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Synthesis and Characterization of Polyaniline:TiO₂ Nanocomposites

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Thin films of polyaniline (PANi) and PANi:titanium oxide (TiO₂) composites have been synthesized by sol–gel spin coating technique. The TiO₂ powder of particle size 50–60 nm was synthesized by sol–gel technique and the polyaniline was synthesized by chemical oxidative polymerization of aniline. The composite films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) Fourier transform infrared (FTIR) and UV-vis spectroscopy, and the results were compared with polyaniline films. The intensity of the diffraction peaks for PANi:TiO₂ composites is lower than that for TiO₂. The characteristic FTIR peaks of PANi were found to shift to a higher wave number in the PANi:TiO₂ composite. These observed effects have been attributed to the interaction of TiO₂ particles with PANi molecular chains. The room temperature resistivity of polyaniline:nano-TiO₂ composite is $3.43 \times 10^3 \Omega \text{ cm}$ and the resistivity of pure nano-TiO₂ particles is $1.60 \times 10^6 \Omega \text{ cm}$.

Keywords FTIR, polyaniline, sol gel, spin coating, TiO₂, X-ray diffraction

INTRODUCTION

In recent years, the development of inorganic/polymer hybrid materials on nanometer scale has received significant attention due to a wide range of

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potential applications in optoelectronic devices [1–3] and in field effect transistors [4]. The inorganic fillers at nanoscale exhibit high surface-to-volume ratio, and thus are expected to modify drastically the electrical, optical and microscopic properties of polymers. In general, the synthesis of a hybrid polymer/inorganic material aims to obtain a new composite material with synergetic or complementary behaviors between the polymer and inorganic material. Polyaniline (PANi) is a most studied polymer because of its relative ease in preparation, good environmental stability [5,6] and tunable conductivity. Nano-TiO₂ also has excellent physical and chemical properties, and it has been used in coating, sensor, solar cell and photocatalyst technology [7–10]. At the present time, there are already reports on the preparation of a polyaniline/nano-TiO₂ composite. Feng et al. synthesized a composite of polyaniline encapsulating nano-TiO₂ particles by in situ emulsion polymerization, and investigated and explained the interaction between polyaniline and nano-TiO₂ particles and the nature of chain growth according to the result of Fourier transform infrared (FTIR) spectra [11]. Xia and Wang prepared a polyaniline/nanocrystalline TiO₂ composite by ultrasonic irradiation; they think that ultrasonic irradiation provides a new way to prepare 0–3-dimensional conducting polymer/nanocrystalline composites [12]. Somani et al. obtained a highly piezoresistive conducting polyaniline/TiO₂ composite by in situ deposition technique at low temperature (0°C) [13]. Since the conducting polyaniline and inorganic semiconducting material TiO₂ in nano form both have a wide range of technological applications, we were motivated to make a composite of PANi and TiO₂ and believed novel properties would result from the molecular level interaction of these two dissimilar chemical components [14,15]. However, to the best of our knowledge no study has been reported on the synthesis and structural, and morphological properties of PANi:TiO₂ composite by sol–gel spin coating method.

In this paper we report on the synthesis, structural, morphological, electrical and optical properties of PANi:TiO₂ composite by sol–gel spin coating method.

EXPERIMENTAL

Synthesis of Polyaniline

Polyaniline was synthesized by polymerization of aniline in the presence of hydrochloric acid as a catalyst and ammonium peroxodisulphate as an oxidant by the chemical oxidative polymerization method. For the synthesis, we took 50 ml, 1 M HCl, and 2 ml of aniline were added into a 250 ml beaker equipped with an electromagnetic stirrer. Then 4.9984 g of (NH₄)₂S₂O₈ (ammonium per oxydisulphate) in 50 ml, 1 M HCl was suddenly added into the above solution. The polymerization temperature ≈0°C was maintained

for 5 h to complete the reaction. Then the precipitate obtained was filtered. The product was washed successively by 1 M HCl followed by distilled water until the wash solution turned colorless. Then it was refiltered and washed once again by distilled water to obtain the emeraldine salt form of polyaniline. To obtain the emeraldine base form of PANi, the dedope ES form of PANi with 0.1 M NH₄OH solution was then dried at 60°C in vacuum for 24 h. Thus, we finally obtained a powder of insulating polyaniline (EB) polymer [16].

Synthesis of Nanocrystalline TiO₂

Nanocrystalline TiO₂ has been synthesized by a sol-gel method using titanium isopropoxide as a source of Ti. 3.7 ml of titanium isopropoxide was added to 40 ml of methanol and the mixture was stirred vigorously at temperature 60°C and stirred for further 1 h, resulting in white powder. The powder was annealed in a tubular furnace at 600°C for 1 h to get the TiO₂ nanopowder with particles of size 50–60 nm.

Synthesis of TiO₂-PANi Nanocomposite

The undoped polyaniline powder was dissolved in *m-cresol*. The solution was stirred for 11 h at room temperature and filtered. A thin film of this filtered undoped PANi was deposited by spin coating method on a glass substrate with 3000 rpm for 40 s and dried on a hot plate at 100°C for 10 min. The TiO₂ composites with undoped PANi were prepared by adding TiO₂ in different weight percentage (0–50 weight %) in a filtered solution of undoped PANi in *m-cresol* and stirring it for 11 h. Thin films of the composite were prepared on glass substrate by spin coating method at 3000 rpm for 40 s.

Characterization and Measurement Methods

X-ray diffraction (XRD) studies were carried out in 2θ range of 20–80° using an X-ray diffractometer (Model: Philips PW3710). The XRD patterns were analyzed by matching the observed peaks with the standard pattern provided by JCPDS file. Fourier transform infrared (FTIR) spectroscopy (Model: Perkin Elmer 100) of TiO₂, PANi and PANi:TiO₂ (50%) composites was studied in the frequency range of 400–4000 cm⁻¹. Morphological study of the films of PANi and PANi:TiO₂ composite was carried out using scanning electron microscopy (SEM Model: JEOL JSM 6360) operating at 20 kV. UV-vis spectra of the samples, which were dispersed in deionized water under ultrasonic action, were recorded on a Simandzu –100 UV-vis spectrophotometer. The resistivity measurements were made on thin films using four probe techniques at room temperature.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of pure polyaniline in the emeraldine base form, titanium oxide powder and PANi:TiO₂ (50%) composite. The XRD pattern of PANi shows a broad peak at $2\theta = 25.30^\circ$ which corresponds to (110) plane of PANi [16]. The patterns show sharp and well-defined peaks, indicating the crystallinity of the synthesized materials. The observed 2θ values are consistent with the standard JCPDS values (JCPDS No. 78–1285 and 86), which enumerate the mixed anatase and rutile tetragonal structure of TiO₂ [17]. The intensity of diffraction peaks for PANi:TiO₂ composites are lower than that for TiO₂. The presence of noncrystalline PANi reduces the mass–volume percentage of TiO₂ and sequentially weakens diffraction peaks of TiO₂. Figure 2 shows SEM micrographs of pure PANi, PANi–TiO₂ (50%)

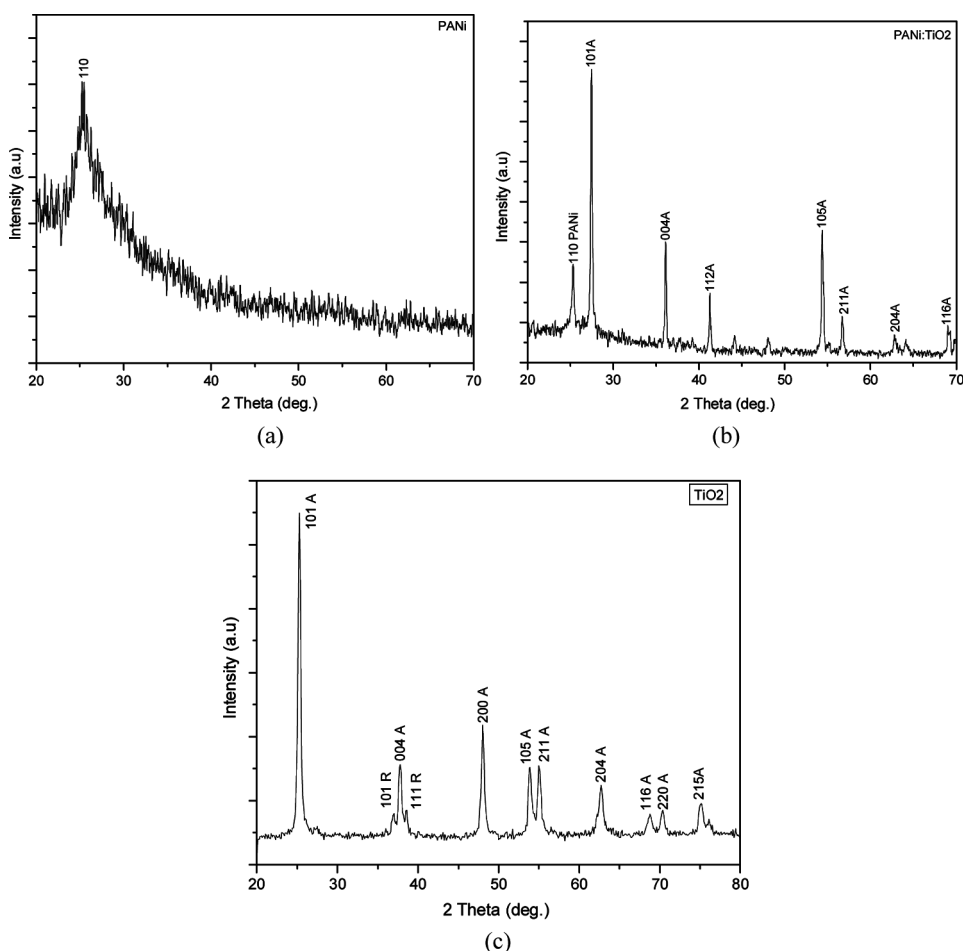


Figure 1: X-ray diffractogram of (a) PANi (EB), (b) PANi:TiO₂ composites, and (c) TiO₂.

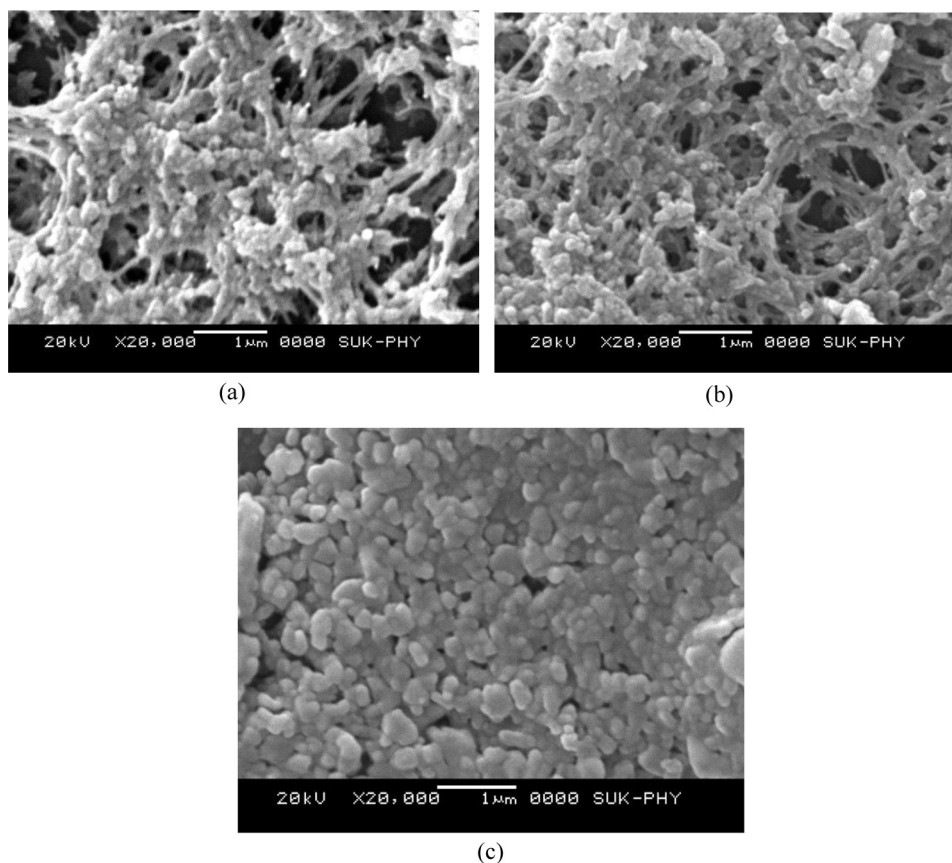


Figure 2: SEM micrographs of (a) pure PANi, (b) PANi:TiO₂, and (c) nano TiO₂.

and nano TiO₂. The SEM image of the composite shows that there is no agglomeration of TiO₂ particles in the PANi matrix, and there is a uniform distribution of the TiO₂ particles in the PANi matrix. According to the SEM images, it was considered that the nanostructured TiO₂ particles embedded within the netlike structure were built by PANi chains. It implies that the composite is highly microporous and is able to increase the liquid–solid interfacial area, and provides a path for the insertion and extraction of ions, and ensures a high reaction rate [18].

Figure 3 shows FTIR spectra of the undoped PANi, PANi-TiO₂ composite and TiO₂ nano particles. The origin of the vibrational bands is as follows: at 3225–3451 cm⁻¹ due to the NH stretching of aromatic amines, at 2845–2914 cm⁻¹ due to aromatic CH-stretching, and at 504 cm⁻¹ due to CH out-of-plane bending vibration. The CH out-of-plane bending mode has been used as a key to identifying the type of substituted benzene. The bands at 1572 and 1489 cm⁻¹ are attributed to the C=N and C=C stretching mode of vibration

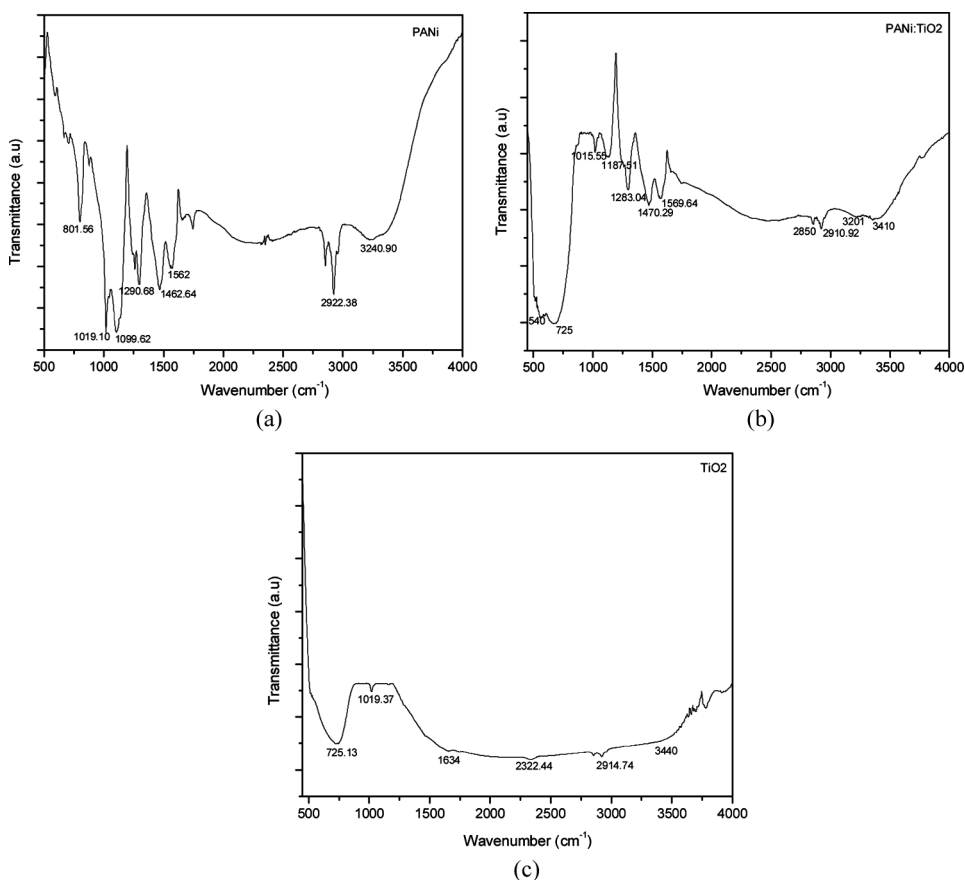


Figure 3: FTIR spectra of (a) PANi (EB), (b) PANi:TiO₂, and (c) nano TiO₂.

for the quinonoid and benzenoid units of polyaniline. The peaks at 1296 and 1239 cm⁻¹ are assigned to the C–N stretching mode of benzenoid ring. The peak at 1239 cm⁻¹ is the characteristic of the conducting protonated form of polyaniline. The bands in the region 1000–1115 cm⁻¹ are due to in-plane bending vibration of C–H mode. The bend at 797 cm⁻¹ originates from out-of-plane C–H bending vibration. The low wave number region exhibits a strong vibration around 725 cm⁻¹ which corresponds to the antisymmetric Ti–O–Ti mode of the titanium oxide.

UV-vis spectra of polyaniline, polyaniline/nano-TiO₂ composite and nano-TiO₂ particles are given in Figure 4. Figure 4(a) shows that three distinctive peaks of polyaniline appear at about 336, 451 and 924 nm, which are attributed to the π - π^* polaron- π^* and π -polaron transition [12,18], respectively. From Figure 4(b), it can be noted that the characteristic peaks of nano-TiO₂ and polyaniline (EB) all appear in the polyaniline/nano-TiO₂ composite. Moreover, the peak at 924 nm is obviously shifted from 924 to 865 nm. It indicates

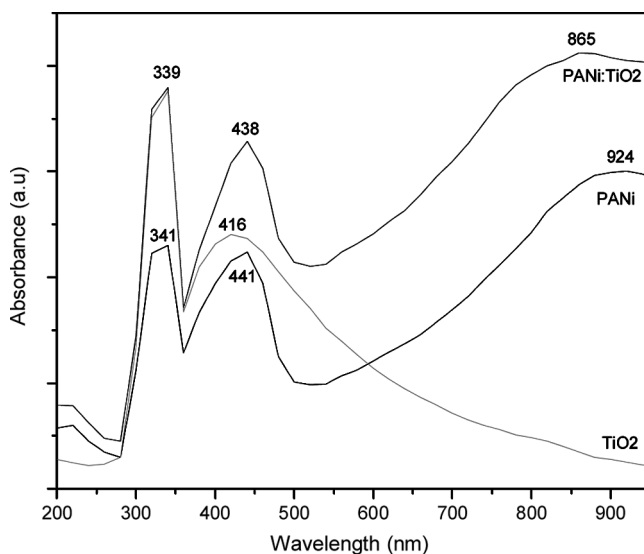


Figure 4: UV-vis absorption spectra of (a) PANi (EB), (b) PANi:TiO₂, and (c) nano TiO₂.

that insertion of nano-TiO₂ particles has the effect on the doping of conducting polyaniline, while this effect should owe to an interaction at the interface of polyaniline and nano-TiO₂ particles.

As seen from Figure 5, the plot of resistivity (ρ) vs. the TiO₂ content of nanocomposite films can be divided into three regions (i) for 0–20 wt% of TiO₂NP region where the resistivity increases slowly, (ii) for 20 wt% to

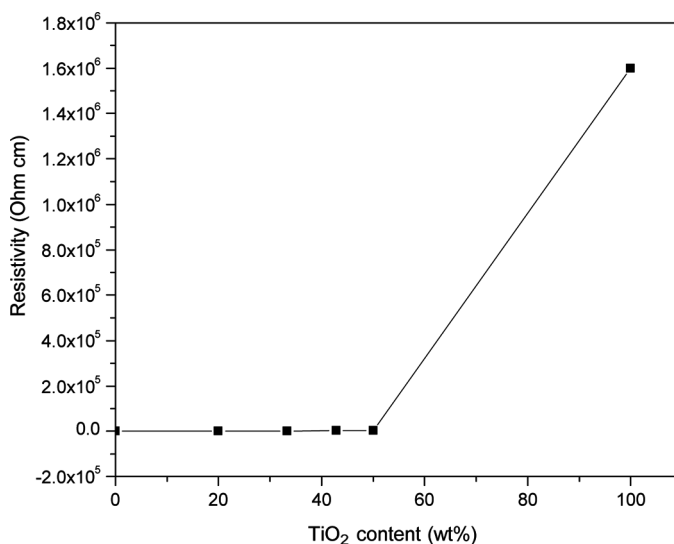


Figure 5: The plot of resistivity (ρ) vs. TiO₂ content of nanocomposite films.

35 wt%, where resistivity decreases rapidly, and (iii) for ≥ 35 wt% resistivity increases dramatically. This dramatic enhancement in resistivity arises because electrons from polar O^{2-} terminated TiO_2 nanoparticle surfaces are transferred to PANi chains, resulting in their reduction. In a highly reduced PANi, since conjugation is lost, charges can become strongly localized in the PANi ring.

CONCLUSION

Thin films of polyaniline and polyaniline: TiO_2 composites were synthesized by sol-gel spin coating techniques. The SEM study of PANi- TiO_2 composite film revealed uniform distribution of TiO_2 particles in the PANi matrix. The absorption peaks in FTIR and UV-vis spectra of PANi: TiO_2 composite films were found to shift to a higher wave number as compared to those observed in pure PANi. The observed shifts were attributed to the interaction between the TiO_2 particle and PANi molecular chains. A change in the value of the lattice parameter of TiO_2 in the PANi- TiO_2 composite was observed which also indicated the presence of interaction between TiO_2 particles and the PANi matrix. The room temperature resistivity measurement shows that the molecular chain constitution of polyaniline is the most important carrier in a polyaniline:nano- TiO_2 composite.

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