

Studies on synthesis and Reduction of Graphene Oxide from Natural Graphite by using Chemical Method

L. M. Manocha*, Hasmukh Gajera and S. Manocha

Department of Materials Science, Sardar Patel University, Vallabh Vidyanagar, Gujarat – 388120, India

Abstract

Graphene is a material with rapidly growing interest. It consists of flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice and is basic building block for all graphitic materials. Interest in Graphene is because of its excellent mechanical, electrical, thermal, optical properties and its very high specific surface area. Studies have been performed on wet oxidation of natural graphite by using Modified Hummers Method followed by exfoliation and reduction in order to synthesise graphene from Graphite Oxide (GO). Acid route has been followed for oxidation whereas reduction has been carried out in water with hydrazine hydrate and Sodium Borohydrate. It results in to a material with characteristics that are comparable to those of pristine graphite. The reaction at every step has been characterized by using FTIR, TGA, XRD, Raman spectroscopy and surface area measurement.

Introduction

Graphene is the name given to a fl at monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice, and is a basic building block for graphitic materials of all other dimensionalities (Fig. 1). It can be wrapped up into 0D fullerenes, rolled into 1D nanotubes or stacked into 3D graphite [1]. It has a large theoretical specific surface area ($2630 \text{ m}^2\text{g}^{-1}$), high intrinsic mobility ($200\,000 \text{ cm}^2\text{v}^{-1}\text{s}^{-1}$), high Young's modulus ($\sim 1.0 \text{ TPa}$) and thermal conductivity ($\sim 5000 \text{ W m}^{-1}\text{K}^{-1}$), and its optical transmittance ($\sim 97.7\%$) and good electrical conductivity for various applications such as for transparent conductive electrodes [2,3], as well as many other potential applications in thermal management and mechanical fields.

Graphene has been studied for over 40 years, specially measurements of transport properties in micromechanically exfoliated layers of graphene [4] as well as a variety of studies involving the use of chemically modified graphene (CMG) to make new materials [5-7]. Graphite oxide (GO) offers potential for the production of CMG on the ton scale [8]. First prepared almost 150 years ago [9], GO has emerged as a precursor offering the potential of cost-effective, large-scale production of graphene-based materials

[7]. In general, GO is synthesized by either Brodie [9], Staudenmaier [10]. Hummers method [11] or some variation of these methods. All three methods involve oxidation of graphite to various levels.

GO is homogeneously dispersed in water due to the oxygen functional groups and it can be exfoliated in water and other solvents. The Sonication and Thermal treatment are used for exfoliation purpose. By nature, GO is electrically insulating and thus cannot be used without further processing as conducting nanomaterial [12]. In addition, the presence of oxygen functional groups make GO thermally unstable [13].

To that end, we have examined the Oxidation of Graphite and Chemical reduction of exfoliated graphene Oxide sheets with Hydrazine hydrate and Sodium Borohydrate and carried out comprehensive studies on this material using TGA, FTIR, Raman Spectroscopy, XRD and Surface area measurement. The experimental results are reported in this paper.

Experimental

Synthesis of Graphite Oxide

GO was synthesized from natural graphite powder ($400 \mu\text{m}$) by modified Hummers Method [14]. The Graphite powder (10 gm) was put into a solution of concentrated H_2SO_4 (360 ml), P_2O_5 (10 gm) and $\text{K}_2\text{S}_2\text{O}_8$ (10 gm) at 80°C . The resultant dark

*corresponding author. E-mail: manocha52@rediffmail.com

blue mixture was stirred constantly over a period of 6 h and allowed to cool to room temperature. The mixture then carefully diluted with distilled water, filtered and washed on the filter until the rinse water pH became neutral. The product was dried in air at room temperature overnight. This pre oxidized graphite was then subjected to oxidation by Hummers method [11].

This pre oxidized powder (10 gm) was put into cold (0°C) concentrated H₂SO₄ (360 ml). KMnO₄ (45 gm) was added gradually with stirring and cooling, so that the temperature of the mixture was not allowed to reach 20°C. The mixture was then stirred at room temperature (30°C) for 24 h. The mixture was then carefully diluted with distilled water and H₂O₂ (30 ml) was added, after which the color of mixture got changed to bright yellow. The mixture was centrifuge and washed to remove acid and other reactants, to give a viscous, brown dispersion of GO in water, which is stable for a period of months and was used to prepare exfoliated GO.

Exfoliation of Graphite Oxide

Exfoliation was achieved by dilution of the GO dispersion with distilled water (1 mg : 1 ml), followed by Sonication (30 min). The thermal exfoliation was achieved by rapidly heating of dried GO in a furnace. The dried GO was loaded in a quartz boat, which was then inserted into a 50 cm long quartz tube with inner diameter 35 mm. The nitrogen gas was flushed in the quartz tube for 10 min. After that quartz tube was rapidly inserted in to the middle heating zone of the furnace which was already heated between

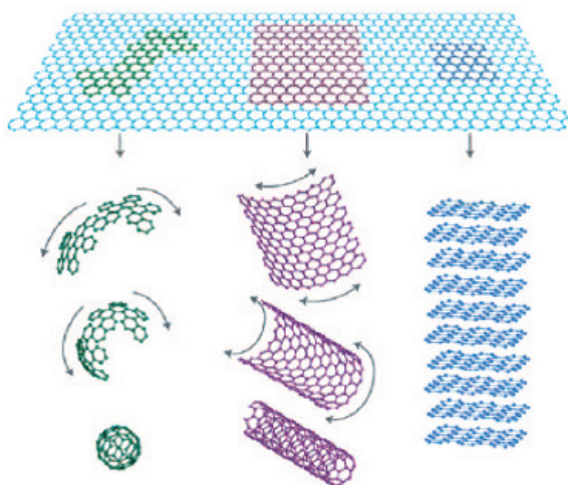


Fig. 1. Schematic diagram of Graphene as a Mother of all graphitic forms

220-250 °C. The quartz tube was kept for 30 sec and quickly removed from the heating zone.

Reduction of Graphene Oxide

The chemical reduction of GO was done by using Hydrazine hydrate and Sodium Borohydrate. In both cases, GO (150 mg) was loaded in 250 ml flask to which 150 ml distilled water was added. This solution was sonicated by using ultrasonic bath cleaner until it became clear without any visible particulate matter in solution to obtain homogeneous dispersion of exfoliated GO (graphene oxide) in water.

In first case, Hydrazine hydrate (1.5 ml) was added in above dispersion and heated at 100°C in oil bath for 24 h. In second case, Sodium Borohydrate (800 mg) was added in GO dispersion and heated at 80 °C in oil bath for 4 h. The reduced GO (r-GO) gradually precipitated out as a black solid mass on surface. This product was isolated by filtration and was with distilled water until the rinse water pH became neutral and dried at 100 °C in oven for 3 h.

Characterization

Thermogravimetric analysis (TGA) was performed on samples to determine the extent of oxidation and reduction process of graphite. TGA was performed under nitrogen flow (100 to 200 ml/min) using TA instrument TGA-SDTA851 (Mettler Toledo) on sample sizes from 5 to 7 mg and the mass was recorded as a function of temperature. SHIMDZU 8300 FTIR spectrometer was used to

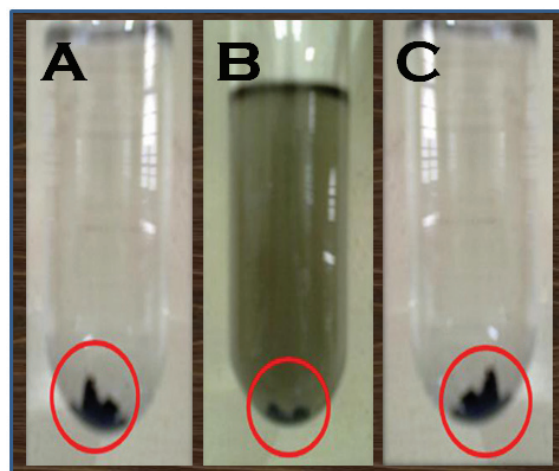


Fig.2. Photographs of r-GO in water A), in DMF B), in THF C)

study the type of chemical groups present in GO and r-GO and sample was prepared by mixing of weighted sample with KBr powder to make pellets. The surface area measurement of graphite oxide and reduced graphene oxide was done by using Methylene blue method. Raman scattering is a fast and non destructive technique for characterization of Graphite samples. The Raman spectra measurements were performed at room temperature with a Renishaw Raman Spectrometer at 785 nm laser with 50× objective. XRD analysis of starting graphite and graphite oxide was performed using XRD Diffractometer (powder) Philips Xpert with Cu K α radiation.

Results and Discussion

Reduction of exfoliated GO

During the reduction process of graphene oxide sheets dispersed in water, the brown-colored dispersion turned black and the reduced sheets aggregate and eventually precipitate.

The precipitation of the reduced sheets occurs, result of oxygen removal and thus increased incompatibility with the aqueous medium. As dissolution of the reduced sheets decreases, the inter sheet hydrophobic interactions cause them to aggregate as well as adhere to the hydrophobic surface. The main purpose of reduction of EGO was to obtain graphene from the graphene oxide. All of our attempts to redisperse them in water and other solvents such as DMF and THF were failed as seen in Fig. 2 respectively.

Thermalgravimetric Analysis

After oxidation of Graphite, the graphite oxide is thermally unstable and during heating weight loss of GO starts. There were two regions in which the weight loss was observed. The first weight loss was observed below and at 100 °C due to presence of water in GO and second weight loss was observed near 200 °C, which is due to oxygen functional groups. These functional groups were introduced during the oxidation of natural graphite. There was 34% weight loss was observed in GO at near 220 °C indicate removal of oxygen function groups.

TGA curve of r-GO SBH shows 15% weight loss at 203 °C which is smaller as compared to the GO curve. It means reduction of GO was not completed in case of Sodium Borohydrate. In case of Hydrazine hydrate, no weight loss was observed during TGA analysis. It means that reduction was completed and mostly oxygen functional groups got removed after reaction.

FT – IR Analysis

Fig. 4 shows FTIR spectra of GO, r-GO SBH and r-GO HH. Graphene oxide exhibits the following characteristic IR features. Strong band is observed at ~ 3440 cm^{-1} which is attributed to the hydroxyl stretching vibrations of the C-OH groups, doublet near ~ 2925 cm^{-1} and ~ 2855 cm^{-1} attributed to the CH₂ or CH₃ groups, a weak peak between 1720 - 1740 cm^{-1} assigned to the C=O stretching vibrations of the-COOH groups, a peak between 1590 – 1620 cm^{-1} assigned to C=C from unoxidized sp² CC

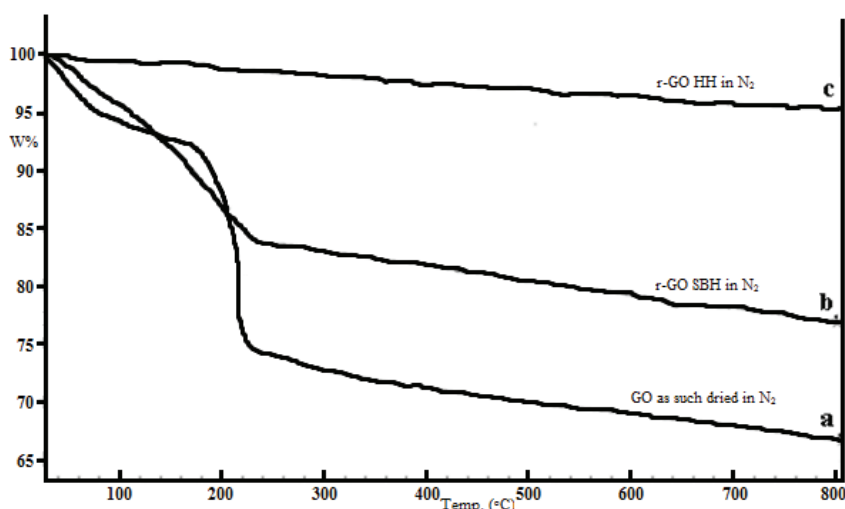


Fig..3. TGA curves - a. GO as such, b. r-GO SBH, c. r-GO HH

bonds, a weak peak at 1396 cm^{-1} assigned to the O-H deformations of the C-OH groups, and a strong band at $1050 - 1095\text{ cm}^{-1}$ attributed to C-O stretching vibrations.

The absence of peaks at 2925 cm^{-1} , 2855 cm^{-1} , $1720-1740\text{ cm}^{-1}$ and weak peak at 1060 cm^{-1} indicate that the alkyl, carboxylic and ester groups attached to the graphene layer have been removed during reduction of GO. Figure 4.b shows more function groups removal as compare to 4.c.

Surface area measurement

Surface area measurement of the exfoliated GO sheets and reduced GO sheets via methylene blue adsorption yielded a surface area value of $1155\text{ m}^2/\text{g}$ and $535\text{ m}^2/\text{g}$ respectively. This high specific surface area is partially an indication of the degree of GO exfoliation. However, it is still lower than the theoretical specific surface area for completely exfoliated and isolated graphene sheets ($2,620\text{ m}^2/\text{g}$). After reduction of Graphene oxide the surface area of r-GO was $535\text{ m}^2/\text{g}$. This is due to the agglomeration of the graphene oxide sheets. This agglomeration can result in the partial overlapping and coalescing of the reduced sheets and lowering the surface area.

Raman spectroscopic study

The significant structural changes occurring during the chemical processing from pristine

graphite to GO, and then to the reduced GO, are also reflected in their Raman spectra. Raman spectroscopy has been used to probe structural and electronic characteristics of graphite materials, providing useful information on the defects (D-band), in plan vibration of sp^2 carbon atoms (G-band) as well as the stacking orders (2D-band). The G band of graphite materials is a doubly degenerate (TO & LO) phonon mode (E_{2g} symmetry) at the Brillouin zone.¹⁵

The Raman spectrum of the pristine graphite, as expected, displays a prominent G band as only feature at 1584.01 cm^{-1} , corresponding to the first order scattering of the E_{2g} mode. In the Raman spectrum of GO, the G band is broadened and shifted to 1604.8 cm^{-1} . In addition, the D band at 1373.28 cm^{-1} became prominent, indicating the reduction in size of the in-plane sp^2 domains as compared to pristine graphite possibly due to the extensive oxidation of graphite. The Raman spectra of reduced GO also contain both G and D bands (1589.3 cm^{-1} and 1371.2 cm^{-1} respectively), however with an increased D/G intensity ratio compared to that in GO. This change suggests decrease in the average size of sp^2 domains upon reduction of the exfoliated GO.¹⁵

XRD study

Figure 6 shows powder XRD results of graphite, Graphite Oxide and 2 h stirred Graphite Oxide. Row graphite showed very strong peak at 26.5° (Fig. 6a) which gives the value of inter layer distance (d-spacing 3.4 \AA). However, after oxidation graphitic

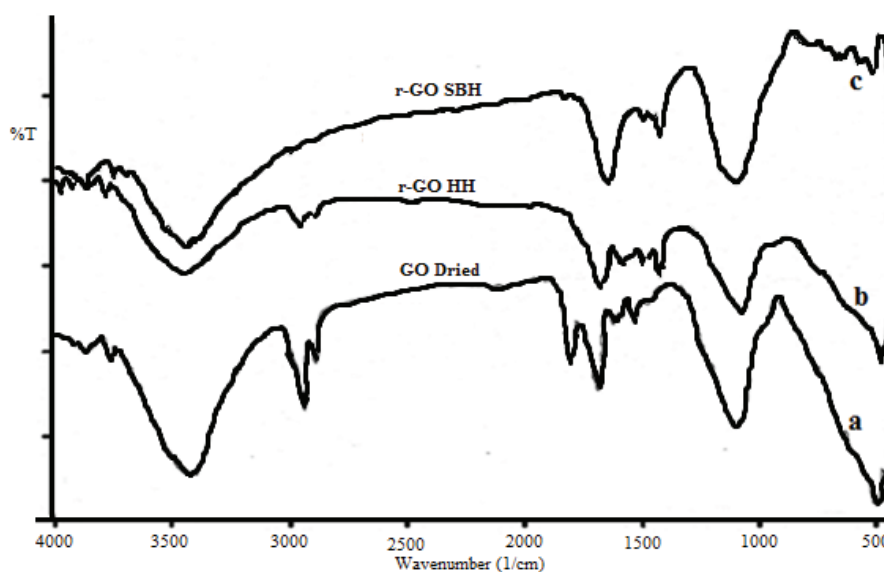


Fig.4. FTIR spectra a. GO as such, b. r-GO HH, c. r-GO SBH

peak disappeared and new peak appeared at 10.43° with d-spacing of 8.48 Å which is larger than inter layer distance of starting graphite. Because the presence of oxygen functional groups attached on both sides of graphene sheet during oxidation reaction, individual graphene oxide sheets are thicker than individual pristine graphene sheet.¹⁶

XRD result of GO 2 h showed that the XRD peak was shifted to 10.25° from 10.48° after 2 h mechanical stirring of graphite oxide. This mechanical stirring will be used for exfoliation of GO to graphene oxide. After 2 h stirring the inter layer distance of GO got increased up to 8.63 Å which is much larger than inter layer distance of starting natural graphite flakes.

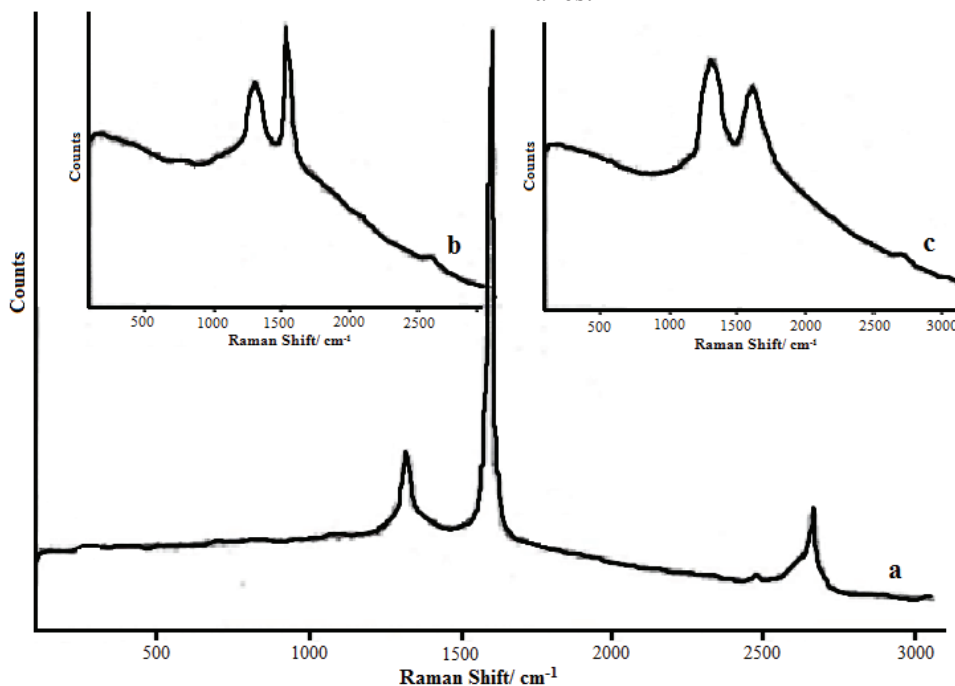


Fig.5. Raman spectra of a. Graphite, b. GO, c. r-GO HH

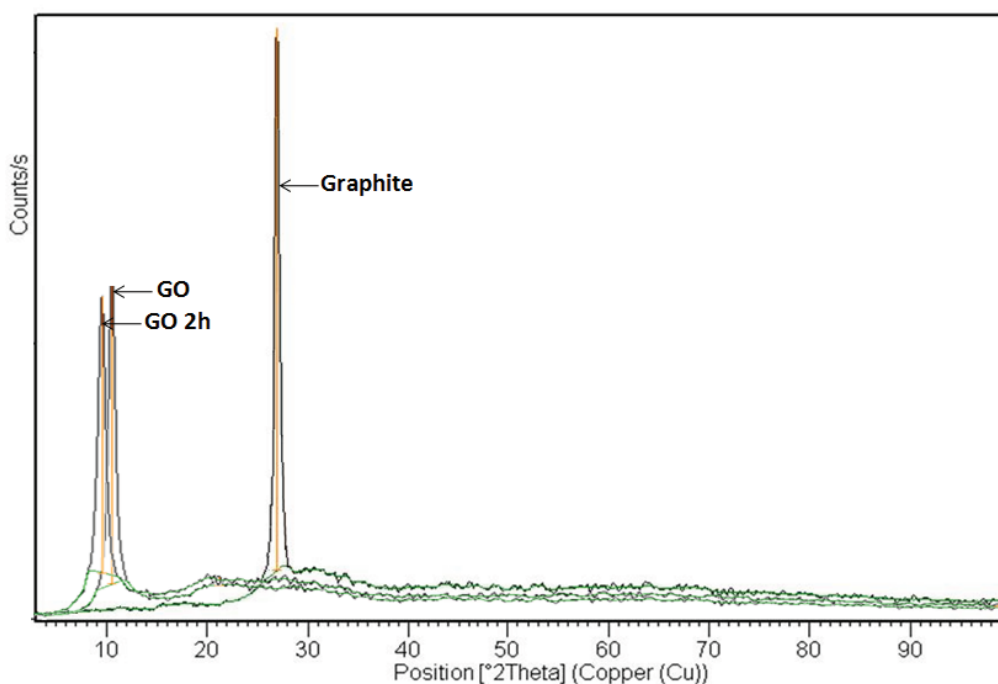


Fig.6. XRD of a. Graphite, b. GO, c. GO 2h

Conclusion

Synthesis of Graphene via 'Chemical routes' may be able to produce fairly large amounts in cost effective manner. In reduction process, the majority of oxygen containing functional groups are removed and reduction of exfoliated graphene oxide results in a material with graphitic characteristics. On the nanoscale, this material consist of thin graphene sheets and possesses a high specific surface area. This reduced graphene oxide sheets may find use in a variety of applications such as electrically conducting filler in nanocomposites, energy storage as well as hydrogen storage.

Acknowledgement

The authors wish to thank UGC for the financial assistance provided under "UGC research fellowship for Meritorious Students Scheme". Also thanks to Sophisticated Instrumentation Centre for Applied and Research Testing for providing testing facilities.

References

1. A. K. Geim, K. S. Novoselov, Nat. Mater. 2007, 6, 183
2. W. Cai, Y. Zhu, X. Li, R. D. Piner, R.S. Ruoff, Appl. Phys. Lett. 2009, 95, 123115
3. X. Li, Y. Zhu, W. Cai, M. Borysiak, B. Han, D. Chen, R. D. Piner, L. Colombo, R. S. Ruoff, Nano Lett. 2009, 9, 4359
4. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, Science 2004, 306, 666
5. S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R.D. Piner, S. T. Nguyen, R. S. Ruoff, Nature 2006, 442, 282
6. S. Watcharotone, D. A. Dikin, S. Stankovich, R. Piner, I. Jung, G. H. B. Dommett, G. Evmenenko, S. E. Wu, S. F. Chen, C. P. Liu, S. T. Nguyen, R. S. Ruoff, Nano Lett. 2007, 7, 1888.
7. S. Park, R. S. Ruoff, Nat. Nanotechnol. 2009, 4, 217
8. M. Segal, Nat. Nano 2009, 4, 612
9. B. C. Brodie, Ann. Chim. Phys. 1860, 59, 466
10. L. Staudenmaier, Ber. Deut. Chem. Ges. 1898, 31, 1481
11. W. S. Hummers, R. E. Offeman, J. Am. Chem. Soc. 1958, 80, 1339
12. S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, R. S. Ruoff, Carbon 2007, 45, 1558
13. H. K. Jeong, Y. P. Lee, M. H. Jin, E. S. Kim, J. J. Bae, Y. H. Lee, Chem. Phys. Lett. 2009, 470, 255
14. N. I. Kovtyukhova, P. J. Ollivier, B. R. Martin, T. E. Mallouk, S. A. Chizhik, E. V. Buzaneva, A. D. Gorchinskiy, Chem. Mater, 1999, 11, 771
15. F. Tuinstra, J. L. Koenig, J. Chem. Phys. 1970, 53, 1126
16. J. Shen, Y. Hu, M. Shi, X. Lu, C. Qin, C. Li, M. Ye Chem. Mater, 2009, 21, 3514

Received 22 June 2010.