

rGO- SnO₂ Composites for Supercapacitor Applications

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Abstract. Reduced graphene oxide (rGO) – SnO₂ composites for supercapacitor applications were synthesized and characterized to understand their utility. Graphene Oxide (GO) was prepared through modified Hummer's method and mixed with SnO₂ precursor solution prepared through Sol –Gel chemistry to attain rGO- SnO₂ composite. The synthesized powder was annealed to get rGO- SnO₂ composite. X – ray diffraction and Raman spectroscopic studies show the successful synthesis of GO, SnO₂ and rGO-SnO₂ composites evidenced by standard signatures. Cyclic Voltammometric studies show interesting results for the composites where the specific capacitance for the composite is 1.62 times higher than that of the pure SnO₂.

1. Introduction

Graphene and related materials are of great interest due to their potential utility in various fields like, integrated circuits, field emitter transistors, lithium ion batteries, transparent conductive electrodes in solar cells, biological and chemical sensors, and polymer composites [1]. Chemically derived Graphene Oxide (GO) has been studied intensely in recent days due to the ease of preparation method and possibility to get bulk of material. Various materials combined with Graphene Oxide and Reduced Graphene oxide (rGO) are studied due to the improvement in physical properties for applications in the fields of sensors, photo catalysis, super capacitors etc.

SnO₂, a wide band gap ($E_g=3.6\text{eV}$) n-type semiconductor, has been a material of interest due to wide ranging applications in sensors and catalysis [2]. Semiconductor composites with graphene oxide are topic of intense research in these days due to high efficiency in lithium ion batteries, supercapacitors, dye degradation and bio sensing applications. SnO₂/graphene composites are also excellent candidates for the development of electrochemical sensors due to high active surface area, high electrocatalytic activity, chemical stability, and interface dominated properties [3].

In this paper an attempt to synthesize graphene oxide, reduced graphene oxide-SnO₂ composites is done and studies through cyclic voltammetry were carried out to understand electrochemical properties.

2. Experimental methods

Graphene oxide (GO) is synthesized from graphite powder by modified Hummers method [4]. Reduced Graphene Oxide (rGO) - SnO₂ composite is prepared by mixing GO and SnO₂ precursor prepared by chemical solution methods. The SnO₂ precursor is prepared by adding 22.56 gm of SnCl₂.2H₂O to 100 ml absolute ethanol (1M solution) and stirring at 60°C for 30 min in a closed vessel to obtain the clear, transparent and homogeneous solution. Now, 9.496 ml of GO is added to 40 ml Tin



Chloride solution in a closed vessel and the admixture is stirred at 80°C for 1h. The obtained powder after drying is washed with de-ionized water several times and finally with ethanol 2-3 times and is dried at 100°C in the oven for 24 hours. rGO-SnO₂ composite achieved by annealing the resultant powders at 500°C temperatures in inert ambient. SnO₂ was prepared through similar method without GO addition.

The X-Ray diffraction measurements are carried out using Rigaku Smartlab (9kW power, Cu $k\alpha=1.54\text{\AA}$) in the 2θ range of 10-80°. The Raman spectra were recorded in the region 416-2000 cm⁻¹ with Micro Raman spectrometer with model No. STR - 500, Cornes Technologies Ltd., Japan. The excitation wavelength of the laser used is 532.8 nm and the grating used is 600 grooves/mm. Cyclic voltammogram (CV) and Electrochemical impedance spectroscopy tests were measured by an electrochemical working station (SP-150, Biologic Science instrument). Cycle stability tests were carried out with a CH instruments electrochemical work station instrument. 0.5 M H₂SO₄ was used as electrolyte with three electrode geometry having material coated glassy carbon electrode as working electrode, Pt wire as counter electrode, Saturated calomel electrode (SCE) as reference electrode with electrode surface are of 0.07 cm².

3. Results and Discussion

The figure 1 shows that the X-Ray diffraction patterns of the samples. The obtained reflections for SnO₂ from Fig. 1 (b) indicate the tetragonal rutile phase of SnO₂ matching with JCPDS Card No. 41-1445. The Fig. 1 (c) indicates that the rGO-SnO₂ composite also exists in the same phase. The peak corresponding with GO is not observed in rGO-SnO₂. This may be due to the less amount of GO in the composite and dominating strong intensity peaks of SnO₂ [5]. Fig. 1 (a) shows the XRD pattern of GO with 2θ value 11.11° which corresponds to (002) reflection with interlayer d-spacing 7.96Å indicating the successful preparation of GO by oxidation of Graphite [6].

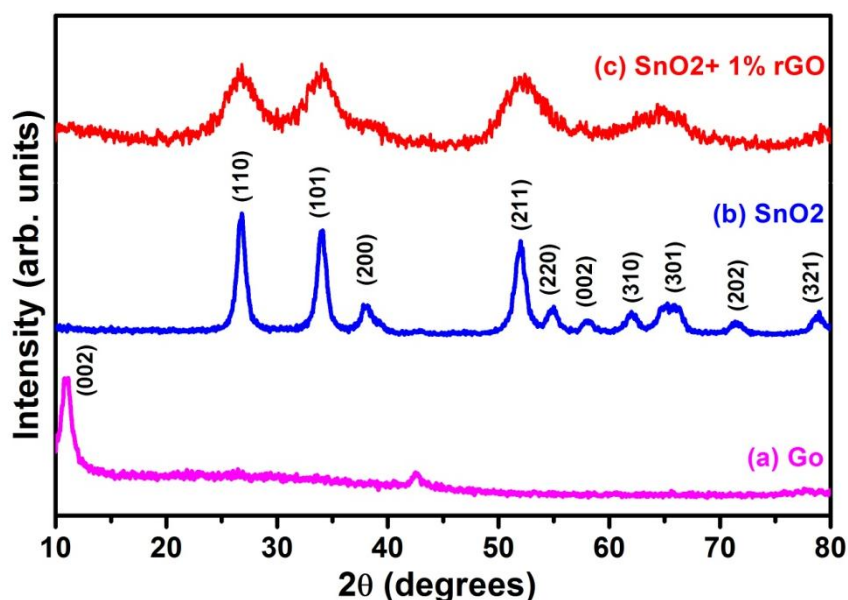


Figure 1. X-Ray Diffraction of (a) GO, (b) SnO₂ and (c) SnO₂ + 1wt% rGO.

The figure 2 shows the Raman spectra of the samples. From Fig. 2 (a), the peaks at 485.1 cm⁻¹, 631.3 cm⁻¹ and 771.1 cm⁻¹ corresponds to the E_g, A_{1g} and B_{2g} vibration modes of SnO₂ respectively [7]. The degree of disorder and the average size of sp² domains are measured in terms of I_D/I_G ratio [8]. From Fig. 2 (b) and 2 (c), the G and D bands of GO and rGO-SnO₂ composites can be seen. From these graphs, the I_D/I_G intensity ratios for GO and rGO-SnO₂ composite respectively are 0.95 and 1.06.

The value of I_D/I_G ratio for composite is more than that of GO due to the formation of sp^2 domains and that GO was reduced due to the addition of Sn during the reaction [1].

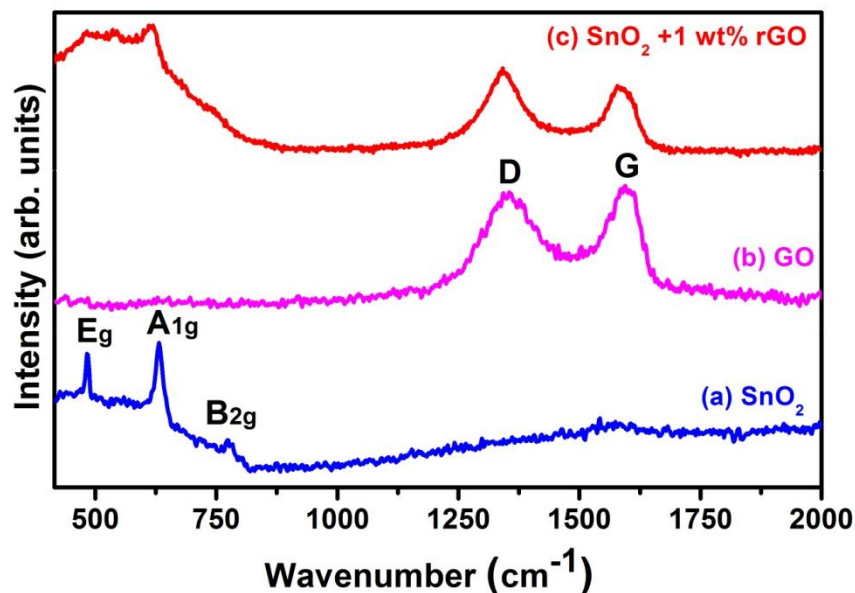


Figure 2. Raman spectra of (a) SnO_2 , (b) GO and (c) $\text{SnO}_2 + 1\text{ wt}\% \text{ rGO}$

The cyclic voltammetric studies for SnO_2 and rGO-SnO_2 composite have been recorded in the potential range of -0.8 – 0.8 V with a scan rate of 1 mV/sec in $0.5\text{ M H}_2\text{SO}_4$ solution.

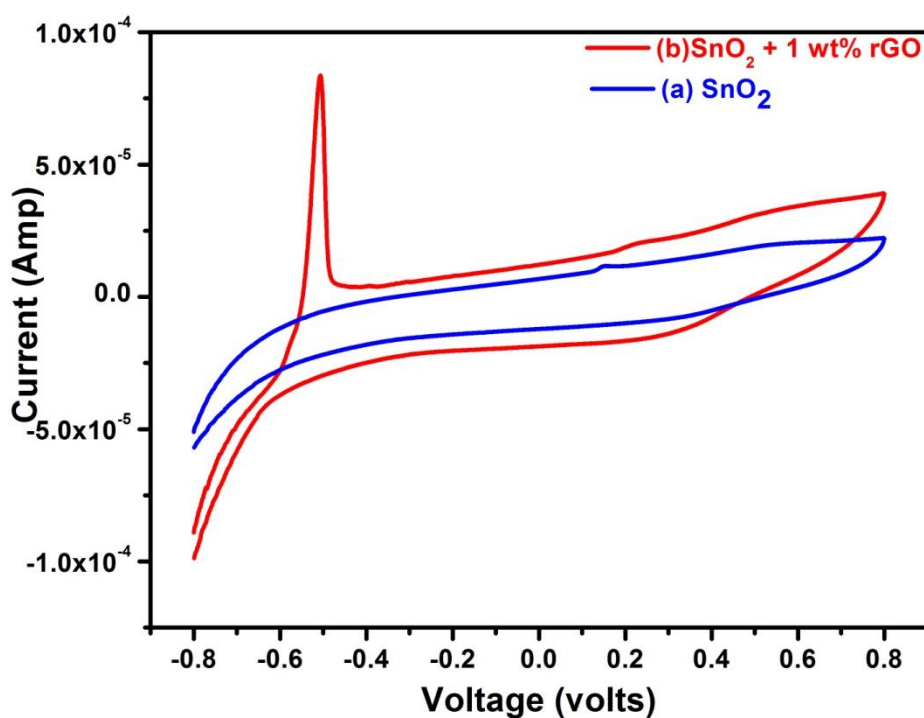


Figure 3. Cyclic voltammogram of (a) SnO_2 and (b) $\text{SnO}_2 + 1\text{ wt}\% \text{ rGO}$.

The specific capacitance of the both samples was found using the formula:

$$C = \frac{\int i(E) dE}{2mv(E_2 - E_1)}$$

where C is capacitance (in farad (F)), $i(E)$ is the instantaneous current (in A), $\int i(E)dE$ is the total voltammetric charge obtained by integration of positive and negative sweep in CV, m is the mass (in gm), v is the scan rate (in V/sec) and (E_2-E_1) is the potential window width (in V). From the Fig. 3, it is evident that the area of the composite curve is more compared to the pure SnO_2 which clearly indicates that the rGO-SnO_2 composite is having more specific capacitance (4.66 F/gm) than that of pure SnO_2 (2.86 F/gm). Here the specific capacitance of the composite is 1.62 times higher than that of pure SnO_2 . So the composite can be used in super capacitor applications since the addition of GO to the SnO_2 enhances its capacitive behaviour [9].

From the electrochemical impedance measurements, Nyquist plots of the Pure and rGO-SnO_2 composite samples are shown in the Figure.4. Accordingly, an equivalent circuit is proposed to simulate the electrochemical behaviour of the samples [10] which is shown in the inset of Fig. 4. The circuit elements are composed of bulk solution resistance (R_1) which is the solution resistance between working electrode and reference electrode, the high frequency semicircle is associated with SEI film resistance (R_2), the middle frequency semicircle is linked to charge-transfer resistance through the electrode-electrolyte interface (R_3), CPE1 and CPE2 are the constant phase elements and the inclined line is associated with the Warburg impedance W_1 [11]. The diameters of high and low frequency regions give the SEI resistance (R_2) and Charge transfer resistance (R_3) directly.

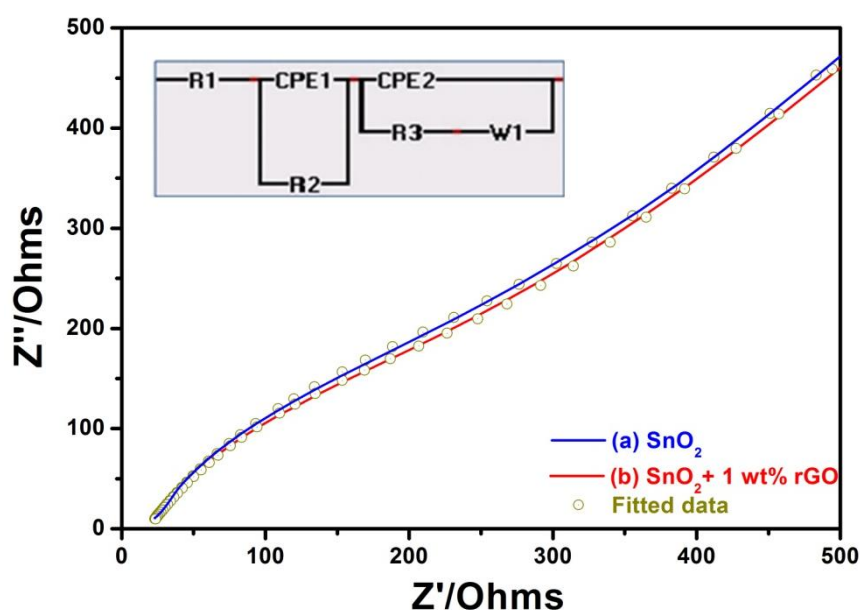


Figure 4. Nyquist plots of (a) SnO_2 and (b) $\text{SnO}_2 + 1\text{wt}\%$ rGO.

Table 1: Bulk solution resistance R_1 , SEI resistance R_2 , and Charge transfer resistance R_3 values of SnO_2 and $\text{SnO}_2 + 1\text{wt}\%$ rGO

Name of the Sample	R_1 (in Ω)	R_2 (in Ω)	R_3 (in Ω)
SnO_2	17.1	178	70902
$\text{SnO}_2 + \text{rGO}$	17.9	168	44577

From the Table 1, it can be seen that the diameters of the semicircles in the high and low frequency regions for the rGO-SnO_2 composite are lower than that of pure SnO_2 . The obtained parameters after fitting tell that the value of the charge transfer resistance R_3 for the composite is much lower than that of the Pure SnO_2 which clearly indicates that improvement of the charge transfer performance of the

composite. Also the value of the SEI film resistance R_2 for the composite is lower than that of the Pure SnO_2 which obviously reveals the high conductivity of the composite than that of pure SnO_2 . Therefore, the presence of GO in SnO_2 not only enhances the conductivity of the composite but also largely enhances the electrochemical activity of SnO_2 [6].

4. Conclusions

The graphene oxide, SnO_2 and rGO- SnO_2 composite are prepared successfully. Pure SnO_2 and rGO- SnO_2 composite exist in the tetragonal phase as confirmed by XRD. Graphene oxide became reduced after the addition of Sn to it confirmed by Raman studies. From CV and Electrochemical Impedance studies, the specific capacitance and conductivity values of composite are found to be higher than that of pure SnO_2 which clearly tells the usage of composite in super capacitor applications.

Acknowledgements

The authors from Department of Pure and Applied Physics thank UGC, New Delhi and DST, Govt. of India for their funding through UGC – SAP 1, and FIST – Level 1 programme, respectively. One of the authors, G. R. Turpu acknowledges UGC, New Delhi for funding vide F.No. 43-407/2014 (SR).

References

- [1] Chen M, Zhang C, Li L, Liu Y, Li X, Xu X, Xia F, Wang W and Gao J 2013 *ACS Appl. Mater. Interfaces* **5** 13333.
- [2] Lavanya N, Radhakrishnan S, Sudhan N, Sekar C, Leonardi S G, Cannilla C and Neri G 2014 *Nanotechnology* **25** 295501.
- [3] Dutta D, Chandra S, Swain A K and Bahadur D 2014 *Anal. Chem.* **86** 5914.
- [4] Hummers W S and Offeman R E 1958 *J. Am. Chem. Soc.* **80** 1339.
- [5] Seema H, Kemp K C, Chandra V and Kim K S 2012 *Nanotechnology* **23** 355705.
- [6] Dubin S, Gilje S, Wang K, Tung V C, Cha K, Hall A S, Farrar J, Varshneya R, Yang Y and Kaner R B 2010 *ACS Nano* **4** 3845.
- [7] Leonardy A, Hung W-Z, Tsai D-S, Chou C-C and Huang Y-S 2009 *Cryst. Growth Des.* **9** 3958.
- [8] Zhao B, Zhang G, Song J, Jiang Y, Zhuang H, Liu P and Fang T 2011 *Electrochimica Acta* **56** 7340.
- [9] Lua T, Zhanga Y, Lia H, Pana L, Lib Y and Sun Z 2010 *Electrochimica Acta* **55** 4170.
- [10] Wang R, Xu C, Sun J, Gao L and Yao H 2014 *ACS Appl. Mater. Interfaces* **6** 3427.
- [11] Gao X, Luo W, Zhong C, Wexler D, Cho S-L, Liu H-K, Shi Z, Chen G, Ozawa K and Wang J-Z 2014 *Sci. Rep.* **4** 6095.