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1. Introduction

Over the last decade, since the invention of graphene by Geim and Novoselov in 2004,¹ graphene and its derivatives have gained unprecedented attention from the scientific and technological community. Its perfect 2D structure and extraordinary electronic, optical, mechanical, and thermal properties make graphene an ideal choice for diverse applications. Flexibility and transparency of the sheet along with high electrical conductivity make graphene an excellent candidate for roll-up and wearable electronic devices.² The remarkable optical properties of graphene have paved the way to its use as filler nanocomposites in photovoltaic³ and optoelectronic devices.⁴ Being anisotropic,⁵ graphene exhibits optical birefringence, which finds wide applications in optical devices such as LCDs, modulators, colour filters and optical grating.⁶ Other promising appli-

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Self-propagated combustion synthesis of few-layered graphene: an optical properties perspective†

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This paper describes a labour efficient and cost-effective strategy to prepare few-layered of reduced graphene oxide like (RGOL) sheets from graphite. The self-propagated combustion route enables the bulk production of RGOL sheets. Microscopic and spectroscopic analyses confirmed the formation of fewlayer graphene sheets of an average thickness of ~3 nm and the presence of some oxygen functional groups with a C/O ratio of 8.74. A possible mechanistic pathway for the formation of RGOL sheets is proposed. The optical properties of the RGOL sample were studied in detail by means of Spectroscopic Ellipsometry (SE). The experimental abilities of SE in relating the optical properties with the number of oxygen functionalities present in the samples are explored. The data were analysed by a double-layered optical model along with the Drude–Lorentz oscillatory dispersion relation. The refractive index (n =2.24), extinction coefficient (k = 2.03), and dielectric functions are obtained using point-by-point analysis and are also checked for Kramers–Kronig (KK) consistency.

cations of graphene include its use in memory devices,⁷ sensors,⁸ biomedical devices,⁹ hydrogen storage,¹⁰ solar cells,¹¹ super-capacitors,¹² transparent electrodes¹³ and environmental clean-up.¹⁴ However, the ability to produce graphene at an affordable cost is the crux to make field level applications a reality.

Several strategies have been developed to produce graphene sheets by mechanical,¹ chemical,¹⁵ and thermal¹⁶ exfoliation methods. The first chemical exfoliation of graphite was performed in 1857 by vaporization of graphite intercalating compounds (GICs) such as bromine¹⁷ and potassium.¹⁸ Since then several attempts were made to produce few-layer graphene sheets in laboratories around the world. The isolation of a single sheet of graphene from a piece of highly oriented pyrolytic graphite (HOPG) using 'scotch tape' was achieved in 2004.¹ Though the technique is still practiced in laboratories, the low production yield and intensive labour requirements limit its practical use. Berger et al.¹⁹ have demonstrated the epitaxial growth of few-layer graphene on SiC surface. The chemical vapour deposition (CVD) method was first reported by Somani et al. (2006)²⁰ with camphor as the precursor. Efforts have also been made to grow graphene on various metal substrates like Ni,²¹ Ru,²² Ir,²³ Cu,²⁴ dielectrics, and insulators²⁵ using methane as the carbon precursor.²⁶ Though the synthesis of graphene on a large-scale on Cu foil is performed through the CVD process, the cost and ease of production is still a major concern when it is required to be produced on an





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industrial scale. Stankovich et al. (2006)²⁷ demonstrated an efficient solution-based route for the scalable synthesis of graphene by reducing graphene oxide (GO)²⁸ with hydrazine hydrate.²⁹ Reduction methods such as thermal,³⁰ microwave,³¹ photo,³² photocatalytic,³³ and solvothermal³⁴ are also reported. Aerosol pyrolysis,35 ionic-liquid assisted electrochemical method,36 electrolytic exfoliation,37 unzipping of CNTs,³⁸ arc discharge method,³⁹ mechanical delamination,⁴⁰ and combustion⁴¹ are other reported methods of synthesizing graphene.⁴² Among these, chemical exfoliation of graphite by intercalation followed by the reduction of graphene oxide (GO) to reduced graphene oxide (RGO) is a widely practiced technique for bulk synthesis.²⁹ Though popular, this wet chemistry method is laborious, time-consuming and requires harsh chemicals for production. Various strategies followed for the synthesis of graphene is summarised in Table S1 of the ESI.†

This paper demonstrates a low-cost strategy to exfoliate graphite through a combustion route. The self-propagated combustion synthesis method proposed here is simple, reliable and quick. This method enables the production of few-layered graphene (RGOL) in bulk quantity compared to the other reported methods. The optical properties of RGOL sheets are explored by Spectroscopic Ellipsometry (SE). The first report on the optical functions of exfoliated single-layer graphene sheet on a silicon and amorphous quartz substrate was authored by Kravets and coworkers.43 Weber et al.44 have analysed exfoliated graphene fragments on a silicon substrate using B-splines parameterization. The ellipsometry of epitaxially grown graphene on Ni, Cu and SiC substrates,45 and CVD grew graphene on Si substrates are explored.⁴⁶ The optical properties of the chemically and thermally reduced graphene oxides are also studied.⁴⁷ However, to the best of our knowledge, no studies have been performed to understand the optical properties of few-layered graphene synthesized through a combustion route. Efforts are also required to understand the effect of oxygen functionalities and defects on the optical properties of graphene.

2. Experimental sections

2.1. Chemicals

All chemicals were used as received without further purification. All solutions were prepared in de-ionized water $(0.056 \ \mu S \ cm^{-1})$. The graphite sample of particle size 2–5 μm was procured from Tamil Nadu Minerals Ltd (TAMIN), India. Potassium persulfate was procured from Rankem Chemicals Pvt. Ltd, India. Glucose was sourced from a local grocery store in Chennai, India.

2.2. Synthesis

The RGOL sheet was synthesized from graphite through a selfpropagated combustion route using glucose ($C_6H_{12}O_6$) and potassium persulfate ($K_2S_2O_8$) as a fuel and an oxidizer, respectively, in a ratio of 1:1:1. Graphite was taken as the carbon precursor and was mixed thoroughly with the fuel and the oxidizer using a mortar and pestle. The fuel to oxidizer ratio was fixed by a trial and error method. The solid homogeneous mixture was compressed to a pellet and it was kept in a ceramic crucible and transferred to a temperature programmed furnace. The furnace temperature was elevated from an ambient condition to 350 °C at a heating rate of \sim 3 °C min⁻¹. The temperature was held at 350 °C for 2 h and then gradually cooled to room temperature at the ambient rate. The obtained sample was washed several times with de-ionized water and stored after drying.

2.3. The proposed mechanism of formation of RGOL sheets

In reality, the mechanism of the combustion process is very complex. Several parameters including the fuel to oxidant ratio, the temperature of the reaction, ignition temperature, maximum flame temperature, chemical composition, and mass of the precursor reagent affect the process. A possible mechanism for the formation of RGOL by the proposed selfpropagated combustion process is explained below.

When the temperature of the system reaches 60-100 °C, the oxidizer K₂S₂O₈ starts to decompose to release oxygen. At this stage, the oxygen groups are expected to become attached to the edge of the graphite sheet to form partially expanded graphite oxide. When the temperature is at 146 °C and above (melting temperature of glucose is 146 °C), the glucose starts to melt, as the graphite sheets are partially expanded and exfoliated, and the fuel (i.e., the melted glucose molecules) tends to intercalate into the partially oxidised graphite sheets. As the temperature increases to ~250 °C (around the ignition temperature of the fuel), the combustion reaction starts, where the glucose reacts with oxygen to form CO_2 and water as per the reaction (R1). The reaction is highly exothermic with the heat of combustion of $-2801 \text{ kJ mol}^{-1}$. The pressure exerted due to the release of CO₂ helps in further exfoliation of graphite oxide. Subsequently, as the temperature reaches 350-400 °C, auto-ignition of the fuel occurs with the release of excess energy and the actual temperature of the system is higher than the set value (called maximum flame temperature). The heat that is liberated is sufficient to trigger graphite oxide for its highly exothermic de-oxygenation reaction. At this temperature, the oxygen groups are mostly reduced and the sheets which are formed are almost similar to reduced graphene oxide (RGO). The combustion of intercalated graphite oxide may be vigorous and propagating. It is also reported that once the exfoliation process is initiated in graphite oxide, the multilayer is ruptured at an accelerating pace. The pressure that is generated by the release of H₂O and CO₂ during combustion of the fuel is 60 MPa and 100 MPa, which exceeds the van der Waals attraction between two GO sheets (2.5 MPa).⁴⁸ This facilitates the exfoliation process.

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + -2801 \text{ kJ mol}^{-1}$$
 (R1)

3. Instrumentation

High-resolution transmission electron microscopy (HRTEM) images of the graphene sample were measured with a JEM

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3010 (JEOL, Japan) transmission electron microscope. Dilute dispersion of the sample was spotted on amorphous carbon film supported on copper grids and dried under ambient conditions. The X-ray photoelectron spectroscopy (XPS) spectrum of the RGOL sheet sample was recorded using ESCA Probe TPD of Omicron Nanotechnology. Polychromatic Mg Ka was used as the X-ray source (hv = 1253.6 eV). The binding energy was calibrated with respect to C 1s at 284.5 eV. Fourier transform infrared (FT-IR) spectrum of the sample was collected using a Nicolet 6700 spectrometer. The spectrum was collected in the range of 650-4000 cm⁻¹. The thermogravimetric analyser (TGA) unit of SEIKO model TG/DTA 6200 (Thermo Gravimetric/Differential Thermal Analysis) was used to measure high-temperature transitions and decomposition peak values. The initial weight of 5.014 mg of the sample was tested at a temperature ranging from 40-800 °C at a heating rate of 10 °C min⁻¹ with N₂ as the carrier gas. A confocal Raman microscope, CRM a300 S (WI Tec GmbH), coupled with an atomic force microscope (AFM) was used for collecting Raman spectra and AFM images. An UVISEL, HORIBA Jobin Yvon ellipsometry system was used to measure the refractive index, thickness and optical constants of the RGOL film. The RGOL film was obtained by vacuum filtration of the sample dispersion, through Whatman cellulose acetate filter paper of pore size 220 nm. Then the filtrate was transferred onto the surface of the glass substrate and dried. The measurements were performed at room temperature with a xenon lamp as the source of radiation. The spectra were obtained with a 0.01 eV resolution in the photon energy range of 0.5 eV to 6 eV using the sensitive photoelastic modulator (PEM) model of an ellipsometer. The instrument is driven by using the powerful and advanced DeltaPsi2 software, designed for accurate and flexible measurement and characterization of thin film structures.

4. Results and discussion

Fig. 1A shows RGOL prepared in bulk quantity (~10 g) and the difference in colour between the pristine graphite (left) and RGOL (right) is shown in Fig. 1B. The shiny texture of graphite is lost after the thermal exfoliation. A detailed characterization of RGOL was done by using various microscopic and spectroscopic techniques. The structural evolution of the graphene derivative, the presence of defects, edge and grain boundaries, and the number of layers can be learned from the Raman spectrum.⁴⁹ Fig. 1C shows the Raman spectrum of graphite and the RGOL sample. As expected, the Raman spectrum of graphite (Fig. 1Ca) displays a prominent G peak at 1575 cm⁻¹ corresponding to the primary in-plane vibrational mode and a less intense sharp 2D peak at 2707 cm⁻¹ is due to the second order overtone of in-plane vibration. The presence of defects and disorders in the crystal symmetries of the precursor graphite is indicated by the occurrence of a small D peak at 1345 cm⁻¹. Fig. 1Bb shows the Raman spectrum of the RGOL sample. There is a red-shift in the G band position when compared to bulk graphite flakes



Fig. 1 (A) Photograph of RGOL sample (10 g), (B) graphite (left) and RGOL sheets (right). (C) Raman spectrum of (a) graphite and (b) RGOL sheets.

and this shift is attributed to the transformation of the bulk graphite crystal to graphene sheets.⁵⁰ The RGOL sheet shows a prominent D peak (~1353 cm⁻¹) with intensity comparable to those of the G peaks ($\sim 1589 \text{ cm}^{-1}$). From the ratio of the peak intensities, $I_{\rm D}/I_{\rm G}$ of the Raman spectrum, the levels of the disorders can be characterised.⁵¹ The I_D/I_G ratio was calculated from the deconvoluted spectra with Lorentzian outlines and the ratios were found to increase from 0.19 for graphite to 1.21 for RGOL sheets. The G band broadens significantly with respect to that of graphite but there is no shift in its peak positions indicating that the thermal treatment has not affected the hexagonal carbon network. Generally, the position and shape of the 2D band define the number of layers stacked as sheets. The 2D band at 2673 cm⁻¹ originating from a twophonon double resonance is indicative of the graphitic nature. The 2D peak appears to be shorter and broader, which is attributed to the destruction of the band structure by the introduction of defects on graphene sheets.⁵² Close to the 2D peak, the sample exhibits a (D + G) peak at 2914 cm⁻¹, which is induced by the presence of smaller disorders. Among the two types of crystal edges, namely armchair and zig-zag structures, only armchair edges have the capability of elastically scattering charge carriers that give rise to an intense D peak.⁵³ The very intense D peak of the Raman spectrum of the RGOL sheet suggests that the prepared sample has armchair crystal edges. Table 2 of the ESI[†] shows the comparison of the measured parameters of RGO synthesized through different approaches.

The UV-Vis absorption spectrum (see Fig. 2A) of the RGOL sheet exhibits a peak at 269 nm, which is attributed to the aromatic C=C bonds of the π -conjugation network similar to RGO prepared by the chemical route.⁵⁴ The inset of Fig. 2Aa shows the aqueous dispersion of 0.01 wt% of the RGOL sheet. The FT-IR spectrum in Fig. 2B shows a broad band in the range of 3200–3400 cm⁻¹ and is attributed to –OH stretching vibrations. The peaks centered at ~2924 cm⁻¹ and 2854 cm⁻¹ correspond to the stretching vibrations of the asymmetric and



Fig. 2 (A) UV-Vis and (B) FT-IR spectrum of the RGOL sheet. The inset in (A) shows the aqueous dispersion of 0.01 wt% of RGOL sheets.

symmetric bands of the alkyl groups ($-CH_2$), respectively. The small sharp peak observed at 1389 cm⁻¹ is due to the C–H vibration due to some defects arising from sp³ hybridization. The presence of defects was also seen in the Raman spectrum of the RGOL sheet in Fig. 1Cb. The C=C bond at ~1639 cm⁻¹ is attributed to the skeletal vibrations of the un-disturbed graphitic domains. The prominent peak centered at 1579 cm⁻¹ corresponds to the aromatic C=C bonding. The absorption band intensities at -C-O (epoxy) and -C-O (alkoxy) groups at 1125 cm⁻¹ and 1089 cm⁻¹, respectively, are weak, indicating that the oxygen groups are concentrated at the edges and not in the basal plane of graphene.⁵⁵

Fig. S1 in the ESI[†] shows the TG plot of the RGOL sample. The TG curve shows the details of weight loss from room temperature to 800 °C. The sample exhibits an initial weight loss of about 5.5% in the temperature range of 30 to 180 °C. This can be attributed to the loss of adsorbed water. The decomposition of the mixture is displayed by a sharp mass loss of about 21.5% from 330 to 430 °C. This is attributed to the loss of edge oxygen functionality in the RGOL sheet.

Fig. 3A shows the XPS survey spectrum of the RGOL sample. The spectrum shows the presence of carbon and oxygen as the only elements. The XPS peaks were fitted to Voigt functions having 80% Gaussian and 20% Lorentzian characteristics after performing Shirley background correction. In Fig. 3Ba, the sp² peak of C 1s is centered at 284.6 eV and has FWHM of 1.72 eV. A small peak at 286.4 eV is assigned to the epoxide group (C-O-C). The less intense peak at 288.3 eV is attributed to the carbonyl (C=O) group that may occur due to the attachment of the oxygen group to the edges of graphite during the combustion process. In Fig. 3Bb, the peaks at 531.1 eV and 532.9 eV of the O 1s spectrum corresponding to C=O and C-O groups, respectively, are shown. The C/O ratio of the sample is calculated from the C 1s and O 1s regions of the survey spectrum and is found to be 8.74. The quantitative analysis of the individual components of carbon and oxygen groups obtained from the fitted results of C 1s and O 1s regions of the XPS spectra is tabulated in Table 1.

Fig. 3C shows the AFM topological image on which the height profile is taken, marked with a red line. The height measurements derived from the AFM image show that the



Fig. 3 (A) XPS survey spectrum of the RGOL sheets, (B) deconvoluted XPS spectrum of C 1s (a) and O 1s (b) (C) AFM image of the RGOL sheets along with the height profile and lateral dimension (D).

 Table 1
 Quantitative analysis of individual components obtained from fitted C 1s and O 1s regions of XPS spectra of the RGOL sheet

| | C 1s | | | O 1s | |
|-----------------|------------------|-------|-------|-------|-------|
| B.E (eV) | 284.6 | 286.4 | 288.3 | 531.1 | 532.9 |
| Assignment | Csp ² | C-OH | C==0 | C==0 | C-O |
| RGOL sheets (%) | 71.08 | 14.06 | 4.58 | 4.93 | 5.32 |

thickness of the sheet is around 1.7 nm that corresponds to the presence of approximately 5 layers of graphene. The lateral dimension of the sheet was found to be $\sim 0.7 \times 1.5 \ \mu\text{m}$. Fig. 4 shows the HRTEM images of the RGOL sample. Fig. 4A shows



Fig. 4 (A) TEM image showing the lateral dimension of few-layered graphene sheet along with folds and wrinkles of RGO, the inset shows the SAED image of the same. (B) HRTEM image showing the lattice fringes of few-layered graphene. (C) and (D) show the presence of tri- and bi-layers of RGOL sheets.

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the low magnification TEM image of the sample. The nanosheets are transparent, wrinkled, and folded at the edge, indicating the presence of few-layered graphene sheets (2-3 layers). The lateral dimension of the graphene sheet was found to be ~500 nm, though, in some regions, some sheets are of micron size (shown in Fig. S2[†]). The inset in Fig. 4A shows the corresponding SAED pattern for the area shown in Fig. 4(A). Well-defined diffraction rings of (1 0 0) and (1 1 0) confirm the crystalline structure of graphene.⁵⁶ It is also worth noting that (1 0 0) spots are brighter than (1 1 0) spots indicating the formation of good quality graphene.⁵⁷ A bright spot can be seen owing to (0 0 2) planes because of defects in sp² carbon. The ordered graphitic lattice fringes (shown by the white line and arrows) are evidently visible in the high-resolution TEM image of the graphene sheet (Fig. 4B). The interlayer spacing between the lattice fringes is found to be 0.34 nm. The HRTEM micrographs in Fig. 4C and D also show the presence of trilayers and bilayers of graphene sheets. The measured thicknesses of double, triple, and a few layers of graphene are 0.7 nm, 1.0 nm and 3.3 nm (Fig. 4B), respectively. This observation is in close agreement with the AFM and ellipsometry data as well. The RGOL layers can be further separated by performing ultra-centrifugation if required, as reported by Coleman *et al.*⁵⁸

5. Optical properties

Spectroscopic ellipsometry is used to determine the film thickness, optical constants, surface roughness, porosity, composition, and uniformity on solid surfaces.⁵⁶ SE measures the amplitude change (ψ) and the difference in the phase shift (Δ) between the incident and reflected light. Fig. 5A shows the measured ψ and Δ , respectively, at the angle of incidence (AOI) of 65°. The optical parameterization technique is followed to obtain the optical constants n and k as a function of wavelength. The method involves (i) constructing a model, (ii) assigning the dispersion relation to each layer and (iii) modeling the parameter and optimising it through an iterative procedure until a good fit with the measured data is obtained. Using this model, the refractive index (n), extinction coefficient

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consistency.⁵⁹ The experimental data of the RGOL sample were studied using a Drude–Lorentz oscillatory dispersion relationship on the three-layered model consisting of the bottom glass substrate, a very thin Cauchy mid sublayer (4 nm) that represents the intercalated air or water between the layers and the top graphene layer. The model parameters were fitted for the lowest

 γ^2 value of 0.03.

Fig. 5B shows an intense peak of the refractive index (n)and the extinction coefficient (k) at 2.24 and 2.03, respectively. The presence of defects in the sample was assessed by analysing the variation of the amplitude of the imaginary part $\langle \varepsilon_2 \rangle$ of the pseudo-dielectric function, $\langle \varepsilon \rangle = \langle \varepsilon_1 \rangle + i \langle \varepsilon_2 \rangle$. The variations in amplitude can give an indication of the defects caused by the oxidation of the sample. Losurdo et al.⁶⁰ have reported that the presence of oxygen functional groups like -C=0 or -C-0 can redshift the $\langle \varepsilon_2 \rangle$ peak from a normal value of 4.8 eV (for pristine graphene).⁴⁶ They observed a red-shift of 0.5 eV for every 10% increase in oxygen functionalities. The sample showed a $\langle \varepsilon_2 \rangle$ peak of 4.6 eV (Fig. 6B), with a shift of 0.2 eV from that of pristine graphene. This perhaps indicates the presence of around 4% of oxygen in the form of -C=O or -O-H. These data are also in close agreement with the % of oxygen groups calculated from XPS data. Fig. 6A shows the absorption spectra of the RGOL sheet at room temperature. The absorption peak at 4.9 eV arises due to the inter-band transition by the resonant excitons.⁶¹ The apparent shift of about 0.4 meV from that of the absorption peak of graphene at 4.5 eV is due to the absence of electron-hole interactions.⁶² These features of the absorption spectra confirm that the synthesized sample consists of few-layered graphene sheets.63

The good optical properties of RGOL sheets indicate its possible applications in photonic materials and in the development of optoelectronic devices such as LEDs and solar cells. Table 2 shows a comparative analysis of the optical constants of the RGOL sheet with those shown in the literature and the data are in close agreement with those in the literature.^{43,64}



Fig. 5 (A) The experimental ellipsometric parameters of $tan(\psi)$ and cos (Δ) of the RGOL sheet. (B) The measured refractive index (*n*) and the extinction coefficient (*k*) of the RGOL sheet.



Fig. 6 (A) Spectra showing the measured absorption coefficient of the RGOL sheet. (B) Spectra of the real (ε_1) and imaginary (ε_2) parts of the complex dielectric function of the sample.

 Table 2
 Comparative analysis of optical parameters of graphene samples

| Author/Ref. | Thickness | n | k 2.03 |
|--|--------------|------|-----------|
| Present work | 0.846 nm | 2.24 | |
| Nelson <i>et al.</i> ⁵ | 4 layers | 2.3 | 2.42 |
| Jellison <i>et al.</i> ⁶⁵ | Single layer | 2.56 | 2.03 |
| Kravets <i>et al.</i> ⁴³ | 0.335 nm | 2.8 | 1.45 |
| Matković <i>et al.</i> ⁶⁴ | Single layer | 2.7 | 1.35 |
| Wurstbauer <i>et al.</i> ⁶⁶ | Single layer | 3.0 | 1.35 |
| Weber <i>et al.</i> ⁴⁴ | 0.34 nm | 3.4 | 3.42 |
| Ochoa-Martínez <i>et al.</i> ⁶⁷ | Multilayer | 3.9 | 3.86 |

6. Conclusion

A single-pot combustion synthesis approach for the successful bulk production of a graphenic material from graphite is demonstrated, with a production efficiency of more than 90%. This method enables the production of few-layered graphene in a short period of time at an affordable cost (INR \sim 430 per kg). We believe that this is a significant step towards the bulk production of few-layered graphene from graphite. The process can be easily scaled up to produce kilograms of graphene in few hours. The data reveal that the as-produced graphene shows excellent optical properties comparable with that of RGO synthesized by the known conventional methods. Achieving the bulk production of dispersible graphene with good optical properties stimulates new research opportunities in developing low-cost filtration membranes, optoelectronics, and photovoltaic devices.

Conflicts of interest

There are no conflicts of interest to declare.

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