A STUDY ON CHARACTERISTICS OF ECOFRIENDLY SYNTHESIS OF GRAPHENE OXIDE USING CITRUS LIMETA AND L-ASCORBIC ACID

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Abstract : In the present work we studied the basic properties of Graphene Oxide and rGO. Graphene oxide was prepared using improved modified Hummer's method. Further reduction of Graphene Oxide was carried out in two ways, by using L-ascorbic acid as a reducing agent and using ecofriendly reducing agent namely aqueous peel extract of CITRUS LIMETA (Sweet lime). Reduced Graphene Oxide (rGO) was obtained using cold maceration, magnetic stirring, sonication and refluxing techniques. Structural and optical characterization of GO and rGO was carried out using XRD, UV-visible, FTIR, SEM. X-ray diffraction, FTIR, UV-visible spectroscopy shows the formation of rGO. The surface morphology of synthesized rGO was studied by SEM analysis. Resistance of the rGO films prepared was measured using resistance meter. Preparation of reduced graphene oxide using aqueous peel extract of CITRUS LIMETA (Sweet lime) is sustainable, cost effective and more ecofriendly than other standard methods of reduction of nanoparticles.

Keywords: ecofriendly synthesis, graphene oxide, reduced graphene oxide, vitamin C

I. INTRODUCTION

Graphene is an extraordinary material due to its thermal, optical, mechanical and transport properties [ ]. Recent progress has shown that the graphene-based materials can have a profound impact on electronic and optoelectronic devices, chemical sensors, biosensors, nanocomposites, and energy storage[ ]. Various methods are reported on the production of graphene such as micromechanical cleavage, graphitization of SiC and solution exfoliation of graphite in organic solvents etc[ ]. However, these methods turn out a poor yield of graphene. Chemical reduction of graphite oxide is a simple, cost effective route with high yield. But this method is not suitable in case of biological applications because of the harmful nature of the reducing agents. Thermal treatment, two step reduction, exfoliation are some other methods reported by researchers [ ]. Due to non ecofriendly and highly toxic nature of the chemicals in these methods stimulated us to think some alternative technique for synthesizing graphene oxide using aqueous peel extract of CITRUS LIMETA (Sweet lime) as a green reducing agent. It contains natural vitamin C and exceptional anti-oxidant as well as antibacterial activity [ ], it is considered as a green substitute to unsafe reducing agents in synthesis of nanomaterials. Further L-ascorbic acid is an isolated nutrient as a part of vitamin C. It was also used in synthesis of GO[ ] to compare the characteristics of rGO. Present work reports simple ecofriendly approach to obtain reduced graphene oxide by chemical reduction of GO using aqueous peel extract of CITRUS LIMETA (Sweet lime) as a green reducing agent.

II. EXPERIMENTATION

Preparation of Grapheme Oxide:

In the present work, improved modified Hummer's method was used for the preparation of graphene oxide (GO) [ ]. It has two phases the solid phase is a mixture of 10 g of graphite powder and 5 g $NaNO_3$. The liquid phase contains 216 ml of concentrated H_2SO_4 mixed with 24 ml concentrated H_3PO_4. The liquid phase ratio was maintained as 9:1 (wt %). After addition of 30 g of potassium permanganate, the mixture was stirred for 1 hour at temperature of 100ºC. Addition of 30 ml of H_2O_2 into the mixture resulting in yellow color represents great level of oxidation. For the complete removal of SO_4^{2-} , solution was repeatedly washed with 5% HCl and DI followed by centrifuge (4000 rpm). Finally the material was air dried for nearly 24 h and a brown black sample was collected.

Preparation of Phytoextracts

Fresh CITRUS LIMETA (Sweet lime), were purchased from local market and washed with DI water to remove the dust particles. The peels of CITRUS LIMETA (Sweet lime) were blended with domestic blender and kept in DI water for cold maceration overnight. The mixture was stirred at 50˚C for 30 min in DI water.

Reduction of GO using aqueous peel extract of CITRUS LIMETA (Sweet lime)

50 mg GO (0.1 mg/ml) was dispersed in DI water via sonication for 45 min. 10 ml (5wt %) aqueous peel extract of CITRUS LIMETA (Sweet lime) was added to the dispersion. The mixture was refluxed for 6 hrs at 50°C, until color changes to brown-black. The mixture was repeatedly washed with DI water and ethanol. The product was centrifuged at 4000 rpm for 20 min and dried at 100°C in oven.

Reduction of GO using L-ascorbic acid

50 mg GO (0.1 mg/ml) was dispersed in DI water via sonication for 45 min. o.1 M L-ascorbic acid was dissolved in DI water. The obtained mixture of GO and L-ascorbic acid (1:1 volume ratio) was homogenized using magnetic stirrer at 60°C for 1 hour. The color of the mixture changes from brown to black. The mixture was centrifuged at 4000 rpm for 10 min. 10 ml of 30 % H_2O_2

was added to the mixture in order to remove remaining ascorbic acid. The mixture was sonicated for 30 minutes at 60°C. The mixture was repeatedly washed with DI water and ethanol. The product was centrifuged at 4000 rpm for 20 min and dried at 100°C in oven.

Characterization

Structural characterization

The samples prepared were characterized by various techniques to investigate their properties. X-ray diffraction (XRD) patterns of the samples were recorded using Phillip, Holland instrument with CuKα_ radiation (0.1541 nm) in the range of 5° to 85° with scanning rate 2° per minute.

Optical characterization

Fourier Transform Infrared (FTIR) and UV-visible spectra of the samples were recorded on Perkin-Elmer FTIR Spectrometer RXI and Shimadzu UV-2450 UV visible spectrophotometer respectively. Scanning electron micrographs (SEM) were recorded on Zeiss scanning microscope instrument operating at 20 kV, at various magnifications.

III Results and discussion:

Structural characterization

XRD analysis

Figure 1 depicts XRD pattern of graphite powder, prepared graphene oxide and reduced graphene oxide.

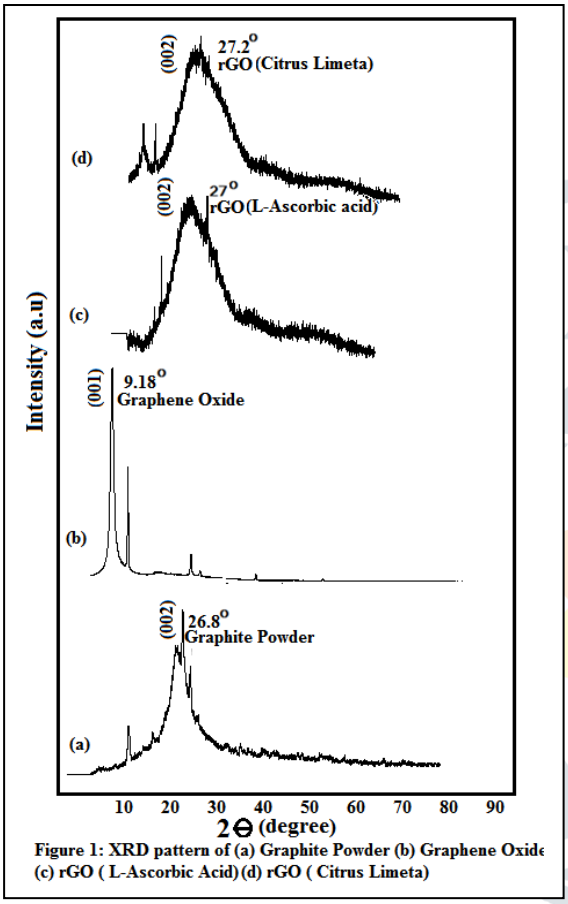

Figure 1: XRD pattern of (a) Graphite Powder (b) Graphene Oxide (c) rGO (L-Ascorbic Acid) (d) rGO (Citrus Limeta)

Figure (1a) represents the XRD pattern for graphite powder along with the characteristic peak [002] at 2θ = ~ 26.8° corresponding to an interlayer distance of 0.39 nm. After oxidation of graphite into GO, the sharp peak of graphite disappears and new peak appears at 2θ ~9.18° corresponding to [001] plane as shown in figure (1b). At this stage interlayer distance increases to 0.54 nm. The increase in interlayer distance is attributed to the formation of functional groups on both sides of loosely stacked graphite sheets. A peak around 26.8° shows presence of a few un-oxidized graphite. [ ]. Fig (1c) depicts layered formation of rGO(L-Ascorbic) sheets with corresponding peak 2θ ~ 27° corresponding to [002] plane.Figure (1d) shows layered formation of rGO (Citrus Limeta) sheets with corresponding peak 2θ ~ 27.2° corresponding to [002] plane. It is observed that XRD peak of natural vitamin C (Citrus Limeta) matches with the XRD peak of L-ascorbic acid. The average crystallite size was estimated according to the Scherer equation

$$D = \frac{0.9\lambda}{\beta Cos\theta}$$

The average crystallite size of rGO using L-Ascorbic acid is 0.49 nm. Similarly average crystallite size of rGO using aqueous peel extract of Citrus Limeta is 0.48 nm

SEM

Figure 2 displays SEM of GO, rGO

Figure (2a) represents SEM of Graphite powder .GO in figure (2b) implies agglomeration of nanosheets containing large number of unevenly placed thin sheets of oxygenated graphene layers. The morphological structure of rGO using L-ascorbic acid resulted in formation of layered rGO sheets as shown in figure (2c) . Reflux treatment on GO using Citrus Limeta peel extract resulted in formation of distinct exfoliated layers of rGO as shown in figure (2d). The EDX result also confirms the elemental composition of elements C and O respectively figure (2e) and figure (2f). The reduction degree calculated by C:O ratios of rGO samples were obtained from EDX analysis . C:O ratio was calculated for rGO using L-ascorbic acid as well as using Citrus Limeta peel extract . In both the cases C:O ratio is >8.

Optical characterization

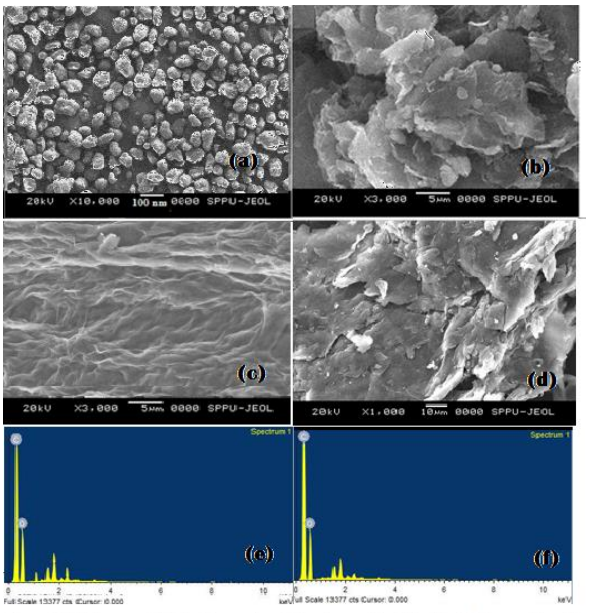

Figure 2: SEM images of (a) Graphite powder (b) Graphene oxide (GO) (c) rGO (L-ascorbic acid) (d) rGO (Citrus Limeta) (e) EDX- rGO (L-ascorbic acid) f) EDX-rGO (Citrus Limeta)

UV-visible analysis

Figure 3 shows UV visible spectra of Graphene oxide and reduced graphene oxide

The absorption peak in figure (3a) was observed at 228 nm depicts π→π*transition of C=C bonds [ ]. The shift in absorption peak from 228 to 272 nm is observed in figure (3b) after the reduction of GO by reflux method using L-Ascorbic acid. Similar shift was noted in figure (3c) at 274 nm for rGO using Citrus Limeta .The shift signifies deoxygenation of the GO sheets and the rebuilding of the sp^2 bonded hybridized carbon structure. This phenomenon shift has been used as a monitoring tool for the reduction of GO. During the reduction of GO, the colour of GO solution changes from yellow brown to black. This is in agreement with the work reported by few researchers [ ].

FTIR analysis:

Figure 4 indicates FTIR spectra of graphene oxide and reduced graphene oxide

The FTIR of graphene oxide GO shows various characteristic absorption bands of oxygen-containing groups which demonstrate the successful oxidation process. A wide-ranging peak at 3452 cm^{-1} indicates the O–H stretching vibrations for hydroxyl groups and water molecules. The IR peaks at 2367 cm^{-1} shows CH_2 stretching of

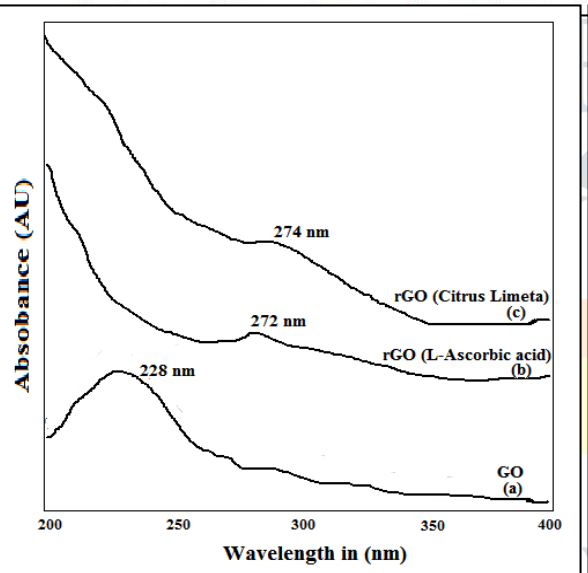

Figure 3: UV visible spectra of (a) GO (b) rGO (L-ascorbic acid) (c) rGO (Citrus Limeta)

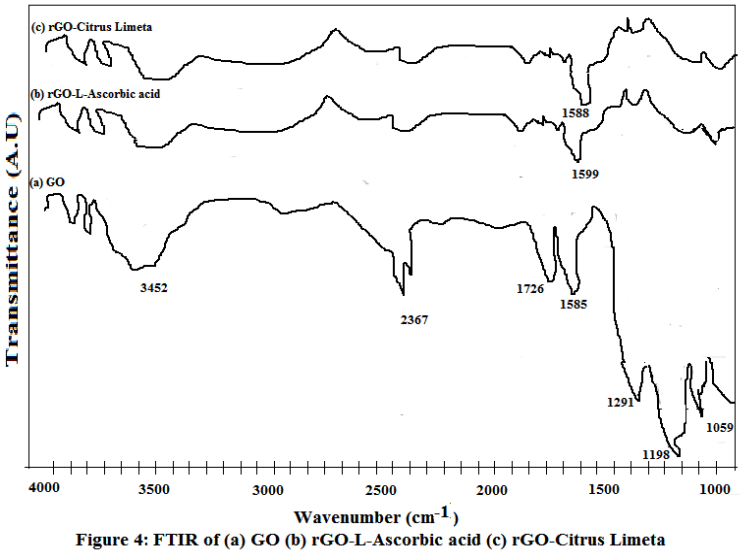

Figure 4: FTIR of (a) GO (b) rGO-L-Ascorbic acid (c) rGO-Citrus Limeta

Graphene Oxide. The high intensity bands for GO show quantity of C–H vibrations. Moreover stretching vibrations in C=O and stretching in C–O for –COOH groups produced at edges of the GO surface appeared at 1726 cm^{-1} and 1585 cm^{-1}, respectively. The stretching vibrations in C–O–C for epoxy groups appear around 1059 cm^{-1}. A tremendous reduction in intensity of absorption of oxygen-containing functional groups is seen in rGO (fig 4b) using L-Ascorbic acid. The same can be seen (fig 4c) for rGO using Citrus Limeta. This also predicts that aqueous peel extract of Citrus Limeta active green reducing agent. The C=O bands in carbonyl group vanished and wide spectrum is maintained. Few residual O-H groups are observed in rGO.

Resistance measurement

Resistance of the rGO films prepared was measured using 6 1/2 digit resistance meter. The resistance of rGO-L-Ascorbic acid was 30 KΩ and that of rGO-Citrus Limeta 29.42 KΩ.

Conclusions

The aqueous peel extract of Citrus Limeta (natural vitamin C) and L-ascorbic acid an isolated nutrient as a part of vitamin C were successfully used as green reducing agent for reduction of graphene oxide (GO) into reduced graphene oxide (rGO). Average crystallite size calculated using Scherer equation is 0.49 nm and 0.48 nm respectively. C:O ratio calculated for rGO using L-ascorbic acid as well as using Citrus Limeta peel extract is almost >8. The resistance of rGO-L-Ascorbic acid was 30 KΩ and that of rGO-Citrus Limeta 29.42 KΩ. Preparation of reduced graphene oxide using aqueous peel extract of CITRUS LIMETA (Sweet lime) is the best sustainable, cost effective and more ecofriendly than other standard methods of reduction of nanoparticles.

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