Dalton Transactions

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Dalton Transactions Dalton Transactions Dynamic Article Links ▶

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

PAPER

Synthesis of carbon black/carbon nitride intercalation compound composite for efficient hydrogen production†

Zhaochun Wu, Honglin Gao, Shicheng Yan,*[a] and Zhigang Zou[a,b]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

The photoactivity of g-C_3N_4 is greatly limited by its high recombination rate of photogenerated carriers. Coupling g-C_3N_4 with other materials has been demonstrated to be an effective way to facilitate the separation and transport of charge carriers. Herein we report a composite of conductive carbon black and carbon nitride intercalation compound synthesized through facile one-step molten salt method. The as-prepared carbon black/ carbon nitride intercalation compound composite was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM), UV-vis absorption spectrum and photoluminescence spectroscopy (PL). The carbon black nanoparticles, homogeneously dispersed on the surface of carbon nitride intercalation compound, efficiently enhanced separation and transport of photogenerated carriers, and thus improving the visible-light photocatalytic activity. The composite of 0.5 wt% carbon black and carbon nitride intercalation compound exhibited a H_2 production rate of 68.9 μmol/h, which is about 3.2 times higher than hydrogen production on pristine carbon nitride intercalation compound.

Introduction

Recently, a metal-free semiconductor, graphite-like carbon nitride (g-C_3N_4) has attracted vast attention. The g-C_3N_4 photocatalyst has an optical band gap of 2.7 eV which can absorb the visible light. More importantly, the conduction band (CB) and valence band (VB) potentials of g-C_3N_4 respectively located at -1.12 and 1.57 eV, which meet the thermodynamic requirement for water splitting.[1] In addition, g-C_3N_4 semiconductor is stable under light irradiation due to the strong covalent bonds between carbon and nitride atoms, indicating that g-C_3N_4 is a promising photocatalyst for application in water splitting as well as organic pollutant degradation.

However, the photoactivity of g-C_3N_4 is low because of the inefficiency in separation and transport of photogenerated carriers and the large optical band gap of 2.7 eV. To overcome the disabilities of g-C_3N_4, a lot of work has been done. Nonmetal or metal elements doping such as S, B, P and Zn were employed to narrow band gap for more light absorption, thus improving the photocatalytic activity.[2,3,4,5] In addition to expand the light absorption, another method to modify the photocatalytic performance of g-C_3N_4 is to enhance the efficiency in separation and transport of photogenerated holes and electrons. In our previous work, coordinating alkali metals into the C–N plane of carbon nitride to form a carbon nitride intercalation compound (CNIC) significantly improved the electrical conductivity of g-C_3N_4, which is beneficial to the separation and transport of the photogenerated carriers.[6] Also, it has been well demonstrated that to build g-C_3N_4-based hybrids with various materials, such as TaON, TiO_2 and graphene,[7,8,9] can promote the separation and transfer of the photogenerated carriers efficiently. Here, we expected to combine a proper material with CNIC to make an efficient photocatalyst for further improvement of photocatalytic activity in solar hydrogen production over carbon nitride.

It has been well known that carbon based materials are quite favourable for enhancing the photocatalytic activity of g-C_3N_4 due to the excellent physical and chemical properties and high affinity with g-C_3N_4. The graphene/g-C_3N_4 composite was prepared by a combined impregnation chemical reduction strategy, exhibited the enhanced visible-light photocatalytic activity.[8] Multi-walled carbon nanotubes modified white g-C_3N_4-H^+Cl^- composite and graphene oxide modified g-C_3N_4 hybrids were prepared, and both showed similar enhancement in visible light photocatalytic performance.[10,11] A common conclusion was given by all these studies that the introduction of the carbon based materials facilitated the separation and transport of photogenerated carriers, and thus enhancing the visible-light photocatalytic activity of g-C_3N_4.

However，the graphene or carbon nanotubes usually have a size scale of several hundred nanometers，which is comparable to the size of g-C_3N_4 host, usually leading to the low interface contact area between the two materials. Furthermore, it is difficult to achieve the uniform distribution of carbon based materials with large size scale on the surface of g-C_3N_4 host. The low contact area and the nonuniform distribution of carbon based materials on surface of g-C_3N_4 usually lead to the inefficient transport of photogenerated carriers from the g-C_3N_4 to carbon materials. To further improve the performance of the g-C_3N_4 composite photocatalyst, a material with uniform distribution on the surface of g-C_3N_4 is expected.

Carbon black is a form of paracrystalline carbon with a high surface area to volume ratio. The particle size of carbon black can be turned from 5 nm to hundreds of nanometers, meaning that it is easy to disperse carbon black with small particle size on the surface of g-C_3N_4 for uniform distribution and large contact area. Herein we report the one-step molten salt synthesis of carbon black/carbon nitride intercalation compound (CNIC) composite photocatalyst by using conductive carbon black and melamine as precursors, and mixture of NaCl, KCl and LiCl as the solvent. The photocatalytic H_2 production experiments exhibited that the carbon black was an excellent candidate for improving photocatalytic activity of carbon nitride intercalation compound.

Experimental Sections

Synthesis and characterizations: All chemicals were reagent-grade and used without further purification, distilled water was used in the whole experiment. Conductive carbon black (HIBLACK 40B2) was provided by Degussa Korea Carbon Black Co. Carbon black/carbon nitride intercalation compound composite catalyst was synthesized through molten salt method

with calcination temperature at 500 °C. 5 g NaCl, 5 g KCl, 5 g LiCl, 1 g melamine and carbon black were put together in the mortar and ground till thoroughly mixed. The weight percentages of carbon black to melamine in the precursors were 0, 0.25, 0.5 and 1.0 wt%, respectively. The resulting carbon black/carbon nitride intercalation compound composite samples were labeled as CC_x, where x = 0, 0.25, 0.5, and 1.0 according to the ratio of carbon black to melamine. The mixture was then heated at 500 °C for 2 hours in semi-closed atmosphere. After that, the product was washed by distilled water several times and then vacuum filtered. Finally, the obtained solid sample was dried at 80 °C for 10 hours.

The as-prepared CC_x composite samples were characterized by x-ray diffractions (XRD) for phase identification on the Rigaku Ultima □ diffractometer and by transmission electron microscope (TEM, FEI Tecnai G2 F30 S-Twin) and field emission scanning electron microscopy (FE-SEM, NOVA230, FEI Ltd.) for microstructural observations. The specific surface area was determined by an adsorption apparatus (Micromeritics TriStar 3000, USA) based on the BET method, calculated from the linear part of the BET plot ranging from P/P_0 = 0.05 to P/P_0 = 0.15. Ultraviolet visible (UV-vis) diffuse reflection spectra were measured using a UV-vis spectrophotometer (Shimadzu UV-2550, Japan) and converted from reflection to absorbance by the Kubelka-Munk method. The bulk conductivity was measured by a standard four probe method under a pressure of 28 MPa. The catalyst powders were pressed into a cylinder with a diameter of 11 mm and height of 10.18 mm. The photoluminescence (PL) spectroscopy was obtained by using the Cary eclipse fluorescence spectrophotometer (USA).

Photocatalytic tests: The photocatalytic reaction under visible light irradiation was carried out in a top-irradiation quartz cell (100 mL). The reaction cell was connected to a closed gas circulation system and the gases evolved were analyzed with an on-line TCD gas chromatograph (GC-8A, Shimadzu, argon carrier). In a typically photocatalytic reaction, 0.1 g of CC_x composite catalyst powder was suspended in 100 mL of aqueous methanol solution (H_2O: CH_3OH = 4:1, in volume). 3 wt% Pt cocatalyst was loaded on the photocatalyst powder by an in situ photodeposition method to promote H_2 production: under light irradiation, an equivalent molar amount of H_2PtCl_6 in solution was reduced to the metallic state and deposited onto the surface of the catalyst, forming the Pt-loaded catalyst. A cutoff filter L42 was used for visible light and a water filter was used to eliminate the temperature effect.

Results and Discussion

The XRD patterns for the as-prepared samples were shown in Fig.1. For the CC_0 sample, the series of diffraction peaks, at 8.3, 12.2, 21.6, 27.7, 32.6 and 36.4° can be assigned to the (*00l*) reflections, suggesting that a carbon nitride intercalation compound was successfully synthesized. Usually, the molten-salt flux is a highly reactive medium, where the mobility of ions in these molten salts is approximately 10^{10} times higher than in the solid state.[12] Therefore, the intercalation structure forms easily during the molten salt heat treatment. The intercalation structure was well demonstrated in our previous report by XPS analysis and theoretical calculations to be the combination of K-Cl-Na.[6] As observed from the XRD patterns, the diffraction peaks of CC_x (x=0.25, 0.5 and 1.0) composite samples are the same with those of pristine CC_0 sample, indicating that carbon black is stable under the heating temperature, that is, there is no direct chemical reaction of melamine with carbon black to occur during thermal treatment. No diffraction peaks of lithium chloride, sodium chloride or potassium chloride were observed in all the carbon black/carbon nitride intercalation compound composite samples, indicating that all the CC_x samples exhibited the single intercalation structure.

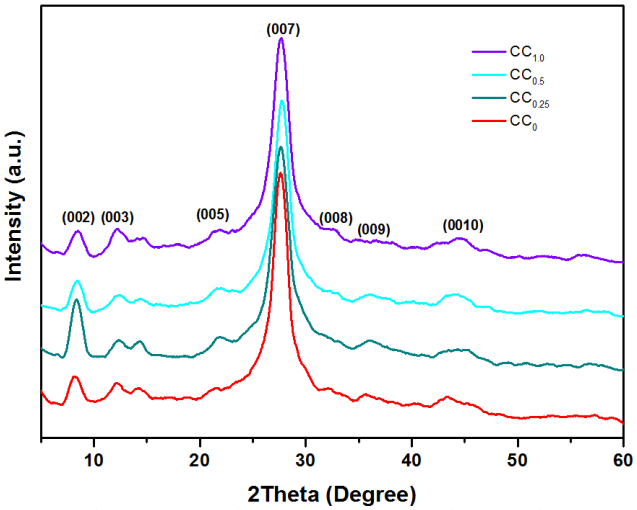


Figure 1. The XRD patterns for CC_x (x=0, 0.25, 0.5, and 1.0) samples.

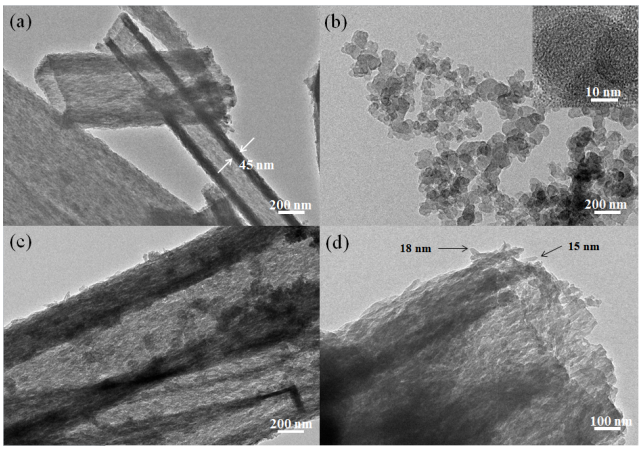


Figure 2. TEM images for CC_0 (a), carbon black (b) and as-prepared $CC_{0.5}$ sample (c, d). Inset of (b) shows the high resolution image for carbon black.

TEM observations were performed to confirm the morphology and microstructure of carbon black and CC_x samples. As shown in Fig. 2a, the pristine CC_0 sample shows the rectangular nanotube morphology. The length of the nanotube reaches as long as several micrometers. And the wall thickness of the nanotube is about 40-50 nm. The carbon black is composed of well-dispersed nanoparticles with diameters about 20-30 nm (Fig. 2b). High-resolution TEM observation indicated no obvious lattice of crystal was observed, further confirming that carbon black is an amorphous carbon material. The morphology of $CC_{0.5}$ sample remains the rectangular nanotube (Fig. 2c), the same as that of CC_0. It can be clearly seen that the carbon black nanoparticles dispersed uniformly on the surface of the wall of C_3N_4 nanotube. From Fig. 2d, it can be observed that the walls of the $CC_{0.5}$ nanotubes exhibited a porous structure, which formed by agglomeration of small C_3N_4 nanoplates. These results confirmed that carbon black as additive does not affect the formation of tubular morphology and porous structure of carbon nitride intercalation compound.

It is interesting to understand the formation of the CC_x nanocube that does not require introducing a template or surfactant molecules. As reported in our previous work,[9] the starting temperature of thermal polycondensation of melamine was determined by differential scanning calorimetry technique to be at 330 °C, which is lower than the melting temperature of mixing salts of NaCl, KCl and LiCl (355 °C). Generally, the crystals of NaCl, KCl and LiCl have cubic morphology. During the heating process, Cl^- on the surface of chloride crystals can react with H^+ in amino functions of melamine, the reaction between Cl^- and amino functions induces the melem forms on the cubic chloride crystals. Subsequently, the mixing salts melt after increasing the temperature over 355 °C and the square profile of the cubic chloride crystals can be maintained during the crystal growth and polymerization of melem. When the temperature rises over 500 °C, the intercalation reaction occurs and carbon nitride intercalation compound nanotubes form.

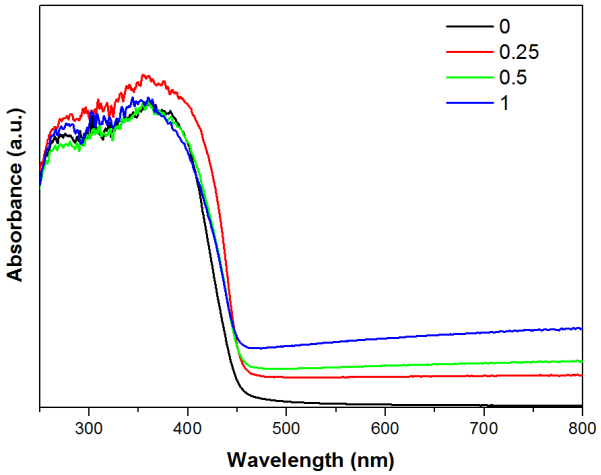


Figure 3. UV-vis absorption spectra of the CC_x (x=0, 0.25, 0.5, and 1.0) samples.

The UV-vis absorption spectra of the CC_x (x=0, 0.25, 0.5, 1.0) samples were measured by UV-vis diffuse reflectance spectroscopy, as shown in Fig. 3. Obviously, the CC_x (x=0.25, 0.5, 1.0) samples show stronger background absorption with increasing carbon black content, which is in agreement with the colour changing from yellow to dark green. The absorption edge for the carbon black coated samples shifts slightly toward longer wavelengths with the increase of conductive carbon black content. The band gaps for the CC_x (x =0, 0.25, 0.5, 1.0) composite samples are estimated to be about 2.68-2.72 eV. The slight difference in band gaps of the CC_x composite samples may be linked to the degree of condensation.[1] Considering that conductive carbon black is a good thermal conductor, different content of conductive carbon black in the sample may result in different thermal conductivity. Thus the samples containing more carbon black were more condensed and exhibited the smaller band gap.

Photocatalytic hydrogen production over various samples loaded with 3 wt% Pt was evaluated under visible-light irradiation (>420 nm) using methanol as the hole scavenger. The CC_0 sample synthesized from melamine without addition of carbon black shows an obvious visible-light photocatalytic activity and the H_2 production reaches an average rate of 16.3μmol/h for 10h light irradiation. As shown in Fig. 4, the photocatalytic hydrogen production is significantly improved by the addition of carbon black in the precursors. Compared to the CC_0 sample, the sample with the addition of 0.25 wt% carbon black exhibits a 2.7 times enhancement in rates of H_2 production. When 0.5 wt% conductive carbon black is added into the precursors, the activity of the final sample increases correspondingly and reaches the acme to be 68.9 μmol/h, 3.2 times higher than that of CC_0 sample. Nevertheless, as carbon content increases further, the activity decreases to be 47.2 μmol/h.

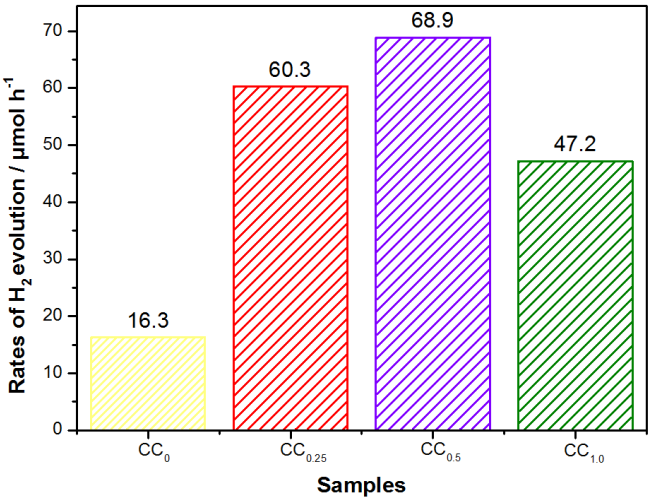


Figure 4. Photocatalytic H_2 production rate for the CC_x (x=0, 0.25, 0.5, and 1.0) samples in methanol aqueous solution under visible-light irradiation.

The BET specific surface areas of carbon black and CC_x samples were investigated by nitrogen adsorption. The BET surface area of carbon black and CC_0 sample is 104.9 and 102.1 m^2/g, respectively. And the BET surface area of carbon black/carbon nitride intercalation compound composite is 104.8 for $CC_{0.25}$, 108.8 for $CC_{0.25}$ and 110.3m^2/g for $CC_{0.25}$, respectively. This indicates that by adding carbon black into the precursors, the surface area of the sample slightly increases. Therefore, the change in photocatalytic activities is not linked with the difference in specific surface area. Comparison experiment was made on pristine carbon black, and it showed no photocatalytic H_2 production activity under visible light irradiation. This indicates that conductive carbon black, which is inactive itself, plays a very important role in enhancing the photocatalytic activity of carbon nitride intercalation compound. The decrease in rate of H_2 production, when the carbon black content is higher than 0.5 wt%, can be attributed to the shielding effect of carbon black. Indeed, the UV-vis absorption spectra for the carbon black coated carbon nitride intercalation compound show the strong background absorption from the blackbody absorption by carbon black (Fig.3). In a contrast test, the H_2 production rate of CC_x sample in triethanolamine (TEOA) solution was evaluated. Similar with the results in methanol solution, $CC_{0.5}$ sample exhibited the higher H_2 production rate than CC_0. In 10 h light irradiation, the average H_2 production rate reached 330 μmol/h for $CC_{0.5}$ sample and 170 μmol/h for CC_0 sample in the TEOA solution, which were much higher than in methanol solution. As is well known, the TEOA is a more excellent electron donor than methanol. During the photocatalytic reaction, it is slightly difficult to provide electron for methanol than TEOA in kinetics.[13] The hole generated on the surface of the catalyst is consumed faster by electron recombination from TEOA than directly to oxidize methanol.

Photoluminescence (PL) analysis is an effective method to investigate the separation efficiency of the photo-generated carriers in a semiconductor because PL emission probably results from the band edge recombination mechanism. Fig. 5 presents the

PL spectrum for pristine CC_0 sample and the $CC_{0.5}$ composite sample with an excitation wavelength of 340 nm. As can be seen from Fig.5, the main emission peak is centred at about 460 nm, which is close to band gap energy of 2.7 eV for carbon nitride intercalation compound, which is indicative of the band edge recombination of electron-hole pairs. Obviously, in comparison with pristine CC_0, the intensity of the PL signal for the $CC_{0.5}$ composite sample is much lower. This indicates that the composite sample has a lower recombination rate of electrons and holes under visible light irradiation. The process can be assumed that the electrons were excited from the valence band to the conduction band and then transferred to carbon black nanoparticles, preventing a direct recombination of electrons and holes. This could be ascribed to that carbon black nanoparticles are good conductor of electricity, thus effectively increasing the separation of photogenerated electron-hole pairs. For more evidences to support the proposed reason for efficient photocatalytic H_2 production over the as-prepared carbon black/carbon nitride intercalation compound, the bulk electrical conductivity was detected by a standard four-probe method, which is easily measurable and usually depending on the carrier transport. The bulk electrical conductivity of $CC_{0.5}$ sample is 2.42 $\times 10^{-7}$ S cm^{-1}, about 2.5 times higher than that of pristine CC_0 (0.684×10^{-7} S cm^{-1}). The higher bulk electrical conductivity facilitates the electron transport, which contributes to the enhancement of photocatalytic activity of carbon nitride intercalation compound.

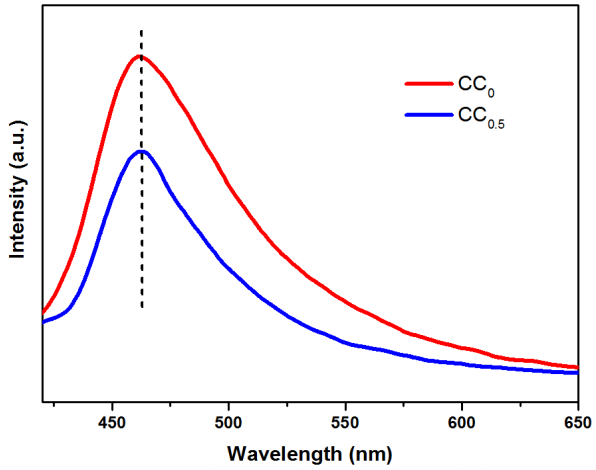


Figure 5. PL spectra for CC_0 and $CC_{0.5}$ samples. Excitation: 340 nm.

Conclusions

In summary, a series of carbon black/ carbon nitride intercalation compound composite photocatalysts have been prepared by heating the mixture of melamine and carbon black in molten salt. The carbon black nanoparticles were homogeneously distributed on the surface of carbon nitride intercalation compound, and acted as conductive channels to efficiently facilitate the separation and transport of the photogenerated charge carriers, thus enhancing the visible-light photocatalytic H_2 production activity of carbon nitride intercalation compound. This study presents that the carbon black modified carbon nitride intercalation compound is a promising high-performance photocatalyst for solar hydrogen production due to the low cost and facile synthesis.

Notes and references

1 X. C. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen and and M. Antonietti, *Nature Mat.,* 2008, **10** , 1038.

2 G. Liu, P. Niu, C. H. Sun, S. C. Smith, Z. G. Chen, G. Q. Lu and H. M. Cheng, *J. Am. Chem. Soc*., 2010, **132**, 11642.

3 S. C. Yan, Z. S. Li, and Z. G. Zou, *Langmuir,* 2010, **26(6)**, 3894.

4 Y. J. Zhang, T. Mori, J. H. Ye and M. Antonietti, *J. Am. Chem. Soc.*, 2010, **132**, 6294.

5 B. Yue, Q. Y. Li, H. Iwai, T. Kako and J. H. Ye, *Sci. Technol. Adv. Mater.*, 2011, **12**, 034401.

6 H. L. Gao, S. C. Yan, J. J. Wang, Y. A. Huang, P. Wang, Z. S. Li and Z. G. Zou, *Phys. Chem. Chem. Phys.*, 2013, **15**, 18077.

7 S. C. Yan, S. B. Lv, Z. S. Li, and Z. G. Zou, *Dalton Trans.*, 2010, **39**, 1488.

8 H. J. Yan and H. X. Yang, *J. Alloy Compd.*, 2011, **509**, 26.

9 Q. J. Xiang, J. G. Yu and M. Jaroniec, *J. Phys. Chem. C*, 2011, **115**, 7355.

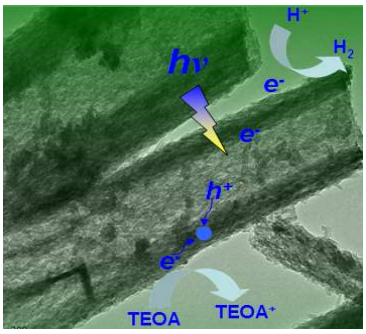
10 Y. G. Xu, H. Xu, L. Wang, J. Yan, H. M. Li, Y. H. Song, L. Y. Huang and G. B. Cai, *Dalton Trans.*, 2013, **42**, 7604.

11 G. Z. Liao, S. Chen, X. Quan, H. T. Yu and H. M. Zhao, *J. Mater. Chem.*, 2012, **22**, 2721.

12 M. S. Dresselhaus and G. Dresselhaus, *Adv. Phys.*, 2002, **51**, 1.

13 M. M. Maitani, C. H. Zhan, D. Mochizuki, E. Suzuki and Y. Wada, *Catal. Sci. Technol.*, 2014, **4**, 871.

Table of contents entry



Carbon black/carbon nitride intercalation compound composite photocatalyst was synthesized by molten salt heating for efficient solar hydrogen production.