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Chemical synthesis of ZnO/PANI nanocomposite and functional properties

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Abstract : A novel ZnO/PANI nanocomposite was successfully synthesized by wet chemical method using ethylenediamine tetra acetic acid (EDTA) as a capping agent. The capping mechanism is discussed based on the chemical reaction between the ZnO nanoparticles, the functional groups of the PANI and capping agent. The XRD analysis revealed that the addition of EDTA makes some effect on the crystallinity of ZnO/PANI nanocomposite. The FTIR spectra confirmed the interaction between EDTA and ZnO/PANI nanocomposite. Surface morphological studies, SEM and TEM showed the morphology of bundlelike ZnO/PANI nanocomposite. HRTEM image showed the grown of (002) planes of the hexagonal ZnO phase with the interplanar distance of 0.24 nm. The change in morphology of the synthesized composite was mainly due to the capping agent. The enhanced fluorescence of ZnO/PANI nanocomposite was observed. From the results it was found that the formation of ZnO/PANI nanobundle was due to the interfacial contact between ZnO, PANI and EDTA.
Keywords: ZnO, PANI, EDTA, FTIR, XRD, SEM, Fluorescence, TEM, HRTEM.

Introduction

Nanosized semiconductor materials have attracted considerable efforts in recent years. Zinc Oxide (ZnO) is one of the extensively studied II–VI semiconductor materials mainly due to its attractive optoelectronic properties such as wide band gap (3.37 eV), and large exciton binding energy (60 meV) at room temperature[1,2]. It has potential applications in various fields such as diode lasers, solar cells, gas sensors and catalyst for electronics[3,4,5,6,7,8,8,9,10]. Furthermore, ZnO is an environmental friendly material which is highly desirable especially for renewable energy and biological applications. Compared to other metal oxide nanomaterials, zinc oxide displays novel nanostructures such as nanosprings, nanobelts, nanorings, nanotetrapods and nanowires[11,12].In recent years, the development of inorganic/polymer hybrid materials on nanometer scale have been receiving significant attention due to a wide range of potential applications in

optoelectronic devices and in field effect transistors. The inorganic fillers at nanoscale exhibit high surface to volume ratio and thus expected to modify drastically the electrical, optical and dielectric properties of polymer. Polyaniline (PANI) is a most studied polymer because of its relative ease in preparation, good environmental stability and tunable conductivity[13]. Among the various synthetic routes, ZnO/PANI nanocomposite is prepared by facile wet chemical synthesis using Ethylene diamine tetra acetic acid (EDTA) as a capping agent. In this work, the EDTA effect on size and morphology of ZnO/PANI nanocomposite is studied. The possible growth mechanism for ZnO/PANI nanostructures is discussed based on our experimental results.

Experimental

Synthesis of ZnO/PANI Nanocomposite

PANI was prepared by the standard oxidation of 0.2M aniline hydrochloride with 0.25M ammonium peroxydisulfate (APS) in an aqueous medium[14]. The prepared PANI (Emeraldine) salt was deprotonated with an excess of 1M ammonium hydrochloride, collected on a filter and dried in air[15]. The preparation of ZnO accomplishes the following steps: 0.3M of sodium hydroxide was dissolved in 50 ml of deionised water under magnetic stirring at 460 rpm at room temperature and 0.025M of EDTA was added to the mixture. After the complete dissolution of EDTA, 0.2M of zinc acetate was added to the solution. The reaction was continued for ten hours and then precipitates were washed with water for several times and centrifuged. Finally, the obtained product was dried at 150°C for five hours. In the preparation of ZnO/PANI nanocomposite, the prepared PANI was mixed with zinc acetate in the middle of the ZnO preparation.

Characterization Techniques

The obtained powder was characterized by X-ray diffraction pattern using the XPERT-PRO diffractometer system with Cu Kα radiation (λ=1.5406 Å) and the 2θ range was scanned from 10 to 80° continuously with rate of 2° per minute. FTIR spectra (SHIMADZU) of EDTA capped ZnO/PANI nanocomposite was studied in the frequency range of 400 - 4000 cm^{-1}. Morphological study of EDTA capped ZnO/PANI nanocomposite was carried out using scanning electron microscopy (JEOL JSM 5600) and Transmission electron microscopy (JEM 2010). Fluorescence spectra of PANI, ZnO and ZnO/PANI nanocomposite was carried out with a spectrofluorometer (RF-5301 pc).

Results and Discussion

XRD analysis

In Fig. 1 the observed XRD pattern of PANI, ZnO and ZnO/PANI nanocomposite were shown. Fig. 1(a) shows the amorphous nature of PANI[16]. Fig.1 (b) shows the sharp diffraction peaks apparent in the figure indicate good crystallinity of zinc oxide nanoparticles and reveals all diffraction peaks, which are perfectly similar to the literature (JCPDS no. 751526)[17]. The observed reflection planes resemble the tetragonal ZnO nanostructure, it can be seen that the reflections are markedly broadened, indicating crystalline size of ZnO nanoparticles of 28 nm by using Scherrer's equation[17]. Fig. 1(c) shows the XRD spectra for the ZnO/PANI nanocomposite. The peaks at 2θ = 35, 39,43,52,53 and 54 correspond to (200), (111), (201), (002), (300) and (211) plane of EDTA. The strong and sharp diffraction peaks of the ZnO/PANI nanocomposite indicate the obtained products are crystalline in nature and it is suggested that zinc oxide crystallites undergo interfacial interactions with PANI and loses its own morphology by the mixing of ZnO/PANI nanocomposites with the complexing agent EDTA.

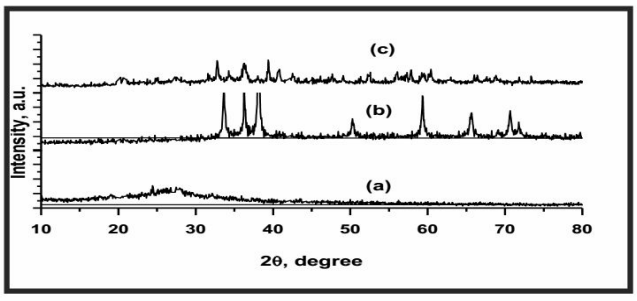

Figure 1 XRD pattern of (a) PANI, (b) ZnO and (c) ZnO/PANI nanocomposite.

FTIR analysis

Fig. 2 shows the FTIR spectra of the PANI, ZnO and ZnO/PANI nanocomposite. FTIR assignments of the samples are given in Table 1. The characteristic bands of PANI assigned as follows: C=N and C=C stretching modes for the quinoid and benzenoid rings occurs at 1570 cm^{-1} and 1481 cm^{-1} (Fig. 2a). The band at 1301 cm^{-1} had been attributed to C-N stretching mode for the benzenoid ring, while the band at 1139 cm^{-1} is assigned to the plane bending vibration of C-H(modes of N=Q=N, Q=NH^{+}-B and B-NH^{+}-B, Q represents the quinoid ring and B represents the benzenoid ring) which is formed during protonation[18, 19]. From Fig. 2b, the peak at 3421 cm^{-1} indicates the presence of -OH residue, probably due to the atmospheric moisture[20]. From Fig. 2c, it is evident that the composite contained contributions from both zinc oxide and PANI. For the bands at 1570 cm^{-1} corresponding to the stretching mode C=N is shifted to higher wavenumber 1581 cm^{-1} and the at 1481 cm^{-1} corresponding to the stretching mode C=C is shifted to lower wavenumber 1475 cm^{-1}. Similarly, the C-H band at 1139 cm^{-1} is shifted into 1029 cm^{-1} and 1089 cm^{-1}, it may be described due to the formation of hydrogen bonding between zinc oxide and NH group on the surface of PANI nanoparticles. This can be explained on the basis of constrained growth and restricted modes of vibration in zinc oxide grown in the presence of PANI. In such case, the oxide particles get absorbed on PANI chain, which were dispersed in the reaction mixture and the formation of nanoparticles proceeds initially on the surface of the polymer chains when EDTA is added to the solution[21]. This leads to the adhesion of the zinc oxide nanoparticles to the polymer chains and also act in the role of coupling of two polymer chains lead to cluster of ZnO/PANI nanocomposites. In order to investigate the presence of capping agent on the synthesised product, for the EDTA capped ZnO/PANI composite, the doublet peak observed at around 1125 cm^{-1} represents the stretching vibrations of CH-OH of EDTA molecule.

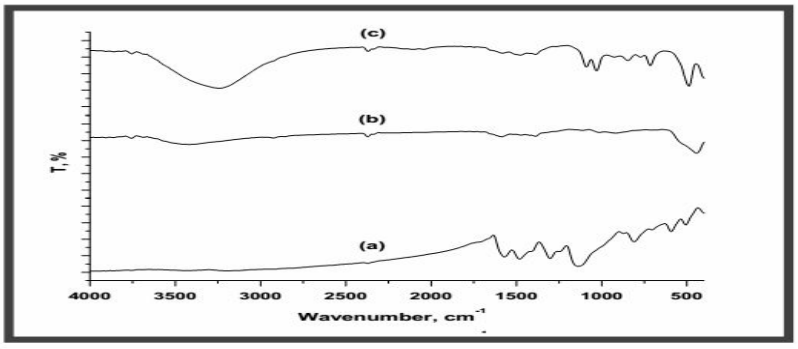

Figure 2 FTIR Spectra of (a) PANI, (b) ZnO and (c) ZnO/PANI nanocomposite.

Table 1. FTIR Spectra of PANI, ZnO and ZnO/PANI nanocomposite

Sample	Benzenoid cm^{-1}	Quinoid cm^{-1}	C-N cm^{-1}	N=Q=N cm^{-1}	C-H cm^{-1}	O-H cm^{-1}
PANI	1481	1570	1301	1139	810	.....
ZnO	.....	.....	.....	.....	.....	3481
ZnO/PANI	1475	1581	.....	1029, 1089	.....	...

Morphological studies

SEM analysis

Fig. 3 shows the SEM images of PANI, ZnO and ZnO/PANI nanocomposite. The micrograph confirms the formation of hybrid material, ZnO/PANI nanocomposite[22]. The micrograph of PANI indicates the agglomerated granular structure (Fig. 3a). Fig. 3b shows the petal-like structure of pure zinc oxide. Fig. 3c indicates the bundle of ZnO/PANI nanocomposite. The change in the surface morphology has been observed with the composition of EDTA in ZnO/PANI nanocomposite. The complex, stringy, interconnected network is a general feature of the morphology of EDTA capped ZnO/PANI nanocomposite. The morphology appears

almost bundle like with ZnO/PANI network surrounded by EDTA due to the strong intermolecular forces between them. The strong interactions between charged PANI chains, EDTA facilitate the formation of nanobundles. In the mechanism of nanobundle formation, EDTA has six reaction sites including four hydroxyl groups which can make coordination bond with Zn^{2+} ion and effectively modify the size and morphology of ZnO/PANI nanocomposite during the synthesis of wet chemical method[1, 13, 16].

TEM analysis

Fig. 4 shows the TEM and HRTEM images of ZnO and ZnO/PANI nanocomposite. The inset shows the ZnO nanoparticles. The HRTEM image indicates the highly uniform dispersion of particles with irregular shaped morphology and could not observe the grain boundaries in the strip (Fig. 4a and 4b). The results indicate that ZnO coexists with PANI and capped by the complexing agent EDTA. The interface between PANI and ZnO is observed clearly with the different boundary edges (Fig. 4c and 4d). However it is found that the very small particles connect with the edges of large particles and it should be noted that the size of the ZnO islands is not uniform. The interplanar spacing in the crystalline petal is 0.24nm, which corresponds to the distance between two (002) planes of the hexagonal ZnO phase, indicating the preferential growth along the (002) direction. The lattice plane fringes of the

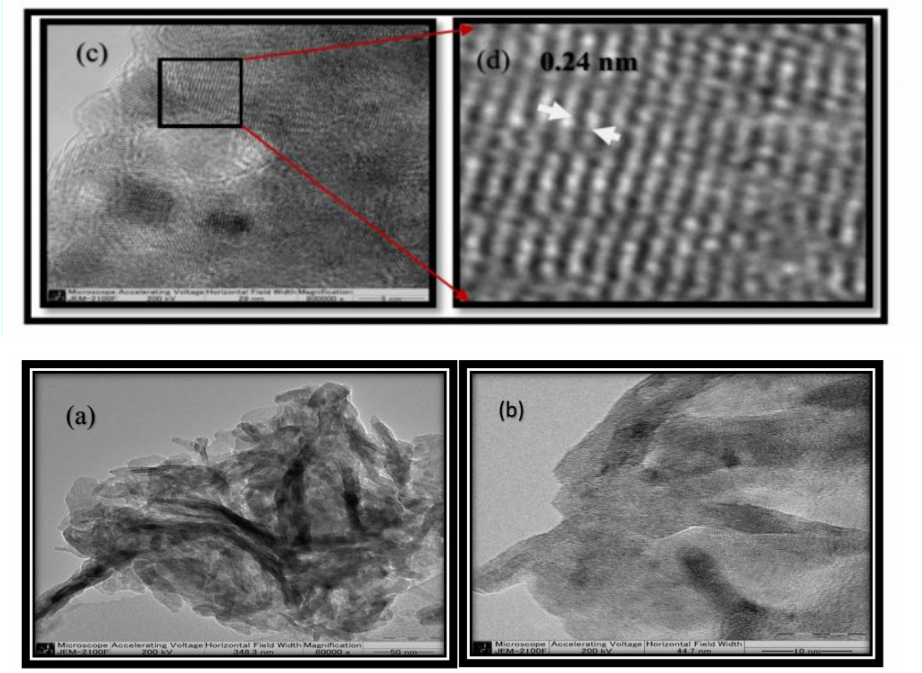

Figure 4 TEM and HRTEM images of ZnO /PANI nanocomposite (a, b). The inset shows the ZnO nanoparticles along the (002) direction (c, d).

ZnO nanoparticles are used to calculate the d- spacing values, indicating the formation of ZnO nanocrystals with different morphology depending on the reaction medium. The distance between the two lattice planes for ZnO were around 0.24 nm, which corresponds to the d- spacing of the (002) crystal planes respectively of the wurtzite ZnO[23].

Fluorescence Spectroscopic analysis

The ZnO/PANI nanocomposite was subjected to fluorescence spectroscopy to observe the excitation and emission phenomenon. Fig. 5 shows the fluorescence spectra of ZnO, PANI and ZnO/PANI nanocomposite which reveal the emission of radiation in the UV region. The emission of ZnO and ZnO/PANI were observed at 389nm with increased intensity. The PANI was observed at 388 nm.

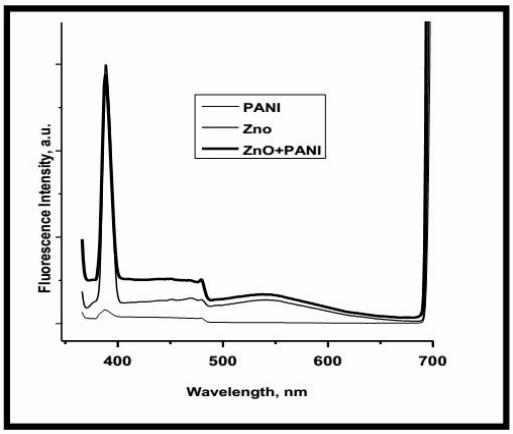

Figure 5 Fluorescence spectra of PANI, ZnO and ZnO/PANI nanocomposite

It is observed that the emission wavelength increases as ZnO increases, hence by adding composition of ZnO with PANI the radiation of desired wavelength can be obtained. Further it is also observed that the emission is very strong (highly intense) of ZnO. Therefore, the PANI with ZnO emits the radiation of 389 nm with high intensity. The result indicates that the composite has violet fluorescence emission[24].

Conclusion

In this paper we have reported the preparation of ZnO/PANI nanocomposite by wet chemical method which usually done by incorporating ZnO in the process of polymerization of aniline. But in this work, the PANI molecules were introduced while the formation ZnO nanoparticles in the presence of EDTA. This new method makes the novel structure of nanocomposite as nanobundle. Morphological changes of different boundary edges were obviously seen in the HRTEM images of ZnO/PANI nanocomposite. The composite compared to PANI and zinc oxide confirmed that the formation of ZnO/PANI nanobundle is distinct. The ZnO crystallites undergo interfacial interactions with PANI and lost its own morphology with the effect of EDTA.

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