

SYNERGIC SYNTHESIS ROUTE FOR THE FABRICATION OF ORGANIC-INORGANIC COMPOSITE FILM

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Abstract

Synergic synthesis for organic-inorganic hybrid matrices has been significantly interested for a wide range of optoelectronic applications. Regarding this, efficient synthesis route for the fabrication of P(Py-2FPy)/TiO₂ composite film has been studied. While inorganic TiO₂ nanoparticle solution was synthesized by low temperature solution method, the fabrication of composite film was prepared by *ex-situ* chemical copolymerization through spin coating technique. The synergic assembly of composite film was identified and characterized by FT-IR, UV-Vis and XRD. The resulted films show that the inorganic TiO₂ nanoparticles can be successfully incorporated into the organic copolymer matrix. In addition, the new fabricated organic-inorganic composite films are scalable. Thus, it can be applied in industry and will be major interest in the area of nanocomposite materials.

Keywords: polypyrrole, 2- formyl pyrrole, TiO₂, *ex-situ* chemical copolymerization and composite film

Introduction

The mixing of organic polymers and inorganic nanoparticles is opening pathways for engineering flexible composites materials that show a better magnetic, electrical, optical, or mechanical property. New strategies to engineer materials that combine the desirable properties of polymers and nanoparticles for the formation of polymer-inorganic nanocomposites have been attempted for last decades. However, there were many challenges for the synthesis techniques since nanoparticles are typically aggregated which can hinder the fabrication of nanocomposites. The nanoparticles must be integrated in a way leading to isolated, well-dispersed primary nanoparticles inside the matrix. There is no debt to establish the processing techniques that are effective on the formation of composites. Thus, synthetic strategies for composite with a high homogeneity are really a challenge. Synthesis of

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composites can be classified into two major groups, chemical and physical methods respectively.

Chemical methods are direct mixing and melt processing of particles with polymers often lead gradients of the incorporated fillers in the matrix. However, this method leads to turbidity/translucency of composite materials because of the agglomeration of the nanoparticles. As a result, *in-situ* polymerization and *in-situ* nanoparticle formation methods have been developed to overcome these problems. Inorganic nanoparticles were directly dispersed in the monomer solution prior to a polymerization processing in *in-situ* polymerization. In this process, inorganic particles tend to phase separate and sediment quickly from the organic polymer. For the good link/interaction at the interface, specific groups have to be linked onto their surface to stabilize nanoparticle dispersions (Althues *et al.*, 2007).

Physical or *ex-situ* polymerization methods are based on liquid particle dispersions. It implies that particles are dispersed into a polymer melt and then composites are obtained by extrusion. Casting methods use a polymer solution as a dispersant and solvent evaporation yields the composite material (Althues *et al.*, 2007). The *ex-situ* synthesis method is more suitable for large-scale industrial applications than the *in situ* method (Guo *et al.*, 2014). The advantages of this method include resulting of higher dispersibility of nanoparticles in the polymer and have long-term stability against aggregation.

The polymer inorganic composites comprise inorganic nanoparticles which are uniformly dispersed in and fixed to a polymer matrix. The interfacial surface area of composite was increased due to higher surface area of nanoparticles. In addition, smaller particle size allows a much more homogeneous distribution of a composite material. However, this may tend to aggregation of the nanoparticles to energetically stabilize composites, thus lowering the homogeneity of particle distribution. In order to minimize interface energies between particles and polymer matrix, several nanocomposites of polymer and nanoparticles surface modification/functionalization and stabilization techniques have been developed that are mainly used in chemical methods. Recently, *in-situ* polymerization and sol-gel methods were used to fabricate a new class of composite polymer with

transparent nano-fillers. This type of material is also sometimes called polymer-inorganic hybrid/nanohybrid. (Zhang *et al.*, 1997; Yuwono *et al.*, 2004; Li *et al.*, 2007).

Depending on the applications, inorganic components including metals (Hopf *et al.*, 1997; Macanas *et al.*, 2007), metal alloys (Fang *et al.*, 2002), metal oxides (Ahmad *et al.*, 2008), ferric oxide (Gangopadhyay *et al.*, 1999; Gass *et al.*, 2006) and ferrite (Prabhakaran *et al.*, 2008) and carbon based materials (Grossiord *et al.*, 2008; Agarwal *et al.*, 2008) and organic matrix including industrial plastics conducting polymers and transparent polymers usually chosen. However, there is no work for fabrication of copolymer composites film according to our concerns.

In this work, P(Py-2FPy)/TiO₂ composites films were prepared *ex-situ* chemical polymerization through spin coating for the electrical application aspects of composite. The synergic synthesis route for the fabrication of composite film is presented by investigating with UV-Vis, FT-IR and XRD measurement. The incorporation of TiO₂ improved the structural, morphological, and conductivity properties of the composite.

Experimental Details

Preparation of the Organic Monomer Solution

(200 mg, 3 mmol) of Py and (286 mg, 3 mmol) of FPy were mixed and dissolved in 2 mL of chloroform (CHCl₃) in a conical flask. They were stirred at the room temperature for 30 min to obtain the monomer solution.

Preparation of the Inorganic TiO₂ Precursor Solution

In the synthesis of TiO₂, titanium isopropoxide (TTIP), 2-propanol and hydrochloric acid (HCl) are used as the precursor, catalyst and solvent. Typically, the first solution of 0.0138 M, 2.53 mL 2-propanol (IPA) was mixed with 2 M, 35 μ L HCl were prepared. Then another solution was prepared by adding 0.23 M, 369 μ L TTIP in 0.0138 M, 2.53 mL, 2-propanol. Then, the first solution is slowly added drop wise to the second solution and was stirred at 800 rpm. After being stirred for six hours at the room

temperature, a clear and transparent TiO₂ nanoparticle dispersion solution was successfully obtained.

Preparation of the Composite Films

486 mg of as-synthesized TiO₂ solution was added to 486 mg of monomer solution. Thus, the weight ratio of inorganic to organic is 1:1. The mixture was continuously stirred for 24 h. Then, the solution containing (13 mmol) trifluoroacetic acid (TFA) and (2 mL) CHCl₃ was additionally put to composite solution at room temperature. After that, the mixed solution was spin-coated onto the Petri dish at 20 rpm using a home-made spin coater until the complete formation of copolymerization. After that, the film was successively washed by excess deionized water and acetone and dried in a vacuum oven for 12 h. Figure 1(a) illustrates the synthesis route scheme of the composite films. The photo of composite film casted in the Petri dish was exhibited in Figure 1(b). The film was a metallic greenish black and insoluble in several solvents.

Characterization Tools

The UV-Vis was performed in order to examine the absorbance values of all synthesized samples. The UV-Vis spectra were obtained by using Shimadzu UV-1800 UV-Vis spectrophotometer. The crystal structure and crystallite size of the samples were confirmed by XRD (model RIGAKU-RINT 2000) using CuK_α radiation (40 kV, 40 mA) over a 2θ range from 10° to 70° on a powder type X-ray diffractometer equipped with a diffracted-beam graphite monochromator. The identification of functional group was investigated by FT-IR. The spectra formations of TiO₂, pure copolymer and composite films were obtained by FT-IR 8400 Shimadzu spectrophotometer using a KBr pallet in the mid IR radiation (4000 cm⁻¹ - 400 cm⁻¹) range with a resolution of 4.0 cm⁻¹.

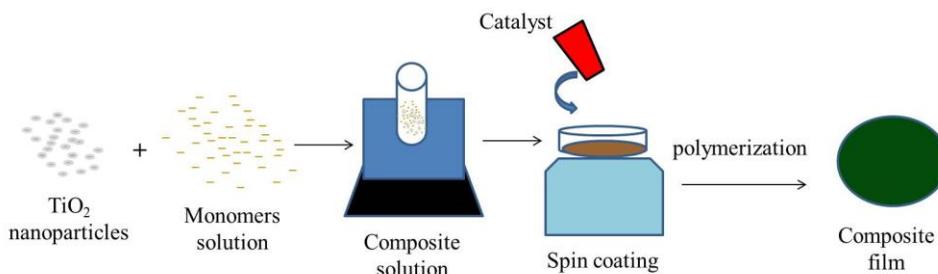


Figure 1:(a) *Ex-situ* synthesis schemes for the preparation of nanocomposites films

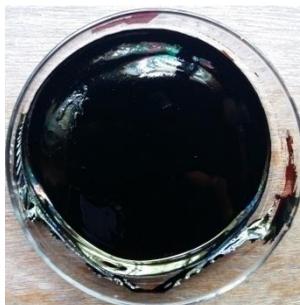


Figure 1: (b) Photo showing copolymer/ TiO_2 composite film

Results and Discussion

The formation of TiO_2 nanoparticles and copolymer film was monitored by ultraviolet-visible (UV-Vis) spectroscopy. The maximum absorption wavelength occurred at 271 nm in Figure 2(a) was confirmed that the product is TiO_2 nanoparticles (Vebber *et al.*, 2016). UV-Vis spectrum of pure copolymer film is shown in Figure 2(b). It was noted that characteristic absorption band of the π - π^* transition of polypyrrole is appeared at around 492 nm. This fact indicated that the FPY group was incorporated into the chemical structure of the conjugated polymer chains. Since Py and FPY had no absorption band at about 500 nm, this could be assigned with π - π^* transition of the C=C double bond, which was formed by the copolymerization. In addition, weaker and broader band was appeared at about 700 nm. This strongly implied that the bipolaron state of polypyrrole was present in the

films. This indicated that such strong acid (TFA) strongly interacted with pyrrole segments to form bipolaron state (Hoshina *et al.*, 2012).

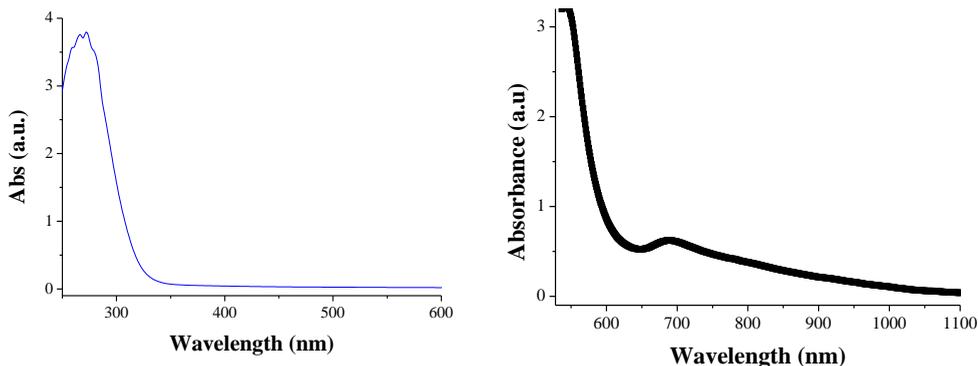


Figure 2: (a) UV-Vis absorption spectrum of as-synthesized TiO₂ nanoparticles **Figure 2:** (b) UV-Vis absorption spectrum of pure copolymer film

The functional groups for all investigated samples were identified by FT-IR. The spectra were shown in Figure 3. The spectrum (a) is for TiO₂ nanoparticles. In this spectrum, the peaks at 3400-3500 cm⁻¹ and 1622-1633 cm⁻¹ in the spectra are due to the stretching and bending vibration of the -OH group. The peak at 1458 cm⁻¹ corresponds to the Ti-O-Ti vibration (Saravanan *et al.*, 2010). The peak at 1354 cm⁻¹ corresponds to the C-H deformation (Colthup *et al.*, 1964., Bellamy *et al.*, 1975). The peak at 1203 cm⁻¹ corresponded to the ν_1 and ν_3 (degenerate splitting) modes that correspond to symmetric and asymmetric stretching modes respectively (Lane 2007). The peaks at 522.73 cm⁻¹ show stretching vibration of Ti-O (Vetrivel *et al.*, (2014-2015)). Absorption peaks found at 480 cm⁻¹ correspond to Ti-O-Ti peak frequency since the regions from 400 to 800 cm⁻¹ are dominated with weak and broad peaks identified to have the frequencies corresponding to bulk titania skeletal (Kuma *et al.*, 2000).

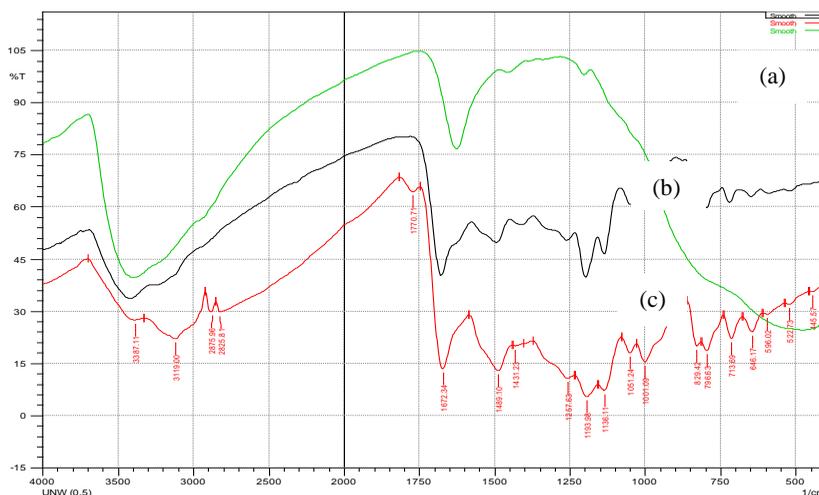


Figure 3: FT-IR spectra of (a)TiO₂ nanoparticles (b) pure copolymer P (Py-2FPy) films without nanoparticles and (c) P(Py-2FPy)/TiO₂ composite films

The FT-IR spectrum (b) shows the pure copolymer film. The peak observed at 3383 cm^{-1} was due to the N-H stretching vibration. The peak at 3128 cm^{-1} was aromatic C-H stretching. The peaks of C=N stretching at $1483\text{--}1402\text{ cm}^{-1}$ were attributed to the formation of the conjugated structure in the film. The peak observed at 1258 cm^{-1} was assigned to -C=CH- stretching from methine group of the copolymer. The peak at 1203 cm^{-1} can be related to C-N stretching of amine group. The peak of C=N appeared at 1138 cm^{-1} . The peak at 1051 cm^{-1} can be attributed to C-H in plane deformation. The peak of the aromatic C-H out-of-plane deformation vibration appeared at $1006\text{--}800\text{ cm}^{-1}$, respectively (Yusuke *et al.*, 2012).

In the spectrum (c), composite film, characteristic peaks of copolymer are observed in the composite films, indicating the formation of copolymer. The two peaks at 2875 and 2825 cm^{-1} correspond to C-H stretching vibration (asymmetric) and C-H stretching vibration (symmetric) from the remaining organic-moiety (Sabzi *et al.*, 2009). In addition to this, the presence of the new peaks at 522.73 and 445.57 cm^{-1} confirmed that inorganic component was well resident in the polymer matrix. The obvious spectral differences between pure polymer and the composite indicate that polymer exhibits a different

polymer chain structure and there are physicochemical interactions between the TiO₂ nanoparticles and PPy-FPy copolymer.

XRD measurement was carried out in order to confirm the crystal structure of TiO₂ nanoparticles. TiO₂ has amorphous structure at the room temperature (Guo *et al.*, 2012). In order to obtain the TiO₂ crystals, as-synthesized TiO₂ was annealed at different temperatures (500 °C, 600 °C and 700 °C). The crystal phases of TiO₂ nanoparticles were observed by XRD measurement. Figure 4 represents the XRD patterns of TiO₂ nanoparticles annealed at 500 °C, 600 °C and 700 °C. The generated TiO₂ nanoparticles contained the phase type anatase, rutile, and brookite. The important roles in the formation of the resulting TiO₂ crystal phases were depended on the starting material, its composition, deposition method and annealing temperature (Mechiakh *et al.*, 2010). Crystallization is often performed by calcination at temperatures above 400 °C since as-synthesized TiO₂ is amorphous (Liao *et al.*, 2010). Only the crystal form of pure anatase was obtained at the annealing temperature 500 °C and a partial phase anatase and rutile was resulted at 600 °C since the weak diffraction peak (110) started to generate in this sample. However, the diffraction peak (110) is more prominent and the (101) peak was weaker when the annealing temperature was increased to 700 °C. This can result the more rutile phase of TiO₂ nanoparticles. Rutile phase can totally transform above 800 °C (Mechiakh *et al.*, 2010). Thus, annealing temperature has one of the major impacts on the crystal phase because the kinetics of reactions taking place was changed and the amount of OH⁻ was varied by temperature and acid (Yin *et al.*, 2004; Cheng *et al.*, 1995; Liet *et al.*, 2002).

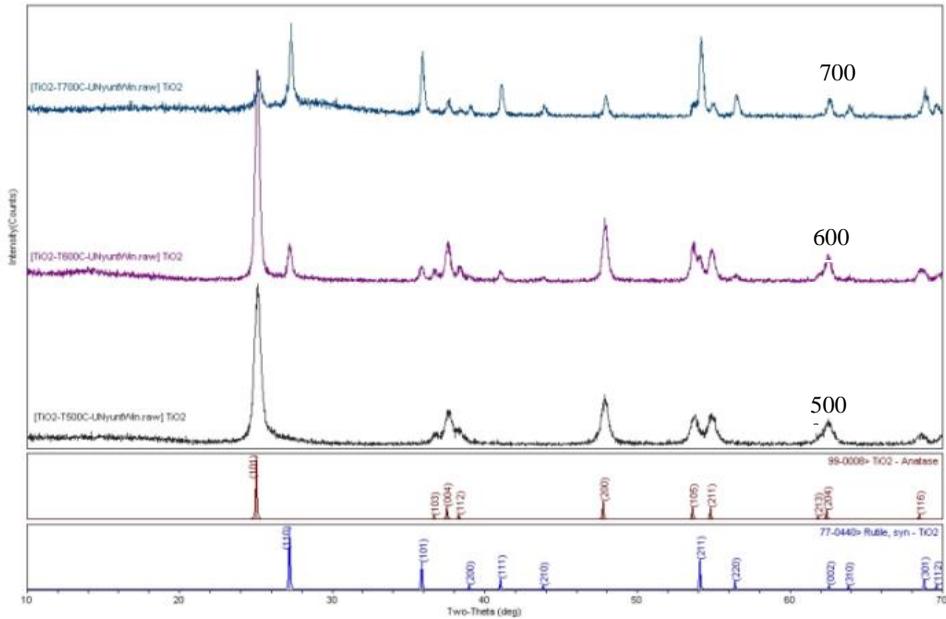


Figure 4: XRD patterns of TiO₂ nanoparticles annealed at 500°C, 600°C and 700°C

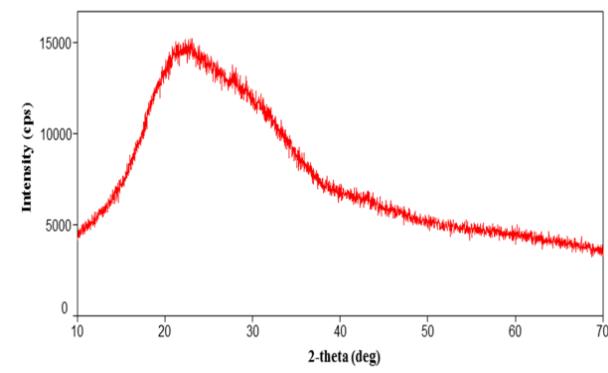


Figure 5: XRD spectrum of pure P(Py-FPy) copolymer film

XRD spectrum in Figure 5 shows the standalone P(Py-Fpy) copolymer film. No diffraction peaks could be detected except only for the broad peak around at the diffraction angle around 23° which is corresponding to amorphous polymer.

Conclusions

The new synthesis route of composite films comprising of TiO₂ nanoparticles in the P(Py-2FPy) copolymer matrix has been presented. While the TiO₂ nanoparticles were synthesized by low temperature solution method, the fabrication of composite film was prepared by chemical copolymerization through spin coating technique. The integration of inorganic components in polymer matrix was confirmed by FT-IR analysis. It can be remarkable that a suitable synthetic method of inorganic nanoparticles is firstly required in order to well dissolve in monomer solutions. Secondly, the enough stirring time is necessary for the homogeneous composite solution. The most important issue is the preparation technique of composite film formation. In this case, it is very important to consider the polymerization methods which are uncomplicated and possibility of film formation. In conclusion, by exploiting the physics of the inorganic nanoparticles, organic polymer and polymeric nanocomposites, the novel and functional composites can be designed and fabricated for new interesting applications such as optoelectronic and magneto-optic applications. It is expected that the use of a new functional composites as P(Py-2FPy)/TiO₂ materials will lead to nanocomposites with the unique combination of inorganic and organic properties.

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