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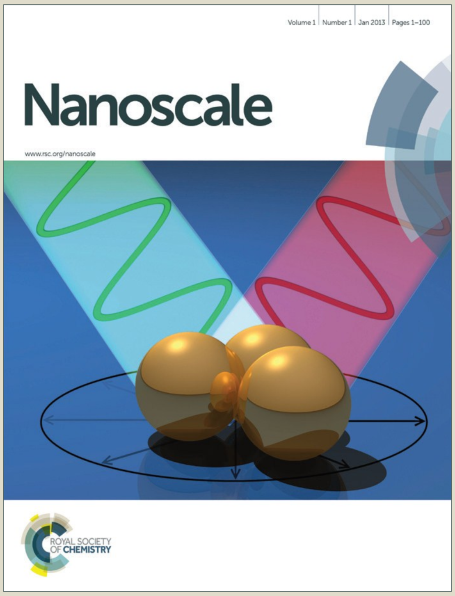

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Journal Name RSCPublishing

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Acid-free and Oxone Oxidant-assisted Solvothermal Synthesis of Graphene Quantum Dots using Various Natural Carbon Materials as Resources

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To prepare carbon-based fluorescence materials such as graphene quantum dots (GQDs), new and effective methods methods are needed to convert one-dimensional (1D) or two-dimensional (2D) carbon materials to 0D GQDs. Here, we report a novel acid-free and oxone oxidant-assisted solvothermal synthesis of GQDs using various natural carbon resources including graphite (G), multiwall carbon nanotube (M), carbon fiber (CF), and charcoal (C). This acid-free method, not requiring the neutralization process of strong acids, exhibits a simple and eco-friendly purification process and also represents a recycling production process, together with mass production and high yield. Newly synthesized GQDs exhibited a strong blue photoluminescence (PL) under 365 nm UV light illumination. The PL emission peaks of all recycled GQDs did not change.

Carbon based materials such as graphite, carbon nanotubes (CNTs), carbon fiber (CF) and coal are attracting attention for future science and technology applications due to their unique electronic, optical, thermal and mechanical properties as well as their chemical stability. In particular, graphene has generated significant interest as a two-dimensional (2D) single atom carbon material because of its large surface area, high carrier mobility, excellent mechanical strength, and superior flexibility.[1-7]

Graphene quantum dots (GQDs) have received tremendous attention in nanoscience and nanotechnology because of their large surface area, low cytotoxicity, excellent solubility and tuneable band gap, that was both theoretically predicted and observed in experimental studies.[8-10] These properties make GQDs attractive for applications in optoelectronics,[11] photovoltaics,[12] bio-imaging[13] and organic light-emitting diodes.[14] GQDs consist of single, double and few- to 10-layer graphene sheets with lateral dimensions less than 100-nm. GQDs show strong quantum confinement because of their edge effect and zero dimensionality (0D) required to induce photoluminescence (PL).[15-17] A variety of methods, such as high resolution electro-beam,[18] microwave irradiation,[19] electrochemical,[20] chemical cutting,[21] and hydrothermal routes[22] have been introduced to synthesize or fabricate GQDs from various carbon-based materials. These materials include graphite or graphene oxide (GO), CNTs, CF, glucose and coal.[5, 23] One-pot solvothermal reduction methods that provide blue luminescent GQDs from GO have recently been reported.[24] However, these methods are limited in that only GO is used as a starting material. Generally, most methods used to prepare GQDs are not direct synthesis routes from graphite but instead require complicated processes wherein GO starting material is exposed to a strong acid.

Recently, Sun et al. reported a facile chemical oxidation method from graphite in a strong acid.[21] Although this method is a direct synthesis route to fabricate GQDs from graphite, it is not a one-pot synthesis. It also requires a strong acid, sulfuric acid. In previous work for the direct synthesis of GQDs, we reported mass production of GQDs by one-pot microwave irradiation from graphite under strongly acidic conditions.[25] Direct synthesis using the chemical cutting method from bulk graphite under a series of strong acids has advantages. However, GQDs purification typically requires Purification also a very long time to ensure acid removal. This purification is complicated and tedious. Purification also includes a neutralization process that requires a strong base, resulting in the formation of a large amount of salt. Therefore, a direct method for synthesizing GQDs from graphite without the use of strong acid oxidants is necessary. A few strategies have been employed recently to solve this problem by potassium intercalation.[26] For example, Suh and co-workers published a description of a direct synthesis of GQDs from graphite by using thermal plasma jet without use of acid condition.

Researchers suggested that these methods can control the size of GQDs.[16] Until now, however, no chemical methods have been developed to directly synthesize GQDs without using a strong acid. Most direct synthesis of GQDs from graphite raw materials uses strongly acidic conditions, such as H_2SO_4 and HNO_3. Graphite and graphite like structures composed of multilayer of grahene sheets stacked by strong π-π interaction. It is difficult to directly convert graphite into nanosized graphene or GQDs. In addition, the direct synthesis of GQDs from raw materials as a carbon fiber and coal without using acid has not been reported. It is desirable to provide an acid-free one-pot direct chemical synthesis method for creating GQDs from natural resources and carbon-based materials such as graphite, MWCNT, CF, and charcoal.

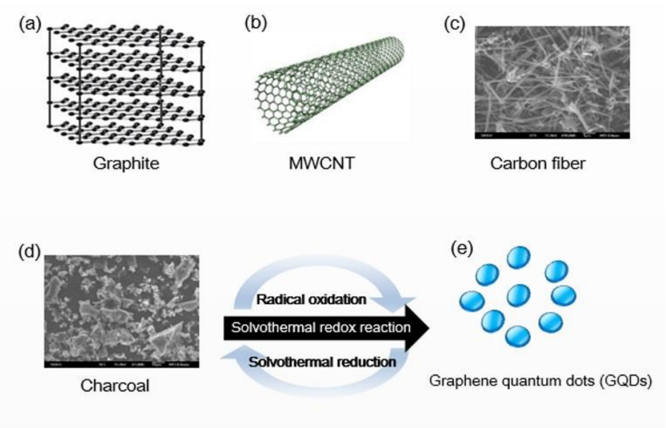

Fig. 1 Schematic representation of GQD preparation by solvothermal redox reaction with an acid-free oxidant, oxone, from four different kinds of carbon sources, including (a) graphite, (b) MWCNTs, (c) CF, and (d) charcoal.

Herein, we report an acid-free method for one-pot direct chemical synthesis of GQDs from all kinds of natural carbon resources using an acid-free oxidant, potassium monopersulfate (also called oxone). The one-pot direct preparation of GQDs was designed using a solvothermal redox reaction method with oxone oxidant for 4 different representative natural resources: graphite (G), MWCNTs (M), CF and charcoal (C). By controlling the redox potential, sulfate radicals ($SO^{\cdot}$-) or hydroxyl radicals ($OH^{\cdot}$) can be generated by oxone.[27] These radicals with solvothermal are responsible of the oxidation-reduction or scission of carbon-carbon bond for acid-free one-pot direct chemical synthesis of GQDs. The mechanism is combination of radical oxidation and solvothermal reduction processes called a solvothermal redox reaction. This reaction can be accelerated by oxone to obtain GQDs by solvothermal redox. Natural carbon materials can be repeatedly broken in a one-pot solvothermal redox reaction using oxone to provide an acid-free reaction for mass production of GQDs. The resulting repeated cycles of oxidation, cleavage, and reduction of natural carbon materials can be turned into very small sized GQDs. GQDs were produced from carbon-based materials as shown in Figure 1, which depicts schematic representations of GQD fabrication from G, M, CF, and C by solvothermal redox reaction with oxone. GQDs were successfully synthesized from the four different carbon based materials using oxone in a one-pot direct chemical synthesis under acid free conditions. These GQDs were randomly broken down during the solvothermal redox reaction. After filtration, the brownish solution of suspended G, M, CF and C became transparent yellowish (Figure S1a-d). However, large GQDs and multilayered GQDs that were not fully broken down were also observed. Thus, the morphologies and fluorescence of the four types of GQDs differ. This method is significantly more straightforward than previous methods in terms of reaction conditions.[24] Furthermore, it also facilitate control of the morphology, size and shape of the GQDs. This one-pot direct solvothermal redox reaction with oxone allows *in situ* rearomatization through carbon-carbon bond formation to produce highly conjugated GQDs in a scalable process suitable for mass production.

Graphite is a well-known carbon-based material consisting of stacks of graphene sheets. Charcoal contains a certain amount of graphite-like stacks of flat graphene sheets (Figure S2a-d). MWCNTs and CF consist of multiple rolled layers of carbon atoms (Figure S2b-c). All of these carbon sources are readily available for the direct preparation of GQDs. A solvothermal redox reaction works best to prepare GQDs from graphite-like flakes or MWCNTs/CF. A large amount of precipitate in each solution of G, M, CF and C remains at the bottom of the reactor. Re-collected G, M, CF and C materials (about 90% w/w) were dried and reused as starting materials after filtration to demonstrate recycling of starting material. After the first solvothermal redox reaction with 10% yield using the re-collected G, M, CF, and C, GQDs were obtained with 6% yield. The PL emission peaks of G-GQDs, M-GQDs, CF-GQDs and C-GQDs did not change, as shown in Figure S3a-d. Since only carbon based materials can be directly exfoliated, the four kinds of recovered carbon-based materials can be recycled repeatedly, resulting in high overall yield compared to other methods. SEM images of the re-collected G, M, CF and C materials show that they retain their original shape, size and structure (Figure S4a-d). This oxone-based method is simple, cost effective, and allows for a non-hazardous purification process that does not require neutralization of strong acid with a strong base.

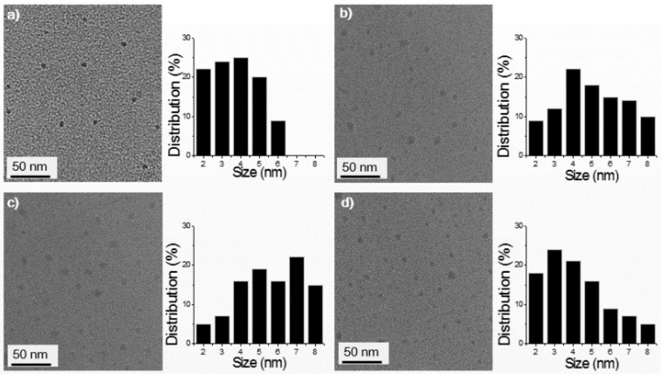

Fig. 2 TEM images of GQDs and size distribution histogram graphs of (a) G-GQDs, (b) M-GQDs, (c) CF-GQDs, and (d) C-GQDs.

Generally, strongly acidic conditions are required to make GQDs from graphite-like flakes or multiple rolled carbon atoms. Strong oxidant agents are often used to prepare graphene oxide, such as H_2SO_4, HNO_3, or H_3PO_4 with $KMnO_4$.[28] However, the use of the strong acids requires the neutralization with a large amount strong base, NaOH, until pH of 7 is obtained. This separation process to obtain pure GQDs is really tedious and time-consuming. Table S1 shows a comparison of acid-assisted and acid-free GQDs methods using raw materials including a graphite, multiwall carbon nanotube, carbon fiber and charcoal. Thus, the use of oxone as an oxidant provides an eco-friendly and cost-effective method for the preparation of GQDs by one-pot direct solvothermal redox reaction of G, M, CF, and C raw materials. High-resolution transmission electron microscopy (HR-TEM) images in Figure 2a-d, show that G-GQDs, M-GQDs, CF-GQDs and C-GQDs are fairly uniform with size distributions of 2-8 nm. Large carbon dots (>20 nm) with about 10% yield. The clear atomic lattice structure of G-GQDs, M-GQDs, CF-GQDs, and C-GQDs exhibit a lattice spacing of 0.25 nm that corresponds to the crystal state, showing many crystalline domains highlighted with circles in Figure S5a-d. The topographic images obtained from a typical tapping mode AFM demonstrated that G-GQDs, M-GQDs and CF-GQDs consisted of 1-3 graphene layers. For C-GQDs, several-layer GQDs (>10 nm) that were not fully cut were observed (Figure S6a-d).

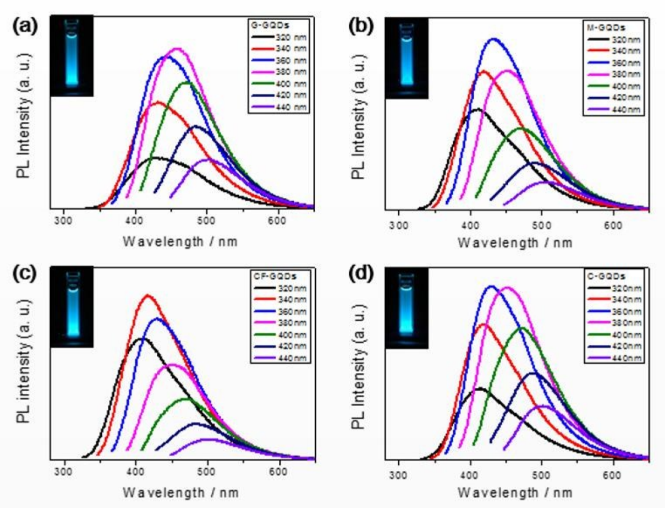

Fig. 3 PL spectra of (a) G-GQDs, (b) M-GQDs, (c) CF-GQDs, and (d) C-GQDs measured at different excitation wavelengths from 320 to 440 nm (inset: photographs of each GQDs solution showing blue fluorescence under UV light at a 365 nm excitation wavelength).

To analyze the photophysical properties of GQDs, UV-visible absorption and photoluminescence (PL) spectral analyses of G-GQDs, M-GQDs, CF-GQDs and C-GQDs diluted in deionized (DI) water were investigated. Typical absorption peaks of G-GQDs, M-GQDs, CF-GQDs and C-GQDs were observed around 267 nm in the UV-vis spectra due to the $\pi \rightarrow \pi^*$ transition of aromatic sp^2 domains, which correspond to chemically reduced GO (Figure S7a-d).[29] According to previous reports, the absorption peak position depends on the synthesis method rather than the size or shapes of GQDs or carbon quantum dots (CQDs).[12, 30] The insets in Figure 3a-d show optical images of the various GQDs, exhibiting blue luminescence under 365 nm UV light illumination. The PL spectra of the various GQDs exhibited shifts in emission peaks with a change in excitation from 320 to 440 nm, demonstrating that all PL emission peaks were dependent on the excitation wavelength. Strong PL emission peaks were observed for G-GQDs and CF-GQDs at 420 nm when excited at 340 nm. Similarly, strong PL emission peaks of M-GQDs and C-GQDs were observed at 430 nm when these were excited at 360 nm.

The correct PL excitation (PLE) spectrum for G-GQDs, M-GQDs, CF-GQDs and C-GQDs was confirmed (Figure S8a-d). Blue emission was attributed to the zigzag effect with a carbene-like triplet ground state $\sigma^1\pi^1$.[21, 26] The photophysical properties of GQDs are affected by a combination of factors including their size, shape, synthesis methods and functionalization.[23, 31, 32] Table S2 indicates the quantum yields (QYs) of G-GQDs, M-GQDs, CF-GQDs and C-GQDs by using Rhodamine B such as reference. The improvement of QYs and yields of GQDs is an important factors for potential applications in bio-imaging source and electrolyte-free electrochromic display.[31, 33] For example, shen *et al*. reported a simple approach for enhancing the QYs of GQDs surface-passivated using polyethylene glycol (PEG). Researcher indicates that QYs of GQDs-PEG was about 28.0 %, which was two times higher than that of pure GQDs.[34] Time-resolved PL spectroscopy demonstrates that the average PL lifetime of G-GQDs, M-GQDs, CF-GQDs and C-GQDs was shortened from 2.94 ns, 3.14 ns, 3.13 ns and 3.4 ns, respectively (Figure S9a-d).

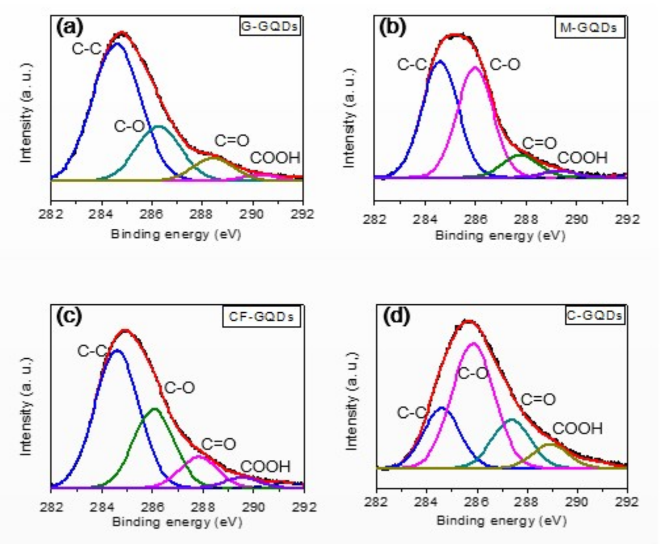

Fig. 4 High resolution XPS spectra of C1s of (a) G-GQDs, (b) M-GQDs, (c) CF-GQDs, and (d) C-GQDs by solvothermal redox reaction with an acid-free oxidant, oxone.

X-ray photoelectron spectroscopy (XPS) was adopted to measure the elemental composition of GQDs. XPS survey spectra for various GQDs showed a predominant C1s peak at 248.8 eV and an O1s peak at 532 eV (Figure S10a-d). Figure 4a-d shows high-resolution XPS spectra of C1s, confirming that carbon components were completely changed to G-GQDs, M-GQDs, CF-GQDs and C-GQDs from G, M, CF and C, respectively. FT-IR also shows the surface functional groups of G-GQDs, M-GQDs, CF-GQDs and C-GQDs (Figure S11a-d). The functional groups on the various GQDs included hydroxyl, graphitic carbon, ether, and carboxylic acid groups based on C=C, C-O, and COOH peaks.

Micro-Raman spectra shown in Figure S12a-d for G-GQDs, M-GQDs, CF-GQDs and C-GQDs samples prepared by a spin casting on Si wafers. The G band peaks of the GQDs at 1590 cm^{-1} are related to the E2g vibrational mode of aromatic domains in the two-dimensional hexagonal lattice structure. The D peaks appeared at 1370 cm^{-1}, providing I_D/I_G ratios of ~0.94, ~0.97, ~0.93 and ~0.96 for G-GQDs, M-GQDs, CF-GQDs and C-GQDs, respectively. Large

I_D/I_G ratios for GQDs prepared by hydrothermal methods have also been observed.[22]

Conclusions

We successfully developed an acid-free one-pot direct chemical synthesis of GQDs from 4 different kinds of carbon (graphite, MWCNT, CF, and charcoal) using a neutral oxidant, oxone. The solvothermal redox method allows oxidative cleavage of all carbon based starting materials and in-situ re-aromatization. To the best of our knowledge, this is the first time that GQDs have been mass produced directly from graphite, MWCNTs, CF and charcoal with an acid-free one-pot direct solvothermal redox method. One of the primary advantages of this method is the simple purification process used to obtain pure GQDs by introducing a neutral oxone oxidant. This process does not require the removal of a large amount salt formed from neutralization of a strong acid. This simple purification method allows repeated solvothermal GQDs production processes using re-collected starting materials, leading to mass production and high yield compared with other methods. The newly synthesized G-GQDs, M-GQDs, CF-GQDs and C-GQDs exhibited a strong blue luminescence, indicating their full re-aromatization. This acid-free one-pot solvothermal redox reaction method should be easily applied to industrial manufacturing using carbon based materials due to its simple purification and mass production capability.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIP) (Grant No. 2006-0050684).

Notes and references

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1 U. N. Maiti, W. J. Lee, J. M. Lee, Y. Oh, J. Y. Kim, J. E. Kim, J. Shim, T. H. Han and S. O. Kim, *Adv. Mater*. 2013, **26**, 40-67.
2 A. K. Geim and K. S. Novoselov, *Nat. Materials*. 2007, **6**, 183-191
3 J. Lu, P. S. Emmeline Yeo, C. K. Gan, P. Wu and K. Loh, *Nat. Nanotechnol.* 2011, **6**, 247-252.
4 X. Cao, Q. He, W. Shi, B. Li, Z. Zeng, Y. Shi, Q. Yan and H. Zhang, *Small*. 2011, **9**, 1199-1202.
5 R. Ye, C. Xiang, J. Lin, Z. Peng, K. Huang, Z. Yan, N. P. Cook, E. L. G. Samuel, C. C. Hwang, G. Ruan, G. Ceriotti, A. R. O. Raji, A. A. Marti and J. M. Tour, *Nat. Commun*. 2013, **4**, 2943.
6 J. Peng, W. Gao, B. K. Gupta, Z. Liu, R. Romero-Aburto, L. Ge, L. Song, L. B. Alemany, X. Zhan, G. Gao, S. A. Vithayathil, B. A. Kaipparettu, A. A. Marti, T. Hayashi, J.J. Zhu and P. M. Ajayan, *Nano Lett*. 2012, **12**, 844-849.
7 F. Liu, M. H. Jang, H. D. Ha, J. H. Kim, Y. H. Cho and T. S. Seo, *Adv. Mater.* 2013, **25**, 3657-3662.
8 S. Kim, S. W. Hwang, M. K. Kim, D. Y. Shin, C. O. Kim, S. B. Yang, J.H. Park, E. Hwang, S. H. Choi, G. W. Ko, S. H. Sim, C. S. Sone, H. J. CHoi, S. K. Bae and B. H. Hong, *ACS Nano*. 2012, **6**, 8203-8208.
9 Y. Li, Y. Zhao, H. Cheng, Y. Hu, G. Shi, L. Dai and L. Qu, *J. Am. Chem. Soc*. 2012, **134**, 15-18.
10 L. Wang, S. J. Zhu, H. Y. Wang, S. N. Qu, Y. L. Zhang, Q. D. Chen, H. L. Xu, W. Han, B. Yang and H. B. Sun, *ACS Nano*. 2014, **8**, 2541-2547.
11 V. Gupta, N. Chaudhary, R. Srivastava, G. D. Sharma, R. Bhardwaj and S. Chand, *J. Am. Chem. Soc*. 2011, **133**, 9960-9963.
12 H. Li, X. He, Z. Kang, H. Huang, Y. Liu, J. Liu, S. Lian, C. H. A. Tsang, X. Yang and S. T. Lee, *Angew. Chem. Int. Ed*. 2010, **49**, 4430-4434.
13 X. Zhai, P. Zhang, C. Liu, T. Bai, W. Li, L. Dai and W. Liu, *Chem. Commun*. 2012, **48**, 7955-7957.
14 W. Kwon, Y. H. Kim, C. L. Lee, M. Lee, H. C. Choi, T. W. Lee and S. W. Rhee, 20 *Nano Letters*. 2014, **14**, 1306-1311.
15 L. Tang, R. Ji, X. Cao, J. Lin, H. Jiang, X. Li, K. S. Teng, C. M. Luk, S. Zeng, J. Hao and S. P. Lau, *ACS Nano*. 2012, **6**, 5102-5110.
16 J. Kim and J. S. Suh, *ACS Nano*. 2014, **8**, 4190-4196.
17 J. Moon, J. An, U. Sim, S. P. Cho, J. H. Kang, C. Chung, J. H. Seo, J. Lee, K. T. Nam and B. H. Hong, *Adv. Mater*. 2014, **26**, 3501-3505.
18 L. A. Ponomarenko, F. Schedin, M. I. Katsnelson, R. Yang, E. W. Hill, K. S. Novoselov and A. K. Geim, *Science*. 2008, **320**, 356-358.
19 L. L. Li, J Ji, R. Fei, C. Z. Wang, Q. Lu, J. R. Zhang, L. P. Jing and J. J. Zhu, *Adv. Funct. Mater*. 2012, **22**, 2971-2979.
20 Y. Li, Y. Hu, Y. Zhao, G. Shi, L. Deng, Y. Hou and L. Qu, *Adv. Mater*. 2011, **23**, 776-780.
21 Y. Sun, S. Wang, C. Li, P. Luo, L. Tao, Y. Wei and G. Shi, *Phys. Chem. Chem. Phys.* 2013, **15**, 9907-9913.
22 B. D. Pan, J. Zhang, Z. Li and M. Wu, *Adv. Mater*. 2010, **22**, 734-738.
23 Z. Zhang, J. Zhang, N. Chen and L. Qu, *Energy Environ. Sci*. 2012, **5**, 8869-8890.
24 S. Zhu, J. Zhang, C. Qiao, S. Tang, Y. Li, W. Yuan, B. Li, L. Tian, F. Liu, R. Hu, H. Gao, H. Wei, H. Zhang, H. Sun and B. Yang, *Chem. Commun*. 2011, **47**, 6858-6860.
25 Y. Shin, J. Lee, J. Yang, J. Park, K. Lee, S. Kim, Y. Park, and H. Lee, *Small*. 2014**, 5**, 866-870.
26 L. Lin and S. Zhang, *Chem. Commun*, 2012, **48**, 10177
27 I. Grcic, S. Papic, N. Koprivanac and I. Kovacic. *Water Research*. 2012, **46**, 5683-5695
28 D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slexander, L. B. Alemany, W. Lu and J. M. Tour, *ACS Nano*. 2010, **4**, 4806-4814.
29 I. K. Moon, J. Lee, R. S. Ruoff and H. Lee, *Nat. Commun.* 2010, **1**, 73.

30 H. Tetsuka, R. Asahi, A. Nagoya, K. Okamoto, I. Tajima, R. Ohta and A. Okamoto, *Adv. Mater*. 2012, **24**, 5333-5338.

31 L. Li, G. Wu, G. Yang, J. Peng, J. Zhao and J. J. Zhu, *Nanoscale.* 2013, **5**, 4015-4039.

32 X. Zhou, S. Guo and J. Zhang, *ChemPhysChem*. 2013, **14**, 2627-2640.

33 E. Hwang, S. Seo, S. Bak, H. Lee, M. Min and H. Lee, *Adv. Mater*. 2014, **26**, 5129-5136.

34 J. Shen, Y. Zhu, X. Yang, J. Zong, J. Zhang and C. Li, *New J. Chem.* 2012, **36**, 97-101.