DOI: 10.1002/ange.201301049

Hydrogen storage

Metal-Free Catalysis of Ammonia–Borane Dehydrogenation/Regeneration for a Highly Efficient and Facilely Recyclable Hydrogen-Storage Material**

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In view of its high chemical energy density and no emissions if derived from recyclable resources, hydrogen is expected to be an essential energy carrier of the future, fixing the gap between intermissive recyclables and rapidly dwindling fossil fuels.[1] Light, safe, and compact storage of hydrogen for on-board applications remains the largest challenge in its implementation.[2] As a result, there has been great motivation to pursue chemical materials that comprise light elements and have a high hydrogen content suitable for on-board applications.[3] Ammonia borane (NH_3BH_3, AB) is considered as one of the most promising chemical hydrogen storage materials,[4] attributed to its high material storage density, low thermolysis temperature,[5] and recently realized regenerability.[6] Nevertheless, poor recyclability, slow kinetics below 100 °C, and simultaneous liberation of excessive deleterious gases upon thermolysis (i.e., borazine, ammonia, and diborane)[7] are main challenges that need to be addressed before this material can be utilized in practical systems.

Initial advances have demonstrated that the promoted rate, extent and purity of H_2 delivery required could be achieved from AB by using a variety of catalytic strategies, such as nanoscaffolds,[8] acids,[9] bases,[10] metal catalysts,[11] among others.[12] Among them, metal catalysts showed superior performances in stimulating AB dehydrogenation. Unfortunately, the presence of metallic catalysts in the decomposed products would lead to a significant negative effect on AB regeneration by the hydrazine route (Supporting Information, Table S1). To overcome the drawbacks above, it seems that an ideal solution is to seek alternative metal-free nanosupports with more accessible surfaces and efficient acidic or basic catalytic sites that could increase AB loading capacity as well as the contact area between the decomposed products (polyborazylene, PB) and the reductants, and could also facilitate the targeted transformation from AB to PB upon dehydrogenation.[6b]

Graphitic carbon nitride (g-C_3N_4, GCN) is an appealing material in which the incorporation of nitrogen atoms into the graphitic-like carbon, can improve the mechanical, chemical inertness, thermal stability, energy applications properties, and especially give rise to basic catalytic function.[13] The introduction of porosity into the bulk GCN by using silica nanoparticles as a template to yield mesoporous GCN (MGCN) gives the as-obtained material more active catalytic sites because of its accessible porous framework with increased surface area.[14] Thus, with the accessible nanoporous structure and basic catalytic activity, MGCN has the potential for achieving the catalysis of AB toward high-performance hydrogen storage. The DFT calculations were conducted to theoretically demonstrate the above assumption. The density of states (DoS) of N atoms of MGCN after incorporating AB molecules showed differences in the p and s orbitals of N atoms near the Fermi level (Supporting Information Figure S1), which indicates a strong interaction between the basic sites of MGCN and the AB molecule introduced, suggesting a potential basis for dispersion of AB nanoparticles on the MGCN. To our knowledge, however, there are no reports on carbon nitride-based materials applied in chemical hydrogen storage. Herein we employ these materials for hydrogen storage.

A MGCN material with high nitrogen content (an average value of 0.72 was determined for the C/N ratio from the elemental analyses, which is comparable to the theoretical value of C_3N_4) and large surface area of 442 m^2g^{-1} (higher than most of currently reported carbon nitride-based materials)[13–15] was applied to load AB through a solution-impregnation route. After being incorporated with AB, the specific surface area of MGCN is lessened to 29 m^2g^{-1} (Figure S2), which indicates the occupation of AB within the porous structure of MGCN. An average loading capacity of 47 wt% AB in the prepared composite (denoted as AB/MGCN) was calculated by elemental analyses performed several times on different batches. AB/MGCN showed a very high AB content which far-exceeds that of most of the reported size-confined systems (Table S2), a uniform distribution and no agglomeration of impregnated AB particles throughout the mesoporous configuration of MGCN was realized (Figure 1 a,b). Further observation using high-resolution transmission electronic microscopy (inset of Figure 1 b) reveals that AB nanoparticles are highly monodisperse with an average diameter of 5 nm, showing a prominent size-controlling role of this MGCN material. This effect is also clarified by X-ray

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[**] This work was partially supported by the Ministry of Science and Technology of China (2010CB631302), the National Natural Science Foundation of China (51071047, 21271046), the Ph.D. Programs Foundation of Ministry of Education of China (20110071110009), and the Science and Technology Commission of Shanghai Municipality (11JC1400700, 11520701100). We thank Dr. Qinfen Gu for his assistance on the DFT calculations conducted on the Multi-modal Australian ScienceS Imaging and Visualisation Environment (MASSIVE) facility.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201301049.

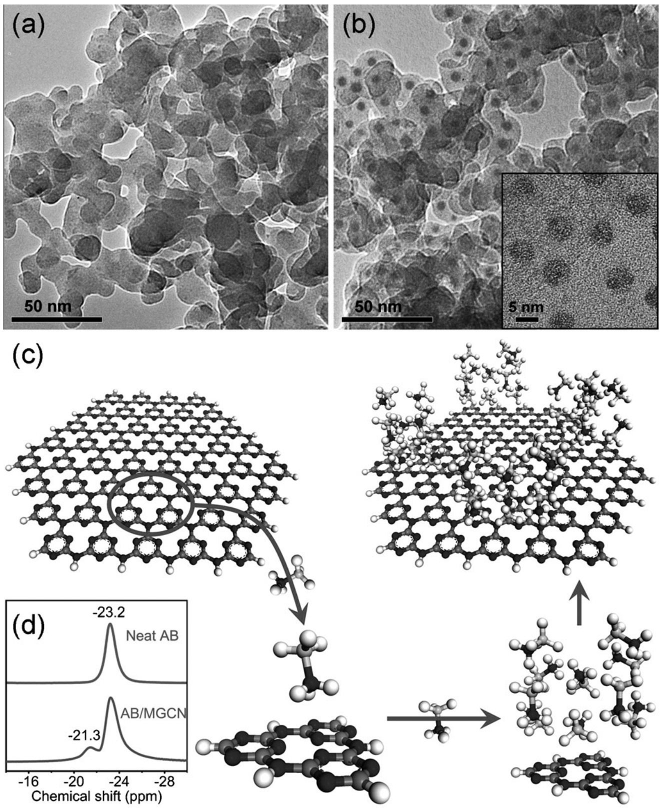

Figure 1. Transmission electronic microscopy images of a) MGCN and b) AB/MGCN (inset: corresponding high-resolution micrograph). c) Proposed mechanism of AB anchoring on the MGCN, supported by the DFT calculations. d) Solid-state ^{11}B NMR spectra of the as-prepared AB/MGCN and neat AB.

diffraction, in which AB is shown to form with an amorphous state in the AB/MGCN (Figure S3). It experimentally illustrates that in addition to the nanoporous architecture of MGCN, its active reaction sites play another crucial role in determining the dispersion and stabilization of AB particles. A possible mechanism of AB incorporation in MGCN, supported by DFT calculations, is proposed and illustrated in Figure 1c (a triazine-based motif was employed to simplify the computations. The other motif, heptazine-based C_3N_4 will be used in an addition theoretical study). The nitrogen functionalities on the surface of MGCN acting as strong Lewis base sites[16] can strongly attract protonic hydrogen atoms (H atoms on N) of some of the introduced AB molecules. The attraction will induce migration of the charges from AB molecules to MGCN, which is demonstrated by the charge distribution computation (Figure S4). The subtle downfield shift of the ^{11}B NMR spectroscopy resonance to $\delta = -21.3$ ppm (in line with its DFT-calculated value) compared with that in AB ($\delta = -23.2$ ppm) further confirms the reaction of initially introduced AB molecules with MGCN (Figure 1d). This shift is also consistent with that of AB reacting with a base,[10a] indicating the catalytic effect arising from the basic sites of MGCN on AB molecule. Depending on the intermolecular dihydrogen bonding network among AB molecules, some other introduced ones are then drawn together. As a consequence, the stabilization of highly dispersed AB particles can be accomplished in MGCN, similar to the observations of MGCN materials firmly anchoring metal nanoparticles.[17]

To compare the thermolysis behaviors of AB/MGCN and neat AB, mass spectrometry (MS), thermogravimetry (TG), and volumetric temperature-programmed desorption (TPD) characterizations were performed. Neat AB starts to dehydrogenate above 100 °C with two peaks centered at 112.8 and 151.5 °C, while AB/MGCN shows a one-step dehydrogenation peaking at around 93.7 °C (Figure 2a), with a complete depression of borazine, ammonia, and diborane emissions. This is also verified by the TG measurements (Figure 2b), in which the weight loss in AB/MGCN is significantly decreased compared to that of neat AB. As shown in Figure 2c, in the AB/MGCN nanocomposite AB generates 2.15 equivalents of H_2 within 120 min at 85 °C. In contrast, little hydrogen evolution from the neat AB is observable under the same conditions. At lower temperatures of 80 °C and 75 °C, respectively, the AB/MGCN composite can release 1.93 equivalents and 1.58 equivalents H_2 in 120 min. The long-time thermostatic TPD results (inset of Figure 2c) showed that an approaching 2.50 equivalent (corresponding to 16.3 wt % in AB) H_2 desorption is exhibited for AB/MGCN in the selected temperatures from 75 to 85 °C. The results for AB/MGCN far-exceed AB/graphene oxide (GO)[6b] (Figure S5) and the other size-confined systems (Table S2), and some ionic-liquid-based catalytic systems[10a,12] with regard to the rate and extent of AB dehydrogenation. This result further clarifies that the hybrid effect of size-confinement and basic functionality afforded by MGCN enormously facilitates the H_2 generation from AB.

Solid-state ^{11}B NMR spectra obtained from different degree thermolysis of AB/MGCN (Figure S6) present a typical base-initiated AB dehydropolymerization route.[10a] The

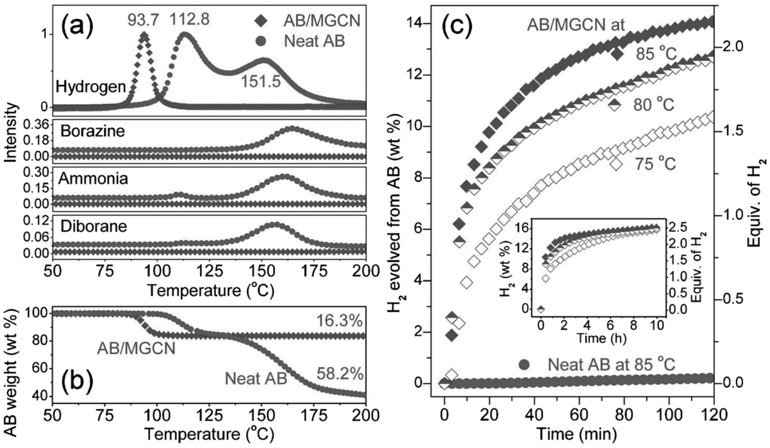

Figure 2. a) MS and b) TG profiles of AB/MGCN and neat AB with a heating rate of 5 °C min⁻¹. c) Thermostatic TPD results of hydrogen released from AB in AB/MGCN at 75, 80, and 85 °C (inset: time-extended thermostatic TPD results. Note that the MGCN was not considered as a gravimetric component during the measurements).

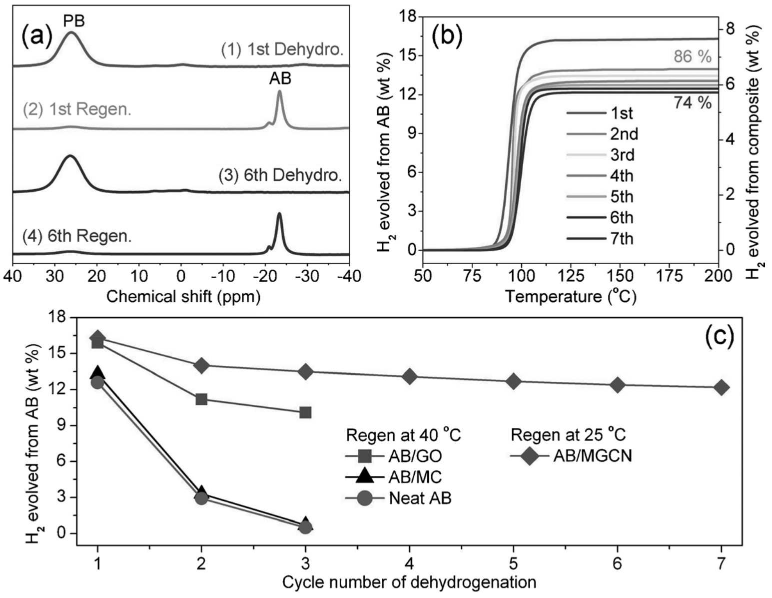

Figure 3. a) Solid-state ^{11}B NMR spectra of AB/MGCN after the first dehydrogenation (1), the first regeneration (2), the sixth de-hydrogenation (3), and the sixth regeneration (4). b) H_2 release results from the starting composite (1st; upper most trace) and multiple-regenerated AB/MGCN (from 2nd to 7th; lowest trace) with a heating rate of 5 °C min^{-1}. c) Cyclic dehydrogenation results of AB/MGCN, AB/GO, AB/MC, and neat AB (Note that the MGCN was not considered as the gravimetric component during the measurements).

final decomposition products, derived from AB losing more than 2.0 equivalents H_2, give rise to a broad resonance centered near $\delta = 26.2$ ppm (Figure 3a(1)) that is characteristic of PB species.[18] It exemplifies that PB is realizable as the signal product of AB dehydrogenation by the basic catalysis of MGCN. After regeneration by hydrogenation with hydrazine, the resonance signal arising from PB species nearly disappears with the regeneration of AB (Figure 3a(2)), implying a efficient regeneration. Moreover, signals of AB and the B species ($\delta = -21.1$ ppm) arising from the interaction between AB and MGCN are still detectable in the products of the sixth regeneration (Figure 3a(4)). This verifies the sustainably catalytic effect of MGCN on AB during its de-/re-hydrogenation cycles. MS studies on each regenerated AB/MGCN composite show identical dehydrogenation performance to that of the pristine material (Figure S7). The high-conversion AB regenerations in MGCN are further demonstrated through the H_2 evolution investigations of the regenerated composites (Figure 3b). It gives that 86% and 74% of AB is converted back for the first and sixth regeneration, respectively, which remarkably outclass that in AB/GO, AB/mesoporous carbon (MC), and neat AB systems with respect to the conversion rates and cycle numbers (Figure 3c and Table S1). Given the high loading capacity of AB in the AB/MGCN composite, a more than 5.7 wt% recyclable dehydrogenation is found for the whole material system, demonstrating an outstanding cycling performance among the chemical hydrogen-storage systems, which encouragingly establishes the basis toward its underlying practicability.

It is notable that a more energy-efficient regeneration route was applied for AB/MGCN in this work. The temperature and length of the hydrazine hydrogenation reaction was improved to room temperature (25 °C) and 12 h, with regard to 40 °C and at least 24 h in initial reports.[6,19] And the corresponding AB regeneration efficiency is comparable to that by using more energy-consuming methods (Figure S8). However, no regeneration has been seen in AB/GO, AB/MC, and neat AB systems upon treatment at room-temperature (Table S1). This indicates that MGCN might also promote the conversion of PB into AB by replacing the energy supplied in the form of heat. To verify this hypothesis, we calculated the energies of the intermediates for the addition of hydrazine (N_2H_4) molecules to a reasonable PB model (i.e., "BNH_2" borazine)[6a] with the presence of MGCN. On the basis of the degree of complication of overall reaction sequence (no less than a hundred reactions), only the initial steps in the reaction were considered. The computational results indicate that these initial reactions are more exothermic (Figure 4) and thus thermodynamically more favorable than those of without MGCN,[6a] which is ascribed to the nitrogen functionalities of MGCN modifying the charge distribution of borazine (Figure S9) and then influencing the reactions between borazine and hydrazine. It confirms the feasibility of room-temperature regeneration of AB with the help of MGCN.

Besides the highly production- and energy-efficient regeneration route at ambient temperature, highly activated as well as recyclable hydrogen generation was established in a MGCN-supported AB system, attributed to the combined activity of size-controlling effect and basic functionality in MGCN. It endows AB with superior hydrogen-storage performances that surpass most of currently reported solid-

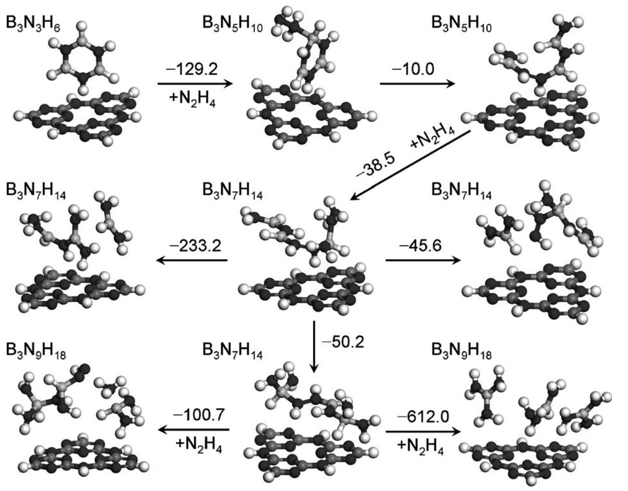

Figure 4. Calculated energies ΔH (kJ mol^{-1} N_2H_4) of possible reactions yielding intermediates and products for the initial introduction of N_2H_4 molecules to borazine in the presence of MGCN.

state hydrogen-storage systems. In spite of the potential advantages, when considering this system to target a realistic application, more intensive research must be devoted toward further improvements, for example, optimizing the synthesis of the composite system or functionalizing the support to promote the guest capacity and the contactable area between dehydrogenated product and reducer, and/or for an improved regeneration means to highly efficiently recharge the spent fuel at lower cost and with less energy-consumption.

Received: February 5, 2013

Keywords: ammonia borane · heterogeneous catalysis · hydrogen storage · mesoporous materials

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[1] a) R. von Helmolt, U. Eberle, *J. Power Sources* **2007**, *165*, 833–843; b) U. Eberle, B. Müeller, R. von Helmolt, *Energy Environ. Sci.* **2012**, *5*, 8780–8798.

[2] a) M. Dresselhaus, I. Thomas, *Nature* **2001**, *414*, 332–337; b) U. Eberle, M. Felderhoff, F. Schüth, *Angew. Chem.* **2009**, *121*, 6732–6757; *Angew. Chem. Int. Ed.* **2009**, *48*, 6608–6630.

[3] a) S. Orimo, Y. Nakamori, J. R. Eliseo, A. Züttel, C. M. Jensen, *Chem. Rev.* **2007**, *107*, 4111–4132; b) U. B. Demirci, P. Miele, *Energy Environ. Sci.* **2011**, *4*, 3334–3341; c) H. W. Li, Y. Yan, S. Orimo, A. Züttel, C. M. Jensen, *Energies* **2011**, *4*, 185–214.

[4] a) F. H. Stephens, V. Pons, R. T. Baker, *Dalton Trans.* **2007**, 2613–2626; b) B. Peng, J. Chen, *Energy Environ. Sci.* **2008**, *1*, 479–483; c) U. B. Demirci, P. Miele, *Energy Environ. Sci.* **2009**, *2*, 627–637; d) A. Staubitz, A. P. M. Robertson, I. Manners, *Chem. Rev.* **2010**, *110*, 4079–4124; e) U. Sanyal, U. B. Demirci, B. R. Jagirdar, P. Miele, *ChemSusChem* **2011**, *4*, 1731–1739; f) G. R. Whittell, I. Manners, *Angew. Chem.* **2011**, *123*, 10470–10472; *Angew. Chem. Int. Ed.* **2011**, *50*, 10288–10289.

[5] F. Baitalow, J. Baumann, G. Wolf, K. Jaenicke-Rößler, G. Leitner, *Thermochim. Acta* **2002**, *391*, 159–168.

[6] a) A. D. Sutton, A. K. Burrell, D. A. Dixon, E. B. Garner, J. C. Gordon, T. Nakagawa, K. C. Ott, J. P. Robinson, M. Vasiliu, *Science* **2011**, *331*, 1426; b) Z. W. Tang, H. Chen, X. W. Chen, L. M. Wu, X. B. Yu, *J. Am. Chem. Soc.* **2012**, *134*, 5464–5467.

[7] G. Wolf, J. Baumann, F. Baitalow, F. Hoffmann, *Thermochim. Acta* **2000**, *343*, 19–25.

[8] a) Y. Li, L. Xie, J. Zheng, X. Li, *Chem. Eur. J.* **2009**, *15*, 8951–8954; b) Z. Y. Li, G. S. Zhu, G. Q. Lu, S. L. Qiu, X. D. Yao, *J. Am. Chem. Soc.* **2010**, *132*, 1490–1491; c) Y. Q. Li, P. Song, J. Zheng, X. G. Li, *Chem. Eur. J.* **2010**, *16*, 10887–10892; d) Z. W. Tang, S. F. Li, Z. X. Yang, X. B. Yu, *J. Mater. Chem.* **2011**, *21*, 14616–14621; e) Z. W. Tang, S. F. Li, W. N. Yang, X. B. Yu, *J. Mater. Chem.* **2012**, *22*, 12752–12758; f) A. Aijaz, A. Karkamkar, Y. J. Choi, N. Tsumori, E. Rönnebro, T. Autrey, H. Shioyama, Q. Xu, *J. Am. Chem. Soc.* **2012**, *134*, 13926–13929.

[9] F. H. Stephens, R. T. Baker, M. H. Matus, D. J. Grant, D. A. Dixon, *Angew. Chem.* **2007**, *119*, 760–763; *Angew. Chem. Int. Ed.* **2007**, *46*, 746–749.

[10] a) D. Himmelberger, C. Yoon, M. Bluhm, P. Carroll, L. Sneddon, *J. Am. Chem. Soc.* **2009**, *131*, 14101–14110; b) W. C. Ewing, A. Marchione, D. W. Himmelberger, P. J. Carroll, L. G. Sneddon, *J. Am. Chem. Soc.* **2011**, *133*, 17093–17099.

[11] a) C. A. Jaska, K. Temple, A. J. Lough, I. Manners, *Chem. Commun.* **2001**, 962–963; b) R. J. Keaton, J. M. Blacquiere, R. T. Baker, *J. Am. Chem. Soc.* **2007**, *129*, 1844–1845; c) N. Blaquiere, S. Diallo-Garcia, S. I. Gorelsky, D. A. Black, K. Fagnou, *J. Am. Chem. Soc.* **2008**, *130*, 14034–14035; d) X. B. Zhang, J. M. Yan, S. Han, H. Shioyama, Q. Xu, *J. Am. Chem. Soc.* **2009**, *131*, 2778–2779; e) G. Alcaraz, S. Sabo-Etienne, *Angew. Chem.* **2010**, *122*, 7326–7335; *Angew. Chem. Int. Ed.* **2010**, *49*, 7170–7179; f) B. L. Conley, D. Guess, T. J. Williams, *J. Am. Chem. Soc.* **2011**, *133*, 14212–14215; g) P.-Z. Li, A. Aijaz, Q. Xu, *Angew. Chem.* **2012**, *124*, 6857–6860; *Angew. Chem. Int. Ed.* **2012**, *51*, 6753–6756.

[12] a) M. E. Bluhm, M. G. Bradley, R. Butterick, U. Kusari, L. G. Sneddon, *J. Am. Chem. Soc.* **2006**, *128*, 7748–7749; b) D. W. Himmelberger, L. R. Alden, M. E. Bluhm, L. G. Sneddon, *Inorg. Chem.* **2009**, *48*, 9883–9889; c) W. R. H. Wright, E. R. Berkeley, L. R. Alden, R. T. Baker, L. G. Sneddon, *Chem. Commun.* **2011**, *47*, 3177–3179.

[13] a) X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.* **2009**, *8*, 76–80; b) Y. Wang, X. Wang, M. Antonietti, *Angew. Chem.* **2012**, *124*, 70–92; *Angew. Chem. Int. Ed.* **2012**, *51*, 68–89; c) Y. Zheng, J. Liu, J. Liang, M. Jaroniec, S. Z. Qiao, *Energy Environ. Sci.* **2012**, *5*, 6717–6731.

[14] a) E. Z. Lee, Y. S. Jun, W. H. Hong, A. Thomas, M. M. Jin, *Angew. Chem.* **2010**, *122*, 9900–9904; *Angew. Chem. Int. Ed.* **2010**, *49*, 9706–9710; b) Y. Zheng, Y. Jiao, J. Chen, J. Liu, J. Liang, A. Du, W. Zhang, Z. Zhu, S. C. Smith, M. Jaroniec, G. Q. Lu, S. Z. Qiao, *J. Am. Chem. Soc.* **2011**, *133*, 20116–20119; c) F. Su, S. C. Mathew, L. Möhlmann, M. Antonietti, X. Wang, S. Blechert, *Angew. Chem.* **2011**, *123*, 683–686; *Angew. Chem. Int. Ed.* **2011**, *50*, 657–660; d) X.-H. Li, X. Wang, M. Antonietti, *Chem. Sci.* **2012**, *3*, 2170–2174; e) J. Zhang, G. Zhang, X. Chen, S. Lin, L. Möhlmann, G. Dołęga, G. Lipner, M. Antonietti, S. Blechert, X. Wang, *Angew. Chem.* **2012**, *124*, 3237–3241; *Angew. Chem. Int. Ed.* **2012**, *51*, 3183–3187.

[15] a) X. Wang, K. Maeda, X. Chen, K. Takanabe, K. Domen, Y. Hou, X. Fu, M. Antonietti, *J. Am. Chem. Soc.* **2009**, *131*, 1680–1681; b) F. Su, S. C. Mathew, G. Lipner, X. Fu, M. Antonietti, S. Blechert, X. Wang, *J. Am. Chem. Soc.* **2010**, *132*, 16299–16301.

[16] X. Jin, V. V. Balasubramanian, S. T. Selvan, D. P. Sawant, M. A. Chari, G. Q. Lu, A. Vinu, *Angew. Chem.* **2009**, *121*, 8024–8027; *Angew. Chem. Int. Ed.* **2009**, *48*, 7884–7887.

[17] a) K. K. Datta, B. V. Reddy, K. Ariga, A. Vinu, *Angew. Chem.* **2010**, *122*, 6097–6101; *Angew. Chem. Int. Ed.* **2010**, *49*, 5961–5965; b) Y. Wang, J. Yao, H. Li, D. Su, M. Antonietti, *J. Am. Chem. Soc.* **2011**, *133*, 2362–2365.

[18] a) P. J. Fazen, J. S. Beck, A. T. Lynch, E. E. Remsen, L. G. Sneddon, *Chem. Mater.* **1990**, *2*, 96–97; b) P. J. Fazen, E. E. Remsen, J. S. Beck, P. J. Carroll, A. R. McGhie, L. G. Sneddon, *Chem. Mater.* **1995**, *7*, 1942–1956.

[19] Z. W. Tang, Y. B. Tan, X. W. Chen, X. B. Yu, *Chem. Commun.* **2012**, *48*, 9296–9298.