SYNTHESIS OF CONDUCTING POLYPYRROLE-TITANIA NANOCOMPOSITES BY THE RADIOLYSIS METHOD

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Introduction

Polymer-inorganic hybrids nanoparticle have attracted great attention, since they have interesting physical properties and potential applications.[1] These particles not only combine the advantageous properties of metals and polymers but also exhibit many new characters that single-phase materials do not have. In order to prepare the nanoscale materials successfully, several approaches have been employed like physical mixing, sol-gel technique, *in situ* chemical polymerization, and γ-irradiation technique.[2] Among the these methods; γ-irradiation technique is a useful means and has been extensively used to generate nanoscale metals and nanocomposites. Moreover, this technique is easily controlled and adaptable, and it cannot induce impurities into the matrix.

Conducting polymers (CP), however, arouse an immense interest among researchers because of their curious electronic, magnetic and optical properties. In terms of CP, polypyrrole (PPy) is one of the most studied polymers due to its environmental stability, relative ease of synthesis, and good electrical conductivity. PPy is the most frequently used in commercial applications, such as batteries, supercapacitors, sensors and corrosion protection.[3] On the other hand, the nanoscale metal particles such as gold, silver and titanium provide a very exciting research field due to their interesting properties. Among them, TiO_2 nanoparticles are appealing because of their excellent physical and chemical properties as well as extensive uses in many areas like coatings, solar cells, and photocatalysts.[4] Here, we report a synthesis route of PPy-TiO_2 that is chemically synthesized by the *in-situ* gamma radiation-induced polymerization method. The morphology and microstructure of the resulting specimen are characterized and the physical properties, including thermal and electrical aspects, are discussed in brief.

Experimental

Pyrrole monomer (Py, 98%, Aldrich) was purified by distillation under reduced pressure and kept below 0˚C prior to use. Titania nanopowder (99.9+%, mixture of anatase & rutile), Ammonium per sulfate (APS, $(NH_4)_2S_2O_8$), hydrochloric acid and other organic solvents were bought from Aldrich as reagent grade and used without further purification. A typical routine synthesis is as follows: 100 ml of 0.1*M* HCl solution containing titania nanopowder (0.2 g) was added to a 500 ml double-neck round bottomed flask equipped with a magnetic Teflon coated stirrer. The mixture was sonicated for 30 min at room temperature. Py (0.0125 *M*) with 50 ml of 0.1*M* HCl was added to the above solution and stirred for 30 min. Then, 50 ml of 0.1*M* HCl solution containing APS (0.013 *M*) was added drop wise, with constant stirring and found a dark-green solution. After removing oxygen by bubbling with pure argon gas for 1 h the solution was irradiated by ^{60}Co γ-ray source. The resultant PPy-TiO_2 nanocomposites were carefully washed with methanol, and distilled water until the filtrate was colorless. The

obtained black powder was dried under a vacuum dryer at room temperature for 24 h. The bulk PPy powders were also synthesized using a similar method and the same mole ratios of monomer to dopant were incorporated into the polymerization without the TiO_2 nanopowder.

Instruments used for characterizations were: Elemental Analysis (EA) (FISON EA-1110), Scanning Electron Microscope (SEM) (Hitachi, S-4300), X-ray Diffraction (XRD) (Philips, X'Pert APD), and Thermal Gravimetric Analysis (TGA) (Dupont, 9900/2100).

Results and Discussion

Gamma-ray irradiation offers several advantages for the initiation of polymerization with inorganic nanoparticles over the conventional chemical methods. Γ-radiation has been applied extensively for the initiation of polymerization, grafting of polymer chains onto polymeric backbones, modification of polymer blends and preparation of interpenetrating polymer networks.[5] In our work, a large number of hydrated electrons and organic radicals including e^-_{aq}, $OH^\bullet$, H_3O^+ and pyrrolium cations were produced during γ-ray irradiation in aqueous solution. These hydrated electrons/radicals initiated the polymerization of free pyrrole existing in the reaction solution from *in-situ* polymerization and polyaniline chains were formed on the surface of titania nanoparticles which grow together to the composite by the aid of high energic γ-ray irradiation. As TiO_2 nanoparticles were electronegative in aqueous solution, the pyrrolium cations might have a possibility to adsorb on the surface of TiO_2 nanoparticles by the electrostatic attraction. Fig. 1 shows typical morphology of PPy-TiO_2 nanoparticles. Electron microscopic images represent the PPy-TiO_2 nanocomposites with the diameter between 50 nm and 300 nm. UV-visible absorption showed two electronic bands at about 320 and 596 nm for bulk PPy and the blue-shifted bands due to the formation of PPy-TiO_2 composites (not given figure here). XRD revealed typical polymer and titania phases in the nanocomposites (Fig. 2). The PPy-TiO_2 composites showed also improved thermogravimetric stability compared to the PPy homopolymer (not shown figure here). Electrical properties were checked by standard four-point probes method and found to be 0.028 S/cm for bulk PPy and 0.0015 S/cm for PPy-TiO_2 nanocomposites.

Conclusion

A simple and easy route for the synthesis of PPy-TiO_2 nanocomposites has been demonstrated in the presence of pyrrole monomer, titanium dioxide nanoparticles and a free-radical oxidant as starting materials, by the *in situ* radiation-induced oxidative polymerization method. PPy-TiO_2 nanocomposites synthesized by this novel method showed very good improved properties and they might be used potentially in industrial basis like charge storage and materials of solar cells for its excellent photovoltaic and absorption properties.

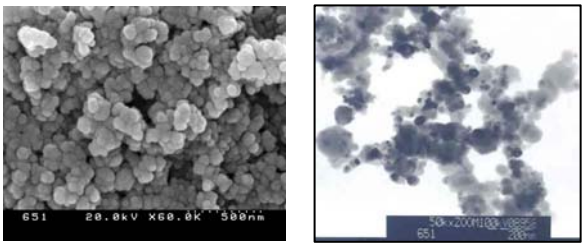

Fig. 1: (a) SEM, and (b) TEM images of PPy-TiO_2 composites.

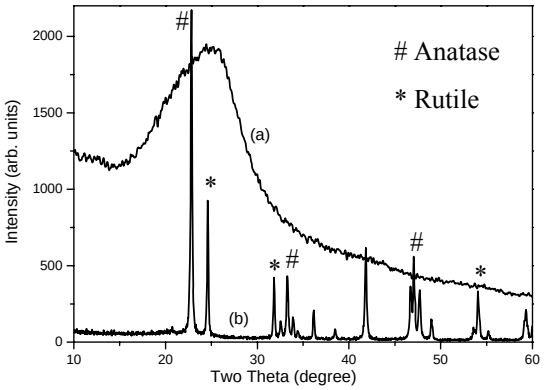

Fig. 2: XRD data of (a) PPy, and (b) PPy-TiO_2 composites.

References

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