High mobility organic semiconductor for constructing high efficiency carbon nitride heterojunction photocatalysts

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Graphitic carbon nitride (CN) has attracted worldwide attention due to its low-cost, environmental friendliness and tunable structures. However, CN photocatalyst still suffers from low charge separation efficiency issue. It is known that mobility is one of the most important factors dominating the charge separation and transport. This work reports a new strategy to address low charge separation issue by coupling high-mobility organic semiconductor and CN. Copper phthalocyanine (CuPc), a classical small molecule organic semiconductor which possesses high mobility, outstanding stability and strong visible-light absorption, was selected to construct CN/CuPc heterojunctions. The CN/CuPc heterojunctions showed a high hydrogen evolution (PHE) rate of 9.0 mmol g⁻¹ h⁻¹ and apparent quantum yield (AQY) of 3.99% (420 nm) and 1.31% (600 nm). This work demonstrates the application prospects of high-mobility organic semiconductors in heterojunction photocatalysis.

Visible-light induced photocatalytic hydrogen evolution (PHE) has attracted tremendous research interests since it provides a sustainable approach to address the forthcoming worldwide energy and environmental crisis.¹ Efficient visible-light absorption, high efficiency and favorable stability are essential requirements for PHE photocatalysts. Besides, in terms of potential commercial application, photocatalysts should also be low-cost and eco-friendly. Recently, graphitic carbon nitride (CN), as a metal-free and visible-light responsive organic photocatalyst, has grabbed intense attentions due to its fascinating features, such as appropriate energy band positions for PHE, high physicochemical stability, reasonable cost, nontoxicity and easy preparation.²⁻⁶ However, pristine CN suffers from deficient visible-light absorption and rapid recombination of photogenerated charges, resulting in moderate photocatalytic efficiency. Rational construction of nano-composites heterojunction has become an effective way to overcome these issues, since it can not only inhibit the hole-

electron pairs recombination but also reinforce visible-light utilization.⁴ Recently, organic semiconductors (OSCs) have been regarded as an immense potential candidate to form efficient CN based organic-organic surface heterojunctions.⁷⁻²³ Thanks to the unique structural tunability of organic molecules, the band position and visible-light absorption capacity of CN/OSCs heterojunctions could be conveniently regulated to enhance the exciton separation efficiency at the interface and broaden the light absorption of the system.

Basically, the reaction processes of PHE can be divided into three steps, namely light absorption, charge transport and surface reaction. Tremendous efforts have been made to improve the light absorption and surface reaction processes, such as nanostructure design and molecular engineering.^{2, 24} However, little attention has been paid to the mobility of OSCs, which has an important influence on the recombination during the carrier transport, and therefore also affects the activity of the photocatalyst. The faster the carriers migrate, the lower the probability of the hole-electron recombination would be. Herein, copper phthalocyanine (CuPc), a classical OSC which possesses high mobility as well as excellent stability and efficient visible-light absorption,²⁵⁻²⁷ was used to construct CN/CuPc pure organic heterojunctions with CN nanosheets through π - π interaction. The heterojunction photocatalysts exhibit extended visible-light absorption and promoted charge transfer. As a result, the PHE rate is significantly increased compared with pure CN, which is also higher than that of the previously reported similar CN based organic heterojunction system that possesses lower mobility,²⁸ indicating the importance of mobility for the performance of organic

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Scheme 1 Schematic of the two-step method for the exfoliation of bulk CN to CN nanosheets.

photocatalysts. To the best of our knowledge, this is the first report about the application of CuPc in organic heterojunction photocatalysts for PHE.

Bulk CN was fabricated by thermal condensation of urea at a temperature of 550°C for 4h. Then a two-step method combining secondary calcination and liquid exfoliation was adopted to obtain CN nanosheet, as shown in Scheme 1. Firstly, the thickness of bulk CN was decreased primarily through a secondary calcination in air. This step which is also known as thermal oxygen etching can break hydrogen bonds between CN layers through gradual oxidation.²⁹ Fig. S2 shows the nitrogen absorption-desorption isotherms of bulk CN and CN after the secondary calcination. As derived from the isotherms, the specific surface area of CN is increased from 140.8 m²/g to 239.7 m²/g after the calcination. Meanwhile, the pore volume is increased from 0.61 cm³/g to 0.93 cm³/g. These data verified the validity of this thermal treatment. Secondly, the obtained CN after secondary calcination was exfoliated into nanosheet via high-power ultrasonic processing in isopropanol for 10h. X-ray diffraction (XRD) was conducted for CN before and after sonication (Fig. S3). The position of (002) peak, which originates from the interlayer stacking of CN nanosheet, shifts from 27.89° to 27.67°, indicating an expanded interlayer distance after sonication. Simultaneously, the full width at half maximum (FWHM) became narrowed, manifesting improved crystallinity of CN which is caused by the better arrangement. The preparation of CN nanosheets by the two-step method was confirmed by the SEM images, as depicted in Fig. 1a and b. After two steps of exfoliation, large-sized and thick CN becomes small and thin nanosheets. The thickness of the ultrasonic treated CN nanosheets was determined by AFM (Fig. S4). The results showed that the CN nanosheet exhibited an ultrathin thickness of ~1.9 nm.

Considering the large conjugated structure of both CN and CuPc, the strong π - π interaction could facilitate the construction of heterojunction. CN/CuPc heterojunction photocatalysts with different ratios of CuPc (0 wt.%, 3 wt.%, 5 wt.%, 7 wt.%, 10 wt.%) were prepared through a simple ultrasonic blending method. The typical TEM image of CN/CuPc (Fig. 1c, 7 wt.% CuPc) illustrates that the heterojunction maintains the nanosheet morphology of CN. TEM-assisted elemental mappings were performed to prove the existence of CuPc in the composite, as shown in Fig. 1d and Fig. S5. The Cu-K mapping indicates that CuPc is uniformly dispersed on CN nanosheets, and the heterojunction structure remains stable even after a series of sample preparation processes.

Fig. 1 SEM images of (a) bulk CN and (b) CN nanosheet obtained by the two-step method. (c) TEM image of CN/CuPc (7 wt.%) composite. (d) Electron image and corresponding TEM-assisted elemental mapping of Cu, C and N of CN/CuPc (7 wt.%) composite.

The absorption spectrum of the heterojunction was measured by UV-vis diffuse reflectance spectroscopy (DRS), as shown in Fig. 2a. As can be seen, pristine CN has an absorption edge of 463 nm, corresponding to an optical band gap about 2.68 eV (Fig. 2b), which is slightly lower than some previously reported values.²⁹⁻³⁰ Considering that the CN fabrication and the initial exfoliation are carried out under air, it can be inferred that this may be caused by the N vacancy defects introduced unintentionally.³¹ While CuPc shows strong characteristic Q-band absorption ranging from 500nm to 800nm. Consequently, the CN/CuPc composites exhibit much broader absorption combining the features of CN and CuPc, rendering the heterojunction with the ability to absorb almost the entire range of visible-light which is essential to improve the photocatalytic activity. Furthermore, the Q-band absorption of CuPc in CN/CuPc shows obvious red-shift compared with that of the pure CuPc, which is an evidence suggesting π - π interaction between CN and CuPc. The interactions between CN and CuPc were further confirmed by the Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). As depicted in Fig. 2c, the pristine CN shows typical FTIR absorption spectra. The peaks from 1200-1600 cm⁻¹ correspond to the stretching vibration of C-N heterocycles in CN, and peak at 811 cm⁻¹ represents the bending vibration of heptazine units. As the proportion of CuPc increases, the CN characteristic peaks become weak gradually, indicating the existence of non-covalent intermolecular interactions.⁷ Fig. 2d shows the Cu 2p XPS spectra of pure CuPc and CN/CuPc (7 wt.% CuPc). The binding energy of Cu 2p_{3/2} for CN/CuPc decreases by 0.3 eV compared with that of pure CuPc. Similar phenomenon is also observed for Cu 2p_{1/2} peak. Since CN is a nitrogen-rich material, the decrease of Cu 2p binding energy may be due to the enhancement of Cu-N interaction, which leads to an increase in the outer electron density of Cu and thus enhances the electronic shielding effect. To prove this inference, N 1s XPS spectra of CN and CN/CuPc were conducted (Fig. S6). The N 1s

Fig. 2 (a) DRS of CN and CN/CuPc heterojunctions. (b) Tauc plot derived from the DRS of CN. (c) FTIR of CN and CN/CuPc heterojunctions. The weight of different samples is the same (3 mg). (d) Cu 2p XPS of CN and CN/CuPc (7 wt.%) heterojunctions.

binding energy in the composites shows obvious increase compared with that of CN, corresponding to the decrease of Cu 2p binding energy.

To explore the photocatalytic activities of the CN/CuPc heterojunctions, the PHE rates of CN loaded with different ratios of CuPc were measured in the presence of triethanolamine (TEOA) as the hole sacrificial agent and without any other cocatalyst (Fig. S7 and Table S1). A 300 W Xenon lamp is used as a light source. A total of 20 mg hybrids was used as the photocatalyst. The pristine CN nanosheets show low PHE rate of $15.2 \mu\text{mol g}^{-1} \text{h}^{-1}$. Initially, as the ratio of CuPc increases, the PHE rate of the heterojunction increase gradually, reaching the maximum rate of $71.2 \mu\text{mol g}^{-1} \text{h}^{-1}$ at 7 wt.%. However, further increasing the content of CuPc leads to a decrease of the PHE rate. This phenomenon is not exceptional since excessive CuPc may obscure the active site.¹² In this case, the optimal ratio of CuPc is determined to be 7%, under which the enhancement of visible-light absorption and the maintenance of the effective active sites could reach a balance. X-ray diffraction (XRD) of the CN/CuPc before and after the reaction were performed to examine the stability of the mixture, as shown in Fig. S8. The XRD spectrum before the reaction shows a simple summation of the two components and remains basically the same after the reaction, indicating that CuPc has not been stripped off after a long time of reaction.

The photocatalytic activity of the heterojunction system could be further improved by adding Pt cocatalyst, as shown in Fig. 3. 5 wt.% Pt was loaded onto the catalysts surface through the photodeposition of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$. Pure CN nanosheet with Pt cocatalyst exhibits a PHE rate of $3.4 \text{ mmol g}^{-1} \text{h}^{-1}$, while the CN/CuPc heterojunction with 7 wt.% CuPc shows a much higher rate of $9.0 \text{ mmol g}^{-1} \text{h}^{-1}$ (Fig. 3a), which is also higher than that of the previously reported CN/VOPc system with lower mobility.²⁸ These results demonstrate the advantages of high-mobility organic semiconductors in improving the CN based PHE photocatalysts. The stability of the CN/CuPc was also

Fig. 3 (a) PHE results of CN and CN/CuPc (7 wt.%) heterojunction, measured under the irradiation of a 300 W Xenon lamp. TEOA is used as the hole sacrificial agent. 5 wt.% Pt is used as cocatalyst. (b) Cycling test of the CN/CuPc (7 wt.%) heterojunctions.

investigated by the cycling test (Fig. 3b). The photocatalytic activity of the composite shows no significant decline after four cycles of irradiation.

To further study the photocatalytic mechanism, it is essential to figure out the electronic interactions between CN and CuPc. The band structure of CN and CuPc were determined by the DRS and Mott-Schottky analysis, as depicted in Fig. 4. The optical gap of CuPc is calculated as 1.40 eV according to the DRS (Fig. 4a and 4b). The flat band position (E_{fb}) of CN and CuPc can be obtained from the Mott-Schottky curves (Fig. 4c and 4d). For CN, the positive slope indicates it is a typical N-type semiconductor, and the E_{fb} (-0.37 V vs RHE) can be approximated as the conduction band (E_c). For CuPc, the negative slope indicates it is a P-type semiconductor and the E_{fb} (0.88 V vs RHE) can be approximated as the valence band (E_v). Thus, straddled band alignment (Type II) which could facilitate the charge transfer is formed, as shown in Fig. 5a. To verify the charge transfer interaction between the two components, photoluminescence (PL), photoresponse and electrochemical impedance spectroscopy (EIS) of CN and CN/CuPc were conducted and compared, as shown in Fig. 5b-d. Pure CN shows strong emission at 469 nm under an excitation wavelength of 335 nm (Fig. 5b). The PL

Fig. 4 (a) DRS of CuPc and (b) corresponding Tauc plots. Mott-Schottky plot of (c) CN and (d) CuPc.

Fig. 5 (a) Schematic of the photocatalytic mechanism of CN/CuPc heterojunction. (b) PL of CN and CN/CuPc heterojunctions under an excitation wavelength of 335nm. (c) Photocurrent responses of CN and CN/CuPc (7 wt.%) heterojunctions. 0.5M Na₂SO₄ solution was used as the electrolyte. 2mg/ml CN/CuPc isopropanol suspension was dripped onto the ITO electrode and baked dry with an infrared lamp. A 300w Xenon lamp was used as the light source. (d) EIS of CN and CN/CuPc (7 wt.%) heterojunctions. 5 mM [Fe(CN)₆]^{3-/4-} (1:1) solution containing 0.1 M KCl was used as the electrolyte. 2mg/ml CN/CuPc isopropanol suspension was dripped onto the glassy carbon electrode and baked dry with an infrared lamp. ESI was tested using a three-electrode system.

intensity decreases with the increase of CuPc content, indicating that the recombination of the photogenerated electron-hole pairs are effectively suppressed in CN/CuPc heterojunction. Fig. 5c exhibits the photocurrent responses of CN and CN/CuPc (7 wt.% CuPc). Compared to CN, higher photocurrent is obtained for CN/CuPc, which can be rationalized by the broader visible-light absorption and efficient charge transfer between CN and CuPc. To confirm the charge transfer process at the heterojunction interface, EIS of CN and CN/CuPc (7 wt.% CuPc) were also performed, the Nyquist plots are depicted in Fig. 5d. The semicircle in the high frequency region represents the charge transfer process at the electrode, and the arc radius indicates the charge transfer resistance (R_{ct}). It is obvious that the CN/CuPc possesses a smaller radius and thus smaller R_{ct} , which means more effective charge transfer and migration for the heterojunction photocatalyst.

The photocatalytic mechanism can be further confirmed by PHE testing irradiated at monochromatic light. As shown in Fig. S9a, Under the irradiation of 600 nm monochromatic light beyond the CN absorption range, the entire system showed a PHE rate of 1.49 mmol g⁻¹ h⁻¹, corresponding to apparent quantum yield (AQY) of 1.31%. This means that there is effective charge transfer between CuPc and CN. The CN/CuPc hybrid under irradiation of 420 nm monochromatic for PHE was also measured (Fig. S9b), exhibiting a high AQY of 3.99%. Furthermore, PHE testing of pure CuPc is also performed to determine which component the hydrogen production capacity is mainly derived from, as depicted in Fig. S10. Using Xenon lamp as the light source, pristine CuPc without Pt loaded has no hydrogen production capacity. After loading 5%Pt, CuPc shows weak PHE performance with a hydrogen production rate of 29.3

μmol g⁻¹ h⁻¹, far below the value of the CN/CuPc system. Therefore, it can be inferred that the main sites of PHE reaction are located on the surface of CN. The role of CuPc in the system is not only to broaden the visible light absorption but also to enhance the charge separation and transfer at the CN/CuPc heterojunction.

Conclusions

In conclusion, CN nanosheet with high specific surface area were prepared through a two-step method. CuPc, a classic organic small molecular semiconductor possessing high mobility, outstanding visible-light absorption and physicochemical stability, was selected to construct CN/CuPc photocatalyst for PHE. Due to the broadened visible-light absorption and the enhancement of charge separation, the heterojunction exhibits a greatly improved PHE rate of up to 9.0 mmol g⁻¹ h⁻¹. The band position was determined and the photocatalytic mechanism of this organic heterojunction system was confirmed through various photoelectrochemical characterizations. This work demonstrates the prospect of high mobility organic semiconductors in photocatalytic reactions, providing a new strategy for the construction of efficient pure organic photocatalyst for PHE.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- 1 J. Qi, W. Zhang, R. Cao, *Adv. Energy Mater.*, 2018, **8**, 1701620.
- 2 W. J. Ong, L. L. Tan, Y. H. Ng, S. T. Yong, S. P. Chai, *Chem. Rev.*, 2016, **116**, 7159-7329.
- 3 J. Wen, J. Xie, X. Chen, X. Li, *Appl. Surf. Sci.*, 2017, **391**, 72-123.
- 4 J. Fu, J. Yu, C. Jiang, B. Cheng, *Adv. Energy Mater.*, 2018, **8**, 1701503.
- 5 H. Huang, K. Xiao, N. Tian, F. Dong, T. Zhang, X. Du, Y. Zhang, *J. Mater. Chem. A*, 2017, **5**, 17452-17463.
- 6 X. Sun, H. Huang, Q. Zhao, T. Ma, L. Wang, *Adv. Funct. Mater.*, 2020, **30**, 1910005.

- 7 J. Chen, C. L. Dong, D. Zhao, Y. C. Huang, X. Wang, L. Samad, L. Dang, M. Shearer, S. Shen, L. Guo, *Adv. Mater.*, 2017, **29**, 1606198.
- 8 L. Ge, C. Han, J. Liu, *J. Mater. Chem.*, 2012, **22**, 11843-11850.
- 9 Y. Guo, S. Song, Y. Zheng, R. Li, T. Peng, *Dalton Trans.*, 2016, **45**, 14071-14079.
- 10 F. He, G. Chen, Y. Yu, S. Hao, Y. Zhou, Y. Zheng, *ACS Appl. Mater. Interfaces*, 2014, **6**, 7171-7179.
- 11 Y. Sui, J. Liu, Y. Zhang, X. Tian, W. Chen, *Nanoscale*, 2013, **5**, 9150-9155.
- 12 D. H. Wang, J. N. Pan, H. H. Li, J. J. Liu, Y. B. Wang, L. T. Kang, J. N. Yao, *J. Mater. Chem. A*, 2016, **4**, 290-296.
- 13 J. Wang, Y. Zheng, T. Peng, J. Zhang, R. Li, *ACS Sustain. Chem. Eng.*, 2017, **5**, 7549-7556.
- 14 Z. Xing, Z. Chen, X. Zong, L. Wang, *Chem. Commun.*, 2014, **50**, 6762-6764.
- 15 H. Yan, Y. Huang, *Chem. Commun.*, 2011, **47**, 4168-4170.
- 16 F. Yu, Z. Wang, S. Zhang, H. Ye, K. Kong, X. Gong, J. Hua, H. Tian, *Adv. Funct. Mater.*, 2018, **28**, 1804512.
- 17 L. Yu, X. Zhang, C. Zhuang, L. Lin, R. Li, T. Peng, *Phys. Chem. Chem. Phys.*, 2014, **16**, 4106-4114.
- 18 X. Zhang, T. Peng, L. Yu, R. Li, Q. Li, Z. Li, *ACS Catal.*, 2015, **5**, 504-510.
- 19 X. Zhang, L. Yu, C. Zhuang, T. Peng, R. Li, X. Li, *ACS Catal.*, 2014, **4**, 162-170.
- 20 W. Zhou, T. Jia, H. Shi, D. Yu, W. Hong, X. Chen, *J. Mater. Chem. A.*, 2019, **7**, 303-311.
- 21 Z. Jiang, G. Dong, R. Wang, C. He, C. Wang, J. Sun, *Sol. RRL*, 2020, **4**, 2000303.
- 22 Y. Shao, X. Xiao, Y. P. Zhu, T. Y. Ma, *Angew. Chem. Int. Ed.*, 2019, **58**, 14599-14604.
- 23 X. Sun, L. Shi, H. Huang, X. Song, T. Ma, *Chem. Commun.*, 2020, **56**, 11000-11013.
- 24 Z. Zhou, Y. Zhang, Y. Shen, S. Liu, Y. Zhang, *Chem. Soc. Rev.*, 2018, **47**, 2298-2321.
- 25 C. Wang, H. Dong, W. Hu, Y. Liu, D. Zhu, *Chem. Rev.*, 2012, **112**, 2208-2267.
- 26 Y. Lin, Y. Li, X. Zhan, *Chem. Soc. Rev.*, 2012, **41**, 4245-4272.
- 27 H. Wang, D. Yan, *NPG Asia Mater.*, 2010, **2**, 69-78.
- 28 Y. Liu, L. Ma, C. Shen, X. Wang, X. Zhou, Z. Zhao, A. Xu, *Chinese J. Catal.*, 2019, **40**, 168-176.
- 29 P. Niu, L. Zhang, G. Liu, H.-M. Cheng, *Adv. Funct. Mater.*, 2012, **22**, 4763-4770.
- 30 J. T. Yin, Z. Li, Y. Cai, Q. F. Zhang, W. Chen, *Chem. Commun.*, 2017, **53**, 9430-9433.
- 31 P. Niu, G. Liu, H.-M. Cheng, *J. Phys. Chem. C*, 2012, **116**, 11013-11018.