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Research Article

Electrochemical performance and material characterization of reduced grapheneoxide (rGO) / titanium dioxide (TiO_2) composite as electrodes for supercapacitors

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ABSTRACT

Reduced Graphene Oxide/ Titanium Dioxide (rGO/ TiO_2) composite was synthesized by one-step hydrothermal reaction with a view to investigating the performance as electrodes for supercapacitors. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM) analysis revealed that graphite oxide (GO) was successfully transformed to reduced graphene oxide (rGO) after hydrothermal reduction and the relevant peak was observed at $2\theta = 26°$. Investigations on electrochemical properties of rGO/TiO_2 based supercapacitors revealed improved performance on charge/discharge cycles in comparison to supercapacitors based on pure TiO_2. Also it has low self- discharge rate with 1.42 V initial voltage and 1.43 V final voltage after nine circles. The specific capacitance of rGO/ TiO_2 composite was 242 Fg^{-1} while that for rGO and TiO_2 are 12.8 Fg^{-1} and 109 Fg^{-1} respectively. After applied current density is increased from 0.024 to 0.127 Ag^{-1}, the specific capacitance of rGO / TiO_2 remains about 80% of its initial voltage. The specific capacity is expected to improve further by using rGO/TiO_2/Polyaniline composite and the investigations are in progress.

Keywords: Graphite Oxide (GO), ReducedGraphene Oxide (rGO), rGO/ TiO_2 composite, Supercapacitors

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1. INTRODUCTION

Titanium Dioxide (TiO_2) has been extensively explored for different applications including catalysis, energy storage and energy conversion devices such as supercapacitors, rechargeable batteries and solar cells owing to its good stability, nontoxicity and low cost [1,2]. It possesses low charge transfer resistance ($R_{ct} = 0.34\ \Omega$) and high specific capacitance ($C_{sp} = 280.3\ Fg^{-1}$) at current density of 1 Ag^{-1}(3). Carbon doped TiO_2 composite is a promising electrode for supercapacitors when compared to sulfur/TiO_2 or R/TiO_2 (R= Ag, Pt, Fe) composites due to good electrochemical performances [4,5].

In order to raise a composite with TiO_2, graphene is a promising material. Graphene is identified as a single layer carbon atom which was first exfoliated from graphite by Novoselov et al. by using a mechanical tape striping method in 2004[6]. Graphene possesses excellent thermal and electrical conductivity as well as earns a high surface area. Because of the unique structure of graphene, it results in relatively higher specific capacitance compared to other carbon materials [7]. Therefore, graphene/TiO_2 composite would results unique properties. Chemical and thermal reduction of graphene oxide has been used at mass production of rGO [8-10].

In the present study, a novel method one-step hydrothermal reaction was followed for synthesis of rGO/TiO_2 composite. The material characterization was done using X-ray diffractrometer (XRD), a Fourier Transformation Infrared Spectrometer (FTIR) and a Scanning Electron Microscope (SEM). The electrochemical properties of rGO/TiO_2 based supercapacitor were investigated.

2. EXPERIMENTAL

2.1 Synthesis of rGO/ TiO_2 composite

Graphite oxide (GO) was synthesized by modified Hummers method [11] using natural graphite (99.5%) from Kahatagaha graphite mine in Sri Lanka. After the oxidation reaction, GO was washed with 5% HCl until sulphate ions could not be detected with $BaCl_2$. Subsequently, GO was washed with distilled water several times to remove ions. Thereafter the residue was dried at 60 °C in vacuum oven over night. GO (1g) was dissolved in distilled water (1600ml) and kept for 30 min under the ultrasonication at room temperature. 2g of TiO_2 (bulk of TiO_2 powder available in the lab) was added into the above solution under the vigorous stirring for 1h. The suspension was transferred into an autoclave, and it was heated at 120°C for 2hrs. The final solution was washed with ethanol and distilled water several times and dried at 80°C for 2hrs. Finally, the black colour composite of rGO/TiO_2 was obtained. The schematic of the experimental procedure of preparation of rGO/TiO_2 composite is shown in Figure. 1.

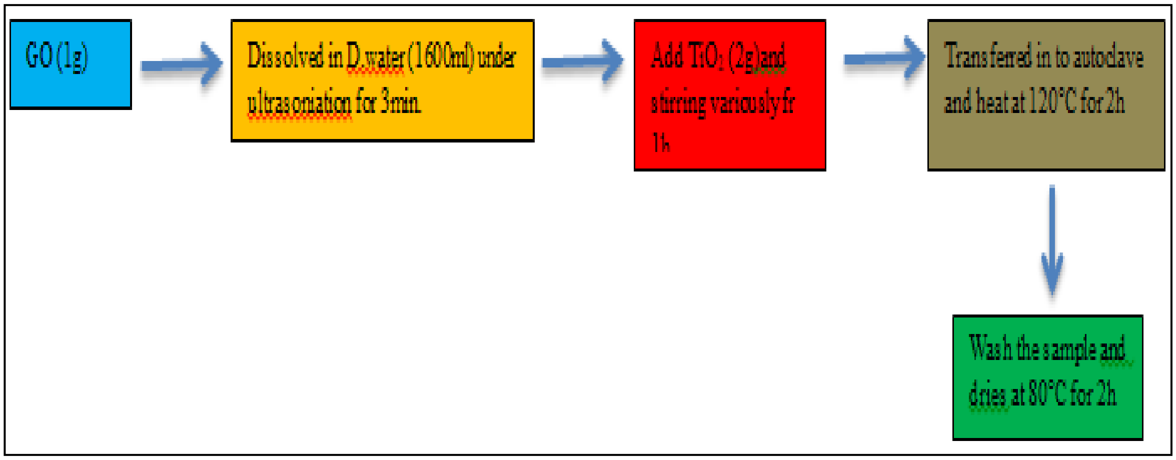

Figure. 1: The schematic of the experimental procedure of formation of rGO/TiO_2 composite

2.2 Electrode constructions and assembling of supercapacitors

Supercapacitor includes three main parts: working electrode (anode), counter electrode (anode) and appropriate electrolyte. To prepare the electrodes, 80% of active material rGO/TiO_2 composite was mixed with 15% of active carbon and 5% of polytetraflurethyleno (PTFE) as a binding agent. Known amount of active material was applied on the surface of two identical stainless-steel electrodes. Two electrodes consisted of a mixture of active material (80%), carbon black (15%) and polyvinylidene fluoride (PVDF) as binder agen**t** (5%). A piece of filter paper (50 um) was used as a separator and 1M H_2SO_4 used as an electrolyte.

2.3 Characterization

The phase composition of rGO and rGO/TiO_2 materials were studied by a Regaku-ultima VI, X-ray diffractometer with Cu Kα (λ= 1542 Å) radiation with range varying from 5° to 100°. Crystallographic information of the materials was obtained with the aid of the ICSD data base. The functional groups of rGO and rGO/TiO_2 materials were analyzed using Bruker Tensor 27 Fourier transformed infrared spectrometer. The morphology of TiO_2 and rGO/TiO_2 materials were studied by a LEOm1420vp scanning electron microscopy. Charge/Discharge performance, cyclic voltammograms, 1st discharge curves and impedance spectra of supercapacitors were obtained using Biologic sp-150 potentiostat / impedance analyzer.

3. RESULTS AND DISCUSSION

3.1 Material Characterization

3.1.1 XRD Analysis

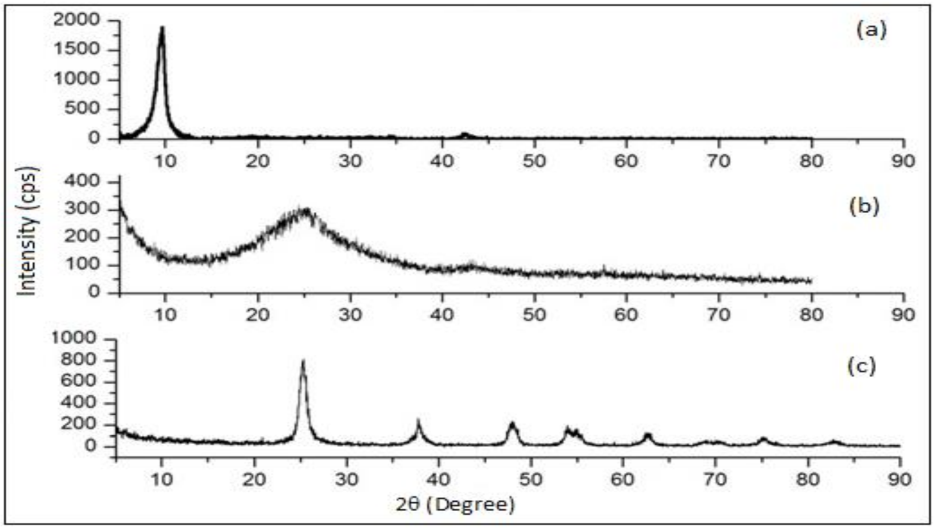

Figure. 2: XRD spectra of (a) GO (b) rGO (b) and rGO/TiO_2 Composite

Figure. 2 shows the XRD spectra of (a) GO (b) rGO and (c) rGO / TiO_2 Composite. The GO had an intense peak at 2θ = 10.5°, corresponding to the (0 0 1) plane as shown in the Fig. 2(a). When the GO was reduced to rGO, the diffraction peak at 2θ = 10.5° was disappeared and a new low intensity broader peak appeared at 2θ = 26° corresponding to the rGO (0 0 2) plane as shown in the Fig. 2(b). For the rGO/TiO_2 composite, as in the Fig. 2(c), a series of characteristic peaks are observed at 2θ = 25.5°, 37.8°, 48.1°, 54.1°, 55.5°, 63.9°, 70.3° and 74.1° relevant to TiO_2, where peak corresponding to rGO is not observed probably due to overlapping with high intense TiO_2 diffraction peaks. All the peaks of X-ray diffraction of anatase phase of TiO_2 could be identified using ICSD collection code 154604.

3.1.2 FTIR analysis

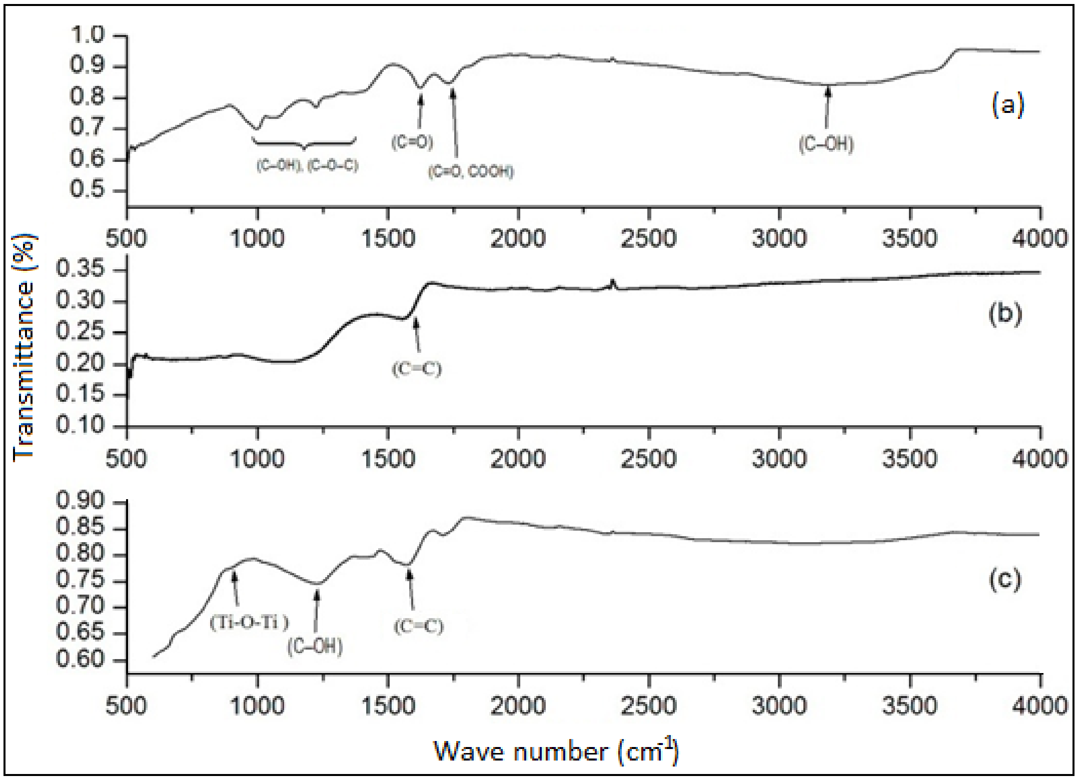

Figure. 3: FTIR spectra of (a) GO, (b) rGO, and (c) rGO/TiO_2 composite

Figure.3 shows the FTIR spectrum of (a) GO, (b) rGO, and (c) rGO/TiO_2 composite which is useful to identify the chemical functional groups in complex composite materials easily. In Figure 3 (a) epoxides (C–O–C) and structural hydroxyls (C–OH) attributed bands were seen at 996 cm^{-1} and 1224 cm^{-1}, and carboxyl (COOH), ketonic species (C=O) and C–O attributed bands can be seen at 1621 cm^{-1} and 1735 cm^{-1}. Band at about 3183 cm^{-1} is attributed to free hydroxyl (C–OH) from water vapour. After reducing GO to rGO and it is found that sp^2-hybridized C=C peak of reduced graphene oxide formed at the band 1552 cm^{-1}. Band at 947 cm^{-1} is attributed to remaining epoxide (C–O–C) attached to the graphene basal plane in Figure. 3(b). In the FTIR of rGO/TiO_2 composite of Figure. 3(c), the, stretching vibration peaks of C=O, C-OH and C-O of GO were fully disappeared after hydrothermal reduction and only the C=C stretching vibration peak is visible at 1501 cm^{-1}. These evidences imply that GO was converted into rGO successfully. The band at 854 cm^{-1} corresponds to the Ti-O-Ti stretching vibration. Further, O-H stretching band is observed at 3450 cm^{-1}. Even though the presence of rGO is not fully recognized using XRD analysis, FTIR spectra clearly illustrated the presence of rGO in the composite.

3.1.3 SEM Analysis

The SEM image of rGO/TiO_2 composite is shown in figure. 4 at 12 K magnification. Though the presence of TiO_2 particles is not visible in the image, crumpled flexible nature of rGO has been shown. Higher magnification through FE-SEM or SEM coupling to EDX would obviously enable observing TiO_2 particles. Further studies are required for such analysis. Nevertheless, the presence of rGO in the composite was clearly confirmed by FTIR spectra.

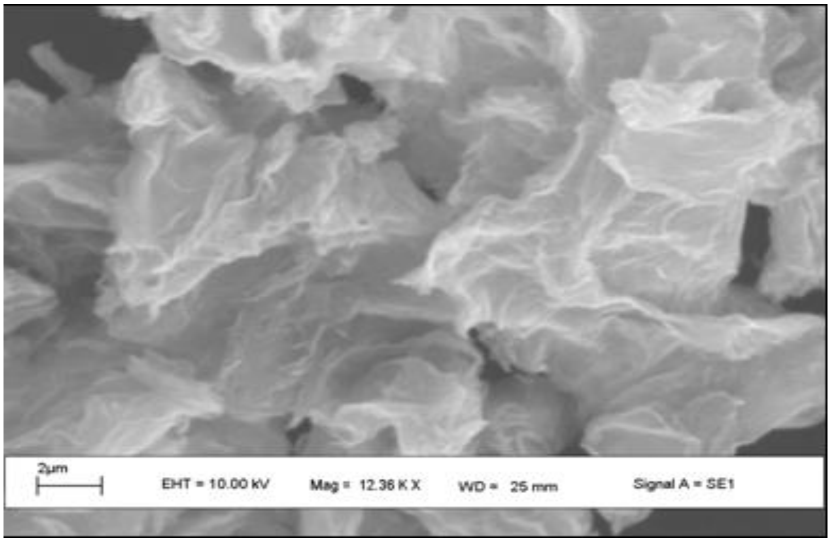

Figure. 4: SEM image of rGO/TiO_2composite

3.2 Electrochemical performance

3.2.1 Charge /Discharge Test

Figure. 5 shows the charge/ discharge curves of TiO_2 and rGO/TiO_2 based supercapacitors at room temperature and 0.1 mA constant current. As expected, the supercapacitor with rGO/TiO_2 electrodes shows better charge / discharge performance compared to supercapacitor with pure TiO_2 electrodes. It achieves 1.42 V initial voltage and 1.43 V final voltage after nine circles. Also, it has low self-discharge rate compare of TiO_2 supercapacitor. Important parameters of each supercapacitor are also listed in Table 1.

Table 1: Important parameters of supercapacitors with electrodes TiO_2 and rGO/TiO_2 after charging/ discharging test

Active Material	Initial Voltage (no load) (V)	Charging Time (min)	Discharging Time (min)	Maximum Initial Charge Voltage (V) (with load)	Minimum Initial Discharge Voltage (V) (with load)	Maximum Charge Voltage (V) (after 9th circle)	Minimum Discharge Voltage (V) (after 9th circle)
TiO_2	1.35	20	20	1.42	1.12	1.43	1.11
rGO/ TiO_2	1.24	20	20	1.37	0.82	1.39	0.81

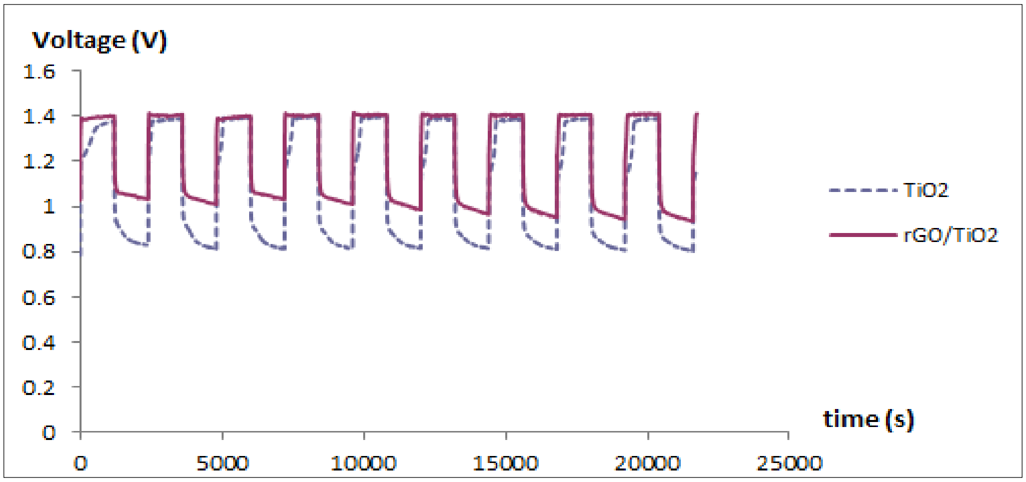

Figure. 5: Charge/ discharge curves of supercapacitors having TiO_2 and rGO/TiO_2 with electrodes under 0.1 mA constant current

3.2.2 Cyclic Voltammetry (CV) Analysis

Figure. 6(a) and (b) show the cyclic voltammograms of supercapacitors with rGO, TiO_2 electrodes. Figure.6(c) shows the 1st and the 20th cyclic voltammogram of supercapacitor with rGO/ TiO_2 composite. The CV tests were performed between -1 to 1V at a scanrate of $1 mVs^{-1}$. The specific capacitance of the electrode can be calculated from CV curve according to the following equation:

$$C_m = \frac{1}{2m\upsilon\Delta V}\int i(V)dV \qquad (1)$$

where C_m is the specific capacitance (F g^{-1}) based on the mass of electroactive materials, m is the weight of active material (g), υ is the scan rate (V s^{-1}), ΔV is the potential window (V) and 'I' is the response current density (A). Specific capacitance of supercapacitor with rGO/ TiO_2 composite shows a significant value compared to that with the individual materials. Calculated capacitance of rGO/ TiO_2 composite is 242 Fg^{-1}. While that for rGO and TiO_2 are 12.8 Fg^{-1} and 109 Fg^{-1} respectively. The anodic and cathodic peak currents ofrGO/ TiO_2 composite can be observed at 6.57 mA and -7.41 mA corresponding to 0.52 V and -0.59 V. The cell voltage of the rGO/ TiO_2 composite can be calculated as a value of 1.11V. Also it shows the good symmetry of the redox peaks after cycles further reveals the excellent rate capability of rGO/ TiO_2 composite.

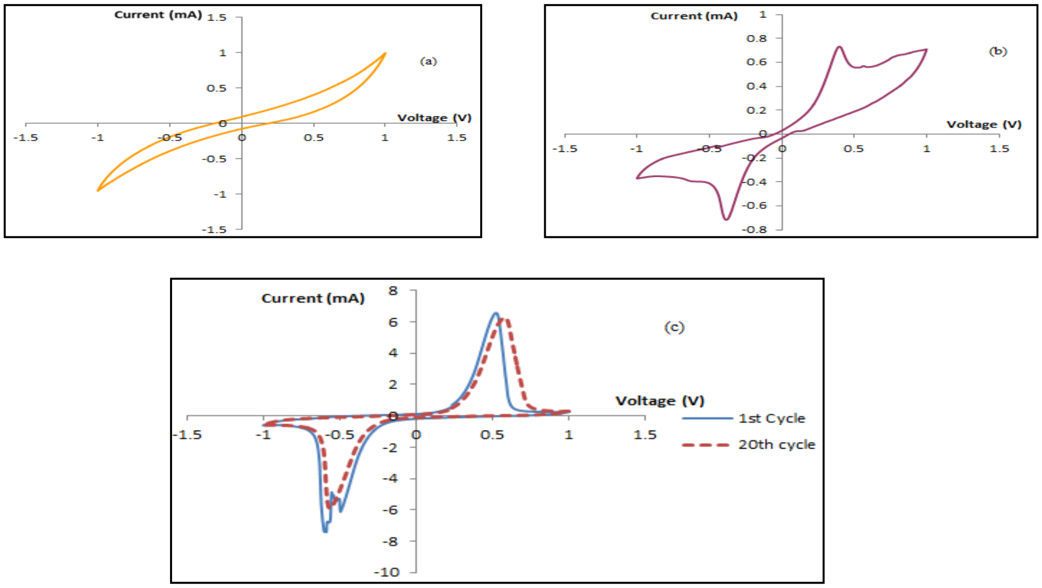

Figure. 6: Cyclic voltammograms of supercapacitors with electrodes (a) rGO, (b) TiO_2, Fig (c) with 1st and 20th cycles of supercapacitors with rGO / TiO_2 composite electrodes. Scan rate 1mVs^{-1}

3.2.3 First Discharge Test

The 1st discharge curves of supercapacitors with rGO/ TiO_2 composite electrodes at different currents are shown in figure. 7. Furthermore the specific capacitance values of active material corresponding to different current densities are shown in table 2. The average specific capacitance values (C_m) of the samples are calculated from the discharge process according to the following equation:

$$C_m = \frac{I \, \Delta T}{m \, \Delta V} \qquad (2)$$

I is the charge / discharge current, Δt is the discharge time, ΔV is the voltage difference, and m is the mass of active material within electrodes. The rGO / TiO_2 composite illustrated a specific capacitance of 247 Fg^{-1}at a current density of 0.024 Ag^{-1}. This is considerable value for two electrode system. The results show that when the applied current density is increased from 0.024 to 0.127 Ag^{-1}, the specific capacitance of rGO/ TiO_2 composite remains about 80% of its initial value.

Table 2: Specific capacitance values of rGO/ TiO_2 composite corresponding to different current densities

Current (mA)	Current Density (Ag^{-1})	Specific Capacitance (Fg^{-1})
0.1	0.024	247
0.2	0.050	239
0.3	0.066	235
0.4	0.096	226
0.5	0.127	199

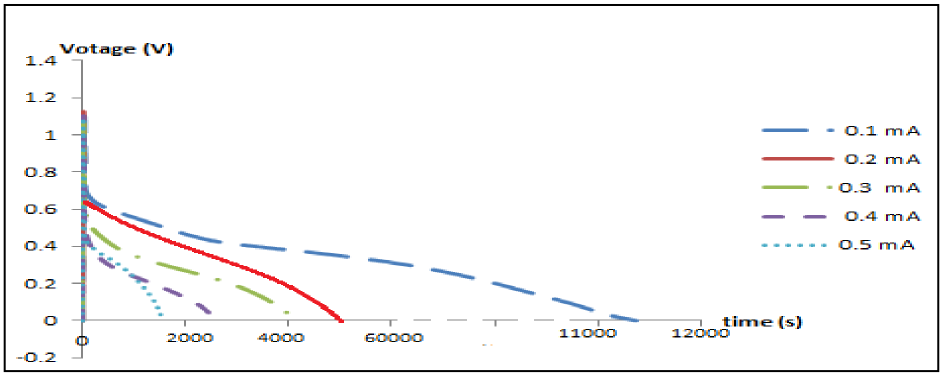

Figure. 7: 1st discharge curves of supercapacitors with rGO/ TiO_2 composite electrodes under different currents

3.2.3 Impedance Analysis

The Nyquist impedance plot of rGO/TiO_2 supercapacitor is shown in figure. 8(a). The possible fitted line for the original curve represented in solid line. The equivalent circuit of the rGO/ TiO_2 composite is shown in fig. 8(b). Where R_1 = 16.36 Ω represent ohmic resistance. R_2 =206.5 Ω , R_3 =8358 Ω and R_4 =18622 Ω represents the charge transfer resistance. Q_1 =2.691 F represents the double layer charge of rGO/ TiO_2 supercapacitor, where a=0.622. C_1= 0.254 F and C_2 =2.164 F Fg^{-1} are the capacitance of active material. Higher charge transfer resistance is observed due to lower conductivity of the current collector which is to be improved.

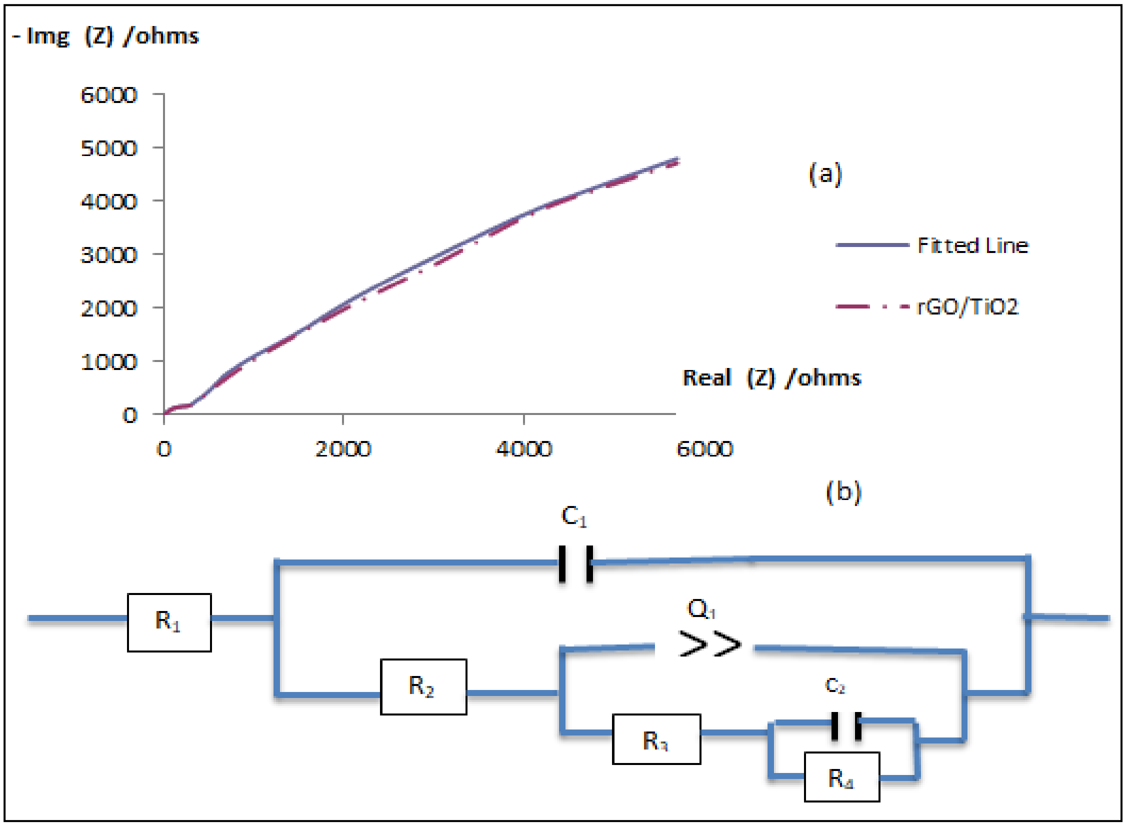

Figure. 8: (a) Impedance plots and (b) Equivalent circuit of supercapacitor with rGO/ TiO_2composite electrodes

3 CONCLUSIONS

The rGO/TiO_2 composite was synthesized by one step hydrothermal reaction without using high temperature calcinations. The phase composition, functional groups and morphology structure of rGO/TiO_2 composite were analyzed by using XRD, FTIR and SEM respectively. The SEM image was showed flexible corrugated nature of rGO sheet while XRD and FTIR verified the presence of individual material in the composite. The specific capacitance of rGO/ TiO_2 composite was 242 Fg^{-1} which is significant value for a two electrode cell. The charge/discharge performance, cyclic voltammetry, 1st discharge test and impedance analysis of rGO/TiO_2 composite demonstrated that rGO/TiO_2 composite have good cycling stability at high charge/ discharge rate. Therefore this composite is suitable for supercapacitors and also for various other applications including gas sensors, batteries. Further research is underway to investigate rGO/Polyaniline/TiO_2 hybrid composite electrodes for supercapacitors with enhanced electrochemical properties.

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