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Study of Effect TiO_2 Thin Film Morphological on Polyaniline/TiO_2 Solar Cell Efficiency

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ABSTRACT

In this work study preparation, structural, optical and electrical properties of polyaniline (PANi), nanocrystalline TiO_2 and PANi: TiO_2 nanocomposites. The TiO_2 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), field emission scanning electron microscopy (FESEM), Fourier transform infrared (FTIR) and UV-Vis spectroscopy and the results were compared with polyaniline films. The intensity of diffraction peaks for PANi: TiO_2 composites are lower than for TiO_2. The characteristic FTIR peaks of PANi were found shift to higher wave number in PANi: TiO_2 composite. These observed effects have been attributed to interaction of TiO_2 particles with PANi molecular chains.

Keywords: PANi, TiO_2; Sol gel; Solar cell

INTRODUCTION

Recently, organic-inorganic hybrid materials have been extensively investigated. Its main reason is to expect to be obtained new kind of composite materials with complementary behaviors, and be used in electronic or nano-electronic devices [1-4]. TiO_2 is one of the typical of n-type semiconductor, while polyaniline is one of the typical conductive polymers, which is usually considered as p-type materials. Because it has good mechanical flexibility and environmental stability, and its conductivity could be controlled with acid/base, it has potential application in many fields, such as lightweight battery electrode, electromagnetic shielding device, anticorrosion coatings, and sensors [5,6]. Additionally, in the fields of sensors, the conductive polymer is one kind of sensitive materials at or near room temperature operating, and has a convenient operating and attractive prospect of development [7-9]. Consequently, it is hopeful to obtain new materials with complementary behaviors between polyaniline and TiO_2.

To now, although a large number of studies on composite materials of polyaniline-TiO_2 have been reported, most of researches on these polymers are still focusing on the preparation of materials and morphology characterization [8-10], such as size and shape of the oxide particles, degree of the dispersion, kind of interaction and interface between the organic and inorganic phase, and so on. A very few reports touched upon the properties of device. Schnitzler et al. [1] have prepared the (Polyaniline-TiO_2) hybrid materials, characterized it by X-ray diffractometric, UV-vis, FTIR spectroscopy, transmission electron microscopy, and electric conductivity measurements and obtained some available information. However, to the best of our knowledge no systematic study has been worked on synthesis, structural, morphological and optoelectronic properties of PANi: TiO_2 composite by sol gel spin coating method. In the present paper we report preparation and deposition of PANi, TiO_2 and PANi: TiO_2 nanocomposite films by chemical polymerization and sol gel spin coating technique. The films, were further investigated for their structural, morphological, electrical and optical properties.

MATERIALS AND METHODS

Preparation of Polyaniline:

Polyaniline was prepared by polymerization of aniline in the presence of hydrochloric acid as a catalyst and ammonium peroxidisulphate (APS) as an oxidant agent by chemical oxidative polymerization method. For the synthesis, we took 50 ml 1M HCl, and 2ml of aniline were added into a 250 ml equipped with electromagnetic stirrer. Then 4.9 g of $(NH_4)_2S_2O_8$ (ammonium peroxidisulphate) in 50 ml, 1M HCl was suddenly added into the above solution. The polymerization temperature ~ 0°C was maintained for 6 hours to complete the reaction. Then the precipitate obtained was filtered. The product was washed successively by 1M HCl followed by deionized water and respectively until the wash solution turned colorless. Then it was re-filtered and washed once again successively by of deionized water, thoroughly to obtain the emeraldine salt ES form of polyaniline. To obtain emeraldine base EB form of PANi, undoped ES form of PANi with 0.1M NH_4OH solution then dried at 80°C in vacuum oven to overnight. Thus, finally obtained powder of insulating polyaniline emeraldine base EB polymer [11].

Preparation of Nanocrystalline (TiO_2):

Nanocrystalline Titanium Oxide has been prepared by used a sol-gel method using titanium isopropoxide as origin of (Ti), 3.7ml of Titanium isopropoxide was added to 30 ml of methanol and mixture was stirred vigorously at temperature 80 ^{0}C and was stirred for further 1 h, we get a white powder. The powder was annealed in tubular furnace at 650 ^{0}C for 1 h, to get the TiO_2 Nano powder having particles of size of 50-60 nm [12].

Preparation of Nanocomposite (TiO_2 /PANi):

The undoped polyaniline powder was dissolved in M-cresol solution. The solution was stirred for 12h at room temperature and filtered. A thin film of this filtered undoped PANi was deposited by spin coating method on a slid glass substrate with 3000 rpm for 30 s and dried on a hot plate at 100 ^0C for 10 min. The TiO_2 composites with undoped PANi were prepared by adding TiO_2 in different weight percentage (0-50 weight %) in filtered solution of undoped PANi in M-cresol and stirring it for 12 hrs. Thin films of the composite were prepared on slid glass substrate by spin coating method at 3000 rpm for 40 s.

Characterization and Measurement Methods:

X-ray diffraction studies were carried out using high resolution an X-ray diffractometer (Model: PANalytical X Pert Pro MRD PW3040). The XRD patterns were recorded in the range of 2θ: 10–70^o with a step width of 0.02^o and step time 1.25 sec by using (CuKα) radiation (λ=1.5406A^o). The XRD patterns were analyzed by matching the observed peaks with the standard pattern provided by a JCPDS file. Fourier Transform Infra-Red (FTIR) spectroscopy (Model: Perkin Elmer Spectrum Gx) of polymer, TiO_2, and PANi: TiO_2 (50%) composite was studied in the frequency range of 400-4000 cm^{-1}. Morphological study of thin films of PANi and PANi: TiO_2 composite was carried out using field effect scanning electron microscopy (FESEM Model: JEOL JSM 6360) operating at 20 kV. UV-visible spectra of samples, which were dispersed in deionized water under ultrasonic action, which were recorded on a Shimadzu - 1800 UV-Visible spectrophotometer. The electrical conductivity and resistivity characteristic study using by four probe techniques at room temperature. (Model Keithley 82), and Solar Simulator which were study by using IV (Model: Keithley-2400 SOURCE METER).

RESULTS AND DISCUSSION

Figure. 1 shows the XRD patterns of Polyaniline pure in the emeraldine base form, titanium oxide powder and PANi: TiO_2 (50 %) composite. The XRD pattern of PANi shows a broad peak at 2θ = 25^o which corresponds to (110) plane of PANi [11]. The patterns show sharp peaks, indicating the crystallinity of the synthesized materials. The observed 2θ values are consistent with the standard JCPDS values (JCPDS No.78-1285), which enumerate the mixed anatase and rutile tetragonal structure of TiO_2 [12]. The intensity of diffraction peaks for PANi: TiO_2 Nano composites are lower than for TiO_2. The present of non-crystalline PANi reduce mass–volume percentage of TiO_2 and sequentially weaken diffraction peaks of TiO_2.

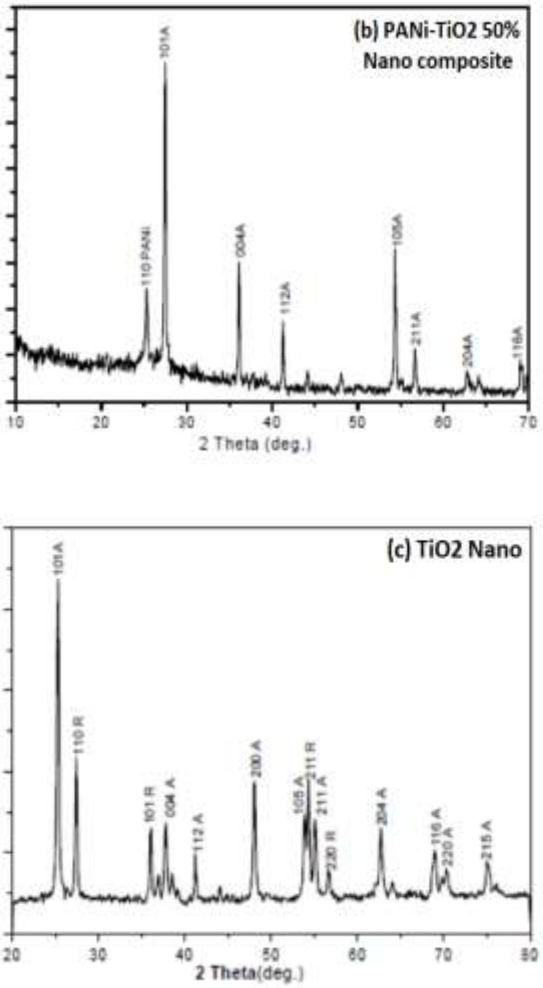
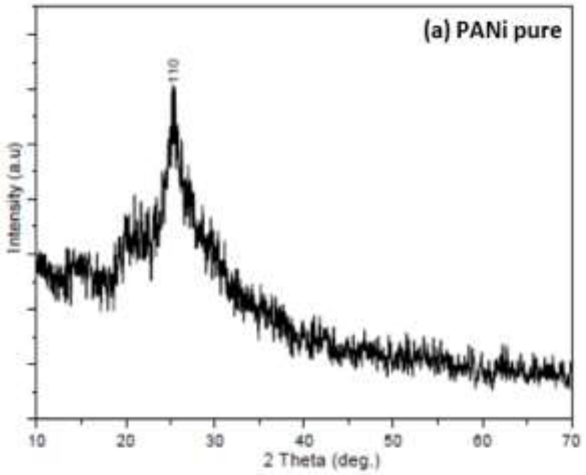
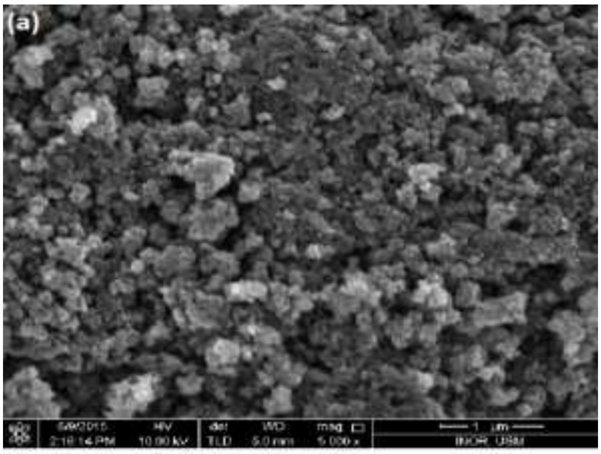


FIGURE 1: XRD DIFFRACTOMETER OF (a) PANi-EB, (b) PANi: TiO_2 COMPOSITES and (c) TiO_2

Figure. 2 shows FESEM microstructure of PANi pure, PANi–TiO_2 (50%) and TiO_2. FESEM image of nanocomposite shows that there is no conglomeration of TiO_2 particles in PANi polymeric chains and there is a uniform distribution of the TiO_2 particles in the Polymer matrix. According to the FESEM results, it was considered that the nanostructured of TiO_2 particles embedded within the net structure built by Polymer chains. It implies that the composite is highly micro-porosity and is able to increase the liquid–solid interfacial area, provides a path for the insertion and extraction of ions, and ensures a high reaction rate [13].





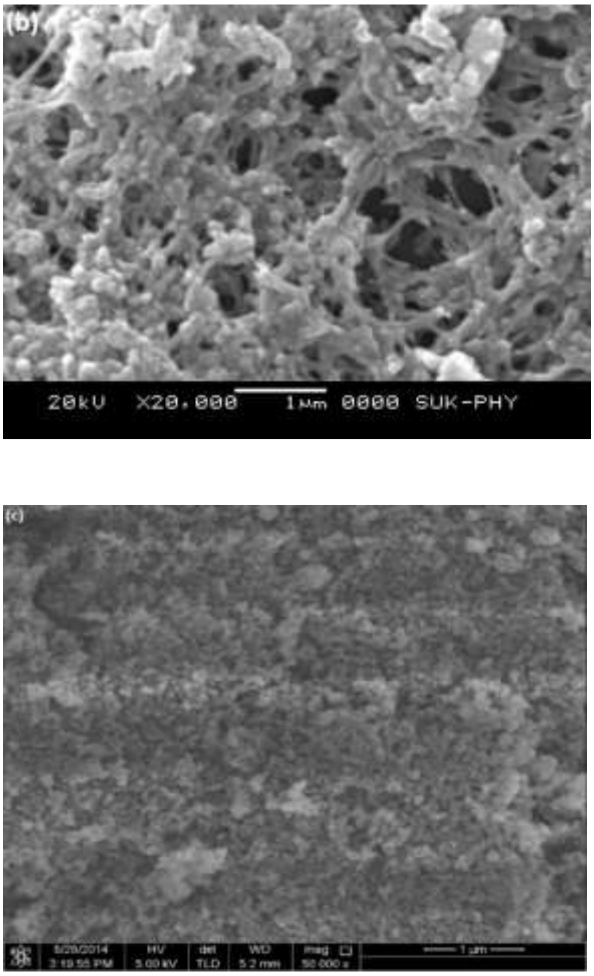
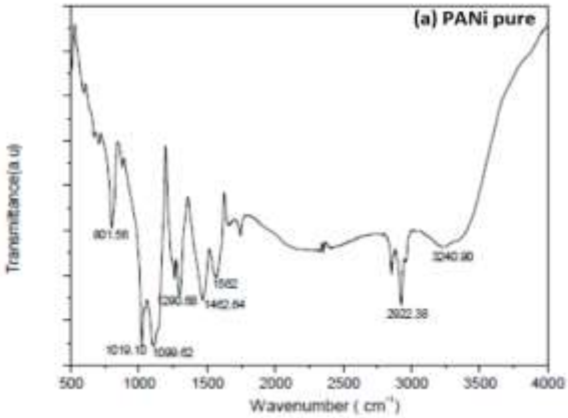


FIGURE 2: FESEM MICROSTRACTURE OF (a) PANi Pure, (b) PANi: TiO_2 and (c) TiO_2 NANO

Figure. 3 show the FT-IR spectra of the pure PANi, PANi-TiO_2 (50%) Nano composite and TiO_2 Nano particles. The origin of the vibrational bands is as follows: 3225–3451 cm^{-1} due to the NH stretching of aromatic amines, at 2845–2914 cm^{-1} due to aromatic CH-stretching, 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 C═N and C═C stretching mode of vibration for the quinonoid and benzeniod units of polyaniline. The peaks at 1296 and 1239 cm^{-1} are assigned to C–N stretching mode of benzeniod ring. The peak at 1239 cm^{-1} is the characteristic of the conducting protonated form of polyaniline [11]. 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 out of plane C–H bending vibration. The low wave number region exhibits a strong vibration around 725 cm^{-1} which corresponds to antisymmetric Ti–O–Ti mode of the TiO_2. [12].



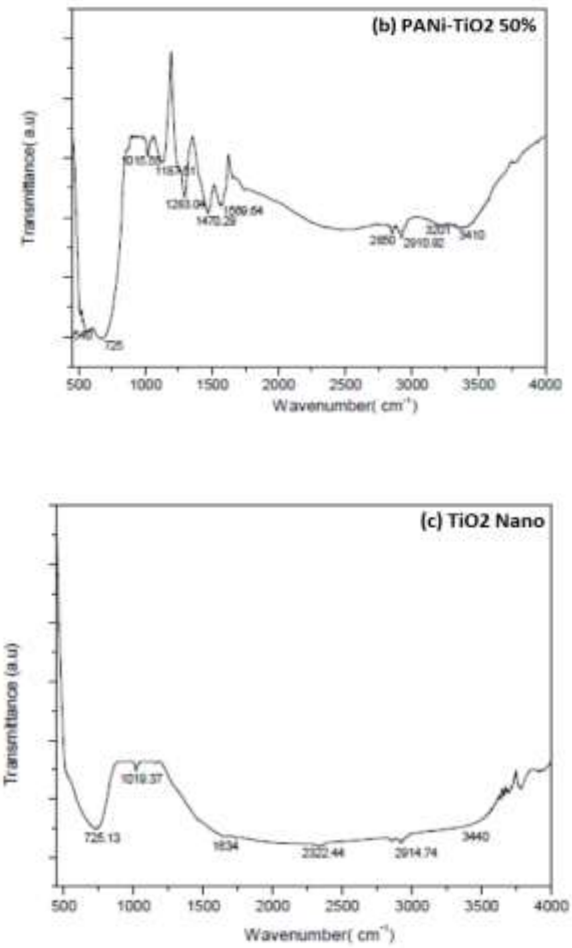


FIGURE 3: FT-IR SPECTROSCOPY OF (a) PANi pure, (b) PANi: TiO_2 and (c) TiO_2 NANO

UV-Vis spectra of polyaniline, polyaniline/nano-TiO_2 composite and nano-TiO_2 particles are given in Figure. 4. Figure.4a shows that three distinctive peaks of polymer PANi appear at about 336, 451 and 924 nm, which are attributed to the π–π*, Polarons- π* and π- Polarons transition [11-13], respectively. Figure. 4b, it can be noted that the characteristic peaks of nano-TiO_2 and polyaniline (EB) all appear in polyaniline/nano-TiO_2 composite. Moreover, the peak at 924 nm is obviously shifted from 924 to 865 nm. It indicates that insertion of nano-TiO_2 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-TiO_2 particles.

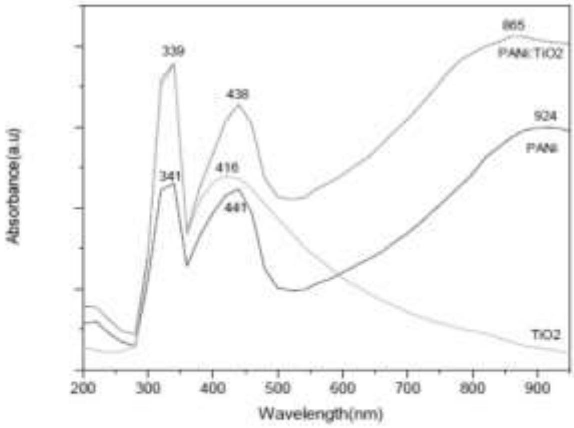


FIGURE 4: UV ABSORPTION SPECTROSCOPY OF (a) PANi pure (b) PANi: TiO_2 and (c) TiO_2 NANO.

The *I-V* characteristics shown in Figure.5 (a) and Figure.5 (b), which are measured by a Keithley 2400 current-voltage source in dark indicate no barrier is apparent at Al/polyaniline or ITO/TiO_2 interface, because their *I-V* characteristics are almost linear. Therefore, we can make a conclusion that ITO and TiO_2, Al and polyaniline form ohmic contact. Figure. 6 shows *I–V* characteristics of the four groups of devices fabricated from different TiO_2 nano-particle concentration in dark, also recorded by Keithley 2400 current voltage source. The curves of a, b and c clearly demonstrate that we have formed a rectifying contact with a current rectification-ratio, therefore we can make a conclusion that a built-in electric field at nano-crystalline Polyaniline/TiO_2 interface has been created, however, the curve of d indicates no built-in electric field is obtained when the ratio of titanium alkoxide, ethanol and deionized water at 4:6:1, because its *I–V* characteristics is almost linear. Figure.7 shows the *I–V* characteristics of the four groups of devices under simulated solar radiation (50 mW/cm^2), the largest short circuit current density of 65.9 μA/cm^2 and open circuit voltage of 0.397 V are obtained from c device.

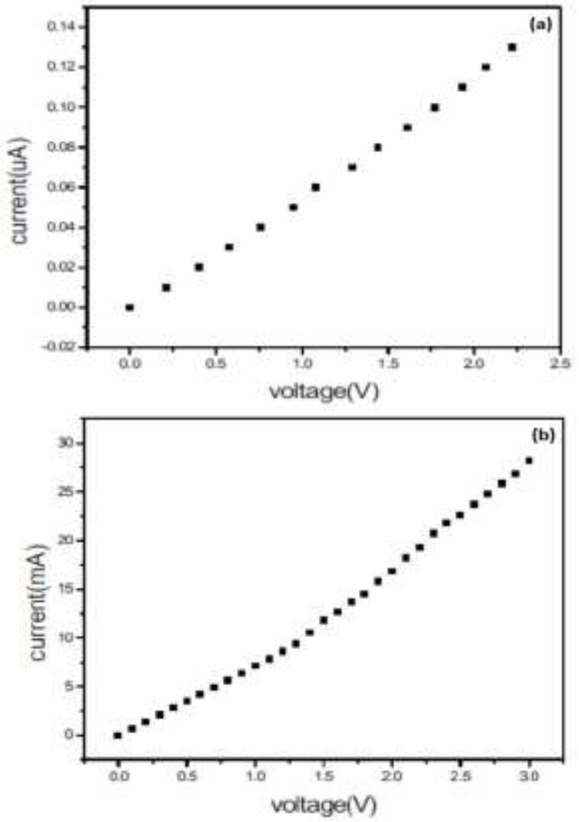


FIGURE 5: THE *I-V* CHARACTERSTICS IN DARK OF DEVICE-TYPE STRACTURE of (a) ITO/NANO-crystalline TiO_2/ITO (b) Al/POLYANILINE-EB/Al

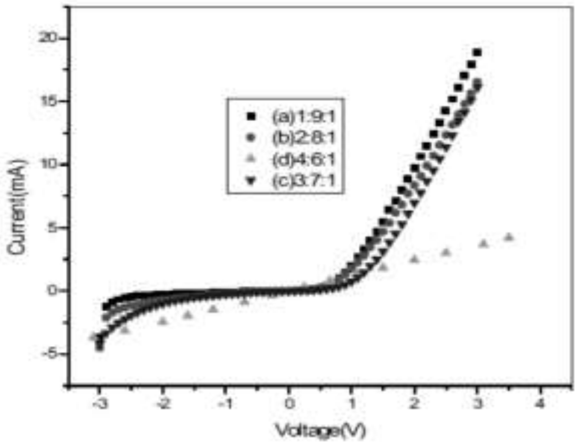


FIGURE 6: *I–V* CHARACTERSTICS of the FOUR GROUPS IN THE DARK.

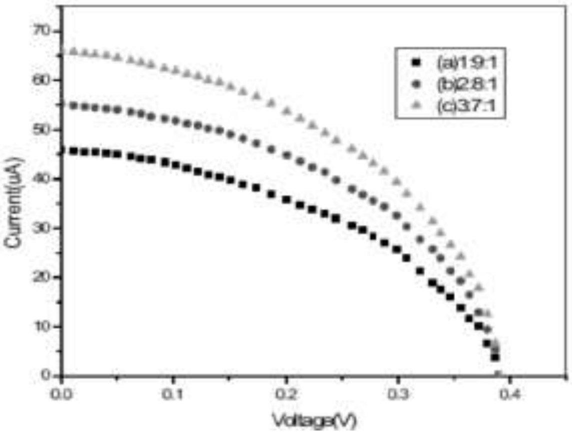


FIGURE 7: *I–V* CHARACTERSTICS OF THE FOUR GROUPS UNDER SIMULATED SOLAR RADIATION (50 mW/cm^2).

CONCLUSION

Thin films of Polyaniline, TiO_2 and Polyaniline: TiO_2 nanocomposites were synthesized by sol gel spin coating techniques. The absorption peaks in FTIR and UV-Vis spectroscopy of PANi: TiO_2 composite film were found shift to the 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 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 polymer chains. The FESEM study of PANi–TiO_2 composite film revealed uniform distribution of TiO_2 particles in Polymer. The heterojunction organic solar cell of TiO_2/ Polyaniline, compared the performance four groups of devices with different TiO_2 nanoparticle concentration. The result in different device performance, and the most suitable sol has been obtained through our research.

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