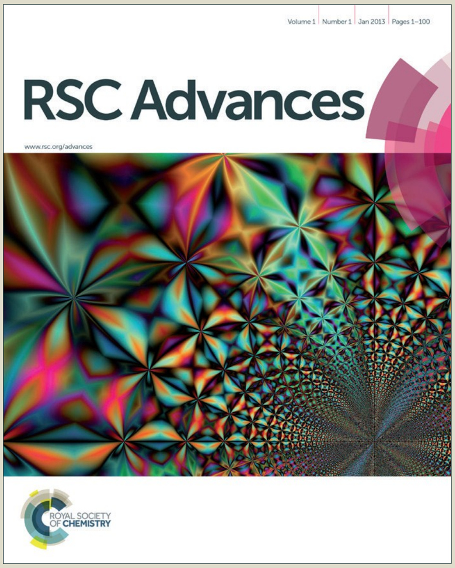
RSC Advances



ROYAL SOCIETY
OF **CHEMISTRY**

www.rsc.org/advances

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Graphitic Carbon Nitride for Photocatalytic Degradation of Sulfamethazine in Aqueous Solution under Simulated Sunlight Irradiation

Huahua Xiao, [a,*] **Junjiang Zhu** [b,c,*] **Arne Thomas** [d]

Received (in XXX, XXX) XthXXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Graphitic carbon nitride (g-CN) is active for sulfamethazine (SMT) degradation under simulated sunlight irradiation, with 70% SMT conversion within 90 min and half-life of SMT 14 times shorter than that in the absence of catalyst, and can be recycled for at least five times with no loss of activity, making it a potential material in practice for SMT removal.

Clinical and veterinary antibiotics are serious pollutant sources in the municipal and agricultural wastewater and receiving waters[1-3]. The biologically activity and ecological impact brought by antibiotics in the wastewater have attracted widespread attentions, especially the drug resistance of pathogenic bacteria caused by antibiotics which are exposed for a long time in the environment[4-6]. Sulfonamides are a class of important bacteriostatic agents commonly used in human and veterinary medicine. For example, sulfamethazine (SMT, whose structure can be found in Figure S1) is largely used for treating livestock diseases and is a predominant sulfonamide found in livestock animal wastewater[7, 8]. Currently, the removal of these antibiotics is mainly by direct photolysis under natural conditions, which however takes long time and may result in derivative lesions. Especially, with the more and more antibiotics used in our life, this becomes more crucial for our environment. It is thus an urgent and essential task to find convenient methods for fast removal of these antibiotics discharged in the wastewater.

Photocatalytic degradation is one of the promising ways for the removal of antibiotics in wastewater[9-11]. For example, TiO_2 has been frequently used as photocatalyst for the reactions[10, 11]. However, the large bandgap energy limits its practical application. In order to utilize the solar energy efficiently, the development of visible light catalysts with small bandgap energy, e.g., Bi_2MoO_6[9], was suggested. Still, these metal oxide photocatalysts suffer a lot of problems in practical applications, such as the aggregation of active metals, the difficulty of morphology control, and the possible metal leaching that causes secondary pollution[12, 13]. The use of a stable metal-free material with strong resistance to harsh environments is therefore a valuable target for the treatment of contaminant in aqueous solution.

Graphitic carbon nitride (g-CN, very often also named after its idealized sum formula "g-C_3N_4" in the literature) has recently been found to be a good visible-light-driven photocatalyst for various reactions including hydrogen evolution from water[14-18], and recently also overall water splitting[19], dye degradation[20, 21] and CO_2 reduction[22, 23]. Especially, this material is stable in acidic, neutral and basic solution[16, 24], which makes it a promising candidate for catalytic removal of pollutants in aqueous solution. In this work we show that, besides the above-mentioned applications, g-CN is also highly active for the degradation of antibiotic SMT in aqueous solution under simulated sunlight, and can be recycled for at least five times with no loss of activity, making it a great potential catalyst for practical applications.

Bulk, supported and mesoporous graphitic carbon nitride, denoted as g-CN, g-CN/SBA-15 and mpg-CN, respectively, were prepared using guanidine hydrochloride as precursor[25, 26] (See experimental in SI). Note that the preparation of mpg-CN using SBA-15 as template is hard, it was prepared with silica gel for substitution. Photocatalytic degradation of SMT was conducted on a XPA-7 photochemical reactor and simulated sunlight irradiation was provided by a 350W xenon lamp. 20 mg catalysts and 20 mL SMT aqueous solution (10 mg L^{-1}, simulating the concentration in real wastewater) were added to a quartz-tube reactor and stirred magnetically. Before irradiation, the suspension was stirred in dark for 30 min to reach an adsorption–desorption equilibrium. The reaction mixture at desired reaction time were extracted (from parallel reactors) and analyzed by a reverse-phase HPLC apparatus. Detailed experimental procedures can be found in the experimental section of SI.

Characterizations of the materials are presented in Figure S2, showing that materials with desired structure and properties were prepared, and were well in accordance to that reported in literature. In brief, X-ray diffraction patterns (Figure S2A) shows that two characteristic peaks at $2\theta = 13.1°$ and $27.3°$ are observed for the bulk and porous g-CN, but are not seen for g-CN/SBA-15 due to the low loading of g-CN. TGA profiles (Figure S2B), show that 14 % weight loss at temperature above 600 ºC is observed for g-CN/SBA-15. In contrast 97% weight loss is observed for the porous g-CN, and 100% for the bulk g-CN. N_2 physisorption isotherms (Figure S2C) indicate that the surface area of bulk g-CN is small (6.8 m^2/g). It increases to 212 m^2/g for mpg-CN and to 501 m^2/g for g-CN/SBA-15.

UV-Vis diffuse reflectance spectra (Figure S2D) show that the morphologies of the materials can influence the light harvesting ability and the absorption band edge changes. The former could be attributed to a scattering effect of porous material, as reported by Wang et al,[27] while the latter could be caused by the different condensation degrees of the material. It has been reported that the condensation degree and the physicochemical properties of g-CN can be altered when prepared under different conditions, although no obvious difference is observable in their textures, detected by XRD or IR for example[24]. By comparison, it could be inferred that g-CN/SBA-15 with the most condensed structure needs to be excited with high energy, while bulk g-CN with less condensed structure can be excited with relatively low energy.

TEM images (Figure S3) show a layer-like structure is observed for the bulk g-CN and pores with size of ca. 16 nm are observed for mpg-CN, and ordered mesopores attributable to SBA-15 are seen for g-CN/SBA-15. This fits well to results reported in literature[25, 27], and suggests that the materials with desired surface morphology and structure are prepared.

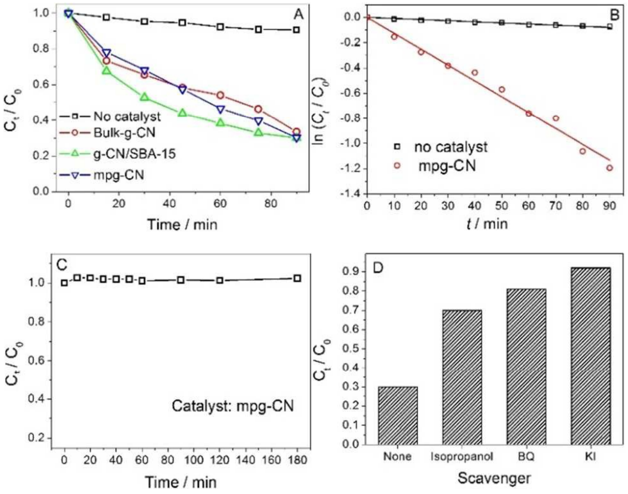


Figure 1. (A) Photocatalytic activity of the g-CN based catalysts for SMT degradation as a function of reaction time. (B) Kinetic data for photocatalytic degradation of SMT in the absence and presence of mpg-CN. (C) Amounts of SMT adsorbed on mpg-CN with the adsorption time. (D) Effect of scavengers on the photocatalytic activity of mpg-CN for SMT degradation. Reaction conditions: SMT = 10 mg L^{-1}; Photocatalyst = 1.0 g L^{-1}; pH = 6.9, t = 90 min.

Figure 1A presents the photocatalytic activities of catalysts for SMT degradation under simulated sunlight irradiation, showing that they are all active for the reaction, with 70% conversion at 90 min, which is comparable to that of metal-containing Bi_2MoO_6 catalyst conducted under similar conditions[9]. By comparison, less than 7% conversion is obtained in blank experiment (without catalyst), suggesting that the SMT degradation is conducted by g-CN catalysis. Kinetic calculation shows that the half-life of SMT is 14 times shorter when the catalyst is added to the reaction (Figure 1B, see details in Table 1), confirming the important role of photocatalyst in the reaction. Product analysis by HPLC-MS shows that 2-(N-p-Amino-phenyl)-amino-4,6-dimethylpyrimidine and 2-Amino-4,6-dimethyl-pyrimidine are the mainly remained intermediates in solution (Figure S4), whose toxicity is far lower than that of SMT[9, 28].

It is noted that the surface morphology or the surface area of catalyst has little effect on the reaction activity. Either the bulk or the supported or the mesoporous g-CN shows 70% conversion at 90 min, despite a slightly higher activity is observed for g-CN/SBA-15 within 90 min. This indicates that in this case a higher surface area and porous structure has no advantage in improving the catalytic efficiency, which is surprising and is in contrast to the reported g-CN based catalysts for hydrogen evolution, for which a higher surface area and introduction of porosity had a significant effect on photocatalytic activity[29, 30].

Table 1. Photodegradation rate constants of SMT conducted over mpg-CN (C_{SMT} = 10 mg L^{-1}, $C_{Cat.}$ = 1 g L^{-1}, t = 90 min)

Entry	H_2O_2 / mmol·L^{-1}	Kinetic equation	Half-life ($t_{1/2}$) / min	Coefficient (R^2)
1 [a]	0	$\ln C/C_0 = -0.0009t$	789.5	0.9688
2	0	$\ln C/C_0 = -0.0126t$	55.0	0.9833
3	0.03	$\ln C/C_0 = -0.0232t$	29.9	0.9801
4	0.06	$\ln C/C_0 = -0.0259t$	26.8	0.9849
5	0.15	$\ln C/C_0 = -0.0416t$	16.7	0.9941
6	0.30	$\ln C/C_0 = -0.0297t$	23.3	0.9877
7	0.60	$\ln C/C_0 = -0.0235t$	29.5	0.9845

[a] No catalyst is added to the reaction

In order to explain this observation, we measured the ability of mpg-CN for SMT adsorption. Before the photocatalytic tests, the catalyst were stirred in SMT solution in the dark and the concentration of SMT before and after the adsorption process was monitored. Figure 1C shows that the concentration of SMT was unchanged even after 180 min, indicating that mpg-CN has negligible ability to SMT adsorption. The same is also observed for g-CN/SBA-15 (not shown here). This could be that both g-CN and SMT have electron-donating groups (e.g., amino and/or methyl groups), therefore SMT will be repelled, instead of be adsorbed, by g-CN. That is, the additional provided surface area actually is ineffective for the reaction, explaining why similar activity is observed for g-CN materials with varied surface areas.

For photocatalytic degradation of organics in aqueous solution, there are three major reactive species participating in the reaction, namely hydroxyl radicals (•OH)[20], holes in the valence band of the photocatalyst (h^+)[31] and superoxide anions (•O_2^-)[21]. To identify their roles in the reaction and study the reaction mechanism, we performed controlled experiments by adding specified scavengers to the reaction, including isopropanol, potassium iodide (KI) and benzoquinone (BQ), which are used to quench •OH, h^+ and •O_2^- species, respectively[32, 33]. Figure 1D shows that all the scavengers can affect the reaction, with a sequence of KI > BQ > isopropanol (see details in Figure S5). This indicate that the described reactive species are all involved in the reaction, and h^+ has the highest and •OH has the lowest contribution to the reaction, with a difference of about three times. As the •OH radical is a strong oxidant which should also exhibit high reactivity to the reaction, it can be doubted that the •OH radical is produced to a large extent in the reaction. Indeed, we found that the contribution of the •OH radical to the reaction is almost zero if we assume that the activity is 100% contributed from the above three species (the calculation process can be found in the experimental section of the SI). In other words, the •OH radical is not produced in the reaction and the SMT is oxidized mainly by the directly produced h^+ and •O_2^- species. Indeed, in a supplementary experiment we found that no activity is observable if KI and BQ were added together, see Figure S6.

To prove the above conclusion that •OH radical is not produced in the reaction, a reference experiment was carried out by adding H_2O_2 to the reaction, which is usually used as a source of producing •OH radicals in photodegradation reactions[34]. Table 1 lists the effect of H_2O_2 concentration on the kinetics of SMT photodegradation, showing that H_2O_2 addition can accelerate the reaction, with the optimum H_2O_2 concentration of 0.15 mmol·L^{-1} and half-life of 16.7 min. Further increase of H_2O_2 concentration leads to decreased reaction rate, which can be explained as H_2O_2 itself has the ability to capture •OH radicals and form less active HO_2• radical[17, 35]. This proves that the •OH radical, if produced, would contribute strongly to the reaction. Hence, the zero contribution calculated above should be that the •OH radical is not produced in the reaction.

Consequently, the decrease in activity by addition of isopropanol could be better explained by the quenching of other reactive species produced in the reaction, even though it is currently not clear which species it exactly is.

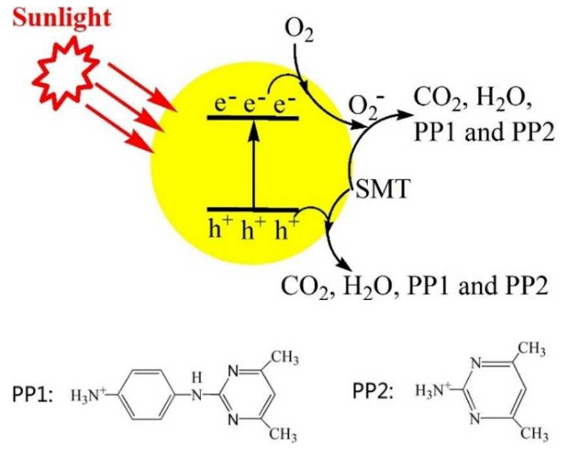


Figure 2. A proposed mechanism for photodegradation of SMT on g-CN conducted in aqueous solution under simulated sunlight irradiation.

On the above basis, a mechanism for SMT photodegradation in aqueous solution over g-CN is proposed, Figure 2. At the beginning, electrons (e^-) at the VB are excited to the CB under simulated sunlight irradiation, accompanying the generation of holes (h^+). The photo-induced electrons will then react and reduce the dissolved oxygen (O_2) on the surface of g-CN to superoxide radical $\bullet O_2^-$, which is a strong oxidizing agent and would oxidize the SMT into CO_2, H_2O and other intermediates (see Figure S4). This happens also for the photo-induced holes (h^+).

In principle for g-CNs with higher surface area (e.g. mpg-CN vs. bulk g-CN) also an increased amount of photo-generated holes and superoxide anions would be expected. However, as SMT is not adsorbing the catalyst's surface, the higher amount of h^+ produced within the porous materials has no beneficial effect on the SMT degradation rate but will be consumed by other pathways. On the other hand, a higher amount of superoxide anions generated by irradiation of porous CNs should result in faster degradation rates, without the adsorption of SMT to the catalyst's surface is necessary in the first step. As it is observed that all three g-CN materials show nearly identical degradation activity it can be thus reasoned that all catalysts are producing already sufficient amount of superoxide anions to reach the maximum degradation rate of SMT in excess of these species. Indeed it has been reported that bulk g-CNs can produce large amounts of superoxide anions in the presence of oxygen[19, 30, 35].

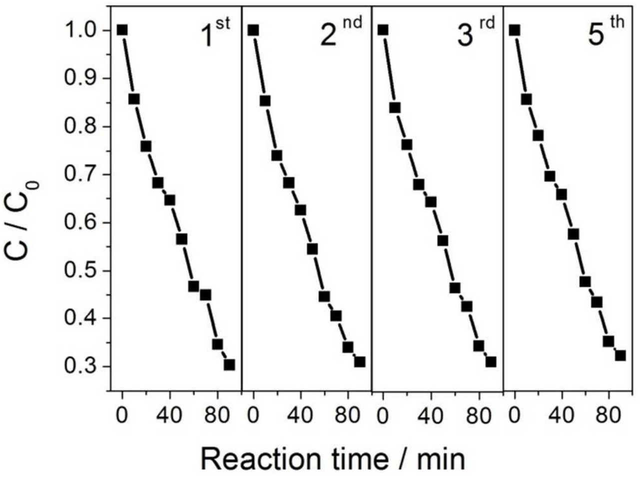


Figure 3. The reusability of mpg-CN for photocatalytic degradation of SMT in aqueous solution. Reaction conditions: SMT = 10 mg L^{-1}; Photocatalyst = 1.0 g L^{-1}; pH = 6.9.

At the end, the reusability of catalyst for the reaction was tested, to see if the catalyst has sufficient potential for industrial application. In each cycle, the reaction solution was centrifuged and the supernatant was poured out, and fresh SMT solution was refilled to the reactor to restart the reaction. No additional treatment on the used catalyst was applied. Figure 3 shows that the catalyst is highly stable for the reaction, and no appreciable loss in the activity is observed even after five cycles, demonstrating that the catalyst is highly reusable for the reaction, and could be a potential candidate for industrial removal of sulfonamides antibiotics in aqueous solution.

In summary, we show that metal-free g-CN is active for photocatalytic degradation of SMT in aqueous solution, leading to a shortened half-life of about 14 times compared to that in the absence of catalyst. Especially the catalyst can be reused directly without appreciable loss in the activity, which makes the material a promising candidate for the removal of SMT in aqueous solution in practical use. Further works on modifying the textural structure and improving the photocatalytic performances of g-CN for the degradation of various antibiotics in aqueous solution will be conducted, to pave the way of its industrialization for wastewater treatment.

Financial support from the National Science Foundation of China (No. 21203254), the Natural Science Foundation of Hubei Province of China (2015CFA138), and the Cluster of Excellence "Unifying Concepts in Catalysis" (EXL 31411), is gratefully acknowledged.

Notes and references

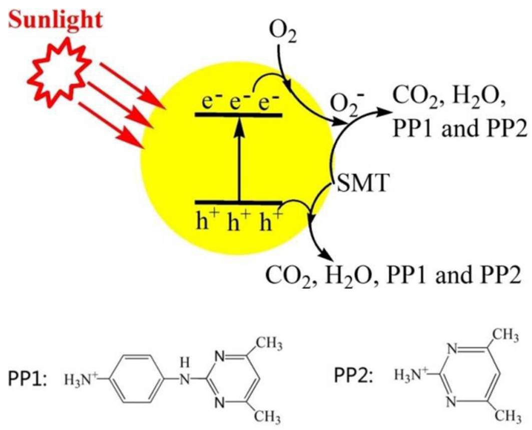
[a] *Faculty of Environmental Science and Engineering, Guangdong University of Technology, Guangzhou 510006, China;* [b] *Institute of Catalysis for Energy and Environment, Shenyang Normal University, Shenyang 110034, China;* [c] *Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs & Commission Ministry of Education, South-Central University for Nationalities, Wuhan 430074, China;* [d] *Department of Chemistry, Technische Universität Berlin, Hardenbergstr. 40, 10623 Berlin, Germany; E-mail: xhh201@163.com, ciaczjj@163.com.*

† Electronic Supplementary Information (ESI) available: Experimental details, Chemical structure of SMT, Characterizations of g-CN, mpg-CN

and g-CN/SBA-15, Product analysis from HPLC-MS, and the detailed effect of scavenger on the activity. See DOI: 10.1039/b000000x/

1 M. J. García-Galán, T. Garrido, J. Fraile, A. Ginebreda, M. S. Díaz-Cruz and D. Barceló, *J. Hydrol.*, 2010, **383**, 93-101.
2 L. Jiang, X. Hu, D. Yin, H. Zhang and Z. Yu, *Chemosphere*, 2011, **82**, 822-828.
3 X. Li, W. Zheng and W. R. Kelly, *Sci. Total Environ.*, 2013, **445-446**, 22-28.
4 W. Baran, E. Adamek, J. Ziemianska and A. Sobczak, *J. Hazard. Mater.*, 2011, 196, 1-15.
5 M. Dalla Bona, V. Di Leva and M. De Liguoro, *Chemosphere*, 2014, 115, 67-74.
6 M. De Liguoro, B. Fioretto, C. Poltronieri and G. Gallina, *Chemosphere*, 2009, 75, 1519-1524.
7 X. Peng, K. Zhang, C. Tang, Q. Huang, Y. Yu and J. Cui, *J. Environ. Monit.*, 2011, **13**, 446-454.
8 Z. Xu, C. Song, Y. Hu and G. Li, *Talanta*, 2011, **85**, 97-103.
9 C. Guo, J. Xu, S. Wang, Y. Zhang, Y. He and X. Li, *Catal. Sci. Technol.*, 2013, **3**, 1603-1611.
10 S. Kaniou, K. Pitarakis, I. Barlagianni and I. Poulios, *Chemosphere*, 2005, **60**, 372-380.
11 P.S. Yap, Y.L. Cheah, M. Srinivasan and T.T. Lim, *Appl. Catal. A: Gen.*, 2012, **427-428**, 125-136.
12 X. Ding, W. Ho, J. Shang and L. Zhang, *Appl. Catal. B: Environ.*, 2016, **182**, 316-325.
13 K. Dai, D. Li, L. Geng, C. Liang and Q. Liu, *Mater Lett*, 2015, **160**, 124-127.
14 S. Chen, C. Wang, B. R. Bunes, Y. Li, C. Wang and L. Zang, *Appl. Catal. A: Gen.*, 2015, **498**, 63-68.
15 Y. Zhong, Z. Wang, J. Feng, S. Yan, H. Zhang, Z. Li and Z. Zou, *Appl. Sur. Sci.*, 2014, **295**, 253-259.
16 X. C. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen and M. Antonietti, *Nat. Mater.*, 2009, **8**, 76-80.
17 K. Kailasam, A. Fischer, G. Zhang, J. Zhang, M. Schwarze, M. Schröder, X. Wang, R. Schomäcker and A. Thomas, *ChemSusChem*, 2015, **8**, 1404-1410.
18 Y.S. Jun, J. Park, S. U. Lee, A. Thomas, W. H. Hong and G. D. Stucky, *Angew. Chem. Int. Ed.*, 2013, **52**, 11083-11087.
19 J. Liu, Y. Liu, N. Liu, Y. Han, X. Zhang, H. Huang, Y. Lifshitz, S.T. Lee, J. Zhong, Z.H. Kang, *Science*, 2015, **347**, 970-974
20 F.T. Li, Y. Zhao, Q. Wang, X.J. Wang, Y.J. Hao, R.H. Liu and D. Zhao, *J. Hazard. Mater.*, 2015, **283**, 371-381.
21 T. Xian, H. Yang, L. J. Di and J. F. Dai, *J. Alloy. Compd.*, 2015, **622**, 1098-1104.
22 Y. He, Y. Wang, L. Zhang, B. Teng and M. Fan, *Appl. Catal. B: Environ.*, 2015, **168-169**, 1-8.
23 Y. He, L. Zhang, M. Fan, X. Wang, M. L. Walbridge, Q. Nong, Y. Wu and L. Zhao, *Sol. Energ. Mat. Sol. C.*, 2015, **137**, 175-184.
24 J. Zhu, P. Xiao, H. Li and S. Carabineiro, *ACS. Appl. Mater. Interfaces*, 2014, **6**, 16449-16465.
25 P. Xiao, Y. X. zhao, T. Wang, Y. Y. Zhan, H. H. Wang, J. L. Li, A. Thomas and J. J. Zhu, *Chem. Eur. J.*, 2014, **20**, 2872-2878.
26 Q. Yang, W. Wang, Y. Zhao, Y. Zhu, J. Zhu and L. Wang, *RSC Adv.*, 2015, **5**, 54978-54984.
27 X. C. Wang, K. Maeda, X. F. Chen, K. Takanabe, K. Domen, Y. D. Hou, X. Z. Fu and M. Antonietti, *J. Am. Chem. Soc.*, 2009, **131**, 1680-1681.
28 M. Perisa, S. Babic, I. Skoric, T. Fromel and T. P. Knepper, *Environ. Sci. Pollut. Res. Int.*, 2013, **20**, 8934-8946.
29 K. Kailasam, J. D. Epping, A. Thomas, S. Losse and H. Junge, *Energ. Environ. Sci.*, 2011, **4**, 4668-4674.
30 P. Zhang, H. Li and Y. Wang, *Chem. Commun.*, 2014, **50**, 6312-6315.
31 C. Chang, Y. Fu, M. Hu, C. Wang, G. Shan and L. Zhu, *Appl. Catal. B: Environ.*, 2013, **142-143**, 553-560.
32 G. V. Buxton, C. L. Greenstock, W. P. Helman and A. B. Ross, *J Phys Chem Ref Data*, 1988, **17**, 513-886.
33 J. Ng, X. Wang and D. D. Sun, *Appl. Catal. B: Environ.*, 2011, **110**, 260-272.
34 Y. Cui, Z. Ding, P. Liu, M. Antonietti, X. Fu and X. Wang, *Phys. Chem. Chem. Phys.*, 2012, **14**, 1455-1462.
35 F. Su, S. C. Mathew, L. Möhlmann, M. Antonietti, X. Wang and S. Blechert, *Angew. Chem. Int. Ed.*, 2011, **50**, 657-660.

Graphical Abstract



Graphitic carbon nitride (g-CN), with either bulk, supported or porous structure, is active for photo-degradation of sulfamethazine (SMT) under simulated sunlight irradiation, with 70% SMT conversion within 90 min and half-life of SMT 14 times shorter than that in the absence of catalyst, and can be recycled for at least five times with no loss of activity, making it a potential material in practice for SMT removal.