Synthesis and Optical Properties of Zinc Ferrite / Polyaniline Nanocomposites

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***Abstract*— A conducting polymer/ ferrite nanocomposite system has been introduced to improve its engineering applicability or physical properties and electrical conductivity over a pure conducting polymer. Such material possesses advantages of both low dimensional system and organic conductors. In this investigation, polyaniline/zinc ferrite (PANI/$ZnFe_2O_4$) nanocomposites of various compositions (PZF-10, 20, 30%) were prepared by the method of in situ polymerization of aniline in aqueous solution of Sulfuric acid, with different percentage of ferrite powder. The structural and optical properties of synthesized PANI/$ZnFe_2O_4$ nanocomposites in terms of X-ray diffraction, Transmission electron microscopy and UV-Visible spectroscopy are studied. Substitution of $ZnFe_2O_4$ content in PANI has a marked effect on structural and optical properties. Particle size estimated by Transmission electron microscopy pattern was well consistent with that of X-ray diffraction results. Energy band gap of all synthesized sample were calculated from UV-Vis absorption spectroscopy.**

Keywords*— $ZnFe_2O_4$ nanoparticles; reflux method; in-situ polymerization; energy band gap

I. INTRODUCTION

Conducting polymer ferrite nanocomposites have attracted significant academic and technological attention because of their unique physical properties and potential applications in nanoelectronics, electromagnetic and biomedical devices. These conducting polymer when interacts with ferrite nanoparticles because of possible interaction between inorganic nanoparticles and polymer matrices may generate some unique properties upon the formation of polymer /ferrite nanocomposites[1]. Among π-conjugated conducting polymers, Polyaniline (PANI) is especially attractive because of its thermal and environmental stabilities [2]. PANI has many applications in various fields such as electromagnetic shielding, microwave absorbing materials, batteries, sensors, corrosion protection. When nanosized filler particles like $ZnFe_2O_4$ nanoparticles combined with PANI matrix, resulting nanocomposites show enhance magnetic and transport properties due to low dimensional magnetic system applications. Nowadays PANI has been successfully synthesizing with different nanocomposites [3-5]. Our aim is to synthesize PANI/$ZnFe_2O_4$ nanocomposites because of its commercial applications in color imaging, ferrofluids, magnetic refrigeration, information storage and medical diagnosis [6]. A.H.Elsayed and coworkers synthesized Polyaniline (PANI-EB) containing MFe_2O_4 (M is an element in a divalent state; M^{2+}= Fe^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, and Zn^{2+}) prepared by chemical method [7]. The electrochemical corrosion protection performance of polyaniline coated Fe_3O_4 pigmented coating material has been studied by J.Alam and M.Kashif by using potentiodynamic polymerization technique[8]. Hossein Eisazadeh and Hamid reza Khorshidi synthesized composite of polyailine containing Fe_2O_3 and CoO with nanometer size using hydroxyl-propylcellulose as surfactant [9]. Hollow polyaniline/Fe_3O_4 microsphere composite with electromagnetic properties were successfully prepared by decorating the surface of hollow polyaniline/ sulfonated polystyrene microsphere with various amount of Fe_3O_4 magnetic nanoparticles [10]. In the present study, we report the synthesis of $ZnFe_2O_4$ nanoparticles by using reflux method and used them for the preparation of PANI/$ZnFe_2O_4$ nanocomposites by using in-situ polymerization method to study structural and optical properties.

II. EXPERIMENTAL

A. Materials

PANI and PANI/$ZnFe_2O_4$ nanocomposites powders were prepared according to the previously reported method [11-12]. Aniline monomer was distilled under reduced pressure and stored below 0^0C, Sulphuric acid (H_2SO_4), Ammonium peroxydisulfate (APS), NaOH, Zinc nitrate [$Zn(NO_3)_2.6H_2O$], Ferric nitrate [$Fe(NO_3)_3.9H_2O$] and starch $(C_6H_{10}O_5)_n$, distilled water, acetone (99%) and methanol (99%) were bought from S.D. Fine-Chem. Ltd. and used as received without further purification. All chemicals were of analytical grade.

PANI/$ZnFe_2O_4$ nanocomposites have been characterized by X-ray diffraction (XRD) analysis conducted on Philips PW1710 automatic X-ray diffractometer with Cu-K_α radiation (λ = 1.5428 Å), with a scanning speed of 10° min^{-1}. The morphology and structure of $ZnFe_2O_4$ and PANI/$ZnFe_2O_4$ nanocomposites were investigated by TEM. The optical absorption spectra of PANI and PANI/$ZnFe_2O_4$ nanocomposites were carried out using UV-1800 double beam UV-VIS spectrophotometer.

B. Synthesis of PANI/ $ZnFe_2O_4$ nanocomposites

$ZnFe_2O_4$ nanoparticles were prepared by the simple reflux method as reported in our earlier article[13]. $ZnFe_2O_4$ nanoparticles have been abbreviated as ZF whereas PANI/$ZnFe_2O_4$ nanocomposites were abbreviated as PZF respectively.

PANI/ $ZnFe_2O_4$ nanocomposites of various compositions were prepared by the method of in-situ chemical oxidation polymerization of aniline in aqueous solution of Sulfuric acid using APS as an oxidant, with different percentage of $ZnFe_2O_4$ powder (10, 20, 30%) at room temperature. 0.1M of pure aniline and APS were dissolved separately in 1M of aqueous H_2SO_4 solution to start the polymerization of aniline and stirred for 1hour. 10, 20, 30% of corresponding nanoferrite was added in resulting solution and sonicated for 1Hr in order to reduce the aggregation of ferrite nanoparticles. Stirr the solution until a good degree of polymerization was achieved. The precipitate produced in the reaction was removed by filtration, washed repeatedly with 1M of H_2SO_4 and dried under vacuum for 24 Hrs. This has been led to the formation of PANI/ $ZnFe_2O_4$ nanocomposites. The different content of PANI/$ZnFe_2O_4$ nanocomposites were abbreviated as PZF-10, PZF-20, PZF-30% respectively for PANI/ $ZnFe_2O_4$ (10%), PANI/ $ZnFe_2O_4$ (20%), PANI/ $ZnFe_2O_4$ (30%).

III. RESULTS AND DISCUSSION

A. X-Ray Diffraction (XRD)

XRD spectra of $ZnFe_2O_4$ nanoparticles, PANI/$ZnFe_2O_4$ nanocomposites and PANI are given in Fig.1. It can be seen from the figure that all the main peaks are related to a single phase spinel structure. The spectra did not show any other peaks for impurities, suggesting the product consists of the pure phase of the material. The broadening nature of the diffraction peaks refers to the small dimension of $ZnFe_2O_4$ nanoparticles. The average crystallite size of $ZnFe_2O_4$ nanoparticles was found by the scherrer formula is 16nm. The XRD pattern for PANI shows amorphous nature in partially crystalline state with two diffraction peak at about $2\theta = 20.3^0$ and 26.1^0[14].

Fig.1 also gives the XRD pattern of PANI/$ZnFe_2O_4$ nanocomposites under investigation. XRD pattern of nanocomposites show crystalline nature due to the presence of ferrite nanoparticles. It can also be observed that the diffraction peaks were broadened initially for pure ferrite and became narrow after the interaction with PANI.

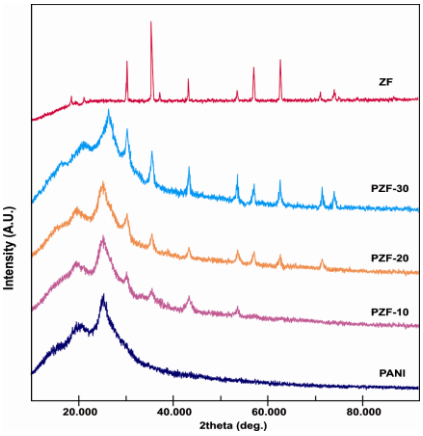

Fig.1. XRD spectra of PANI, $ZnFe_2O_4$ (ZF) and PANI/$ZnFe_2O_4$ nanocomposites

B. Transmission electron microscopy

Fig. 2a,2b and 2c,2d shows TEM and SAED pattern of $ZnFe_2O_4$ nanoparticles and PANI/$ZnFe_2O_4$ nanocomposites (PZF-30%). It is clearly seen from the TEM pattern $ZnFe_2O_4$ nanoparticles have triangular morphology whereas that of PANI/$ZnFe_2O_4$ nanocomposites show s same morphology suggesting coating of PANI on $ZnFe_2O_4$ nanoparticles. The particle size of $ZnFe_2O_4$ nanoparticles observed by TEM pattern was 20 nm, which is consistent with the XRD result estimated by Scherrer formula, while PANI/$NiZnFe_2O_4$ nanocomposites having particle size of 50 nm. Selected area electron diffraction (SAED) pattern of $ZnFe_2O_4$ nanoparticles and PANI/$ZnFe_2O_4$ nanocomposites (PZF-30%) were shown in Fig.2c and 2d. It consist of concentric rings indicating (hkl) reflection.

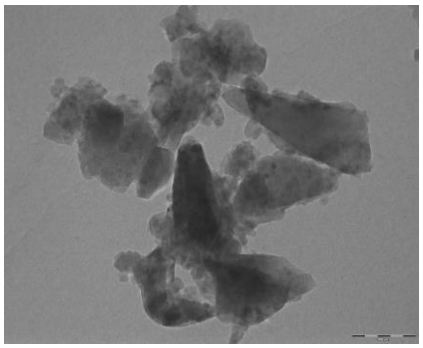

Fig.2a. TEM image of $ZnFe_2O_4$

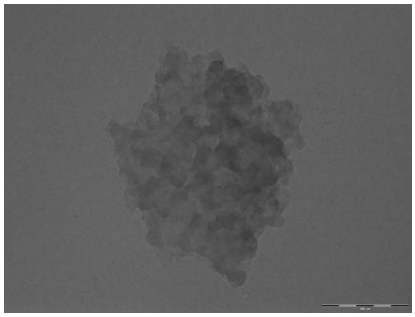

Fig.2b. TEM image of PANI/$ZnFe_2O_4$ nanocomposite(30%)

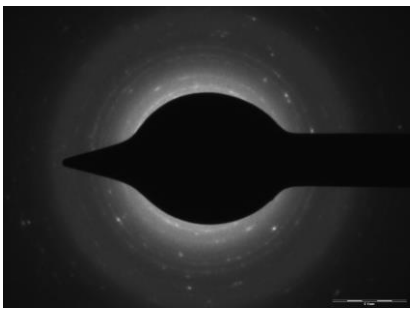

Fig.2b. SAED pattern of $ZnFe_2O_4$

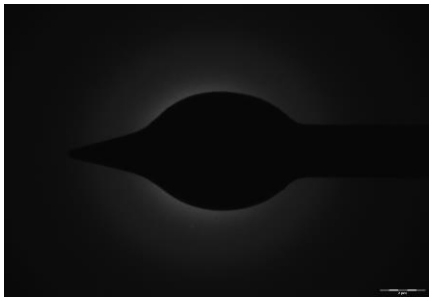

Fig.2b. SAED pattern of PANI/$ZnFe_2O_4$ nanocomposite(30%)

C.UV-Visible spectroscopy

Fig.3 shows UV-Visible spectra of PANI and PANI/$ZnFe_2O_4$ nanocomposites. UV-Visible spectra of PANI show two characteristic absorption bands at around 323 and 630 nm. Absorption peaks of PANI/$ZnFe_2O_4$ nanocomposites at 330nm, 345nm, 354nm and 610nm, 618nm, 623nm are attributed to π to π* transition of benzoid ring and exciton absorption of quinoid ring, respectively [15]. Formal absorption peak of the nanocomposites are shifted to a longer wavelength showing red shift with increasing ferrite content in the sample whereas latter peak are shifted to smaller wavelength showing blue shift with increasing ferrite content in the sample. These results suggest that there is good interaction between $ZnFe_2O_4$ nanoparticles and PANI chain. Band gap calculated for formal and latter peak was mentioned in Table.1.

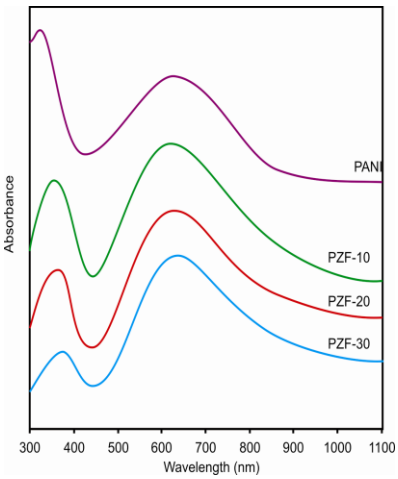

Fig.3. UV-Visible spectra of PANI and PANI/$ZnFe_2O_4$ nanocomposites

TABLE I. Wavelength for maximum absorbance and corresponding optical band gaps for PANI and PANI/$ZnFe_2O_4$ nanocomposites

Materials	***λmax(nm)***		***Band energy (eV)***	
PANI	323	630	3.84	1.97
PZF-10	330	610	3.76	2.03
PZF-20	345	618	3.59	2.00
PZF-30	354	623	3.50	1.99

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