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The novel and efficient reduction of graphene oxide using *Ocimum sanctum* L. leaf extract as an alternative renewable bio-resource

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The efficient, rapid, bio-inspired synthesis of reduced graphene oxide (rGO) nanosheets was explored using green leaf extract of *Ocimum sanctum* L. (Tulsi leaves). This mild biorenewable reducing agent containing eugenol, ascorbic acid, and polyols also acts as a stabilizer for the prepared rGO. Characterization of the synthesized graphene nanosheets was performed using XPS, TEM, SEM, XRD, FT-IR, Raman and UV-vis spectroscopy studies. The catalytic application of the prepared rGO was established through the fruitful reduction of α , β -unsaturated aldehydes to the corresponding allylic alcohols in aqueous media. Excellent yields of pure products (92%) in addition to regioselective reduction were practically observed.

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Introduction

Graphene, a 2D carbon material arranged in a single layered hexagonal lattice, has demonstrated tremendous electronic, mechanical and thermal properties.¹ These supreme qualities of graphene give it great promise in areas of application such as the fields of devices and composites.² Many excellent studies related to the catalytic applications of graphene, including metal-free catalysts,^{3a} graphene-based electrocatalysts,^{3b-d} and photocatalysts,^{3e} have been well reported. Up to now, many strategies⁴ have been adopted for the synthesis of graphene, such as chemical vapor deposition (CVD),^{4a} micro-mechanical exfoliation,^{4b} epitaxial growth,^{4c} the thermal reduction of graphene oxide,^{4d} electric arc discharge,^{4e} the chemical reduction of exfoliated graphene oxide, etc.4f Of these methods, the chemical reduction of graphene oxide is conceded a versatile and suitable method for the bulk production of rGO at low cost. Unfortunately, hydrazine,^{5a} hydroquinone,^{5b} and sodium borohydride^{5c} are toxic and hazardous chemicals with respect to both human health and the environment.

As a consequence, continuous exertions have been focused on alternative approaches and nature-based reducing agents, such as vitamins,⁶ reducing sugars,⁷ amino acids,⁸ proteins,⁹ hormones,¹⁰ bacteria,¹¹ and various plant extracts,¹² for obtaining rGO. The mild reducing efficiencies of natural products not only



The leaf extract of Tulsi (*Ocimum sanctum* L.) contains eugenol, ascorbic acid, polyphenols, *etc.*,^{13a,b} which have natural reducing abilities, and get oxidized to the corresponding relatively more stable and unreactive quinone moieties with no agglomeration of the prepared rGO. Recently, we have reported the bio-reduction of GO using cashew leaf extract.^{13c} In a continuation of our interests in methodology development,¹⁴ especially using nanomaterials as catalysts,¹⁵ we next explored green leaf extracts of Tulsi for the facile and green reduction of GO. Herein, we report for the first time tulsi leaf extract as a reducing agent for the reduction of GO (Fig. 1).

A plausible mechanism for reduction has been proposed *via* SN^2 nucleophilic attack involving the electrophilic carbon of epoxide and reactive hydroxyl groups in GO, followed by the elimination of water molecules (Scheme 1).¹⁶ Graphene oxide has been prepared *via* the oxidation of graphite powder according to a modified Hummers' method.¹⁷ The reduction of GO using *Tulsi* leaf extract was performed under heating conditions at 70 °C for 4 h. This proposed method for the reduction of exfoliated GO has several advantages over other reported green



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Table 1 Comparative study of the C/O atomic ratios obtained from XPS elemental analysis of rGO produced using different reducing agents

Reducing agent	GO reduction process	Condition	C/O atomic ratio	Ref.
Gallic acid	400 mg of GO dispersed in 100 mL of water, sonicated for 2 h, added NH_3 · H_2O (1.2 mL)	RT, 24 h 95 °C, 6 h	GO: 2.56; RT-rGO: 3.89 HT-rGO: 5.28	20 <i>a</i>
<i>Hibiscus sabdariffa</i> L. extract	80 mg of GO (0.4 mg mL^{-1}) dispersed in 200 mL of extract, ultrasound for 1 h, heating		GO: 2.3; RT-rGO: 3.0	20 <i>b</i>
			HT-rGO: 3.01	
Tea solution	50 g of GO dispersed in 100 mL of tea solution, sonicated for 30 min, refluxing	90 °C, under N ₂ atmosphere	GO: 1.43; TPG: 2.84	20 <i>c</i>
Sugarcane bagasse extract	300 mg of GO dispersed in 600 mL of DI, ultrasound for 30 min, 400 mL of aqueous solution of SBE, followed by 600 μ L of ammonia solution	95 °C, 12 h	GO: 2.03; rGO: 3.37	20 <i>d</i>
Drained water from soaked mung beans	100 mg of GO dispersed in 100 mL of DI water, 100 mL of drainer water from soaked mung beans	RT, 24 h	GO: 2.3; rGO: 6.6	20e
<i>Pulicaria glutinosa</i> plant extract	200 mg of GO dispersed in 40 mL of DI water, 10 mL of plant extract (0.1 g mL^{-1})	98 °C, 24 h	GO: 1.25; rGO: 1.86	20 <i>f</i>
Tannin acid	To a GO suspension in water, tannin acid was added (400 wt% relative to GO) with sonication for 30 min	80 °C, 10 h	rGO: 2.44	20g
<i>Lycium barbarum</i> extract	To 100 mg of GO suspension in 100 mL of DI water, 100 mL of <i>Lycium barbarum</i> extract was added	95 °C, 24 h	rGO: 6.5	12k
Chrysanthemum extract	To a 0.1 mg mL ^{-1} GO suspension, 100 mL of chrysanthemum extract was added	95 °C, 24 h	rGO: 6.6	12l
Tulsi leaf extract	10 mg of GO dispersed in 10 mL of DI water, 40 mL of leaf extract was added (1 mg mL ^{-1})	70 °C, 4 h	GO: 1.94; TRGO: 3.10	Present work



Fig. 1 A schematic representation of the synthesis of TRGO.



Scheme 1 A plausible mechanism for the reduction of GO with Tulsi leaf extract.

methods^{12a-c,18} in terms of the extent of reduction, temperature and time. The envisaged method for the reduction of GO has an advantage regarding the enhanced dispersion of Tulsi leaf reduced graphene oxide (TRGO) in water, which is expected due to the already oxidized biomolecules present in Tulsi leaf extract stabilizing TRGO.

Results and discussion

The reduction of GO using Tulsi leaf extract was performed in water at 70 $^{\circ}$ C for 4 h. In a typical experiment, 40 mL of leaf extract was added to 10 mL (1 mg/1 mL) of an aqueous dispersion of GO under vigorous stirring, increasing the reaction temperature up to 70 °C over the next 4 h. As the reaction proceeded, the brownish color of the GO suspension slowly changed to black and finally, over the next 3.5 h, it turned dark black, indicating the formation of graphene (Fig. 1). The mixture was kept under the same reaction conditions for an additional half an hour to allow the GO to be well reduced. Herein, we prepared four different samples of Tulsi leaf extract reduced graphene oxide (TRGO) using different volumes of leaf extract while the amount of GO suspension in all four sets was kept constant at 10 mL (1 mg mL⁻¹). These four sets are: TRGO 1 (10 mL of leaf extract); TRGO 2 (20 mL of leaf extract); TRGO 3 (30 mL of leaf extract); and TRGO 4 (40 mL of leaf extract). The best reduction was observed using TRGO 4, hence, it was used as a catalyst in the catalytic hydride transfer reaction. The extent of reduction of GO into rGO induced by Tulsi leaf extract was confirmed via spectral analysis, viz., UV-vis spectra, FTIR spectra, XRD pattern, Raman spectra, XPS, TEM and SEM-EDX analysis.



Fig. 2 (A) UV-vis spectra obtained for exfoliated graphene oxide (GO), chemically reduced graphene oxide (CRG) *via* NaBH₄, and Tulsi leaf reduced graphene oxide (TRGOs). (B) Digital photographs of aqueous dispersions of GO and TRGO 4. (C) FTIR spectra of GO, TRGO 4 and aqueous leaf extract.

Preliminary characterization was done using UV-vis spectroscopy (Fig. 2A). In the UV-vis spectra, two absorbance peaks were observed at 232.2 nm and 307 nm for GO, which are attributed to the $\pi \to \pi^*$ transition of graphitic C=C bonds and a very weak shoulder absorbance due to the $n \rightarrow \pi^*$ transition of C=O bonds, respectively. There were no satisfactory changes in the peak positions of TRGO 1 and TRGO 2, while a dramatic change in the absorption peak of TRGO 3 was noticed. Meanwhile, a new absorption peak appeared at 282 nm and started shifting towards the red end with increasing leaf extract volume. A newly appearing distinct peak indicates that electronic conjugation in reduced GO is re-established. TRGO 4 shows better reduction, with a corresponding characteristic peak at 288.1 nm. It is clearly noticed that the absorption peak shows a larger red shift (288.1 nm) than seen from other reported chemical methods (e.g., NaBH₄ as a reducing agent: 267 nm),^{5c} as well as several green methods.^{6a,8a,b,11b,12a,19}

In the FTIR spectra (Fig. 2C), GO characteristic bands appearing at 3422.73 cm⁻¹ reveal the presence of hydroxyl groups in GO, while peaks at 1716.82, 1219.83 and 1057.56 cm⁻¹ are obtained for $\nu_{\rm COOH}\text{,}$ $\nu_{\rm C-O(epoxy)}$ and $\nu_{\rm C-O(alkoxy)}\text{,}$ respectively. A sharp peak at 1626.13 cm⁻¹ can be assigned to aromatic C=C stretching and one at 1389.02 cm^{-1} to the bending vibrations of -OH groups of water molecules adsorbed on GO. The intensities of FTIR absorption peaks corresponding to oxygen functionalities such as ν_{COOH} , $\nu_{\text{O-H}}$, $\nu_{\text{C=O-H}}$ significantly decrease and the absorptions of epoxy groups even vanish entirely, indicating that most oxygen containing functional groups are eliminated during reduction. Furthermore, a new band appearing at 1553.56 cm⁻¹ is attributed to the restoration of aromatic rings. The FTIR spectrum of leaf extract was also recorded to investigate possible interactions between biomolecules present in the leaf extract and the prepared rGO. FTIR analysis of the leaf extract showed two sharp absorption peaks centered at 3479.70 and 1634.36 cm⁻¹. It is well reported that the absorbance peak at 1634.36 cm⁻¹ from the amide I band of proteins arises due to carbonyl stretching in proteins and that at 3479.70 cm⁻¹ arises from -OH stretching in alcohols and phenolic compounds present in leaf extract. The presence of possible proteins and polyphenolic compounds acting as reducing and stabilizing agents for the prepared rGO is demonstrated.

An SEM image of TRGO 4 shows well exfoliated flake-like sheets (Fig. 3A) and EDX analysis confirms the presence of 22 atomic% oxygen in the rGO, with a carbon to oxygen atomic ratio (C/O) of \sim 3.50 (Fig. 3B). This could be attributed to the presence of unreduced oxygen-containing functional groups on the surfaces of the reduced graphene oxide sheets. The prepared reduced graphene oxide was fully analyzed *via* TEM observations. A low magnification TEM image suggest that the reduced graphene oxide layers are very transparent, silky and crumbly in nature (Fig. 3C). In a HRTEM image of TRGO 4 (Fig. 3D), the ordered graphic lattices are clearly visible. The selected area electron diffraction (SAED) pattern is shown in the inset of Fig. 3D, with hexagonal diffraction patterns that confirm its crystalline structure.

XRD analysis of GO (Fig. 4A) shows that a characteristic peak appears at 11.63° , which highlights the introduction of



Fig. 3 (A) An SEM image of TRGO 4. (B) EDX data for TRGO 4. (C) A low magnification TEM image of TRGO 4 and (D) A HRTEM image of TRGO 4: the inset shows the SAED pattern of TRGO 4.



Fig. 4 (A) XRD patterns of GO and TRGO 4. (B) Raman spectra of GO and TRGO 4.

oxygenated functional groups with an interlayer spacing (*d*) of 7.61 Å. Upon reduction, the interlayer distance (3.24 Å) decreases due to the removal of oxygen functionalities, and the reappearance of a quite broad peak at $2\theta = 23.53^{\circ}$ (Fig. 4A) is slightly different from that observed for graphite ($2\theta = 26.65^{\circ}$, d = 3.34 Å); this corresponds to the (002) plane, showing the reduction of GO and restoration of an ordered crystal structure. Furthermore, the small peak at 11.63° in TRGO 4 reveals the presence of a small amount of residual oxygen functionalities during reduction, which is also supported by the literature.^{20b}

In Raman spectra, GO shows the G band at 1601.02 cm⁻¹ and the D-band at 1365.32 cm⁻¹, while in the case of TRGO 4, two characteristic bands are observed: the G band at 1586.33 cm⁻¹ is usually assigned to the E_{2g} phonon of sp² atoms and the D band at 1358.12 cm⁻¹ (A_{1g} symmetry mode) is attributed to structural defects induced by hydroxyl or epoxide bonds on the graphene oxide surface. Amusingly, in the case of TRGO 4, the D-band and G band of GO is shifted to the lower end. The intensity ratio of the D band to the G band (I_D/I_G) indicates the degree of disorder, such as those involving defects. The I_D/I_G intensity ratio of GO is found

to be 0.95 (Fig. 4B), while it increases significantly to 1.005 in TRGO 4 due to a decrease in the literal size of the obtained reduced graphene oxide sheets.

To evaluate the structural information and confirm the removal of oxygen functionalities, X-ray photoelectron spectroscopy (XPS) analysis of GO and TRGO 4 was conducted (Fig. 5). The C 1s XPS spectrum of GO (Fig. 5B) shows that two large Lorentzian peaks are found in GO at 283.56 eV, corresponding to C-C/C==C of the aromatic ring and C-C/C==C of aromatic ring components, and 285.63 eV, corresponding to C-O (1,2-epoxide and alkoxy functionalities), with peaks at 287.12 eV and 288.05 eV corresponding to C=O and O-C=O, respectively. XPS elemental analysis of GO also shows the presence of 66.1% carbon and 33.9% oxygen, with an atomic ratio of carbon to oxygen (C/O ratio) of 1.94 (Fig. 5A). Compared with GO, the spectrum of reduced GO (TRGO 4) exhibits decreased intensities for the C 1s peaks of carbon binding to oxygen functionalities (Fig. 5C). Epoxy, alkoxy (C-O), O-C=O, etc. are greatly weakened, which demonstrates the effective deoxygenation of GO, which is in accordance with the results from FTIR and elemental analysis. The carbon content from sp² C-C makes up 73.09% of the total carbon in TRGO 4, which is much higher than the 66.1% in GO. The higher C/O ratio of TRGO 4 (3.10) suggests that the oxygen containing components are partially removed during reduction, which was also consistent with the obtained results from XRD analysis.

Furthermore, the O 1s signal of GO was deconvoluted into three peaks corresponding to quinone (529.79 eV), oxygen double-bonded to carbon (C=O) at 531.33 eV, and oxygen single-bonded to carbon, such as in the case of hydroxyl and epoxy functionalities, at 533.18 eV (Fig. 6A). The complete removal of the peak at 533.18 eV related to oxygen singlebonded to carbon in TRGO 4 (Fig. 6B) suggests the successful reduction of hydroxyl or epoxy functionalities upon the Tulsi leaf extract assisted reduction of GO. A comparative study of the C/O atomic ratios obtained from the XPS elemental analysis of



Fig. 5 (A) XPS survey spectrum of GO and TRGO 4, (B) the deconvoluted C 1s spectrum of GO, and (C) the deconvoluted C 1s spectra of TRGO 4.



Fig. 6 (A) The deconvoluted O 1s spectra of GO; and (B) the deconvoluted O 1s spectra of GO TRGO 4.

prepared rGO using various green reducing agents shows that the C/O atomic ratio of TRGO 4 sample was close to that using gallic acid (C/O of 3.89),^{20a} Hibiscus sabdariffa L. extract (C/O of 3.01),^{20b} and Sugarcane bagasse extract (C/O of 3.37),^{20d} and much higher than those using tannin (C/O of 2.44),^{20g} Pulicaria glutinosa plant extract (C/O of 1.86),^{20f} and tea solution (C/O of 2.84) (Table 1).^{20c}

The reduction of carbonyl compounds into their corresponding alcohols is an important organic transformation. The reduction of α,β-unsaturated carbonyl compounds has been widely carried out using sodium borohydride. This reaction is highly solvent dependent and generally does not result in useful regioselectivity. It can follow two pathways: addition to the carbonyl group (1,2-addition) to give allylic alcohols; or addition to the conjugated double bond (1,4-addition) to afford saturated carbonyl compounds.²¹ To tune the reducing power and selectivity of the metal hydride NaBH₄ for the 1,2-reduction of conjugated carbonyl compounds, numerous hydroborate agents have been reported.²² The search for a novel metal-free and green supporting catalyst to NaBH₄ that allows convenient, cost effective and efficient reduction under mild conditions is very crucial. In this context and as a continuation of our studies into synthetically useful green processes,¹⁴ especially graphene fabrication and catalysis,¹⁵ we anticipate applying Tulsi leaf extract reduced graphene (TRGO 4)/NaBH₄ as a new reducing agent for the regioselective reduction of α,β -unsaturated carbonyl compounds (Scheme 2). Thus, a mixture of (E)-cinnamaldehyde (1 equivalent), NaBH₄ (0.5 equivalent) and TRGO 4 (10 mg) was taken in water and stirred for 7 min at room temperature and, surprisingly, appreciable conversion into (E)-cinnamyl alcohol (the 1,2-addition product) without the formation of saturated alcohol (the 1,4-addition product) was achieved (Table 2, entry 1). Upon increasing the catalyst loading from 10 mg to 15 mg, the yield of the product increases up to 92% (Table 2, entry 2). However, a further increase in the catalyst amount did not increase the



Scheme 2 The reduction of cinnamaldehyde using TRGO 4 in water.

Table 2 The optimization of the reaction conditions for the reduction of cinnamaldehyde in aqueous media

$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Entry	Catalyst	Amount (mg)	Time ^a	Yield ^{b,c} (%)
2 TRGO 4 15 7 min 92 3 TRGO 4 20 7 min 92 4 5 h 5^d TRGO 4 20 5 h 6^e 5 h 7^e TRGO 4 20 5 h 8^f TRGO 4 15 7 min 92 9^g CRG 20 20 min 89	1	TRGO 4	10	7 min	68
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	TRGO 4	15	7 min	92
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	TRGO 4	20	7 min	92
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4	_	_	5 h	_
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5^d	TRGO 4	20	5 h	_
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6 ^e	_	_	5 h	_
8 ^f TRGO 4 15 7 min 92 9 ^g CRG 20 20 min 89	7^e	TRGO 4	20	5 h	_
9 ^g CRG 20 20 min 89	8 ^f	TRGO 4	15	7 min	92
	9 ^g	CRG	20	20 min	89

^{*a*} Stirring time. ^{*b*} Yield of the isolated and purified product. ^{*c*} Characterized *via* spectral (FTIR, ¹H NMR and ¹³C NMR) data. ^{*d*} Without NaBH₄. ^{*e*} Stirring under reflux conditions without NaBH₄. ^{*f*} Stirring under reflux conditions.^g Chemically reduced graphene oxide.

conversion rate (Table 2, entry 3) and, hence, 15 mg of TRGO 4 was taken as the optimum catalyst loading (Table 2, entry 2). Also, increasing the reaction temperature under reflux conditions did not increase the yield and conversion rate (Table 2, entry 8). The reduction process did not take place either in the absence of TRGO 4 or NaBH₄, even after 5 h stirring at room temperature (Table 2, entries 4 and 5) or under reflux conditions (Table 2, entries 6 and 7).

Furthermore, just for comparison, we also tried chemically reduced rGO in the aforementioned conversion and we obtained the corresponding alcohol in relatively lower yield than with the prepared TRGO 4 (Table 2, entry 9). The reason for the higher catalytic efficiency of TRGO is presumably due to its higher catalytic surface area. The defects and unsaturated carbon atoms at its edges provide TRGO 4 with a higher catalytic surface area. These factors make TRGO 4 a highly active catalyst and avoid the possibility of agglomeration, which explains the higher conversion rate using TRGO 4 than chemically reduced rGO (Table 2, entries 3 and 8). The catalyst was then recovered from the first reaction batch via centrifuging, washed with ethanol, and dried under vacuum at below 50 °C, and it could be reused by mixing with fresh NaBH₄ for five subsequent reaction batches without any significant loss of activity (Fig. 7). We did not face any difficulties or accidents or any unpleasant moments while performing this reaction process. The reduction of cinnamaldehyde to cinnamyl alcohol was confirmed via FTIR (Fig. 8), ¹H NMR (Fig. 9) and ¹³C NMR



Fig. 7 Reusability experiments involving the TRGO catalyst.



Fig. 8 FTIR spectrum of (E)-cinnamyl alcohol.



Fig. 9 ¹H NMR spectrum of (E)-cinnamyl alcohol

(Fig. 10) spectroscopy and it is also in good agreement with reports in the literature.23

Seven sets of equivalent protons are found in the ¹H NMR spectrum of cinnamyl alcohol. A 1H multiplet at 6.25-6.32 is assigned to one α-H, while a doublet at 6.53-6.56 is attributed to one β -H, and a coupling constant of 15.6 Hz shows that the α - and β -Hs are both *trans* to each other. Three sets of equivalent protons appear at a low field, indicating that they were more deshielded due to being directly attached to the benzene ring (the 2H doublet at δ 7.31–7.33, the 2H multiplet at δ 7.21–7.28 and the 1H multiplet at δ 7.15–7.20 ppm); a 2H double-doublet appears for $-CH_2$ at δ 4.24–4.26 (J = 4.6 Hz, 1.2 Hz). A singlet at δ 1.94, attributed to -OH, was found in the ¹H NMR spectrum.



Fig. 10 ¹³C NMR spectrum of (E)-cinnamyl alcohol.

In summary, our work offers a convenient, cost effective and green method for the reduction of GO using biomolecules present in Tulsi leaf extract as bio-renewable mild reducing agents for GO. This simple method has the sufficient advantages of reestablishing the electronic configuration in reduced graphene sheets, along with trace amounts of unreduced oxygen functionalities in GO. Moreover, the developed rGO is an efficient catalyst with NaBH₄ in water for the regioselective synthesis of α , β -unsaturated alcohols. Thus, the reported protocol would be a practical green alternative to existing procedures for the synthesis of allylic alcohols, catering for the needs of academia as well as industry.

Experimental

General information

All chemicals used in this study were of analytical grade, commercially available, and used without further purification. Graphite (CAS No. 1E4011854, particle size: $<100 \mu$ m) was purchased from SD-Fine. Green leaves of Tulsi were collected from Guru Ghasidas Central University campus, Bilaspur, C.G. India.

UV-vis spectroscopic measurements were performed with an aqueous dispersion of graphene oxide (GO), chemically reduced graphene oxide (CRG) and Tulsi leaf extract reduced graphene oxide (TRGO) in deionized water, and the absorbance was detected using a Shimadzu, UV-1800 UV-vis spectrophotometer (wavelength range: 200–800 nm). FTIR spectra were recorded using a Thermo Nicolet, Avatar 370 spectrometer with a resolution of 4 cm⁻¹ and samples in KBr form. X-ray diffraction (XRD) analysis was conducted on a Bruker AXS D8 X-ray diffractometer with CuK α radiation ($\lambda = 1.5406$ Å).

A transmission electron microscope (JEOL 2100F) with an accelerating voltage of 200 kV and a probe size of under 0.5 nm was used to examine the morphology. The scanning electron microscopy data with EDX images were obtained using a VEGA 3 TESCAN, EDX (Bruker) instrument. XPS measurements of powder samples were performed *via* XPS with Auger Electron Spectroscopy (AES) Module apparatus (PHI 5000 Versa Prob II, FEI Inc.). Raman spectra were recorded on a micro-Raman spectrometer (Renishaw plc, UK) using a 514 nm argon ion laser. The ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Advance III 400 MHz instrument in CDCl₃ solvent, using TMS as an internal standard. Chemical shifts were reported in ppm (δ) and coupling constants (f) in Hz.

Synthesis of graphene oxide

Graphene oxide (GO) has been synthesized *via* the oxidation of graphite flakes using a modified Hummers' method.¹⁷ About 1 g of graphite flakes was slowly added to concentrated sulfuric acid (23 mL) while stirring in an ice bath, followed by addition of about 0.5 g of sodium nitrate. And then, 3 g of potassium permanganate was added slowly, keeping the temperature within 0–5 $^{\circ}$ C to avoid any possible explosion. Stirring was

continued for 30 min a room temperature and a thick paste was formed. This was then diluted with distilled water (46 mL) under stirring conditions. The temperature of the solution was raised to about 98 °C and then the mixture was stirred for 4 h. Finally, it was cooled down and 100 mL of deionized water was added, followed by the slow addition of 3 mL of H_2O_2 (30%). The color of the solution changes from dark brown to yellowish brown. The overall solution was exfoliated under stirring followed by centrifuging at 3000 rpm to collect the solid mass at the bottom. The prepared materials were repeatedly washed with 50 mL of warm deionized water and 30 mL of 5% HCl to completely remove residual salts and acids. Finally, the brown mass was collected and dried at 50 °C under vacuum to obtain solid graphene oxide.

Preparation of an aqueous extract of O. Sanctum L. (tulsi leaf)

2.5 g of fresh *O. sanctum* leaves were washed, chopped and allowed to warm at 35 $^{\circ}$ C for 20 min with 100 mL of distilled water. A wine-red solution was obtained, cooled down and filtered with No. 1 Whatmann filter paper to yield leaf extract. The pH of the extract was measured as 5.0 and further used for the green reduction of GO.

Reduction of GO with the aqueous extract of *O. Sanctum* L. (tulsi leaf)

About 10 mg of GO was dispersed in 10 mL of deionized water (1 mg mL⁻¹) in a round bottom flask and this was stirred for 30 min to obtain a brown colored homogeneous dispersion. For the reduction process, 10 mL of leaf extract was added to the suspension and the whole solution was stirred at 70 °C. The solution gradually started changing color from brown to black upon heating and, after 4 h, a dark black solution was obtained. The reaction was discontinued, and the mixture was cooled down to room temperature. The resulting solution was centrifuged at 3500 rpm for 30 min. And the solid was collected and washed several times with a DI water and ethanol mixture. Finally, the black solid was dried under vacuum at 50 °C. The obtained product is designated as TRGO (Tulsi leaf extract reduced graphene oxide).

Procedure for the reduction of cinnamaldehyde

About 88 μ L of cinnamyl aldehyde (1 mmol) was added to a magnetically stirred suspension of TRGO 4 (15 mg) in DI water (2 mL) in a round bottom flask. About 0.5 mmol of NaBH₄ was then added to this reaction mixture and it was allowed to stir at room temperature for approximately 7 min. After the completion of the reaction as indicated by TLC, the catalyst was separated *via* simple filtration using Whatmann filter paper No. 1, and the reaction mixture was extracted with ethyl acetate (3 × 5 mL) and distilled water (20 mL), and finally dried over anhy. Na₂SO₄. The evaporation of the solvent using a rotary evaporator afforded the pure product. Characterization data of cinnamyl alcohol: white powder (92%);

IR (KBr): $\nu_{\rm max}$ 3360, 3004, 22942, 2839, 1483, 1459, 1263, 1156, 1039, 782 cm⁻¹; ¹H NMR (400 MHz; CDCl₃/TMS): δ : 7.31–7.33 (d, 2H arom, *J* = 7.9 Hz), 7.21–7.28 (m, 2H arom), 7.15–7.20

(m, 1H arom), 6.53–6.56 (d, 1H_{β}, *J* = 15.6 Hz), 6.25–6.32 (m, 1H_{α}), 4.24–4.26 (dd, 2H, *J* = 4.6 Hz, 1.2 Hz), 1.94 (s, 1H, OH); ¹³C NMR (100 MHz; CDCl₃/TMS): δ : 138.18, 132.73, 129.35, 128.84, 127.03, 124.20, 62.83; EIMS (*m*/*z*): 134 (M⁺). Anal. calcd for C₉H₁₀O: C, 80.56, H, 7.51; found: C, 80.23; H, 7.69.

Conflicts of interest

There are no conflicts to declare.

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