



SPECTROSCOPIC AND THERMAL INVESTIGATIONS OF POLYANILINE-TiO₂ NANOCOMPOSITE

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Abstract

Polyaniline(PANI)-Titanium dioxide(TiO₂) nanocomposite was prepared by one-step in situ polymerization method in presence of TiO₂ and was characterized via FTIR spectra, UV-Vis. spectra thermogravimetric analysis and scanning electron microscopy. SEM micrographs showed that the nanocomposite exhibited spherical morphology with particle sizes about 70 nm. Both FTIR and UV-Vis. spectra indicate that polyaniline and TiO₂ are not simply blended. The thermal decomposition temperature of PANI is ~420 °C in PANI- TiO₂ nanocomposite, which is lower than that of PANI (~465 °C).

Keywords : Polyaniline, TiO₂, in situ polymerization, Thermal decomposition temperature.

Introduction

Organic-inorganic nanocomposites for synergetic behaviour and a wide range of potential use have triggered great interest and concern of the related academic organizations and researchers over the past decade.¹⁻² Specially nanocomposites of organic conjugated polymers and inorganic nanocrystals have attracted great attention due to a large number of potential applications such as photonics, photoelectronics and catalysis.³ Among the conducting polymers, polyaniline(PANI) is often used as an organic part to prepare nanocomposites because of its low cost, easy preparation, controllable unique properties by oxidation and protonation state, excellent environmental stability and potential application in electronic devices.⁴

Among the inorganic nanoparticles, titanium dioxides(TiO₂) nanoparticles are appealing because of their excellent physical and



chemical properties, as well as extensive applications in diverse areas, such as coatings, solar cells and photocatysts.⁵

In this paper, a simple method for the synthesis of PANI-TiO₂ nanocomposite, which could be easily applied industrially. PANI-TiO₂ nanocomposite was prepared by one-step in situ polymerization method. The nanocomposite was characterized by FTIR, UV-Vis, SEM and thermogravimetric analysis.

Experimental

Aniline was distilled before use. All the chemicals were of analytical reagent grade and were used as received.

Preparation of PANI

Synthesis of PANI was carried out by chemical peroxidation method⁶⁻⁷ 0.1 mole of aniline was dissolved in 1M HCl to form 0.1M aniline hydrochloride. To this reaction mixture 0.1M of ammonium persulphate [(NH₄)₂S₂O₈] which acts as the oxidant was added slowly with continuous stirring for 4-6 h at 0-5°C to polymerize. The precipitated powder recovered was vacuum filtered and washed with deionized water. Finally the resultant precipitate was dried in an oven for 24 h to achieve a constant weight.

Preparation of PANI- TiO₂ nanocompostie

Synthesis of PANI-TiO₂ nanocomposite was carried out by one-step in situ polymerization⁸⁻⁹. 0.1 mole of aniline was dissolved in 1M HCl to form aniline hydrochloride. Titanium dioxide (TiO₂) powder was added to the above solution with vigorous stirring in order to keep TiO₂ powder was added to the above solution with vigorous stirring in order to keep TiO₂ homogeneously suspended in the solution. To this reaction mixture, 0.1 M of ammonium persulphate which acts as the oxidant was added slowly with continuous stirring for 4-6 h at 0-5 °C to polymerize. The precipitated powder recovered was vacuum filtered and washed with



deionized water. Finally the resultant precipitate was dried in an oven for 24 h to achieve a constant weight.

Characterization

The FTIR spectra were recorded on Shimadzu FTIR-8101A Spectrophotometer. The UV-Vis. absorption spectra were recorded on UV-1800 Shimadzu automatic recording double beam spectrophotometer . The morphology of nanocomposites was examined on JSM-6380A scanning electron microscope. TGA of nanocomposite was carried on TGA/SDTA 851 Mettler Toledo instrument at a heating rate of $15^{\circ}\text{C min}^{-1}$ in nitrogen atmosphere.

Results and Discussion

Figure 1 shows FTIR spectra of TiO_2 , PANI and PANI- TiO_2 nanocomposite. From fig. 1(a), the broad peak from 400 to 700 cm^{-1} is the characterisitic band of TiO_2 . The characteristic bands of PANI (Fig.1(b)) are assigned as follows : the band at 3413 cm^{-1} is attributed to N-H stretching mode, C=N and C=C stretching modes for the quinoid and benzenoid rings occur at 1585 cm^{-1} and 1504 cm^{-1} , the bands at about 1288 cm^{-1} and 1244 cm^{-1} have been attributed to C-N stretching mode for the benzenoid ring, while the band at 1101 cm^{-1} is assigned to an in plane bending vibration of C-H which is formed during protonation¹⁰. It is evident that the FTIR spectra of PANI- TiO_2 nanocomposite (fig.1(c)) contains contributions from both TiO_2 and PANI. However, some bands of PANI have shifted due to interaction with TiO_2 . The bands at 1585 cm^{-1} , 1504 cm^{-1} and 1288 cm^{-1} , corresponding to the stretching mode of C=N, C=C and C-N, all shift to lower wavenumbers and N=H stretching band at 3413 cm^{-1} shifts to higher wavenumber. Similarly the band at 1101 cm^{-1} also shifts to 1120 cm^{-1} . These changes suggest that C=N, C=C and C-N bands become weaker in PANI- TiO_2 nanocomposite while the N-H band becomes stronger. The results confirm that there is strong

interaction between the PANI and TiO₂ and the presence of TiO₂ prompts the doping of PANI.

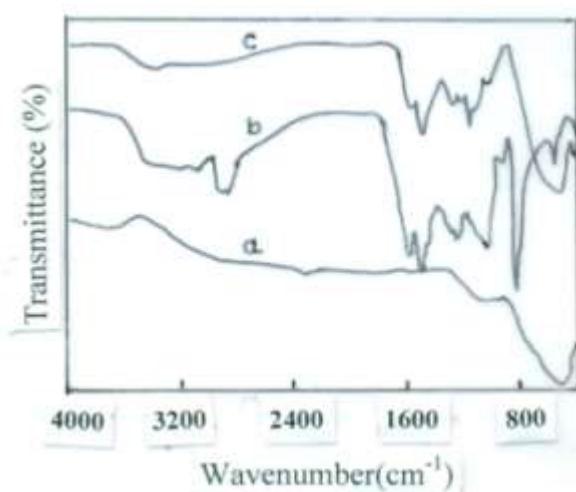


Figure 1. FTIR spectra of (a) TiO₂ (b) PANI and (c) PANI-TiO₂

The UV Vis. absorption spectra of TiO₂, PANI and PANI-TiO₂ nanocomposite are shown in figure 2. (fig 2(C)). The PANI-TiO₂ nanocomposite (Fig.2(c)) can strong absorb not only the ultraviolet light but also the visible light. The characteristics bands of PANI (fig 2 (b)) at 365-370 nm and 535 nm, which are attributed to $\pi-\pi^*$ transition of benzenoid ring, polaron- π^* respectively¹¹. The absorption peaks of the PANI-TiO₂ nanocomposite at characteristics peaks of PANI become stronger

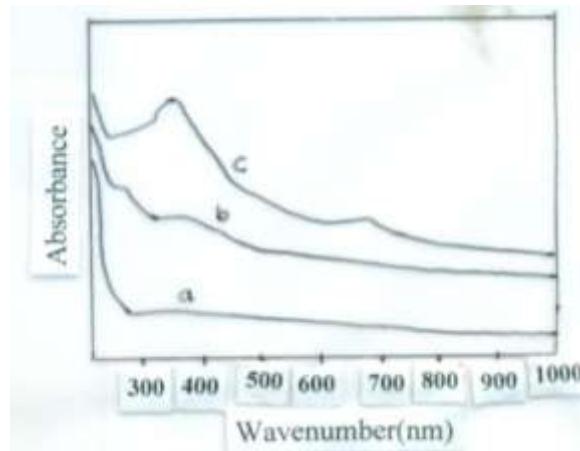


Figure 2. UV-Vis. spectra of a TiO₂ (b) PANI and (c) PANI-TiO₂



Figure 3 shows the scanning electron micrograph (SEM) of PANI and PANI-TiO₂ nanocomposite. It can be found from Fig. 3(a) that the PANI exhibit spherical morphology with particle sizes of about 50 nm, while PANI-TiO₂ nanocomposite approaches spherical with particle sizes of about 70 nm (Fig 3 (b)).

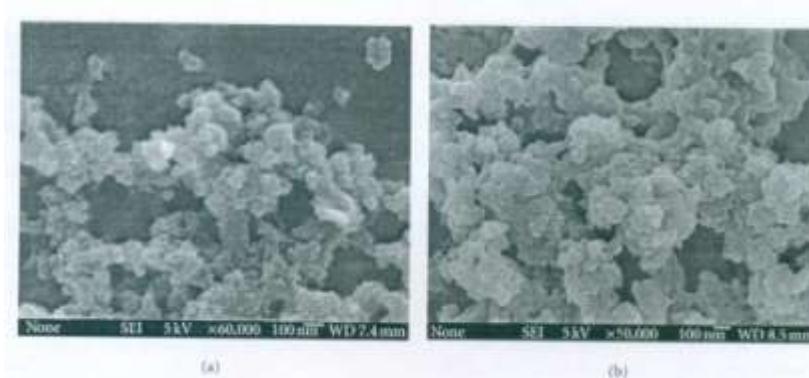


Figure 3. SEM images of (a) PANI and (b) PANI-TiO₂

Figure 4 illustrates the thermogravimetric curves of PANI and PANI-TiO₂ nanocomposite. Fig.4(a) reveals that the sharp weight loss for PANI began at nearly 120 °C and continued until 700 °C, due to the thermal degradation of PANI chains on a large scale. The thermal decomposition temperature of PANI is ~420 °C in PANI-TiO₂ nanocomposite, which is lower than that of PANI (~465 °C). The lower temperature is associated with the effect of TiO₂ upon PANI.

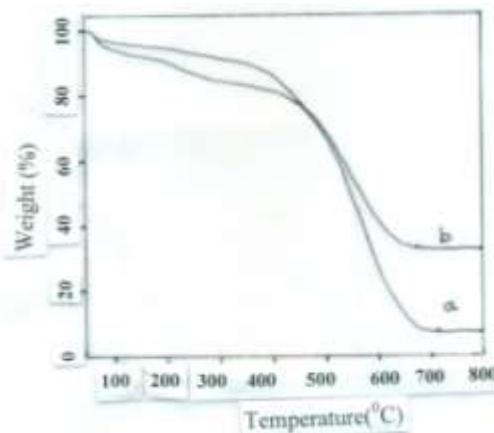


Figure 4 Thermogravimetric curves of (a) PANI and (b) PANI-TiO₂



Conclusions

PANI-TiO₂ nanocomposite has been successfully prepared by one-step in situ polymerization in presence of TiO₂. PANI and TiO₂ are not simply blended in this nanocomposite. An interaction existed between TiO₂ and PANI macromolecules. It is confirmed that the diameter of the resulted PANI-TiO₂ nanocomposite is about 70 nm. FTIR and UV-Vis. spectra indicate that the polyaniline and TiO₂ are not simply blended in this nanocomposite. This method is simple and inexpensive and it can be easily applied industrially.

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