

Facile Synthesis of Highly Transparent Polymer Nanocomposites by Introduction of Core–Shell Structured Nanoparticles

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A high transmittance is the prerequisite for optically functional materials to be successfully used in practical applications. However, introduction of inorganic nanoparticles even at low contents into transparent polymers often leads to opaque nanocomposites due to light scattering caused by the nanoparticles because of the refractive index (RI) mismatch between nanoparticles and polymer matrices. This article reports for the first time a strategy for facile synthesis of highly transparent polymer nanocomposites by introduction of core–shell structured nanoparticles with the same RI. This strategy is based on the assumption that the core–shell structured nanoparticles can be regarded as integral nanofillers that have one refractive index in the polymer medium. In this study, core–shell structured silica–titania (S–T) nanoparticles were synthesized through coating titania with continuous feeding via hydrolysis of tetrabutyl orthotitanate (TBOT) to silica core prepared according to Stöber's method by base-catalyzed hydrolysis of tetraethylorthosilicate (TEOS) in ethanol solution. The transmittance of the S–T/epoxy nanocomposites synthesized by introduction of the S–T nanoparticles into a transparent epoxy matrix was studied as a function of the titania coating content. The optimal transmittance of the nanocomposite was successfully attained at the shell weight content of 36.5% in terms of the filler–matrix RI matching principle.

Introduction

Optically transparent polymer materials have been widely used in various devices such as optical lenses,¹ liquid-crystal displays,² dental restorations,³ and optoelectronic packages.⁴ With the rapid development of these technologies, both enhanced mechanical and physical properties are desired. Introduction of inorganic nanoparticles is an effective way to enhance mechanical and physical properties of transparent polymers. Indeed, improvement in strength and stiffness,^{1,5,6} thermal expansion coefficient and thermal conductivity,⁴ and UV-shielding and UV-resistance^{7–9} of optically functional materials has been achieved by introduction of inorganic nanoparticles. On the other hand, for optically functional materials, a high transmittance is the prerequisite so that they can be successfully used in practical applications. Unfortu-

nately, it is hard to maintain the high transmittance of transparent polymer matrices due to light scattering caused by the nanoparticles because of the mismatch of refractive index (RI) between the nanoparticles and the polymer matrix. For discrete spherical particles embedded in a transparent polymer matrix, the reduction of transmitted light intensity due to light scattering can be described by¹⁰

$$\frac{I}{I_0} \sim \exp \left[\frac{-3V_p x r^3}{4\lambda^4} \left(\frac{n_p}{n_m} - 1 \right) \right] \quad (1)$$

where x is optical path-length, V_p is particle volume fraction, r is particle radius, λ is light wavelength, and n_p and n_m are refractive indices of the particles and matrix, respectively. Equation 1 shows that in the absence of matching refractive index the light intensity reduces dramatically as r increases. That is, scattering losses can be minimized only for composites containing fine particles 1–2 orders of magnitude smaller than the wavelength of light.^{11,12} But as the particle size decreases, particle agglomeration becomes severe and deteriorates the particle dispersion in the polymer matrix.¹³ Such agglomerates persist in the composite and scatter visible light, leading to turbidity. Therefore, mere reduction of particle size is definitely inefficient to avoid scattering and thus turbidity.

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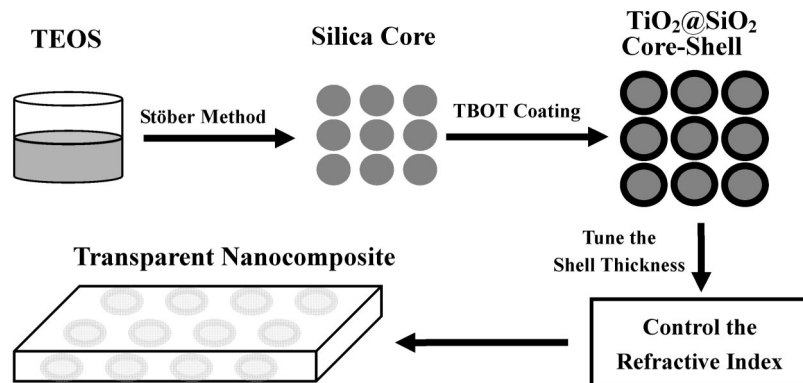


Figure 1. Schematic diagram for the preparation of the transparent S-T/epoxy nanocomposite.

Moreover, from eq 1, it is clear that optically transparent nanocomposites with the same transparency as the polymer matrix can be obtained when the refractive index perfectly matches between the inorganic fillers and the polymer (namely $n_p = n_m$). However, the RI is an intrinsic material property; in general, the RI of inorganic nanofillers is greatly different to that of pure transparent polymers, which would inevitably lead to light scattering and easily result in opaqueness even if at a very low nanoparticle content (less than 0.5 wt %).^{9,14} The RI mismatch, in the case of thin film materials, can be compensated by decreasing the particle size much below the wavelength of visible light, and hence the transparency can be maintained at a relatively high level, especially by very small film thickness.¹⁵ Nonetheless, from eq 1, it is easy to see that the transmitted light intensity decreases dramatically with the increase of the specimen thickness. This is probably why in many fundamental research works transparent polymer nanocomposites have most often been made in films with very small thicknesses.^{1–7} However, in practical applications, optical devices such as optical lenses, optoelectronic packages, and so forth may not be made in thin films. For bulky nanocomposites, this compensation of decreasing particle size is very limited. Consequently, it seems very difficult if not impossible to synthesize highly transparent polymer nanocomposites by introduction of normal inorganic nanoparticles.

Although the refractive index is an intrinsic material property, it may be tuned in the case of core-shell structured nanoparticles by assuming that they can be regarded as integral nanofillers that have one refractive index in the polymer medium. Therefore, it is possible in principle to readily prepare highly transparent polymer nanocomposites by introduction of core-shell structured nanoparticles with the same RI as that of the transparent polymer matrix. Now analysis about the refractive index of core-shell structured

nanoparticles is conducted below. The refractive index (RI) of a multicomponent nanocomposite takes the average value of the refractive indices of the components and can be approximately calculated by¹¹

$$n_{\text{composite}}^2 = \sum_i n_i^2 V_i \quad (2)$$

where n_i and V_i are the RI and volume fraction of the individual components, respectively. Core-shell structured nanoparticles can be regarded as representative elements forming the multicomponent nanocomposite. It follows that the refractive index of the composite core-shell structured nanoparticles can be reasonably calculated by eq 2. Therefore, the RI of a core-shell structured nanoparticle can be controlled over the range of RIs of its components.

In this study, silica and titania are selected to fabricate the RI tunable core-shell structured nanoparticles because silica and titania have been widely used as fillers for nanocomposites owing to their excellent mechanical, thermal, and optical properties to improve the physical and mechanical properties of transparent polymers.^{1,5,7,15–17} Moreover, the RIs of silica and titania are respectively 1.42–1.46^{18–21} and 2.5²² in the visible light wavelength range so that silica-titania (S-T) core-shell structured nanoparticles can give a broad range of RI that can match most transparent polymer matrices. Transparent epoxy with a refractive index of 1.54 was chosen as the matrix material since it is an important optoelectronic encapsulating material, but its physical and mechanical properties have to be improved for wider applications.^{4,9,17} This strategy is reported for the first time in this article for facile synthesis of highly transparent epoxy nanocomposites via introduction of core-shell structured nanoparticles with controlled refractive index.

Experimental Section

The silica core was synthesized according to Stöber's method by base-catalyzed hydrolysis of tetraethylorthosilicate (TEOS) in ethanol solution. Direct coating of the thin titania shell on silica core was performed with continuous feeding via hydrolysis of

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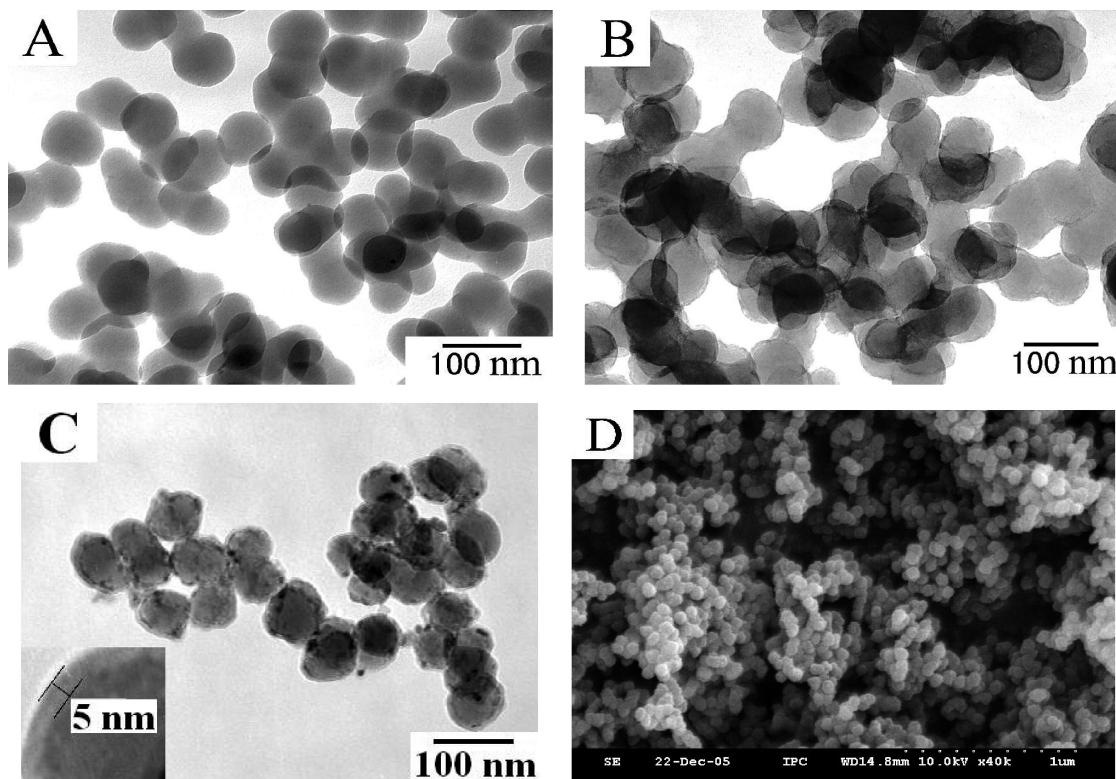


Figure 2. TEM images of (A) pure silica, (B) coated silica by titania with a weight percentage of 36.5 wt % before annealing, (C) TEM image, and (D) SEM image of coated silica by 36.5 wt % titania after annealing for 2 h at 600 °C.

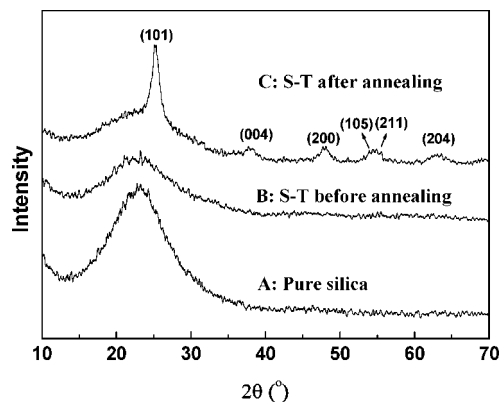


Figure 3. XRD patterns of pure silica and coated silica particles with titania of a weight percentage of 36.5 wt % before and after annealing for 2 h at 600 °C.

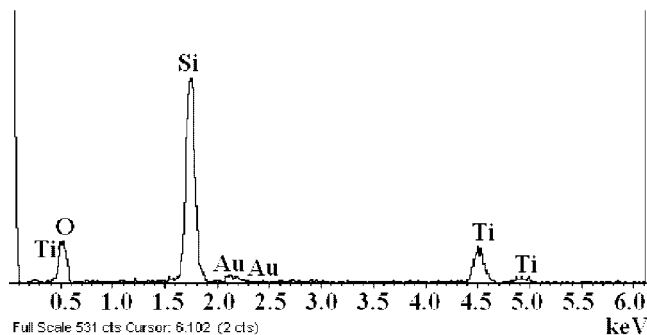


Figure 4. EDS spectrum of core-shell structured S-T nanoparticles.

tetrabutyl orthotitanate (TBOT) in ethanol solution. Annealing at 600 °C for 2 h was performed to obtain core-shell structured silica-titania (S-T) nanoparticles with a diameter of about 59 nm.

The as-prepared core-shell structured S-T nanoparticles were then dispersed in epoxy curing agent EP-400B (hexahydrophthalic anhydride, Bao & Lin Optoelectronic Co. Ltd. of China) using an ultrasonic technique for 1 h at 50 °C, and the resulting mixture was mixed with epoxy EP-400A (bisphenol A type epoxy resin, Bao & Lin Optoelectronic Co. Ltd. of China). The resulting mixture was well stirred until homogeneous and then poured into a stainless steel mold and heated in an oven for 1 h at 140 °C and 10 h at 100 °C. The thickness of fabricated samples was ~4 mm.

TEM images of nanoparticles were taken with a Hitachi 800 TEM. SEM images and the EDS spectrum of the nanoparticles were taken with a Hitachi S-4300 SEM. The mean particle sizes of 100 particles were estimated with the software Photoshop 7.0. XRD patterns were recorded on a RINT 2000 wide-angle goniometer with Cu K α radiation ($\lambda = 1.5406$ Å). The optical properties of S-T/epoxy nanocomposites were studied by UV-vis spectrophotometer (Model Lambda 900). TEM study of S-T/epoxy nanocomposites was conducted on a JEOL 2011 electron microscope. An atomic force microscope (AFM; Nanoscope IIIa, Digital Instruments Co.) was used to investigate the surface morphology of the pure epoxy and epoxy nanocomposites. AFM images were taken with 3×3 μm scan area from the prepared samples.

Results and Discussion

Figure 1 is the schematic diagram for the preparation of the transparent S-T/epoxy nanocomposite. Stöber's method was used to prepare the silica core, which was then coated with a titania shell via the hydrolysis of tetrabutyl orthotitanate (TBOT). According to eq 2, the RI of the core-shell structured S-T nanoparticles can be tuned by controlling the shell thickness or weight percentage of titania. Finally, the transparent S-T/epoxy nanocomposite was prepared from the transparent epoxy (EP-400) and the as-

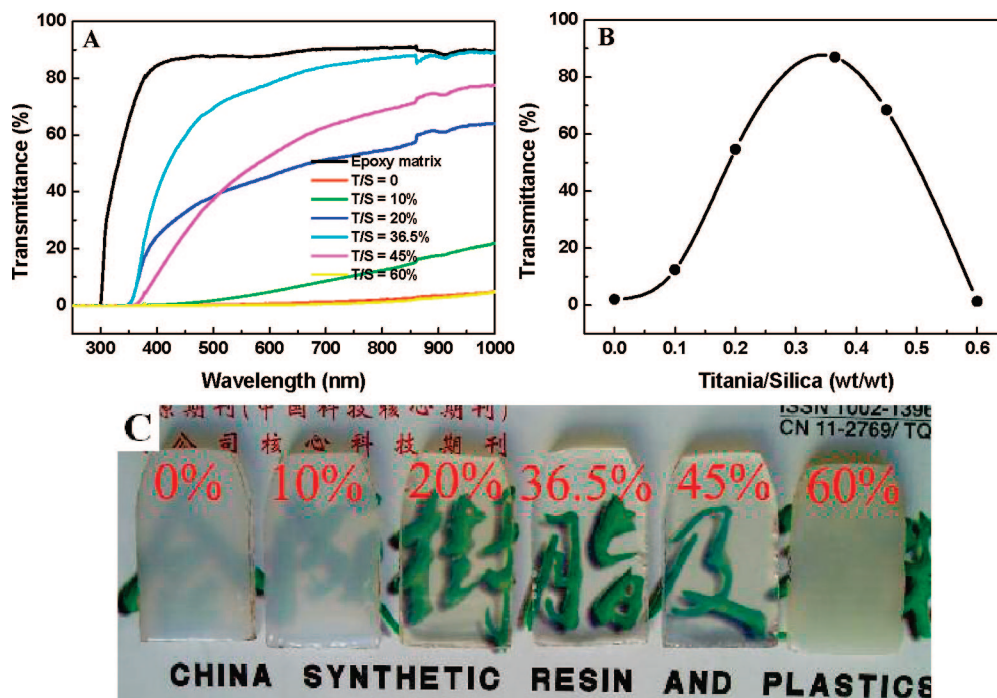


Figure 5. (A) UV-vis transmittance spectra of the epoxy matrix and the S-T/epoxy nanocomposites, (B) transmittance of the S-T/epoxy nanocomposites at 800 nm, (C) photo of the nanocomposites as a function of the shell weight percentage.

prepared core-shell structured S-T nanoparticles via the in situ polymerization method. The 1 wt % content of core-shell structured S-T nanoparticles was chosen as a representative example with no loss of generality since the addition of 1 wt % uncoated silica nanoparticles to the transparent epoxy (EP-400) matrix has already led to an almost totally opaque nanocomposite. This is the same as reported previously that addition of inorganic nanoparticles of a low content less than 0.5 wt % to a transparent polymer matrix could lead to an opaque nanocomposite.^{9,14} For higher contents (e.g., 2 and 10 wt %) of core-shell structured S-T nanoparticles, similar results were obtained and would not be repeated here for simplicity.

Figure 2A shows the transmission electron microscopy (TEM) image of pure silica prepared by the Stöber method. The silica nanoparticles with uniform size were spherical with smooth surface, and the average particle size measured from 100 particles was about 59 nm. TEM micrographs of the core-shell structured S-T nanoparticles with a coating of 36.5 wt % titania on the silica core (the core is considered as the filler while the shell is regarded as the matrix) before and after annealing at 600 °C for 2 h are given in Figure 2B,C, respectively. Clearly, titania was uniformly coated on the surface of the silica core since titania-coated silica particles became larger and rougher compared to pure silica particles, and no isolated titania particles were observed. The rough surface of the core-shell structured S-T nanoparticles was attributed to shell crystallization.²³ The dark color was caused by overlapping of nanoparticles as shown in Figure 2 A–C. After annealing, the mean diameter of the S-T nanoparticles was increased to about 69 nm obtained from 100 nanoparticles. In the inset of Figure 2 C, a typical core-shell structured S-T nanoparticle was shown with a shell

thickness of ~5 nm as a representative example. Figure 2D is a scanning electron micrograph of the core-shell structured S-T nanoparticles with a coating of 36.5 wt % titania on silica after annealing, confirming the uniformity and spherical shape of the S-T nanoparticles.

Figure 3 shows the XRD patterns of pure silica and coated silica with titania of a shell weight percentage of 36.5 wt % before and after annealing for 2 h at 600 °C. It will be shown later that the shell weight percentage of 36.5% is the one leading to the optimal transmittance for the nanocomposites. The XRD pattern of pure silica shows a broad peak at ~23°, indicating it is amorphous.²⁴ The XRD pattern of nonannealed S-T nanoparticles shows that the titania coating layer was also amorphous since no extra diffraction peaks appear except the broad amorphous silica peak around 23°. After annealing for 2 h at 600 °C, the characteristic peaks of anatase phase (JCPDS File No. 21-1272) appear, showing the titania coating of the S-T nanoparticles has been transformed from the amorphous phase to the anatase phase successfully.¹⁷ The corresponding broad background peak on the low angle side is due to the presence of the amorphous silica core. Moreover, no other phases could be detected, indicating that formation and reversion of oxygen bridged heterometal bonds like Si–O–Ti–O, Si–O–Si–O, and Ti–O–Ti–O bonding possibly with a chemical shift of the ppm level²⁵ that might probably take place at the boundary of silica core and titania shell could be ignored.

Figure 4 is the EDS spectrum of the core-shell structured S-T nanoparticles, showing that the nanoparticles are composed of silicon, titanium, and oxygen. Some amount of elemental gold is observed in the EDS spectrum because the surface of the nanoparticles is treated by spraying gold in

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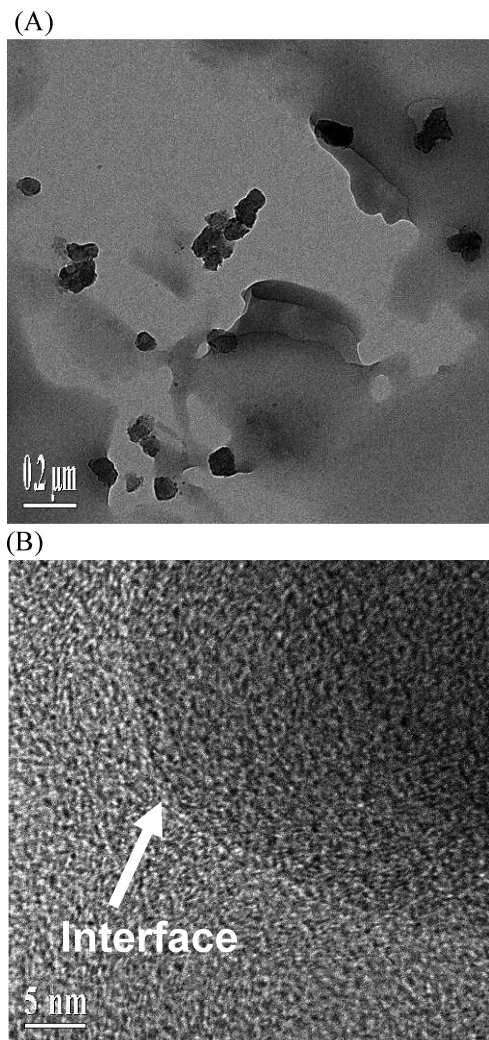


Figure 6. TEM images for (A) the dispersion of nanoparticles in the nanocomposite and (B) the nanoparticle–polymer interface adhesion.

the SEM experiment. The quantitative analysis shows that the atomic ratio of Si:Ti is about 2.17:1, which is slightly lower than the calculated atomic ratio of 2.28:1 from the stoichiometric composition of the 36.5 wt % of titania shell. This is because titania is on the surface layer of the core–shell structured nanoparticle with a diameter of about 69 nm while EDS mainly measures the surface layer elements and the elements in the core may not be completely detected.

The UV–vis transmittance spectra of pure epoxy matrix and S-T/epoxy nanocomposites with the 1 wt % filler content are shown in Figure 5A, where core–shell structured S-T nanoparticles have a titania shell content of 0, 10, 20, 36.5, 45, and 60 wt %. It can be clearly seen that epoxy nanocomposites filled with pure silica nanoparticles even having a smaller size compared to core–shell structured nanoparticles is almost totally opaque within the whole UV–vis range. Moreover, the transmittance of the S-T/epoxy nanocomposites varies as the shell content changes as shown in Figure 5A. As the titania shell content increases, the visible light transmittance at 800 nm of the S-T/epoxy nanocomposites increases up to a high value of 87% when the titania coating content is 36.5 wt % as shown in Figure 5B. Further increase in the weight percentage of titania shell leads to

the reduced transmittance of S-T/epoxy nanocomposites. The effect of the titania shell content on the corresponding transparency of the nanocomposites is exhibited in Figure 5C, which is consistent with Figure 5A,B. And the highest transparency is observed at the 36.5 wt % titania shell content.

From the above results, it is clear that introduction of core–shell structured nanoparticles can lead to development of highly transparent polymer nanocomposites. For polymer nanocomposites, nanoparticle dispersion, particle–polymer interface, sample surface roughness, and particle–polymer refractive index difference may have effects on the transmittance of the epoxy nanocomposites, and these effects are discussed below.

The dispersion of core–shell structured S-T nanoparticles in the epoxy nanocomposites and the nanoparticle–epoxy interface adhesion were analyzed by TEM as shown in Figure 6. As pointed out above, it is normally very hard to avoid nanoparticle agglomeration especially when nanoparticles are very small. It can be seen in Figure 6 that there are some degree of nanoparticle agglomeration though the nanoparticles are well dispersed in the epoxy matrix. For the RI mismatching cases, the particle agglomerates correspond to larger particles consisting of smaller nanoparticles, and thus the particle agglomeration would have a negative effect on the transmittance of the nanocomposite, reducing the transmittance of the transparent epoxy matrix. On the other hand, Figure 6 also shows that the nanoparticle–matrix interface adhesion is excellent. Hence, the effect of the particle–matrix interface on the transmittance is negligible.

The 2D and 3D AFM images of the surface topography obtained for the pure epoxy and nanocomposite samples are shown in Figure 7. It can be seen from Figure 7A,B that the sample surface prepared from pure epoxy is quite smooth and thus the light scattering due to the effect of surface roughness would be small. So, a high transmittance of pure epoxy resin has been observed as shown in Figure 5A. On the other hand, the addition of inorganic nanoparticles to a polymer would lead to an increase in viscosity, resulting in a rough surface of the nanocomposite samples as shown in Figure 7C,D. The surface roughness would have an effect on the light scattering, reducing the transmittance of the transparent epoxy matrix.

Now the effect of the refractive index on the transmittance of the nanocomposites is discussed as the major factor. From the statistical analysis of 100 nanoparticles using the software Photoshop 7.0 based on the TEM images shown in Figure 2A,C, the silica core and titania shell diameters (D_{Silica} and $D_{\text{S-T}}$) are estimated to be ~ 59 nm and ~ 69 nm, respectively. In the following calculation, it will be shown that the shell layer of the core–shell structured nanoparticles is not closely compacted but is composed of titania and air. So, the RI of core–shell structured S-T nanoparticles, $n_{\text{S-T}}$, should be calculated via the effective medium theory as expressed in eq 2:

$$n_{\text{S-T}}^2 = n_{\text{Silica}}^2 V_{\text{Silica}} + n_{\text{Titania}}^2 V_{\text{Titania}} + n_{\text{Air}}^2 V_{\text{Air}} \quad (3)$$

where n_{Silica} , n_{Titania} , and n_{Air} are the RI of silica, titania, and air, respectively. V_{Silica} , V_{Titania} , and V_{Air} are respectively the

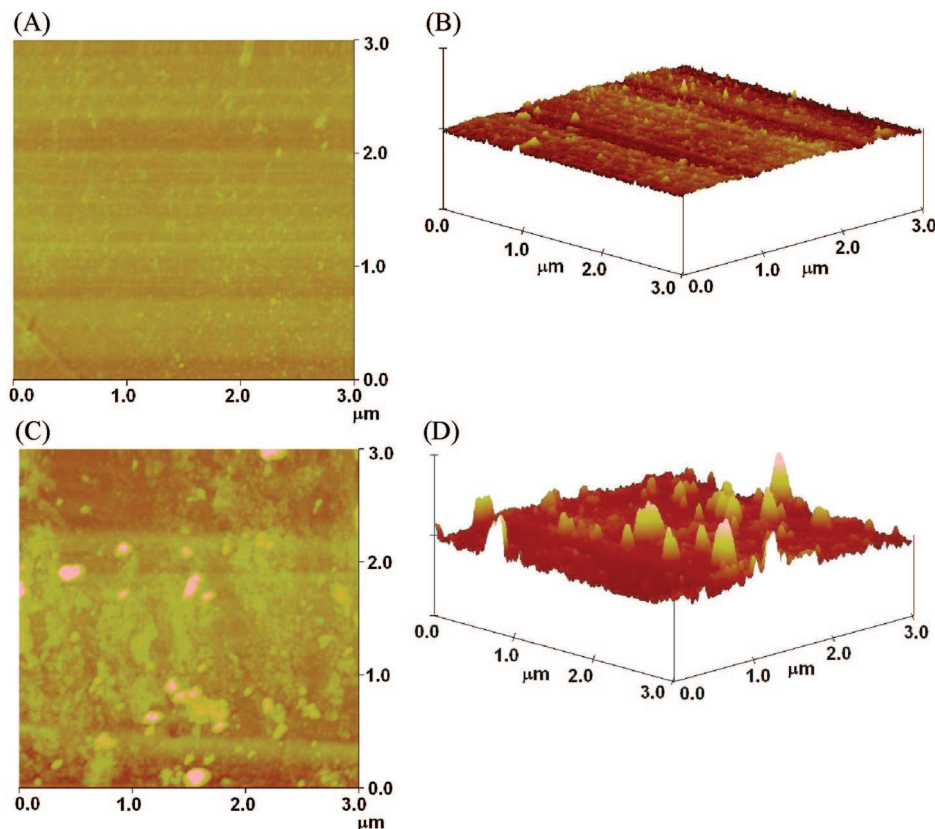


Figure 7. AFM images of the surface topography for the pure epoxy (A, B) and the epoxy nanocomposite containing 1 wt % S-T nanoparticles with the titania coating of a content of 36.5 wt % (C, D). The full height scale is 100 nm in the 3D AFM image, and it can be seen that the surface roughness is very small for the case of pure epoxy while the surface of the nanocomposite containing S-T nanoparticles is somewhat rough.

corresponding volume fractions of silica core, titania shell, and air and can be determined by

$$V_{\text{Silica}} = \left(\frac{D_{\text{Silica}}}{D_{\text{S-T}}} \right)^3 = 62.5\% \quad (4)$$

$$V_{\text{Titania}} = \frac{36.5 \text{ wt } \% \times V_{\text{Silica}} \rho_{\text{Silica}}}{\rho_{\text{Titania}}} = 12.9\% \quad (5)$$

$$V_{\text{Air}} = 1 - V_{\text{Silica}} - V_{\text{Titania}} = 24.6\% \quad (6)$$

where D_{Silica} (~ 59 nm) and $D_{\text{S-T}}$ (~ 69 nm) are the diameters of silica and S-T nanoparticles. ρ_{Silica} and ρ_{Titania} are respectively the densities of silica and titania and equal 2.2 g/cm^3 and 3.89 g/cm^3 ; $n_{\text{Silica}} = 1.42\text{--}1.46$, $n_{\text{Titania}} = 2.5$, and $n_{\text{Air}} = 1$ in the visible light wavelength range.²⁶ Equation 6 shows that there indeed exists air in the shell layer. Hence, we can obtain $n_{\text{S-T}} = 1.52\text{--}1.54$ using eqs 3–6, which is very close to the RI (1.54–1.55) of the transparent epoxy.^{9,27} This is why the highest transmittance and transparency of the S-T/epoxy nanocomposite have been observed at the 36.5 wt % titania shell content as shown in Figure 5B,C. Compared to the pure transparent epoxy, the best visible light transmittance for the refractive index matching case is slightly lower, partly resulting from the surface roughness as shown in Figure 7. Another reason is that the titania shell cannot be perfectly uniformly coated on the surface of all S-T nanoparticles,

leading to a slightly lower transmittance compared to pure transparent epoxy. The effect of particle dispersion on the transmittance should be negligible since the transmitted light intensity is independent of the particle size for the RI matching case as expressed in eq 1.

Here it should be pointed out that the RI of transparent polymer matrices is generally in the range of 1.5 to 1.7, which is within the tunable range of the RI of the core-shell structured S-T nanoparticles, and thus introduction of core-shell structured S-T nanoparticles will readily lead to the development of various transparent polymer nanocomposites. Moreover, this strategy can be extended to facile synthesis of other transparent composite systems based on transparent polymers such as transparent epoxy, polymethylmethacrylate, and so forth filled with core-shell structured nanoparticles of silica/ZnO and silica/ZnS, in which the RI of ZnO and ZnS are respectively 1.9–2.0⁹ and 2.4.²⁸

Conclusions

In conclusion, this article has reported for the first time a strategy for facile synthesis of highly transparent polymer nanocomposites via introduction of core-shell structured nanoparticles. Core-shell structured silica-titania (S-T) nanoparticles with controlled refractive index have been synthesized through coating titania with

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continuous feeding via hydrolysis of TBOT to silica core preprepared according to Stöber's method by base-catalyzed hydrolysis of TEOS in ethanol solution. The highly transparent S-T/epoxy nanocomposite with an 87% transmittance at 800 nm has been successfully synthesized by incorporation of the S-T composite nanoparticles with a matching refractive index into a transparent epoxy matrix. In principle, this strategy can be extended to facile synthesis of other transparent polymer nanocomposite systems based on transparent polymers such as transparent epoxy, polymethylmethacrylate, and so forth filled with core-shell structured nanoparticles of SiO_2/ZnO and SiO_2/ZnS since the refractive index of transparent polymers is

generally in-between that of the components in these core-shell nanoparticle systems.

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