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Synthesis of Multifunctional graphene exhibiting excellent sonochemical dye removal activity, green and regioselective reduction of cinnamaldehyde

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Abstract

The present synthetic protocol focused on the green, cost-effective and bio-synthesis of multifunctional graphene by employing a highly biomedical plant, *Kigelia Africana* stems aqueous extract as a reducing and stabilizing agent. The synthesized graphene is characterized by UV-Visible, FT-IR, XRD, Raman, HR-SEM and HR-TEM techniques. Thus synthesized grapheme sample demonstrated excellent dye removal activity by adsorbing Rhodamine B and Alizarin Red dyes, where most of the dyes are removed within 5 min by the sonochemical process. Further, the graphene established regioselective and efficient reduction of cinnamaldehyde to cinnamyl alcohol in an aqueous medium with excellent yields (94 %).

Keywords: Graphene; *Kigelia Africana*; FT-IR; XRD; Raman; green synthesis

1Introduction

Graphene has been envisaged as a superior multifunctional material owing to its properties such as huge surface area, high flexibility and superior conductivity [1]. The use of plant extracts for reduction of graphene oxide (GO) to reduced graphene oxide (rGO) is the best method to access graphene because they are massively available at low cost, renewable reagents, easy to prepare and handle, efficient mild reducing agents and are environment friendly, thus reduces pollution [2-3]. Furthermore, plant extracts also work as stabilizing agents by preventing agglomeration and also preserves the hydrophilic nature of graphene sheets [4-6]. Various plant extracts-Carrot, Grapes, Aloe-Vera, Tulsi, Custard apple, Betel, Amla are employed as green reducing agents in the production of graphene and its composites [1-8]. Therefore, in continuation of our green synthetic methods [1,7,8], we

envisaged the use of *Kigelia Africana* (KA) (highly medicinal plant) stem extract, as a reducing agent for the synthesis of rGO that displayed superior multifunctional activities in sonochemical dye removal and catalytic reduction of aldehydes.

2. Experimental

2.1 Green synthesis of graphene

About 1 g of KA stem powder in 100 mL of water was boiled at 50 °C for 20 min, the cooled solution was then filtered to get brown colour KA stem extract. The mixture of 60 mL of KA stem extract and 100 mL of GO [1] dispersion (1 mg/mL) was refluxed at 80 °C with varying reaction time intervals. The air cooled solution was centrifuged at 10,000 rpm, the precipitate was washed with water and ethanol, followed by vacuum drying gave the black colour powder with 80 % yield. Three different samples of KA stem extract reduced graphene oxide (KRG) using different reaction time intervals of 3,6 and 9 h (**Fig.1**) were prepared.

Fig. 1

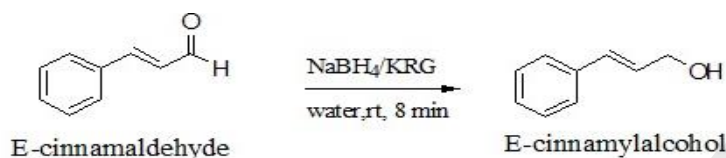
2.2 Sonochemical dye removal studies

Two different dyes viz., Rhodamine B (RB) and Alizarin Red (AR) were used to investigate the dye removal capability of KRG and compared with GO. In a model experiment, 10 mg of KRG was dispersed into 100 mL of 5 ppm dye solution and sonicated for 45 min. Known volumes of the reaction mixture were drawn after regular time intervals (0, 5, 10, 15, 30, 45 min) and analyzed using UV-Vis spectroscopy.

2.3 Reduction of aldehydes to alcohols

The KRG was presumed to exhibit a regioselective reduction of α,β -unsaturated aldehydes to corresponding alcohols leaving the double bond untouched. In a typical reduction protocol, 0.095 mL of *trans*-cinnamaldehyde (1 mmol) and 0.05 g of NaBH₄ (0.5 mmol) were added to 2 mL of KRG (15 mg in water) dispersion and stirred at room

temperature for 8 min. On completion of the reaction, KRG was separated by filtration, the filtrate was extracted with ethyl acetate followed by vacuum dry afforded *E*-cinnamyl alcohol (Scheme 1).



Scheme 1: Reduction of cinnamaldehyde with KRG/NaBH₄.

2.4 Characterization techniques

UV-Vis data was acquired with a JASCO V-550 (Japan) spectrophotometer. Infra-red spectral analysis was performed on an FT-IR 5300, JASCO instrument. XRD studies were done using Bruker D8 advance diffractometer (USA), with Cu-K α radiation. Raman data was acquired using a Micro-Raman spectrometer, Raman-SR-TEC-IG, USA. The morphological studies were executed with HR-TEM; FEITecnai T20G2S TWIN, USA). HR-SEM images were obtained with a VEGA 3 TESCAN instrument. The ¹H NMR and ¹³C NMR spectra were recorded on Bruker Advance III instruments at 400 and 100 MHz.

3. Results and discussion

The primary visual confirmation for the reduction of GO to KRG during the reaction was observed by a colour change from brownish-yellow to dark-black. The characteristic UV-Vis absorption peaks of GO appeared at 237.6 and 284.4 nm were attributed to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of C=C and C=O moieties (Fig. 2a). After reduction for 3 h, the GO did not appear to be reduced as evidenced by its UV-Vis spectral peaks (236.4 and 282 nm). However, a dramatic change in the UV-Vis peak positions was observed after 6 h, which showed the disappearance of the previous peaks and the appearance of a new broad peak at 261 nm. Further, continuing the reduction for 9 h, GO was completely reduced to form KRG

(266.1 nm) and the extensive conjugation of graphene had been re-established by forming more number of C=C double bonds (**Fig. 1**).

The FT-IR spectra of GO showed prominent stretching peaks of O-H (carboxyl, hydroxyl) at 3400 cm^{-1} , C=O and C=C peaks at 1631 and 1406 cm^{-1} , the epoxy, alkoxy, alcohol C-O peaks at 1268 and 900 cm^{-1} (**Fig. 2b**). The reduction of GO to KRG will reduce all these functional groups thereby the corresponding frequencies will disappear or shows reduced intensities. The FT-IR spectra of KRG after 6 and 9 h reduction clearly showed the decrease in the intensities of all these peaks.

The complete reduction of GO results in the removal of all oxygen containing functional groups from the surface of the GO and forms C=C double bonds to regenerate the extended conjugation of graphene sheets. Due to this, the sharp peak of GO will disappear and a new broad peak corresponding to exfoliated graphene sheets will appear in the XRD patterns. The XRD spectra (**Fig. 2c**) of GO displayed a single peak at a 2θ value of 11° (d-spacing $0.8\text{-}1.0\text{ nm}$). The reduction of GO to KRG was not successful after 3 h (peak at 10.2° similar to GO) whereas, after 6 h, KRG showed an additional broad peak at a 2θ value of 23.6° along with GO peak. This new peak was ascribed to the graphene sheets. The complete reduction of GO to well-exfoliated KRG sheets was observed after 9 h where the GO peak was disappeared and the KRG broad peak appeared at a 2θ value of 26° .

Generally, pure GO shows a sharp G band in Raman spectra at $1580\text{-}1600\text{ cm}^{-1}$, whereas rGO shows both G and D ($\sim 1300\text{ cm}^{-1}$) bands representing the defects in rGO. These two peaks of KRG (9 h) appeared at 1605 and 1292 cm^{-1} respectively (**Fig. 2d**), which were consistent with the literature reports. The I_D/I_G ratio was measured to be 1.19.

Fig. 2

The HR-SEM images (**Fig. 2e-f**) showed the well-exfoliated sheets of KRG (9 h) with curved and defect edges. The HR-TEM images (**Fig. 2g-j**) further established the formation of well exfoliated and transparent sheets of KRG, and their two-dimensional sheet structure. The inset was selected area electron diffraction pattern for the KRG with a hexagonal diffraction pattern.

Therefore all the characterization techniques proved that the prediction of using KA stem extract for the reduction of GO to KRG was successful. Thus prepared KRG (9 h) was utilized for dye removal from water by sonochemical process and also in the green reduction of cinnamaldehyde.

4 Dye elimination studies

The modern industrialization has seen the release of several dyes into the near by water bodies leading to the contamination of the water. Recently, graphene is envisaged to be the best catalyst for water purification and the rGO obtained by green synthetic routes was employed for this by Upadhyay *et al.* (Grape extracts) [3], Gourav *et al.* (Aloe vera extract) [5], Suresh *et al.* (Cinnamon, Spinach, Clove extracts) [14-16]. This sound literature knowledge led us to develop a new dye removal activity with KRG by the sonochemical process.

The UV-Vis analysis of the dye removal studies by KRG was presented in **Fig. 3**. The RB dye was almost removed within 10 min of sonication and complete removal was observed after 45 min, whereas GO took 45 min to reduce the intensity to 80 % and the complete removal of the dye was not possible with GO even after prolonged sonication. Similar results were observed for AR dye where almost 100 % dye removal was observed within the first 5 min for KRG while the same was not possible for GO. The C/C_0 Vs time graphs of both RB and AR clearly indicated that KRG was far better catalyst than GO with 100 % dye removal

capacity. The dye removal activity could be attributed to the proper adsorption of dye on to the large surface area of two-dimensional KRG sheets.

Fig. 3

5 Reduction of aldehydes to alcohols

The intriguing nature of efficient organic transformations, recyclability, use of water solvent and the emergence of a variety of nanocatalysts in recent literature is a great advance towards nanocatalysis in organic transformations. Employing such nanocatalysis for regioselective reduction of carbonyl compounds to alcohols greatly reduces the environmental pollution and cost of production [17]. In a model experiment, we have used 10 mg of KRG and 50 mg of NaBH₄ to reduce 10 μ L of cinnamaldehyde and got only 25 % yield (**S.No.1, Table 1**) of cinnamyl alcohol as the single product. Several reaction conditions and catalyst loading endeavoured as shown in **Table 1** to improve the yield. Increasing the catalyst to 10 mg has reasonably improved the yield (57 %, **S.No.2**) but a good yield of 94 % (**S.No.3**) was observed with 15 mg of KRG. Other reaction conditions resulted either in decomposition or no progress in the reaction. Thus, we have optimised with 15 mg of KRG at room temperature as the best reaction condition to get a maximum yield of 94 %. The KRG catalyst provides higher surface area which allows the interaction of more number of cinnamaldehyde molecules. Further, the conjugated electronic arrangements [17] in KRG enables the selective binding of double bond and aldehyde moieties in cinnamaldehyde that facilitates fashionable 1,2-reduction by NaBH₄.

Table 1. Various reaction conditions and progress of the reduction with KRG/NaBH₄catalyst.

S.No	Catalyst	Amount of catalyst (mg)	Reaction time (min)	Yield (%)
1	KRG+NaBH ₄	5	30	28
2	KRG+NaBH ₄	10	20	57
3	KRG+NaBH ₄	15	10	94
4	KRG+NaBH ₄	20	8	75
5	Only KRG	15	120	-
6	Only KRG	20	120	-
7	Only KRG (Reflux)	20	120	-
8	Only NaBH ₄	25	120	-

Conclusions

The present research demonstrated an expedient, cost-effective, sustainable synthesis of multifunctional graphene by utilizing *KA* stem aqueous extract, a green reducing agent. The obtained graphene exhibited excellent dye removal capacity (100 % in 5 min) in sonochemical dye removal application using Rhodamine-B and Alizarin red dyes. Further, the graphene regioselectively reduced *trans*-cinnamaldehyde to *trans*-cinnamyl alcohol by NaBH₄ in the aqueous medium. The indigenous methodology is useful in water purification and green catalysis applications.

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Conflict of interest

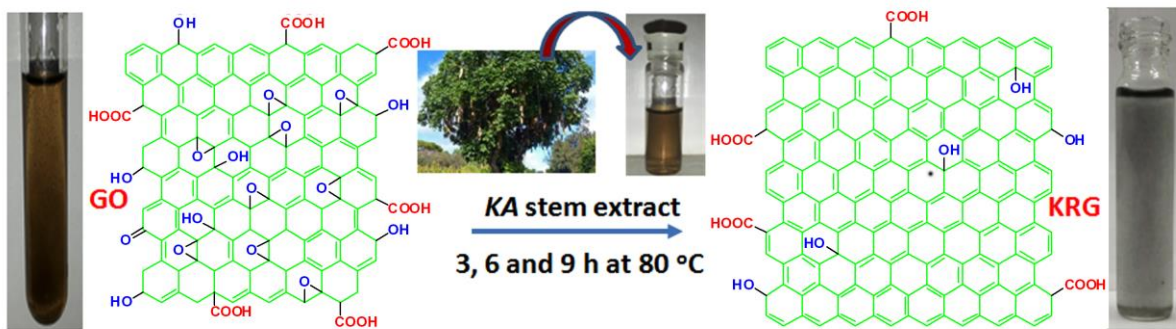
The authors declare no conflict of interest.

References

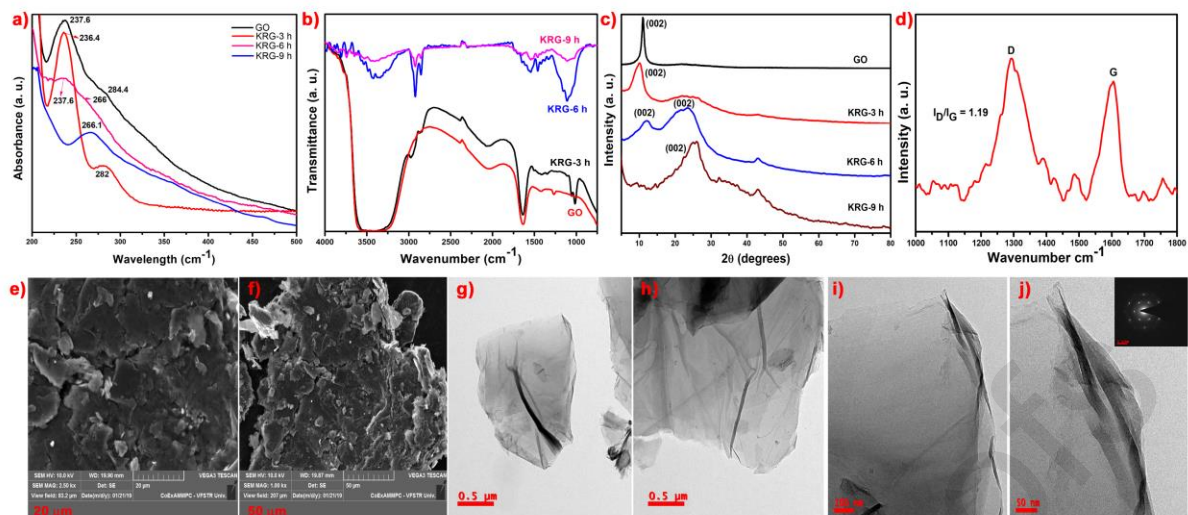
1. B. Chandu, VSS. Mosali, B. Mullamuri, HB. Bollokolla, Carbon Lett. 21 (2017) 74-80.
2. CK. Chua, M. Pumera, Chem. Soc. Rev.43 (2014) 291–312.

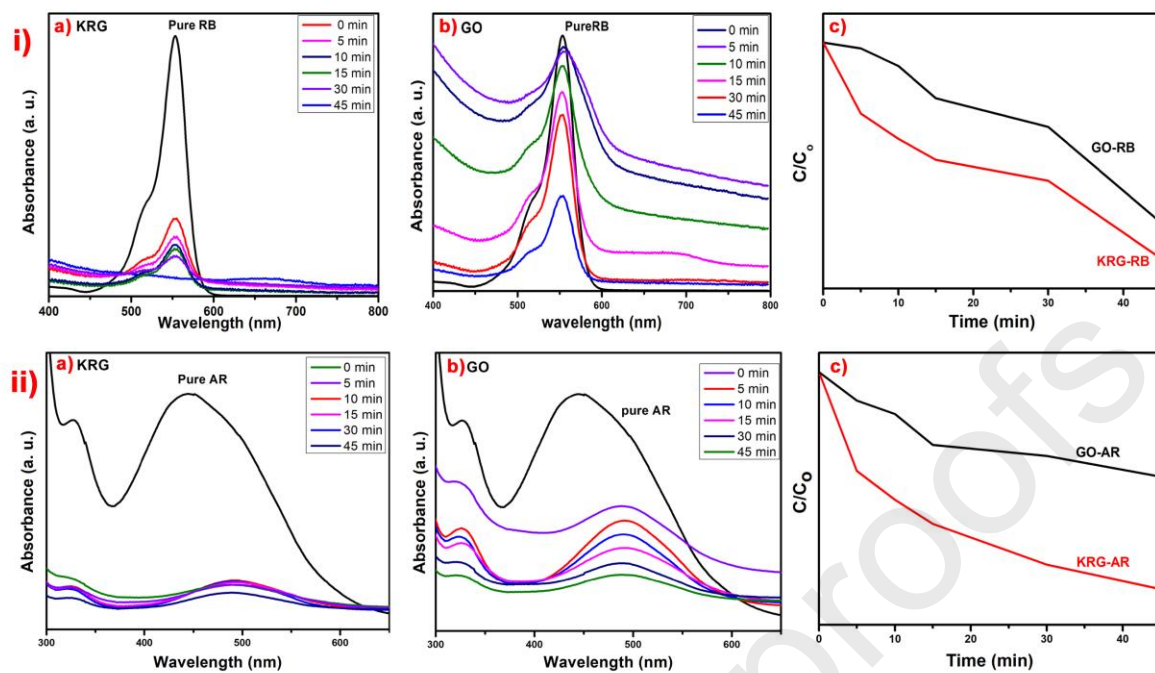
3. RK. Upadhyay, N. Soin, G. Bhattacharya, S. Saha, A. Barman, SS. Roy, *Mater. Lett.* 160 (2015) 355-358.
4. S. Mahata, A. Sahu, P. Shukla, A. Rai, M. Singh, VK.Rai, *New J. Chem.* 42 (2018) 19945-19952.
5. G. Bhattacharya, S. Sas, S. Wadhwa, A. Mathur, J.Mc Laughlin, SS. Roy, *RSC Adv.* 7 (2017) 26680-26688.
6. T. Kuila, S. Bose, P. Khanra, AK. Mishra, NH. Kim, JH. Lee. *Carbon* 50 (2012) 914–921.
7. B. Chandu, S. Nurbasha, HB. Bollikolla, *ChemistrySelect* 2 (2017) 11172-11177.
8. B. Chandu, Ch.Jalaja, K. Raghuram, HB. Bollikolla, *Mater. Technol.* 33(2018),730-736.
9. PB. Ashishie, AA. Chinyere, AA. Ayi, CO. Oseghale, ET. Adesuji, AH. Labulo, *Internat. J. Phys. Sci.* 13(2018) 24-32.
10. AE. Olufemi, OI. Omotayo, AB. David, I. Monjeed, O. Adebola, S. Bilikis, A. Temitope. *Journal of Pharmaceutical Research International.* 18(2017) 1-10.
11. S. Saini, H. Kaur, B. Verma, SK. Singh, *Natural product radiance*, 8(2009) 190-197.
12. U. Sharma, Singh, *Asian J pharm Clin Res.* 3(2010) 73-75.
13. IE. Cock, *Pharmacogn. Commn.* 6(2016) 115-117.
14. D. Suresh, MA. Udayabhanu, HP. Kumar, H. Nagabhushana, SC. Sharma. *Mater. Lett.* 151 (2015) 93-95.
15. D. Suresh, PC. Nethravathi, H. Nagabhushana, SC. Sharma. *Ceramics International* 41 (2015) 4810-4813.
16. D. Suresh, MA. Udayabhanu, H. Nagabhushana, SC. Sharma, *Mater. Lett.* 142 (2014) 4-6.
17. VK. Rai, S. Mahata, SR. Bhardiya, P. Shukla, A. Rai, M. Singh, *Tetrahedron Lett.* 60 (2019) 524–529.

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Highlights

- Green and cost-effective synthesis of graphene using *Kigelia Aficana* stem extract
- The obtained graphene showed excellent dye removal activity using sonochemical process
- The graphene showed green and regio-selective reduction of cinnamaldehyde

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AUTHORS CONTRIBUTIONS

Chandra Mohan Kurmarayuni:- Principal author who made the experimental work

Swarnalatha Kurapati:- Collection of bulk sample material

Syed Akhil:- carrying out raman spectra

Basavaiah Chandu:- Analysis of the work

**Bala Murali Krishna Khandapu:- managing of work progress and instrumentation
work**

Prabhakar Koya:- HR-SEM work

Hari Babu Bollikolla:- planning of the work and draft preparation