Carbon Quantum Dots

Deutsche Ausgabe: DOI: 10.1002/ange.201510945
Internationale Ausgabe: DOI: 10.1002/anie.201510945

Invisible Security Ink Based on Water-Soluble Graphitic Carbon Nitride Quantum Dots

Zhiping Song, Tianran Lin, Lihua Lin, Sen Lin, Fengfu Fu, Xinchen Wang, and Liangqia Guo**

In memory of Jiaxi Lu

Abstract: *Stimuli-responsive photoluminescent (PL) materials have been widely used as fluorescent ink for data security applications. However, traditional fluorescent inks are limited in maintaining the secrecy of information because the inks are usually visible by naked eyes either under ambient light or UV-light illumination. Here, we introduced metal-free water-soluble graphitic carbon nitride quantum dots (g-CNQDs) as invisible security ink for information coding, encryption, and decryption. The information written by the g-CNQDs is invisible in ambient light and UV light, but it can be readable by a fluorescence microplate reader. Moreover, the information can be encrypted and decrypted by using oxalic acid and sodium bicarbonate as encryption reagent and decryption reagent, respectively. Our findings provide new opportunities for high-level information coding and protection by using water-soluble g-CNQDs as invisible security ink.*

Data security has become an important issue in economic and military fields as well as in our daily lives. Stimuli-responsive PL materials can change their optical outputs of spectra and lifetime in response to external stimuli and possess extra security features that are difficult to mimic and duplicate, and thus they have been widely used as security inks for applications in the fields of optical data recording, data storage and data security.[1]

A variety of PL materials have been developed and used as security inks. For example, organic dyes[2] have been widely used as fluorescent inks, albeit they are limited by poor photostability and small Stokes shift. Conjugated polymers dots[3] and inorganic quantum dots[4] have also been employed as alternatives of conventional organic fluorescent dyes to improve the fluorescent patterns due to their tunable fluorescent properties, narrow emission bandwidth, and superior photostability. Lanthanide-doped up-converting nanoparticles have recently been employed to fabricate high-security anti-counterfeiting patterns under near-infrared (NIR) excitation; however, there are concerns on the long-term toxicity and/or potential environmental hazards of these lanthanide-based fluorescent inks.[5]

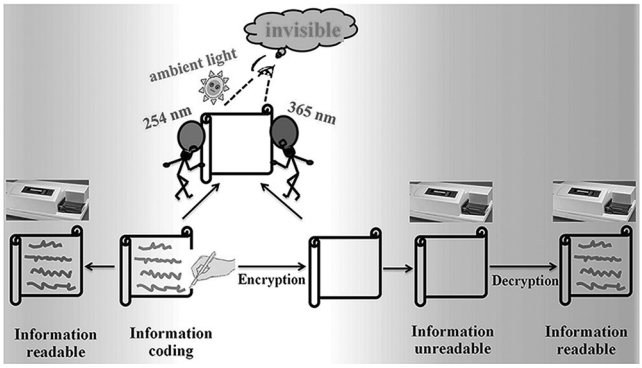
Recently, carbon dots have emerged as a new type of fluorescent ink because of their facile preparation and highly-stable fluorescence, low toxicity, and low costs.[6] Coding these carbon dots in one or two dimensions has been suggested as a potential strategy to prevent tampering or counterfeiting, but theses coding techniques were comparatively less effective at protecting confidential information because the information written by these inks is visible by naked eyes either in ambient light[2b–c] or under the excitation by UV,[1a–d,2a,c,6a–d,f] visible[4b,6e] or NIR light.[1e,5] Therefore, it still calls for the development of new stimuli-responsive PL materials with more confidential and reliable features for high-level information coding and security protection.

Graphitic carbon nitride ($g\text{-}C_3N_4$) is the most stable allotrope of binary carbon nitride phases and has recently attracted great interest due to its unique electronic properties.[7] Melon-based $g\text{-}C_3N_4$ can be prepared in large scale by the condensation of *N*-containing precursors, including cyanamide, dicyandiamide, melamine, urea, and thiourea.[8] The thus obtained defective $g\text{-}C_3N_4$ polymers have been well-demonstrated to function as a new family of sustainable photocatalysts, while still applicable for bioimaging and sensing fields after being fabricated in the form of $g\text{-}C_3N_4$ nanosheets and g-CNQDs.[8–10] Similar to carbon dots, fluorescent $g\text{-}C_3N_4$ nanosheets and g-CNQDs have the advantages of easy preparation, high quantum yield, good biocompatibility, low costs, low cytotoxicity, and high photostability. For all these benefits, we are very positive to apply these emerging nanomaterials as fluorescent ink for data security applications.

Here, we introduced g-CNQDs as invisible security ink for information coding, encryption, and decryption (Scheme 1). The information written by using the water-soluble g-CNQDs is invisible under both ambient light and UV-light illumination (with wavelengths of 254 and 365 nm). The encoded information is readable by a fluorescence microplate reader, and it can be further encrypted and decrypted by quenching and recovering the fluorescence of the g-CNQDs ink. Thus, this process can provide a threefold protection in maintaining the secrecy of information. First, the security ink is almost transparent in the visible light range, and thus the information written using this security ink is colorless and invisible under ambient light. Second, the security ink emits fluorescence with a peak in the UV range, which is significantly different from the previous fluorescent inks.[1–6] Thus, the information is also invisible by naked eyes under the illumination of an easy-

[*] Z. Song, T. Lin, L. Lin, Dr. S. Lin, Prof. F. Fu, Prof. X. Wang, Prof. L. Guo
Ministry of Education Key Laboratory of Analysis and Detection for Food Safety, State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry
Fuzhou University, Fuzhou 350116 (P.R. China)
E-mail: xcwang@fzu.edu.cn
lqguo@fzu.edu.cn

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201510945.



Scheme 1. Schematic illustration of information coding, reading, encryption, and decryption process.

to-get UV lamp (such as 254 and 365 nm lamps), but it is readable by using a fluorescence microplate reader. Third, by applying encryption reagents on the top of the g-CNQDs ink to quench the fluorescence, the information is unreadable. Interestingly, the information can be readable again after using an appropriate decryption reagent. Therefore, the coding information is strictly confidential. Compared with traditional fluorescent inks, this new g-CNQDs security ink can provide a high-level information coding and protection.

The g-CNQDs solution was prepared by the chemical oxidation of bulk g-C_3N_4 with HNO_3, followed by hydrothermal treatment and ultrasonic exfoliation. Typical TEM image (Figure 1 a) shows that the diameters of g-CNQDs are in the range of 1–5 nm with mean diameters of about 2 nm.

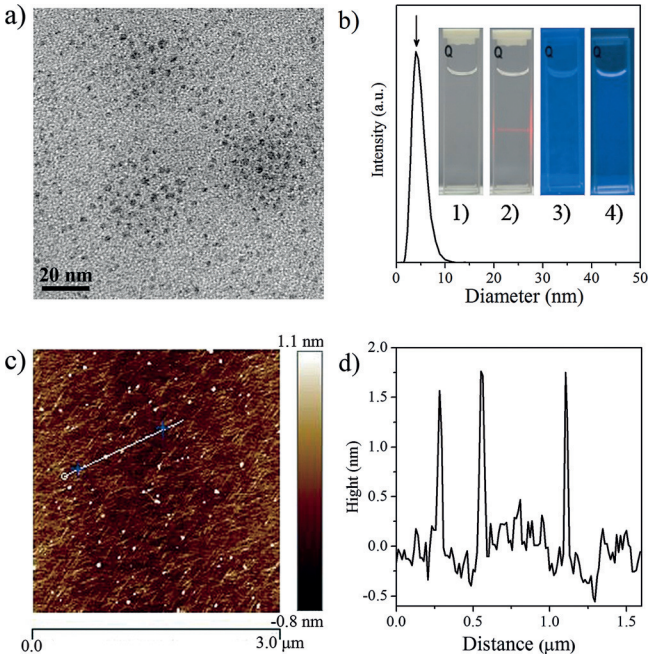


Figure 1. a) TEM image of g-CNQDs. b) Particle size distribution obtained by dynamic light scattering. Inset: Photographs of 1) an aqueous g-CNQDs solution (20 μg mL^{-1}) under ambient light. 2) Tyndall effect generated by a red laser, under illumination using 3) a 365 nm lamp, and 4) a 254 nm lamp. c) AFM image, and d) the corresponding height image of the g-CNQDs.

The g-CNQDs solution shows a typical Tyndall effect, which was indicated by a red laser beam (635 nm) passing through the transparent solution (Figure 1 b, inset). Moreover, the as-prepared g-CNQDs solution does not emit visible fluorescence under UV illumination at 254 and 365 nm (Figure 1 b, inset). The particle size of g-CNQDs was also cross checked by ZetaPlus analysis (Figure 1 b). The most probable dynamic diameter of g-CNQDs is 4 nm, which is larger than that measured by TEM due to the Brownian movement and hydration effect in the solution. The AFM images (Figure 1 c–d) affirm that the thickness of g-CNQDs is ca. 1.7 nm.

XPS spectrum (Figure 2 a) was carried out to examine the chemical composition of g-CNQDs, which shows three

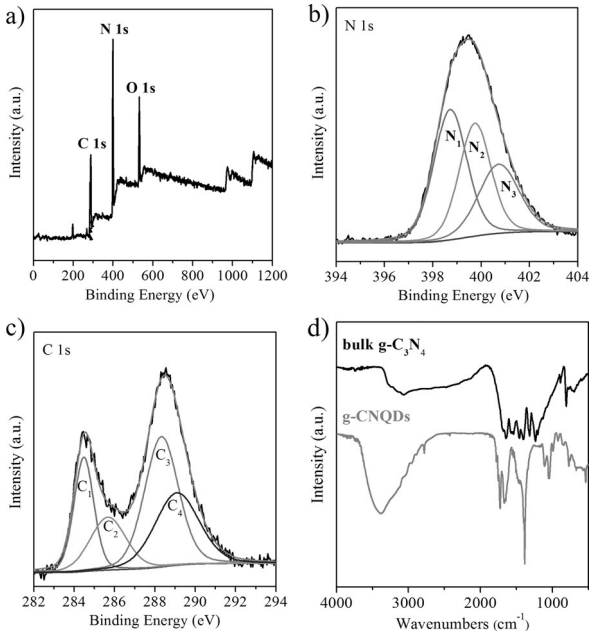


Figure 2. a) XPS survey spectrum, b) N 1s core-level spectrum, c) C 1s core-level spectrum of g-CNQDs, and d) FT-IR spectra of bulk g-C_3N_4 and g-CNQDs.

dominant peaks at 288.9, 401.0, and 532.7 ev, corresponding to C1s, N1s, and O1s, respectively. The high-resolution XPS N1s core-level spectrum (Figure 2 b) of g-CNQDs can be deconvoluted into three peak components with binding energies (BEs) at 398.74, 399.75, and 400.71 eV, respectively. These BEs belong to the pyridinic nitrogen (C=N−C), pyrrolic nitrogen (C−N−C), and quaternary nitrogen (N−$(C)_3$), respectively.[10e–g,11] The XPS C1s core-level spectrum (Figure 2 c) can be deconvoluted into four peak components with BEs at 284.72 (C1), 285.42 (C2), 288.17 (C3) and 288.87 eV (C4), attributable to C−C, C−O, N−C=N, and O−C=O, respectively. As compared with the XPS data of bulk g-C_3N_4 (Figure S1), additional oxygen-rich groups were observed on the as-prepared g-CNQDs sample due to the oxidation treatment. These results, together with the presence of N−C=N bonds, indicate that the basic substructure of g-CNQDs is the heptazine heterocyclic ring unit.

FT-IR spectrum (Figure 2 d) was used to verify the chemical structure and surface functional groups of g-

CNQDs. The broad adsorption peak at 3380 cm^{-1} corresponds to the stretching vibration of O-H and N-H. The peak at 1750 cm^{-1} is assigned to the stretching vibration of C=O. Absorption bands at 1473 and 1384 cm^{-1} are assigned to typical stretching vibration modes of C=N and C–N heterocycles, while the bands at 1108, 1043 cm^{-1} can be ascribed to the stretching vibration of C-O. The peak at 800 cm^{-1} is the characteristic breathing mode of the tri-s-triazine rings.[10d–f] These results indicate that oxygen- and nitrogen-containing groups such as hydroxyl, carboxylic acid, and amine exist in g-CNQDs, imparting a hydrophilic surface on g-CNQDs to make it highly dispersible in aqueous solution.[12]

The UV–visible spectrum of g-CNQDs solution (Figure S2a) exhibited a large peak between 200 to 270 nm with a shoulder peak at approximately 245 nm, because of π–π* electronic transitions from HOMO to LUMO of graphitic carbon nitrides containing tri-s-triazine ring.[10e] The density functional theory (DFT) calculations show that the HOMO of g-CNQDs is consisted mainly of N p orbitals, whereas the LUMO is the hybridized state of C and N p orbitals (Figure 3). The calculated band gap is 4.33 eV corresponding

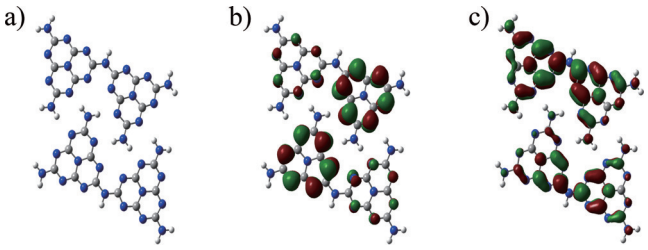


Figure 3. a) The optimized structure of melon-based g-C_3N_4. b) The HOMO and c) LUMO of melon (blue, gray, and white colored atoms represent N, C, and H, respectively).

to the optical absorption edge at 286 nm, which was significantly larger than that of bulk counterpart, mostly probably because of the quantum size effects.[13] Notably, there is virtually no absorption over the whole visible light range, which is preferable as invisible security ink to maintain the secrecy of information. The excitation spectrum (Figure S2a) showed a maximal luminescence at ca. 245 nm. A narrow and symmetrical fluorescence peak at 367 nm was observed when the aqueous solution of g-CNQDs was excited at 245 nm (Figure S2a). Distinctly different from most previous fluorescent g-C_3N_4 nanosheets[9a,10b–d] and g-CNQDs[11] with blue fluorescence, the emission peak of our g-CNQDs is in the UV-light range. The blue shift of absorption and emission peaks of g-CNQDs (Figure S3) might be ascribed to the quantum confinement effect with the conduction and valence band shifting in the opposite directions.[9a,10f,12] The emission peaks of the as-prepared g-CNQDs at various excitation wavelengths show no obvious shift and remain at 367 nm (Figure S2b). This excitation-independent emission behavior reveals that the fluorescent properties of g-CNQDs solution are dependent on the surface states rather than the morphology, and the surface states of the g-CNQDs should be rather uniform.[14] As shown in Figure S2c-d, the as-prepared g-CNQDs emitted strong fluorescence under neutral condition (pH 5–7) and weak fluorescence at acid condition. This pH-dependent fluorescence property corroborates the fact that the fluorescence emission is caused by the transition between lone-pair (LP) valence band on the nitrogen atoms and π* conduction band.[12] At acid condition, lone-pair electron on N is protonated, and thus partly deactivating the fluorescence of g-CNQDs.

Inspired by the above exceptional optical properties of g-CNQDs, we are very interested to use g-CNQDs as fluorescent ink. Firstly, oxalic acid ($H_2C_2O_4$), a colorless organic solid acid with middle strong acidity and low toxicity, was chose to quench the fluorescence of g-CNQDs. As shown in Figure S4a, the fluorescence of g-CNQDs solution decreased with the concentration of oxalic acid and was almost completely quenched when the concentration of oxalic acid increased to 20 mmol L^{-1}. Next, sodium bicarbonate ($NaHCO_3$, a white solid alkaline with weak alkalinity and low toxicity) was used to recover the fluorescence of g-CNQDs. As shown in Figure S4B, the fluorescence increased with the concentration of $NaHCO_3$ due to the neutralization reaction between the protonated g-CNQDs and $NaHCO_3$. Subsequently, we tested the fluorescence quenching and recovering of g-CNQDs in the solid-state for real application in a filter paper. After g-CNQDs solution was loaded onto the filter paper, the fluorescence of solid-state g-CNQDs was recorded by a fluorescence microplate reader with the excitation wavelength of 250 nm. Results show that the g-CNQDs can also emit strong fluorescence on the filter paper (Figure S4c, curve 1). Upon further addition of $H_2C_2O_4$ solution onto the filter paper, the fluorescence of g-CNQDs (curve 4 in Figure S4c) can be quenched close to the background of filter paper (curve 3 in Figure S4c). However, after the addition of $NaHCO_3$ solution, the fluorescence of g-CNQDs can be recovered (curve 2 in Figure S4c), which was similar to the phenomenon in solution. Interestingly, the fluorescence quenching and recovery of g-CNQDs on the filter paper can be repetitive by the alternate addition of $H_2C_2O_4$ and $NaHCO_3$, respectively (Figure S4d). Thus, by addition of $H_2C_2O_4$ and $NaHCO_3$ solution, the solid-state fluorescence of g-CNQDs can be switched off and on. This pH-dependent stimulus-responsive property of g-CNQDs in solid state, which is invisible by naked eyes under ambient light and UV light, is unique and therefore holds great promise for applications in information coding, encryption, and decryption.

On the basis of these findings, a novel strategy for information coding, encryption and decryption was designed by using water-soluble g-CNQDs solution as invisible security ink. First the filter paper was cut into the same size of a 96-well plate. Then, 96 circles were drawn on the filter paper by a white wax crayon according to the model of 96-well plate and then toasted on a hot plate to melt the wax, resulting in 96 circles with hydrophobic edges on a filter paper to restrict aqueous solution within the circle (Figure S5). g-CNQDs solution was dropped onto some circles on the filter paper to code the desired information (a pattern of three characters "FZU", for example). After the filter paper was dried, the visibility of the characters on the filter paper was almost negligible under ambient light and under the excitation of

254 nm and 365 nm lamps (Figure S6), reflecting the fact that g-CNQDs are invisible and emit fluorescence mainly in the UV range under the excitation of UV light.

In the next set of experiment, we applied a fluorescence microplate reader to read the encoded information. Strong fluorescence of the g-CNQDs on the filter paper could be recorded at the position loaded with g-CNQDs solution, together with a very weak background fluorescence of the filter paper at the positions without loaded g-CNQDs (Figure S7a). The threshold of the fluorescence intensity at the maximal emission of the g-CNQDs (367 nm) can be set higher than the background fluorescence of the filter paper (300 counts in this example) to rule out the background effect of the filter paper. The threshold can thus be used as a key to "read" the encoded information. Namely, a position on the filter paper with g-CNQDs was set to blue color, while another position without g-CNQDs was set to white color. Thus, a pattern of "FZU" was obtained (Figure 4a).

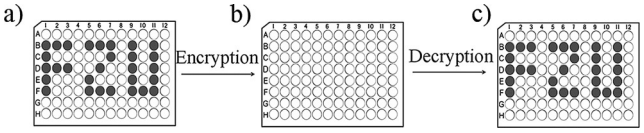


Figure 4. Information reading after coding, encryption, and decryption.

The information can be encrypted by using $H_2C_2O_4$ as encryption reagent. After loading $H_2C_2O_4$ onto each circle on the filter paper, the fluorescence of g-CNQDs were quenched to the background fluorescence of filter paper (Figure S7b). No pattern of information could be obtained (Figure 4b) after the encryption process. Nevertheless, the encrypted information can be decrypted by using $NaHCO_3$ to neutralize the acidified g-CNQDs. After further loading of $NaHCO_3$ onto each circle on the filter paper, strong fluorescence of g-CNQDs can be recorded again at the position where g-CNQDs solution was originally loaded (Figure S7c). Clearly, a pattern of three characters "FZU" could be obtained again as shown in Figure 4c. Remarkably, information coding, encryption and decryption can be realized by using g-CNQDs solution as invisible security ink, $H_2C_2O_4$ as encryption reagent, $NaHCO_3$ as decryption reagent.

To conclude, water-soluble g-CNQDs were successfully applied as invisible security ink for information coding, encryption and decryption. The information written using this security ink cannot be visible under ambient light and UV light, and can be readable by a common fluorescence microplate reader quickly. The information can be further encrypted by applying $H_2C_2O_4$ and can be decrypted by $NaHCO_3$. In contrast to conventional fluorescent ink, the information coded by this security ink is more reliable in maintaining secrecy of information. In addition, the fluorescent ink, encryption and decryption reagents are facile, low-cost, and environmental-friendly. Therefore, we believe that nanostructured g-C_3N_4 will open a new avenue for applications in the field of anti-counterfeiting, information storage, and secret communication.

Acknowledgements

This work was financially supported by NSFC (grant numbers 21577017 and 21425309), the National Basic Research Program of China (grant number 2013CB632405), Program for New Century Excellent Talents in Fujian Province University, and the Science and Technology Project of Fujian Province, China (grant number 2015Y0045).

Keywords: carbon nitride · data security · fluorescence · fluorescent ink · semiconductors

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 2773–2777
Angew. Chem. **2016**, *128*, 2823–2827

[1] a) A. Kishimura, T. Yamashita, K. Yamaguchi, T. Aida, *Nat. Mater.* **2005**, *4*, 546–549; b) T. Mutai, H. Satou, K. Araki, *Nat. Mater.* **2005**, *4*, 685–687; c) B. Yoon, D.-Y. Ham, O. Yarimaga, H. An, C. W. Lee, J. M. Kim, *Adv. Mater.* **2011**, *23*, 5492–5497; d) D. R. Whang, Y. You, W.-S. Chae, J. Heo, S. Kim, S. Y. Park, *Langmuir* **2012**, *28*, 15433–15437; e) Y. Lu, J. Zhao, R. Zhang, Y. Liu, D. Liu, E. M. Goldys, X. Yang, P. Xi, A. Sunna, J. Lu, Y. Shi, R. C. Leif, Y. Huo, J. Shen, J. A. Piper, J. P. Robinson, D. Jin, *Nat. Photonics* **2014**, *8*, 32–36.

[2] a) H. H. Pham, I. Gourevich, J. K. Oh, J. E. N. Jonkman, E. Kmacheva, *Adv. Mater.* **2004**, *16*, 516–520; b) X. Zhu, R. Liu, Y. Li, H. Huang, Q. Wang, D. Wang, X. Zhu, S. Liu, H. Zhu, *Chem. Commun.* **2014**, *50*, 12951–12954; c) X. Hou, C. Ke, C. J. Bruns, P. R. McGonigal, R. B. Pettman, J. F. Stoddart, *Nat. Commun.* **2015**, *6*, 6884.

[3] K. Chang, Z. Liu, H. Chen, L. Sheng, S. X.-A. Zhang, D. T. Chiu, S. Yin, C. Wu, W. Qin, *Small* **2014**, *10*, 4270–4275.

[4] a) L. Sun, H. Shi, W. Li, H. Xiao, S. Fu, X. Cao, Z. Li, *J. Mater. Chem.* **2012**, *22*, 8221–8227; b) Z. Lu, Y. Liu, W. Hu, X. W. Lou, C. Li, *Chem. Commun.* **2011**, *47*, 9609–9611.

[5] J. M. Meruga, W. M. Cross, P. S. May, Q. A. Luu, G. A. Crawford, J. J. Kellar, *Nanotechnology* **2012**, *23*, 395201.

[6] a) L. Zhu, Y. Yin, C.-F. Wang, S. Chen, *J. Mater. Chem. C* **2013**, *1*, 4925–4932; b) S. Gao, Y. Chen, H. Fan, X. Wei, C. Hu, L. Wang, L. Qu, *J. Mater. Chem. A* **2014**, *2*, 6320–6325; c) J. Wang, C.-F. Wang, S. Chen, *Angew. Chem. Int. Ed.* **2012**, *51*, 9297–9301; *Angew. Chem.* **2012**, *124*, 9431–9435; d) Q. Lou, S. Qu, P. Jing, W. Ji, D. Li, J. Cao, H. Zhang, L. Liu, J. Zhao, D. Shen, *Adv. Mater.* **2015**, *27*, 1389–1394; e) S. Qu, X. Wang, Q. Lu, X. Liu, L. Wang, *Angew. Chem. Int. Ed.* **2012**, *51*, 12215–12218; *Angew. Chem.* **2012**, *124*, 12381–12384; f) X. Chen, Q. Jin, L. Wu, C. Tung, X. Tang, *Angew. Chem. Int. Ed.* **2014**, *53*, 12542–12547; *Angew. Chem.* **2014**, *126*, 12750–12755.

[7] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.* **2009**, *8*, 76–80.

[8] a) Y. Zheng, L. Lin, B. Wang, X. Wang, *Angew. Chem. Int. Ed.* **2015**, *54*, 12868–12884; *Angew. Chem.* **2015**, *127*, 13060–13077; b) Y. Wang, X. Wang, M. Antonietti, *Angew. Chem. Int. Ed.* **2012**, *51*, 68–89; *Angew. Chem.* **2012**, *124*, 70–92.

[9] a) X. D. Zhang, X. Xie, H. Wang, J. J. Zhang, B. C. Pan, Y. Xie, *J. Am. Chem. Soc.* **2013**, *135*, 18–21; b) Q. Zhang, J. Xie, Y. Tian, J. Wang, Y. Xie, *Adv. Mater.* **2014**, *26*, 4438–4443; c) J. Zhang, Y. Chen, X. Wang, *Energy Environ. Sci.* **2015**, *8*, 3092–3108.

[10] a) Y. R. Tang, H. J. Song, Y. Y. Su, Y. Lv, *Anal. Chem.* **2013**, *85*, 11876–11884; b) H. Huang, R. Chen, J. Ma, L. Yan, Y. Zhao, Y. Wang, W. Zhang, J. Fan, X. Chen, *Chem. Commun.* **2014**, *50*, 15415–15418; c) J. Tian, Q. Liu, A. M. Asiri, A. O. Al-Youbi, X. Sun, *Anal. Chem.* **2013**, *85*, 5595–5599; d) M. Rong, L. Lin, X. Song, T. Zhao, Y. Zhong, J. Yan, Y. Wang, X. Chen, *Anal. Chem.* **2015**, *87*, 1288–1296; e) Y. Tang, Y. Su, N. Yang, L. Zhang, Y. Lv,

Anal. Chem. **2014**, *86*, 4528 – 4535; f) S. Barman, M. Sadhukhan, *J. Mater. Chem.* **2012**, *22*, 21832 – 21837.
[11] J. Zhou, Y. Yang, C.-Y. Zhang, *Chem. Commun.* **2013**, *49*, 8605 – 8607.
[12] Z. Zhou, Y. Shen, Y. Li, A. Liu, S. Liu, Y. Zhang, ACS Nano 2015, 9, 12480 – 12487.
[13] G. Zhang, J. Zhang, M. Zhang, X. Wang, *J. Mater. Chem.* **2012**, *22*, 8083 – 8091.
[14] Y. Dong, H. Pang, H. Yang, C. Guo, J. Shao, Y. Chi, C. M. Li, T. Yu, *Angew. Chem. Int. Ed.* **2013**, *52*, 7800 – 7804; *Angew. Chem.* **2013**, *125*, 7954 – 7958.

Received: November 25, 2015
Published online: January 19, 2016

