SYNTHESIS AND ANALYSIS OF PANI / TiO$_2$ HYBRID FILMS BY VARIED SPIN RATES

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PANI/TiO$_2$ hybrids were synthesized by sol–gel chemical method through the oxidative polymerization. PANI/TiO$_2$ hybrid films with different spinning rates were produced by spin coating method. UV studies indicate two characteristic bands at 361 and 402 nm, which can be attributed to the π–π*,polaron–π* and π–polaron transitions. From FTIR, it is evident that the position of the peaks associated with PANI was influenced by the content of TiO$_2$ nanoparticles and the bands corresponding to the benzenoid and quinonoid ring in PANI were found to be shifted towards higher wave numbers. From the AFM images, it was observed that the surfaces of the films become rougher when the spin rate decreases leading to the formation of highly ordered polymer films with thickened active layer for improved light harvesting.

1. Introduction

Heterogeneous conducting polymer nanocomposites, especially organic-inorganic nanocomposites, have drawn the attention of scientists over the preceding years due to a wide range of potential use of these composites. Conducting polymer composites with some suitable compositions of one or more insulating materials led to achieve desirable properties. These materials are especially important owing to their bridging role between the world of conducting polymers and that of nanoparticles. For application of conducting polymers, knowing how these conducting polymer composite will affect the behavior in an electric field is a long-standing problem and of great importance. Conducting polymers such as polyaniline and polypyrrole exhibit excellent electrical conductivities and outstanding thermal stability, while their chemical solubility and mechanical properties are poor leading to a reduced processability.TiO$_2$ can influence its photovoltaic properties. The use of composites is believed to increase the electrical conduction of the polymer and in addition, to improve its stability, which is of prime importance in devices.

Various PANI/TiO$_2$ nanocomposites have been prepared by using chemical or electrochemical polymerization of aniline in the presence of nano-colloidal TiO$_2$. Polymer/inorganic hybrids have attracted much attention due to their potential applications in many areas, such as thin-film field-effect transistors and solar cells. They provide better electrical properties due to the direct interfacial interaction of polymers with inorganic materials where the polymers act as donors and inorganic parts as acceptors [1, 2]. The PANI/TiO$_2$ hybrid system has extensively been studied by many researchers [3-6].

However, in spite of the significant progress, the synthesis of PANI/ TiO$_2$ hybrids with the nanoscale structures, including nanofibers, nanotubes, nanorods, nanosheets and nanoparticles is still of major concern [7–10].

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So far, a lot of attempts have been made to achieve chemical oxidative polymerization of aniline on the surface of TiO_2 nanoparticles in the presence of hydrochloric acid [11–23]. In view of that TiO_2 colloidal sols prepared have also been used to achieve the chemical oxidative polymerization of aniline on the surface of individual TiO_2 nanoparticles at highly acidic conditions [24–30]. In particular, facilitating the interaction of PANI with individual TiO_2 nanoparticles at the nanometer scale remains a dispute because nanoparticles frequently undergo agglomeration due to the fundamental driving force to reduce their high surface energy [31].Therefore, only a small surface area of nanoparticles becomes available for interfacial interactions with PANI. In this regard, a uniform dispersion of crystalline TiO_2 nanoparticles into PANI is essential to achieve outstanding PANI/TiO_2 hybrid materials.

In the present work an attempt has been made to generate p–n heterojunction with nano-crystalline TiO_2 (n-type) and polyaniline as the hole conductor to obtain a novel material with complementary behaviours between PANI and TiO_2.The morphology and electrical properties were analyzed in relation to the various spin rates of this synthesized hybrid solutions by spin coating method.

2. Experimental

2.1Materials
Merck branded Aniline monomer, the oxidant APS (Ammonium per sulphate) and Sulphuric acid (H_2SO_4), Microscope glass slides were purchased and used without further purification. Nano TiO_2 powder (100 nm) was purchased from Sigma Aldrich for the synthesis.

2.2 Sol-Gel and Spin Coating Method of PANI/ TiO_2 Hybrid Films
Initially, dispersion of necessary quantity (80%) of TiO_2 nano powder was carried out in distilled water under ultrasonication for 2 hrs. For synthesis 0.1 M of aniline monomer was added drop-wise to the TiO_2 solution and the resulting solution was kept under mild stirring for 2 hrs. This resulted in aniline/TiO_2 sols. 0.1M of $((NH_4)_2S_2O_8$ was separately dissolved in 1M solution of sulphuric acid and finally added to the aniline-TiO_2 sols. The solution was stirred for 12 h, which was considered long enough to cause the oxidative polymerization of aniline on the surface of the TiO_2 nanoparticles. The resulting, dark-green PANI/ TiO_2 hybrid nanomaterials were washed with ethanol 5 times and then sonicated for 45 min.

2.3 Substrate preparation
Due to the low thickness of the polymeric thin layer, substrate cleaning is of great importance. At the beginning, the glass slides were cut out in given dimensions followed by washing by de-ionized water and soap. Then, they were consecutively put for 20 minutes in acetone, propanol and methanol in the ultrasonic bath and washed using deionised water. Finally, the substrate was dried in the oven at 80° C for 15 minutes to remove the excess water.

The prepared solutions were deposited on glass substrates by the spin coater by varying the spin rates as 2000 rpm, 3000 rpm, 4000 rpm, and 5000 rpm. The glass substrates were annealed at 120˚C for 20 minutes to form hybrid films.

3. Results and discussion

PANI/TiO_2 hybrid films with different spinning rates viz., 2000 rpm, 3000 rpm, 40000 rpm and 5000 rpm were synthesized using sulphuric acid (H_2SO_4) by chemical oxidation method. Due to the slow-spinning rate, the polymer chains have long time to self-organize leading to the highly ordered polymer, the thickened active layer results in an improved light harvesting. The effects of the slow-spinning process on the absorption spectra, the polymer crystallinity, and the thickness dependence are discussed below.

The bonding characteristics were investigated by Fourier transformed infrared spectroscopy (FTIR, Bruker Vertex 80 V) and UV–vis spectroscopy (UV–vis, UV-2550

Shimadzu), the morphology by AFM studies and their electrical conductivity was measured at room temperature by a standard four-probe method, using a Keithley 2180 nanovoltmeter and Keithley 2400 source meter. The results are discussed.

3.1 UV-Vis absorption spectrum of PANI/TiO$_2$ nano hybrids

Fig 3.1 shows the UV-Vis spectrum of the PANI/TiO$_2$ hybrid films with different spinning rates viz., 2000 rpm, 3000 rpm, 4000 rpm and 5000 rpm formed with 80 % of TiO$_2$ solution. The characteristic absorption bands of the films are observed over the wavelength range from 300 nm to 750 nm.
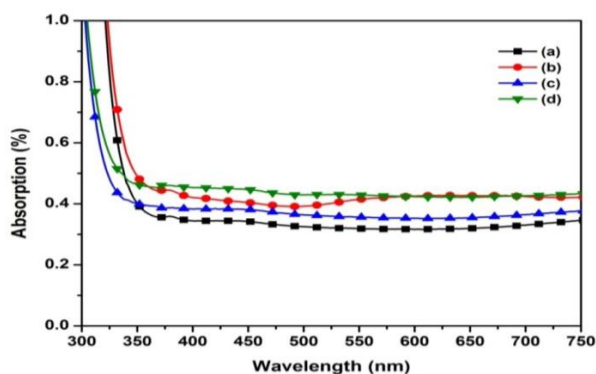

Fig. 3.1 UV-Vis absorption spectrum of PANI/TiO$_2$ hybrids of spin rates a) 5000rpm
b) 4000 rpm c) 3000 rpm d) 2000 rpm

It is clear from the figures that the absorption in the UV region increases with the film thickness (for low spin rates). Both the FTIR and UV–vis observations strongly suggest a possibility of the enrichment in the electrochemical stability due to the realization of the chemical bonding between PANI and TiO$_2$. The characteristic bands of the doped PANI thin film prepared appear at 361 and 402 nm, can be attributed to the π– π*, polaron–π* and π–polaron transitions, respectively [32-34], which indicates that encapsulation of nano-TiO$_2$ particles has the effect on the doping of conducting PANI, while this effect should be constrained to an interaction at the interface of PANI and nano-TiO$_2$ particles [35].

3.2 Fourier transforms infrared spectroscopy analysis of PANI/TiO$_2$ hybrids

Fourier transform infrared spectroscopy analysis of PANI/TiO$_2$ hybrids was scanned from 4000 to 800 cm^{-1} using thermonicolet V-200 FTIR Spectrometer by KBr pellet technique. Fig . 3.2 shows the FTIR spectra of and PANI/TiO$_2$ hybrid films with different spin rates.
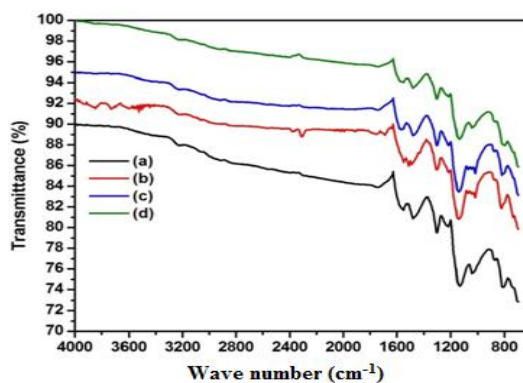

Fig. 3.2 Fourier transforms infrared spectroscopy analysis of PANI/TiO$_2$ hybrids of spin rates
a)   5000 rpm b) 4000 rpm c) 3000 rpm and d) 2000 rpm

The bands assigned at 1477, 1302 and 806 cm^{-1} correspond to the stretching modes of C=C, C–N and C–C bonds of the benzenoid rings, while the bands at 1560 and 1241 cm^{-1} respectively correspond to the C=N and C–N stretching modes of the quinonoid rings in PANI. The broad bands at 3444 cm^{-1}and 1130 cm^{-1} attributed to the N–H stretching mode and plane bending vibration of the C–H bond, respectively [36].

It is evident that the position of the peaks associated with PANI was influenced by the content of TiO$_2$ nanoparticles. In particular, the peaks corresponding to the benzenoid and quinonoid rings in PANI shifted toward higher wave numbers. The band shift indicates that chemical bonding was established between PANI and TiO$_2$, which might ultimately boost the chemical stability of the hybrid. During the chemical polymerization, some of the nitrogen atoms in PANI are expected to form coordinated compounds with the exposed titanium atoms on the surface of TiO$_2$ [37]. The strong ionic (or covalent) bonding between the nitrogen and the titanium would restrict the vibration modes of the PANI chains. Moreover, the electron withdrawing nature of TiO$_2$ may delocalize some of the electrons around the nitrogen present in PANI [38]. These phenomena likely cause the observed shifts of the benzenoid and quinonoid peaks toward higher wave numbers in the FTIR spectra.

3.3 AFM STUDIES of PANI/TiO$_2$ hybrids

In order to further understand the morphological changes that occur in the polymer layer upon different spinning rate, the AFM images of the polymer films of the slow spinning rate (2000 rpm), and high spinning rate (5000 rpm) were recorded using AFM (model: Solver Pro M of NT-MDT working in semi-contact mode).

The film is accompanied by much micrometric and nanometric roughness. In fact, such structure has been produced from the presence of TiO$_2$ nanoparticles during the polymerization process and film substrate is a result of polymer growth and special structure of TiO$_2$ nanoparticles. So, the film can be present as large surface area. As is well known, properties of a broad range of materials and performance of different devices depend strongly on their surface characteristics.

From the images, it was observed that the surfaces of the films exhibited a certain degree of roughness and the film became rougher when the spin rate decreases from 5000 to 2000 rpm and thickness of the active layer increases from 240 to 400 nm.

The bright areas are interpreted as TiO$_2$ rigid nanomaterials and the darker areas as polymers of soft materials. Lowering the spin-coating rate is a straight and simple way to realize the low-cost and high-efficiency hybrid solar cells because it lengthens the drying time and thickens the active layer at one time [39].

The rough surface has been explained as a signature of polymer self-organization, which in turn enhances ordered structure formation in the film. Therefore, the rough surface suggests a higher degree of ordering. Furthermore, the enhanced ordering of molecular structure correlates to an increased hole mobility, resulting in balanced carrier transport in the active layer [34]. The film with slow spinning rate (2000 rpm) shows not only a high roughness but also a coarse texture with broad hill-like features of 35 nm.
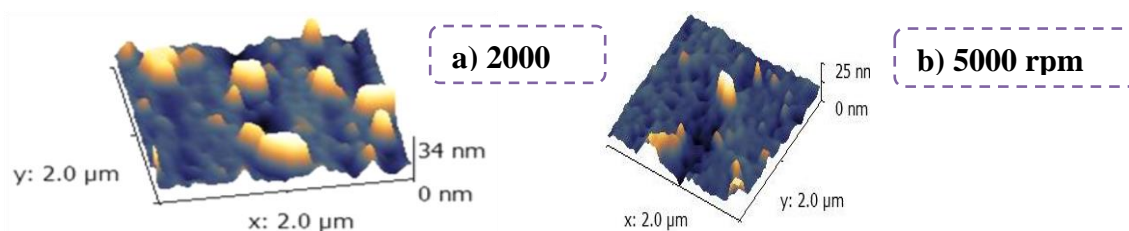

Fig. 3.3.1 AFM images of PANI/TiO$_2$ hybrids of spin rates a) 2000 rpm and b) 5000 rpm
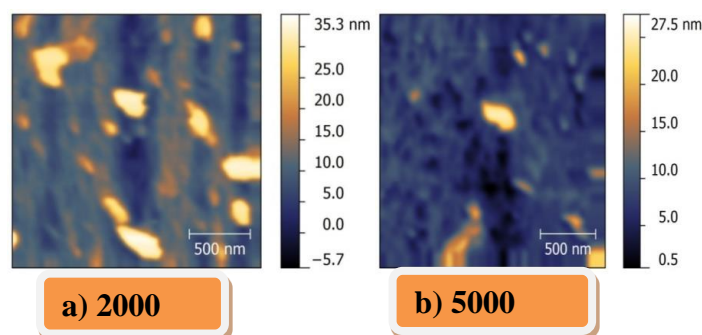
Fig. 3.3.2 AFM images of PANI/TiO$_2$ hybrids of spin rates a) 2000 rpm and b) 5000 rpm.

The fast-spun film shows less roughness compared to the slow spun film. The rms roughness, of the fast-spun surface is 2.97nm. Upon slow spinning, the rms roughness of the surface increases to 5.94 nm due to slow drying. However, there is no white colour region, which is the height of 34 nm, in the AFM image of the film with fast-spin rate and shows less roughness compared to the other film.

3.4 Electrical conductivity measurements of PANI/TiO$_2$ hybrids

Their electrical conductivity was measured at room temperature by a standard four-probe method, using a Keithley 2180 nano voltmeter and Keithley 2400 source meter.

Table. 1 Electrical conductivity of PANI/TiO$_2$ hybrids

Sample	Conductivity (S/cm)
PANI/TiO$_2$(2000 rpm)	0.87S/cm
PANI/TiO$_2$(3000 rpm)	0.76S/cm
PANI/TiO$_2$ (4000 rpm)	0.60S/cm
PANI/TiO$_2$(5000 rpm)	0.43S/cm

The electrical conductivity of the PANI/TiO$_2$ hybrids was measured and the result is summarized in Table 1. PANI/TiO$_2$ of spin rate 2000 rpm shows the largest conductivity value of 0.87 S/cm, probable for the generation of more effective network for charge transport.

The enhancement in Jsc can be attributed to two important factors. Due to the slow-spinning rate, the polymer chains have long time to self- organize leading to the highly ordered polymer, the thickened active layer results in an improved light harvesting [39].

4. Conclusions

PANI/TiO2 hybrids were synthesized by sol–gel chemical method through the oxidative polymerization of aniline through adding well-dispersed TiO2 nanoparticles. PANI/TiO2 hybrid films with different spinning rates viz., 2000 rpm, 3000 rpm, 40000 rpm and 5000 rpm were produced by spin coating method.

UV studies indicate two characteristic bands for the doped PANI thin film at 361 and 402 nm, which can be attributed to the π– π*, polaron–π* and π–polaron transitions. This confirms that the encapsulated nano-TiO2 particles has the effect on doped conducting PANI. From FTIR, it is evident that the position of the peaks associated with PANI was influenced by the content of TiO2 nanoparticles. In particular, the bands corresponding to the benzenoid and quinonoid ring in PANI were found to be shifted towards higher wave numbers. The band shift indicates that chemical bonding was established between PANI and TiO2, which might ultimately boost the chemical

stability of the hybrid. From the AFM images, it was observed that the surfaces of the films exhibited a certain degree of roughness and the film become rougher when the spin rate decreases from 5000 to 2000 rpm and consequently thickness of the active layer increases from 240 to 400nm. Lowering the spin-coating rate is a straight and simple way to realize the low-cost and high-efficiency hybrid solar cells because it lengthens the drying time and thickens the active layer at one time. PANI/TiO2 hybrid films formed at spin rate 2000 rpm shows largest conductivity 0.87 S/cm, and leads to the formation of effective network for charge transport which in turn enhances the current density. Due to the slow-spinning rate, the polymer chains have long time to self-organize leading to the formation of highly ordered polymer films with thickened active layer for improved light harvesting.

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