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An easy two step chemical route synthesis of nanocomposites of ZnO/MWNTs thin film electrode and Supercapacitor

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Abstract

An easy chemical route technique is proposed to prepare hybrid nanocomposites of ZnO/MWNTs nanocomposites in two steps. The technique uses dip and dry approach followed by a facial successive ionic layer adsorption and reaction (SILAR). Scanning electron microscopy (SEM) and X-ray diffraction (XRD) are used to characterize the morphology and structure of ZnO/MWNTs hybrids nanocomposites. The results show that the ZnO nanodots have high porus and cluster uniformly on MWNTs. Serving as a free-standing electrode, the electrochemical performance of of ZnO/MWNTs hybrids nanocomposites at different electrolytes are studied by cyclic voltammetry, It is found that the of electrochemical performance of ZnO/MWNTs hybrids nanocomposites in H_2SO_4 electrolyte gives high performance in energy storage applications.

Keywords: Multiwalled carbon nanotubes, ZnO, Thin Film, Electrolyte, Supercapacitor

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1. Introduction

Electricity generated from renewable sources, such as solar ,wind power and tidal offers huge potential for meeting every demands .But access to solar ,wind power and tidal energy is intermittent, where as electricity must be reliably available for whole day. Even second to second fluctuations can cause major disruptions that cost millions of rupees annually. Electrochemical storage devices will therefore be significant for effectively leveling the cyclic nature of renewable energy sources. Supercapacitor, as a novel energy storage device, is emerging potential to substitute or complement batteries in applications that require high power densities [1-3]. Supercapacitor is nothing but the combination of advantages of both conventional capacitors, which have high power density and rechargeable batteries, which have high energy density.

Conducting polymers, Transition metal oxides [4,8] and metal sulphides have been widely employed for electrochemical capacitors with high power density, taking advantage of their fast redox kinetics. Among the transition metaloxides, ZnO is found to be one of the better alternate materials due to its higher surface area, good redox property, controllable size and shape, and structural identities.[9,10] But, the poor conductivity, low mechanical and chemical stability of these materials usually demand the addition of conductive multiwalled carbon nano tubes (MWNTs) to enhance its charge transfer rate and supporting matrix/substrate. To increase energy, as well as power density, transition metal oxides must be deposited within MWNTs to form faradic pseudocapacitors. In particular, ZnO nanostructures are promising materials in optics, optoelectronics, sensors, supercapacitors, and actuators due to their semiconducting, piezoelectronic, and piezoelectric properties [11, 12]. Nanostructured ZnO possesses high specific surface area, biocompatibility and excellent electrochemical activity, making it desirable for high performance supercapacitors.

Cyclic voltammetry (CV) is used to assess the quality of electrochemical capacitors and of electrodes for electrochemical capacitors Cyclic voltammetric curves for ideal capacitor is perfect rectangular shape and for non ideal electrochemical capacitor is nearly rectangular or different from rectangular or like more rectangular shape [13-15]. Deviations of CV curves of ideal capacitors from rectangular shape are mainly due to their electric resistance and to redox processes to their electric resistance and to redox processes

In this work, we report, an easy two step chemical route technique dip and dry approach followed by a facial successive ionic layer adsorption and reaction (SILAR) for synthesis of ZnO/MWNTs nanocomposites thin film electrode. This methods utilizes maximize the active material utilization ratio and decrease the diffusion length significantly. This result helps to get high specific

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capacitance and excellent rate capabili different ty. Effect of different aqueous electrolyte on ZnO/MWNTs nanocomposites thin film electrode was studied by using cyclic voltammetry.

2 Materials and Experimental details

2.1 Materials used

Carbon nanotubes (CNTs) (>95% purity, outer diameter from 15-20 nm and length from 5-15 μm) were purchased from Nano Amor (Housten, TX) . Mostly chemicals used in this study were of reagent grade purchased from Sigma-Aldrich and used without further purification. Zinc nitrate (Sigma-Aldrich), Ammonia solution 25% (Merck), H_2SO_4 (Sigma-Aldrich), KOH (Sigma Aldrich) , NaOH (Sigma -Aldrich), KCl (Sigma -Aldrich) and NaCl (Sigma -Aldrich).

2.2 Substrate cleaning:

Substrate cleaning plays an important role in the deposition of thin films. Extreme cleaning of the substrate is required for deposition of material, as the contaminated surface provides nucleation sites, facilitating growth resulting into non-uniform films. Electrically conducting substrate is the necessary requirement for the deposition towards application as supercapacitor. The 5.0 cm X 1.0 cm dimensions of stainless steel (SS) substrates were used for the deposition of films.

2.3 Preparation of MWNTs solution

Firstly, MWNTs were refluxed in H_2O_2 at 333K for 48h to remove the amorphous carbon derivative and to generate oxygenated functional group. These functionalized MWNTs were well dispersed into the solution containing distilled water and Triton X-100 using ultrasonicator. The obtained stable dispersed MWNTs solution for the preparation of MWNTs thin films were used.

2.4 Deposition Coating of MWNTs thin film on SS substrate

Relatively simple & reliable method' Dip and dry' approach coating technique is used to coat the MWNTs solution on highly polished and cleaned substrates for 10 min . The MWNTs gets adsorbed on the surface of stainless-steel substrate (SS). The thickness of thin film can be controlled by the repetition in dipping the substrate in the MWNTs solution. Further these MWNTs coated stainless steel substrate were dried immediately in air OR in IR lamp and to make it ready for further deposition.

2.5 Preparation of ZnO/MWNTs nanocomposites thin film electrode

Firstly, functionalized MWNTs in distilled water with Triton X-100 was sonicate to obtain stable dispersion. For the „dip and dry" process, cleaned SS substrates were dipped in prepared MWNTs solution for suitable time. During the process, MWNTs get adsorbed on the surface of SS substrate. Further these MWNTs coated SS were dried under Infrared (IR) lamp. This process was repeated by few times in order to obtain the uniform coating of MWNTs onto SS substrate. Further, these MWNTs coated SS substrates were used for further deposition of zinc oxide (ZnO). The layer of ZnO was deposited onto MWNTs by using successive ionic later adsorption and desorption (SILAR) method. The SILAR method was used for the synthesis of ZnO in which a beaker contains the aqueous cationic solution of zinc nitrate complexed with ammonia as source of zinc whereas other beaker contains distilled water which was maintained at 80° C as an anionic solution. Well dried SS coated MWNTs films were used as substrate for the ZnO deposition. MWNTs coated SS substrate was immersed in the cationic solution, the zinc complex ions get adsorbed on the walls of MWNTs due to attractive forces between ions in the solution and that on the surface of the MWNTs. These forces may be cohesive or van-der Waals or chemical attractive. Further, the MWNTs coated SS substrate with pre-adsorbed Zn complex ions immersed in a hot water solution maintained at 80° C to get zinc hydroxide by the reaction. This completes one SILAR cycle for formation of ZnO layer. Such 40 cycles were repeated to increase the overall film thickness. Finally, these films were annealed at 200° C for the removal of hydroxide phase and also to remove the Triton X-100 in MWNTs. Thus, the uniform and well-adherent ZnO/MWNTs nanocomposites thin film electrodes were obtained on the SS substrates after annealing.

2.6 Characterization techniques

The prepared samples was characterized by X-ray diffraction on a 'X' Pert Pro (PANAlytical) difractometer. with an diffraction angle 2θ between

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20 °and 80°. Surface morphologies of ZnO/MWNTs films were examined by using field emission scanning electron microscopy (FE-SEM, Model: Hitachi S 4800) attached with an energy dispersive X-ray analysis (EDAX) to measure the sample composition. Electrochemical measurements were conducted in a three electrode cell which consist of a 25 ml beaker equipped with a reference electrode (vs,Ag/AgCl), counter electrode (platinum), and a working electrode (TiO_2/MWNTs thin film) using potensiostat (Gamry Instrument PWR600) .

2.7. Electrochemical study

In order to study the effect of electrolytes on supercapacitive performance of ZnO/MWNTs nanocomposites thin film electrode, cyclic voltammetry (CV) experiment was performed.These supercapacitive performance were studied in different electrolytes viz 1 M solution of NaOH, NaCl, KCl, KOH and H_2SO_4 at 50 mVs^{-1} scan rate as shown in fig. 1The specific capacitance of the samples was estimated from the integrated charge from the CV data using the equation.

$$C_s = \frac{1}{mv(V_c - V_a)} \int_{Va}^{Vc} I_m dV$$

Where, C_s is the specific capacitance ($F.g^{-1}$), v is the potential scan rate (mVs^{-1}), (V_c -V_a) is the potential range (V, vs, Ag/AgCl) and I_m denotes the response current ($mAcm^{-2}$) based on the mass of the ZnO/MWNTs material on SS substrate.

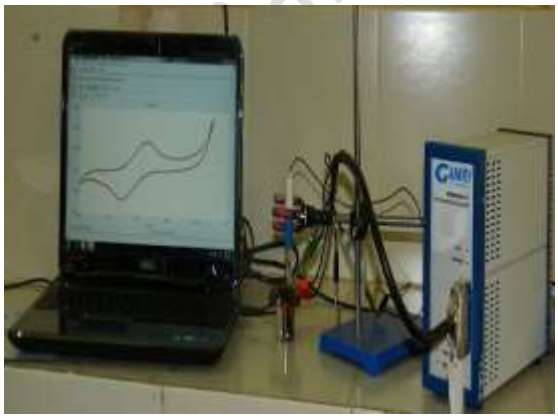

Fig. 1. Cyclic voltammetry setup

3. Results and discussion

3.1. Structural and compositional analysis

Structural analysis of bare stainless steel (SS), CNTs and CNT-ZnO nanodot thin films are carried by x-ray diffraction technique is shown in Fig.2. It is seen that XRD pattern exhibits major peaks of stainless steel at 44.19º, 50.42º, 64.25º and 74.35º marked with triangles (Δ). Very minute peak corresponding to MWNTs and ZnO were observed at 25.61º and 31.74º, respectively. This means that the ZnO/MWNT nanocomposites thin films showed amorphous nature, which is one of the prime requirements for supercapacitor [15]. Only high intensity peaks of stainless steel were observed. There were no other contamination or impurity peaks observed in XRD analysis.

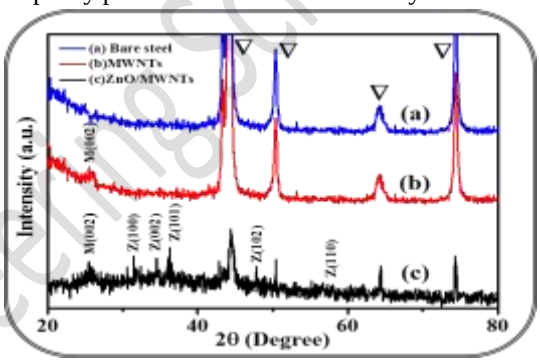

Fig.2 XRD of stainless steel, MWNTs and ZnO/MWNTs

Fig. 3 shows typical EDAX pattern for ZnO/MWNT nanocomposites thin film electrode.The elemental analyses were carried out for C, Zn and O [15]. The strong peak of C was found with small elemental peaks due to Zn and O. Thus the existence of C, Zn and O was confirmed from the EDAX spectrum. The average atomic percentage of C: Zn: O is listed in the inset of Fig.3.

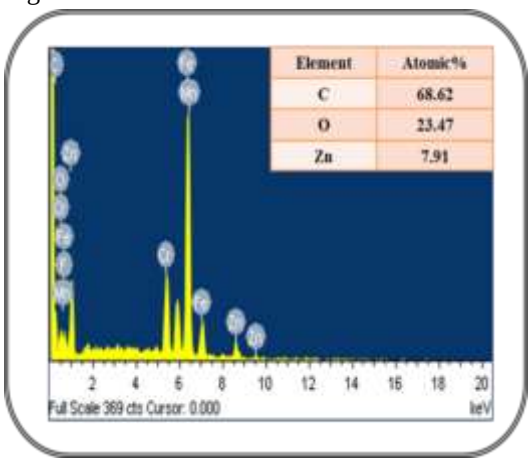

Fig.3 EDAX of ZnO/MWNTs nanocomposites

3.2 Surface morphological study

Fig. 4 shows FESEM images of ZnO/MWNTs films at 500nm magnifications. It is seen that, the outside surface of MWNTs is uniformly anchored with ZnO nanoparticles. No aggregation of ZnO was seen in the porous area between MWNTs network, indicating that the nucleation occurs predominantly on the outer surfaces of MWNTs and just some micrometres long MWNTs are uniformly entangled to form uniform three dimensional interconnected networks.

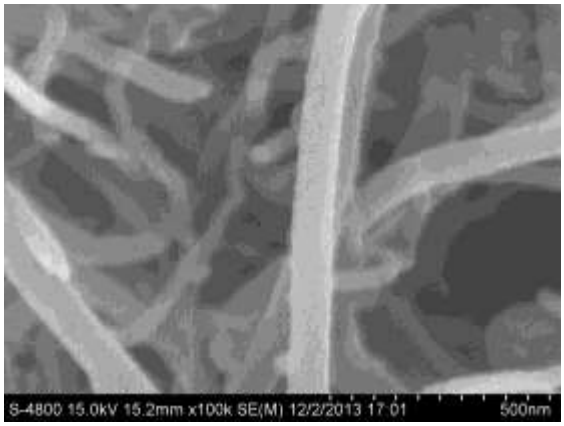

Fig. 4 FESEM image of ZnO/MWNTs

3.2 Effect of Electrolyte

An importance factor that has to be considered in order to prove the capacitance, the change in the electrolyte will have direct effect on the capacitance value. The effect electrolyte on

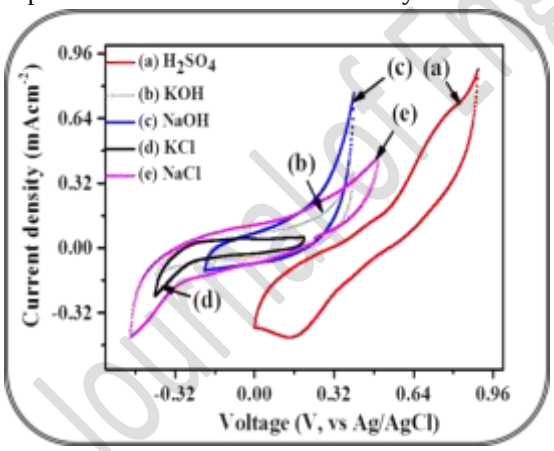

Fig.5 Cyclic voltammetry of ZnO/MWNs nanocomposites

Supercacitance of ZnO/MWNTs nanocomposites thin film electrodes was studied on the scan rate of 50 mVs^{-1}.In order to check the effect of electrolytes, the electrochemical behaviour of ZnO/MWNTs thin film electrode were evaluated in aqueous electrolyte viz. 1 M solution of H_2SO_4, KOH, NaOH, KCl and NaCl . For each electrolytes, cyclic voltammetry curves was obtained. Fig.5. shows the CV of ZnO/MWNTs thin film electrodes at different electrolyte.

The rectangular-like profiles with redox peak and mirror-image characteristics of the CV curves reveal the pseudocapacitive behaviour as reported by others [15], indicating that the deposited ZnO/MWNTs thin film electrodes are promising electrode materials for use in supercapacitors.

It is observed from all CV curves of all electrolytes, the H_2SO_4 electrolyte gave the largest current than the other electrolytes. In all cases, the electrode exhibited symmetric CV characteristics in forward and reverse sweeps.

4. Conclusions

In conclusions, we described a new two step approach of a ZnO/MWNTs nanocomposites electrodes were fabricated by dip and dry approach followed by a facial successive ionic layer adsorption and reaction (SILAR). Nearly, the rectangular shape of a cyclic voltammetry curves for each electrolyte were obtained. Maximum current in cyclic voltammetry was obtained for H_2SO_4 electrolytes. Such freestanding ZnO/MWNTs nanocomposites electrodes demonstrate excellent performance for supercapacitor in H_2SO_4 electrolytes. This study suggests that the MWNTs coating with the ZnO nanomaterials would open new routes for the applications of supercapacitors. Thus these encouraging results suggest that ZnO/MWNTs nanocomposites can serves as promising electrode materials for high performance supercapacitors.

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