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# ONE-POT SYNTHESIS OF CONDUCTING GRAPHENE POLYMER COMPOSITES AND ITS STRAIN SENSING APPLICATION (PREPRINT)

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**14. ABSTRACT**
In-situ reduction of graphite oxide in polymer powder has been implemented using focused solar electromagnetic radiation. Graphene has proved that it can act as alternative filler in nanocomposites due to its high electronic transport properties and its use in advanced polymer composites for EMI shielding applications. With an applied load, strain measured and corresponding change in resistance of the reduced graphite oxide-polymer composites has been observed. The morphological, structural, electrical,
thermal, and electromechanical characteristics of the reduced graphene-PVDF were studied. A gauge factor was obtained demonstrating a promising application as a strain sensor in structural health monitoring.

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# One-pot synthesis of conducting graphene polymer composites and its strain sensing application

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**Insitu reduction of graphite oxide in polymer powder has been implemented using focused solar electromagnetic radiation. The simultaneous reduction of graphite oxide, melting of the polymer and embedding of reduced graphite oxide nano flakes in polymer offers a new way of synthesizing conducting polymer composites. An electromechanical application of the present reduced graphite oxide-PVDF nanocomposite has been proposed with a gauge factor of 12.1.**

Graphene is a two dimensional monolayer of carbon atoms arranged into a hexagonal lattice and it possesses extraordinary properties[1] such as unique electron transport performance,[2] fascinating elasticity and stiffness.[3] Graphene has proved that it can act as alternative filler in nanocomposites due to its high electronic transport properties and its use in advanced polymer composites for EMI shielding applications.[4-5] Especially high aspect ratio combined with high electrical conductivity promises graphene as an ultimate lightweight nanofiller in polymer compared to carbon nanotubes.[6-7] In order to fully transfer these excellent properties of graphene also called reduced graphite oxide to a polymer and form a nanocomposite with high performance. Many factors are involved especially preparation method, orientation, dispersion and the interface between polymer and nanofiller (graphene). It is well known that graphene with its high surface area and surface energy and a strong tendency to van der Waals and π-π interactions tend to aggregate and hence, their dispersion in a polymer is very difficult.[8-9] Graphene is ready to form irreversible aggregations, or even restacks to form graphite through interlayer cohesive energy. Large scale production and homogeneous dispersion of graphene seem to be insurmountable by the direct blending approaches and it obviously reduces the possibility of graphene polymer products at an industrial scale.[10] Many efforts[11] have been made to synthesize graphene as thin as possible and to disperse them homogeneously in polymer matrix which is essential for preparing electrically conducting graphene composites. Till now, there are no reports on the preparation of conducting graphene polymer composites in dry state, without the usage of any solvents.

In this communication, we report a simple straightforward one step method for the preparation of conducting graphene polyvinyliedene fluoride (PVDF) composites starting from graphite oxide (GO) and PVDF. The synthesis is entirely a dry route consisting of graphite oxide, PVDF powder, converging lens and ever existing solar radiation. This method can be exploited for the preparation of graphene-polymer composites by replacing PVDF with other thermoplastic polymers such as PMMA, PET, PC, PE, PEEK,

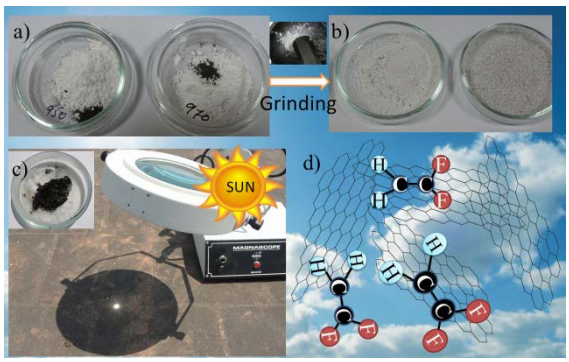


Fig.1: a) Optical images of PVDF and graphite oxide mixture with different concentrations, b) Homogeneous mixture of PVDF and GO after grinding, c) Magnascope with 130 mm lens with schematic of natural SUN (source of power), inset shows the black mixture containing PVDF along with graphene and d) Schematic representation of graphene and PVDF structure.

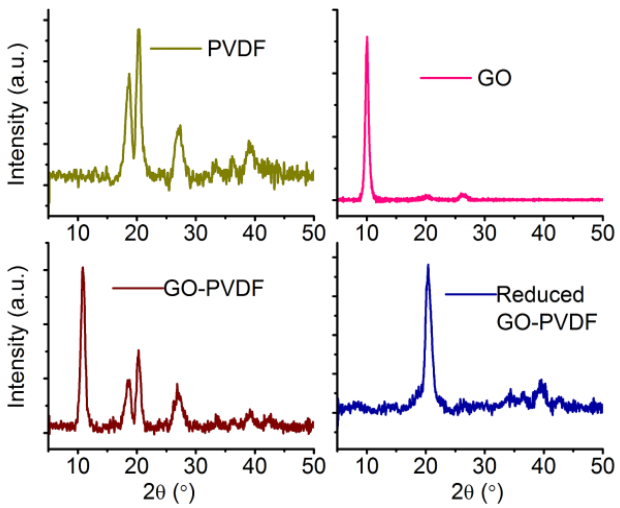


Fig. 2 Powder X-ray diffractograms of PVDF, GO, GO-PVDF and PVDF containing reduced graphite oxide.

When GO was mixed with PVDF, the colour of the total mixture was still in white in nature (Fig. 1b) due to the addition of small amount of GO. As soon as focused solar radiation falls on this

composite, the irradiated portion becomes black (Fig. 1c) due to photo-reduction and exfoliation of graphite oxide into reduced graphite oxide in the presence of polymer. One of the key points in this experiment is that PVDF melts at 166°C and focused solar radiation can easily melt this polymer while reducing and exfoliating graphite oxide. Simultaneous actions of melting, reduction and exfoliation are major advantages in the present approach. The total time needed for the entire synthesis is only 5 min which is much better than the reported methods for synthesis of conducting graphene polymer composites.[12-14] Also the current method of preparation in completely dry state is a novel one, as no such reports are available in the literature. By blending the ratio of graphite oxide and PVDF, various composites have been prepared with different weight fractions of reduced graphite oxide. For example, initially 990 mg of PVDF and 10 mg of GO powder were mixed together and photo-reduction was performed over this composite to attain fixed weight fraction of reduced graphene. Depending upon the yield of graphene by this solar technique, fixed weight fraction of reduced graphite oxide in polymer was obtained. Similarly 6-7 composites were prepared by increasing the amount of GO in PVDF matrix. After photo reduction over these composites, all the composites are subjected to the hot melting press to make thin films out of it.

Figure 2 shows the powder X-ray diffractograms of graphite oxide, PVDF powder, PVDF-GO mixture and reduced graphite oxide in PVDF. XRD pattern of GO powder shows a large inter planar spacing (d) of 8.36 Å compared with graphite inter planar spacing of 3.4 Å. This increase in d value can be due to oxygen functional groups of GO and water molecules held between the interlayer galleries of hydrophilic GO and it is well supported by the literature.[15] The XRD spectrum of pure PVDF powder was also shown and it clearly contains two major peaks at 18.7° and 20.3°. These are clear indication of α and β phase of commercial PVDF powder. Figure 2c shows the XRD of GO-PVDF which contains characteristic peaks of graphite oxide and PVDF polymer. This GO-PVDF mixture was irradiated with focused solar radiation and XRD spectra was taken. Quite interestingly, we did not observe any signatures of graphite oxide and α phase of PVDF and PVDF was completely crystallized into β crystalline (fig. 2d) phase after irradiating with focused solar radiation. This suggests that solar exfoliation favours the formation of β phase of PVDF. When graphite oxide is added to the PVDF and performed photo chemical reduction, most preferably beta phase is forming due to less binding energy of beta phase to the surface attachment of reduced graphene. It is well supported by theoretical calculations.[16]

The chemical changes brought about by solar reduction in graphite oxide and PVDF mixture have been characterized by thermo gravimetric analysis (TGA). Fig. 3 shows the TGA for reduced graphite oxide along with PVDF and reduced graphite oxide in the presence of PVDF. In the case of graphite oxide, main mass loss was observed around 200°C and it can be due to thermally labile functional groups. However, we did not observe any considerable amount of mass loss in the case of reduced graphite oxide in the presence of PVDF, which validates our hypothesis. Another interesting thing we have observed is that the onset decomposition temperature of reduced graphite oxide is enormously increased by ~35°C compared with bare PVDF onset decomposition temperature. It can be due to effective load transfer between polymer base and nanofiller. The addition of nanofillers especially carbon nanotubes and graphene to the polymers, these nanofillers penetrates into the complex polymer structures and it modifies the structure of the polymer such that thermal stability improves. The strength of the composite is depends on how this nanofiller can penetrated thorough the polymer so that maximum load transfer between nanofiller and polymer can be achieved. This is also called as reinforcement effect.

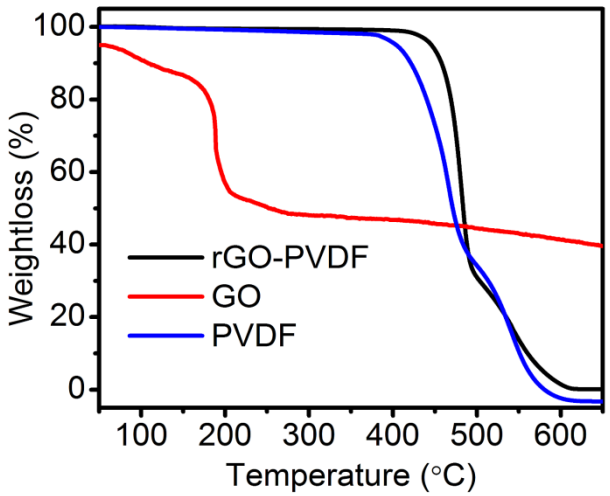


Fig.3: Thermo gravimetric spectra of PVDF, Graphite Oxide (GO) and reduced graphite oxide-PVDF in $O_2$ atmosphere at the rate of 10°C/min

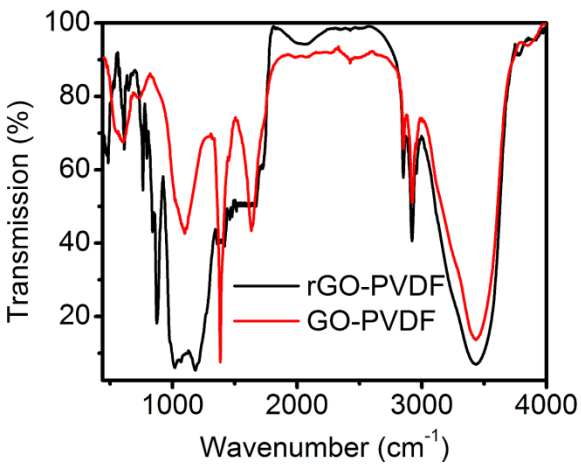


Fig. 4 FTIR spectra of Graphite Oxide-PVDF and reduced Graphite Oxide-PVDF composite after photo reduction

FTIR of graphite oxide-PVDF composite and reduced graphite oxide-PVDF composite after photo reduction was shown in above figure 4. It is well known that graphite oxide is insulting in nature due to its physical damage of conjugated structure due to treatment of with strong acids and it leads to attachments of various carbonyl, carboxyl and hydroxyl functional groups. FTIR spectra of GO-PVDF show the presence of functional groups from GO side and spectroscopic information of PVDF structure. The most characteristic features of the spectra are a broad band was observed at 3452 $cm^{-1}$ which is due to O-H stretching vibrations, and the band at 1735 $cm^{-1}$ is due to the C=O stretching

vibrations from carbonyl and carboxyl groups and an intense band at 1365 $cm^{-1}$ due to C-OH vibrations, a band at 1106 $cm^{-1}$ which is due to C-O stretching vibrations are observed in FTIR of GO-PVDF composite in addition to that, peaks at 616 and 764 $cm^{-1}$ are observed and these are corresponding to the α-PVDF polymorph. It clearly confirm the existence of GO and PVDF. After photo reduction of GO-PVDF composite, the functional groups corresponding to the carbonyl, carboxyl and hydroxyl groups are completely disappeared and also a new peak start appeared at 837 $cm^{-1}$ and 487 $cm^{-1}$ which are corresponding to the β-PVDF polymorph. Our FTIR results corroborate the XRD results.[17-19]

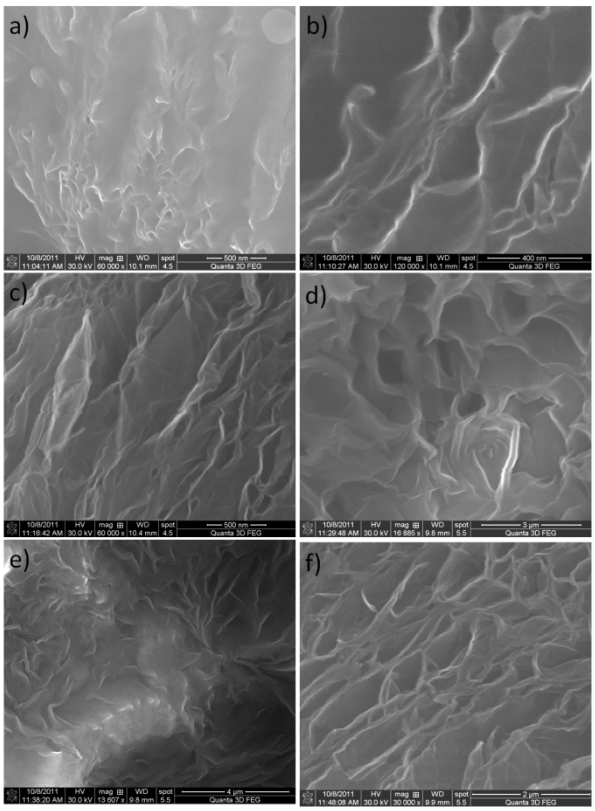


Figure 5 Field emission scanning electron micrographs of the reduced graphite oxide in PVDF matrix.

Fig. 5 (a-f) shows the micrographs of the reduced graphite oxide-PVDF composites, which confirms the layered structure of reduced graphite oxide in PVDF polymer and further EDX (Fig. S4) confirms the removal of oxygen (reduction) from GO.

The reduced graphene in PVDF was formed as a film by pressing and pasting it over aluminium specimen and it has been tested for strain gauge factor evolution. The sensitivity of a strain gauge can be estimated by the gauge factor as shown in equation 1. Gauge factor of a strain gauge can be defined as the relative change in resistance to the mechanical strain.

$$\text{Strain sensitivity (Gauge factor)} = \frac{\Delta R}{R_o \varepsilon} \text{-------- (1)}$$

Where ΔR is change in resistance under mechanical strain, $R_o$ is the resistance of the nanocomposite with no strain applied and ε is the mechanical strain.

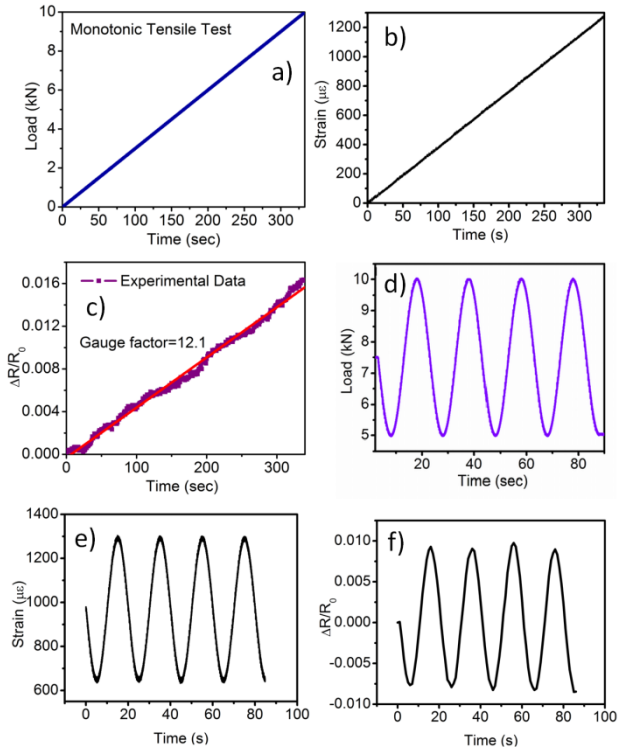


Fig. 6: a-c) Monotonic test over reduced graphite oxide-PVDF film and corresponding induced strain and change in resistance of the composite film. d-f) Tensile-compressive test from 5 kN-10 kN of the same composite film.

Figure 6a-c shows the load applied, strain measured and corresponding change in resistance of the reduced graphite oxide-polymer composites. It is clear from fig. 6c that the fractional change in resistance of the reduced graphite-PVDF composite is changing linearly with time. In addition, strain also varies linearly with time as shown in fig. 6b. From the measured resistance data ($R_o$~230Ω), strain gauge factor was calculated. A change in resistance of 2.78 Ω was observed for 1000 με of mechanical strain. A gauge factor of 12.1 has been obtained which is high compared with the reported literature on graphene as a strain sensor.[14, 21, 22] The conventional strain gauges are having a gauge factor of 2. The fatigue test over this nanocomposite suggests that change in resistance follows the change in strain. The change in resistance of the composite can be due to two reasons. The first one is: when tensile strain is applied on the composite, the number of local conducting interconnections varies due to the physical movement of the reduced graphite oxide nanofillers in PVDF matrix and consequently conducting path for electrons will get disturbed so that hike in resistance is observed. The second reason for rise in resistance of the composite is that when tensile strain is applied, rGO experiences the same and change in the density of states of rGO occurs and this results in the increase of band gap in graphene.[23]

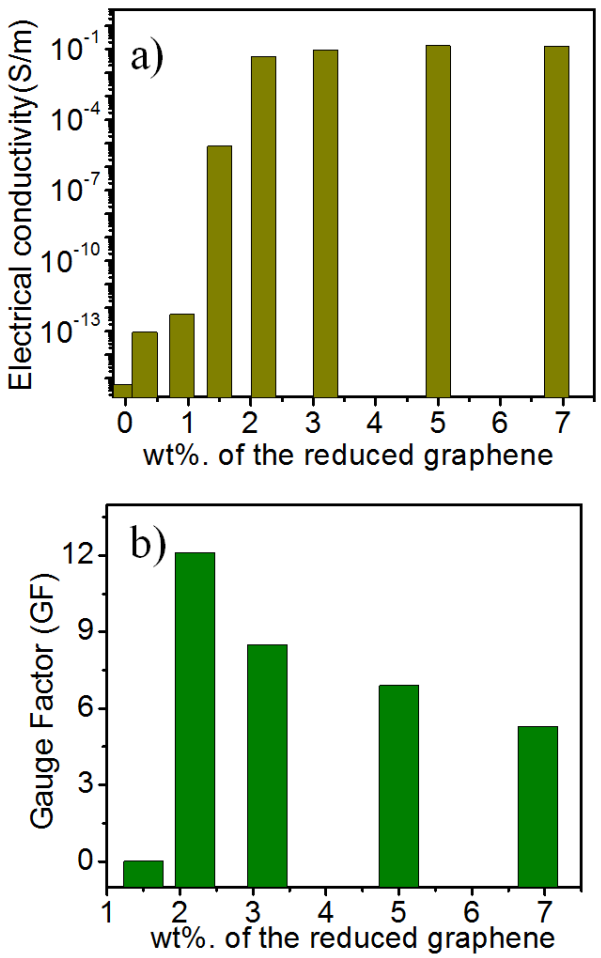


Fig. 7: a) Electrical conductivity of the reduced graphite oxide (rGO) in PVDF with different weight fractions of rGO and b) Gauge factors of the corresponding composites with different weight fraction of rGO.

It is well reported in literature that graphite oxide is an insulator due to its disrupted conjugative network of hexagonal carbon structure.[11] And PVDF is a highly electrically insulating material with polymorphs in its crystal structure having highest chemical resistance.[16] The electrical conductivity of the reduced graphite oxide (2.2 wt. % of reduced graphite oxide) in the presence of PVDF increased enormously to about ~0.04 S/m which is 14 orders of magnitude more in electrical conductivity in compared with PVDF conductivity shown in figure 7a. In another case with 0.9 wt. % of reduced graphite oxide, conductivity was very low due to poor dispersion of nanofiller in the polymer. When sufficient concentration of nanofiller was achieved in the polymer, percolation in electrical conductivity was observed. This high conductivity of the reduced graphite oxide-PVDF composite at low nanofiller loading can find many electrical applications. In order to understand the effect of loading of reduced GO in PVDF under focused solar radiation, different sets of samples have been synthesized by varying the amount of GO in PVDF. The electrical conductivities of the reduced GO-PVDF composites were calculated and are shown in Fig. 7a. The increment in electrical conductivity of the reduced GO-PVDF composites with the amount of rGO can be attributed to the conductivity and percolation effect of rGO in PVDF. The percolation threshold in electrical conductivity was achieved with >2 wt. % rGO. We have also measured through plane conductivity of these nanocomposites by passing a current through thickness and geometry of the composites as shown in Fig. S3. The observed conductivity values suggest that the synthesized nanocomposites are well conductive in nature and the through plane conductivity is almost equal to the in-plane electrical conductivity of the nanocomposites as shown in Fig. 5a. The effect of weight fraction of rGO in PVDF on gauge factor is shown in Fig. 7b. For 1.5 wt. % rGO in PVDF, the composite shows high resistance and the gauge factor is low whereas for optimal concentration of 2.2 wt. % of rGO, the gauge factor rises to a very high value (12.1) due to sufficient interconnections of conductive rGO nanofillers connecting each other in PVDF matrix and due to its onset of electrical percolation and individual and sufficient fillers are available to experience the applied strain. As the concentration of rGO increases still further in PVDF matrix, saturation of these conducting fillers leads to a composites in which the physical movement of the fillers are attenuated by the adjacent fillers with applied strain. That's why change in resistance decreases and it leads to decrease in gauge factor of the final composite.

## Conclusion

In conclusion, graphite oxide was completely reduced in polyvinylidene fluoride (PVDF) in dry state using photo-chemical reduction. The simultaneous reduction and ultra-fast melting of polymer avoids the restacking of graphene. The synthesised composites are highly conducting in nature and exhibits lower percolation thresholds. The morphological, structural, electrical, thermal, and electromechanical characteristics of the reduced graphene-PVDF were studied. A strain gauge factor of 12.1 was obtained as promising application as a strain sensor in structural health monitoring.

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## Notes and references

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References

1. A. K. Geim and K. S. Novoselov, Nat Mater, 2007, 6, 183-191.
2. X. Du, I. Skachko, A. Barker and E. Y. Andrei, Nat. Nanotechnol., 2008, 3, 491-495.

3. C. Lee, X. Wei, J. W. Kysar and J. Hone, Science, 2008, 321, 385-388.
4. S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen and R. S. Ruoff, Nature, 2006, 442, 282-286.
5. V. Eswaraiah, V. Sankaranarayanan and S. Ramaprabhu, Macromol. Mater. Eng., 2011, 296: 894–898.
6. T. Wei, G. Luo, Z. Fan, C. Zheng, J. Yan, C. Yao, W. Li and C. Zhang, Carbon, 2009, 47, 2296-2299.
7. K. P. Loh, Q. Bao, P. K. Ang and J. Yang, J. Mater. Chem., 2010, 20, 2277-2289.
8. D. Vuluga, J.-M. Thomassin, I. Molenberg, I. Huynen, B. Gilbert, C. Jerome, M. Alexandre and C. Detrembleur, Chem. Commun., 2011, 47, 2544-2546.
9. S. Park and R. S. Ruoff, Nat. Nanotechnol., 2009, 4, 217-224.
10. H. Wu, W. Zhao, H. Hu and G. Chen, J. Mater. Chem., 2011, 21, 8626-8632.
11. V. Eswaraiah, S. S. Jyothirmayee Aravind and S. Ramaprabhu, J. Mater. Chem., 2011, 21, 6800-6803.
12. S. Ansari and E. P. Giannelis, J. Polym. Sci., Part B: Polym. Phys., 2009, 47, 888-897.
13. S. Kim, I. Do and L. T. Drzal, Macromol. Mater. Eng., 2009, 294, 196-205.
14. V. Eswaraiah, K. Balasubramaniam and S. Ramaprabhu, J. Mater. Chem., 2011, 21, 12626-12628.
15. S. Park, J. An, J. R. Potts, A. Velamakanni, S. Murali and R. S. Ruoff, Carbon, 2011, 49, 3019-3023.
16. S. Yu, W. Zheng, W. Yu, Y. Zhang, Q. Jiang and Z. Zhao, Macromolecules, 2009, 42, 8870-8874.
17. J. I. Paredes, S. Villar-Rodil, A. Martínez-Alonso and J. M. D. Tascón, Langmuir, 2008, 24, 10560-10564.
18. Y. Si and E. T. Samulski, Nano Lett., 2008, 8, 1679-1682.
19. D. Shah, P. Maiti, E. Gunn, D. F. Schmidt, D. D. Jiang, C. A. Batt and E. P. Giannelis, Adv. Mater., 2004, 16, 1173-1177.
20. V. Eswaraiah, V. Sankaranarayanan and S. Ramaprabhu, Nanoscale Res. Lett., 2011, 6, 137.
21. Y. Lee, S. Bae, H. Jang, S. Jang, S.-E. Zhu, S. H. Sim, Y. I. Song, B. H. Hong and J.-H. Ahn, Nano Lett., 2010, 10, 490-493.
22. Y.-J. Kim, J. Y. Cha, H. Ham, H. Huh, D.-S. So and I. Kang, Curr. Appl Phys., 2011, 11, S350-S352.
23. Z. H. Ni, T. Yu, Y. H. Lu, Y. Y. Wang, Y. P. Feng and Z. X. Shen, ACS Nano, 2008, 2, 2301-2305.