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## ARTICLE

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### Eco-friendly synthesis of graphene using the aqueous extract of *Amaranthus dubius*

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An eco-friendly process of reduction of graphene oxide using aqueous extract of *Amaranthus dubius* under refluxing method is herein reported. The colour change of the graphene oxide (GO) solution from brown to black was noted during the reduction of graphene oxide. UV-Visible spectrophotometer was used to monitor the formation of reduced graphene oxide (AKRGO). The crystallite size of nanographene was confirmed by XRD analysis and Scherrer's formula. FTIR spectral analysis revealed the reduction of graphene oxide using aqueous extract of *Amaranthus dubius*. The morphology of the synthesized graphene was examined by SEM analysis.

**Keywords:** Graphene, XRD, SEM, FTIR, nanoparticles.

**1. Introduction :** Graphene, a novel and an exciting material composed of  $sp^2$  bonded carbon atoms densely packed in a honeycomb crystal lattice have received significant attention in recent years, due to its excellent properties like high current density, good electrical conductivity, ballistic transport, large theoretical specific surface area, chemical inertness, optical transmittance, high thermal conductivity and super hydrophobicity at nanometer scale [1-2].

The covalent bonds formed by  $sp^2$  hybridised orbital's in graphene is responsible for its extraordinary mechanical strength, making it possible to have stable free-standing graphene sheets, being only one atomic layer thick. Its band gap and magnetic properties can be tailored by changing its edge structure and by chemical modification of its interior or edges. These features have made graphene an ideal for diverse applications such as energy-storage capacitors, sensors and transistors [3].

Graphene is characterized as the thinnest material in our universe explored a wide range of applications in various industries such as photovoltaic cells, capacitors, sensors, transparent

conductive electrodes and novel nanocomposites [4]. Due to its high charge mobility, low noise, large detection area and biocompatibility, graphene finds applications in bio sensing, drug and gene delivery, imaging, antibacterial materials to scaffold for cell culture and biomedical fields [5]. In recent years, several procedures have been adopted for producing graphene. The chemical reduction of GO is the commonly used method compared to all other methods. The main disadvantage of chemical method is the irreversible aggregation of the product graphene oxide and high toxic nature of the reducing agents making it unfit for biological related applications. In order to overcome the aforesaid difficulties, green nanotechnology is of late used widely by researchers. Very few reports are available on the reduction of GO by using tea solution [6], glucose [7], polyphenol alcohol [8], wild carrot root [9], reducing sugar [10], melatonin [11], bacteria [12-13], vitamin C [14 - 15], amino acid [16] and bovine serum albumin [17]. There are no reports on the use of plant extracts in the formation of graphene.

Hence we report a simple and eco-friendly synthesis of reduced graphene oxide using

aqueous extract of *Amaranthus dubius* as reducing agent. The confirmation of formation of graphene has been established through spectral measurements viz. UV-visible spectra, XRD, FTIR, SEM and Raman spectra. The stability of the synthesized graphene has been made through zeta potential and particle size analysis.

## 2. Experimental :

**2.2 Materials :** Graphite powder was purchased from Loba chemicals, India. *Amaranthus dubius* (plant) were collected from retail shop in Coimbatore.

## 2.3 Methods :

**2.3.1 Preparation of plant extract :** Fresh plant of *Amaranthus dubius* (20 g) was washed, blended in a mechanical blender and stirred continuously for 30 min, maintaining the temperature at 50°C. The mixture was filtered using Whatmann filter paper and refrigerated at -4°C.

**2.3.2 Preparation of graphene oxide :** Graphene oxide was prepared by oxidizing the graphite with potassium permanganate and concentrated sulphuric acid. Graphite powder (2 g) and 46 mL of concentrated sulphuric acid was stirred in a magnetic stirrer for 2h in an ice-bath. 6 g of potassium permanganate was added gradually over a period of 30 min with vigorous stirring under the temperature of 20°C for 2h. Then 92 mL of double distilled water was added to the mixture and maintaining the temperature below 100°C for 30 min. Finally 30% hydrogen peroxide (280 mL) was added till the brown solution turned pale yellow colour. The obtained product was filtered, washed with 10% Hydrochloric acid solution to remove the metal ions followed by repeated washing with distilled water till the pH of the solution is neutral. The purified graphene oxide was filtered and dried.

**2.3.3 Synthesis of graphene using phytoextract :** The stable graphene oxide was prepared by sonicating 60 mg in 120 mL of distilled water for 30 min. 10 mL of aqueous extract of *Amaranthus dubius* was added to the stable graphene oxide solution and refluxed until the brown colour solution changes to black.

**2.4 Characterization :** The UV-visible spectra were analyzed using Double Beam Spectrophotometer – 2202 (Systronics). X-ray diffraction study was carried out by X' Pert Pro system with Cu K radiation ( $\lambda=1.54060 \text{ \AA}$ ) operated at 45 kV and 30 mA over the range of  $2\theta = 2 - 70^\circ$  with scanning rate  $2^\circ$  per min. The FTIR spectra was performed using Fourier Transform Infrared spectroscopy 8400S (Shimadzu). The particle size and zeta potential were analyzed using NanoPartica SZ-100 series (Horiba) and maintained at a temperature of 25° C for 2 min. Scanning Electron Microscope (e-SEM, FEI Quanta 250) was used to examine the morphology of the reduced graphene oxide (AKRGO) coated on the glass substrate. The Raman spectrum was obtained using R-3000 QE with an optical resolution of  $6 \text{ cm}^{-1}$ .

## 3. Results and discussion :

**3.1 Phyto-mediated reduction of graphene oxide :** The graphene oxide (GO) was reduced to graphene (AKRGO) by using the aqueous extract of *Amaranthus dubius* under refluxing. The agglomeration occurred on addition of plant extract and dispersed finally after 1 h of refluxing. The brown colour solution changes to black after 4 h of refluxing with precipitation. The complete reduction of graphene oxide takes place only after 9 h of continuous refluxing. It was noted that the temperature, concentration of the phytoextract and time of reaction may play a foremost role in the synthesis of graphene.

**3.2 UV-Visible spectroscopy :** The reduction of graphene oxide was also monitored by UV-Visible spectroscopy. The UV-Visible spectrum of graphene oxide shows an absorption band at 236 nm and a weak shoulder at 300 nm corresponding to  $\pi - \pi^*$  transitions and C=O bonds respectively. *Amaranthus dubius* assisted graphene had a red shift of 278 nm which confirms the reduction of graphene oxide (Figure 1). It was observed that the optical absorption of reduced graphene oxide (AKRGO) was higher than that of graphene oxide (GO). The concentration of graphene and graphene oxide to form a stable dispersed solution may significantly manipulate the absorption bands obtained in UV-Visible spectroscopy.

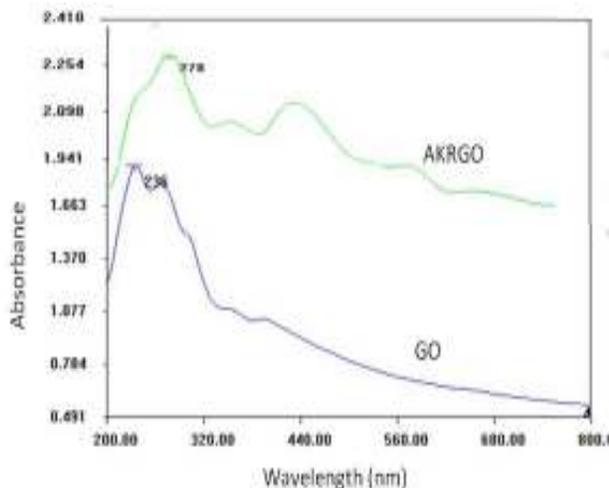


Figure (1): UV-Visible spectra of graphene oxide (GO) and reduced graphene oxide using *A. dubius* (AKRGO)

**3.3 X-ray diffraction (XRD) analysis :** The structural changes of graphene oxide upon reduction were analyzed using the patterns obtained by X-ray diffraction study. Graphite has a strong diffraction peak at about  $26.52^\circ$  which represents an interlayer distance of 0.34 nm. In graphene oxide (GO) this peak disappears and a new weak diffraction peak appeared at  $10.51^\circ$  with an interlayer space (d-spacing) of 0.84 nm. This indicates that the graphene oxide retains a layered structure. The distance between the layers increases, due to the formation of hydroxyl, epoxy and carboxyl groups which causes intercalation of water molecules. It is observed that reduced graphene oxide exhibited a peak at  $28.8^\circ$  corresponds to the interlayer distance of 3.16 Å and disappearance of  $10.81^\circ$  in the XRD pattern of AKRGO is shown in Figure (2). This can be attributed to the successful reduction of the GO by aqueous extract of *Amaranthus dubius*. The crystallite size of nanographene was determined using Debye-Scherrer's equation as given below -

$$D = k\lambda / \beta \cos\theta \text{ (nm)}$$

where,  $k$  = constant (0.9),  $\lambda$  = wavelength of the X-ray (Å),  $\beta$  = full width half maximum (radians),  $\theta$  = diffraction angle (degrees).

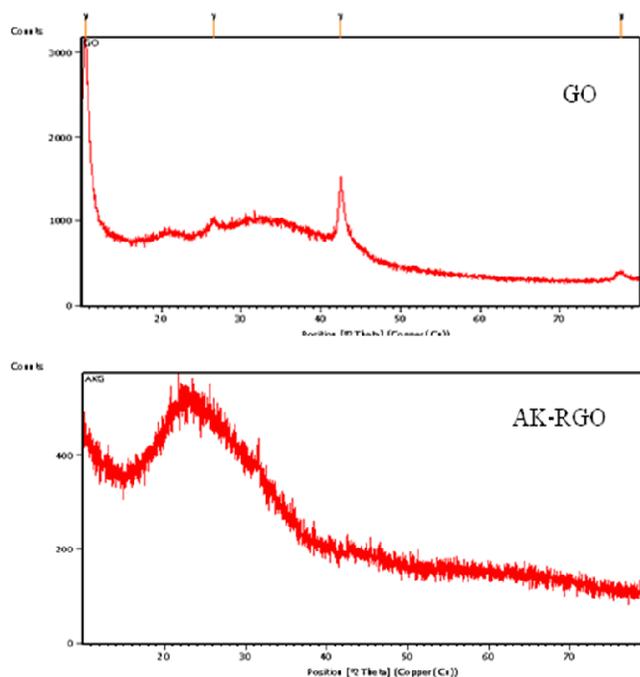


Figure (2): XRD patterns of graphene oxide (GO) and *A. dubius* assisted graphene (AKRGO).

**3.4 FTIR analysis :** The FTIR spectra of graphene oxide (GO) and graphene (AKRGO) are shown in Figure (3). The two peaks at  $1720 \text{ cm}^{-1}$  and  $1610 \text{ cm}^{-1}$  was assigned to carbonyl and aromatics respectively for graphene oxide. The disappearance of the foresaid peaks was observed in Figure (3), which revealed the reduction of graphene oxide using the aqueous extract of *Amaranthus dubius*.

**3.5 Raman spectroscopy :** Raman spectroscopy is a useful tool in determining the finger print region of graphene. Figure (4) represents the Raman shift of synthesized graphene (AKRGO) which shows a D band at  $1350 \text{ cm}^{-1}$ . The pristine graphite with large grain size has no detectable D band at around  $1350 \text{ cm}^{-1}$  [18]. The D band was noted at  $1350 \text{ cm}^{-1}$  indicating small crystallite size of graphene (AKRGO) with some impurities [19]. The G band of synthesized graphene was shifted to  $1641 \text{ cm}^{-1}$  instead of  $1587 \text{ cm}^{-1}$  which manifests that G peak is strongly temperature dependent. The sensitivity of G peak will depend on the local change in temperature accompanied by the variation of laser excitation power focused on the graphene [20]. The complete loss of 2D peak ( $\sim 2670 \text{ cm}^{-1}$ ) accompanied by peak broadening

and  $20\text{-}30\text{ cm}^{-1}$  shift of G band suggest that the graphene flakes are composed of layers of 5-20 thickness [21]. In the present study, the absence of 2D and shift of D peaks ( $1641\text{ cm}^{-1}$ ) signifies the formation of few layer graphene.

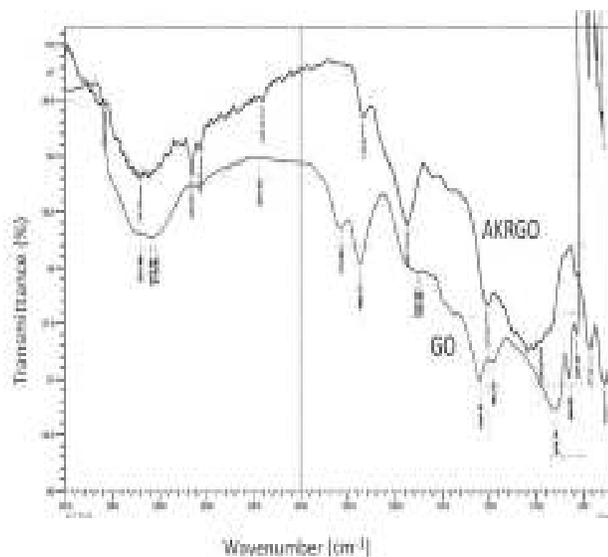


Figure (3): FTIR spectra of synthesized graphene (AKRGO) (a) and graphene oxide (b)

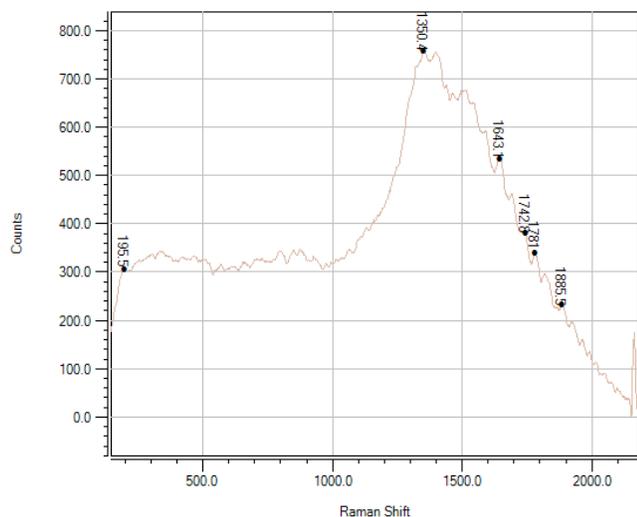
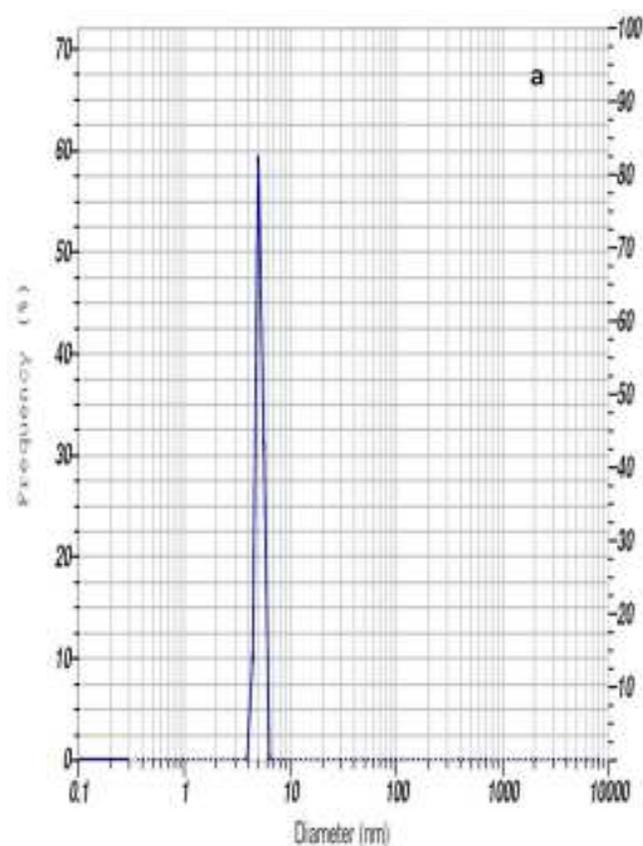


Figure (4): Raman shift of reduced graphene oxide (AKRGO)

### 3.6 Particle size and zeta potential analysis :

The particle size of the synthesized nanographene confirmed by particle size analyzer was 4.8 nm (Figure 5a). The zeta potential measurement is a useful parameter to characterize the stable dispersions of the graphene. The Zeta-potential value of particles which are lower than  $-30\text{ mV}$

will possess strong repulsive forces [22]. The zeta potential values of neutral nanoparticles lies in-between  $-10$  and  $+10\text{ mV}$  and strongly cationic and anionic NPs possess the values greater than  $+30\text{ mV}$  or less than  $-30\text{ mV}$ . In the present study the Zeta-potential value for the synthesized graphene (AKRGO) is  $-47.4\text{ mV}$  which indicates the formation of anionic nanoparticles (Figure 5b). The negatively charged nanoparticles will have the affinity to permeate membranes and cause disruption of cell wall [23]. Thus the foresaid properties of the synthesized graphene (AKRGO) may be utilized in the drug delivery applications.



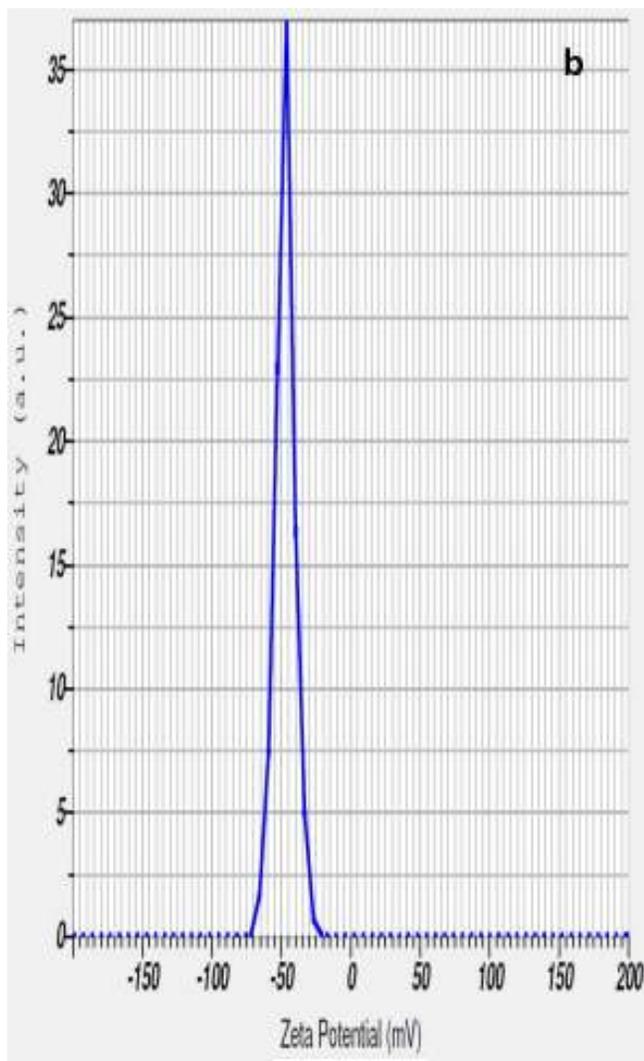
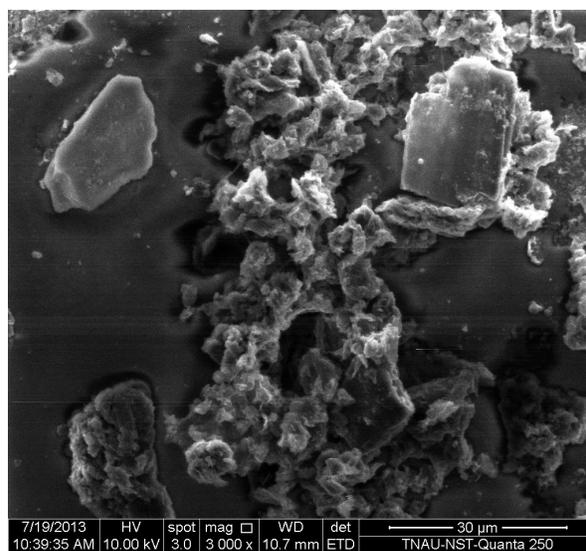


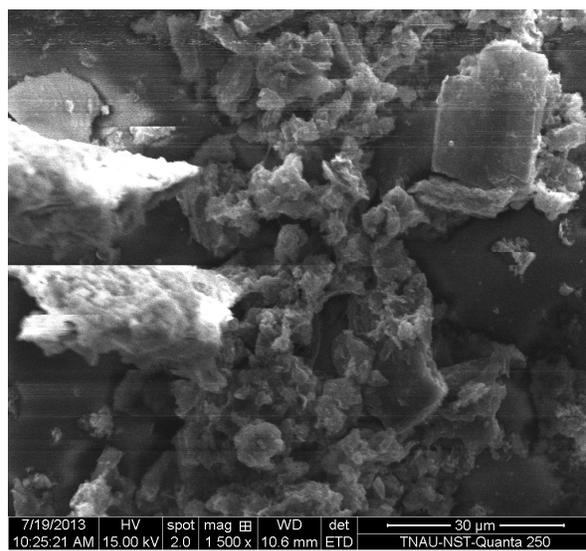
Figure (5): Particle size (a) and Zeta potential measurements (b) of synthesized graphene - AKRGO

**3.7 SEM – EDAX analysis :** The SEM–EDAX image of the reduced graphene oxide using the aqueous extract of *Amaranthus dubius* is shown in Figure (6). Reduced graphene oxide suspension (AKRGO) obtained after centrifugation was coated on the glass substrate and heated followed by vacuum drying. The suspension composed of platelets shows a fluffy and crumpled morphology (Figure 6a & b). The high magnification SEM image displays thin and wrinkled platelets of transparent layers (Figure 6c). The surface of the AKRGO looks like smooth transparent nanosheets as that of normal graphene (Figure 6c).

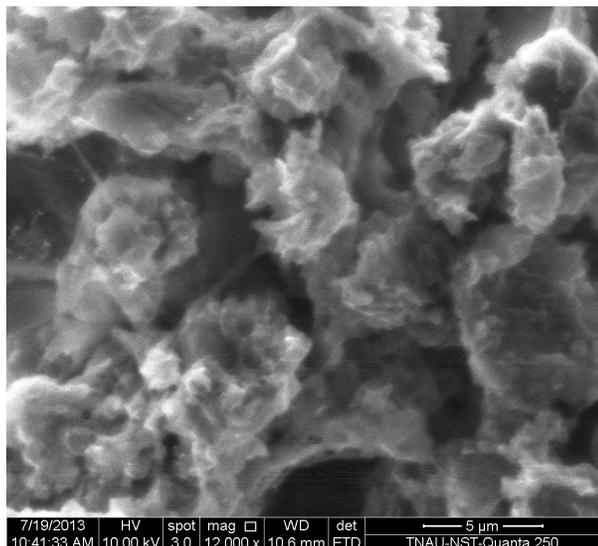
The EDAX spectrum of AKRGO reveals that graphene mainly consists of elemental carbon and some other elements such as Na, Mg, Al, Ca and Si as impurities (Figure 6d). These impurities might have come from the experimental procedure adopted in the synthesis of graphene. The EDAX spectra of graphene oxide disclosed the oxygen content to be 34.5 atom % as given in Table (2) and the atomic ratio of carbon to oxygen as 1.7. The EDAX measurements of the synthesized graphene confirms the reduction of graphene oxide using the extract of *Amaranthus dubius* as seen from the significant reduction of oxygen content (20 atom %) and decreased C/O ratio compared to that of graphene oxide is given in the Table (2).



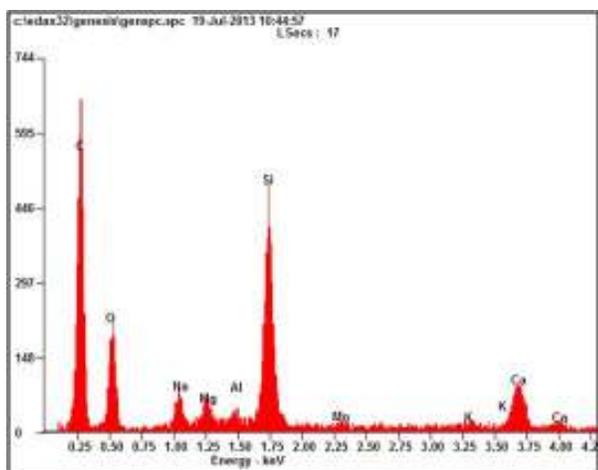
(a)



(b)



(c)



(d)

Figure (6): SEM images (a, b, c) of graphene (AKRGO) at different magnifications and EDAX spectrum (d).

Table (2): EDAX measurements of GO and AKRGO

Sr. No.	Material	C (at. %)	O (at. %)	C/O ratio
1	Graphene Oxide	62.7	34.5	1.7
2	Synthesized Graphene (AKRGO)	75.6	20.2	3.7

**4. Conclusion :** An environmentally benign synthesis of graphene was achieved using the aqueous extract of *Alternanthera sessilis*. The UV-Visible and FTIR spectra of AKRGO reveals that the phytoconstituents present in this extract

plays a vital role in the reduction of graphene oxide to graphene. The particle size analyzer confirms the size of nanographene to be around 5 nm. The Raman spectrum demonstrates that the synthesized graphene was few layers composed of very small crystallites. The fluffy morphology and stable dispersion of graphene (AKRGO) was confirmed by SEM analysis and zeta potential measurements. The resources involved in this method are feasible for the large scale production of graphene compared to that of chemical reduction. Thus, biosynthesized nanographene which finds more applications in biomedical fields as nanocarriers in drug delivery system and therapeutic agents can be efficiently prepared by this green technique.

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