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A LOW-COST ROUTE FOR SYNTHESIS OF REDUCED-GRAPHENE OXIDE THIN FILMS FOR TRANSPARENT CONDUCTING ELECTRODES BY SPRAY-PYROLYSIS

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Graphene and other two-dimensional (2D) materials are promising materials for photonics and optoelectronics applications. A significant requirement for these applications is to develop cost effective and industrial scale production processes, while providing a balance between fabrication and final material quality. In this paper, we are reporting the replacement of indium tin oxide (ITO) with reduced graphene oxide (r-GO) for transparent conducting electrodes for optoelectronic devices. We have synthesized graphene oxide (GO) by modified Hummers method and deposited on quartz substrate by spry-pyrolysis to fabricate thin film of GO. These thin films were reduced by aluminum and sodium borohydrate. For characterization of fabricated thin films UV-VIS spectrophotometer, Atomic force microscopy (AFM) and Four-point probe were used.

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1. Introduction

Transparent conducting electrodes (TCEs) are electrodes that are highly transparent (more than 80%) to visible spectrum and offer good conductivity as well. Other parameters associated with transparent electrodes are of suitable work-function (4.9 eV to 5.2 eV), chemical stability and low cost Fabrication [1]. Now a days, these electrodes have been extensively used in many modern optoelectronic devices such as Touch screens, Liquid crystal displays (LCDs), Organic Light Emitting Diodes (OLEDS) [2,3] and solar cells [4]. Light interacts in or out with these devices through these TCEs. All these devices need transmission and current injection at the same time. These optoelectronic devices share similar structure and TCE is one of the top upper layers.

Recently, transparent conductive electrodes are fabricated by metal oxides, whereas the most broadly used oxide being Indium tin oxide (ITO). These ITO`s based electrodes are possessed by low sheet resistance with 85% optical transparency in the visible range [5]. These metal oxides are well studied and refined for more than 50 years [6,7,8]. ITO offers several vital drawbacks related to its material properties and cost, it has ceramic nature, which means extremely low strains can produce micro-cracks in ITO films and these cracks degrade film conductivity significantly [9,10,11]. Trace amounts of salts and acids in the environment cause corrosion of ITO layer, so it suffers severe lifetime issues [12,13]. ITO films possess comparatively high index of reflection when combined with lower index substrates, which causes undesirable reflection [14]. Anti-reflection coating stacks are developed to overcome this problem but these can be quite expensive. Due to the poor mechanically flexibility, it can't be used on flexible substrates. Moreover, many organic optoelectronic devices can't perform well due to the poor electrical contact with its films.

The high cost connected with ITO is the major threat to remain dominant in transparent electrodes market [15,16]. So, due to the lessening of Indium resources the use of ITO is a key reason for raising costs of many optoelectronic devices. Usually, its films are deposited via

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Vacuum sputtering, which is a slow and inefficient process. In this process, only 3-30% of sputtered Indium target reaches the substrate while remaining stays left on the walls of the sputtering chamber [17]. Moreover, flexible electrode technology got more attention due to the amazing development in flexible optoelectronic technologies which can produce devices on flexible substrates instead of conventional glass substrate. ITO does not support substrate bending due to its brittleness and thus other materials are explored to exchange ITO.

Graphene was emerged in 2004 as promising Transparent Conductor, when highly oriented pyrolytic graphite was repeatedly peeled by cellophane tape [18]. It is a sp^2 hybridized monolayer of carbon atoms closely packed into a hexagonal structure. This material is a gifted transparent conductor and may replace traditional Indium tin oxide electrodes in optoelectronic devices due to its optical and electrical properties [19,20,21] that came from its sp^2 hybridization. It has enormously high room temperature carrier mobility ($\approx 20\ 000\ cm^2\ v^{-1}s^{-1}$) potentially unmatched by any other material [22] and only 2.3% of visible light is absorbed by it. Electrons in discrete graphene sheets delocalize over the entire sheet, providing ballistic charge transport with minor optical absorption [23].

2. Experimental work

All materials, sulfuric acid, hydrochloric acid, graphite powder, sodium nitrate, potassium permanaganate and hydrogen per oxide used in this work were purchased from Sigma-Aldrich. For synthesize of graphite oxide Hummers method was followed [24]. Graphite powder (5g) was subjected with sodium nitrate (2.5 g) in sulphuric acid (115ml of 98% concentrated), the prepared mixture was strirred for 40 minutes and cooled in ice bath and then subjected with oxidizing agent potassium permanaganate and temprature was maintained below 20°C, during the reaction the colour was slightly changed from black to dark green.

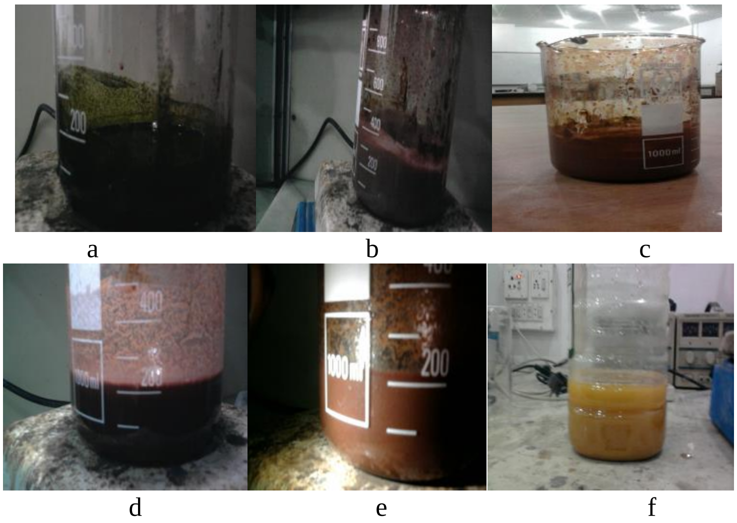

Fig. 1. Different steps of Hummers method indicating oxidation of graphite

Mixture was removed from icebath after the careful addition of potassium permanganate and strirred for 30 minutes with 35°C raise of temprature, this was the medium temprature stage. At this stage emission of dimaganeseheptoxide gas took place due to the reaction of potassium permanganate with sulphuric acid. After the completion of medium temperature stage the deionized water (250 ml) was added gradually (75 minutes) into the mixture and temperature was raised to 98°C. This was the high temperature stage. The color of mixture changes to reddish brown indicates the extent of oxidation. Finally, Oxidation of graphite was completed by addition of deionized water (400 ml) and hydrogen per oxide (50 ml of 35% concentrated) to remove the ions present in the solution while the temperature was maintained at 98°C, at the end of reaction the bright yellow color was the indication the successful oxidation. The stepwise changes in color are shown in Fig. 1**.**

The bright yellowish mixture was filtered and washed various times with 200 ml of 1M hydrochloric acid (HCl) solution followed by 500 ml of deionized water and dried.

To convert graphite oxide into GO, the graphite oxide powder was exfoliated in deionized water by ultra-sonication in a ratio 5 mg/ml for 6 hours into the centrifuge at 8000 rpm for 30 minutes. Top 75% of the suspension was decanted to yield graphene oxide suspension. The conversion process is shown in the Fig. 2.

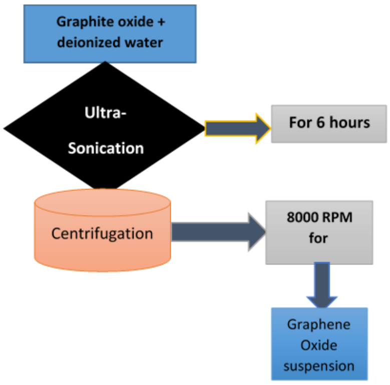

Fig. 2 Conversion of GO into graphene oxide

To deposit graphene oxide on quartz, pretreatment was performed. Quartz substrates (1cm ×1cm) were washed in acetone, deionized water and isopropanol by ultra-sonication bath. At the end of washing cycle these substrates were dried under nitrogen steam and subjected to Piranha solution (7:3 H_2SO_4:H_2O_2 mixture, caution tremendously corrosive and very exothermic) for 40 min. Finally, these substrates were dried again under nitrogen steam and stored in air tight boxes. Graphene oxide suspension (10 mg/ml) was sprayed on quartz substrates (1cm ×1cm) and these substrates were left for drying for 24 hours to get GO thin films. GO thin films were reduced by Aluminium powder and sodiumborohydrate. GO thin film was dipped in a mixture of 0.5 gram aluminium powder and 20 ml of 35% concentrated sulphuric acid for 40 minutes. After 40 minutes film was washed with deionized water and stored in air tight environment. GO thin film was immersed in 50 ml of 150 mM sodium-borohydrate solution for 2 hours. After 2-hour film was washed with deionized water and stored in air tight environment. Experimental work of graphene oxide (GO) thin films was divided in five different steps, the summery of these all steps is shown in Fig. 3.

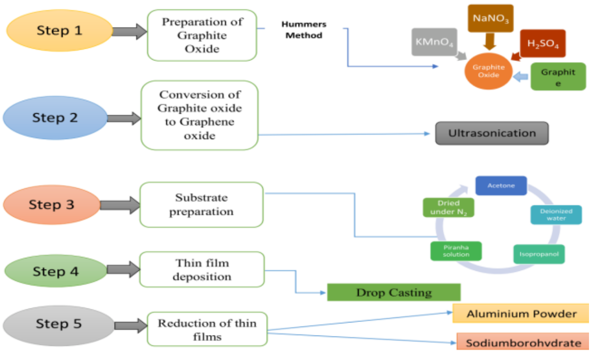

Fig. 3. Different steps involved in the synthesis of r-GO

3. Results and discussion

3.1. Optical properties

The optical properties of thin films were studied by UV-VIS spectrophotometer. Fig. 4 (a, b) shows absorption spectra of GO and r-GO. The spectrum of GO has an absorption peak is around 240 nm and after reduction shifted towards the higher wavelengths due to the partial removal of oxygen containing groups and partial restoration of sp^2 network in aromatic carbon. This is the red shift which is due to electronic configuration of reduced GO. The strong absorption peak at 240 nm is attributed to π-π^* transition of aromatic C-C ring. The spectra for r-GO shows red shift at 268 and 275 nm, these two peaks are attributed to n-π^* for C-O bond.

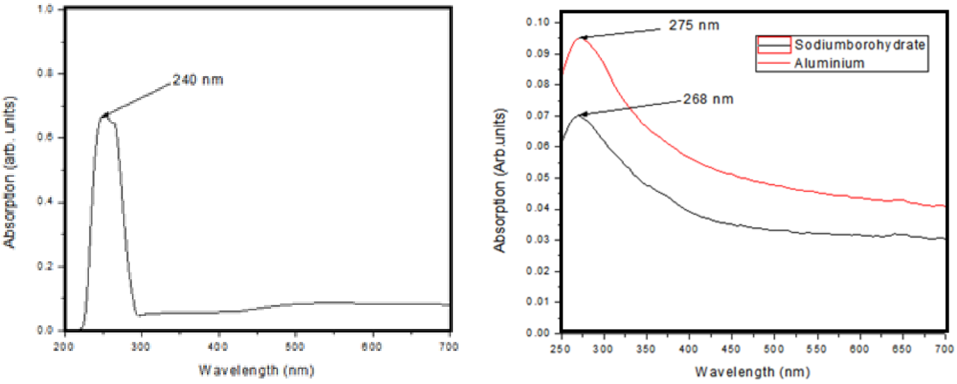

Fig. 4. Absorption spectra as function of wavelength of GO (a) and r-GO (b)

The red shift is greater for aluminum powder, which shows that aluminum removed oxygen containing groups more efficiently than sodium-borohydrate.

Transmission spectra of r-GO films are shown in Fig. 5, it is observed from the transmission spectra that the transparency of r-GO thin by aluminum powder is 90%, whereas by sodium-borohydrate the transparency is 93%.

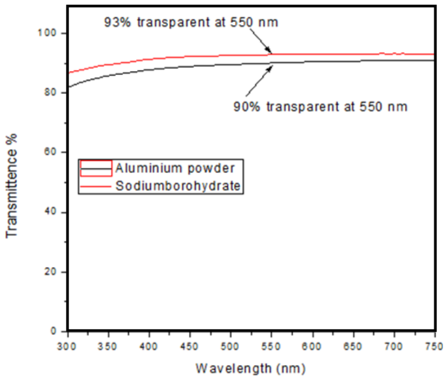

Fig. 5. Transmission spectra r-GO by aluminum powder and sodium-borohydrate.

3.2. Atomic Force Microscopic (AFM)

AFM was used to characterize surface roughness as well as for topography. As shown in Fig. 6, the Surface root mean square roughness (R_q) is 7.0 nm for GO on quartz substrate, which were reduced to 6 nm and 3.7 nm after the treatment with sodium-borohydrate and aluminum respectively. The removal of oxygenated functional groups with the treatment of sodium-borohydrate and aluminum were mainly responsible for the reduction of surface roughness. Although the defects cannot be completely removed after treatment, due to the very well aligned structure of the films, the surface roughness was much lower than that of the film produced by other techniques, such as spin [13,14], dip coating [17], and transfer printing [15,16,24].

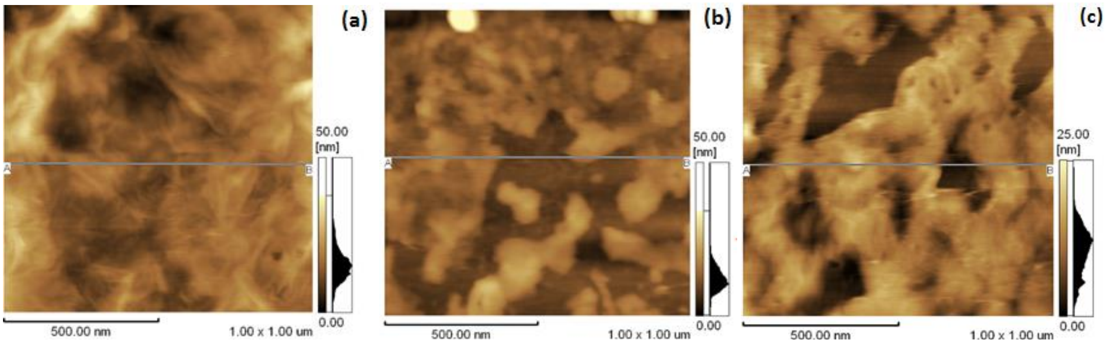

Fig. 6. Surface root mean square roughness (R_q) of GO (a) and r-GO with by sodiumboro hydrate (c) and r-GO with aluminium powder

The AFM images shows a topography of GO and r-GO in 3D is presented in Figure 7. It is clear from AFM images that bright and dark areas form hills and valley. The GO films are expected to be thicker due the presence of covalently bonded oxygen and the displacement of sp^{3} hybridized carbon atom above and below the original graphene plane, after the treatment roughness and thickness is reduced due to the removal of oxygen containing functional groups.

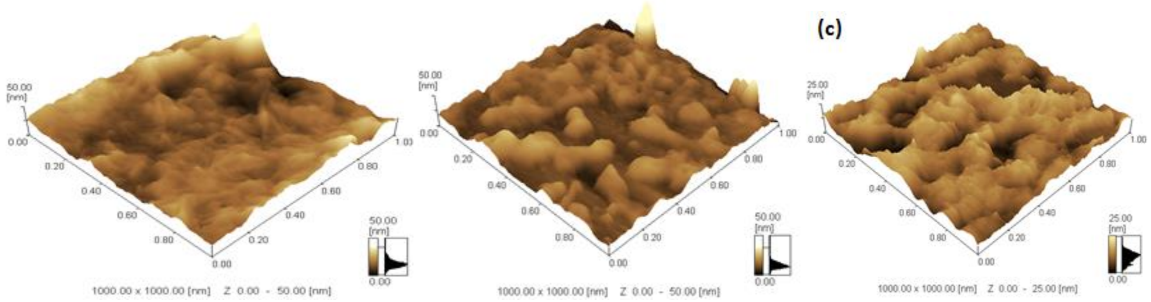

Fig. 7. AFM images of GO, r-GO by sodium-borohydrate and r-GO by aluminum

3.3. Electrical properties measurement

The electrical properties of synthesized samples were calculated by Four-probe method. The result shows that the sheet resistance of the films before the treatment was relatively high ($20\times10^{9}\Omega$/sq), after the treatment with aluminum and sodium-borohydrate the sheet resistance was significantly reduced of (4.53×10^{6}-6.5×10^{6} Ω/sq), which is 10^{3} times lower than as that of before treatment. The functional group of oxygen was removed by treatment, which in turn restored the p-electron system in graphene. In the treatment, the aluminum and sodium-borohydrte cleaned the GO films with a beneficial effect on electrical conductivity. The functional groups of aluminum and sodium-borohydrate acted as electron acceptors, allowing the Fermi level to move toward the valence band and thus increasing the hole density in graphene, giving rise to a reduced electrical resistivity. The optical and electrical properties were enhanced by the treatment of both aluminum and sodium-borohydrate. Sheet resistance observed in our study by spray pyrolysis was significantly reduced with high optical transparency above 90%. Sheet resistance and conductivity of GO and r-GO thin films is calculated by four-point probe method and presented in Table 1

Table 1: Electrical properties measurement by Four-probe method

Sample name	Sheet resistance (Ω sq^{-1})	Conductivity (Scm^{-1})
GO	20×10^{9}	6.15×10^{-5}
r-GO (Sodium-borohydrate)	6.52×10^{6}	153
r-GO (Aluminum powder)	4.53×10^{6}	220.7

High sheet resistance associated with GO films is due to the incomplete reduction of oxygen containing functional groups. However, sheet resistance of r-GO film reduced by aluminium powder is lower than the sodium-borohydrate reduced GO film.

4. Conclusions

Thin films of graphene oxide were fabricated by spray pyrolysis and further reduced with aluminum powder and sodium borohydrate, due to which a significant change in optical, electrical and morphological was observed. The optical transparency and electrical conductivity of GO thin films were improved by chemical treatments. The treatment helped to remove the impurities on the graphene oxide thin films. while functional groups acted as electron acceptors thus increasing the hole density in graphene oxide.

The electrical conductivity of the resulting graphene oxide films was increased along with improvement of the optical transmittance up-to 93% (at 550 nm). As with high transparency and good conductivity with low surface roughness these synthesized sample could be used as transparent conducting electrodes in the photovoltaics and optoelectronics.

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