60 wt % $Cu_{2-x}Se/g\text{-}C_3N_4$ heterojunctions had the atom percentage of surface Cu(I) and Cu(II) as 4.86:1.[17] The asymmetric peak at 54.2 eV contains Se3d 5/2 and Se3d 3/2 peaks was representative of the Se3d binding energy for lattice Se^{2-} (Fig. 4D).[17]

The C 1s spectra can be deconvoluted (in Fig. 4E). The major C peak at 288.20 eV was identified as sp^2-bonded carbon (N–C=N), and the weaker one at 284.69 eV corresponded to graphitic carbon which was usually observed on the XPS characterization for carbon nitrides.[18] The N 1s spectrum (Fig. 4F) could be fitted into three binding energies. Signals at 398.7 eV showed occurrence of C–N=C groups and 399.85 eV was related to either N–$(C)_3$ groups or amino groups ($(C)_2$–N–H). The 401.2 eV peak was weak and corresponded to N of N–$(C)_3$ in the aromatic cycles and 404.20 eV peak was attributed to the π –excitations.[8c, 19]

The as-prepared $Cu_{2-x}Se/g\text{-}C_3N_4$ heterojunctions have enhanced absorption throughout the visible to NIR light range (Fig. 5A). $Cu_{2-x}Se$ had the LSPR property at the NIR range, while the $g\text{-}C_3N_4$ shows the optical absorption threshold at ca. 460 nm. It was the LSPR property [10] and the optical absorption threshold [4] that made the $Cu_{2-x}Se/g\text{-}C_3N_4$ composites showed a broad and strong absorption in the visible light region and even extended to near-infrared region. This result indicated that $Cu_{2-x}Se/g\text{-}C_3N_4$ could absorb photons with different energies owing to the interaction between $Cu_{2-x}Se$ and $g\text{-}C_3N_4$, which were beneficial to the sunlight photocatalytic process.

In order to estimate the photocatalytic effect of the as-prepared $Cu_{2-x}Se/g\text{-}C_3N_4$ heterojunctions, methylene blue (MB), a common organic pollutant, was selected under visible-light irradiation (λ > 420 nm) (Fig. S5-S12, ESI†). As shown in Fig. 5B, there was almost no decreasing concentration of MB during the adsorption-desorption process due to the low surface area of the photocatalysts (Table S1) and the surface areas do not play a significant role in enhancing the photocatalytic activity of the $Cu_{2-x}Se/g\text{-}C_3N_4$. Fig. 5C revealed that the relationship between ln (C_0/C) and irradiation time was linear, indicating that the photocatalytic degradation of MB followed the pseudo-first-order kinetics.

$$\ln (C_0/C) = kt \quad (1)$$

Where C_0 and C were the equilibrium concentration of adsorption and the concentration of MB at the exposure time, t, respectively, and k was the apparent rate constant. The $Cu_{2-x}Se/g\text{-}C_3N_4$ heterojunctions composite with 60% mass ratios of $Cu_{2-x}Se$ (60 wt % $Cu_{2-x}Se/g\text{-}C_3N_4$) exhibited the highest photocatalytic rate

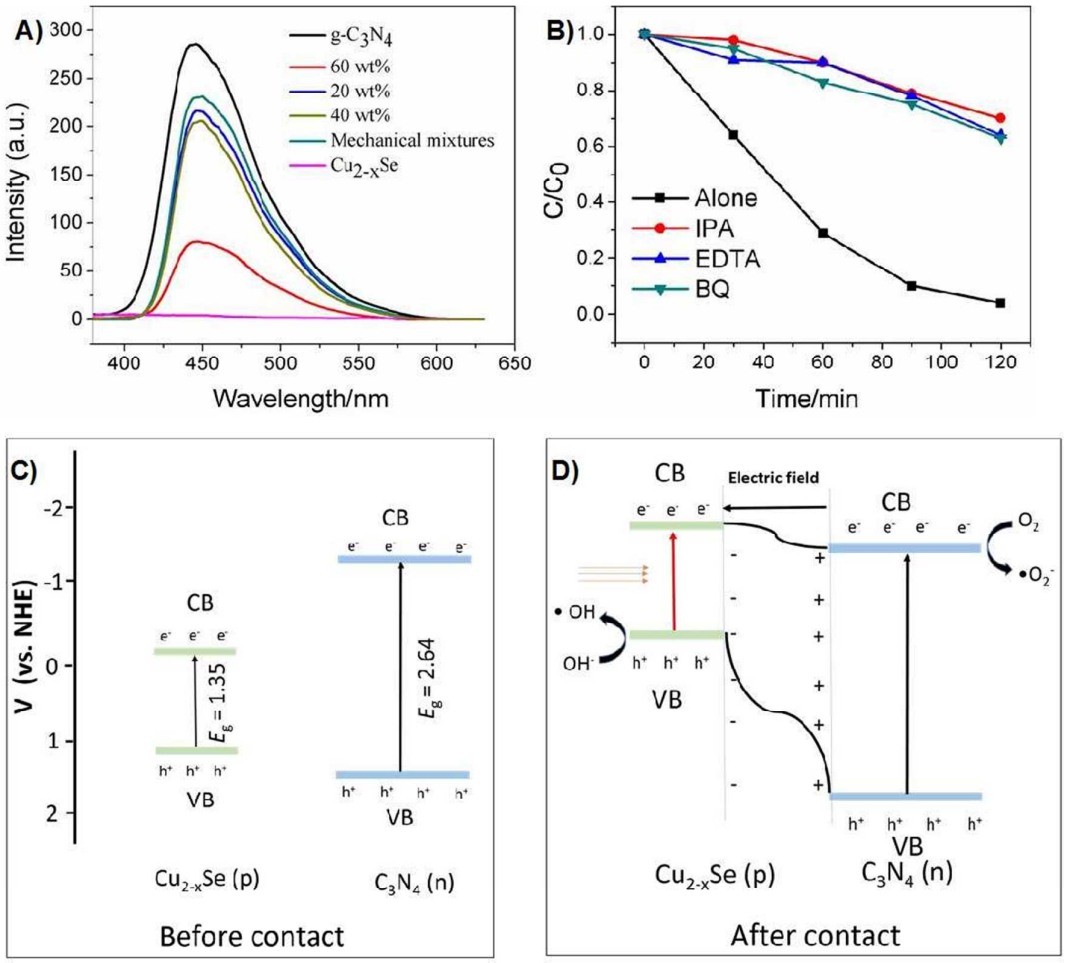


Fig.6 Investigation of the photocatalytic mechanism. (A) The fluorescence spectra of the g-C_3N_4, $Cu_{2-x}Se$, $Cu_{2-x}Se$/g-C_3N_4 samples (with the mass of g-C_3N_4 as 12 mg in 50 mL 2 mM NaOH solution) and mechanical mixtures of 18 mg $Cu_{2-x}Se$ and 12 mg g-C_3N_4 in 50 mL 2 mM NaOH solution (equal to the 60 wt% $Cu_{2-x}Se$). (B) Photocatalytic degradation of MB over $Cu_{2-x}Se$/g-C_3N_4 heterojunctions alone and with the addition of IPA, EDTA, and BQ. (C) The energy band structure diagram of $Cu_{2-x}Se$ and g-C_3N_4 before heterojunction. D) The energy band structure diagram of $Cu_{2-x}Se$/g-C_3N_4 heterojunctions

constant (*k*), which was almost 6.1 and 2.8 times as high as that of individual $Cu_{2-x}Se$ and g-C_3N_4, respectively (Table S1). The $Cu_{2-x}Se$/g-C_3N_4 photocatalyst can be recycled several times (Fig. 5D) and was also very stable (Fig. S13, 14).

Fluorescence measurements, which were usually employed to investigate the migration, transfer and recombination processes of photogenerated electron–hole pairs in semiconductors.[20] A lower PL intensity is a general indication of a lower recombination of electron–hole pairs, resulting in higher photocatalytic activity.[21] the bare g-C_3N_4 had a strong emission peak at 440 nm (Fig. 6A), which decreased remarkably in $Cu_{2-x}Se$/g-C_3N_4 composites with the increase mass ratio of $Cu_{2-x}Se$. Meanwhile, the FL of the mechanical mixtures of the same mass content of g-C_3N_4 with 60 wt% $Cu_{2-x}Se$ were measured. It showed relatively weaker emission peak than g-C_3N_4 but stronger emission peak than all the $Cu_{2-x}Se$/g-C_3N_4 heterojunctions measured. While, the characteristic emission peak of $Cu_{2-x}Se$/g-C_3N_4 (60 wt%) was the most weak, indicating that the recombination of electron–hole pairs in $Cu_{2-x}Se$/g-C_3N_4 was hindered most greatly.

The photocatalytic activity of the photocatalyst always contributed to the active species such as photogenrated holes, •OH radicals, and $•O_2^-$ in the photocatalytic process.[8] Therefore, in order to examine the role of these reactive species, a series of radicals trapping experiments using isopropyl alcohol (IPA, 2 mM),[22] ethylenediaminetetraacetate (EDTA, 2 mM),[23] and p-benzoquinone (BQ, 0.5 mM),[24] which are known as effective •OH, holes, and $•O_2^-$ scavengers for photocatalytic reaction, respectively, were applied to investigate the species involved in the process of photocatalytic degradation. Fig. 6B showed that holes, •OH radicals and $•O_2^-$ indeed functioned during the catalytic process. In such case, a reasonable photocatalytic mechanism could be proposed.

Based on the results above, a possible photocatalytic mechanism of $Cu_{2-x}Se$/g-C_3N_4 heterojunctions under visible light irradiation was proposed and illustrated in Fig. C, D. The potentials of VB and CB of a semiconductor material can be estimated according to the following empirical equations,[25]

$$E_{VB} = \chi - E^e + 0.5E_g \qquad (2)$$

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

Wherein E_{VB} is the valence band edge potential, χ is the electronegativity of the semiconductor, which is the geometric mean of the constituent atoms, E^e is the energy of free electrons on the hydrogen scale (about 4.5 eV vs NHE). The χ values for $Cu_{2-x}Se$ and g-C_3N_4 were 4.96 and 4.64 eV, respectively. The band gap energy of $Cu_{2-x}Se$ and g-C_3N_4 in our experiment was 1.35 eV and 2.64 eV (Fig. S4, inset and see details in ESI†) of The E_{VB} of $Cu_{2-x}Se$ and g-C_3N_4 were calculated to be 1.14 and 1.46 eV, respectively. The E_{CB} of of $Cu_{2-x}Se$ and g-C_3N_4 were estimated to be −0.21 and −1.18 eV, respectively. It is well known that the photocatalytic activities of photocatalysts, to a great extent, depend on the separation and transport of photogenerated charge carriers. When the p-$Cu_{2-x}Se$ and n-C_3N_4 were combined to form the p–n heterojunction, an interfacial electric field could be built in the interface between p-$Cu_{2-x}Se$ and n-C_3N_4.[26]That fact caused an efficient separation of photogenerated electrons and holes to enhance the photocatalytic activity. Furthermore, because of the more positive potential of Cu^{2+}/Cu^{1+} (0.153 V), the photogenerated electrons on the CB of $Cu_{2-x}Se$ may in situ reduce Cu^{2+} to metallic Cu^{1+}, which also migrated the electron to inhibit the recombination of the photoexcited pairs. In such case, the photogenerated electrons on the CB of the g-C_3N_4 and $Cu_{2-x}Se$ can reduce the oxygen to generate active species $\bullet O_2^-$($O^2/\bullet O_2^-$, − 0.046 V vs SHE) due to their more negative potential, which can further oxidize MB. Subsequently, it would combine with H^+ to produce H_2O_2, finally decomposing into hydroxyl radicals •OH radicals.[27] These •OH radicals also played an additional role for the MB degradation. The holes in the VB of g-C_3N_4 diffused to the surface of catalyst particles and transferred to VB of $Cu_{2-x}Se$ to accomplish the separation of electron−hole pairs, which would be readily scavenged by H_2O or OH^-, leading to •OH radicals, and accelerated the MB degradation. These results matched well with the trapping experiments showing that the all the holes, •OH radicals and $\bullet O_2^-$ were involved in the process of the photocatalytic reaction.

Conclusions

In summary, efficient $Cu_{2-x}Se$/g-C_3N_4 plasmonic photocatalysts were successfully synthesized by a simple solvent-thermal method. The $Cu_{2-x}Se$ nanoparticles were dispersedly decorated on the surface of bulk g-C_3N_4. This novel heterojunctions were demonstrated to promote transfer and separation of photogenerated charge carriers driven by the band offsets, resulting in a significant enhancement in the photocatalytic activity for MB degradation under visible light irradiation. Furthermore, all the holes, •OH radicals and $\bullet O_2^-$ were the active species in the degradation process. This study might provide a new perspective for the design of high-performance photocatalysis by plasmonic semiconductor heterojuncted with g-C_3N_4. And the nanostructure $Cu_{2-x}Se$/g-C_3N_4 heterojunctions can also be envisaged for further sustainable energy applications.

Acknowledgements

This study was financially supported by the National Natural Science Foundation of China (NSFC, Grant No.21375109) and Chongqing Postdoctoral Science Foundation funded project (Xm2014021).

Notes and references

§ Jing Han and Hong Yan Zou contributed to this work equally.

1 a) M. R. Hoffmann, S. T. Martin, W. Choi and D. W. Bahnemann, Chem. Rev., 1995, 95, 69; b) M. D. Hernández-Alonso, F. Fresno, S. Suárez and J. M. Coronado, *Energy Environ. Sci*., 2009, **2**, 1231; c) L. Q. Ye, J. Y. Liu, Z. Jiang, T. Y. Peng and L. Zan, *Appl. Catal., B* 2013, **142**, 1.
2 A. Fujishima and K. Honda, *Nature,* 1972, **238**, 37.
3 a) H. Zhang, X. Fan, X. Quan, S. Chen and H.Yu, *Environ. Sci. Technol*. 2011, **45**, 5731; b) W. Wang, H. Du, R. Wang, T. Wen and A. Xu, *Nanoscale* 2013, **5**, 3315; c) S. K. Cushing, J. T. Li, F. K Meng, T. R. Senty, S. Suri, M. J. Zhi, M. Li, A. D. Bristow and N.Q. Wu, *J. Am. Chem. Soc.,* 2012*,* **134***,* 15033; d) Z. W. Liu, W. B. Hou, P. Pavaskar, M. Aykol and S.B. Cronin, *Nano Lett*. 2011, **11**, 1111.
4 a) F. Scotognella, G. Della Valle, A. R. Srimath Kandada, D. Dorfs, M. Zavelani-Rossi, M. Conforti, K. Miszta, A. Comin, K. Korobchevskaya, G. Lanzani, L. Manna and F. Tassone, *Nano Lett.*, 2011, **11**, 4711.; b) Y. Zhao, H. Pan, Y. Lou, X. Qiu, J. Zhu and C. Burda, *J. Am. Chem. Soc.*, 2009, **131**, 4253; c) A. Comin and L. Manna, *Chem. Soc. Rev.*, 2014, **43**, 3957; d) X. Liu, C. Lee, W. C. Law, D. Zhu, M. Liu, M. Jeon, J. Kim, P. N. Prasad, C. Kim and M. T. Swihart, *Nano Lett*., 2013, **13**, 4333; e) X. Liu, X.Wang, B. Zhou, W. C. Law, A. N. Cartwright and M. T. Swihart, *Adv. Funct. Mater*., 2013, 23, 1256; f) S. Q. Lie,; H. Y. Zou, Y. Chang, and C. Z. Huang, *RSC Adv*., 2014, **4**, 55094; g) W. L. Li, S. Q. Lie, Y. Chang., X. Y. Wan, T. T. Wang, J. Wang, and C. Z. Huang, *J. Mater. Chem. B*, 2014, **2**, 7027.
5 a) J. Kundu and D. Pradhan, *ACS Appl. Mater. Interfaces*, 2014, **6**, 1823; b) Q. W. Shu, L. Jing, M. X. Gao, J. Wang and C. Z. Huang, *CrystEngComm*., 2015, **17**, 1374.
6 a) H. G. Kim, P. H. Borse, W. Y. Choi and J. S. Lee, *Angew. Chem., Int. Ed.*, 2005, **44**, 4585; b) H. G. Kim, P. H. Borse, J. S. Jang, E. D. Jeong, O. S. Jung, Y. J. Suh and J. S. Lee, *Chem. Commun.*, 2009, 5889; c) A. Kudo and Y. Miseki, *Chem. Soc. Rev*., 2009, **38**, 253; d) G. Wang, B. B. Huang, L. Wang, Z. Y. Wang, Z. Z. Lou, X. Y. Qin, X. Y. Zhang and Y. Dai, *Chem. Commun*., 2014, **50**, 3814; e) R. Marschall, *Adv. Mater*., 2014, **24**, 2421.
7 a) X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen and M. Antonietti, *Nat. Mater*., 2008, **8**, 76; b) Y. Zhao, F. Zhao, X. P. Wang, C. Y. Xu, Z. P. Zhang, G. Q. Shi and L. T. Qu, *Angew. Chem. Int. Ed*., 2014, **53**, 13934; c) Y. Zheng, L. H. Lin, X. J. Ye, F. S. Guo and X. C. Wang, *Angew. Chem. Int. Ed*., 2014, **53**, 11926; d) S. Kumar, S. Tonda, , B. Kumar, A. Baruah and V. Shanker, *J. Phys. Chem. C*, 2013, **117**, 26135; e) J. Liu, Y. Liu, N. Y. Liu, Y. Z. Han, X. Zhang, H. Huang, Y. Lifshitz, S. T. Li, J. Zhong and Z. H. Kang, *Science*, 2015, **347**, 970.
8 a) S. W. Cao and J. G. Yu, *J. Phys. Chem. Lett*., 2014, **5**, 2101; b) H. Xu, J. Yan, Y. Xu, Y. Song, H. Li, J. Xia, C. Huang and H. Wan, *Appl. Catal.,B*, 2013, **129**, 182; c) Y. F. Li, L. Fang, R. Jin, Y. Yang, X. Fang, Y. Xing and S. Y. Song, *Nanoscale*, 2015, **7**, 758; d) S.W. Zhang, J. X. Li, M. Y. Zeng, G. X. Zhao, J. Z. Xu, W. P. Hu and X. K. Wang, *ACS Appl. Mater. Interfaces,* 2013, **5**, 12735; e) Y. Feng, J. C. Shen, Q. F. Cai, H. Yang and Q. H. Shen*, New J. Chem.,* 2015*,* **39***,* 1132; f) I. Aslam, C. Cao, M. Tanveer, W. S. Khan, M. Thair, M. Abid, F. Idrees, F. K. Butt, Z. Ali and N. Mahmood, *New J. Chem.,* 2014*,* **38**, 5462.
9 X. D. Zhang, X. Xie, H. Wang, J. J. Zhang, B. C. Pan and Y. Xie, *J. Am. Chem. Soc*., 2013, **135**, 18.
10 a) D. Dorfs, T. Härtling, K. Miszta, N. C. Bigall, M. R. Kim, A. Genovese, A. Falqui, M. Povia and L. Manna, *J. Am. Chem. Soc.*, 2011, **133**, 11175; b)S. Q. Lie, D. M. Wang, M. X. Gao and C. Z. Huang, *Nanoscale*, 2014, **6**, 10289.

11 Y. L. Tian, B. B. Chang, J. L. Lu, J. Fu, F. N. Xi and X. P. Dong, *ACS Appl. Mater. Interfaces*, 2013, **5**, 7079.
12 Z. T. Deng, M. Mansuripur and A. J. Muscat, *J. Mater. Chem.*, 2009, **19**, 6201.
13 S. C. Yan, Z. S. Li and Z. G Zou, *Langmuir* 2009, **25**, 10397.
14 P. Niu, L. Zhang, G. Liu and H. Cheng, *Adv. Funct. Mater.*, 2012, **22**, 4763.
15 A. Beran, G. Giester and E. Libowitzky, *Miner. Petrol.*, 1997, **61**, 223.
16 I. Kriegel, C. Y. Jiang, J. Rodriguez-Fernandez, R. D. Schaller, D. V. Talapin, E. da Como and J. Feldmann, *J. Am. Chem. Soc.*, 2012, **134**, 1583.
17 S. C. Riha, D. C. Johnson and A. L. Prieto, *J. Am. Chem. Soc.*, 2011, **133**, 1383.
18 J. A. Singh, S. H. Overbury, N. J. Dudney, M. J. Li and G. M. Veith, *ACS Catal.*, 2012, **2**, 1138.
19 T. Y. Ma, Y. Tang, S. Dai and S. Z. Qiao, *Small*, 2014, **10**, 2382.
20 J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 3rd ed., Springer: New York, 2006.
21 a) Y. F. Chen, W. X. Huang, D. L. He, Y. Situ and H. Huang, *ACS Appl. Mater. Interfaces,* 2014, **6**, 14405; b) J. S. Xu, T.J. K. Brenner, Z. P. Chen, D. Neher, M. Antonietti and M. Shalom, *ACS Appl. Mater. Interfaces,* 2014, **6**, 16481**.**
22 L. Jin,G. Zhu, M. Hojamberdiev, X. Luo, C. Tan, J. Peng, X. Wei, J. Li and P. Liu, *Ind. Eng. Chem. Res.*, 2014, **53**, 13718.
23 M. S. Elovitz and U. V. Gunten, Ozone, *Sci. Eng*, 1999, **21**, 239.
24 Y.Zhang, N. Zhang, Z. Tang and Y. Xu, *Chem. Sci.*, 2013, **4**, 1820.
25 a) X. Lin, X. Y. Guo, W. L. Shi, L. N. Zhao, Y. S. Yan and Q. W. Wang, *J Alloys Compd.*, 2015, **635**, 256; b) X. Lin, X. Y. Guo, W. L. Shi, L. N. Zhao, Y. S. Yan and Q. W. Wang, *Catal. Commun.*, 2015, **66**, 67; c) F. Guo, W. L. Shi, X. Yan, Y. Guo and G. B. Che, *Sep. Puri. Tech.,* 2015, **141**, 246.
26 a) Z. J. Sun, Q. D. Yue, J. S. Li, J. Xu, H. F. Zheng and P. W. Du, *J. Mater. Chem*. A, 2015, **3**, 10243; b) S.S. Yi, X. Z. Yue, D. D. Xu, Z. P. Liu, F. Zhao, D. J. Wang and Y. H. Lin, *New J. Chem.*, 2015, **39**, 2917.
27 H. T. Ren, S. Y. Jia, Y. Wu, S. H. Wu, T. H. Zhang and X. Han, *Ind. Eng. Chem. Res.*, 2014, **53**, 17645.