Materials Research Express

PAPER

Preparation of graphite phase carbon nitride (g-C$_3$N$_4$) micro-nano bouquet by thermal polymerization

Feiwen Ma$^{1,2}$, Yuchun Ji$^{1,2}$, Bingsai Liu$^{1,2}$, Jilin Wang$^{1,2,3}$*, Bing Zhou$^{1,2}$, Guoyuan Zhen$^{1,2}$, Fei Long$^{1,2,3,*}$ and Zhengguang Zou$^{1,2}$

1 School of Materials Science and Engineering, Key Laboratory of New Processing Technology for Nonferrous Metals and Materials of Ministry of Education, Guilin University of Technology, Guilin 541004, People’s Republic of China
2 Guangxi Key Laboratory of Optical and Electronic Materials and Devices, Guilin University of Technology, Guilin 541004, People’s Republic of China
3 Collaborative Innovation Center for Exploration of Hidden Nonferrous Metal Deposits and Development of New Materials in Guangxi, Guilin University of Technology, Guilin 541004, People’s Republic of China

* Authors to whom any correspondence should be addressed.
E-mail: jilinwang@glut.edu.cn, longf@glut.edu.cn and feiwen0908@163.com

Keywords: thermal polymerization, carbon nitride, micro-nano bouquets, structure

Abstract

A novel kind of g-C$_3$N$_4$ micro-nano bouquets were successfully prepared via a simple method using melamine and ammonium chloride as raw materials. X-ray diffraclome (XRD), field emission scanning electron microscope (FESEM), X-ray energy spectrometer (EDX), transmission electron microscope (TEM), high resolution transmission electron microscopy (HRTEM), fourier transform infrared spectrometer (FT-IR) and x-ray photoelectron spectroscopy (XPS) were used to characterize the as-synthesized samples. The results indicated that the samples presented graphitic C$_3$N$_4$ micro-nano bouquets. Every microstructure was composed of many petals cross gathered along with the different directions. And the tip of every single petal contained quantities of nano bouquet structures with smaller diameters. In addition, abundant nanoparticles/nanorods distributed and intertwined together on the surface of the nano bouquet structure, and then formed cocoon-like porous morphology. Besides, based on the experimental results, the reasonable chemical reactions and the corresponding growth mechanism during the preparation process of g-C$_3$N$_4$ micro-nano bouquets were proposed. Finally, the UV–vis results showed that the sample was a wide band gap (about 3.11 eV) semiconductor.

1. Introduction

In the early 1990s, Hemley et al theoretically predicted that C$_3$N$_4$ has five structures, namely α-C$_3$N$_4$, β-C$_3$N$_4$, c- C$_3$N$_4$, p- C$_3$N$_4$ and g- C$_3$N$_4$ in graphite phase [1]. Among them, organic pollutant degradation and photocatalytic hydrogen production have good prospects [2–6], graphite-phase g-C$_3$N$_4$ is widely used as a nonmetallic photocatalyst in recent years due to its semiconductor properties, special optical properties, energy storage capacity [7], gas adsorption capacity and other physical and chemical properties [8–10].

Previous studies have reported a variety of synthesis methods of graphite-phase g-C$_3$N$_4$ materials, including template method [11–15], thermal polymerization method [16–20], mechanical ball mill method [21] and solvent thermal method [22–27]. For example, Liu et al took porous alumina as a template to prepare g-C$_3$N$_4$ nanotubes, but there were many aluminum oxide impurities in the final products, and the experimental process was relatively complex and inconvenient to operate [12]. Wang et al [13] prepared mesoporous g-C$_3$N$_4$ by taking three-dimensional cubic mesoporous silica as template and melamine as precursor. Wang [11] et al used calcium carbonate particles as hard templates and calcined melamine to prepare blocky g-C$_3$N$_4$. However, a certain amount of carbon dopant remained in the samples. Lqbal, W et al [16] used one-step method to prepare g-C$_3$N$_4$ nanosheets using melamine and ammonium sulphate as the bubble template in air. Lu [17] et al took
urea as raw material and polymerized it into g-C3N4 tablets in muffle furnace. For mechanical ball mill method [21], it generally requires long time ball mill under the protection of high-pressure nitrogen. Carbon, iron and other elements in ball mill existed in various forms of impurities and compounds and were difficult to remove. Solvent-thermal method could ensure the reasonable proportion of products and the impurities were easier to remove. This method generally requires the solvent as a liquid phase reaction medium, which is suitable for the preparation of g-C3N4 [25, 26].

Herein, a novel high-pressure thermal polymerization method was reported to prepare g-C3N4 micro-nano bouquets in a high-temperature and high-pressure reactor. XRD, FTIR, EDS, XPS, FESEM, TEM and HRTEM were used to characterize the phase, element composition, valence and bonding characteristics, macroscopic morphology and microstructure of the samples. In addition, UV–vis was used to study the ultraviolet luminescence characteristics and band gap of the samples. Finally, on the basis of the experimental results, the chemical reaction process and growth mechanism of g-C3N4 micro-nano bouquets in the preparation process were also discussed.

2. Experimental

2.1. Materials synthesis

Melamine (C3H6N6 99%) and Ammonium Chloride (NH4Cl 99%) (China Pharmaceutical Group Co., Ltd) were of analytically pure grade and used without further purification. In a typical experiment process, the reagents were put into the reaction kettle. The crude product was collected after high pressure thermal polymerization for 5 h at 450 °C (heating rate of 5 °C min⁻¹) in the tubular furnace. The obtained sample was dispersed in 50ml deionized water. Then, 40ml hydrochloric acid (12 mol l⁻¹) and 2ml nitric acid (15 mol l⁻¹) were added into suspension and stirred for 12 h at 80 °C. After that, g-C3N4 micro-nano bouquets were obtained with a yield of about 5% by centrifugation, washing and drying for 24 h at 80 °C.

2.2. Characterization

Phase analysis of the sample was performed by x-ray powder diffractometer (XRD, X. Pert PRO MRD, Cu-k radiation x-ray source, lambda = 1.5406A, voltage 40 kV, 40 mA). Element composition valence state and bonding properties of the samples were through x-ray energy (EDS) along with FESEM instruments, Fourier transform infrared spectrometer (FTIR Nicolet Nexus) and x-ray photoelectron spectroscopy analysis (XPS, ESCALAB 250xi spectrometer). Secondary structure and microstructure of samples were observed on the field emission scanning electron microscope (FESEM, Hitachi S4800) and high resolution transmission electron microscopy (TEM/HRTEM, JEM-2100F); The band gap of the sample can be measured by ultraviolet and visible spectrophotometer (UV–vis, UV-3600).

3. Results and discussion

3.1. Morphological characterization of micro-nano bouquets

Figures 1(a)–(d) shows the FESEM images of g-C3N4 micro-nano bouquets ((a) - low magnification, (b), (c), (d) - high magnification). The sample displayed a novel micro-nano bouquets, which was composed of multiple petals intersecting and gathering together in different directions (figures 1(a), (b)), while the end of every single petal contained many nano-bouquet with smaller diameters (indicated by black arrow). The micro-nano bouquets presents the phenomenon of agglomeration (figure 1(a)), which was because that the sample powders were directly sprinkled on the conductive adhesive during the sample preparation process. Each petal was about 5 m in length and 1 m in diameter. As shown in the enlarged images of the petals (figures 1(b)–(d)), the top of the petals was a nano-bouquet with a smaller diameter of less than 500 nm. Besides, some ends of these micro-nano bouquets presented hollow depressed structures (dotted circles). The outer layer of serrate thin wall had a thickness of less than 30nm. And a large number of solid nanoparticles could be observed at the other ends of these micro-nano bouquets (pointed by white arrows). The appeared two different ends might be attributed to the different etching degree during the growth process of the micro-nano bouquet. In addition, it is worth noting that the surface of the bouquet samples were relatively rough, which was attributed to the appearance of a large number of nanoparticles/nanorods existed on the surface. These nanoparticles/nanorods were randomly distributed and interwoven together, forming a cocoon-like pore structure on the surface of the bouquet. These nanoparticles/nanorods could increase the specific surface area of the micro-nano bouquets and enhance the chemical reactivity of the product. Of course, it could also be found that some of the micro-nano bouquet presented a smooth surface with only a few holes (as shown in figure b). This phenomenon could also be caused by the different etching degree of the nano-bouquet during the growth process. The higher the etching degree, the more nanoparticles/nanorods were formed, the rougher of the surface. More holes would be formed finally.
Figure 2 shows the EDS map scanning images of g-C$_3$N$_4$ micro-nano bouquets. The structure of micro-nano bouquets contains C, N and O elements. The obvious sample morphology could be observed by scanning the N element scanning, while it was not obvious by scanning the C element surface. This was due to the use of carbon conductive adhesive in EDS sample preparation process. The existence of O element was due to the absorption of water vapor in the air on the large surface area of this special structure. Therefore, EDS mapping scan proved that the sample was carbon nitride.

Figure 3 shows the TEM (3(a) and 3(b)) and HRTEM (3(c) and 3(d)) images of g-C$_3$N$_4$ micro-nano bouquets. As shown in figures 3(a) and (b), the top part of the bouquet presented a transparent sawtooth shape (marked by dotted box in figure 3(a)), indicating that the outer wall of the bouquet was relatively thin and could
be easily penetrated by the electron beam. In addition, a small amount of solid conical shape appeared at the top of the bouquet (pointed by dotted box in figure 3(b)), which might be caused by different etching degrees. Figures 3(c) and (b) displayed the HRTEM images of a single serrated structure and a solid tapered end respectively. The results showed that the surface of the two structures was relatively rough, the atomic arrangement and lattice fringe were not clear, and the crystallinity was poor. The crystal plane spacing of the sample was measured to be about 0.303 nm, corresponded to be the (002) crystal plane of g-C₃N₄. Therefore, the TEM and HRTEM images analysis results of the samples were consistent with that of the FSEM results mentioned above.

3.2. Phase characterization of micro-nano bouquets

Figure 4 shows the typical XRD (a), FTIR (b) and XPS (c), (d) spectra of the samples. From the XRD spectrum figure 4(a), the diffraction peak located at 26.8° was corresponded to (002) crystal plane of g-C₃N₄ (when the d value was 0.322 nm) [28]. Four obvious absorption peaks (figure 4(b)) located at 3445, 1631, 1316 and 834 cm⁻¹ in the FTIR spectra. The peaks at 834 cm⁻¹ was ascribed to the deformation vibration mode of triazine ring, and the 1316 cm⁻¹ and 1631 cm⁻¹ diffraction peaks were attributed to the contraction vibration mode of C–N and C=–N respectively [29, 30]. The wide absorption peak at 3445m⁻¹ was generally due to surface hydrolysis and oxidation. In order to further study the chemical bond characteristics of the sample, XPS tests were also performed, as shown in figures 4(c) and (d). The binding energy of C1s spectrum fitting was located at 283.60 eV, 285.31 eV and 287.24 eV (A, B and C peak), corresponded to sp³ hybridization of C–C, C=–N and C–N respectively. N1s spectrum could be decomposed into two peaks of 397.55 eV and 399.20 eV (D and E peak), attributed to sp³ hybridization of N-C bond and sp² hybridization of N=–C bond, respectively [31–33]. Therefore, FTIR and XPS analysis results also proved that the prepared sample was g-C₃N₄ from different perspectives.

3.3. Chemical reaction process and growth mechanism of micro-nano bouquets

In the synthesis process of g-C₃N₄ micro-nano bouquets, the following chemical reactions might occur:

$$C₃H₆N₆ \rightarrow C^* + N^* + H₂ \quad (1)$$

$$NH₄Cl \rightarrow N^* + H₂ + HCl \quad (2)$$

$$C^* + N^* + H₂ \rightarrow [C^* - N^*] \quad (3)$$

$$[C^* - N^*] \rightarrow C₃N₄ \quad (4)$$

Firstly, the decomposition of melamine began at about 350 °C. With the increase of temperature, C₃H₆N₆ was resolved into the active C* and N* (equation (1)) finally. At the same time, NH₄Cl will be reduced to NH₃ and HCl at about 170 °C [16, 34–36] and further decomposition to active N* and H₂ (equation (2)). The decomposition of C₃H₆N₆ and NH₄Cl in the reaction process will produce a large number of gaseous substances (such as C*, N* and H₂), and then create a high-pressure growth environment. According to the growth
mechanism of Vapor-solid (VS), g-C₃N₄ micro-nano bouquets began to grow under special high temperature and pressure conditions (equation (4), figure 5(a)). Attributed to generated excessive activity gaseous substances N≡ and H₂, micro-nano structure surface layer of the new generation of g-C₃N₄ bouquets would be etched by these gas under the condition of high temperature and high pressure. Thus, nanoparticles and nano short stick appeared on the surface of the sample. These nanoparticles and nano short rods intertwined followed formed a kind of interesting silkworm cocoon hole structure. And the exact formation mechanism still needs further research. This supposition could tentatively be supported by the observation of the HRTEM and SEM images.

Figure 5 shows the reasonable growth mechanism and FSEM images of g-C₃N₄ at different growth stages. As can be seen from figure 5(a), the surface and end of g-C₃N₄ micro-nano bouquets without be etched were relatively smooth. With the beginning of the etching process, the nanoparticle and nanorod structure first appeared on the surface (pointed by dotted box in figure 5(b)). However, the end began to crack without obvious etching (pointed by dotted box in figure 5(c)). With the prolongation of etching time, obvious nanoparticles and splitting phenomenon appeared at the end of the single micro-nano bouquet (framed by dotted line in figure 5(d)). In the later stage of etching, surface and end etching were obvious, and the nanoparticles grew together to form interwoven cocoon-shaped structures (figure 5(e)). At the same time, the end was split into several one-dimensional structures with smaller diameters (figure 5(f)).

3.4. Ultraviolet-visible (UV–vis) spectra and forbidden band widths of micro-nano bouquets

Figure 6 shows the UV–visible absorption spectrum and the calculated band gap value of g-C₃N₄ micro-nano bouquets. According to the literature, g-C₃N₄ is a direct bandgap semiconductor [33]. The corresponding bandgap value (illustrated in figure 6) was calculated to be 3.11 eV, which was different from the value of g-C₃N₄ (about 2.7 eV) prepared in the literature [37]. This might be due to structural differences and internal defects that lead to changes of the band gap of graphite phase carbon nitride (2.88–2.97 eV). In addition, calculated based on the first-principles of density functional theory, Xu et al. [38] calculated that the band gap was about 3.1 eV, which was consistent with that measured in this paper. Therefore, the prepared g-C₃N₄ micro-nano flower bundle structure would have a good application prospect in the high-temperature wideband gap semiconductor field, such as ultraviolet light emitting devices, high-power electronic devices with high-frequency which could be used at high temperature.

![Figure 4](image_url)
4. Conclusion

A g-C₃N₄ micro-nano bouquets was prepared by high pressure thermal polymerization method using traditional materials. Single micro-nano bouquets was composed of multiple petals intersecting and gathering together in different directions, and the end of single petal contained many nano-bouquets with smaller diameter. In addition, the surface of single micro-nano bouquets contains a large number of nanoparticles and nanorods, which was randomly distributed and interwoven together, followed formed cocoonliked pore
structure on the surface of the micro-nano bouquet. These unique morphological and structural features can further improve the surface roughness and specific surface area of g-C3N4. It could also serve as surface active sites and enhance chemical reactivity of the sample. Besides, on the basis of the experimental results, the main chemical reaction process, reasonable growth mechanism and corresponding growth model involved in the preparation of g-C3N4 micro-nano bouquets were also proposed. Finally, Uv-vis results showed that g-C3N4 micro-nano bouquets was a wideband gap semiconductor (band gap value was 3.11 eV). This interesting material will have good application prospects in high-temperature wideband gap semiconductor field, such as high-frequency high-temperature, high-power electronic devices and ultraviolet light emitting devices. The authors declare no conflicts of interest.

Acknowledgments

The authors acknowledge the financial support from National Natural Science Foundation of China (No.51972071), Guangxi Natural Science Foundation (2018GXNSFAA050032), Non-ferrous metals and materials processing new technology Ministry of education key laboratory open fund project (No. 19KF-5 and No.19AA-14), Guangxi Young and Middle-aged Teachers’ Basic Ability Promotion Project(No.2018KY0256).

ORCID iDs

Jilin Wang https://orcid.org/0000-0001-8385-253X

References

[1] Teter DM and Hemley RJ 1996 Low-compressibility carbon nitrides Science 271 53–5
[2] Kaurthik KV, Reddy CV, Reddy KR, Ravishankar R, Sanjeev G, Kulkarni R V, Shetti N P and Raghu A V 2019 Barium titanate nanostructures for photocatalytic hydrogen generation and photodegradation of chemical pollutants J. Mater. Sci.- Mater. Electron. 30 20646–53
[3] Patil SB, Basavarajappa P S, Ganganagappa N, Jyothi M S, Raghu A V and Reddy KR R 2019 Recent advances in non-metals-doped TiO2 nanostructured photocatalysts for visible-light driven hydrogen production, CO2 reduction and air purification Int. J. Hydrogen Energy 44 13022–39
[4] Reddy KR, Jyothi MS, Raghu A V, Sadhu V and Aminabhavi TM 2019 Nanocarbons-Supported and Polymers-Supported Titanium Dioxide Nanostructures as Efficient Photocatalysts for Remediation of Contaminated Wastewater and Hydrogen Production Nanophotocatalysis and Environmental Applications (Environmental Chemistry for a Sustainable World 30) ed A Asiri and E Lifthouse (Inamuddin: Springer, Cham) 139–69 978-3-030-12618-6
[5] Shwetharani R, Chandan H R, Sakar M, Balakrishna GR, Reddy KR and Raghu A V 2020 Photocatalytic semiconductor thin films for hydrogen production and environmental applications Int. J. Hydrogen Energy 45 18289–308
[6] Srinivas M, Venkata RC, Kakarla RR, Shetti NP, Reddy MS and Anjanapura VR 2019 Novel Co and Ni metal nanostructures as efficient photocatalysts for photodegradation of organic dyes Mater. Res. Exp. 6 125502
[7] Park S S, Chu S W, Xue C P, Zhao D Y and Ha C S 2011 Facile synthesis of mesoporous carbon nitrides using the incipient wetness method and the application as hydrogen adsorbent J. Mater. Chem. 21 10801–7
[8] Cao S and Yu J U 2014 g-C3N4-based photocatalysts for hydrogen generation J. Phys. Chem. Lett. 5 2101–7
[9] Cao Y, Xing Z, Li Z, Wu X, Hu M, Yan X, Zhu Q, Yang S and Zhou W 2018 Mesoporous black TiO2_x–yAg nanocomposites coupled with g-C3N4 nanosheets as 3D/2D ternary heterojunctions visible light photocatalysts J. Hazard. Mater. 343 181–90
[10] Hong Y, Li C, Li D, Fang Z, Luo B, Yan X, Shen H, Mao B and Shi W 2017 Precisely tunable thickness of graphitic carbon nitride nanosheets for visible-light-driven photocatalytic hydrogen evolution Nanoscale 9 14103–10
[11] Chen D M, Yang J and Ding H 2017 Synthesis of nanoporous carbon nitride using calcium carbonate as templates with enhanced visible-light photocatalytic activity Appl. Surf. Sci. 391 384–91
[12] Suchitra S M and Udayashankar NK 2017 Synthesis and photocatalytic properties of graphitic carbon nitride nanofibers using porous anodic alumina templates Mater. Res. Express 4 124001
[13] Wang Y G, Wang F, Zuo Y H, Zhang X D and Cui L F 2014 Simple synthesis of ordered cubic mesoporous graphitic carbon nitride by chemical vapor deposition method using melamine Mater. Lett. 136 271–3
[14] Li J, Cao C and Zhu H 2007 Synthesis and in vitro anticogulation activity of hollow carbon nitride microspheres Diamond & Related Materials 16 359–63
[15] Bai X J, Cao C B, Xu X Y and Yu Q A 2010 Synthesis and characterization of crystalline carbon nitride nanowires Solid State Commun. 150 2148–53
[16] Jiao W, Qiu R, Lei J, Wang L, Zhang J and Anpo M 2017 One-step large-scale highly active g-C3N4 nanosheets for efficient sunlight-driven photocatalytic hydrogen production Dalton Trans. 46 10678–84
[17] Lu J, Wang Y, Huang J F, Cao L Y, Li Y Y, Hai G J and Bai Z 2016 One-step synthesis of g-C3N4 hierarchical porous structure nanosheets with dramatic ultraviolet light photocatalytic activity Materials Science and Engineering B-Advanced Functional Solid-State Materials 214 19–25
[18] Wang Y, Wang X and Antonietti M 2012 Polymeric graphitic carbon nitride as a heterogeneous organocatalyst: from photochemistry to multipurpose catalysis to sustainable chemistry Angew. Chem. Int. Ed. Engl. 51 68–89
[19] Zhao R, Gao J, Mei S, Wu Y, Wang X, Zhai X, Yang J, Hao C and Yan J 2017 Facile synthesis of graphitic C3N4 nanoporous-tube with high enhancement of visible light photocatalytic activity Nanotechnology 28 495710
[20] Zheng Y, Liu J, Liang J, Jaroniec M and Qiao S Z 2012 Graphitic carbon nitride materials: controllable synthesis and applications in fuel cells and photocatalysis Energy & Environmental Science 5 6717–31
[21] Zhu K X, Wang W J, Meng A, Zhao M, Wang J H, Zhao M, Zhang D L, Jia Y P, Xu C H and Li Z J 2015 Mechanically exfoliated g-C3N4 thin nanosheets by ball milling as high performance photocatalysts RSC Adv. 5 56239–43
[22] Guo Q X, Xie Y, Wang X J, Lv S C, Hou T and Liu X M 2003 Characterization of well-crystallized graphitic carbon nitride nanocrystals via a benzene-thermal route at low temperatures Chem. Phys. Lett. 380 84–7
[23] Khabashesku V N, Zimmerman J L and Margrave J L 2000 Powder synthesis and characterization of amorphous carbon nitride Chem. Mater. 12 3264–70
[24] Li Y, Zhang J, Wang Q, Jin Y, Huang D, Gai Q and Zou G 2010 Nitrogen-rich carbon nitride hollow vessels: synthesis, characterization, and their properties J. Phys. Chem. B 114 9429–34
[25] Xin G and Meng Y L 2013 Pyrolysis synthesized g-C3N4 for photocatalytic degradation of methylene blue Journal of Chemistry 2013 187912
[26] Zhang X, Xie X, Wang H, Zhang J, Pan B and Xie Y 2013 Enhanced photoresponsive ultrathin graphitic-phase C3N4 nanosheets for bioimaging J. Am. Chem. Soc. 135 18–21
[27] Zimmerman J L, Williams R, Khabashesku V N and Margrave J L 2001 Synthesis of spherical carbon nitride nanostructures Nano Lett. 1 731–4
[28] Lowther J E 1998 Defective and amorphous structure of carbon nitride Phys. Rev. B 57 5724–7
[29] Wu D W, Fu D J, Guo H X, Zhang Z H, Meng X Q and Fan X J 1997 Structure and characteristics of C3N4 thin films prepared by rf plasma-enhanced chemical vapor deposition Phys. Rev. B 56 4949–54
[30] Zhao X A, Ong C W, Tsang Y C, Wong Y W, Chan P W and Choy C L 1995 Reactive pulsed-laser deposition of cnx films Appl. Phys. Lett. 66 2652–4
[31] Guo Q, Xie Y, Wang X, Zhang S, Hou T and Lv S 2004 Synthesis of carbon nitride nanotubes with the C3N4 stoichiometry via a benzene-thermal process at low temperatures Chem Commun (Camb) 1 26–7
[32] Lee D Y, Kim Y H, Kim I K and Baik H K 1999 The effects of substrates on carbon nitride thin films prepared by direct dual ion beam deposition Thin Solid Films 355 239–45
[33] Marton D, Boyd K J, Al-Bayati A H, Todorov S S and Rabalais J W 1994 Carbon nitride deposited using energetic species: a two-phase system Phys. Rev. Lett. 73 1118–21
[34] Dai J, Xu L Q, Fang Z, Sheng D P, Guo Q F, Ren Z Y, Wang K and Qian Y T 2007 A convenient catalytic approach to synthesize straight boron nitride nanotubes using syneric nitrogen source Chem. Phys. Lett. 440 253–8
[35] Qian Q L, Wang J L, Gu Y L, Li J, Zhao G W, Zhang L P and Pan X Y 2011 Convenient synthesis of Fe-filled boron nitride nanotubes by SHS method Mater. Lett. 65 866–8
[36] Wang J L, Zhang L L, Long F, Wang W M, Gu Y L, Mo S Y, Zou Z G and Fu Z Y 2016 Solvent-free catalytic synthesis and optical properties of super-hard phase ultrafine carbon nitride nanowires with abundant surface active sites RSC Adv. 6 23272–8
[37] Zhang J, Chen X, Takanabe K, Maeda K, Domen K, Epping J D, Fu X, Antonietti M and Wang X 2010 Synthesis of a carbon nitride structure for visible-light catalysis by copolymerization Angew. Chem. Int. Ed. Engl. 49 441–4
[38] Xu Y and Gao S P 2012 Band gap of C3N4 in the GW approximation Int. J. Hydrogen Energy 37 11072–80