Fabrication of reduced graphene oxide modified poly(3,4-ethylenedioxythiophene) polystyrene sulfonate based transparent conducting electrodes for flexible optoelectronic application

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Abstract

Present article reports on reduced graphene oxide (rGO) modified poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) based transparent conducting electrodes for flexible optoelectronic applications. PEDOT: PSS samples embedded with different rGO concentrations i.e. 0, 1, 2, 3, 4, 5 wt% were prepared and later on, bar coated on polyethylene terephthalate substrate using a 30 μm wire size bar. Various parameters including sheet resistance, bending test (outside and inside bending), optical transmittance etc. were estimated. Our analysis indicates that the samples with 1 wt% rGO possess improved results i.e. low sheet resistance ($315 \pm 8 \Omega/\text{sq.}$) and high transmittance ($\sim 74\%$). Additionally, the sample shows low electrical resistance variation up to 12% (maximum increase) during outward bending and 9% (maximum decrease) during inward bending of the sample for bending curvature from 20 to 100 m^{-1} .

Keywords Transparent conducting electrode · Poly (3 · 4-ethylenedioxythiophene): poly (styrene sulfonic acid) · Dimethyl sulfoxide · Optoelectronics devices · Bar coating

1 Introduction

Transparent conducting electrode (TCE) is an essential part of various optoelectronic devices such as light-emitting diodes, photovoltaic cells, touch screens, solar cells, and flat-panel displays [1–3]. Among various TCEs, Indium tin oxide (ITO) is most preferred as it wealth with attracting characteristics like high transmittance ($\sim 90\%$) and low sheet resistance ($\sim 10 \Omega/\text{sq.}$) [4]. Still, the quest to develop improved materials for flexible TCE applications is on, as ITO possesses practical limitations of its brittle nature. Additionally, limited indium resources restrict the prolonged run use for future flexible optoelectronics

devices. Hence, there is a requirement of alternate material for ITO as TCE. Several TCE materials like transparent conducting polymers (TCPs), metal nanowires, carbon nanotubes, and graphene have been explored for replacing ITO [4, 5]. Among these materials, both graphene and TCPs play a vital role due to their lightweight, low sheet resistance, high transparency, and flexibility [6–8]. Chemical vapor deposition (CVD) is the most preferred technique to deposit graphene. However, the CVD technique requires high temperatures ($\sim 1000^\circ\text{C}$) operation under a high vacuum, making it infeasible to deposit graphene directly on flexible (polymer) substrates [9]. Some of the transfer processes have been explored to deposit graphene on

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polymer substrates using CVD [10], however challenges remain persists in discovering suitable mechanisms for graphene films transfer on flexible substrates without developing cracks during the transfer process, obtaining large-area graphene film with a clean surface and achieving a low-cost transfer process. To undertake CVD technique issues, several solutions have been proposed for the graphene deposition [11, 12]. Nevertheless, yet no process has been precise enough to deposit graphene on a flexible substrate. Among TCPs, Polyaniline (PANI), Polypyrrole (PPy), and PEDOT: PSS are well-known polymers [13–16], but PEDOT: PSS is most preferred materials because of its low sheet resistance and high transmittance [14, 16]. The conductivity of PEDOT: PSS can be enhanced by chemical treatment with some solvent including sulfuric acid, formic acid, Polyethylene Glycol, N,N-dimethyl formamide, xylitol, tetrahydrofuran, methoxyethanol, and dimethyl sulfoxide (DMSO) [17–26], [27]. Despite this, PEDOT:PSS has several problems such as inhomogeneous electrical properties and poor long-term stability [28, 29].

In the present work, for achieving a flexible TCE as an alternate of ITO, rGO modified PEDOT: PSS TCE was fabricated on a flexible PET sheet using a bar coating technique with high performance and stability. At first, graphene oxide (GO) was synthesized using modified Hummer's method and then rGO was synthesized by reducing the GO using L-ascorbic acid. The different proportion of synthesized rGO was mixed in PEDOT: PSS solution and deposited on a PET sheet using bar coating technique as explained in Sect. 2. The deposited film was further exposed to the DMSO solution. Vibrational analysis including Raman spectra, FTIR absorption measurement; sheet resistance, flexibility, of the fabricated electrodes was estimated. The results and conclusion of the work is discussed in Sect. 3, 4 respectively.

2 Materials and methods

Materials: graphite powder, PEDOT: PSS (1.3 wt% dispersion in water) were obtained from Sigma Aldrich (USA); dimethyl sulfoxide (DMSO), and polyethylene terephthalate (PET) film were used for making transparent conducting films. In addition to this, soap solution, isopropyl alcohol (IPA), deionized (DI) water, and nitrogen gas were used to prepare the PET substrate for film deposition.

At first, PET substrates (2.5 cm × 2.5 cm) were cut and cleaned by sonication in soap solution then rinsed in DI water, after that the substrate was sonicated in isopropyl alcohol, and then rinsed in DI water. The substrates were dried with nitrogen and treated with oxygen plasma for 5 min each to enhance the wettability and adhesive strength of the substrate. Graphene oxide (GO) was

synthesised using a modified Hummer's method. In brief, 3 g graphite was dissolved in 60 ml of concentrated H₂SO₄ using stirring at room temperature for 24 h. Thereafter, the solution was placed in an ice bath to maintain the solution temperature up to 10 °C. Then 3 g of NaNO₃ was added to the solution and stirred for 30 min by sustaining the temperature 10 °C in an ice bath, and took out the solution from the ice bath, and stirred it again for 1 h at room temperature. After that, the solution was diluted with 240 ml of DI and stirred it for 30 min and again diluted the solution with 1 L of DI, after that 45 ml of H₂O₂ slowly added drop by drop for 30 min. The resulted solution was washed with HCl (5%wt): 65.2 ml of HCl in 84.8 ml of DI and filtered with a paper filter and washed to achieve neutral pH. The resulted product was dried at 80 °C in the oven for 48 h to receive GO powder. Thereafter, reduced graphene oxide (rGO) was synthesised by reducing the GO using L-ascorbic acid. Aqueous suspension of GO was prepared by ultra-sonicating 500 mg of GO in 1 L DI for 2 h. Thereafter, 500 mg of ascorbic acid was added and the solution was sonicated for the next 24 h. The resulting suspension was filtered and washed with DI water multiple times and dried at 60 °C in a vacuum oven.

Different concentrations 0%, 1%, 2%, 3%, 4%, and 5% (wt%) of rGO was mixed in PEDOT: PSS and sonicated for 4 h each. The prepared solution was deposited on a PET sheet using a bar coating and treated with DMSO. DMSO is a high boiling solvent and strongly enhanced the conductivity of PEDOT:PSS layer [30]. Respective change in sheet resistance and transmittance of the deposited layers were observed. A schematic diagram of the experiment is given in Fig. 1.

2.1 Characterization techniques

The deposited films of rGO modified PEDOT: PSS on PET substrates were characterized by different methods. The sheet resistance of the deposited samples was estimated by the four-probe (Vijayanta Electronics, India) technique. The analysis of surface roughness of the layer was carried out by Atomic Force Microscopy (AFM) using a machine of model Pro 47, provided by NT-MDT spectrum instruments Russia. The optical transmittance measurements were carried out on UV–Vis Spectrophotometer (Rescholar, India). The optical images were taken by optical microscope (Olympus BX53M) and the molecular vibrations of synthesised GO and rGO were characterised by Raman spectroscopy via Raman Spectrometer setup (WI Tec Alpha300 RAS) and FTIR absorption via FTIR spectrometer (PerkinElmer Spectrum Two) available in BML Munjal University, Gurugram. The bending test of the deposited samples was performed by taking the relative variation of electrical resistance using Keithley 2450 as a function of

Fig. 1 Schematic diagram of rGO + PEDOT: PSS solution bar coating processes on PET sheets

bending curvature for both sides including outer bending and inner bending.

3 Results and discussion

In this work, rGO/PEDOT: PSS based transparent conducting electrodes were prepared. In rGO synthesis process, first of all GO was synthesised using modified Hummer's

method and then it was reduced in rGO form using L-ascorbic acid. The resulted GO and rGO were characterised and analysed by Raman and FTIR spectroscopy shown in Fig. 2. Raman spectra of GO and rGO present a D-band at 1310 cm^{-1} and a G-band at 1609 cm^{-1} . The D peak shows the presence of defects and amorphous structure and the G peak shows the ordered sp^2 bond as reported by Pimenta et al. [31]. Due to the double resonance, D' peak at 1730 cm^{-1} is presents in Raman spectra of both GO and

Fig. 2 a Raman spectra of synthesised GO and rGO samples (b) FTIR spectrum of synthesised GO and rGO

rGO [32]. From the Fig. 2a, it was observed that the intensity ratios ($I_{D\text{ band}}/I_{G\text{ band}}$) for GO were 0.6 while 0.64 for rGO which is slightly high than GO, and showed the number of defects increases during reduction due to the restoration of numerous graphitic domains from the amorphous regions of graphite oxide as also reported in accordance with [31, 32].

The FTIR spectrum of synthesised GO is shown in Fig. 2b and indicates the presence of C-O (alkoxy) vibration stretch at 1048 cm^{-1} and 1110 cm^{-1} ; C=C vibration at 1620 cm^{-1} ; C=O vibration at 1713 cm^{-1} and O-H stretch at 3397 cm^{-1} . In the case of rGO sample the FTIR spectrum comprising minor peaks at 1056 cm^{-1} , 3333 cm^{-1} while slightly strengthened peak at 1647 cm^{-1} as reported by Aboulkas et al. [33]. These observations confirmed the formation of rGO.

The synthesised rGO was mixed in PEDOT: PSS solution using different concentrations 0%, 1%, 2%, 3%, 4%, and 5% referred as S0, S1, S2, S3, S4, and S5 respectively. These solutions are sonicated for 4 h before deposition. The prepared solution was deposited on a PET sheet using a bar coating with a bar of wire size $30\text{ }\mu\text{m}$. The sheet resistance of the deposited layer was measured. The alteration in sheet resistance with the rGO concentration in PEDOT: PSS is reported in Fig. 3a. The sheet resistance at rGO concentration 1% (wt%) in PEDOT: PSS showed a sheet resistance of $315 \pm 8\text{ }\Omega/\text{sq.}$ which is the lowest among other samples.

The transmittance of all the samples S0, S1, S2, S3, S4, and S5 were measured using an absorption spectrophotometer as shown in Fig. 3b, and found that the optical transmittance of the S1 in the visible region is higher in comparison to S2, S3, S4, and S5 samples. When the rGO concentration increases, the optical transmittance appears to be reduced. From Fig. 3, it is observed that the sample S1 has low sheet resistance ($315 \pm 8\text{ }\Omega/\text{sq.}$) and high

transmittance ($\sim 74\%$) in comparison to the rest of the rGO modified PEDOT: PSS samples shows a good combination for using as TCE. The combination of sheet resistance ($315 \pm 8\text{ }\Omega/\text{sq.}$) and transmittance ($\sim 74\%$) of S1 sample is much better than that was reported by Liu. et al. (sheet resistance $600\text{ }\Omega/\text{sq.}$ and transmittance $\sim 80\%$ for Graphene/PEDOT:PSS) and Kiyong et al. (sheet resistance $2.3\text{ k}\Omega/\text{sq.}$ and transmittance $\sim 80\%$ for rGO/PEDOT:PSS) in their individual work [34–36].

To analyse the uniformity or surface roughness of the deposited layer, AFM characterisation using Atomic Force Microscopy (AFM) using a machine of model Pro 47, provided by NT-MDT spectrum instruments Russia and optical images of the samples were recorded with an optical microscope (Olympus BX53M) as shown in Figs. 4, 5. The surface images reveal that the surface roughness increases with increasing the concentration of rGO in PEDOT: PSS. Sample S1 shows better quality in comparison to other samples including S2, S3, S4, and S5.

The flexibility and reliability of the deposited samples were tested by bending test using beakers of different diameters including 10, 8, 6, 4, 3 and 2 cm with bending curvature 20, 25, 33, 50, 67, and 100 m^{-1} . Both inner bending and outer bending of the samples were performed by the equation given below that defined the relative variation of electrical resistance [37]:

$$\frac{\Delta R}{R_0} = \frac{(R - R_0)}{R_0}$$

where R_0 is the resistance of the unbent sample [bending curvatures (p) = 0] and R is the resistance of the bent sample at different bending curvatures (p) values.

In this measurement, the variation in electrical resistance of the fabricated flexible transparent conducting

Fig. 3 **a** Sheet resistance of rGO modified PEDOT: PSS film **b** Transmittance of rGO modified PEDOT: PSS hybrid film

Fig. 4 AFM images of the prepared samples

samples was measured and shown in Fig. 6. Sample S1 indicate the least variation in electrical resistance (12% max. increases), in comparison to the other samples. Sample S2 indicate variation $\sim 15\%$ (increases); sample S3 showed variation $\sim 16.5\%$ (increases); sample S4 showed variation $\sim 17.4\%$ (increases) and sample S5 showed variation $\sim 20\%$ (increases) in electrical resistance for bending outer curvatures from 20 to 100 m^{-1} shown in Fig. 6a. The increase in resistance on outward bending is due to tensile stresses that tend to separate the layer particles from each other [38].

In a similar way, electrical resistance variation as a function of inward bending curvatures of rGO/PEDOT: PSS hybrid layer was measured and shown in Fig. 6b. Sample S1 shows minimum electrical resistance variation ($\sim 9\%$ decreases), in comparison to the other prepared samples including sample S2 showed variation $\sim 12.5\%$, sample S3 showed a variation $\sim 14\%$ (decreases), sample S4 showed a variation $\sim 16\%$ (decreases) and sample S5 showed a

variation $\sim 17\%$ (decreases) in electrical resistance for inward bending curvatures from 20 to 100 m^{-1} . The inward bending may create an overlap of the crumpled graphene films that results in a decrease in resistance [39].

Henceforth, the sample S1 is reported having the least sheet resistance ($315 \pm 8\text{ }\Omega/\text{sq.}$), high transmittance ($\sim 74\%$), better smooth surface, and lowest variation in electrical resistance during the inward (9% max. decreases) and outward bending (12% max. increases) in comparison to rest of the samples (S2, S3, S4, and S5). Hence, the sample S1 looked reliable and better for flexible TCE applications.

4 Conclusions

ITO is the most preferred TCE because of its high transmittance and low sheet resistance. However its brittle nature and limited indium resources restrict its use for future

Fig. 5 Optical microscopic images of the prepared samples

Fig. 6 **a** Variation in Electrical resistance of deposited samples for outer bending **b** Electrical resistance variation of deposited samples for inner bending

flexible optoelectronics devices. Hence, there is a requirement of alternate material for replacing ITO as TCE. Keeping this in view, the rGO modified PEDOT: PSS based TCE were deposited on a flexible PET sheet using a bar coating technique for achieving a flexible TCE as an alternate of ITO. The sheet resistance, optical transmittance, bending test (outside and inside bending) and surface roughness of the rGO modified PEDOT: PSS samples were measured. Our analysis reveals that the sample S1, having a concentration of rGO 1 wt% in PEDOT: PSS, showing better results i.e.

low sheet resistance ($315 \pm 8 \Omega/\text{sq.}$) and high transmittance ($\sim 74\%$) with low electrical resistance variation 12% (max. increases) for outward bending and 9% (max. decreases) for inward bending of the sample for bending curvature from 20 to 100 m^{-1} . Therefore, the sample with rGO 1 wt% in PEDOT: PSS is reported for its potential use as flexible TCE for optoelectronics applications.

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Compliance with ethical standards

Conflicts of interest The authors declare that they have no conflict of interest.

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