



# Self assembly of functionalised graphene nanostructures by one step reduction of graphene oxide using aqueous extract of *Artemisia vulgaris*



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## ABSTRACT

We report self assembly and organisation of graphene sheets to form a macroscopically ordered array of graphene layers using one step reduction of graphene oxide. Aqueous extract of dry leaves of *Artemisia vulgaris* is used for de-oxygenation of graphene oxide. The reduced graphene oxide samples are investigated for two different reflux times viz. for 6 h and 12 h. It is found that for an efficient reduction of graphene oxide and for the minimal damage to the crystal structure 6 h of reflux is the most favourable. Besides reducing graphene oxide, the phytochemicals also functionalise the graphene layers with electron withdrawing groups by virtue of which three dimensional nanostructures are formed on its surface.

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## 1. Introduction

Owing to their unique optical, electrical and chemical properties, graphene oxide (GO) and reduced graphene oxide (rGO) have attracted much research interests in the field of electronics and optoelectronics [1–3]. Unlike pure graphene, GO is an insulator where the attached oxygen containing moieties act as strong scattering centres for the Dirac fermions [4]. Removal of these functional groups is necessary for the partial restoration of graphene's electrical and optical properties [5]. Although chemical reduction of GO is one of the promising approach for the large scale graphene synthesis, it requires toxic and strong reducing agents such as hydrazine and sodium borohydride [6,7]. Green reduction techniques have shown promising avenues towards synthesis of rGO [8,9]. Many alternate routes using plant extracts and biomolecules have been reported for the reduction of GO including reduction by green tea [7], glucose, fructose and ascorbic acid [10], aqueous peel extract of orange [6], wild carrot [11], etc. These rGO samples comprise of few to multiple layers of graphene with partially restored electrical and optical properties.

Three dimensional (3D) graphene architectures and their nanocomposites have displayed wide range of applications in the field of building transistors, flexible touch screens, solar cells, batteries, supercapacitors, sensors and bio-devices [12–16]. Many synthesis routes have been reported for their fabrication including graphene on silicon nanocone arrays [17], via boiling GO [18] and rose-like ZnO/rGO composites [19]. However, isolation of these 3D graphene structures and their assembly on a desired substrate remain a challenge till date.

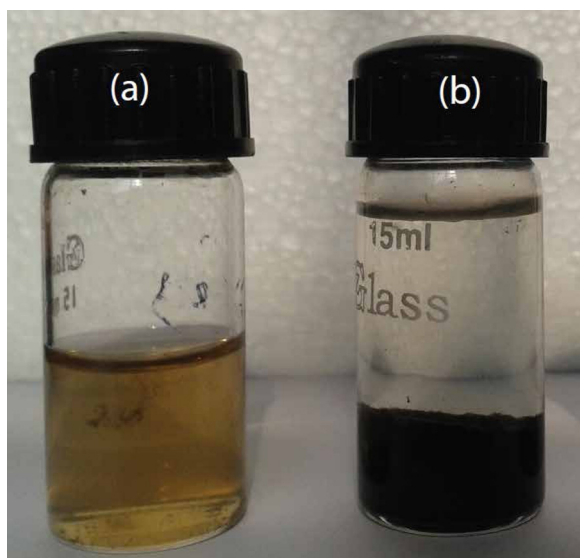
*Artemisia vulgaris* (AV), is known for its medicinal and antioxidant properties. AV extracts are ethno-pharmacologically used for the treatment of diabetes, epilepsy, respiratory and gastrointestinal disorder [20,21]. In this article, a self assembled 3D reduced graphene oxide architectures are constructed by one step bio-reduction of water dispersible GO using AV extracts. This synthesis route produces template-free 3D hedgehog like nanostructures of rGO on the graphene surface without using any external precursors.

## 2. Materials and method

Modified Hummers and Offeman method was adopted for the synthesis of graphite oxide [6,22]. 40 mg of graphite oxide powder was dispersed in 80 ml of deionised water and ultrasonicated for an hour to obtain orange–brown coloured stable aqueous dispersion of GO as can be seen from Fig. 1(a). Dry leaves of AV were finely

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**Fig. 1.** (a) Stable dispersion of GO and (b) sedimentation of rGO-6 in water as observed after few hours of preparation.

cut and washed separately with deionised water and were boiled for 3 min in 40 ml of the water. The extract was left to cool down at room temperature and subsequently filtered using Whatman filter paper with a pore size of 11  $\mu\text{m}$ . This filtrate was considered as the plant extract for the synthesis of rGO.

The prepared GO and rGO samples were characterised at room temperature by using PANalytical X.Pert Pro X-ray diffractometer with Ni-filtered  $\text{CuK}\alpha$  radiation of wavelength 1.54  $\text{\AA}$ , Bruker FTIR with spectral resolution of  $4\text{ cm}^{-1}$ , Renishaw inVia RM2000 Raman spectrometer with 514.5 nm as the excitation wavelength and 30 mW laser power. The photoluminescence (PL) spectra were recorded by Perkin Elmer LS55 spectrometer where the excitation wavelengths ranged between 250 nm and 400 nm and the emission spectra were recorded between 455 nm and 610 nm. Electron paramagnetic resonance (EPR) measurements were performed using Bruker A200 X-band CW spectrometer. The operating microwave frequency was 9.867 GHz and power was 2 mW. Field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) images were obtained using Carl Zeiss Ultra-55 with field emission electron gun working at 5 kV and Technai equipped with thermo-ionic electron gun working at 200 kV respectively.

### 3. Results and discussion

#### 3.1. Reduction of GO

To the stable dispersion of GO (0.5 mg/ml), 8 ml of the plant extract was added and was continuously stirred for 20 min. The mixture was then refluxed at  $90\text{ }^\circ\text{C}$  for up to 12 h. After 4 h of reflux, the solution turned black in colour. The change in colour from orange–brown to black upon refluxing affirms the reduction of GO [6]. In addition to GO, rGO samples refluxed for 6 h and 12 h are discussed in detail in the following sections. Suffix “6” and “12” in rGO represents reflux time of the solution in hours.

Fig. 1(a and b) displays the dispersion of GO and rGO-6 in water. Formation of thin film-like aggregates occur in samples refluxed for 6 or more hours. These films show hydrophobicity and tend to settle at the bottom of the vials even after sonication. Depending upon the presence of multiple polar functional groups in GO and rGO, their dispersion in water varies. This is why, we claim that the observed hydrophobicity in rGO after prolonged reflux is due to the

**Table 1**  
Observed XRD parameters of GO and rGO samples.

Samples	$2\theta$ ( $^\circ$ )	$d$ ( $\text{\AA}$ )
GO	$9.81 \pm 0.01$	9.01
rGO-6	$26.68 \pm 0.01$	3.34
	$28.33 \pm 0.01$	3.15
rGO-12	$5.48 \pm 0.05$	16.11
	$6.28 \pm 0.03$	14.06
	$8.86 \pm 0.01$	9.97
	$25.17 \pm 0.01$	3.53
	$26.84 \pm 0.01$	3.32

removal of functional groups from GO during the green reduction process.

#### 3.2. X-ray diffraction (XRD) analysis

An intense XRD peak for graphite at  $2\theta = 26.57^\circ$  corresponding to (002) reflection and interlayer d-spacing of 3.38  $\text{\AA}$  is observed from Fig. 2(d). XRD patterns of GO, rGO-6 and rGO-12 are also shown in Fig. 2(a, b and c) respectively. The observed peak positions and the d-spacings for GO, rGO-6 and rGO-12 are listed in Table 1. GO exhibits a broad peak at  $2\theta = 9.81^\circ$  corresponding to  $d = 9.01\text{ \AA}$  of (002) plane with a full width at half maxima (FWHM) of  $0.708^\circ$ . It is evident that the d-spacing in GO has increased from that of a crystalline graphite sample upon oxidation. The presence of only one XRD peak at  $2\theta = 9.81^\circ$  in GO suggests complete oxidation of graphite [6,23].

In Fig. 2(b), the peaks centred at  $26.68^\circ$  and  $28.33^\circ$  in rGO-6 are attributed to (002) plane whose interplanar distances are smaller than that of GO. The decrease in the interplanar spacing is attributed to the efficient removal of intrinsic functional groups such as C–O, C–OH and OH from the basal planes of GO. The removal of these oxygen containing groups shall be corroborated with the FTIR spectrum of rGO-6 in the following section. The observed d-spacing in rGO-6 is also smaller than that of the parent graphite sample used for the preparation of GO. An illustration is presented in Fig. 2(e, f, g and h) which shows the change in the interplanar spacing of graphite, GO and rGO-6 samples. The peak at  $28.33^\circ$  for rGO-6 is the most intense and has FWHM of  $0.109^\circ$  which is smaller as compared to that of the GO. In addition, we have observed peaks at higher  $2\theta$  values centred at  $40.52^\circ$ ,  $50.18^\circ$  and  $66.38^\circ$  corresponding to reflection from (100), (102) and (104) planes respectively. The XRD patterns suggest that the synthesised rGO-6 sample is highly crystalline in nature with an ordered array of layers in (002) direction [24].

In rGO-12, XRD peaks appear at  $25.17^\circ$  and  $26.84^\circ$ . These peaks are observed to be weak and broad as compared to rGO-6 indicating loss of long range ordering in the rGO crystal. With an extended reflux of 12 h, additional peaks at  $5.48^\circ$ ,  $6.28^\circ$  and  $8.86^\circ$  are also seen. It suggests that prolonged interaction with the phytomolecules in water during the reduction process increases the interlayer spacing in the rGO sample. It could be attributed to the intercalation of water molecules and/or phytomolecules within the graphitic planes during the reflux process which in turn increases the d-spacing in rGO-12 [7,24–28].

#### 3.3. Fourier transform infrared (FTIR) analysis

GO contains functional groups such as hydroxyl (–OH), epoxy (–O–), carbonyl (=O) decorated on its basal plane which are responsible for increasing the interplanar distance whereas its periphery is decorated with carboxylic (–COO) group when synthesised by Hummers and Offeman method [5,29].

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