Thermally reduced graphene oxide/thermoplastic polyurethane nanocomposites as photomechanical actuators

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ABSTRACT

Optically triggered actuators offer unique advantages like wireless actuation and remote control when compared to other type of actuators. They are extremely useful where stimulus other than electricity or heat is preferred. Thermally reduced graphene oxide (TRGO)/thermoplastic polyurethane (TPU) composite actuators were prepared by simple solution casting technique. The photomechanical actuation properties of the composites were studied under infrared illumination. It was found that the photomechanical response can be tuned by controlling the applied prestrain and the filler loading. Even with a low filler loading of 2 wt. % TRGO, the composite exhibited a very high photomechanical strain of 50.2% with an excellent stress of 1680 kPa at a prestrain of 220%. These high values were achieved at a very low light intensity of 16mWcm^{-2}. The high values of strain obtained with very good generative forces indicate that this is a promising material for light triggered actuators for many potential applications including robotics and biomedical devices. Copyright © 2013 VBRI press.

Keywords: Nanocomposites; actuators; graphene; photomechanical.

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Introduction

Actuators are materials or devices which can undergo shape or mechanical change in response to an appropriate external stimulus [1]. Polymers are one of the most widely studied actuator materials. Unlike conventional ceramic actuators, polymer actuators can give larger displacements even though the generative force will be comparatively less. Moreover, polymer actuators offer many advantages like low cost, light weight and good processability. They have also stroke, force and efficiency similar to that of human muscles. They have found variety of applications in many technological fronts including micro robotics and artificial muscles [2, 3]. Depending on the type of stimulus, polymer actuators can be electrical, thermal, chemical or optical actuators. In the recent years, there has been considerable interest in developing optically triggered polymer actuators due to their advantages like wireless actuation and remote control [4]. Optically triggered polymer actuators are extremely useful when stimulus other than electricity or heat is preferred especially in biomedical field.

Light triggered polymer actuators can be either pure polymers or polymer composites. In both cases, the actuator material system should have an 'energy transfer' unit and a 'molecular switch' unit [5]. The energy transfer unit absorbs the light energy and transfers to the molecular switch unit which undergoes the mechanical change. The molecular switch unit is the polymer network itself whereas the energy transfer unit can either be a functional group as in the case of pure polymers or a filler material as in composites [6]. When compared to a pure polymer actuator material, polymer composite actuators have the advantage of improved mechanical and thermal properties and tunable actuator properties. In the last few years many polymer composite systems were reported for optical actuator applications [7-12]. Even though many polymer systems

including ionomers [8], polysiloxanes [9, 10] and Liquid crystal elastomers (LCE) [11] were used as the matrix for composite based actuators, thermoplastic polyurethanes (TPU) have many advantages over other polymers. TPU has two-phases: a hard segment and a soft segment. The soft segment which is a thermally reversible phase, can store large strains by fixing a transient shape. The original shape can be recovered due to the presence of a hard segment [12]. Thus TPU is an ideal candidate for actuator application. Carbon nanotubes (CNT) are the most widely studied energy transfer units for optical actuators. Many researchers have reported the use of CNT/PDMS [1, 4, 9], CNT/LCE [1, 11] and CNT/TPU [12] composites as optically triggered actuators. However, the inherent bundling nature of CNTs, high cost, poor dispersibility and intrinsic impurities have made them less attractive for practical applications.

Graphene, a single atom thick layer of graphite, is one of the most promising alternatives for CNTs due to their unique electrical, thermal and optical properties [13-15]. Graphene can be effectively utilized as a nanofiller for improving the mechanical, thermal, optical and electrical properties of composites even at very low loadings [16-21]. Graphene could also find a variety of applications in different types of actuators [22-28]. Due to the sp^2 carbon network of graphene, it possesses excellent thermal conductivity and IR absorption. Recently, a few research groups have utilized the unique properties of graphene as an energy transfer unit in light triggered polymer composite actuators [29-33]. Different members of the graphene family including graphene oxide, graphene ribbons and functionalized graphene can also be used as efficient fillers for photomechanical actuators. The IR absorption characteristics of graphene materials and the unique properties of TPU can be combined to develop an IR triggered actuator with significantly enhanced actuator performance. However, not much work was carried out in this direction. Recently, one work was reported on the photomechanical properties of sulfonated graphene/TPU and isocyanate-graphene/TPU composites by a research group [33]. They had to chemically functionalize graphene in order to get a reasonably good performance. Nevertheless, a more quantitative and detailed study of the optical actuation characteristics of graphene/TPU composites are not yet carried out. It is reported that thermally reduced graphene oxide (TRGO) has very high IR absorption characteristics [34]. In the present study, high performance photoactuators were prepared using TRGO/TPU nanocomposites. These nanocomposites were prepared through a simple solvent casting route. A detailed study on the photomechanical actuation properties of TRGO/TPU composites at various prestrains with different filler loading was carried out.

Experimental

Materials

Natural graphite flakes (94.1% C, + 50 Mesh) were obtained from Hind Minerals, India. Sulphuric acid (H_2SO_4, 98% GR), ortho phosphoric acid (H_3PO_4, 85 % pure), potassium permanganate ($KMnO_4$, 99% GR), hydrogen peroxide (H_2O_2, 30% GR) and N, N-Dimethyl

formamide (DMF, 99.5% GR) were purchased from Merck, India. Thermoplastic polyurethane (TPU, Desmopan 380S) was obtained from Bayer Material Science, India.

Synthesis of thermally reduced graphene oxide

Graphite oxide was synthesized from natural graphite flakes using an oxidising mixture of concentrated sulphuric acid and ortho phosphoric acid [35]. To a mixture of 1 mole of graphite flakes in concentrated H_2SO_4 (678 ml) and H_3PO_4 (75 ml), 0.433 moles of $KMnO_4$ was added slowly while keeping the reaction mixture in an ice bath and stirred for 2 h. Then the mixture was heated at 50°C in a water bath for 45 minutes and stirring was continued at room temperature. After 24 h, 450 ml of ice water was added slowly to the reaction mixture which results in an increase of temperature of the system to about 98°C. The stirring was continued for another 2 h and then, hydrogen peroxide (20 ml) was added. The solid collected from the reaction mixture was washed few times with 5% HCl solution followed by distilled water. For each washing, solid was suspended by ultra-sonication and was collected by centrifugation. The resultant graphite oxide was then readily exfoliated to completely water dispersed graphene oxide (GO) by ultra-sonication, which was dried in an air oven at 100°C to get GO sheet. Thermal reduction of graphene oxide was done in a preheated muffle furnace at 850°C for 1 min.

Preparation of thermally reduced graphene oxide-polymer composite

The thermally reduced graphene oxide (TRGO) powder was uniformly dispersed in N, N-Dimethyl formamide (DMF) by ultrasonication. A polyester based Thermoplastic polyurethane (TPU) was dissolved in DMF. To the polymer solution, TRGO dispersion in DMF was added and uniformly mixed using a mechanical stirrer followed by ultrasonication. The resultant slurry was then cast on a stainless steel mould preheated at 100°C and dried at 120°C for 2h. The TRGO/TPU nanocomposite films were then peeled off from the mould. Composite films with varying weight percentage of filler loading were prepared under same conditions.

Characterization

X-ray diffraction (XRD) analysis of the samples were carried out using Ni filtered Cu Kα radiation (λ = 0.154 nm) using Bruker X-Ray diffractometer (Model D5005, Germany) at 40 kV and 30 mA. The samples were scanned in step mode with 2° min^{-1} scan rate. Fourier transform infra red spectroscopy (FT-IR, Avatar 370, Thermo Nicolet, Germany) were carried out to understand the formation of Graphene oxide and thermally reduced graphene oxide. The samples were prepared with KBr. A minimum of 60 scans were acquired with a resolution of 4 cm^{-1}. Back ground spectrum was captured before measurements and base line corrections were made using software. The morphology of the TRGO and composite films was studied using Scanning electron microscopy (SEM, SU 6600, Hitachi, Japan). The TRGO/TPU composite film was fractured in liquid nitrogen and the SEM image of the fractured surface was recorded. High Resolution Transmission Electron Micrographs (HR

TEM) of TRGO sample was also taken using a transmission electron microscope (JEM 2100, JEOL, Japan). TRGO dispersion in DMF was used for taking the TEM images. The samples were prepared on a carbon coated copper grid. The mechanical properties of the composites were studied using Universal Testing Machine (Autograph, Shimadzu, Japan). The specimens were cut in dumbbell shape as per ISO 37 (type 4) standard. The samples were subjected to uniaxial tension at a displacement rate of 200 mm/min with a gauge length of 12 mm. All the measurements were recorded at room temperature.

Photomechanical actuation measurement

An invitro Muscle test system (1205A, 5.0 N, Aurora Scientific Inc., Canada) was used to measure the photomechanical actuation properties of the composites. The measurement system consists of dual mode system with lever arm (model 305 C) and 805A invitro test apparatus. An infrared (IR) lamp (Beurer GmbH, Germany) with red filter was used as the light source. 20mm length and 5mm width strips were cut from the TRGO/TPU nanocomposite sheets. The thickness of the samples was about 0.1 mm. The samples were given pre-strain at 100°C for 4h. The actuation measurement was carried out after keeping the pre-strained samples at room temperature for 8h. The tips of the samples were placed between the grips of *in vitro* Muscle test system. The stress and strain of the samples were measured at various pre-strains. For all measurements, the power density of the light source was kept constant at 16 mWcm^{-2}.

Results and discussion

Characterization of GO and TRGO

When graphite is converted to graphene oxide (GO), the interlayer spacing between the graphitic layers is increased, which will be reflected in the X-ray diffraction (XRD) pattern. Graphite gives an XRD peak at 2θ = 26.3° corresponding to a d spacing of 0.34 nm (**Fig. 1(a)**). In the case of GO, the peak is shifted to 2θ = 11.2° which corresponds to an increased d- spacing of 0.79 nm. The absence of any other peak of graphite confirms the complete conversion of graphite into GO. When GO is thermally reduced, due to high degree of exfoliation, the typical peak related to the interlayer spacing of the GO is completely disappeared. This indicates a nearly complete reduction of graphene oxide into graphene. The Fourier transform infra red (FT-IR) spectrum of GO (**Fig. 1(b)**) confirms the introduction of oxygen functionalities like hydroxyl, epoxy and carboxylic groups on oxidation of graphite. The significant peaks in GO which confirms the conversion of graphite into GO are peaks at 3418 cm^{-1} (due to water -O-H stretching vibration), 1069 cm^{-1} (-C-O stretching), 1168 cm^{-1} (epoxy group), 1600 cm^{-1} (skeletal vibrations from unoxidized graphitic domains) and 1720 cm^{-1} (stretching vibrations from C=O). When GO is thermally reduced, there is no significant peak observed in the FTIR spectrum corresponding to the oxygen functional groups which indicates a nearly complete reduction. The SEM image (**Fig. 1(c)**) of the TRGO clearly reveals its

highly exfoliated structure. As can be seen in the HR-TEM image (**Fig. 1(d)**), TRGO contains single and few layer graphene sheets. Selected area electron diffraction (SAED) pattern of the single layer show hexagonal packing of the graphene.
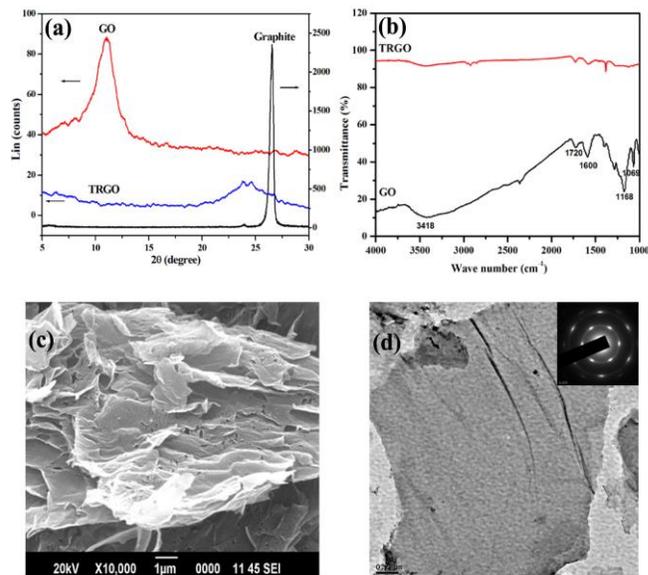
Fig. 1. (a) XRD patterns of Graphite, GO and TRGO (b) FTIR spectra of GO and TRGO (c) SEM of TRGO (d) HR-TEM of TRGO with SAED pattern in the inset

Characterization of TRGO/TPU nanocomposites

As can be observed from the SEM image of TRGO/TPU composite (**Fig. 2**), the TRGO platelets are uniformly dispersed in the TPU matrix. Since graphene has a tendency to restack due to Vander Waals surface forces and due to its low wettability owing to its low surface energy, dispersing graphene as such in a polymer matrix is difficult. Hence, TRGO was first dispersed in DMF by bath sonication and this dispersion was added to polymer solution and sonicated to get uniform dispersion of TRGO in TPU matrix.
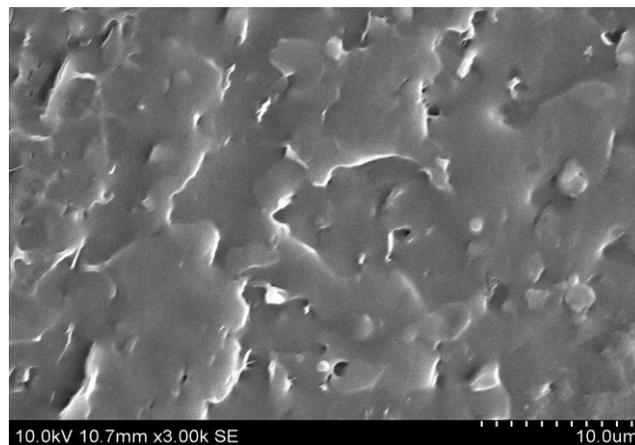
Fig. 2. SEM image of TRGO/TPU composite.

The uniformity of the filler particles in the polymer matrix ensures the improved properties as a composite

material. The TRGO/TPU composites exhibit better mechanical properties when compared to virgin TPU (**Table 1**).

Table 1. Mechanical properties of TRGO/TPU composites.

TRGO loading (wt.%)	Tensile strength (N/mm^2)	Elongation at break (%)	Tensile modulus (N/mm^2)
0	46.6824	808.5053	5.7746
0.5	54.8339	1029.5158	5.3259
1.0	47.7235	894.1147	5.3437
2.5	45.8184	745.473	6.1601
3.0	35.8687	567.7343	6.3306
3.5	25.2426	346.3205	7.3863
4.5	21.0126	390.6958	5.3782

The tensile strength and the elongation are improved at lower filler loading but decreases at higher filler loading. Since TRGO has very high surface to volume ratio, they can impart reinforcement to the polymer matrix at very low concentrations itself. At high concentrations of TRGO, due to the high volume fraction of TRGO, the polymer matrix gets diluted and hence the mechanical properties are decreased. However, in all concentrations, the modulus is not affected very much which is a well desired property for an actuator material.

Photomechanical response of TRGO/TPU composites

under IR light

The TRGO/TPU composite films are found to show fast photomechanical response under IR illumination when a prestrain is given. The actuation was much less without any prestrain, but exhibited large displacement and high generative force at higher prestrains. The photomechanical stress and strain of the composites at different prestrains are shown in the **Fig. 3**. The photomechanical stress is calculated with respect to the dimensions of the sample after giving prestrain.

For all prestrains, samples show contraction in response to IR light. Photomechanical strain increases with prestrain but there is an optimum prestrain for maximum photomechanical stress. When compared to virgin TPU, the photomechanical actuation remarkably increases with TRGO as filler. Virgin TPU is transparent to IR light and hence shows negligible photomechanical response. TRGO acts as an energy transfer unit. TRGO can absorb IR light and effectively transfer the absorbed energy into the polymer matrix, which makes a large difference in the photomechanical responses of the composite. The IR absorption of TRGO/TPU composites mainly depends on two factors: the restoration of sp^2 carbon network in TRGO and the homogeneous distribution of TRGO in the polymer matrix. The restoration of sp^2 carbon network is achieved by the thermal reduction of graphene oxide. There is a strong absorption of IR light in TRGO due to the resonant induction by edge oxygen motion of mobile electrons localized in the vicinity of the oxygen.[35] Maximum IR

absorption of the composite is ensured by the homogeneous distribution of the TRGO platelets in the polymer matrix. TPU has hard segments and soft segments. On giving a prestrain, the soft segments can undergo strain induced crystallization and the mechanical energy can be stored. On IR irradiation, TRGO absorbs the energy and transfers to the polymer matrix. The non - radiative decay of the absorbed IR photons can increase the internal temperature which can melt the strain – induced polymer crystallites of TPU which act as physical crosslinks which secure the deformed shape[33]. This results in actuation by the triggering and subsequent release of mechanical energy stored in the material when in deformed state. Both the photomechanical stress and strain increases at lower filler loading but deceases as the filler loading is further increased which is complementary to the observations in mechanical properties.
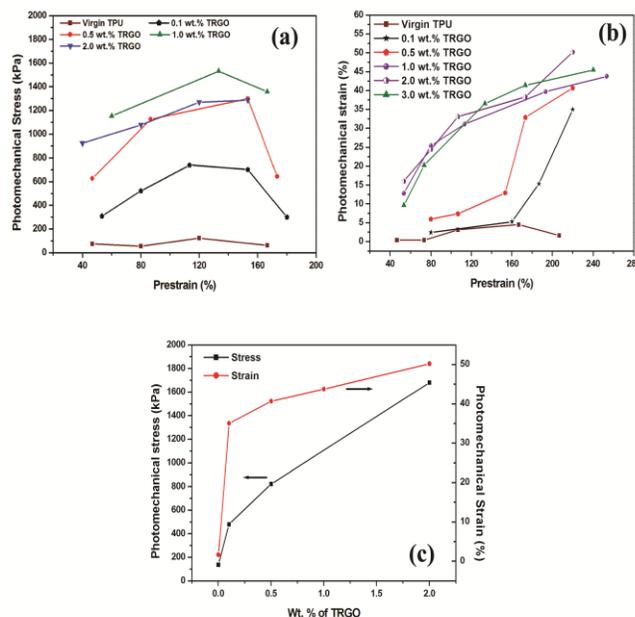
Fig. 3. The photomechanical (a) stress and (b) strain of TRGO/TPU composites at different prestrains (c) stress and strain at different filler loading at a prestrain of 220%.

From **Fig. 3**, it can be observed that TRGO/TPU composites give very high photomechanical response. For instance, at ~120% prestrain, 1.0 wt % TRGO/TPU composite gives a photomechanical force as high as 0.383 N with a stress of 1532 kPa and can contract about 31% of its length i.e., it can lift a weight of 39.08 g to a height of 10.8 mm. Even though there are very few works reported on graphene polymer composite photomechanical actuators, comparison of the properties reveals that TRGO/TPU composites of this work perform considerably better as photoactuators. Previously, Graphene nano platelet/PDMS composites were reported to show a stress change of less than 40 kPa at 2 wt% filler loading.[29] Even with the use of single layer graphene, a total stress change of only about 50 kPa was obtained for 1 wt% graphene/PDMS composites.[31] These are extremely low values when compared to the photomechanical stress obtained for TRGO/TPU composites in this work. The TRGO/TPU composites exhibit superior photomechanical characteristics even when

compared to functionalized graphene –TPU composites in which 1 wt. % sulfonated graphene – TPU composites were reported to give a force of 0.21 N (for a sample of dimension ~30 mm x 5 mm x 0.05 mm) at a prestrain of 200%, which corresponds to a photomechanical stress of 840 kPa.[33] The intensity of IR light used was 30 mWcm^{-2}. However, in the present work, 1 wt. % TRGO/TPU composites exhibits much better photomechanical response. We could obtain a photomechanical stress of 1357 kPa (0.475 N) at 166 % prestrain even at a lower light intensity of 16 mW cm^{-2}. Similarly a photomechanical strain as high as 50.2% is obtained for 2 wt% TRGO/TPU composites at 220% prestrain with a stress of 1680 kPa. This indicates that at a prestrain of 220%, under IR irradiation, it can lift 42.85g to a height of 25 mm. The photomechanical response of the composites with time is given in **Fig. 4 (a)** and **(b)**. The time required for photomechanical response is also reduced when TRGO loading is increased. At higher loading the composites show very fast photomechanical response of less than 1s.
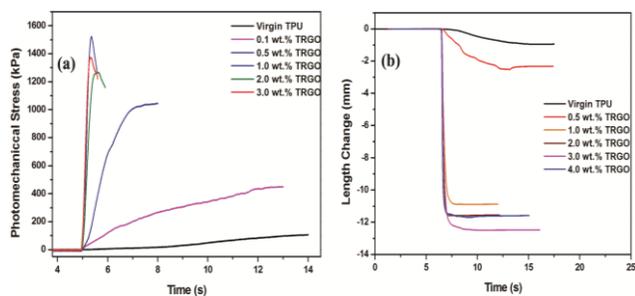
Fig. 4. The photomechanical response of the TRGO/TPU composites with time (a) stress (b) Length change (at a prestrain of ~120%).

Conclusion

The photomechanical actuation properties of Thermally Reduced Graphene Oxide (TRGO)/Thermoplastic Polyurethane (TPU) composites were studied using IR light source. The composites were found to exhibit fast photomechanical response. All the samples show contraction on IR irradiation at a given prestrain. The photomechanical strain increased with prestrain. The photomechanical properties of TPU was found to increase with wt.% of TRGO up to about 2 wt%. Further increase in TRGO concentration resulted in reduction in properties. The response time was also improved as the TRGO content was increased. 1 wt.% TRGO/TPU composite exhibited Photomechanical stress and strain as high as 1532 kPa and 31% respectively. Similarly a photomechanical strain as high as 50.2% is obtained for 2 wt% TRGO/TPU composites at 220% prestrain with a stress of 1680 kPa. Hence this can find potential application as light triggered actuators in many fields including robotics.

Reference

1. Ahir, S. V.; Squires, A. M.; Tajbakhsh, A. R.; Terentjev, E. M. *Phys. Rev. B* **2006**, *73*, 085420.
   DOI: 10.1103/PhysRevB.73.085420
2. Gerratt, A. P.; Bergbreiter, S. *Smart Mater. Struct.* **2013**, *22*, 014010
   DOI: 10.1088/0964-1726/22/1/014010
3. Brochu, P.; Stoyanov, H.; Niu, X.; Pei, Q. *Smart Mater. Struct.* **2013**, 22, 055022
   DOI: 10.1088/0964-1726/22/5/055022
4. Lu, S.; Panchapakesan, B. *Nanotechnology* **2007**, *18*, 305502.
   DOI: 10.1088/0957-4484/18/30/305502
5. Lendlein, A.; Jiang, H.; Junger, O.; Langer, R. *Nature* **2005**, *434*, 879.
   DOI: 10.1038/nature03496
6. Jiang, H.; Kelch, S.; Lendlein, A. *Adv. Mater.* **2006**, *18*, 1471.
   DOI: 10.1002/adma.200502266
7. Ahir, S. V.; Huang, Y.; Terentjev, E. M. *Polymer* **2008**, *49*, 3841.
   DOI: 10.1016/j.polymer.2008.05.005
8. Levitsky, I. A.; Kanelos, P. T.; Woodbury, D. S.; Euler, W. B. *J. Phys. Chem. B* **2006**, *110*, 9421.
   DOI: 10.1021/jp0606154
9. Ahir, S. V.; Terentjev, E. M. *Phys. Rev. Lett.* **2006**, *96*, 133902.
   DOI: 10.1103/PhysRevLett.96.133902
10. Ahir, S. V.; Terentjev, E. M. *Nature Mater.* **2005**, *4*, 491.
    DOI: 10.1038/nmat1391
11. Yang, L.; Setyowati, K.; Li, A.; Gong, S.; Chen, J. *Adv. Mater.* **2008**, *20*, 2271.
    DOI: 10.1002/adma.200702953
12. Koerner, H.; Price, G.; Pearce, N. A.; Alexander, M.; Vaia, R. A. *Nature Mater.* **2004**, *3*, 115.
    DOI: 10.1038/nmat1059
13. Geim, A. K.; *Science* **2009**, *324*, 1530.
    DOI: 10.1126/science.1158877
14. Stankovich, S.; Dikin, D. A.; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S. *Nature* **2006**, *442*, 282.
    DOI: 10.1038/nature04969
15. Atul Tiwari. *Adv. Mat. Lett.* **2012**, *3*, 172
    DOI: 10.5185/amlett.2012.2002
16. Kuila, T.; Bhadra, S.; Yao, D.; Kim, N. H.; Bose, S.; Lee, J. H. *Prog. Polym. Sci.* **2010**, *35*, 1350.
    DOI: 10.1016/j.progpolymsci.2010.07.005
    Parlak, O.; Tiwari, A.; Turner, A.P.F.; Tiwari, A. *Biosensors and Bioelectronics*, **2013**, *49*, 53.
    DOI: 10.1016/j.bios.2013.04.004
17. Shivakumar Gouda, P. S.; Raghavendra Kulkarni, Kurbet S. N.; Dayananda Jawali. *Adv. Mat. Lett.* **2013**, *4*, 261.
    DOI: 10.5185/amlett.2012.9419
18. Ansari, S.; Kelarakis, A.; Estevez, L.; Giannelis, E. P. *Small* **2010**, *6*, 205.
    DOI: 10.1002/smll.200900765
19. Xie, X.; Bai, H.; Shi, G.; Qu, L. *J. Mater. Chem.* **2011**, *21*, 2057.
    DOI: 10.1039/C0JM03926H
20. Chaturvedi, A.; Tiwari, A.; Tiwari, A. *Adv. Mat. Lett.* **2013**, *4*, 656.
    DOI: 10.5185/amlett.2013.4469
21. Patil, B. N.; Acharya, S. A. *Adv. Mat. Lett.* **2013**.
    DOI: 10.5185/amlett.2013.fdm.16
22. Xie, X.; Qu, L.; Zhou, C.; Li, Y.; Zhu, J.; Bai, H.; Shi, G.; Dai, L. *ACS Nano* **2010**, *4*, 6050.
    DOI: 10.1021/nn101563x
23. Zhu, S. E.; Shabani, R.; Rho, J.; Kim, Y.; Hong, B. H.; Ahn, J. H.; Cho, H. J. *Nano Lett.* **2011**, *11*, 977.
    DOI: 10.1021/nl103618e
24. Park, S.; An, J.; Suk, J. W.; Ruoff, R. S. *Small* **2010**, *6*, 210.
    DOI: 10.1002/smll.200901877
25. Shin, K. Y.; Hong, J. Y.; Jang, J. *Chem. Commun.* **2011**, *47*, 8527.
    DOI: 10.1039/C1CC12913A
26. Lian, Y.; Liu, Y.; Jiang, T.; Shu, J.; Lian, H.; Cao, M. *J. Phys. Chem. C* **2010**, *114*, 9659.
    DOI: 10.1021/jp101337h
27. Jung, J. H.; Jeon, J. H.; Sridhar, V.; Il-Kwon Oh. *Carbon* **2011**, *49*, 1279.
    DOI: 10.1016/j.carbon.2010.11.047
28. Zhang, N.; Li, R.; Zhang, L.; Chen, H.; Wang, W.; Liu, Y.; Wu, T.; Wang, X.; Wang, W.; Li, Y.; Zhao, Y.; Gao, J. *Soft Matter* **2011**, *7*, 7231.
    DOI: 10.1039/C1SM05498H
29. Loomis, J.; King, B.; Burkhead, T.; Xu, P.; Bessler, N.; Terentjev, E. M.; Panchapakesan, B. *Nanotechnology* **2012**, *23*, 045501
    DOI: 10.1088/0957-4484/23/4/045501

30. Wu, C.; Feng, J.; Peng, L.; Ni, Y.; Liang, H.; Heb, L.; Xie, Y. *J. Mater. Chem.* **2011**, 21, 18584.
DOI: 10.1039/C1JM13311J

31. Loomis, J.; King, B.; Panchapakesan, B. *Appl. Phys. Lett.* **2012**, *100*, 073108.
DOI: 10.1063/1.3685479

32. Rajendra, K.; Ashok, M. R. *Chem. Commun.* **2013**, *49*, 734.
DOI: 10.1039/C2CC38417E

33. Liang, J.; Xu, Y.; Huang, Y.; Zhang, L.; Wang, Y.; Ma, Y.; Li, F.; Guo, T.; Chen, Y. *J. Phys. Chem. C* **2009**, *113*, 9921.
DOI: 10.1021/jp901284d

34. Acik, M.; Lee, G.; Mattevi, C.; Chhowalla, M.; Cho, K.; Chabal, Y. J. *Nature Mater.* **2010**, *9*, 840.
DOI: 10.1038/nmat2858

35. Marcano, D. C.; Kosynkin, D. V.; Berlin, J. M.; Sinitskii, A.; Sun, Z.; Slesarev, A.; Alemany, L. B.; Lu, W.; Tour, J. M. *ACS Nano* **2010**, 4, 4806.
DOI: 10.1021/nn1006368