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Synthesis of tin oxide/graphene (SnO_2/G) nanocomposite and its electrochemical properties for supercapacitor applications

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ABSTRACT

Tin oxide/graphene (SnO_2/G) nanocomposites were prepared by a simple wet chemical route and the as prepared nanocomposites were characterized by X-ray diffraction (XRD), High Resolution Transmission Electron Microscopy (HRTEM) and Fourier transform infrared spectra (FTIR). The characterized results showed the tetragonal structure of SnO_2 nanostructures on uniform distribution on graphene sheets with a particle size of ~50 nm. The reduction of graphene oxide to graphene during SnO_2/G synthesis was confirmed from FTIR analysis. HRTEM analysis showed that the individual SnO_2 nanoparticles deposited on graphene sheets. The electrochemical performances of SnO_2/G nanocomposites towards supercapacitors were studied in 6M KOH electrolyte. A maximum specific capacitance of 818.6 F/g was obtained for SnO_2/G-a composite at 5 mV/s scan rate suggesting that the presence of graphene matrix in SnO_2 nanoparticles have enhanced the electrochemical behaviour of SnO_2. The galvanostatic charge/discharge studies confirmed the good cyclic stability of the composite electrode. These excellent electrochemical properties suggested that the SnO_2/G nanocomposites could be used for high energy density supercapacitor electrode materials.

1. Introduction

In response to the global warming issue, energy storage has become a huge challenge to the global power systems. Recently, a lot of efforts have been undertaken to develop new energy storage devices like supercapacitors, which can provide high energy density than conventional capacitors and high power density than batteries [1]. There are two energy storage mechanisms for supercapacitors: (i). Electric double layer capacitors, wherein energy storage arises mainly from the separation of ionic charges at the interfaces between electrodes and electrolyte solution [2]. (ii). Pseudocapacitors uses transition metal oxides and conducting polymers, which undergoes reversible faradic reactions [3]. As well known, ruthenium oxide (RuO_2) exhibits a high pseudocapacitance, but its high cost and environmental harmfulness leads to the limit of its practical applications in supercapacitors [4]. Hence the development of new materials at low cost for supercapacitors is still a challenge and needs to be addressed. In recent days, considerable efforts have been devoted by researchers to develop alternative electrode materials like MnO_2 [5], NiO [6], Co_3O_4 [7] and SnO_2 [8], etc.

Among the various metal oxide nanomaterials, SnO_2 based nanomaterials have attracted a considerable attention as a promising electrode material for supercapacitors due to its low cost and high power density. SnO_2 has potential applications in various fields like sensors [9] and solar cells [10]. Especially, SnO_2 appears to be a promising electrode material for energy storage devices like lithium ion batteries and supercapacitors due to its superior electrochemical performance [11]. Though SnO_2 gives better response towards specific capacitance of supercapacitors, it is still limited to practicality due to the poor transportation of the electrolyte ions within the SnO_2 matrix and its poor electrical conductivity. Various reports have demonstrated that the carbon based materials like carbon nanotube and graphene enhance the electronic conductivity of metal oxides. In recent years, one atom-thick layered crystalline with honeycomb structure of sp^2-bonded carbon called graphene is a good candidate for supercapacitor electrode material due to its superior electrical conductivity ($\sim 10^6$ S cm^{-2}) [12], high surface area (2630 m^2 g^{-1}) [13] and high thermal conductivity (5000 Wm^{-1} K^{-1}) [14]. In addition, it can minimize the contact resistance between the electrode and current collector, unlike the case of carbon nanotube [15]. Graphene is an ideal carbon electrode material for electric double layer

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supercapacitors because it is capable of storing an EDL capacitance value of up to 550 F/g, provided the entire surface area viz. 2630 m^2/g is fully utilized. Another advantage of graphene in a supercapacitor electrode is the notion that both major surfaces of graphene sheets on exterior surfaces are readily accessible by electrolyte. Many SnO_2/graphene hybrids with various structures have been reported for supercapacitor applications. Li et al., prepared SnO_2/graphene using a one-pot synthesis approach, which showed a specific capacitance of 34.6 F/g [16]. Wang and group worked reported on the microwave assisted one-pot synthesis of SnO_2/graphene, which gave rise to the specific capacitance of 99.7 F/g [17]. Lim et al., reported solvothermal synthesis of SnO_2/graphene nanocomposites and achieved a maximum specific capacitance of 363.3 F/g [8]. In view of these findings, more investigations need to be done to improve the specific capacitance of the nanocomposites to meet the criteria for excellent supercapacitors.

In this report, a simple wet chemical route has been adopted for the synthesis of SnO_2/graphene nanocomposites and further extended to study its electrochemical behaviour towards supercapacitor applications. During the preparation of graphene, the surface charge of graphene oxide is highly negative when dispersed in ethylene glycol. After adding $SnCl_2{\cdot}2H_2O$ into GO stable solution, positive charge of Sn^{2+} ions were anchored onto the surface of GO sheets via electrostatic interaction especially along the edges of the nanosheets. The GO sheets acted as an oxidizing agent, oxidizing Sn^{2+} to SnO_2 on the surface of GO sheets, while GO got simultaneously reduced to graphene by ethylene glycol. Afterwards, high purity of SnO_2 nanoparticles were obtained at 500 °C under Ar atmosphere. The superior electrochemical performance of SnO_2/G composites could be ascribed to the synergistic effect of graphene matric and SnO_2 nanoparticles.

2. Experimental methods

2.1. Materials

AR grade of Tin (II) chloride dehydrate ($SnCl_2{\cdot}2H_2O$), sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), sulphuric acid (H_2SO_4, 99%), sodium borohydride ($NaBH_4$), hydrogen peroxide (H_2O_2, 30%), sodium hydroxide (NaOH), potassium hydroxide (KOH) were purchased from Sigma-Aldrich. All the solutions were prepared by using Milli-Q water (pH 7.2).

2.2. Preparation of SnO_2/graphene (SnO_2/G) nanocomposites

Graphene oxide was synthesised using modified Hummer's method according to our previous report [19]. Briefly, 160 mg of GO was dispersed in 80 ml of ethylene glycol and sonicated for 1 h to form a stable GO solution. Then 80 ml of $SnCl_2{\cdot}2H_2O$ (5 mM) aqueous solution was added to GO suspension. Afterwards, the mixed solution was transferred into a round bottom flask and refluxed at 190 °C for 6 h. The resultant black colour product was washed and centrifuged with de-ionized water and ethanol. Final product was dried at 60 °C for 12 h. The sample was named as SnO_2/G-a. Similarly, other nanocomposites viz. SnO_2/G-b and SnO_2/G-c were synthesized by a similar method, wherein b and c represents different GO concentrations of 320 mg and 480 mg respectively so as to have a higher ration of graphene concentration in the matrix.

2.3. Materials characterization

X-ray diffraction system (BRUKER, D8 Advance, Germany) was used for the X-ray analysis with Cu-Ka radiation (λ = 1.540° A). Step scanning was done with 2θ intervals from 10° to 65°. Fourier transform infrared spectra were recorded using Spectrum one: FTIR-spectrometer in the range 450–4500 cm^{-1} to characterize the functional groups of the composites. Transmission electron microscopy (TEM) images were captured with a microscope (JEOL, 3010) at an acceleration voltage of 200 kV.

2.4. Electrochemical measurements

All the electrochemical measurements were carried out in an electrochemical analyzer (CHI 600C work station, version 5.01) using a three electrode system in 6 M KOH as electrolyte solution under ambient conditions. The potentials and current were measured with respect to Ag/AgCl (sat.KCl) as the reference. Carbon paper (Purchased from Cabot, USA) and Pt wire were used as the working and counter electrode respectively. The cyclic voltammetry measurements were performed at various scan rates in the potential range from −0.4 to 1.0 V. The working electrode was prepared as follows: In brief, a known amount of active material was dispersed in 5 wt% of nafion and the mixture was coated on a carbon paper (3 cm × 1 cm × 0.1 cm). The total surface area of the active material coated was 0.5 cm^2. The mass of the active material on electrode was 2 mg/cm^2. Then, the electrode was dried for 3 h at room temperature.

3. Results and discussion

XRD pattern of graphene oxide, pure SnO_2 and SnO_2/G-a are shown in Fig. 1. A sharp diffraction peak at 2θ = 10.6° in graphene oxide (inset picture) could be seen corresponding to the interlayer distance of 8.1 Å. This expanded interlayer distance in comparison with that of graphite (3.6 Å) indicating the presence of oxygen, carboxyl functional groups on GO sheets during Hummer's process [18]. The diffraction peaks of SnO_2 nanoparticles at 26.5, 34.4, 52.1 and 64.1° are clearly distinguishable and could be indexed to (110), (101), (211) and (301) planes of tetragonal structure (JCPDS 41-1445) [19]. Interestingly, no diffraction peaks due to graphene could be observed in SnO_2/G composite, which might be due to the exfoliation of GO sheets at 190 °C. During exfoliation, the regular stacks are destroyed and thus disappearance or weak diffraction peaks could be observed in graphene [20]. In addition, the attached SnO_2 nanoparticles on graphene sheets prevent the aggregation and restacking of graphene and due to the SnO_2 nanoparticles in the composite, the diffraction of carbon atoms in graphene is weakened. Thus, the SnO_2 nanoparticles covering the graphene sheets gave a strong diffraction of SnO_2 only in the composite and

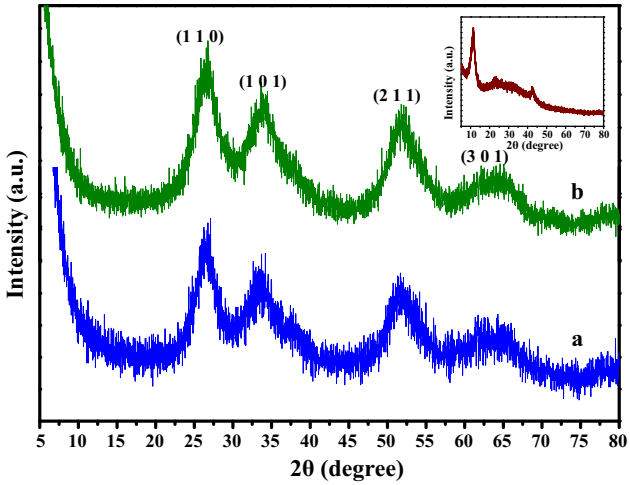

Fig. 1. XRD pattern of (a) Pure SnO_2 (b) SnO_2/G-a nanocomposite and GO (Inset picture).