

Heterostructure Formation of Polyaniline/ZnO Nanoparticulate Thin Film using Electrophoretic Deposition Technique

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Introduction

ZnO is one of the most promising materials among metal oxides that show quantum confinement effects [1] in an experimentally accessible range particle sizes. It has immense potential for a wide range of technological applications in the field of emission displays, gas sensors, photovoltaic devices etc [2–4]. On the other hand, amongst conducting polymers, polyaniline (PANI) is one of the most studied electrically conducting polymers because of its good processibility, environmental stability and potential in the field of catalysis, biosensors, batteries, and electronic technology [5]. PANI has a unique feature due to the presence of reactive –NH– groups in the polymer chain which imparts chemical flexibility to the system and improves the processibility to a large extent. High quality Schottky junctions or p-n junction diodes are required for realizing the performance of optical and electronic devices based on ZnO. Considerable literature on the fabrication of Schottky contacts using high work function metals (Au, Pd, Pt, etc) and n-type ZnO have been reported [6-8].

This study deals with the fabrication of inorganic/organic heterostructure diodes using electrophoretic process for depositing organic materials (PANI, p-type) film on inorganic n-type ZnO nanoparticulate thin film substrate with top Pt thin layer contact. The I-V characteristics measurements, both forward and the reverse biased were performed to confirm the formation of Pt/PANI/ZnO p-n heterostructure diodes.

Experimental

2.1 Synthesis of ZnO nanoparticles

In a typical experiment; 0.3 mole zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$, Aldrich, 98% assay) and 2 mole thiourea (NH_2CSNH_2 , Aldrich) were dissolved in 100 ml deionized water and stirred for 30 min. The solution was then transferred in a three-necked refluxing pot and refluxed for 12 h at 90°C. After refluxing, the white precipitate was washed several times with methanol and annealed in an ambient air at 700°C, for one hour at the annealing rate of 5° C/min.

2.2 Synthesis of Polyaniline

Chemical oxidative polymerization of aniline was performed by taking conc. 1 N HCl solution with constant stirring at room temperature. A separate solution of 1M ammonium peroxydisulfate (APS) was prepared in the aqueous medium. Prior to mixing, both the reactants were pre-cooled on an ice-bath container. Thereafter, 20 ml of aqueous APS solution was slowly added (drop wise) to 20 ml of as prepared aniline solution with constant stirring at room temperature (298 K). The stirring was continued for 10 h. The obtained PANI (emeraldine salt (ES)) was filtered and washed with distilled water and dried at 50°C in vacuum oven.

2.3 Electrophoretic Deposition of Polyaniline

A stock solution of PANI (1 mg/ml) was prepared by dissolving PANI powder in formic acid. Further, 10 ml of 10 mg/l PANI colloidal suspension was prepared by adding 100 μ l of the stock solution into 9.9 ml of acetonitrile. Gentle shaking or brief sonication of the reaction mixture for a while was sufficient to disperse the PANI colloids.

2.4 Fabrication of p-n hetero structure

The nanocrystalline ZnO slurry was obtained by using of 0.5 g synthesized ZnO nanoparticles powder (particles size 50-70 nm) with the incremental addition of 2 ml polyethylene glycol (4 wt% PEG, Fluka, average MW of 20,000) solution. Each time, the aqueous PEG solution (0.1 ml) was continuously added to ZnO nanoparticles for achieving uniform slurry. Lump free slurry was formed. The ZnO nanoparticulate thin film with an active area $\sim 0.25 \text{ cm}^2$ was attained by simple doctor blade technique on FTO substrate and dried at 40°C under nitrogen. Finally, the ZnO deposited FTO substrates were subjected to sintering at 450°C for 30 min in a muffle furnace. These substrates were then subjected to the electrophoretic deposition of PANI to achieve the fabrication of p-n heterostructure.

Results and Discussion

The penetration of the PANI molecules into the crystalline ZnO nanoparticulate thin film upon electrophoretic deposition could be seen from Fig.1 (a). The accumulation of ZnO nanoparticles occur after the deposition of PANI which confirms the substantive interaction and of electrophoretic deposited PANI into the crystalline ZnO nanoparticulate thin film substrates. Fig.1 (b) shows a schematic diagram of PANI/ZnO p-n heterostructure diode where PANI (p-type) is electrophoretically deposited on the ZnO (n-type) nanoparticulate thin film with top Pt thin layer contact.

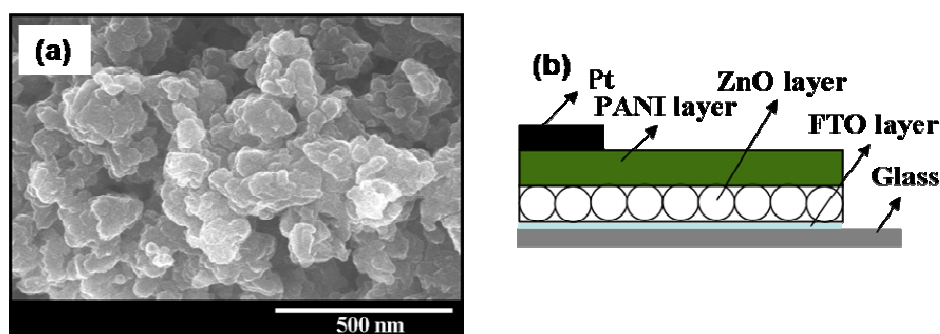


Figure 1: (a) Surface FE-SEM images of PANI/ ZnO nanoparticulate thin film (b) A schematic representation of p-n heterostructure diode of Pt/PANI/ZnO.

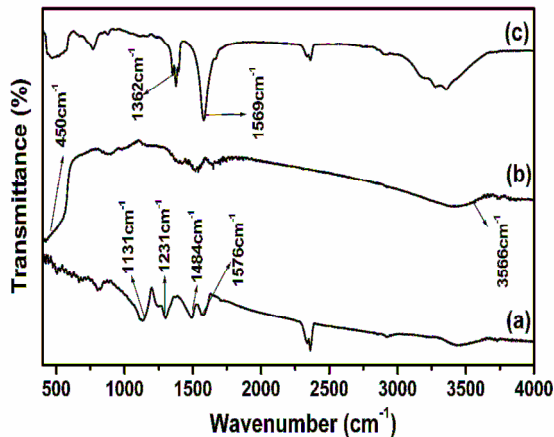


Figure 2: Typical FTIR spectra of (a) pristine PANI (b) ZnO nanoparticles and (c) PANI/ZnO nanoparticulate thin film.

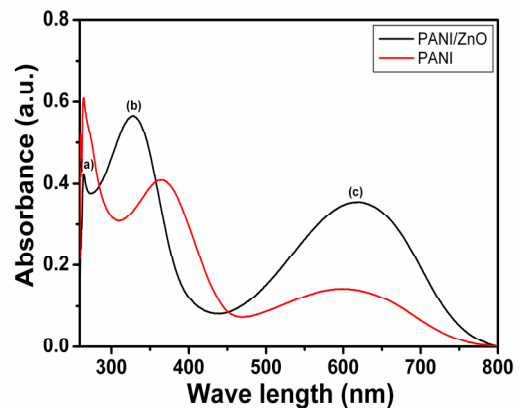


Figure 3: UV-Vis spectra of pristine PANI and PANI/ZnO nanoparticulate thin film.

Fig. 2 shows the FTIR spectrum of synthesized ZnO nanoparticles. The broad peak between 3343 and 3566 cm^{-1} is associated to the adsorbed H_2O molecule where as, the band at around 450 cm^{-1} corresponds to ZnO. Fig. 2 (a) depicts the characteristic peaks at 1576 cm^{-1} , 1484 cm^{-1} , 1231 cm^{-1} and 1131 cm^{-1} , correspond to C=C stretching mode of the quinoid rings, C=C stretching mode of benzenoid rings, C-N stretching mode and N=Q=N (where Q represents the quinoid ring) stretching respectively. On comparison, the presence of peak at $\sim 450\text{ cm}^{-1}$ and the shifted characteristic peaks at around 1569 cm^{-1} and 1362 cm^{-1} in PANI/ZnO nanoparticulate thin film confirm the bonding between the hydroxyl groups and the imine groups of the PANI molecules.

UV-Vis spectra, shown in Fig. 3 clearly exhibits the characteristic bands of PANI at 328 nm and 362 nm in PANI/ZnO nanoparticulate thin film and pristine PANI substrates respectively and are ascribed to $\pi-\pi^*$ transitions. However, the band at 604 and 618 nm is referred to $n\rightarrow\pi^*$ transitions and represent the polarons formation into the conducting PANI. In case of PANI/ZnO nanoparticulate thin film, the peak (a) retains its position, slight red shift for peak (b) is noticed and considerable large blue shift in peak (c) is ascribed to the selective interactions between ZnO and the quinoid ring of ES, facilitating charge transfer from quinoid unit of ES to ZnO via highly reactive imine groups.

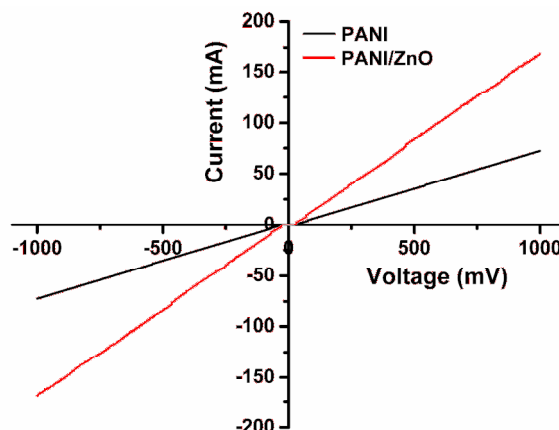


Figure 4: I-V characteristics of pristine PANI and PANI/ZnO nanoparticulate thin film

Current-voltage (I-V) measurements of PANI/ZnO heterostructure was carried out at 298 K with an applied voltage ranges from -1 V to +1 V. Fig. 4 shows the forward and reverse bias I-V characteristics of pristine PANI and PANI/ZnO heterostructure. The I-V characteristics of PANI exhibit almost the symmetrical behavior both in the reverse and the forward bias and the current increases linearly with the increased applied voltage. It is attributed that the formation of polarons and bipolarons in PANI increases rapidly and ultimately, contributing to the higher current in PANI at the high applied voltage. The PANI/ZnO heterostructure reveals that the forward bias current increases by a factor two with an increase in the applied voltage. On comparison with PANI, PANI/ZnO heterostructure obtains a high current which may due to the decrease in the width of the depletion layer at the interface of PANI and ZnO layer and contributes to the typical ohmic system. Thus, it is confirmed that a p-n heterostructure at nanostructured PANI/ZnO interface has been created.

Conclusion

A simple and easy route for the fabrication of PANI/ZnO p-n heterostructures has been demonstrated using electrophoretic deposition technique. The electrophoretic deposition is an effective method to broaden the absorption in visible light range for PANI/ZnO substrates. The I-V characteristics exhibit moderate rectifying and non-linear behavior of PANI/ZnO heterostructure with Pt contact layer. However, a typical ohmic behavior is observed at the interfaces of PANI and ZnO layers without Pt contact layer by I-V characterizations. A simple and the cost effective electrophoretic deposition technique provides the improved performance of the p-n heterostructure devices.

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