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Enhanced photoluminescence in transparent thin films of polyaniline–zinc oxide nanocomposite prepared from oleic acid modified zinc oxide nanoparticles

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ABSTRACT

Oleic acid capped zinc oxide (ZnO) nanoparticles have been synthesized by a wet chemical route. The chemical oxidative method is employed to synthesize polyaniline (PANI) and PANI/ZnO nanocomposites doped with four different dopants such as orthophosphoric acid (H_3PO_4), hydrochloric acid (HCl), naphthalene-2-sulphonic acid and camphor sulphonic acid (CSA). The samples have been structurally characterized by X-ray diffraction (XRD), field emission scanning electron microscopy and Fourier transform infrared (FT-IR) spectroscopic techniques. A comparison of the photoluminescence (PL) emission intensity of PANI and PANI/ZnO nanocomposites is attempted. The enhanced PL intensity in PANI/ZnO nanocomposites is caused by the presence of nanostructured and highly fluorescent ZnO in the composites. It has been observed that, among the composites, the H_3PO_4 doped PANI/ZnO nanocomposite is found to exhibit the highest PL intensity because of the higher extent of (pi) conjugation and the more orderly arrangement of the benzenoid and quinonoid units. In the present work, transparent thin films of PANI and PANI/ZnO nanocomposite for which PL intensity is found to be maximum, have been prepared after re-doping with CSA by the spin-coating technique. The XRD pattern of the PANI/ZnO film shows exceptionally good crystallanity compared to that of pure PANI, which suggests that the addition of ZnO nanocrystals helps in enhancing the crystallanity of the PANI/ZnO nanocomposite. There is a significant increase in the PL emission intensity of the PANI/ZnO nanocomposite film making it suitable for the fabrication of optoelectronic devices.

1. Introduction

Polyaniline (PANI) has been one of the highly pursued conducting polymers due to its unique properties such as good electrical conductivity, interesting optical properties, excellent environmental stability and ease of synthesis [1–4]. Recently, it is also being used extensively as hole-injecting electrodes in polymer light emitting diodes (PLEDs) [5–8]. It has been reported that PANI doped with orthophosphoric acid exhibits quite high photoluminescence emission intensity [9]. The optical and opto-electronic properties of PANI can be tuned appropriately by suitable doping and also by preparing composites with appropriate materials. PANI has become one of the most technologically and industrially important conducting polymers owing to its unique processability together with the availability of relatively inexpensive precursors and better yields of polymerization.

Semiconductor nanoparticles have been under continuous scientific interest because of their unique quantum nature which influences the optical properties of materials to a significant extent. Among them, ZnO is a well known semiconductor with a wide and direct band gap of about 3.37 eV and a large exciton binding energy of 60 meV at room temperature which makes it a significant material for optical and optoelectronic applications [10]. ZnO has been reported to have excellent optical properties such as very good transparency in the visible region and excellent photoluminescence emission all through the visible region. Moreover, ZnO has potential applications in gas sensors [11], catalysts [12,13], microwave absorption [14] and ultraviolet (UV) shielding [15]. Therefore, incorporation of ZnO nanoparticles into polymer matrices can provide high performance materials suitable for device fabrication.

The present study is an attempt to synthesize PANI and PANI/ZnO nanocomposites both in bulk and thin film forms and analyze their photoluminescence emission characteristics. PANI/ZnO nanocomposites are prepared by in-situ polymerization of aniline in the presence of oleic acid (OA) modified ZnO nanoparticles. Oleic acid modified ZnO nanoparticles have been synthesized by the wet chemical method.

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Oleic acid is used for the surface modification of ZnO nanoparticles by introducing a long aliphatic chain and also the carbon – carbon double bonds. It is observed that OA modified ZnO nanoparticles can disperse well in organic solvents. In previous studies reported by our group, PL enhancement has been observed in oleic acid modified ZnO nanorods [16] and oleic acid modified PANI [17]. These findings form the motivation for the present work in which attempts have been made to explore in depth the effect of oleic acid modification on the photoluminescence characteristics of the PANI/ZnO nanocomposite.

Though, extensive work has already been carried out on PANI/ZnO nanocomposite films grown by solution casting [18], vacuum deposition [19] and spin-coating techniques [20–22], no detailed studies exist on the photoluminescence properties of transparent PANI/ZnO nanocomposite thin films deposited by the spin-coating technique. In a recent paper, studies on sandwiched polyaniline (PANI)/ZnO/PANI free-standing nanocomposite films have been reported with high PL emission intensity and reasonably good conductivity [23]. However, all these reports deal with investigations on rather thick films of thickness in the micrometer range. Spin coating is a more advantageous technique where the film thickness can be controlled by suitably adjusting the viscosity of the solution and the spinning speed and get homogeneous films with thickness around a few hundreds of nanometers. The present work is focused on the comparative study of the photoluminescence characteristics of PANI and PANI/ZnO nanocomposites. Transparent films of camphor sulphonic acid (CSA) re-doped PANI and PANI/ZnO nanocomposites could be realized by the spin-coating technique and detailed studies have been carried out on the photoluminescence properties of these films. In this context, the present work is significant and these transparent nanocomposite films with high luminescence intensity offer prospects of applications in different fields of nanophotonics.

2. Experimental details

2.1. Sample preparation

2.1.1. Synthesis of oleic acid capped zinc oxide nanoparticles

A simple wet chemical method was adopted for the synthesis of ZnO nanoparticles. Synthesis by a chemical route has the advantage of being more economical compared with the complex epitaxial methods. In addition, oleic acid was used as the capping agent to prevent growth and modify the size and shape of ZnO nanoparticles. Zinc acetate dehydrate was mixed with sodium hydroxide in 1:2 molar ratio in the presence of oleic acid under magnetic stirring for 2 h. The colloidal solution thus obtained was filtered and dried in hot air oven at 50 °C to get the white ZnO powder which was used for structural analysis and also for preparing PANI/ZnO nanocomposites.

2.1.2. Preparation of PANI and PANI/ZnO nanocomposites

To prepare doped samples of PANI and PANI/ZnO nanocomposites, distilled aniline (AR grade, Spectrochem Pvt Ltd, Mumbai, India) was dissolved in the dopant acid solution. Four different acids such as orthophosphoric acid (H_3PO_4), hydrochloric acid (HCl), naphthalene-2-sulphonic acid (NSA) and CSA were used as the dopants. The oxidizing agent ammonium persulphate (Laboratory Rasayan, extra pure, India) was added drop-wise under constant stirring at 0 °C. During the stirring, oleic acid capped zinc oxide powder was added for synthesizing the PANI/ZnO nanocomposite. The monomer to oxidizing agent ratio was kept at 1:1. After complete addition of the oxidizing agent, the reaction mixture was kept under constant stirring for 4 h. Precipitated powder was filtered and washed with distilled water until the filtrate was colourless. Finally, the green powder obtained was dried in an oven at 80 °C for 12 h.

2.1.3. Preparation of CSA re-doped PANI and PANI/ZnO nanocomposite thin films

H_3PO_4 doped PANI and PANI/ZnO nanocomposite samples were de-doped using 1 M ammonia solution and then re-doped using CSA (1 M). These re-doped samples were dissolved in m-cresol (LR, Laboratory Rasayan, Sd fine Chem. Limited, Mumbai), stirred and ultra-sonicated to obtain good solutions. Films were then coated on ultrasonically cleaned and optically flat glass slides by the spin-coating (Spin 150) technique with 1000 rpm for 30 s to get good quality transparent films. The thickness of the films can be controlled by suitably adjusting the coating time and speed of the spin coating unit. The thickness of these films was recorded using a Veeco Dektak 6 M stylus profiler.

2.2. Characterization

Field emission scanning electron microscopy (FESEM) images of the samples were obtained using a HITACHI SU 6600 microscope with an accelerating voltage of 20 kV. The surfaces of the ZnO nanoparticles, PANI and PANI/ZnO nanocomposite samples were studied using FESEM. X-ray diffraction (XRD) analysis of the samples was done using a Rigaku X-ray diffractometer with Cu-Kα (1.5418 A°) radiation operating at 30 kV and 20 mA. Scanning was carried out in the 2θ range from 10°–70° at a scan speed of 2° per minute. FT-IR spectra of the samples were obtained with an AVTAR 370 DTGS FT-IR spectrophotometer in the wave number range 400–4000 cm^{-1}. Thermo gravimetric analysis (TGA) of PANI and PANI/ZnO nanocomposite samples was carried out on a Diamond TG/DTA instrument. Samples were heated to 800 °C at a scan rate of 10 °C per minute in nitrogen atmosphere. UV–VIS- NIR absorption spectra absorption spectra were recorded on a Jasco-V 500 spectrophotometer in the wavelength range 200–800 nm. The photoluminescence emission spectra of the samples were obtained with Fluoromax-3 Spectrofluorimeter using Xe lamp as excitation source.

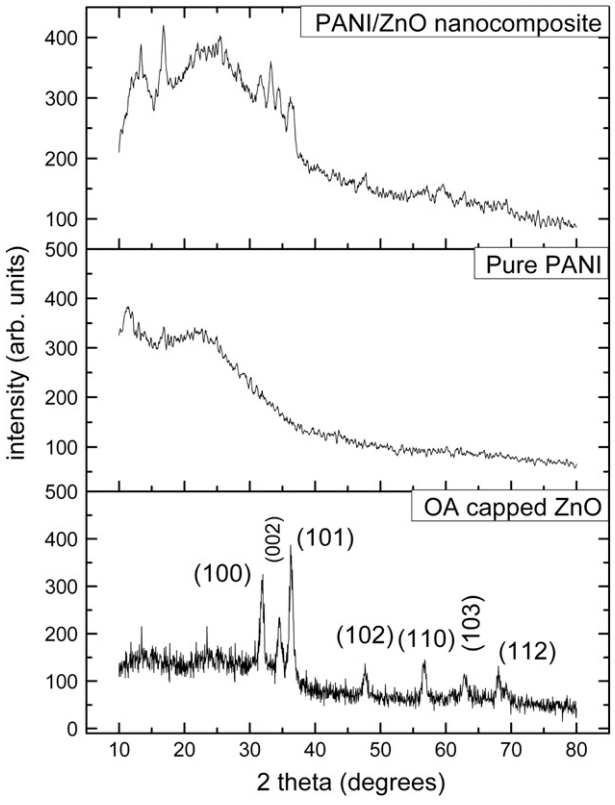

Fig. 1. XRD patterns of OA capped ZnO, pure PANI (H_3PO_4 doped) and PANI/ZnO nanocomposite (H_3PO_4 doped).