

# Developed Polyaniline/Zinc Oxide Nanocomposites for Supercapacitive Applications

G V Chavan\*

Department of Applied science and Humanities

Mauli Group of Institution college of Engineering & Technology,Shegaon-India

\*corresponding Author *Email: gvchavan46@gmail.com*

**Abstract:** Supercapacitors are electronic devices, which are used to store extremely large amounts of electrical charge. This work devoted to synthesis and characterization of polyaniline/ZnO nanocomposites. The materials are synthesized by using chemical method and characterized through XRD analysis. The concentration of ZnO is varies between 20-80 wt. % range with an interval of 20 wt. % . The average polymer chain separation for polyaniline was found to be  $4.41 \text{ \AA}$ . The polymer chain separation value was estimated using the XRD analysis, which suggests the as-synthesized composite materials have high specific capacitance value. Therefore, the materials are useful in the application of supercapacitor.

**Keywords:** Polyaniline; Zinc oxide; Super-capacitive application.

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## I. INTRODUCTION

Super capacitor is also called ultra capacitor or electrochemical capacitor. Super capacitors are electronic devices, which are used to store extremely large amounts of electrical charge. Super capacitors are important energy storage devices having higher energy density and higher power density compared to batteries and conventional capacitors[1].

Li *et al.* demonstrate the design and fabrication of novel nanorchitectures of  $\text{MnO}_2/\text{Mn}/\text{MnO}_2$  sandwich-like nanotube arrays for super capacitors. The as-synthesized materials serve as highly conductive cores to support the redox active two-double  $\text{MnO}_2$  shells with a highly electrolytic accessible surface area and provide reliable electrical connections to  $\text{MnO}_2$  shells. The maximum specific capacitances of 937 F/g at a scan rate of 5 mV/s by cyclic voltammetry (CV) and 955 F/g at a current density of 1.5 A/g by chronopotentiometry were achieved for the  $\text{MnO}_2/\text{Mn}/\text{MnO}_2$  sandwich-like nanotube arrays in solution of 1.0 M  $\text{Na}_2\text{SO}_4$  [2]. Frackowiak *et al.* demonstrated multiwalled carbon nanotube (CNT) electrodes modified by the oxidative treatment to polypyrrole. This show that a maximum specific capacitance of 170 F/g in 1 M  $\text{H}_2\text{SO}_4$  used as an electrolyte solution. The single-walled carbon nanotube-Polypyrrolenanocomposite electrode shows much higher specific capacitance than pure Ppy and as-grown SWNT electrodes, this because of the uniformly coated Ppy on the SWNTs. The SWNT powder was synthesized by dc arc discharge under a helium pressure of 100 Torr, where a graphite rod of ~6 mm in diameter having a concentric hole ~4 mm diameter filled by a mixture of the graphite powder with 5 wt % Ni, Co, and FeS~1:1:1, was discharged with a bias of 22 V and a current of 55 A [3]. Pedro Gomez-Romero *et al.* was synthesized the combination of conducting polymers and electroactive molecular [4] or extended inorganic species to form nanocomposite hybrid materials represents an opportunity for the design of materials with improved properties (stability, charge

propagation dynamics) and enhanced energy storage capabilities. The hybrid electrodes were prepared as thin films on carbon foil using chemical–Electrochemical (Ch–ECh) method and electrochemical method. The results show that the resulting hybrid polymer displays the combined activity of its organic and inorganic components to store and release charge in a solid state electrochemical capacitor device.

Wang *et al* was achieved a capacitance value of  $144 \text{ F g}^{-1}$  at the scan rate of  $200 \text{ mV s}^{-1}$  for single-wall carbon nanotube/PPyfilm[5]. The Mi *et al* was examined electrochemical performance of organometallic-functionalized carbon nanotube-based Ppynanocomposites [6]. Zhang *et al* was synthesized PPy/grapheme nanocomposites via in situ polymerisation [7]. The structural features of the nanocomposite are described in FTIR and Raman spectroscopic analysis. Wang *et al* was synthesized a nanocomposite of graphene oxide doped with PANI via in situ polymerization to improve the electrochemical capacitance performance of PANI [8]. Graphene oxide was synthesized using natural graphite (30  $\mu\text{m}$ ) by a modified Hummers method [9]. Li *et al* was prepared grapheme nanosheets by the exfoliation of graphene oxide by microwave irradiation [10]. The electrochemical performance shows that the graphenenanosheets with undestroyed framework are effective to enhance the electrochemical capacitance of the composite. Lu *et al* demonstrated that hydrogenated  $\text{TiO}_2$  nanotube arrays served as a good scaffold to support  $\text{MnO}_2$  nanoparticles, leading to a specific capacitance of 912 F/g at a scan rate of 10 mV/s [11]. The Al doped ZnO and ZnO nanowire arrays grown directly on stainless steel substrates were fabricated by a facile hydrothermal method. The extraordinary super capacitor performance and the cost-effective and scalable synthesis approach suggest that Al-ZnO/ $\text{MnO}_2$  hybrid electrode could be considered as promising electrode material for super capacitor applications. Yang *et al.* was prepared PPy/GO composite galvanostatically, and the resulting film was subjected to post electrochemical

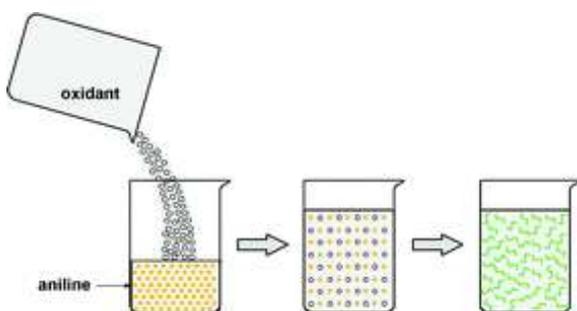
reduction to form PPy-reduced GO film [12]. Bose *et al* used the most commonly method for the synthesis of PPy and graphene nanocomposites is in situ polymerization [13, 14]. Huang *et al* was synthesized Graphene oxide using a simplified Hummer’s method [15]. The ZnO nanodots were deposited onto the carbon nanotubes film by ultrasonic spray pyrolysis (USP) technique. Excess ZnO in CNT–ZnO nanocomposite is deteriorate the capacitive performance by destroying the network structure of the CNT matrix and lowering the conductivity of the electrode. Liu *et al* was demonstrated the preparation of a composite material consisting PANI and silicon nanoparticles [16]. Liu *et al* were fabricated Flexible capacitor sheets using by electrochemical etching method [17]. In this work we developed ZnO nanocomposite. And results of the present work indicate the nanocomposite materials will be allocable for super capacitor.

## II. EXPERIMENTAL

### 2.1 Synthesis of materials:

#### 2.1.1. Synthesis of Polyaniline:

Polyaniline can be synthesized by electrochemical and chemical oxidative polymerization methods [18]. The chemical oxidative polymerization process is of importance since this is the most feasible route for the production of polyaniline on a large scale [19,20]. In this work we used the oxidative polymerization method. The aniline monomer (1M) and ammonium persulphate (1 M) were taken as starting chemicals. The chemical used in this work were of AR grade (SD Fine India). The desired quantity of ammonium persulphate was dissolved in distilled water separately and added in drop wise manner in aniline monomer at room temperature under constant stirring. This reaction mixture was kept for overnight (12 h) under constant temperature to achieve good quality polymerization. The final product appears greenish which was collected on a filter paper and washed with distilled water. The synthesized polyaniline was dried at room temperature. Fig. 1 represent preparation of polyaniline by oxidative polymerization method. The as-synthesized powder was characterized by XRD analysis using RigakuMiniflex-II in the 2θ range 10-70°.



**Fig1: Preparation of polyaniline by Oxidative polymerization method**

#### 2.1.2 Preparation of Composites

In the present work, various compositions were prepared by varying the concentration of ZnO nanoparticles. ZnO nanoparticles were directly procured from SD Fine,

India. The weight % method was adopted for the preparation of composites. The concentration of ZnO was varies between 20-80 wt.% range with an interval of 20 wt.%.

## 2.2 CHARACTERIZATION:

### 2.2.1 XRD:

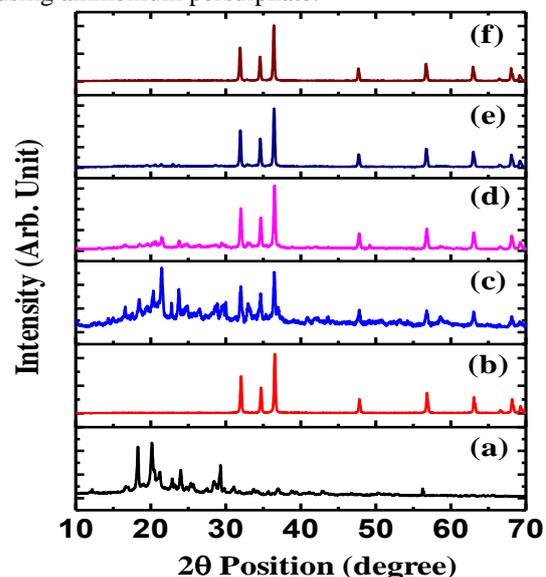
The X-ray powder diffractometer (XRD) is rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized and average bulk composition is determined.

X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg’s Law ( $n\lambda=2d\sin\theta$ ). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample.

## III. RESULTS & DISCUSSION

### 3.1 XRD Analysis

Figure (a) represents the XRD pattern of as-synthesized polyaniline. Pattern consist some sharp peaks between 15-30°. This shows that good degree of crystallization is present in the as-synthesized polyaniline using ammonium persulphate.



**Fig. 2 XRD pattern of polyaniline doped ZnO.**

The sharp peak present over the broad hump is observed in the pattern. This shows that final product acquired semi-crystalline nature. The prominent peaks appear at 18.41, 20.02, 23.99, 29.44 and 56.33 2θ Position was used to compute polymer chain separation. The relation between polymer chain separation (R) and diffraction peak position is given by Eq.1.

$$R = (5\lambda) / (8\sin\theta) \quad (1)$$

Where,  $\lambda$  is wavelength of X-rays (1.54 Å).

The values of polymer chain separation for respective diffraction peaks are listed in Table 1. The average polymer chain separation of prepared polyaniline was found to be 4.41 Å.

Figure (b) represents the XRD pattern of as-synthesized ZnO. Pattern consist some sharp peaks between 30-40°. The sharp peak is observed in the pattern. This shows the final product acquired crystalline nature. The concentration of ZnO varies between 20-80 wt. % range with an interval of 20 wt. % as shown fig (c), (d), (e) and (f) respectively. The values of polymer chain separation for the respective diffraction peaks are listed in Table 1. The average polymer chain separation of concentration of ZnO for 20wt.%, 40wt.%, 60wt.% and 80wt.% are 3.234Å, 3.454Å, 2.71Å and 2.674Å respectively.

**Table 1. Represent the Significant Peaks and Average polymer chain separation**

S. N	Sample	Significant Peaks					Average Polymer Chain Separation
		1	2	3	4	5	
1	Polyaniline	6.06	5.53	4.63	3.79	2.04	4.41Å
2	ZnO	-	-	-	-	-	-
3	20 Wt.%	3.92	3.56	3.23	3.08	2.38	3.234Å
4	40 Wt.%	5.16	3.46	3.20	3.07	2.38	3.454Å
5	60 Wt.%	3.50	3.23	3.08	2.02	1.72	2.71Å
6	80 Wt.%	3.53	3.22	3.07	1.85	1.70	2.674Å

#### IV. CONCLUSIONS

In the present work, we successfully synthesized the polyaniline by oxidative polymerization route using ammonium persulphate as an oxidant and various compositions were prepared by varying the concentration of ZnO nanoparticles. The average polymer chain separation for polyaniline was found to be 4.41 Å. This synthesized polyaniline/ZnO nanocomposite are useful for super capacitive application

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