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To cite this article: Mahesh Soni et al 2017 J. Phys. D: Appl. Phys. 50 124003

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Photo-catalytic reduction of oxygenated graphene dispersions for supercapacitor applications

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Received 15 October 2016, revised 14 January 2017 Accepted for publication 27 January 2017 Published 24 February 2017



Abstract

Reduced graphene oxide (rGO) obtained from aqueous graphene oxide (GO) tends to agglomerate with time and hinders the commercial scale applications for high-density energy storage. Here, we report a photo-catalytic reduction of GO dispersions in N-Methyl-2-Pyrrolidone (NMP) under deep UV light ($\lambda \sim 253$ nm) for 60 min. The obtained hydrophobic rGO dispersions are electrochemically stable for more than 160 d and exhibit a high Brunauer–Emmet–Teller (BET) surface area of ~260 m² g⁻¹. The NMP being a dipolar aprotic solvent serves as an electron donor and its high dipole moment enhances the electrochemical stability of rGO. Furthermore, the fabricated supercapacitor exhibits a high specific capacitance, charge retention, energy and power density of ~220 F g⁻¹ (current density of 0.5 A g⁻¹), up to 1000 charging/discharging cycles, 7.32 Wh kg⁻¹ and 130 W kg⁻¹, respectively. The high stability of dispersion and electrochemical performance of synthesized rGO is envisaged for potential applications in high density energy storage and conductive inks for flexible electronics.

Keywords: supercapacitor, reduced graphene oxide, conductive ink, photo-catalytic reduction

S Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

1. Introduction

Recently, two-dimensional (2D) layered materials have become a prime research focus worldwide in order to explore alternatives for technological applications, such as nanoelectronics, photo-transistors, ultra-fast photonics and photovoltaics [1–3]. Energy storage in batteries and supercapacitors is an equally important area where these materials have been extensively explored. Meeting the increasing demands of portable systems with fast charging/discharging rates, electrochemical stability, long-term retention and low maintenance cost are the major challenges in the field [4–9]. However, the materials with specific requirements are not explored extensively. Additionally, the strategies for large-scale synthesis of good quality materials retaining the long-term stable homogenous dispersion and 2D morphology with a high yield have not been successfully achieved.

Among the family of one-dimensional (1D) and 2D materials, such as carbon nanotubes (CNTs) and oxygenated graphene (GO), reduced graphene oxide (rGO) composites are potentially reliable materials for next-generation devices [6, 7, 10]. In particular, CNT-based composites are well studied in the literature [9, 11–16]. Besides this, GO has a long history of scientific attention since its first synthesis by

Brodie et al [17] in 1855 and later by Hummer et al [18] in 1958. The synthesis was performed using a chemical reaction between graphite and oxygen containing compounds followed by standard sonication and washing steps. Recently, research on GO has sparked the pace after the flourishing of graphenerelated research [19]. The increased interest is because of the ability of GO to remain dispersed as atomically thin sheets in water. To date, GO has been successfully tested and employed in numerous applications in electronics, photovoltaics and biomedical applications owing to its excellent electronic, thermal, optical and mechanical properties [20–25]. In this context, the GO nanosheets have been studied for decoration with functional groups containing oxygen (epoxy, hydroxyl, phenol, ketone, ether, carboxyl and carbonyl) on the basal plane and edges [26]. The presence of various functional groups on GO attributes to the solubility in organic/inorganic solvents and the removal of functional groups reveals the flocculation and precipitation. Moreover, the electrical conductivity of GO can be enhanced through the reduction of functional groups containing oxygen in GO, resulting in rGO.

To date, a large number of techniques and reducing agents have been proposed for the production of rGO from aqueous GO [27–31]. Several groups have reported on the photo-catalytic reduction of GO dispersed in polyvinyl pyrrolidone (PVP) and N,N-Dimethylformamide (DMF) with the UV irradiation for 48 and 4h [32, 33]. GO reduction from the aforesaid techniques results in agglomeration, unstable homogenous dispersion, the high production cost of rGO and are incompatible for flexible substrates. Moreover, these processes involve unpleasant reaction conditions, long reduction time with the use of harmful and strong reducing agents. Therefore, it is challenging to explore a novel, cost effective approach to achieve the environment-friendly production of high quality, electrochemically stable rGO dispersion.

To address these challenges, the present work demonstrates a facile, cost effective and photo-catalytic reduction of aqueous GO dispersions in a mixture of water and N-Methyl-2-pyrrolidone (NMP) under the exposure of UV light over a period of 60 min. The NMP, being a dipolar aprotic solvent [34, 35] serves as an electron donor to GO and its high dipole moment (~3.75) [36] enhances the electrochemical stability for the longer time, leading to a kinetically stable dispersion of rGO for upto 160 d. Consequently, the aqueous rGO synthesized using the solution process is found to be advantageous for high density energy storage applications with a high specific capacitance of ~220 F g⁻¹ and a charge retention of upto 1000 charging/discharging cycles.

2. Methods

2.1. Materials

Graphite (size < 50 μ m, 99.999% pure), potassium permanganate (KMnO₄), sodium nitrate (NaNO₃), hydrochloric acid (HCl) and hydrogen peroxide (H₂O₂) were obtained from Merck. Sulphuric acid (H₂SO₄) was purchased from Fisher Scientific and NMP from Alfa Aesar. De-ionized (DI) water with a resistivity of 18.2 MΩ.cm (from Elga Labwater) was used for cleaning and solution preparation. Deep UV light (G64HO75, 130 w, 253 nm) from Arklite with an intensity of ~5 mW cm⁻² at a distance of 5 cm (measured from UVC Light Meter 850010, SPER Scientific make), was used as a source for the reduction of GO. During the irradiation, the temperature of the UV chamber was maintained around 30 °C–40 °C.

2.2. Synthesis of GO powder

GO was prepared using the modified Hummers method as discussed in an earlier report [26]. In brief, the oxidation of graphite involves an extensive chemical attack between graphite powder and oxygen containing compounds H₂SO₄, NaNO₃ with a very slow addition of KMnO₄ under constant stirring in an ice bath (below 10 °C). The solution was then diluted with the slow addition of DI water (100 ml) at 95 °C. To terminate the reaction, the above solution was treated with 100 ml DI water and 3 ml H₂O₂ (30%), followed by centrifugation and repeated washing with DI water (until pH ~7). The final yellow dispersion was dried in a hot oven at 50 °C to get GO powder. The GO dispersions at a concentration ranging from 0.1–1 mg ml⁻¹ was sonicated (Rivotek, 33 KHz) with DI water for 1 h and used (supplementary information, S1 (stacks.iop.org/JPhysD/50/124003/mmedia)).

2.3. Reduction of graphite oxide by NMP

Initially, an aqueous pale yellow GO dispersion was tested for the photo-catalytic reduction under deep UV irradiation upto 4 h, but no significant changes were noticed (mostly in colour) indicating a negligible reduction of GO. Later, 1 ml NMP was added to the aqueous GO dispersion of the same batch and kept under deep UV exposure for 60 min and examined at 5 min intervals (supplementary figures S1 and S2). The distance between the deep UV lamp and the solution was ~5cm. Here, with the evolution of irradiation time, the colour of the dispersion changes from pale-yellow to dark brown, which finally turns black after 60 min of exposure indicating the possible conversion of GO to rGO.

2.4. Material characterizations

The Fourier transform infrared (FTIR) spectra were recorded on dried powder using an Agilent Technologies Cary 600 Series FTIR Spectrometer. X-ray diffraction (XRD) measurements were carried out using a Rigaku SmartLab rotating anode powder XRD equipped with Cu-K_{α} radiation. UV–Vis spectra were recorded on a Shimadzu UV-2450 spectrophotometer. Raman spectroscopy was performed on a LabRAM HR Evolution confocal Raman spectrometer (Horiba, Japan) using green (532 nm) laser excitation in the range (800– 2000 cm⁻¹). For Raman measurements, the aqueous solutions were sonicated and drop-casted on cleaned p-Si wafers. For contact angle (CA), a water drop of ~15 μ l was gently placed on the drop-casted GO (/r-GO) films deposited over a glass substrate. The measurements were carried out using a Phoenix 300 system (SEO, Korea). The x-ray photoelectron spectra



Figure 1. Schematic diagram of the overall synthesis process of the reduction of GO to rGO, in the presence of deep UV light.

(XPS) were recorded on a PHI Versa Probe 5000 instrument. The aqueous rGO suspension was vacuum filtered followed by freeze-drying and the obtained powder was degassed at 250 °C before the estimation of the Brunauer–Emmet–Teller (BET) surface area using a Quantachrome Autosorb 1C instrument. Atomic force microscopy (AFM) tapping mode measurements were performed on Dimension Icon from Bruker. The thermal properties of rGO were characterized by TGA (TA Instrument SDT Q600). TEM images were obtained with a TECNAI-G2 operated at 120 KV.

2.5. Charge storage and reliability test for supercapacitor

The electrochemical and cyclic voltammetry measurements were performed using a standard three electrode cell (CH 604E, CH Instruments), with Ag/AgCl, Pt wire gauze and glassy carbon electrode (GCE) used as a reference, counter and working electrodes, respectively. The GCE (diameter 3 mm) was fine polished with gel of Al₂O₃ powder in DI water and fine emery paper followed by repeated washing with DI water and air drying. The reference electrode was dipped in 1 M KCl solution for 2–3 min and washed with DI water several times. For loading rGO (0.1 mg ml⁻¹) onto the GCE, a 40 μ l uniform solution of rGO dispersion (2 ml) in Nafion (10 μ l), was drop-casted and dried at 80 °C.

3. Results and discussions

The schematic process flow for synthesis of rGO from aqueous GO-NMP dispersion in the presence of deep UV is shown in figure 1. The final black colour solution is perhaps due to a decrease in the polar functionalities of GO in the presence of NMP [34]. The dipolar aprotic nature of NMP provides a platform for electron–hole pair generation in the system. The generated electron-hole pairs photo-catalytically interact with the inherently present oxygen containing

cess enhances, significantly, under the UV exposure. The reduction of oxygen containing functional groups is expected to result in the narrowing of the GO band gap, observed earlier [33, 37]. As demonstrated by the FTIR spectrum, the GO sheet is covered with hydroxyl (-OH), epoxy (C-O-C), carbonyl (C=O) and carboxyl (O = C-OH) groups at 3370, 1380 1738 and 1053 & 993 cm⁻¹, respectively. On the other hand, for rGO a significant decrease in the intensity of absorption bands peaks corresponding to oxygen functional groups (at 1330 cm^{-1} due to C–O stretching, and 1000 cm^{-1} due to C-O stretching) confirming the photo-catalytic reduction of GO [38] using NMP. Thus, after the reduction to rGO, the functional groups containing oxygen are removed partially or entirely (figure 2(a)), with the existence of the characteristic (C = C) absorption band peak at 1624 (for GO) and 1652, 1573 (for rGO) cm^{-1} [39]. Similarly, the formation of rGO is supported by UV-Visible absorption spectra (shown in supplementary figure S3). Furthermore the formation of rGO from GO was confirmed by XRD as shown in figure 2(b). The GO shows a diffraction peak at $2\theta = -9.3^{\circ}$ (d-spacing-9.49Å) [32, 36], while rGO has a broader (002) peak at $2\theta \sim 23.3^{\circ}$ (d-spacing ~3.81Å) [40]. The larger interlayer spacing of GO is attributed to the presence of hydrocarbons as surface contaminants, oxygen containing functional groups and trapped H₂O molecules at the edges and basal plane [41]; on the other hand the smaller interlayer spacing of rGO suggests the reduction of GO [32, 36].

functional groups of GO (figure 1), thus the reduction pro-

To understand the evolution of rGO from GO and photo-catalytic reduction, Raman studies have been carried out for GO and GO + NMP under UV exposure at intermediate intervals of 10, 15, 20, 30, 45 and 60 min. Raman spectra, in figure 2(c), show two peaks around 1345 and 1590 cm⁻¹, corresponding to first order D and G bands, respectively [33, 36]. The G band peak corresponds to E_{2g} symmetry of sp² hybridised carbon atoms, while the D band corresponds to the breathing mode of sp² hybridised carbon atoms in the



Figure 2. Characterization data of rGO and GO: (a) FTIR absorption band spectra; (b) XRD spectrum; (c) Raman spectroscopy for GO and GO + NMP after 10, 15, 20, 30, 45 and 60 min (UV exposure); (d) XPS spectra of GO and rGO. CAs of GO + NMP; (e) as prepared (27.9°) (f) after 30 min (63.7°) and (g) after 60 min (101.7°), of UV exposure time. (The dotted lines guide the trends.)

hexagonal ring along with the local defects and disorder. The intensity ratio of the D and G bands (I_D/I_G) is an important and major factor to distinguish GO and rGO for structural defects/disorders [32, 33, 38]. We have observed a noticeable enhancement in (I_D/I_G) from ~0.98 to 1.29 for GO to rGO (60 min exposure) (supplementary table s1), which confirms the reduction of GO (figure 2(c)) [42]. The ratio of I_D/I_G in the present work is found to be higher in comparison with the results reported by other techniques [32, 33, 38, 42, 43]. The $I_D/I_G > 1$ of rGO signifies (i) the decrease in the average size of the sp² hybridized carbon atom after GO reduction, (ii) the formation of a large number of smaller graphitic domains than the ones present in GO before reduction leading to large quantities of structural defects and (iii) the increased fraction of graphene edges [42, 44]. The XPS investigations (figure 2(d)), for GO show a carbon/oxygen (C/O) ratio of 2.61, which increases to 4.33 after 60 min of deep UV exposure. The increased C/O ratio indicates the removal of hydrophilic oxygen containing functional groups present in GO. The C_{1s} XPS spectrum of the GO and rGO is as shown in supplementary figure S4. With attached surface functional groups containing oxygen, GO is hydrophilic in nature while rGO is hydrophobic in nature [30]. The hydrophobicity of the rGO film is confirmed by the CA measurements (figures 2(e)-(g)). The smaller CA ~ 27.9° of the water droplet on the GO film is indicating a hydrophilic nature, whereas for GO + NMPfilms after 30 and 60 min of UV exposure, the CA is higher, ~63.7° and ~101.7°, respectively, illustrating the hydrophobicity. We believe that the characterization data supports the formation of rGO after photo-catalytic reduction under UV exposure. The successful reduction quality of as-synthesized

rGO was assessed by TGA curves. The TGA plots of GO and rGO are shown in figure S5. The GO samples show major weight loss between 100 °C and 200 °C, owing to the loss of residual water between adjacent GO sheets and the release of CO, CO₂ and steam from the most labile functional groups during pyrolysis, hence it is thermally unstable [45]. In contrast, the rGO sample exhibits higher thermal stability than GO. The major weight loss was ~20% at temperatures around 300 °C. However, there is still a significant weight loss for rGO between 300 °C and 600 °C attributed to the absence of most oxygen functional groups, suggesting that even the reduction process cannot remove the most stable functionalities, in agreement with previous reports [45]. A comparison of UV exposure time for various photo-reduction methods has been presented in table 1, showing that the present strategy for photo-catalytic reduction produces a good quality rGO. Interestingly, the 60 min of UV exposure time is a minimum among other techniques.

The photograph of the kinetically stable dispersion of GO and rGO, kept undisturbed for 90 d and 160 d has been shown in figure 3. Konios *et al* have investigated the stability of GO and rGO dispersions in a wide range of organic solvents and found stable dispersion existing for 20 d only [36]. In the present case, the dispersion is found to be stable up to 160 d, which is important for application in conductive ink for printed electronics. The reason for such a high stability is understood carefully. Here, the rGO has been photo-catalytically reduced in GO-NMP dispersions, whereas the rGO has been dispersed after formation in the previous reports [36]. To understand the effect of the pH on the stability of dispersion, the rGO was dispersed in both acidic and basic medium. In line with the

Photo-reduction strategy	UV/Laser exposure	$I_{\rm D}/I_{\rm G}$ for rGO	Ref
PVP	48 h		[32]
N,N-Dimethylformamide (DMF)	4 h	1.06	[33]
$50 \text{ ml} (1 \text{ mg ml}^{-1}) \text{ N}$, N-Dimethylformamide (DMF), Tetrathiafulvalene (TTF) (0.25 mol) and Sc(SO ₃ CF ₃) ₃ (0.6 mol) metal ions	—	1.02	[38]
5 ml Zn(II)TTPOH, IPA solution $(0.05 \text{ mg ml}^{-1})$, and 1 ml ethanolamine	3 h	1.095	[42]
GO dispersion along with OH^- , N_2H_4 exposed with UV lamp (254 nm wavelength)	Up to 9 h	_	[46]
(0.1 mg ml ⁻¹) GO dispersion and ammonia solution excited with 248 nm, KrF excimer laser, (maximum pulse energy of 700 mJ)	5 min	_	[47]
GO film on PET substrate excited by UV Lamp (115 V, 60 Hz, 2.5A)	1–24 h	_	[48]
GO film on PET substrate excited by industrial-grade 1064 nm Nd:YAG laser in an ambient environment.	—	—	[49]
$(0.1-1 \text{ mg ml}^{-1})$ GO dispersion and 1 ml NMP	1 h	1.29	Present work

Table 1. Comparison of different photo-reduction strategies for GO.



Figure 3. Photograph of GO and rGO dispersions after (a) 90 d and (b)160 d, showing stable and uniform long-time stability. (c) TEM image of as dispersed rGO nanosheet.

earlier reports [50], the rGO dispersion agglomerates in the acidic medium, while it remains stable in the basic medium, even after 48 h (as shown in figure S6). The pictorial view of the TEM images for the aqueous rGO dispersed in NMP is shown in figure 3(c). The rGO dispersion contains multilayer (3–5) layers of rGO ($t \sim 1.5 \pm 0.2$ nm) as estimated from the AFM image (as shown in supplementary figure S7). The TEM and AFM image confirms the homogenous dispersion of the rGO nanosheets in NMP with a lateral dimension of around 2–3 μ m.

To understand the supercapacitor performance, for energy storage application, the electrochemical characterization current density (A/g)-Potential (V), Galvanostatic charge/ discharge and electrochemical impedance spectroscopy (EIS) have been performed on aqueous rGO in 1 M H₂SO₄. Figure 4(a) shows the current density (A/g)-potential (V) curves, at scan rates of 10, 50, 100, 200 mV s⁻¹, depicting a rectangular shape within the potential range (-0.2-1 V). The excellent capacitance (charge transfer) characteristics have been observed due to the presence of residual functional groups in rGO after reduction. The galvanostatic charge/discharge curves follow the identical behaviour for all the current densities (0.5, 1, 2, 4, 8, 10 A g^{-1}) advocating excellent charge storage capabilities (figure 4(b)). The weight-specific capacitance $C_{\rm sp} = \frac{I}{m} \left(\frac{\delta t}{\delta V} \right)$ is an important parameter to quantify the performance of the active supercapacitor materials [51, 52]. Here *m* is the mass of the active material on the electrode, *I* is the applied current, $\delta V/\delta t$ is the slope of the discharge curve. The estimated C_{sp} at various current densities (0.5, 1, 2, 4, 8) and 10 A g^{-1}) are found to be 220, 120, 80, 70, 55 and 50 F g⁻¹, respectively. The $C_{\rm sp}$ of present work is comparable with previously reported graphene quantum dots (~236 F g^{-1}) [8], and considerably higher than rGO, few layer graphene, porous carbon composite, nitrogen-doped activated carbon/carbon nanotubes (N-AC/MWCNTs), carbon nanotubes-carbon nanofibers (CNTs/CNFs) and activated carbon [51-58]. The retention characteristics, examined by galvanostatic charging/ discharging techniques (C_{sp} versus no. of cycles) at current densities of 0.5 A g^{-1} , suggest ~10% change in the value of $C_{\rm sp}$ of the initial value after 1000 cycles, leading to superior capacitance characteristics (figure 4(c)). For super capacitor applications, energy and power density are the critical parameters that determine the charge storage capability and rate of energy transfer [58]. The energy and power density for the rGO-based supercapacitor are computed to be 7.32 Wh kg^{-1} and 130 W kg⁻¹, respectively, and are comparable to the previous reported results [58]. Additionally, when the power density of the rGO-based supercapacitor reaches to 650 W kg^{-1} , the corresponding energy density is ~ 2 Wh kg⁻¹, demonstrating promising supercapacitor characteristics. Hence, the devices can be employed for the commercial scale fabrication of supercapacitors. The Ragone plots (energy density versus power density) for the fabricated rGO-based supercapacitor is as shown in the inset of figure 4(b).

Additionally, the superior electrochemical reversibility, along with the high rate capability is investigated by the Nyquist



Figure 4. Electrochemical characterization of aqueous rGO in 1 M H₂SO₄ (a) current density-potential curves at different scan rates of 10, 50, 100, 200 mV s⁻¹, (b) galvanostatic charge/discharge curves at current densities of 0.5, 1, 2, 4, 8, 10 A g⁻¹. The inset shows the ragone plots for the fabricated supercapacitor. (c) Retention of capacitance versus no. of cycles for rGO at the current density of 0.5 A g⁻¹. The inset shows the values of weight-specific capacitance (C_{sp}) at 0.5, 1, 2, 4, 8, 10 A g⁻¹, (d) Nyquist plot of EIS at an open circuit potential of 5 mV. The frequency is varied from 0.1M to 0.1 Hz. Z' is the real impedance and Z'' is the imaginary impedance. The inset shows the equivalent circuit.

plot of EIS measurement performed at an open circuit potential of 5 mV. The EIS spectrum resembles a semicircle in the high frequency region and a straight line in the low frequency region. The straight line (Warburg slope) observed in the low frequency region attributes to the rapid diffusion of ions to the electrode, hence resulting in a better capacitive behaviour [6, 59]. The inset in figure 4(d) shows the equivalent circuit diagram for the EIS analysis. The equivalent circuit comprises of a series transfer resistance (R_s) , a parallel combination charge transfer resistance (R_{ct}) , a capacitive element (C_p) and a constant phase element (CPE) as a result of double layer capacitance. From the Nyquist plot, the value of R_s (~9.4 Ω) estimated from the left intercept of the semicircle (at high frequencies), and the value of R_{ct} is ~12 Ω computed from the right intercept (($R_{\rm s} + R_{\rm ct}$), after the diameter of the semi-circle), at the real axis. The two values suggest a high conductivity of synthesised rGO for supercapacitor application. The porosity and accessible surface area of the active material are vital factors in controlling the movement of ions for supercapacitor applications. In the present case, the rGO has a high specific surface area of $\sim 260 \text{ m}^2 \text{ g}^{-1}$ with a pore volume of $0.21 \text{ cm}^3 \text{ g}^{-1}$ as estimated from the BET surface area measurements (supplementary figure S8). The obtained surface area in the present study is considerably higher than the previously reported values 12.7, 136, 230 m² g⁻¹ [52, 60, 61]. The BET measurements suggest a high surface area, pore volume and porosity, thus justifying the results for the supercapacitor performance [15, 58].

4. Conclusions

In conclusion, the study reports a facile and photo-catalytic reduction strategy of GO in NMP under the exposure of UV light at low temperatures. The major outcome is long time stability of the rGO dispersion up to 160 d. The high surface area of the synthesized rGO enables high accessibility for the ion movements leading to a better electrochemical performance with high specific capacitance (~220 F g⁻¹) for supercapacitor applications. The proposed strategy is useful for large-scale production, homogenous dispersion of rGO for supercapacitors and conductive ink in flexible electronics applications.

Acknowledgments

Authors thank IIT mandi for research facilities. SKS would like to acknowledge DST, India for DST/TSG/2015/634 grant. AS would like to acknowledge DST-SERB, India for YSS/2014/1038 grant.

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