Polyaniline Doped Zinc-Oxide Nanocomposite for Electrochemical Super-Capacitor Applications

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Abstract

Zinc oxide nanoparticles were synthesized via sol-gel approach. Synthesized crystalline Zinc Oxide nanoparticles with size 20nm are uniformly deposited on the surface of Polyaniline prepared by the method of in situ chemical oxidative polymerization. Synthesized Zinc Oxide/PANI nanocomposite was investigated by X-ray diffraction and transmission electron microscopy. X-Ray Diffraction study revealed that the structure of Zinc Oxide nanoparticle is hexagonal with space group P63mc.TEM image of Zinc Oxide/PANI nanocomposite shows that Zinc Oxide nanoparticles are uniformly embedded in PANI matrix. These results highly indicate ZnO nanoparticles used as an electrode material and provide higher specific capacitance and energy density for electrochemical Super-capacitor applications.

Keywords: ZnO, ZnO/PANI, XRD, TEM.
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Introduction

Transition metal oxides have gained more interest as electrode materials in Supercapacitor applications in the last decades due to their extremely high theoretical capacity ($372mAhg^{-1}$) with the conventional carbon materials [1]. Among them, Zinc oxide (ZnO) has a wide band gap semiconductor of 3.3eV with large exciton binding energy of 70 meV. ZnO has broad range of applications in the manufacturing of magnetic materials, alkaline battery anodes, dye-sensitized solar cells, semiconductors, solid oxide fuel cells (SOFC), antiferromagnetic layers, p-type transparent conducting films, electrochromic films, heterogeneous catalytic materials and gas sensors [2-3]. ZnO is unique material possesses advantage such as high specific energy, high chemical stability, facile preparation, morphologic diversity and prolonged lifecycle. Therefore, research towards finding new anode materials for super-capacitor applications has been accelerated. The high-energy density materials can be achieved by either increasing charge capacity of the anode or increasing the working potential of the anode materials. Recently, conducting polyaniline has been studied as an additive to improve the performance of anode materials in Supercapacitor applications [4]. When ZnO nanoparticles incorporated in PANI matrix, would result from synergistic effect from the faradic capacitance of the ZnO and double layer capacitance of the PANI [5]. In the present study, we have synthesized ZnO and ZnO/PANI nanocomposite and characterized by XRD and TEM. Further electrochemical properties were investigated for super-capacitor applications.

Synthesis of ZnO/PANI nanocomposite

Zinc oxide (ZnO) nanoparticle was synthesized via sol-gel approach as given in reference [6]. The synthesized 40 wt % of ZnO nanoparticles will be incorporated in PANI matrix by an in-situ chemical oxidative polymerization method [7]. We have chosen 40 wt% of ZnO/PANI comparison with other loadings because it provides optimal dispersion and interfacial interactions between ZnO and PANI chains leading to improved properties.

In a typical procedure, 0.931 gm. of aniline dissolved in 100 ml of 1.388ml of H_2SO_4 solution and stirred for 1 hour, then mixed with 10 ml of sonicated zinc oxide nanoparticles by further sonication for 30 min. increased sonication time

can lead to a decrease in particle size, resulting in more uniform distribution. 100 ml of 1M of H_2SO_4 solution containing 2.28 gm. $(NH_4)_2S_2O_8$ (APS) are then slowly added drop wise to well dispersed suspension mixture for 2 hours with a continuous stirring. Concentration of the material can impact material properties like mechanical strength, thermal conductivity and optical properties ultimately affecting the materials performance in various applications.

After 3 hours, a good degree of polymerization will have achieved as observed by the change in colour from blue to blackish green. The precipitate produced in the reaction will be removed by filtration, washed repeatedly with 1M of H_2SO_4 and dried under vacuum for 24 hours. The conductive emeraldine salt (ES) form of ZnO/PANI nanocomposite powder will be obtained.

Discussions

Figure 1 shows the X-ray diffraction spectra of ZnO and ZnO/PANI nanocomposite. After addition of ZnO nanoparticles in PANI matrix, amorphous nature of PANI changes and found crystallinity distributed in ZnO/PANI nanocomposite due to nucleating effect of ZnO. XRD pattern of ZnO nanoparticles consist of diffraction peaks for 2θ = 31.789˚, 34.439˚, 36.277˚, 47.581˚, 56.639˚, 62.896˚, 67.8˚, 69.12˚, 77.00˚ which corresponds to the (100), (002), (101), (102), (110), (103), (200), (201) and (202) plane of hexagonal phase of ZnO respectively [8]. The peaks clearly indexed the formation of ZnO structure from JCPDS powder diffraction card file. A most intense peak at 2θ = 36.27^0 was obtained along (1 0 1) orientation. The patterns are in accordance with the typical zincite structure ZnO diffraction (hexagonal phase, space group P63mc, with lattice constant a = 3.249 A^0).

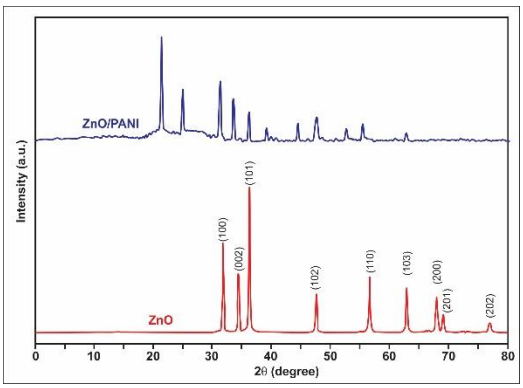

Figure 1: XRD spectra of ZnO and ZnO/PANI nanocomposite.

The diffraction peaks of ZnO nanoparticles and ZnO/PANI composites have been indexed to the hexagonally Wurtzite structured ZnO which were well matched with that in JCPDS data (36-1451). The average crystallite size of ZnO and ZnO/PANI nanocomposite was calculated using Scherer's formula [9] from the diffraction peaks. The XRD pattern of ZnO/PANI nanocomposite shows the two broad peaks are observed at 2θ = 20.73° and 25.62° indicated that ZnO crystallites have been uniformly mixed within the polymer chain.

Table1: XRD analysis Properties and crystallite size

Product	2Θ Degree	FWHM	hkl	Crystallite size (nm)
ZnO	36.28	0.281	(100)	20
ZnO [10]	36.50	0.056	(100)	21.8
ZnO/PANI	20.73	0.270	(020)	21
ZnO/PANI[10]	19.08	0.448	(020)	21.8

The TEM images of the synthesized ZnO and ZnO/PANI nanocomposites have been shown in figure 2 (a) and 2 (b) respectively. The shapes of the ZnO particles are nearly spherical and obviously demonstrate aggregation of the particles. The aggregation of particles should have been originated from the large specific surface area and high surface energy of ZnO nanoparticles [11]. Aggregation can enhance the electrochemical stability of the material, reducing the likelihood of electrochemical degradation and improving the lifespan of the device. As can be seen in Fig. 2b, the morphology of ZnO is irregular and the ZnO nanoparticles were attached with PANI matrix during polymerization [12]. The TEM image of ZnO/PANI nanocomposite indicate that the transformation of highly branched like polyaniline which have granular-like structure. The TEM image also reveals the presence of ZnO in polyaniline which is homogeneously distributed throughout the polyaniline.

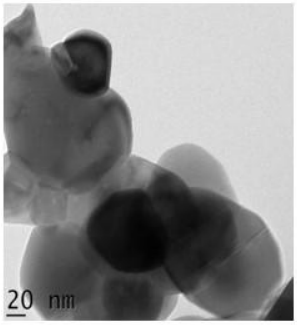

Figure 2 (a): TEM image of ZnO

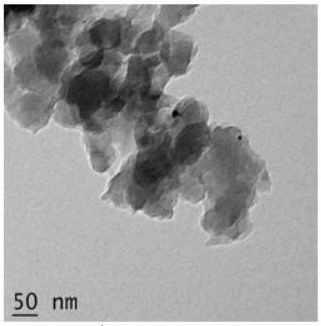

Figure 2 (b): TEM image of ZnO/PANI nanocomposite

Conclusion and Future Prospective

XRD and TEM showed good interaction between PANI and ZnO nanoparticles. Due to this synergistic effect of PANI and nano dimension of ZnO such nanocomposites can be useful as soft electromagnetic materials, catalyst for Li-ion battery, super-capacitor, gas sensor, and photo electrolysis and electrochromic device, colour imaging, magnetic refrigeration, electromagnetic shielding, rechargeable batteries, light emitting diodes, nonlinear optical devices, sensor for medicine and pharmaceutics apparatus.

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