Angewandte Chemie International Edition

DOI: 10.1002/anie.201106656

Photocatalysis

Co-Monomer Control of Carbon Nitride Semiconductors to Optimize Hydrogen Evolution with Visible Light**

*Jinshui Zhang, Guigang Zhang, Xiufang Chen, Sen Lin, Lennart Möhlmann, Grzegorz Dołęga, Grzegorz Lipner, Markus Antonietti, Siegfried Blechert, and Xinchen Wang**

The development of stable systems to generate chemical fuels through water splitting by sunlight is a key challenge of modern materials chemistry, one that is driven by increasing energy demands and climate change. The central problems are to design chemically stable light-harvesting antenna molecules and co-factors, and then to assemble these active components into an integrated photosystem. Various substances have been examined as visible-light converters, including metal–organic dyes,[1] inorganic semiconductors,[2] and conjugated polymers.[3] The last are of particular interest, as they are much closer to biological systems in composition and are potentially sustainable, as well as cheap and easily processable. Principally, properties such as the HOMO and LUMO position and the resulting band gap can be precisely chemically engineered by synthesizing the constituents. To date, in spite of the wide availability of conducting polymers developed for photovoltaics,[4] the impact of these polymers on water splitting technology remains minor, because ordinary conducting polymers are usually unstable to visible light irradiation in conjunction with exposure to oxygen and water.

A recent study has explored metal-free, polymeric graphitic carbon nitride (g-C_3N_4) for the generation of hydrogen from a protic solution with visible light.[5] This carbon nitride (CN) polymer was not only found to be a stable semiconductor, but also to be capable of achieving both half reactions of water splitting, meaning that the band-gap covers both the water reduction and water oxidation potentials. This is indeed a rare and lucky case. However, the activity of pristine g-C_3N_4 remains moderate.[5]

Several strategies, such as nanostructuring,[6] doping,[7] cocatalyzing,[5,8] and copolymerization,[9] have been exploited to improve the photocatalytic activity and selectivity of carbon nitride. Indeed, it was shown that by copolymerizing simple barbituric acid with the carbon nitride precursor through a Schiff base reaction, the performance of g-C_3N_4 could be enhanced, which is an effect resulting from extension of the optical absorption of the polymer to cover more of the visible light range.[9] However, in this case the HOMO was decreased in energy, thus lowering the oxidation potential, which is presumably the most difficult step in achieving overall water splitting with organic semiconductors. This is why the design of appropriate comonomers with diverse chemical composition and structure to allow for modification of the band structure and optoelectronic properties of carbon nitride is still a relevant and promising task.

Herein, we advance this strategy by employing a variety of new monomer building blocks with the desired compositions and electronic structures for chemical incorporation into the conjugated polymeric network of g-C_3N_4. Most precursors of carbon nitride polymers contain cyano groups, amino groups, or both, with the simplest case being cyanamide, which can undergo multiple thermal condensations to form stable aromatic carbon nitrides based on tri-*s*-triazine subunits.[10] Therefore, we synthesized organic molecules bearing amino and/or cyano functionalities to integrate them directly into the carbon nitride polymers (Scheme 1). This design may allow ample choice of organic anchoring groups, being a potentially valuable way to alter the physical and chemical properties of the resulting heterogeneous organocatalysts.

As the photocatalytic properties of bulk g-C_3N_4 originate from its π-conjugated system as a result of the sp^2 hybridization of C and N, it is desirable to extend the delocalization of the π electrons and to change the intrinsic semiconductor properties by grafting aromatic groups on the surface of g-C_3N_4. 2-Aminobenzonitrile (ABN) **1** was selected as a precursor because it reacts with dicyandiamide (DCDA) to give 2,4-diaminoquiazoline **2**.[11] A plausible mechanism is nucleophilic attack of the amino group on the carbon center of DCDA, to form intermediate **i**. The active cyanamide species is thereby formed by reversing the condensation of DCDA.[12] A second nucleophilic attack would then lead to the cyclized compound **2** (Scheme 1). 2,4-Diaminoquiazoline **2** has a similar structure to melamine, which is known to undergo reaction to form melem in the presence of additional DCDA at elevated temperatures.[13] Experimentally, a series of ABN-functionalized g-C_3N_4 polymers was synthesized by changing the amount of ABN added to DCDA for copolymerization. The samples thus obtained were denoted CN-ABN_X (X is the amount of ABN weighed in) and were subjected to various physical analytical techniques and

---

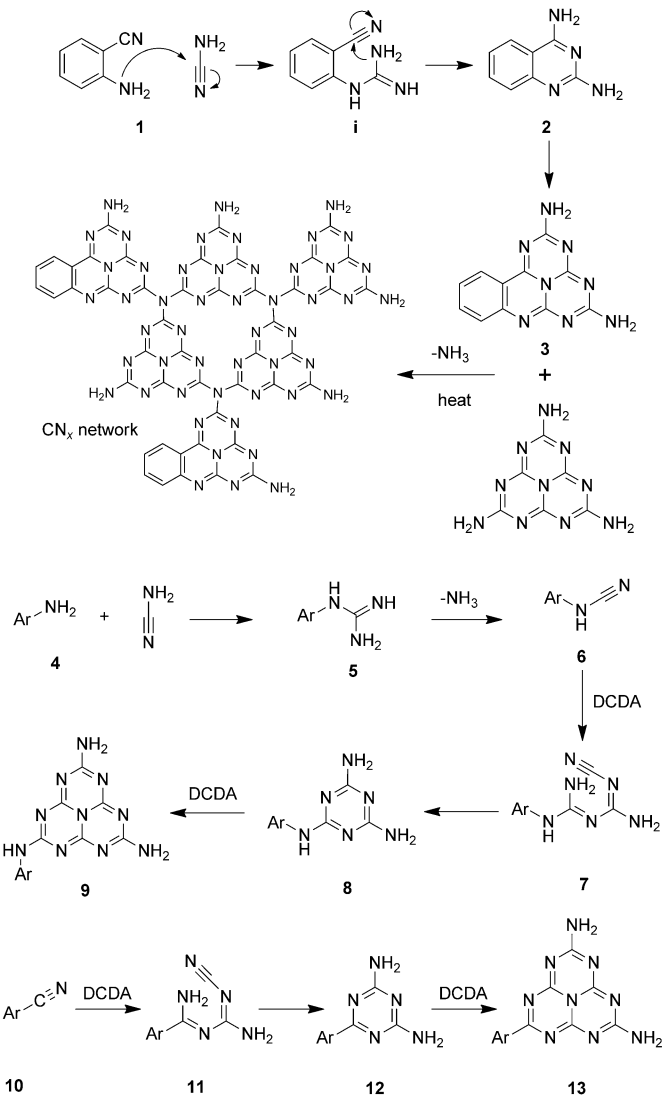
[*] J. Zhang, G. Zhang, X. Chen, Dr. S. Lin, Prof. X. Wang
Research Institute of Photocatalysis, State Key Laboratory
Breeding Base of Photocatalysis, Fuzhou University
Fuzhou 350002 (China)
E-mail: xcwang@fzu.edu.cn

Prof. M. Antonietti
Department of Colloid Chemistry
Max-Planck Institute of Colloids and Interfaces
Research Campus Golm, 14476 Potsdam (Germany)

L. Möhlmann, Dr. G. Dołęga, Dr. G. Lipner, Prof. S. Blechert
Institute of Chemistry, Technical University Berlin
Strasse des 17. Juni 135, 10623 Berlin (Germany)

[**] Supported by the National Natural Science Foundation of China (21033003 and 21173043), PCSIRT (0818), and the Light2Hydrogen Project.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201106656.



Scheme 1. The copolymerization of dicyandiamide/cyanamide with 2-aminobenzonitrile, aniline, and benzonitrile. The linkers (3,9,13) can be integrated into the classic condensation process of g-C_3N_4.

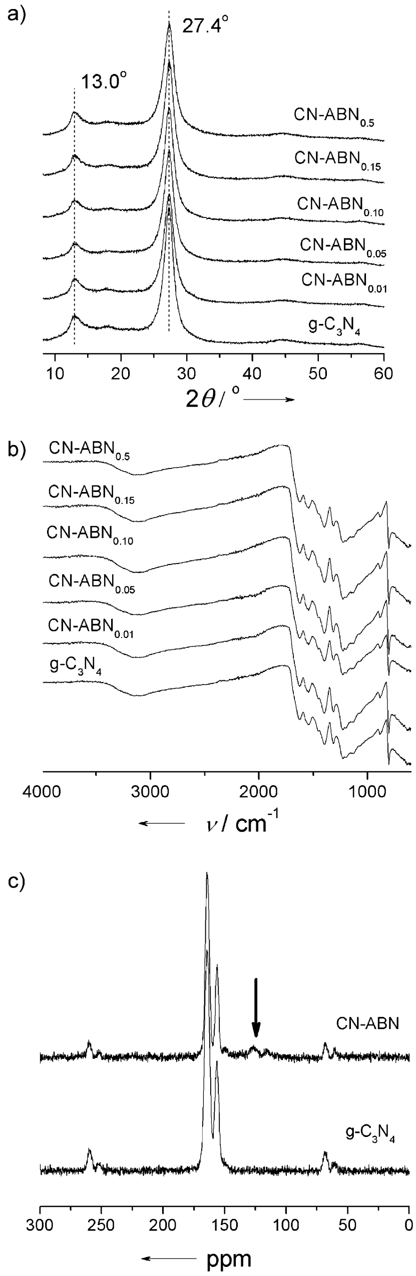


Figure 1. Analysis of CN-ABN, with g-C_3N_4 as reference. a) XRD patterns; b) FTIR spectra; c) solid-state ^{13}C NMR spectra.

performance characterization for hydrogen evolution from a protic solution under visible-light irradiation.

X-ray diffraction (XRD; Figure 1a) patterns of CN-ABN_X and g-C_3N_4 show that the structures are highly related; they are characterized by a dominant peak at 27.4° related to the (002) interlayer reflection of a graphitic structure, with a small reflection peak at about 13° attributable to the in-plane repeat units of heptazine.[5a] The FTIR spectra of CN-ABN_X (Figure 1b) shows all the feature-distinctive stretch modes of aromatic CN heterocycles at 1200 to 1600 cm^{-1} together with the breathing mode of the triazine units at 810 cm^{-1}, which is once again very similar to that of g-C_3N_4. It is clear that modification with ABN does not alter the bulk structure or the core chemical skeleton of g-C_3N_4 too much, provided that the amount of ABN added is below 10%. Chemical analysis, however, revealed an increase in the C/N molar ratio from 0.73 for g-C_3N_4 to 0.78 for CN-$ABN_{0.5}$, indicating the incorporation of the aromatic carbon species into the carbon nitride structure. This additional carbon is further confirmed by the solid-state ^{13}C NMR spectra (Figure 1c). New peaks assigned to the incorporated aromatic carbon in the carbon nitride networks are clearly found at approximately 115 ppm and 126 ppm. Interestingly, the increased carbon amount also alters the electron paramagnetic resonance (EPR) spectra of the materials in the dark; the EPR signal gradually increases as the amount of organic monomer added increases (Figure 2). All samples exhibit one single Lorentzian line with a g value of 2.0034 attributed to an unpaired electron on the carbon atoms of the aromatic rings within π-bonded nanosized clusters.[14] An enhanced EPR signal was observed when g-C_3N_4 and CN-$ABN_{0.1}$ were

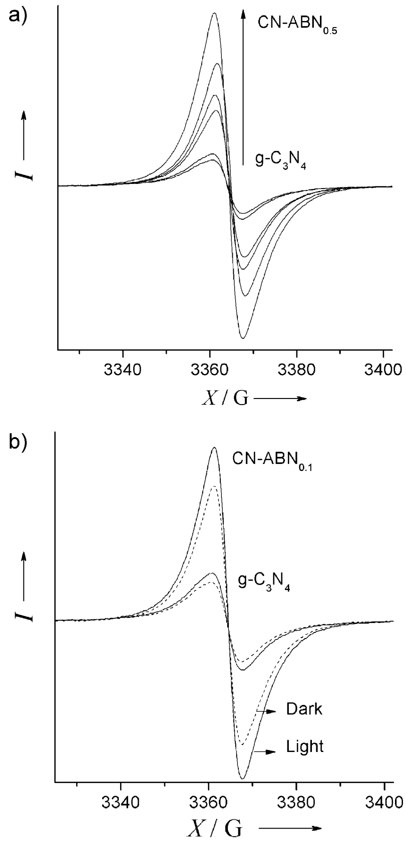


Figure 2. EPR spectra of g-C_3N_4 and CN-ABN_X samples. a) In the dark; b) under visible light ($\lambda > 420$ nm).

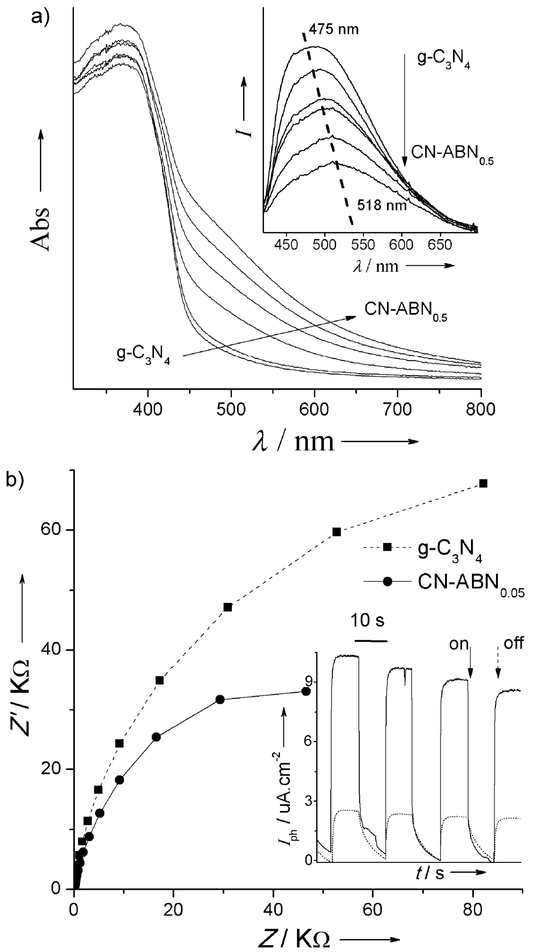


Figure 3. (Photo)electrochemical properties of CN-ABN_X vs. g-C_3N_4. a) Optical absorption of CN-ABN_X and g-C_3N_4 samples; inset shows the photoluminescence spectrum of CN-ABN_X and g-C_3N_4 samples under 400 nm excitation; b) EIS Nyquist plots for CN-$ABN_{0.05}$ and g-C_3N_4; inset shows the periodic on/off photocurrent response of CN-$ABN_{0.05}$ and g-C_3N_4 modified fluorine-doped tin oxide glass (FTO) at 0.4 V bias vs. Ag/AgCl in a 0.2 M Na_2SO_4 solution containing 10 vol.% triethanolamine.

irradiated with visible light, indicating efficient photochemical generation of radical pairs in the semiconductor.

The incorporation of phenylene groups into g-C_3N_4 modifies the π-electron delocalization in the conjugated system, and thus changes the intrinsic optical/electronic properties of the resulting CN-ABN polymers. With increasing ABN content, a remarkable red shift of the optical absorption from about 460 nm (for g-C_3N_4) to about 700 nm (for CN-$ABN_{0.5}$) was observed. Also, the photoluminescence peak of the samples gradually shifts towards longer wavelength with increasing ABN content. This is a strong indication of π-conjugation extension, which lowers the band gap; this is also supported by the results of theoretical calculations (see the Supporting Information).

We also examined the (photo)electrochemical properties of CN-ABN polymers by electrochemical impedance spectroscopy (EIS). Nyquist plots of CN-$ABN_{0.05}$ in the dark gave significantly decreased semicircles compared to g-C_3N_4. This suggests a significantly improved electronic conductivity in the non-photoexcited state. This result is supplemented by photocurrent (I_{ph}) measurements that show an enhancement in the I_{ph} of CN-$ABN_{0.05}$ over g-C_3N_4 by a factor of five. The incorporation of all-carbon aromatics obviously facilitates charge transfer and separation (Figure 3b).

The activity of the g-C_3N_4 reference in terms of hydrogen evolution rate (HER) was 18 $\mu mol\,h^{-1}$ under visible light irradiation of greater than 420 nm (as controlled by a cut-off filter; see the Experimental Section for reaction details), which is well below those of CN-ABN_x samples (HER = 120, 147, 140, 81 $\mu mol\,h^{-1}$ for $x = 0.01, 0.05, 0.1, 0.15$, respectively). Interestingly, CN-$ABN_{0.5}$ showed a HER of only 43 μmol/h, indicating that, a low degree of copolymerization is optimum to keep the favorable catalytic properties of the carbon nitride scaffold.

Figure 4a shows the wavelength dependence of the HER for g-C_3N_4 and CN-$ABN_{0.05}$. This data not only convincingly shows that g-C_3N_4 and CN-$ABN_{0.05}$ are active agents for photocatalytic hydrogen generation, but it also shows a stable improvement in the HER of CN-$ABN_{0.05}$ over the whole range of optical activity. The active wavelength of CN-$ABN_{0.05}$ is actually extended to wavelengths as long as 600 nm. The stability of CN-$ABN_{0.05}$ was examined by performing experiments on the photocatalyst under similar conditions after recycling (Figure 4b). A slight deactivation with time is observable in all run curves, a fact which we attribute to the protonation of more active sites. However, after recycling, the curves again start with a higher primary

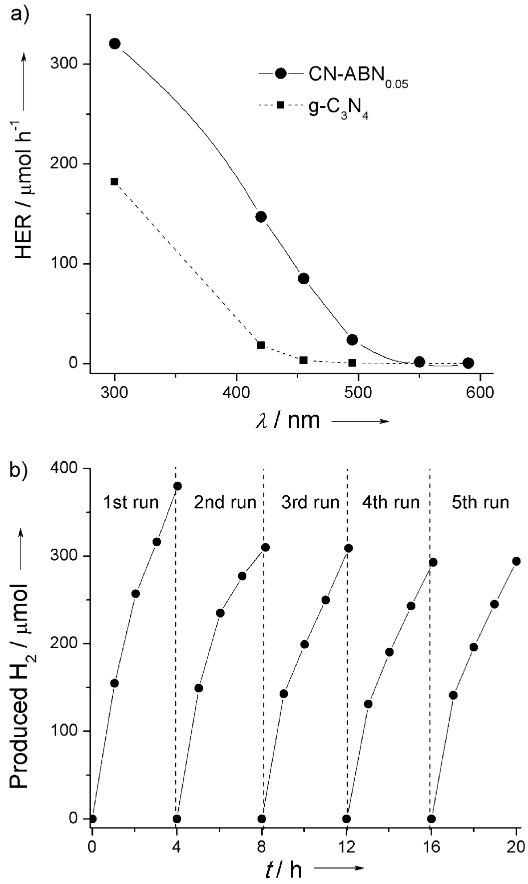
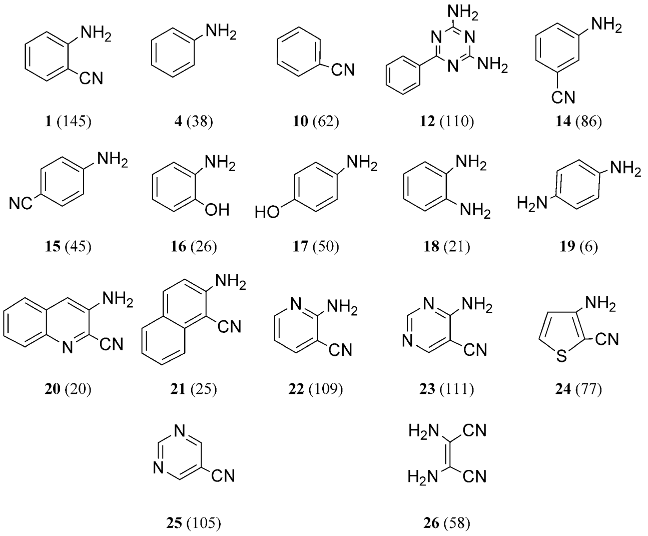


Figure 4. Stability and activity analysis of CN-ABN$_X$ vs. g-C_3N_4. a) Wavelength dependence of the HERs of g-C_3N_4 and CN-ABN$_{0.05}$ loaded with 3 wt% Pt; b) stability test of Pt/CN-ABN$_{0.05}$ photocatalyst with prolonged visible light irradiation ($\lambda > 420$ nm) for 20 h.



Scheme 2. Monomers adopted for the functionalization of g-C_3N_4. The numbers in parentheses are the HERs (µmol h^{-1}) of g-C_3N_4 modified with the corresponding monomer. The HER of g-C_3N_4 is 18 µmol h^{-1}.

activity, in which the overall hydrogen produced per repeat only depends on the onset of the slight deactivation bend. The decrease in activity after the first run is due to the loosened interface connection between cocatalysts and photocatalysts, resulting in a less efficient electron transfer. Recovery of the photocatalytic activity can be achieved by sintering the samples to strengthen the interface contact. The total H_2 production in this experiment reached 1.6 mmol, corresponding to an overall turnover frequency (TOF) of 52 h^{-1} per added Pt atom. Note that the active H_2 generating cocatalyst is presumably a Pt nanoparticle, which would then have a much higher TOF.

To generalize this concept, we examined other amino cyano compounds (**20**–**24**; Scheme 2) to prepare a variety of functional g-C_3N_4 polymers modified with different aromatic or heteroaromatic units. Aromatic compounds were also used that either have only amino/cyano groups (**4**, **10**, **12**, **18**, **19**, **25**; Scheme 2) or have the amino and cyano groups *meta* or *para* to one another, instead of *ortho* (**14**, **15**; Scheme 2). These compounds are able to react with DCDA by nucleophilic addition and can thereby be potentially integrated into the C_3N_4 structure.[15] All functionalized samples (except for monomer **19**) show an enhanced HER over pure g-C_3N_4 to varying extents, but ABN was found to be the most efficient co-monomer. However, direct comparison of the HERs of different monomers is less straightforward, as other structural parameters besides molecular connectivity also change, such as the specific surface area and intermolecular packing. For example, the anchoring monomers decrease the connectivity within the polymerization of melem and generate defects that can increase the surface area and create mesopores in the carbon nitride network, which can play a role as active sites for photocatalysis. More detailed investigations are required for real quantitative statements.

A more important feature of the functionalization by copolymerization with organic compounds bearing amino cyano moieties is the ability to graft other functional groups on the carbon nitride surface (for example, non-aromatic monomers, such as diaminomaleodinitrile **26**). In principle, this would also enable electronic coupling to sensitizers or system modification by strongly interacting dyadic heterostructures. Such an effort could be guided by theoretical calculations, which aid in understanding and scaling the manipulation of carbon nitride substructures. This bottom–up fabrication can be combined with template synthesis using silica nanoparticles to fabricate nanostructured carbon nitride photocatalysts, as demonstrated by mesoporous CN-ABN (MCN-ABN; see the Supporting Information). In principle, the modified carbon nitrides can also be employed in other applications of catalysis and photocatalysis, such as selective oxidative amine coupling[16] or alcohol oxidation[17].

Received: September 19, 2011
Revised: December 19, 2011

Keywords: carbon nitrides · copolymerization · photocatalysis · polymer semiconductors · water splitting

[1] For example, see: a) Q. Wang, S. M. Zakeeruddin, M. K. Nazeeruddin, R. Humphry-Baker, M. Grätzel, *J. Am. Chem. Soc.* **2006**, *128*, 4446; b) A. F. Heyduk, D. G. Nocera, *Science* **2001**, *293*, 1639.

[2] For example, see: a) F. F. Osterloh, *Chem. Mater.* **2008**, *20*, 35; b) K. Maeda, K. Domen, *Chem. Mater.* **2010**, *22*, 612; c) X. B. Chen, S. H. Shen, L. J. Guo, S. S. Mao, *Chem. Rev.* **2010**, *110*, 6503; d) A. Kudo, Y. Miseki, *Chem. Soc. Rev.* **2009**, *38*, 253.

[3] For example, see: a) M. G. Schwab, M. Hamburger, X. L. Feng, J. Shu, H. W. Spiess, X. C. Wang, M. Antonietti, K. Müllen, *Chem. Commun.* **2010**, *46*, 8932; b) T. Shibata, A. Kabumoto, T. Shiragami, O. Ishitani, C. Pac, S. Yanagida, *J. Phys. Chem.* **1990**, *94*, 2068; c) D. L. Jiang, C. Choi, K. Honda, W. S. Li, T. Yuzawa, T. Aida, *J. Am. Chem. Soc.* **2004**, *126*, 12084.

[4] For example, see: a) C. J. Brabec, S. Gowrisanker, J. J. M. Halls, D. Laird, S. J. Jia, S. P. Williams, *Adv. Mater.* **2010**, *22*, 3839; b) C. Li, M. Y. Liu, N. G. Pschirer, M. Baumgarten, K. Mullen, *Chem. Rev.* **2010**, *110*, 6817; c) X. W. Zhan, D. B. Zhu, *Polym. Chem.* **2010**, *1*, 409.

[5] a) X. C. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.* **2009**, *8*, 76; b) K. Maeda, X. C. Wang, Y. Nishihara, D. L. Lu, M. Antonietti, K. Domen, *J. Phys. Chem. C* **2009**, *113*, 4940; c) J. S. Zhang, J. H. Sun, K. Maeda, K. Domen, P. Liu, M. Antonietti, X. Z. Fu, X. C. Wang, *Energy Environ. Sci.* **2011**, *4*, 675.

[6] a) X. C. Wang, K. Maeda, X. F. Chen, K. Takanabe, K. Domen, Y. D. Hou, X. Z. Fu, M. Antonietti, *J. Am. Chem. Soc.* **2009**, *131*, 1680; b) X. F. Chen, Y. S. Jun, K. Takanabe, K. Maeda, K. Domen, X. Z. Fu, M. Antonietti, X. C. Wang, *Chem. Mater.* **2009**, *21*, 4093.

[7] a) X. C. Wang, X. F. Chen, A. Thomas, X. Z. Fu, M. Antonietti, *Adv. Mater.* **2009**, *21*, 1609; b) X. F. Chen, J. S. Zhang, X. Z. Fu, M. Antonietti, X. C. Wang, *J. Am. Chem. Soc.* **2009**, *131*, 11658; c) Z. X. Ding, X. F. Chen, M. Antonietti, X. C. Wang, *ChemSusChem* **2011**, *4*, 274.

[8] Y. Di, X. C. Wang, A. Thomas, M. Antonietti, *ChemCatChem* **2010**, *2*, 834.

[9] J. S. Zhang, X. F. Chen, K. Takanabe, K. Maeda, K. Domen, J. D. Epping, X. Z. Fu, M. Antonietti, X. C. Wang, *Angew. Chem.* **2010**, *122*, 451; *Angew. Chem. Int. Ed.* **2010**, *49*, 441.

[10] a) A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J. O. Müller, R. Schlögl, J. M. Carlsson, *J. Mater. Chem.* **2008**, *18*, 4893; b) E. Kroke, M. Schwarz, E. Horath-Bordon, P. Kroll, B. Noll, A. D. Norman, *New J. Chem.* **2002**, *26*, 508.

[11] W. Zerweck, W. Kunze, DE-B 737931, **1943**.

[12] A. Kawasaki, Y. Ogata, *Tetrahedron* **1966**, *22*, 1267.

[13] a) H. May, *J. Appl. Chem.* **1959**, 340; b) B. Jürgens, E. Irran, J. Senker, P. Kroll, H. Müller, W. Schnick, *J. Am. Chem. Soc.* **2003**, *125*, 10288.

[14] M. Tabbal, T. Christidis, S. Isber, P. Merel, M. A. E. Khakani, M. Chaker, A. Amassian, L. Martinu, *J. Appl. Phys.* **2005**, *98*, 044310.

[15] a) Y. Q. Peng, G. H. Song, *Tetrahedron Lett.* **2004**, *45*, 5313; b) R. Horwitz, *J. Am. Chem. Soc.* **1958**, *80*, 431.

[16] F. Z. Su, S. C. Mathew, L. Mohlmann, M. Antonietti, X. C. Wang, S. Blechert, *Angew. Chem.* **2011**, *123*, 683; *Angew. Chem. Int. Ed.* **2011**, *50*, 657.

[17] F. Z. Su, S. C. Mathew, G. Lipner, X. Z. Fu, M. Antonietti, S. Blechert, X. C. Wang, *J. Am. Chem. Soc.* **2010**, *132*, 16299.