

Thiolated graphene – a new platform for anchoring CdSe quantum dots for hybrid heterostructures†

Cite this: *Nanoscale*, 2013, 5, 3615

Joyashish Debgupta^a and Vijayamohanan K. Pillai^{*b}

Received 21st January 2013

Accepted 3rd March 2013

DOI: 10.1039/c3nr00363a

www.rsc.org/nanoscale

Effective organization of small CdSe quantum dots on graphene sheets has been achieved by a simple solution exchange with thiol terminated graphene prepared by diazonium salt chemistry. This generic methodology of CdSe QD attachment to any graphene surface has remarkable implications in designing hybrid heterostructures.

Graphene, the ideal one atom thick 2D carbon sheet, has drawn considerable attention in recent times owing to its unique properties such as high conductivity, room temperature quantum Hall effect, availability of Dirac fermions,¹ ballistic transport over a large area and moreover its high tensile strength.² It can also be utilized in fabricating thin layer electrodes in flexible electronics and optoelectronics, and also as transparent electrodes³ due to a peculiar blend of mechanical, electrical and thermal properties. On the other hand, CdSe quantum dots (QDs) are well known for their unmatched optoelectronic properties owing to quantum confinement effects.⁴ Since this effect is very sensitive to the size, shape and nature of materials, their tunability has been a boon in exploring applications like sensitized solar cells, LEDs, biological sensors, bioimaging and many more.⁵ Graphene–CdSe QDs due to their unique blend of opto-electronic features (band gap values) thus can form a very important class of hybrids which can be exploited in many applications starting from solar cells, photocatalysis, photoelectrochemical water splitting⁶ to photo-detectors, selective organic transformations⁷ and so on.

Although there are a few reports on the attachment of CdSe QDs on a graphene surface,⁸ the real challenge lies in the controlled attachment of QDs onto the graphene surface with pre-defined areal density. This is a result of the fact that the

surface of graphene, obtained from graphene oxide by complete reduction, contains a lower number of functional groups to anchor the QDs. Polymer wrapping of graphene sheets, hydro-thermal methods and *in situ* generation of QDs on graphene⁹ are a few limited methods that have been available so far for the decoration of QDs on 2D graphene sheets. One major limitation of such methods is that monodispersed QDs can hardly be achieved. Moreover, in some cases, the interaction between QDs and graphene is purely by physical adsorption causing extensive reorganization. These limitations can be avoided by a rational and controlled functionalization of graphene sheets before attaching CdSe quantum dots. Among many functionalization strategies, diazonium-salt functionalization of graphene¹⁰ has been proven to be one of the most easy and effective methods of graphene surface modification which has potential to chemically tailor the graphene surface with desired functionality (by using suitable precursors) to allow further modification on the surface of graphene. This also provides sufficient solubility of graphene in various solvents to ease the fabrication of hybrid materials. Furthermore, this strategy has an additional benefit that the areal density can be enhanced by a layer-by-layer approach to create multidimensional hybrid structures of CdSe and graphene with accurate dimensional control.¹¹

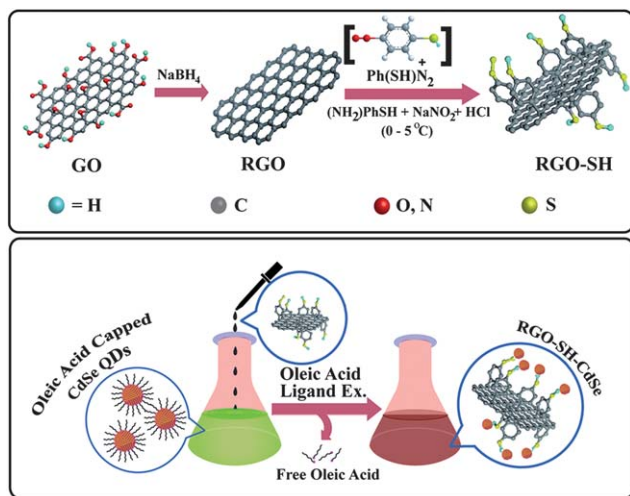
Here we use this novel methodology (Scheme 1) to selectively make thiol (–SH) terminated graphene sheets (Section S1†) by reacting graphene with the diazonium salt of 4-aminothiophenol (4-ATP) followed by building-up of CdSe quantum dots. Since the –SH group has strong affinity towards CdSe QDs (both –SH and CdSe are soft), oleic acid capped CdSe QDs with pre-defined sizes have been effectively exchanged with these thiolated graphene materials by mixing in solution, to make CdSe–graphene hybrids. These hybrids are characterized using FTIR, UV-VIS, photoluminescence (PL), TEM and cyclic voltammetry. The hybrids show effective PL quenching of CdSe QDs with a good photoresponse (using an 80 W tungsten lamp).

A comparison of the FTIR spectra of reduced graphene oxide (RGO), 4-aminothiophenol (4-ATP) and thiol modified graphene (Fig. 1) shows a less intense characteristic peak for the –SH

^aPhysical and Materials Chemistry Division, National Chemical Laboratory, Pune-411008, India. Fax: +91 20 2590 2636; Tel: +91 20 2590 2566

^bCentral Electrochemical Research Institute, Karaikudi, Tamil Nadu, India-630006. E-mail: vk.pillai@ncl.res.in

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3nr00363a



Scheme 1 Synthesis of RGO and -SH terminated RGO followed by CdSe attachment through chemical exchange with oleic acid.

group ($\sim 2530\text{ cm}^{-1}$) in 4-ATP (very weak at 2569 cm^{-1}). However, the peak for thiol is rather broad. This is in accordance with the information available in the literature that the -SH peak is very difficult to observe in FTIR and moreover, vibrational peaks of graphene (especially the remaining -COOH groups) are so strong that those can mask the actual -SH peak. The presence of the -SH group hence confirms the successful grafting on the graphene surface. The spectrum of the 4-ATP molecule however shows (other than the -SH peak) several peaks corresponding to =C-H deformation of a benzene ring (825 cm^{-1}), C=C in plane vibration ($1625, 1497\text{ cm}^{-1}$), aromatic =C-H stretching (3026 cm^{-1}) and finally the N-H stretching (3375 cm^{-1}) of the charged aromatic amine group.¹² The absence of a N-H stretching peak as well as the presence of both S-H and C-H stretching peaks ensure proper functionalization, presumably with the loss of the -NH₂ group as a molecular N₂ during aromatic electrophilic reaction (C-C bond formation) on the graphene surface. In order to further confirm the presence of -SH groups and to check the grafting density, EDAX mapping has been employed. Accordingly, Fig. 1 shows the elemental mapping of the thiolated graphene revealing an almost

complete coverage of S (or -SH group). From the quantitative analysis of EDAX, $\sim 4\text{ wt\%}$ sulphur (S) has been estimated for the case of 1 : 1 wt% of graphene to 4-ATP. This approximately indicates about an $\sim 10^{18}$ to 10^{20} number of -SH units per gram of graphene surface.

Cyclic voltammetry was employed to characterize the RGO before and after -SH grafting. Distinct redox peaks, for the oxidation and reduction of ferrocene methanol (Fig. S3†), were observed in the case of RGO which is a good electron carrier. Interestingly, when the same coating is subjected to thiol functionalization for 2 h, the current for the redox peaks are found to decrease. This is because the surface of the RGO gets modified with -Ph-SH groups, which in turn hinders the diffusion of ferrocene methanol molecules towards the RGO surface and as a result the current drops. Integrating the area of the oxidation peak gives $\sim 10^{-7}\text{ mol cm}^{-2}$ surface coverage of the -PhSH group on the surface of RGO. This is reflected also in the higher charge transfer resistance associated with RGO after thiol modification. Moreover, the diffusion coefficient of ferrocene methanol, obtained from the low frequency straight line portion (by plotting the overall modulus of Z vs. $\omega^{-1/2}$ in Fig. S4†), suggests the poor diffusion of the molecules to the electrode surface (RGO here) due to the presence of the thiol group (pinning). The thiol groups impede the incoming flux of ferrocene methanol molecules to the RGO surface and thereby results in the higher charge transfer resistance.¹³ A water contact angle study on pristine graphene and on RGO-SH shows the increased hydrophobic character on -PhSH grafting (water contact angle increases from 82° to 91° after functionalization) (Fig. S5†). The surface energy of RGO was calculated, before and after -PhSH grafting, using the Owens-Wendt method suggesting an increase (33.1 to 40.3 mJ m^{-2}) after functionalization.¹⁴ However, the polar or non-dispersive component of the surface energy decreases (5.5 to 0.6 mJ m^{-2}) after functionalization with a concomitant increase in dispersive or non-polar component (27.6 to 39.8 mJ m^{-2}).

Raman mapping (Fig. 2) has been used extensively to characterize the functionalized RGO and the hybrids. To generalize the scheme, three different sizes of CdSe QDs were chosen (namely 3.8 nm , 4 nm and 4.9 nm) and exchanged with the -SH functionalized graphene (RGO-SH) hybrid. As has been

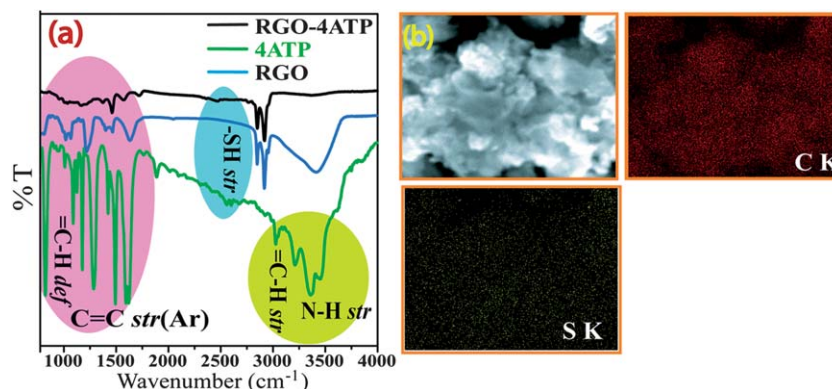


Fig. 1 (a) FTIR spectra of RGO, -SH grafted RGO and 4-ATP, and (b) elemental mapping for the RGO functionalized with the -PhSH group.

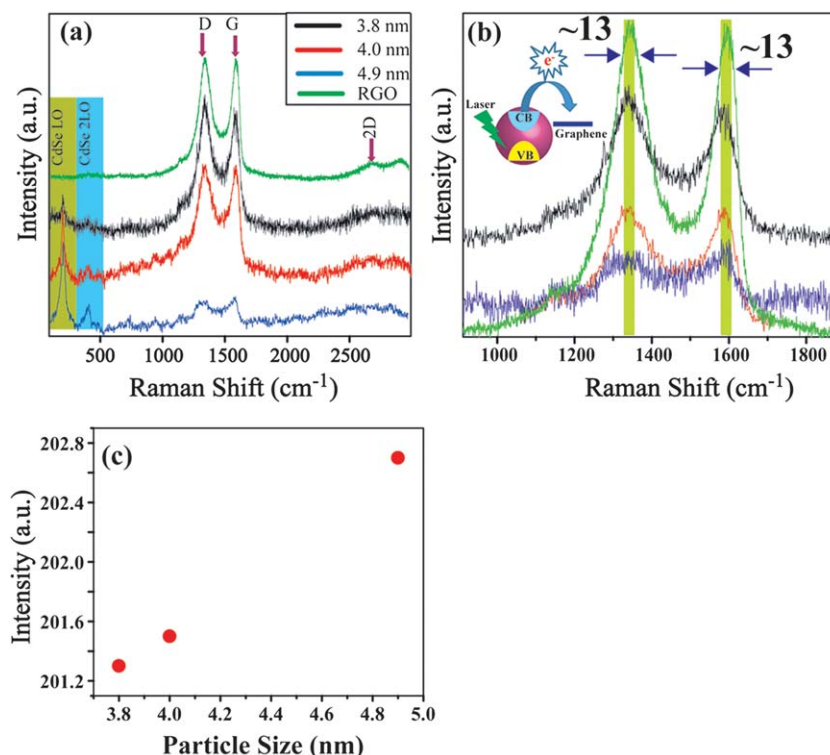


Fig. 2 (a) Micro Raman spectra of CdSe-RGO-SH hybrids with 514 nm Ar^+ laser using 50 \times objective, (b) enlarged portion of D and G bands of RGO showing charge transfer from CdSe to RGO, and (c) variation of peak positions of CdSe QDs with particle size.

indicated in Fig. 2(a), all the three hybrids show two characteristic phonon modes of vibration on excitation—one at 1333.1 cm^{-1} and another at 1582.8 cm^{-1} . The first one is identified as the D-band or defect induced band which appears due to in plane longitudinal phonon vibration or breathing mode of k -point phonons of A_{1g} symmetry and the latter one is the G-band or graphitic band arising due to E_{2g} phonon mode for the sp^2 carbon network of the graphene plane. However, when compared with pristine RGO without any thiol functionalization and CdSe QD decoration, there is an $\sim 13 \text{ cm}^{-1}$ shift of both D as well as G-bands towards lower wavenumber or energy (Fig. 2(b)). This red shift (equivalent to 1.6 meV) implies softening of phonons of RGO due to electron enrichment on graphene because of charge transfer to graphene.¹⁵ The excitation source 514 nm laser has sufficient energy (2.41 eV) to excite the valence band electrons of CdSe QDs and the work function of graphene (-4.5 eV), being favorable with the conduction band positions of these QDs (-4.17 to -4.38 eV for 3.8 nm to 4.9 nm particles), excited electrons can be transferred to graphene, thereby rendering the graphene surface electron rich. This consequently results in red shift in the D and G-band positions of the graphene. Interestingly, the I_D/I_G ratio (1.01 in this case) remains the same both for pristine RGO as well as for functionalized and CdSe decorated RGO confirming that the nature and amount of defect remain the same before and after the functionalization. On the other hand, the appearance of the 2D band, which is the overtone band of the D-band, in all samples, indicates that the number of layers is not disturbed

significantly due to functionalization.¹⁰ A typical crystallite size of $\sim 16.6 \text{ nm}$ has been estimated from the I_D/I_G ratio, which basically represents the distance between two successive defect points. Other than the D-and G-bands, the Raman spectra of the hybrid materials also bear the feature of CdSe QDs in the 100–500 cm^{-1} region. The peak at 201–202 cm^{-1} is attributed to the longitudinal optical (LO) phonon mode of CdSe and that at 400–405 cm^{-1} is the overtone of LO mode which is termed CdSe 2LO. As Fig. 2(c) suggests, the LO peak shows a slow red shift with the decrease in particle size, in accordance with the previous report.¹⁵ The appearance of the LO peak within 201–201 cm^{-1} , as compared to 210 cm^{-1} for bulk CdSe, suggests the invariance of the size and shape for the attached QDs.¹⁵

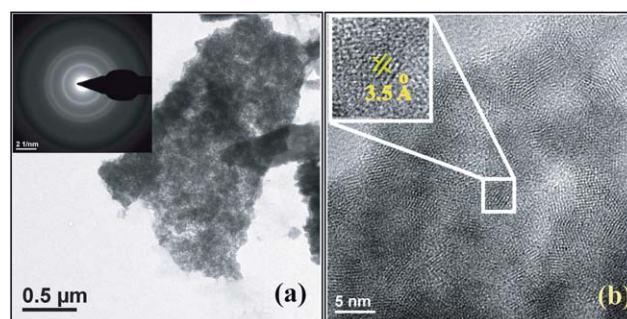


Fig. 3 High resolution TEM micrograph of the CdSe QD (4.9 nm) and RGO-SH hybrid. (a) Low magnification and (b) high magnification image. The inset of (a) shows the SAED pattern of the QDs.

Fig. 3 is a representative high resolution TEM image of the hybrid (CdSe-4.9 nm). Interestingly, a complete coverage of the graphene sheet is observed and the d -spacing (3.58 Å) confirms the crystalline nature of the CdSe particles. This value is also consistent with that obtained for free CdSe QDs (calculated from the analysis of the X-ray diffraction study in S11). The selected area electron diffraction pattern (SAED) shown in the inset of Fig. 3(a) also suggests the cubic phase formation (zinc blende phase, JCPDS card no. 19-0191) and supports the XRD observation. This comparative study of TEM along with PXRD suggests the preservation of the CdSe crystal structure and morphology even after the ligand exchange. Furthermore, the size of the QDs obtained matches well with that calculated from the first excitonic peak position from the UV-VIS data (S6†).

Fig. S6† shows a comparative analysis of the absorbance spectra of CdSe QDs (4.9 nm) with that of the hybrid with RGO-SH in solution. Interestingly, the excitonic peak position ($1s_e$ – $1s_h$ transition) is invariant before and after the exchange with RGO-SH suggesting the preservation of size as well as electronic structure upon ligand exchange. For example, CdSe QDs (only 4.9 nm has been shown) show photoluminescence (PL) emission at around 592 nm while upon the addition of a controlled amount of RGO-SH into the CdSe QD solution, the PL decays systematically with an increase in concentration (Fig. S7†). This effective PL quenching could be ascribed perhaps to the formation of Schottky junction.¹⁵

All the above data suggest the importance of effective functionalization of a graphene surface with 4-ATP in order to prepare -SH terminated graphene using simple solution chemistry. More specifically, chemical anchoring of CdSe QDs can be achieved by the exchange method, which is possible due to the strong affinity of -SH groups towards CdSe (soft-soft interaction). Moreover, the short -PhSH moiety helps the QDs remain very close to the graphene surface, facilitating enhanced electron transfer from CdSe while receiving some assistance from the phenyl group of -PhSH. However, there is always the probability of restacking due to the tendency of H-bonding among -SH groups of one RGO sheet with that of the other, but can be alleviated by proper sonication procedures. We are currently studying the photovoltaic performance of these hybrids.

Conclusions

In conclusion, we report the synthesis of a unique CdSe-graphene heterostructure revealing synergistic optical properties by employing a novel methodology of functionalizing chemically converted graphene using the diazonium salt of 4-aminothiophenol. Robust CdSe QD decoration has been achieved by a simple solution exchange procedure, which has a remarkable potential to control both the size of the QD on RGO as well as the graphene quality. Effective PL quenching suggests proper Schottky junction formation. The thiol terminated graphene can be a potential candidate for 3-D heterostructure (CdSe-graphene) formation by using a layer-by-layer strategy and so it will be very useful for making a photosensitive device. The hybrid is expected to perform well in the area of sensitized solar cells, solar water splitting, photodetectors, etc. Especially, the

presence of graphene gives flexibility to the device obtained from such hybrids.

Acknowledgements

JD sincerely acknowledges University Grants Commission and CSIR, India for a fellowship. We are also thankful to Dr S. Pal, Director, NCL for support and infrastructure. We also thank Ketan, Anuj, Pandiaraj for SEM and TEM analyses.

Notes and references

- (a) K. S. Novoselov, Z. Jiang, Y. Zhang, S. V. Morozov, H. L. Stormer, U. Zeitler, J. C. Maan, G. S. Boebinger, P. Kim and A. K. Geim, *Science*, 2007, **315**, 1379; (b) K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos and A. A. Firsov, *Nature*, 2005, **438**, 197.
- C. Lee, X. Wei, J. W. Kysar and J. Hone, *Science*, 2008, **321**, 385.
- G. Eda, G. Fanchini and M. Chhowalla, *Nat. Nanotechnol.*, 2008, **3**, 270.
- L. Brus, *J. Phys. Chem.*, 1986, **90**, 2555.
- (a) A. P. Alvisatos, *Science*, 1996, **271**, 933; (b) A. Kongkanand, K. Tvrđy, K. Takechi, M. Kuno and P. V. Kamat, *J. Am. Chem. Soc.*, 2008, **230**, 4007; (c) Y. Araki, K. Ohkuno, T. Furukawa and J. Saraie, *J. Cryst. Growth*, 2007, **301**, 809; (d) D. M. Willard, L. Lori, J. J. Carillo and A. V. Orden, *Nano Lett.*, 2001, **9**, 469.
- (a) S. Sun, L. Gao, Y. Liu and J. Sun, *Appl. Phys. Lett.*, 2011, **98**, 931121; (b) M. L. Chen, Z. D. Meng, L. Zhu, C. Y. Park, J. G. Choi, T. Ghosh, K. Y. Cho and W. C. Oh, *J. Nanomater.*, 2012, **2012**, 21.
- (a) N. Zhang, Y. Zhang, X. Pan, X. Fu, S. Liu and Y. J. Xu, *J. Phys. Chem. C*, 2011, **116**, 18023; (b) K. Yu, G. Lu, K. Chen, S. Mao, H. Kim and J. Chen, *Nanoscale*, 2012, **4**, 742; (c) N. Zhang, Y. Zhang, X. Pan, M. Q. Yang and Y. J. Xu, *J. Phys. Chem. C*, 2012, **116**, 18023.
- (a) Y. Lin, K. Zhang, W. Chen, Y. Liu, Z. Geng, J. Zeng, N. Pan, L. Yan, S. Wang and J. G. Hou, *ACS Nano*, 2010, **6**, 3033; (b) Y. Wang, H. B. Yao, X. H. Wang and S. H. Yu, *J. Mater. Chem.*, 2010, **21**, 562; (c) Y. T. Kim, H. J. Han, B. H. Hong and Y. U. Kwon, *Adv. Mater.*, 2010, **22**, 515; (d) W. I. Park, C. H. Lee, J. M. Lee, N. J. Kim and G. C. Yi, *Nanoscale*, 2011, **3**, 3522.
- (a) J. Yan, Q. Ye, X. Wang, B. Yu and F. Zhou, *Nanoscale*, 2012, **4**, 2109; (b) Y. Lin, K. Zhang, W. Chen, Y. Liu, Z. Geng, J. Zeng and J. G. Hou, *ACS nano*, 2010, **4**, 3033; (c) Q. Li, B. Guo, J. Yu, J. Ran, B. Zhang, H. Yan and J. R. Gong, *J. Am. Chem. Soc.*, 2011, **133**, 10878; (d) Q. Xiang, J. Yu and M. Jaroniec, *Nanoscale*, 2011, **3**, 3670; (e) W. Wang, J. Yu, Q. Xiang and B. Cheng, *Appl. Catal., B*, 2012, **119**, 109; (f) Q. Xiang, J. Yu and M. Jaroniec, *Chem. Soc. Rev.*, 2012, **41**, 782.
- (a) M. Fang, K. Wang, H. Lu, Y. Yang and S. Nutt, *J. Mater. Chem.*, 2009, **19**, 7098; (b) J. R. Lomeda, C. D. Doyle, D. V. Kosynkin, W. F. Hwang and J. M. Tour, *J. Am. Chem. Soc.*, 2008, **130**, 16201.

- 11 M. Alazemi, I. Dutta, F. Wang, R. H. Blunk and A. P. Angelopoulos, *Carbon*, 2010, **48**, 4063.
- 12 (a) J. Sharma, N. K. Chaki, S. Mahima, R. G. Gonnade, I. S. Mulla and K. Vijayamohanan, *J. Mater. Chem.*, 2004, **14**, 970; (b) R. M. Silverstein, F. X. Webster and D. J. Kiemle, *Spectrometric Identification of Organic Compounds*, John Wiley & Sons, 7th edn, 1963.
- 13 (a) L. Bao, L. Sun, Z. L. Zhang, P. Jiang, F. W. Wise, H. D. Abruña and D. W. Pang, *J. Phys. Chem. C*, 2011, **115**, 18822; (b) G. K. Ramesha and S. Sampath, *J. Phys. Chem. C*, 2009, **113**, 7985.
- 14 (a) F. M. Fowkes, *J. Phys. Chem.*, 1980, **84**, 510; (b) J. Debgupta, B. A. Kakade and V. K. Pillai, *Phys. Chem. Chem. Phys.*, 2011, **13**, 14668.
- 15 (a) C. Casiraghi, J. Robertson and A. C. Ferrari, *Mater. Today*, 2007, **10**, 44; (b) J. Debgupta, D. B. Shinde and V. K. Pillai, *Chem. Commun.*, 2012, **48**, 3088; (c) I. V. Lightcap and P. V. Kamat, *J. Am. Chem. Soc.*, 2012, **134**, 7109.