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Amorphous/crystalline g-C₃N₄homojunctionfor visiblelight photocatalysisreaction with superior activity

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Amorphous/crystalline g- C_3N_4 homojunctionwas prepared for the first timeat high temperature, in which the ratio of crystalline g- C_3N_4 in the homojunction was optimized. The homogenous junction with a matchedenergy level structure sulted in superiorphotocatalytic performance for the degradation of organic pollutants and H₂ evolution from splitting waterundervisible light irradiation.

Graphitic carbon nitride $(g-C_3N_4)$ as a metal-free visible light photocatalyst has been widely investigated due to its unique semiconductor band structure and excellent chemical stability.¹The suitable band edge of g-C₃N₄is possible to photocatalytic degradation of organic pollutants and hydrogen production via water splitting under visible light irradiation.² However, bulk g-C₃N₄fabricated by conventional calcination method at high temperature has small specific surface area and low crystallinity.³ The quick recombination of photogenerated electrons and holes in bulk g-C₃N₄limited the applications.⁴Efforts have been made to modify the bulk g-C₃N₄, such as nano-modification, special morphology control, ion doping and surface heterojunction construction.⁵ It is common to produce ultrathin g-C₃N₄through heat-treatment at high temperature using a hot gas flow to delaminate $g-C_3N_4$ from layer to layer.⁶However, main attention focused on the change of morphology, ignoring the influence of temperature on the crystallinity and energy level of $g-C_3N_4$.

In fact, it is found that the g-C₃N₄ calcined at high temperature not only has an ultra-thin layered structure but also high degree of polymerization, in which g-C₃N₄ has higher crystallinity and fewer crystal defects and is beneficial to the internal charge transfer. It has been found that theg-C₃N₄calcinedat high temperature has different band gap and edge position compared with the one obtained at low

temperature. For example, He *et al.*⁷ prepared crystallineg- C_3N_4 through the addition of dopamine, which improved hydrogen production performance under visible light. However, increase of crystallinity of g-C₃N₄ requires the introduction of admixture. Other efforts have been made to fabricate surface as $MoS_2/mpg-C_3N_4$,⁸ heterojunction construction, such g-C₃N₄/ZnGaNO,¹⁰ g-C₃N₄/BiOBr,¹¹ Co₃O₄/CNS,⁹ g- $C_3N_4/AgX(X=Br, I)$ ¹² but, these junctions are mainly composed of g-C₃N₄/inorganic semiconductors. Organic g-C₃N₄polymer is generally not easy to bond to the inorganic semiconductor surface and thus not conducive to the charge transfer at the organic-inorganic interfaces.¹³

Crystalline $g-C_3N_4$ (CGCN) and amorphous $g-C_3N_4$ (AGCN) as polymers are fabricated at different temperature with a similar composition. CGCN and AGCN have different energy level structure, which is conducive to the formation of closecoupled copolymers. In this paper, CGCN was used as seeds to optimize the morphology of AGCN, produce ultra-thin nanosheets, and form amorphous/crystalline g- C_3N_4 homojunction (A-CGCN) via polymerization of melemon the surface of CGCN. The homojunction results in the orientation transfer of electron and hole in the different crystal plane and displays superior photocatalytic performance. Namely, A-CGCN was prepared without any pretreatment and admixture for the first time.

The A-CGCN composites were obtained via polymerization of melemon the surface of CGCN (as seeds). The synthesis process of A-CGCN composites is shown in Scheme 1 (also in Experimental section, ESI⁺). The samples was prepared by controlling the calcination procedures and parameters (Table S1, ESI⁺). A two-step process was used to produce thin g-C₃N₄nanosheets with high crystallinity. Amorphous GCN (A₆₀₀GCN) was fabricated at 600 °C. Crystalline GCN (CGCN) was obtained after heating A₆₀₀GCNat 750 °C. A further high temperature treatment could delaminate A₆₀₀GCN and increase the crystallinity. Afterwards, CGCN was calcined in the presence of melamine at 650 °C to obtain an amorphouscrystalline GCN (A-CGCN)ultra-thin layer using CGCN as seeds. At high temperature, melem could form amorphous GCN on

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Scheme 1 Preparation illustration of A-CGCN composites.

the surface of CGCN to generate a A-CGCN junction. The amorphous-crystalline $g-C_3N_4$ homo-junction (A-CGCN), which is composed of AGCN and CGCN with a similar composition but different crystal structure, has different energy band structure was finally created.

Fig. 1a, b, and c show the transmission electron microscopy (TEM) images of samples AGCN, CGCN and A-CGCN, respectively. All of samples revealed thin nanosheet morphology. Compared with sample AGCN, the size of sample CGCN is small because of treatment at much high temperature. As expected, ultra-thin AGCN nanosheets (Fig. 1c) were formed after the thermal polymerization. The specific surface area of sample CGCN was found to be the largest $(119.1 \text{ m}^2/\text{g})$ due to the treatment at much high temperature (750 °C). The specific surface area of sample A-CGCN (87.6 m²/g) was significantly increased compared with sample AGCN (57.7 m²/g) from the Brunauer Emmett Teller (BET) analysis (Fig. S1 and Table S2, ESI⁺). CGCN has a larger specific surface area than A-CGCN but its performance is worse, so the improvement of A-CGCN performance is mainly due to the formation of homojunctions. That is, the effect of the specific surface area is secondary in the experiment, and the main effect is due to the proper homojunction and good crystallinity.

The X-ray diffraction (XRD) patterns of samples AGCN, CGCN and A-CGCN are presented in Fig. 1d. It is noteworthy that two characteristic peaks at 12.8° and 27.9° for samples AGCN, CGCN and A-CGCN corresponded to the (100) and (002) planes, respectively. The former is the characteristic peak caused by the periodic arrangement of the triazine in $g-C_3N_4$, the latter is the stacking of the conjugated aromatic system of carbon nitride, suggesting that samples AGCN, CGCN and A-CGCN maintain $g-C_3N_4$ phase. The XRD peak intensity of sample CGCN (10506) is high compared with sample AGCN (6646). This demonstrates that calcination at high temperature improved the crystallinity of $g-C_3N_4$. Sample A-CGCN (8637) revealed higher peak intensity than that of sample AGCN because of addition of CGCN. X-ray photoelectron spectroscopy (XPS) analysis further indicates the elemental composition and existence state of samples. The full XPS spectra of samples A-CGCN, AGCN, and CGCN were tested (Fig. S2, S3 and S4, ESI^T). The result indicates that these samples contain only three elements of C, N and O. No other extra peak was observed. The peak of O element is ascribed to the H₂O adsorbed on the



Fig. 1TEM images and XRD patterns of samples. TEM images of samples AGCN (a), CGCN (b), A-CGCN(c). (d) XRD patterns. (e) HRTEM image of A-CGCN. SAED patterns of AGCN(f), CGCN (g), A-CGCN (h).

surface of the sample. The C 1s spectrum (Fig.S2b, ESI[']) indicates that the two peaks at 284.3 and 287.5eV correspond to the standard reference carbon (C-C) and sp^2 hybridization at C in N=C-(N)₂, respectively (the spectrum of N 1s in Fig. S2c, ESI⁺). The four peak positions corresponding to C-N=C (398.1eV, Pyridinie-C), N-(C)3 (399.6eV, Pyrrole-C), N-H group (400.6 eV, Graphitic-C) and π -excitation (403.8 eV).¹⁴ The XPS analysis indicates sample CGCN and AGCN revealed similar elemental composition and existence state with sample A-CGCN.

Fig. 1e shows the high resolution transmission electron microscopy (HRTEM) image of sample A-CGCN. Phase AGCN and CGCN have different crystallinity due to different calcination temperatures. The HRTEM image of phase CGCN displays that the lattice distance ofg-C₃N₄ layer is 0.324 nm, corresponding to the (002) inter planes. Phase CGCN exhibited clear lattice fringes compared with AGCN, exhibiting that CGCN has better crystallinity. To further study the crystallinity of samples, the selected area electron diffraction images of samples AGCN, CGCN and A-CGCN are shown in Fig. 1f, g and h. As expected, sample AGCN is relatively more amorphous shown by absence of diffraction spots or rings (Fig. 1f). The presence of some clear diffraction rings in Fig. 1g indicates sample CGCN is with high crystallinity. Because sample A-CGCN contains a small amount of CGCN, a weak diffraction ring was observed in Fig. 1h. This result suggests that A-CGCN forms in the CGCN after the thermal polymerization process.

The energy band structure of samples determined by UV-vis diffuse reflectance test (UV-vis DRS) and the XPS valence band

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Fig. 2 (a) UV-vis DRS and (b) plots of $(\alpha hv)^{1/2}$ vs photon energy of AGCN, CGCN and A-CGCN. (c) XPS valence band spectra of samples AGCN and CGCN. (d) Schematic illustration of electron-hole separation and transport at A-CGCN heterojunction interface and in AGCN and CGCN.

(VB) spectroscopy shown in Fig. 2 are investigated for the discussion of photocatalytic mechanism. The band edge of A-CGCN is located between AGCN and CGCN, which further confirmed the electronic coupling of these two components in the A-CGCN homojunction via polymerization. The tangents to the cross section of plots of $(\alpha hv)^{1/2}$ vs photon energy generally show the band gap width are 2.59, 2.76 and 2.7 eV for samples AGCN, CGCN and A-CGCN (Fig. 2b), respectively. The different band gaps of AGCN and CGCN make it possible to prepare a homogenous junction with a matched energy level structure.

The energy band structures of samples AGCN and CGCN are further characterized by XPS valence band analysis (Fig. 2c).¹⁵ It shows that the valence band positions of AGCN and CGCN differ by 0.5 eV. According to the band gaps of AGCN and CGCN obtained from Fig. 2b, the difference between AGCN and CGCN in the conduction band position is 0.33 eV. Photocatalytic mechanism is proposed in Fig. 2d based on the band gap data.

In the case of visible light irradiation, the electrons in the valence band are excited and transferred to the conduction band while holes are left in the valence band. Because the different conduction band and valence band of AGCN and CGCN are 0.33 and 0.5 eV, respectively (Fig. 2d), the transfer of electrons on the AGCN conduction band to the conduction band of CGCN occurred while the holes on the valence band of CGCN was transferred to the valence band of AGCN. The driving force of this charge transfer is the potential difference between AGCN and CGCN. This directional transfer of electrons and holes results in the major accumulation of electrons on the CGCN and the concentration of holes mainly on the AGCN. The spatial separation of these charges would be beneficial to reduce the recombination rate of electron-hole pairs. In addition, CGCN has high crystallinity and few internal defects, making it easier for electrons to migrate to the CGCN surface in the reduction reaction, which is consistent to



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Fig. 3 (a) Photocatalytic degradation of RhB renderings and (b) fitting histogram of photocatalytic degradation of RhB; (c) effect of capture agent on the photocatalytic activity of A-CGCN;(d) H₂ production curves and (e) apparent rate constants for H₂ evolution of AGCN and A-C_{x%}GCN(X = 0.5, 4, 6, 10) samples under visible light (λ > 420 nm); (f)stability test of A-C_{6%}GCN for four cycling H₂ evolution.

photoluminescence (PL) spectra (Fig. S5, ESI[†]).Namely, the weakening of the luminescence peak of sample CGCN is ascribed to the better crystallinity, which facilitates electron transfer to the sample surface. The weakening of the emission peak of A-CGCN is mainly due to the accumulation of holes and electrons on CGCN and AGCN, respectively, resulting in the separation of space.

The visual evaluation of photocatalytic performance improvement is characterized by photocatalytic degradation of organic pollutants and H₂ evolution from splitting water under visible light irradiation ($\lambda \ge 420$ nm). Fig. 3a and b show the results of RhB degradation under visible light. A-CGCN has the best degradation effect and degrades 100% within 10 min. In contrast, AGCN and CGCN degrade 30 and 70%, respectively. The histogram of sample A-CGN (Fig. 3b) shows that the degradation rate of sample A-CGN is 5.7 times high compared with sample AGCN. Furthermore, the photocatalytic testing of samples AGCN and CGCN were carried out after physically mixing, the effect is much worse than the effect of A-CGCN. It is confirmed that the formation of type II homogeneous junctions by AGCN and CGCN can obviously improve its performance.

In order to further study the photocatalytic reaction mechanism and active species, the active species capture experiment was performed (Fig.3c). AgNO₃, triethanol amine (TEOA), para-benzoquinone (BQ), tertiary butanol (TBA) were

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used as capture agents for e^{-} , h^{+} , O_{2}^{-} and $\cdot OH$, respectively. When AgNO₃ and BQ were added to the photocatalytic system, there is no significant effect in the photocatalysis. On the contrary, the photocatalytic effect decreased apparently when TEOA and TBA were added to the solution. However, the inhibition of photocatalytic performance after addition of TBA is not as effective as TEOA. In the photocatalytic system of A- $C_{0.5\%}$ GCN, the main active substances are h⁺ and the secondary active substance is ·OH. The electron-hole separation and transport at A-CGCN heterojunction interface and in AGCN and CGCN was indicated in Fig. 2d. The electrons and holes are spatially and directionally separated, resulting in an increase in the concentration of holes and electrons. Most of the holes are directly used to degrade RhB, and the remaining holes react with H_2O to form $\cdot OH$ and then oxidative decompose RhB. Meanwhile, electrons do not combine with surfaceadsorbed O_2 to form O_2^- , but rather exists in the form of an excited state, which is more advantageous to the reaction of e with H_2O to produce H_2 , improving the performance of photocatalytic hydrogen production. To eliminate the effect of heat on the degradation efficiency during photocatalysis, sample ACGN* is kept at 60 °C under the dark (Fig. S6, ESI+).

To investigate the effect of amount of CGCN on the photocatalysis activity, the ratio of CGCN in A-CGCN junctions was adjusted (Table S1, ESI^T). In addition, Pt was loaded on A-CGCN for H₂ generation from splitting water. The results indicate that the ideal loading of Pt is 2 wt% and the optimized weight ratio of CGCN in A-CGCN was 6% (Figs. S7 and S8, ESI⁺). Fig. 3d and e show the H₂ evolution from splitting water, displaying a significant performance difference between AGCN and A-CGCN, in which the efficiency of sample A-CGCN (1179 μ molh⁻¹g⁻¹) is 57 times of that of sample CGCN (20.5 μ molh⁻¹g⁻¹) ¹). This is ascribed to the formation of A-CGCN junctions because the hydrogen generation efficiency of sample AGCN+CGCN obtained by physically mixing AGCN and CGCN is similar to sample AGCN (Fig. S8, ESI⁺). The photocatalytic performance improvement of sample A-CGCN is ascribed to the following reasons, AGCN and CGCN are polymers with the same crystal structure, through polymerization reaction to form A-CGCN is more closely linked, II) the potential difference between AGCN and CGCN promotes the spatial separation of electrons and holes, reducing the recombination rate, III) CGCN reveals fine crystallinity and few internal defects, resulting in efficient electron transfer to the surface. Furthermore, after four cycles, the hydrogen generation efficiency of sample A-CGCN was not degraded obviously as shown in Fig. 3f and their morphology was not changed(Fig. S9, ESI⁺), indicating sample A-CGCN is with high stability.

In conclusion, an optimized calcination condition at high temperature delaminated $g-C_3N_4$ and improved the crystallinity, which leads to a different energy band structure without changing crystal structure. A two-step calcination process made superior thin $g-C_3N_4$ with fine crystallinity and large surface area. A-CGCN homojunctions with a compatible phase ratio were created by a two-step polymerization of melem using crystalline $g-C_3N_4$ nanosheets as seeds. The A-CGCN revealed a superior photocatalytic performance for the

degradation of organic pollutants such as RhB. The hydrogen generation efficiency of sample A-CGCN with 6% CGCN is 57 times high compared with that of AGCN nanosheets under visible light irradiation. The result is expected to be utilizable for improvement of the construction and property of $g-C_3N_4$ composites.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

- (a) X. Wang, K. Maeda and A. Thomas, *Nature*, 2009, **8**, 76;
 (b) G. Liu, P. Niu and C. Sun, *J. Am. Chem. Soc.*, 2010, **132**, 11642;
 (c) T. Xiong, W. Cen and Y. Zhang, *ACS Catal.*, 2016, **6**, 2462;
 (d) Y. Chen, Q. Zhou and G. Zhao, *Adv. Funct. Mater.*, 2017;
 (e) W. J. Ong, L. L. Tan and Y. H. Ng, *Chem. Rev*, 2016, **116**,7159.
- 2 (a) K. Dai, L. Lu and C. Liang, *Appl. Catal. B-Environ.*, 2014, 156, 331; (b) X. Chen, W. Lu and T. Xu, *Chem. Eng. J.*, 2017, 328, 853; (c) S. Cao and J. Yu, *J. Phys. Chem. Lett.*, 2014, 5, 2101; (d) Q. Tay, P. Kanhere, C. F. Ng, *J. Mater. Chem. A*, 2015, 27, 4930; (e) J. Zhang, Y. Wang and J. Jin, *ACS Appl. Mater. Inter.*, 2013, 5, 10317.
- 3 (a) D. Feng, Y. Cheng and J. He, *Carbon*, 2017, **125**, 454; (b) H.
 Shi, G. Chen and C. Zhang, *ACS Catal.*, 2014, **4**, 3637; (c) M.
 Bellardita, E. I. García-López, G. Marcì, *Appl. Catal. B-Environ.*, 2018, **220**, 222.
- 4 H. Shi, G. Chen and C. Zhang, ACS Catal., 2014, 4, 3637-3643.
- 5 (a) X. Chen, Y. Jun, K. Takanabe, K. Maeda, K. Domen, X. Z. Fu

M. Antonietti and X. Wang, *Chem. Mater.*, 2009, **21**,4093; (b) J. Zhang, F, Guo and X. Wang, *Adv. Funct. Mater.*, 2013, **23**, 3008; (c) X. Li, J. Zhang, X. Chen, A. Fischer, A. Thomas, M. Antonietti and X. Wang, *Chem. Mater.*, 2011,**23**, 4344; (d) J. Sun, J. Zhang, M. Zhang, M. Antonietti, X. Fu and X. Wang, *Nat. Commun.*, 2012,**3**, 1139; (e)G. Jiang, C. Zhou, X. Xia, F. Yang, D. Tong, W. Yu and S. Liu, *Mater. Lett.*, 2010, **64**, 2718.

- 6 S. W. Cao, Y. P. Yuan, J. Fang, Int. J. Hydrogen Energ, 2013, 38, 1258.
- 7 F. He, G. Chen and Y. Yu, Chem .Commun., 2015, 51, 6824.
- 8 Y. Hou, A. Laursen, J. Zhang, G. Zhang, Y. Zhu, X. Wang, S. Dahl and I. Chorkendorff, *Angew. Chem. Int. Ed.*, 2013, 52, 3621.
- 9 J. Zhang, M. Grzelczak, Y. Hou, K. Maeda, K. Domen, X. Fu, M. Antonietti and X. Wang, *Chem. Sci.*, 2012, **3**, 443.
- 10 M. Yang, Q. Huang and X. Jing, *Mater. Sci. Eng. B*, 2012, **177**, 600.
- 11 J. Fu, Y. Tian, B. Chang, F. Xi and X. Dong, J. *Mater. Chem.*, 2012, **22**, 21159.
- 12 H. Xu, J. Yan, Y. Xu, Y. Song, H. Li, J. Xia, C. Huang and H. Wan, Appl. Catal. B: Environ., 2013, **129**, 182.
- 13 F. He, ACS Appl. Mater. Inter., 2014, 6, 7171.
- 14 J. Meng, J. Pei and Z. He, *RSC Advances*, 2017, **7**, 24097-24104.
- 15 F. Dong, Z. Zhao and T. Xiong, ACS Appl. Mater. Inter., 2013, 5, 11392.