# Synthesis and characterization of $TiO_2$/polystyrene hybrid nanoparticles via admicellar polymerization

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The research of nanocomposite systems has been recognized as one of the noble methods to embed either inorganic or organic particles into polymeric matrixes [1, 2]. In order to disperse inorganic compound effectively either physicochemical [3] or chemical [4–8] processes have been developed by synthesizing colloidal nanocomposites made of inorganic particles surrounded by polymeric materials. In this study the admicellar polymerization was adopted as a chemical process to prepare organic–inorganic composites. Admicellar polymerization, a term derived from adsorption and micelle, defines a class of *in situ* polymerizations taking place inside the surfactant bilayers adsorbed on various substrates, typically inorganic particles with hydrophilic surfaces.

Admicellar polymerization is a three-step chemical process: admicelle formation, monomer adsolubilization [9], and polymerization. The first step is the forming of an admicelle, which includes the adsorption of cationic surfactants on a negatively charged surface. In the second step, monomer adsolubilization process, the hydrophobic monomer is fed into the hydrophobic interior of the admicelle. This process can occur either after the formation of the admicelle or concurrently with surfactant adsorption. The final step is the polymerization. Proper initiator should be added to the reactor.

In this letter, titanium dioxide ($TiO_2$) core particles were covered with polystyrene (PS) shell in order not only to change the hydrophilic characteristics of the $TiO_2$ surface to hydrophobic but also to enhance the dispersion of $TiO_2$ particles in the oil medium. The nature of the coating on the $TiO_2$ particles was characterized by infrared spectroscopy (FT-IR, Perkin Elmer System 2000), Raman spectroscopy (FT-Raman, Bruker, RFS 100/S), thermogravimetric analysis (TGA, TA instrument, Q 50), and scanning electron microscopy (SEM, Hitachi, S-4300).

Cetyltrimethylammonium bromide (CTAB, Aldrich) was used as a cationic surfactant at a concentration of 0.9 mM, which is lower than the critical micellar concentration (CMC). Hydrophilic $TiO_2$ (R-900, Dupont) particles were added to the cationic surfactant solution with stirring for 24 hrs. After treatment of the $TiO_2$ surface in a surfactant solution, styrene (Aldrich) monomer was added to the mixture and then, stirring was continued for 24 hrs. Finally, the initiator, pottasium persulfate (KPS) (Daejung Chemicals) possessing anionic characteristics was added and the reaction mixture was heated up to 70 °C for 12 hrs under continuous stirring. After the admicellar polymerization, the resultant product was repeatedly washed using distilled water and then dried in a vacuum oven for 3 days.

In order to verify the chemical structure of the coating onto the $TiO_2$ core, an FT-IR spectral analysis was performed. Fig. 1 shows the FT-IR spectra of the pristine PS spheres which were synthesized separately, $TiO_2$ nanoparticles, and $TiO_2$ nanoparticles coated with PS. Characteristic peaks of the PS attributable to the C—H stretching in vicinity of 3000 $cm^{-1}$, aromatic C—C stretching around 1470 $cm^{-1}$, C—H out-of–plane bending at 765 $cm^{-1}$, and aromatic C—C out-of–plane bending at 700 $cm^{-1}$ were observed. Aromatic carbon overtones were also visible in 1700-2000 $cm^{-1}$ [10]. These characteristic peaks were also observed for the $TiO_2$ particles coated with PS. On the other hand, the characteristic peak of $TiO_2$ at 500–750 $cm^{-1}$ disappeared in the case of the $TiO_2$ coated with PS. Fig. 2 shows the Raman spectra of the same samples as in Fig. 1. Both the high spectral region and the low spectral region were blown up for clarity. In the high spectral region, both PS and $TiO_2$ coated with PS show the Raman shifts at 3020–3070 $cm^{-1}$ characteristic to the C—H stretching, at 2920–2940 $cm^{-1}$ due to the $-CH_2-$ anti-symmetric stretching, and at 2850–2860 $cm^{-1}$ due to the $-CH_2-$ symmetric stretching. However, $TiO_2$ does not show any characteristic peaks in this region. In the low spectral region, both PS and the $TiO_2$ coated with PS also yield the same results in the characteristic Raman shifts: peak at 1015–1045 $cm^{-1}$ due to the C—H in-plane band, and peak at 990–1010 $cm^{-1}$ due to the ring breathing (absent in ortho-and para-disubstituted compounds) [11]. The characteristic Raman shifts occur at 143, 235, 447, and 612 $cm^{-1}$ for rutile $TiO_2$ [12]. These bands then disappeared in the $TiO_2$ particles coated with PS. As a result of the surface treatment of $TiO_2$ particles, it is expected that the dispersability of the particles in the oil phase would be enhanced and the density of the coated particle would be reduced. In fact, the $TiO_2$ particles coated with PS was dispersed much better in the oil phase than the untreated $TiO_2$ particles. The surface characteristics of $TiO_2$ were changed from hydrophilic to hydrophobic,

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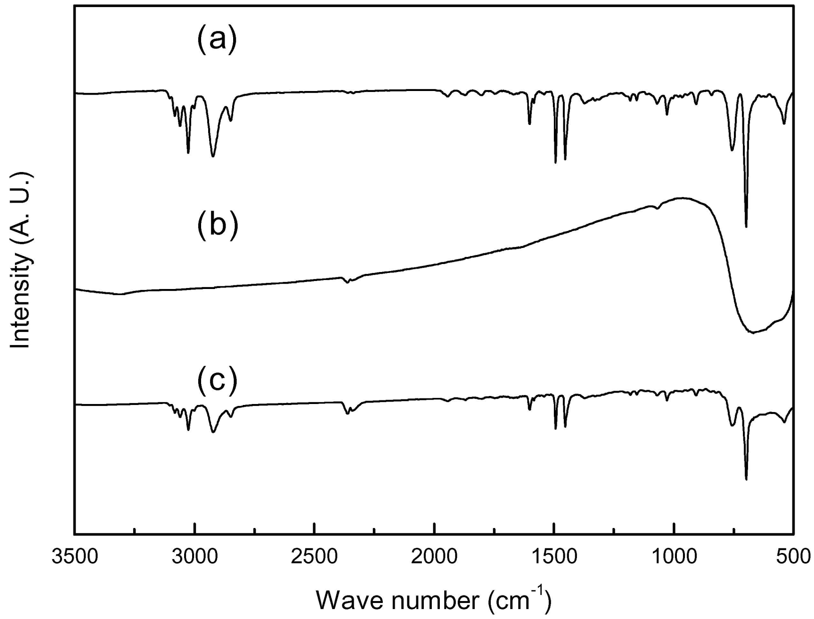

*Figure 1* FT-IR spectra of (a) polystyrene, (b) $TiO_2$, and (c) $TiO_2$ coated with polystyrene.

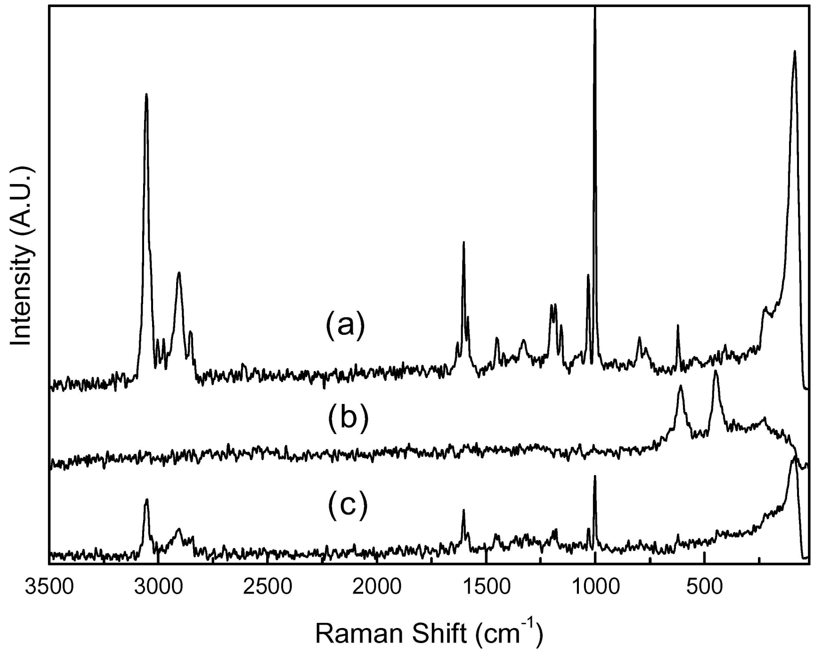

*Figure 2* FT-Raman spectra of (a) polystyrene, (b) $TiO_2$, and (c) $TiO_2$ coated with polystyrene.

resulting from the polymer coating onto the hydrophilic $TiO_2$. The density of the $TiO_2$ coated with PS was measured by pycnometer at 30 °C to be 2380 kg/m$^3$, which was lower than that of the pristine $TiO_2$ (4000 kg/m$^3$). Fig. 3 presents the SEM images of both pristine $TiO_2$ and $TiO_2$ coated with PS. The diameter of the pristine $TiO_2$ was about 200–400 nm and the surface was not very smooth. The size of the $TiO_2$ particles treated with PS is similar to that of the pristine $TiO_2$. However, the surface of the PS-coated $TiO_2$ was smoother compared with that of pristine $TiO_2$, and much smaller PS spheres were adsorbed on some of the particles. Based on the findings by FT-IR, Raman spectroscopy, and SEM, it can be confirmed that the $TiO_2$ nanoparticles were coated with a thin layer of PS. Thermal analysis of the $TiO_2$ particles coated with PS was performed by TGA (Fig. 4). The heating rate was 20 °C/min, purging with air. The PS that was coated on the $TiO_2$ particles, began to decompose around 300 °C and about 77% of the total weight was removed at 400 °C.

In summary, $TiO_2$ particles coated with PS were prepared by the admicellar polymerization method [13]. From both FT-IR and FT-Raman spectra, the characteristic bands of the coated $TiO_2$ particles were identical to the ones of PS. After the surface treatment, the characteristics of the $TiO_2$ surface was changed from hydrophilic to hydrophobic. In addition, the density of the particles was decreased and the dispersion of the $TiO_2$ particles in oil was enhanced as a result of the PS coating on the $TiO_2$ nanoparticles.

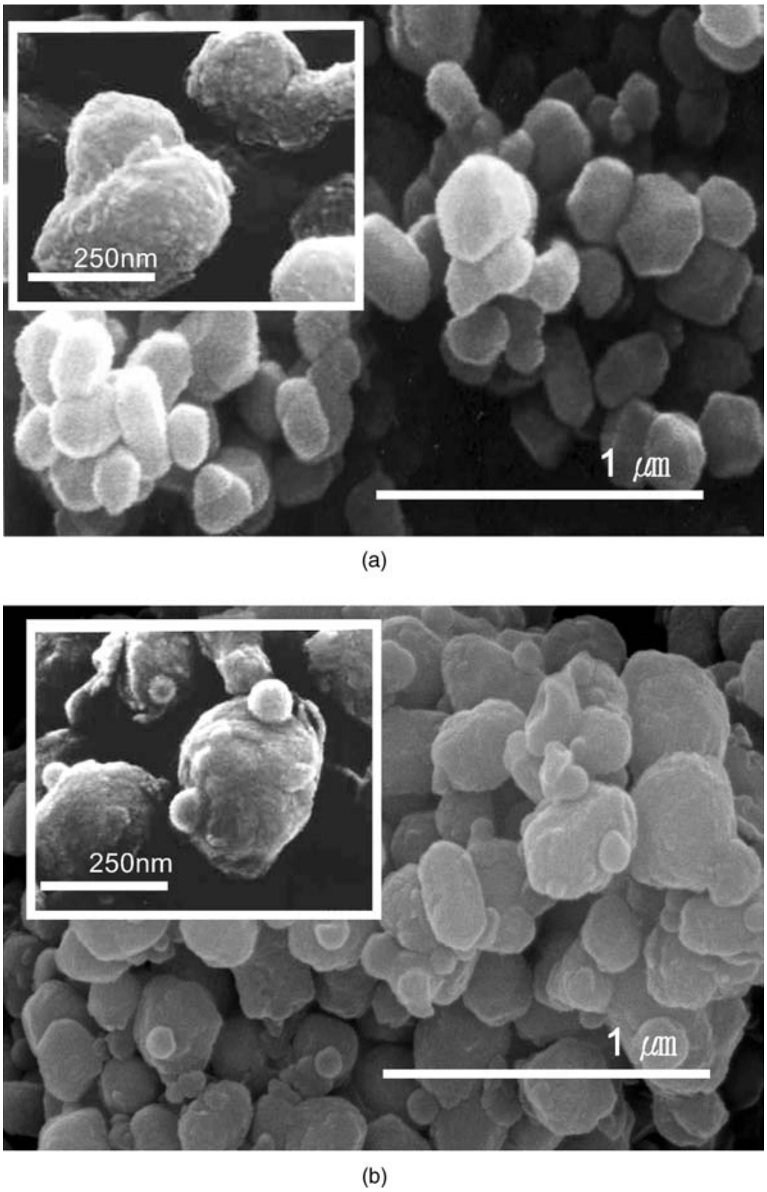

*Figure 3* SEM images. $TiO_2$ particle (a), $TiO_2$ coated polystyrene (b).

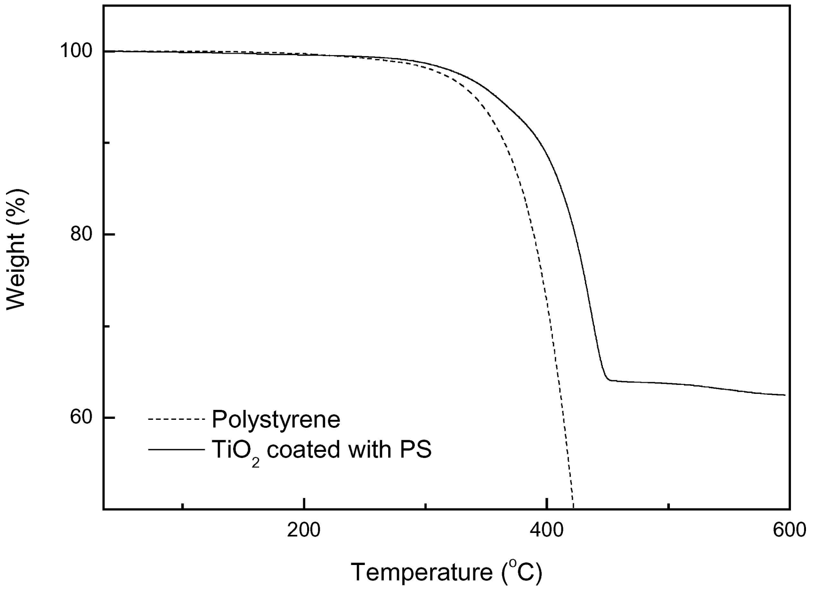

*Figure 4* TGA spectrum of $TiO_2$ coated with polystyrene.

## Acknowledgment

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