Chemical Physics Letters 706 (2018) 647–651

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

Strengthening of photovoltaic and supercapacitive properties of graphene oxide-polyaniline composite by dispersion of α-Al_2O_3 nanoparticles

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ARTICLE INFO

Article history:
Received 3 May 2018
In final form 8 July 2018
Available online 10 July 2018

Keywords:
Graphene oxide
Polyaniline
Photovoltaic
Supercapacitive properties

ABSTRACT

It is demonstrated that the dispersion of α-Al_2O_3 nanoparticles in graphene oxide (GO)-polyaniline (PANi) composite results in significant enhancement of photovoltaic and supercapacitive properties. In order to improve PV and SC properties of GO-PANi composite, 0.5 wt% of α-Al_2O_3 nanoparticles were added in composite. Both PV and SC properties of composites becomes strengthen by addition of 0.5 wt% of α-Al_2O_3 nanoparticles. The GO-PANi/α-Al_2O_3 composite shows power conversion efficiency (%η) 9.31%, which is significantly higher than pure α-Al_2O_3 nanoparticles and GO-PANi composite. The GO-PANi/α-Al_2O_3 composite achieve considerable specific capacitance of the order 715.5 Fg^{-1} at scan rate of 2 mV s^{-1}.

1. Introduction

The widespread use of inorganic photovoltaic cell is still limited because of complications in modification of band gap of inorganic materials and high processing costs [1]. Different approaches using organic or polymer materials such as conducting polymer, graphene and metal oxides have received considerable attention because of their low cost, light weight and flexibility [2]. Whereas supercapacitor is a new class of device, which comes under the category of energy storage devices, and fulfill the technological gap between conventional capacitor and battery. Supercapacitor has some outstanding features like power density, rapid store/release of energy, good charge/discharge life cycles, and Eco friendliness. For supercapacitor application, carbon nanomaterials such as carbon nanotubes and graphene are extensively used, due to their high specific surface area and good electrical conductivity [3].

The use of carbon nanostructures with the conducting polymer is also investigated as supercapacitive material extensively. Yu et al investigated the polyaniline/graphene composite as electrode material for supercapacitors. The electrochemical capacitance of composite has value 596.2 Fg^{-1} and after 1500 cycles at a current density of 2 A g^{-1}, only 16.3% drop in the initial capacitance is observed [4]. Wang et al synthesized PANi with different morphologies and combined with graphene to use as electrode materials of supercapacitors. The result of the study shows that sheet-like Graphene/PANi composites can deliver specific capacitances of 532.3–304.9 Fg^{-1} at scan rates of 2–50 mV/s [5]. Wu et al prepared the Polyaniline/graphene hydrogel composites for supercapacitor application with macroscopically phase-separated structure, which exhibits the high specific capacitance and excellent rate performance. This work concludes the PANi is mainly outside the graphene hydrogel matrix, can enhance the rate performance of the composites [6]. Cong et al prepared the graphene–PANi paper and employed for the supercapacitor application. The composite paper has considerable specific capacitance (763 Fg^{-1}) and good cycling stability [7]. Moussa et al reviewed comprehensively the recent developments in polyaniline/graphene nanocomposites as supercapacitor electrodes. This work underlined the polyaniline/graphene nanocomposites have great potential in electrochemical energy storage applications, especially supercapacitors [8]. Theophile et al reported the successful preparation of Poly(vinyl alcohol)-graphene oxide and Poly(vinyl alcohol)-reduced graphene oxide composite for supercapacitor application. The results of the study indicates that Poly(vinyl alcohol)-reduced graphene oxide composite (190 Fg^{-1}) deliver good supercapacitive properties than Poly(vinyl alcohol)-graphene oxide (13 Fg^{-1}) composite [9]. Loeblein et al a novel material having oxidized-three-dimensional-graphene, with a band gap of 0.2 eV. This material found suitable for electrode application in dye-sensitized solar cells where electrode has stringent work-function requirements [10]. Li et al successfully

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https://doi.org/10.1016/j.cplett.2018.07.018
0009-2614/

fabricated the PANi nanotubes-based supercapacitors having maximum areal capacitance of 237.5 mF cm^{-2} (scan rate = 10 mVs^{-1}) with maximum energy density of 24.31 mW h cm^{-2} (power density = 2.74 mW cm^{-2}). Under bending condition, supercapacitor shows excellent performance. After 2000 cycles, the capacitor maintains 95.2% of the initial capacitive value [11].

Feng et al prepared the graphene/polyaniline nanocomposites by using one-step hydrothermal method. The graphene/PANi nanowire composites exhibit the excellent electrochemical properties having specific capacitance 724.6 F/g higher than the graphene/PANi nanocomposite (602.5 F/g). This study demonstrated that morphology of materials also plays key role in optimization of electrochemical properties [12]. Zhou et al reported the effect of morphology on electrochemical properties using materials system nanoflake-like and nanobelt-like α-MoO_3/graphene nanocomposites. The results of the investigation demonstrated that α-MoO_3 nanoflakes/graphene exhibited better supercapacitive (up to 360 Fg^{-1}) performances than α-MoO_3 nanobelts/graphene [13].

In the light of above discussion, we planned to investigate the photovoltaic and primary electrochemical properties of α-Al_2O_3/PANi-GO composite. In this work, we studied the PV cell properties such as fill factor and power conversion efficiency and supercapacitive properties such, cyclic voltammetry (CV) curve, areal capacitance and cycle stability performance of composite materials. The main accomplishment of present work is that we achieved considerable value of power conversion efficiency and specific capacitance for α-Al_2O_3/PANi-GO composite.

2. Experimental

2.1. Materials preparation and characterization

In the present study, all AR-grade (SD Fine, India) chemicals were used for the preparation materials without further purification. The chemical oxidative polymerization was adopted for the preparation of Polyaniline (PANi). The method of preparation of PANi is reported previously [14]. In this process, aniline monomer and ammonium persulphate were used with molar ratio 1:1 M for preparation of PANi in aqueous media. The addition of aniline monomer in oxidant under constant magnetic stirring results in dark greenish precipitated. As obtained precipitated was washed two times with distilled water and dried in oven for overnight. The fine powder of PANi was used for the preparation of composites. The graphene oxide (GO) used in this work was prepared by previously reported method [15]. The ex-situ approach was adopted for the preparation of composites. The GO loaded PANi composite was prepared by taking equal wt.% of both contents. Whereas, α-Al_2O_3 loaded-GO/PANi composite was prepared by taking 0.5 wt% concentration of α-Al_2O_3 nanoparticles. Both the composites prepared in organic media (Acetone).

The X-ray diffraction (XRD) patterns of as-prepared materials were recorded on Rigaku Miniflex-II using CuK_α radiation (λ = 1.54 Å). The morphology of samples was investigated using scanning electron microscope (SEM) images obtained from JEOL JSM-7500F.

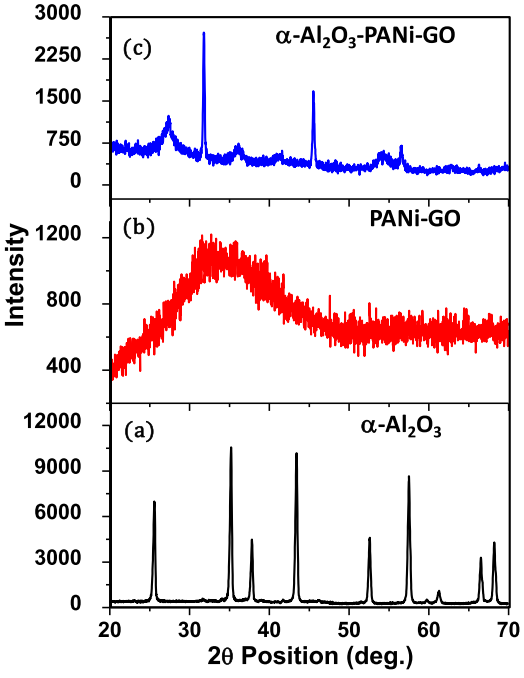

Fig. 1. XRD pattern of α-Al_2O_3 nanoparticle, PANi-GO and α-Al_2O_3/PANi-GO composite.

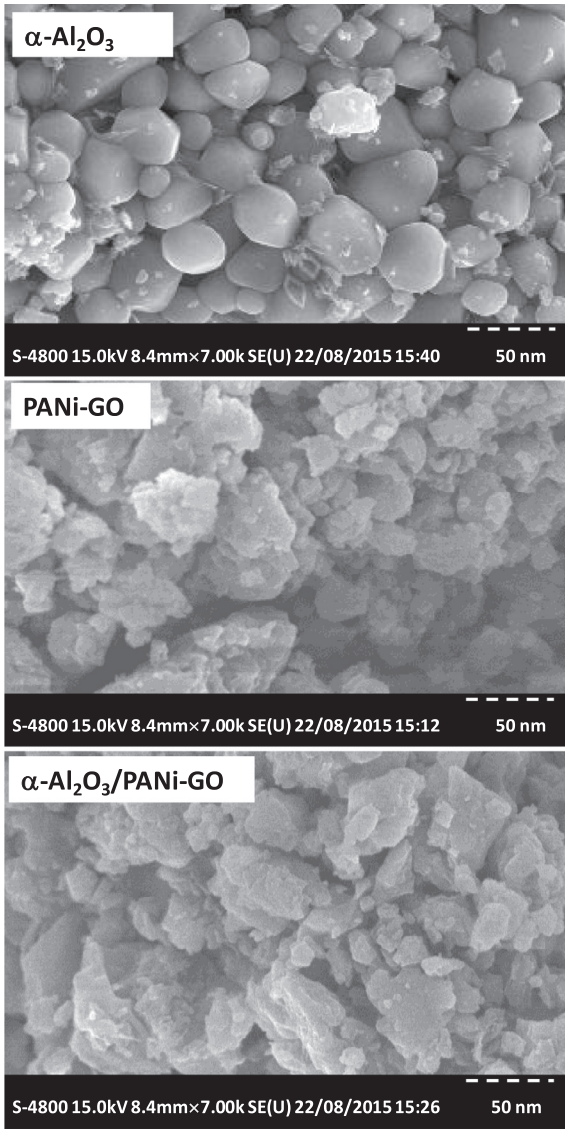

Fig. 2. FE-SEM images of α-Al_2O_3, PANi-GO and α-Al_2O_3/PANi-GO composite.

2.2. Supercapacitive study

Electrochemical measurements such as cyclic voltammetry (CV), areal capacitance and capacitance retention analysis were carried out using three-electrode cell systems (CHI 660 D, CH Instruments). As-prepared materials were used as the working electrode, platinum wire as counter electrode and Ag/AgCl as the reference electrode.

2.3. Photovoltaic (PV) study

PV cell required for testing was prepared by doctor blade technique. During the fabrication of PV cell, indium tin oxide (ITO) coated glass plate were used as transparent electrode and aluminum as metallic electrode. The photovoltaic properties of as-fabricated PV cell such as fill factor (FF) and power conversion efficiency (%η) confirmed by measuring short circuit current (Isc), open circuit voltage (Voc) and I_{max} and V_{max} from IV characteristics of PV cells.

3. Results and discussion

3.1. Characterization of materials

Fig. 1(a) shows the XRD pattern of α-Al_2O_3 nanoparticles, which is in good agreement with PDF Card No-01-081-1667. No other peaks for impurities were detected in pattern. The average crystallite size was computed by considering all prominent diffraction peaks using the Debye-Scherrer equation, which found to be 37.3 nm [16]. Fig. 1(b) depicts the XRD pattern of PANi-GO composite. The XRD pattern shows noisy behavior of diffraction peaks, which confirms the composite exhibited amorphous nature. In addition to this composite comprises broad hump between 2θ-range 20–30°. Fig. 1(c) shows the XRD pattern of α-Al_2O_3 nanoparticles loaded PANi-GO composite. Pattern clearly indicates the presence of signature peaks of α-Al_2O_3 and GO. This indicates the nice incorporation of α-Al_2O_3 in PANi-GO composite.

Fig. 2 represents the SEM images of α-Al_2O_3, PANi-GO and α-Al_2O_3/PANi-GO composite. SEM image of α-Al_2O_3 shows the nanoparticles have irregular shape with well separated boundaries. The average crystallite size estimated using XRD analysis is in good agreement with SEM study. The SEM images of PANi-GO and α-Al_2O_3/PANi-GO composite have almost identical morphology like petals or sheets structure.

3.2. PV study of materials

Fig. 3(a–c) shows IV characteristics of PV cell fabricated using the active PV material, α-Al_2O_3, PANi-GO and α-Al_2O_3/PANi-GO composite respectively and the PV parameters reflected by materials are listed in Table 1. From results, it is concluded that α-Al_2O_3 loaded PANi-GO composite achieve higher short circuit current (I_{sc}) than pure α-Al_2O_3 and PANi-GO. This might be attributed to the good dispersion of α-Al_2O_3 in PANi-GO composite and good charge–transfer process within composite, which is evident in the higher value of Isc [17]. There is a significant enhancement in

Table 1
PV parameters of α-Al_2O_3, PANi-GO and α-Al_2O_3/PANi-GO composite.

Material	I_{max} (mA)	V_{max} (V)	I_{SC} (mA)	V_{OC} (V)	FF	%η
α-Al_2O_3	23.8	0.2	23.8	0.7	0.285	1.61
PANi-GO	86	0.2	86	0.7	0.285	5.81
α-Al_2O_3/PANi-GO	137.7	0.2	137.7	0.8	0.25	9.31

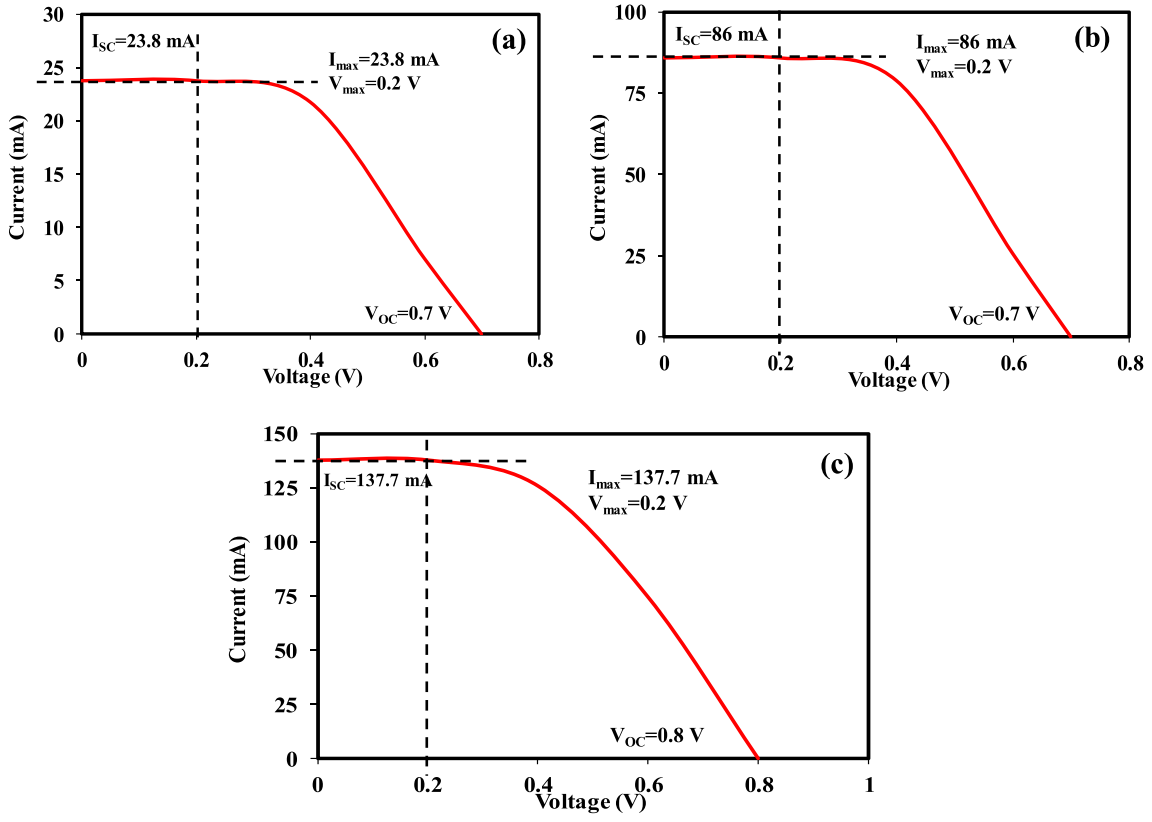

Fig. 3. PV response of (a) α-Al_2O_3, (b) PANi-GO (c) α-Al_2O_3/PANi-GO composite.

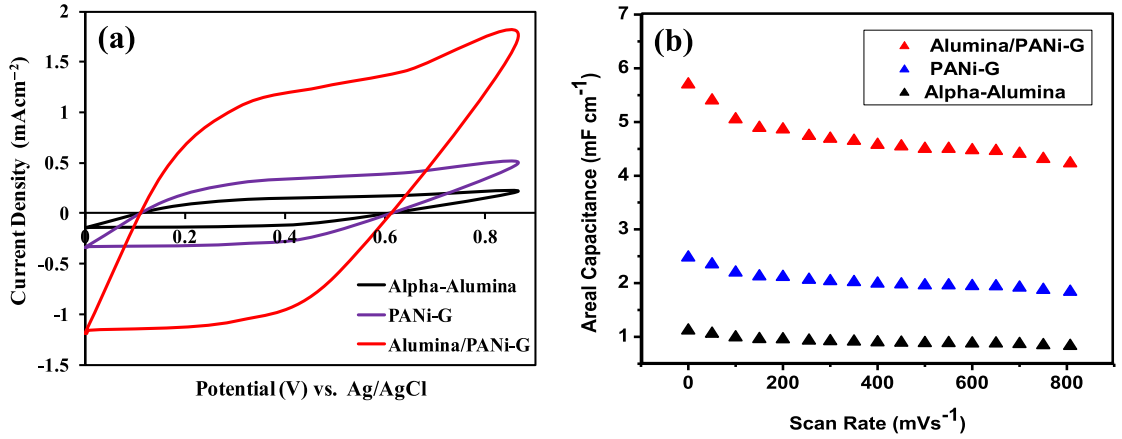

Fig. 4. (a) CV curves and (b) Areal capacitance as a function of scan rate of the α-Al_2O_3, PANi-GO and α-Al_2O_3/PANi-GO recorded at a scan rate of 2 mV s^{-1}.

%η resulted due to the addition of α-Al_2O_3 in PANi-GO composite. The highest value of %η is 9.31% for α-Al_2O_3/PANi-GO composite, whereas %η is 5.81% for PANi-GO composite and 1.61% for α-Al_2O_3.

3.3. Supercapacitive study of materials

Fig. 3a shows the cyclic voltammetric (CV) curves of α-Al_2O_3, PANi-GO and α-Al_2O_3/PANi-GO recorded at a scan rate of 2 mV s^{-1}. The CV curves clearly shows the α-Al_2O_3/PANi-GO composite have superior supercapacitive properties over pristine α-Al_2O_3, PANi-GO composite. The superior supercapacitive properties of α-Al_2O_3/PANi-GO composite can be attributed to oxidation/reduction of surface hydroxyl groups [18]. Specific capacitance has been estimated using the relation (Eq. (1)) [19],

$$Cs = \frac{I}{m \times v}(Fg^{-1}) \quad (1)$$

where I is the average current during anodic and cathodic scan (A), m is the mass of the electrode (g) and v is the scan rate (V). In our case, the highest value of specific capacitance was found to be 715.5 Fg^{-1} at a scan rate of 2 mV s^{-1} for α-Al_2O_3/PANi-GO composite.

Fig. 3b shows the variation of calculated areal capacitance of the α-Al_2O_3, PANi-GO and α-Al_2O_3/PANi-GO composite as a function of scan rate. Here also plot clearly depicts that α-Al_2O_3/PANi-GO composite has several fold higher capacitance over the pristine α-Al_2O_3, PANi-GO composite. The significant enhancement in electrochemical performance was attributed to two main processes occurring in the composite. First is that composite possesses improved carrier density, which results in good electrical conductivity. Second is the increase of density of hydroxyl groups on α-Al_2O_3/PANi-GO composite [20]. The absence of redox peak indicates that capacitance was mainly contributed by non-faradaic redox reactions.

As shown in Fig. 4, the capacitance drops in pristine α-Al_2O_3 and PANi-GO composite is significantly more than α-Al_2O_3/PANi-GO composite. The α-Al_2O_3/PANi-GO composite electrode exhibits an excellent long-term stability with 95.83% capacitance retention after 7000 cycles. The good capacitance ability of α-Al_2O_3/PANi-GO composite is ascribed to enhanced electrical conductivity and highly stable surface redox reaction [21] (see Fig. 5).

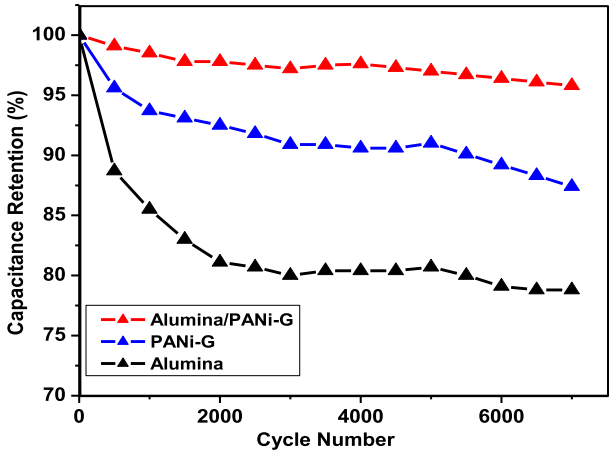

Fig. 5. Cycle performance of the alpha-Al_2O_3, PANi-GO and α-Al_2O_3/PANi-GO composite measured at a scan rate of 2 mV s^{-1} for 7000 cycles.

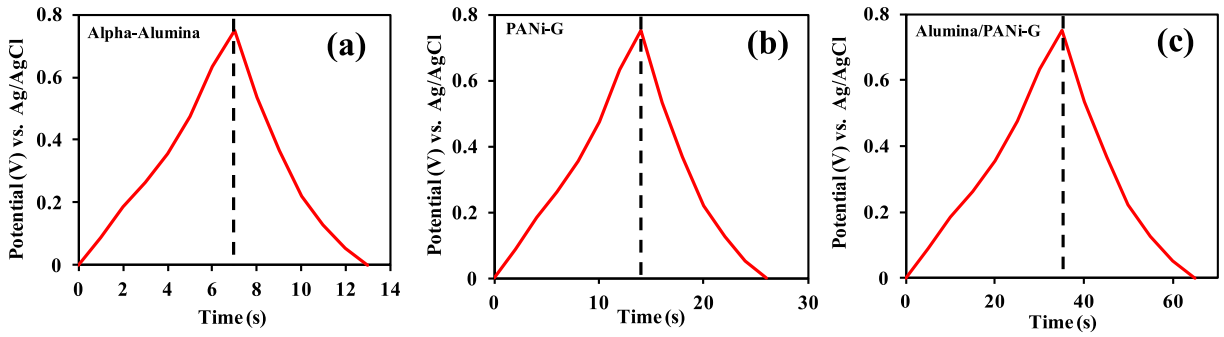

Fig. 6. Galvanostatic charge/discharge curves of the (a) alpha-Al_2O_3, (b) PANi-GO and (c) Al_2O_3/PANi-GO collected at a current density of 10 μAcm^{-2}.

Electrochemical study of alpha-Al_2O_3, PANi-GO and Al_2O_3/PANi-GO samples were extended by measuring charge/discharge measurements. Fig. 6(a–c) shows the galvanostatic charge/discharge (GCD) curves of alpha-Al_2O_3, PANi-GO and Al_2O_3/PANi-GO samples, respectively. The GCD curves of Al_2O_3/PANi-GO sample is nearly symmetric and significantly lengthy than alpha-Al_2O_3 and PANi-GO. This indicates capacitive properties of Al_2O_3/PANi-GO sample superior than alpha-Al_2O_3 and PANi-GO. Improved performance of Al_2O_3/PANi-GO attributed to synergetic state between alpha-Al_2O_3 and PANi-GO.

4. Conclusions

In summary, we have successfully demonstrated that the photovoltaic and supercapacitive performance of GO-PANi/α-Al_2O_3 composite is superior over the α-Al_2O_3 and PANi-GO composite. GO-PANi/α-Al_2O_3 composite based PV cell shows significant power conversion efficiency of the order of 9.31%, which much higher than α-Al_2O_3 and PANi-GO composite. The GO-PANi/α-Al_2O_3 composite exhibits the considerable specific capacitance of the order 715.5 Fg^{-1}. The GO-PANi/α-Al_2O_3 composite retain 95.83% capacitance after 7000 cycles, which shows the good cycling stability of composites. The GCD characteristics of Al_2O_3/PANi-GO sample improved due to synergetic effect between α-Al_2O_3 and PANi-GO composite. At present work is underway for the optimization of the electrochemical performance GO-PANi/α-Al_2O_3 composite.

Acknowledgment

The authors appreciate the help of Dr. S.K. Omanwar Head, Department of Physics, Sant Gadge Baba Amravati University, Amravati for providing necessary facilities for the work.

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