Monodisperse SiO_2/TiO_2 Core-shell Colloidal Spheres: Synthesis and Ordered Self-assembling

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Monodisperse SiO_2/TiO_2 core-shell spheres have been prepared with conventional sol–gel method. The thickness of titania coatings on SiO_2 spheres was 30 nm, corresponding to 56.48 wt % titania loading and 1.66 effective refractive index of the composite particles. The relative standard deviation of composite spheres diameters distribution is 3.79%. The composite spheres were assembled, by gravity sedimentation, into three-dimensionally ordered colloidal crystals, which showed photonic band gap determined by UV–vis transmission spectrum.

It was generally accepted that the preparation of monodisperse titania spheres by conventional sol–gel method is very difficult,[1] because of the fast hydrolysis rate of titania precursor.[2,3] In our previous work, larger size SiO_2/TiO_2 composite spheres[4] and $SiO_2/TiO_2/SiO_2$ complex spheres[5] had been obtained, but the composite particles were not be able to be assembled into photonic crystals. In this paper the monodisperse SiO_2/TiO_2 colloidal spheres have been synthesized using conventional sol–gel method by control of the addition rate of water[6,7] into the reaction solution.

The monodisperse silica spheres of 256 nm were prepared by a seeding technique[5] on the basis of the hydrolysis and condensation of tetraethoxysilane (TEOS). SiO_2/TiO_2 composite spheres were synthesized by putting the silica particles into ethanol at room temperature, pouring tetrabutyl orthotitanate (TBOT) into the SiO_2–ethanol dispersion and adding double-distilled (DI) water dropwise into the solution at the rate of 0.003 mL/min and then brining the temperature to the boiling temperature. The number density of the SiO_2 particles in the ethanol was 3.615×10^{10}/mL and the initial concentration of the TBOT was 0.009 mol/L. The ethanol suspension was refluxed for 1.5 h, then stirred continuously for 1.5 h. Thus formed SiO_2/TiO_2 composite spheres were separated centrifugally from the reaction solution, washed with DI water. Finally, the SiO_2/TiO_2 composite colloidal crystal, showing bright pink color under sunshine, was obtained by gravity sedimentation of the composite particles dispersing in DI water.

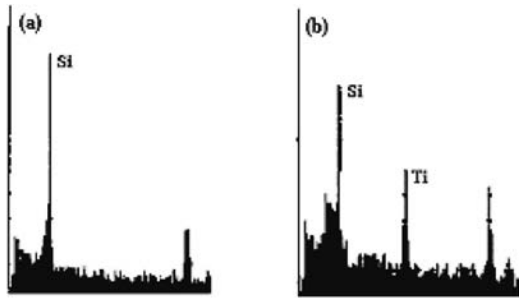

Figure 1. Energy dispersive X-ray fluorescence spectra: (a) plain silica spheres, and (b) the composite SiO_2/TiO_2 spheres.

Table 1. Relative contents of Si and Ti elements in plain SiO_2 and composite spheres measured by EDXS

Sample	Si content/wt %	Ti content/wt %
SiO_2 cores	≈100.0	≈0.0
TiO_2/SiO_2 spheres	73.886	35.739

The Si and Ti elements of the composite spheres were analyzed by energy-dispersive X-ray fluorescence spectrum (EDXS), as shown in Figure 1 and the relative contents of these elements are shown in Table 1.

The thickness of TiO_2-coating layer is calculated with gravity sedimentation rate and transmission electron microscopy (TEM), the results are shown in Table 2. Figure 2 are the TEM images of the spheres.

As shown in Table 2, the diameter measured by gravity sedimentation agrees well with that obtained by TEM.

The data of gravity sedimentation is obtained with the following formulas:

$$\nu = gd^2(\rho - \rho_0)/18\eta \quad (1)$$

$$d^3\rho = d_1{}^3\rho_1 + (d^3 - d_1{}^3)\rho_2 \quad (2)$$

where Eq 1 is stokes formula;
ν: Sedimentation velocity;
ρ_0, η: Density, viscosity of water;

Table 2. Diameter and TiO_2-coating thickness of core-shell spheres based on TEM and gravity sedimentation rate

Sample	Stockes diameter (based on gravity sedimentation rate) /nm	Mean TEM diameter /nm	Relative standard deviation of diameters based on TEM /%	TiO_2 coating thickness /nm	Titania loading[a] /wt %
SiO_2 cores	259	256	4.13	—	—
TiO_2/SiO_2 spheres	320	316	3.79	30	56.48

[a]Titania loading is calculated according to TEM diameter, the density of SiO_2 cores is 1.9 g/cm^3, and the density of amorphous TiO_2 is set as 2.5 g/cm^3.[5]

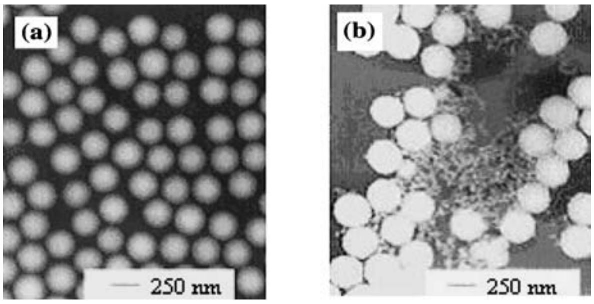

Figure 2. TEM images: (a) the plain SiO_2 particles, and (b) the composite SiO_2/TiO_2 spheres.

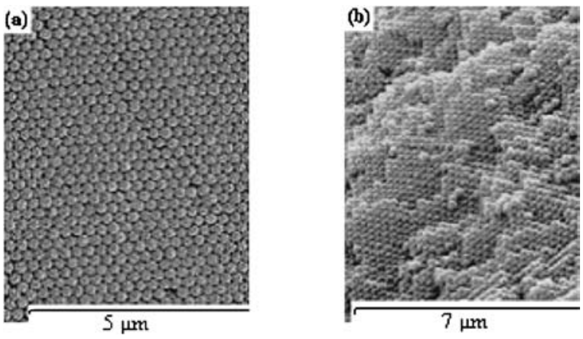

Figure 3. SEM images of the SiO_2/ TiO_2 colloidal photonic crystal: (a) the upper surface, and (b) the inner-section surface.

g: Gravity acceleration;
d, ρ: Diameter, density of composite spheres;
d_1, ρ_1: Diameter, density of core;
ρ_2: Density of coating layer;

The refractive index of composite spheres can be calculated with the formula[9] of

$$n_e{}^2 = (n_1)^2 f_1 + (n_2)^2 f_2$$

where n_e is the effective refractive index, n_1 and n_2 are the refractive index of component 1 and 2, respectively, and f_1 and f_2 are the volume fraction of component 1 and 2 in the spheres, respectively. On the basis of the above equation and the refractive indices of silica[8] (1.45) and amorphous titania[1] (1.88), the effective refractive index of the composite SiO_2/TiO_2 spheres is calculated to be 1.66, which is higher than that of silica (1.45) and polystyrene (1.59).

During the synthesis of the composite SiO_2/TiO_2 spheres some new TiO_2 nuclei formed, which are much smaller than the composite spheres, as shown in Figure 2b. The gravity sedimentation assembling process got rid of the small TiO_2 nuclei from the SiO_2/TiO_2 colloidal photonic crystal with selection technique.[10] SEM images of the SiO_2/TiO_2 colloidal photonic crystal are shown in Figure 3.

As shown in Figure 3, the crystal structure is face-centered-cubic (fcc) lattice, and the upper surface [111] of the colloidal photonic crystal, shown in Figure 3a, and the inner-section surfaces, shown in Figure 3b, exhibit large-range monocrystal array at each layer of colloidal photonic crystal.

The UV–vis transmission spectrum of the SiO_2/TiO_2 colloidal photonic crystal is shown in Figure 4. It is clear that there is a deep valley at 600 nm. Because titania has no absorption[11] above 400 nm and silica has no absorption[12] at ca. 600 nm, the band gap is the photonic band gap of the SiO_2/TiO_2 colloidal photonic crystal. As far as we know, there has not been report on the successful fabrication of colloidal photonic crystals with SiO_2/TiO_2 composite spheres.

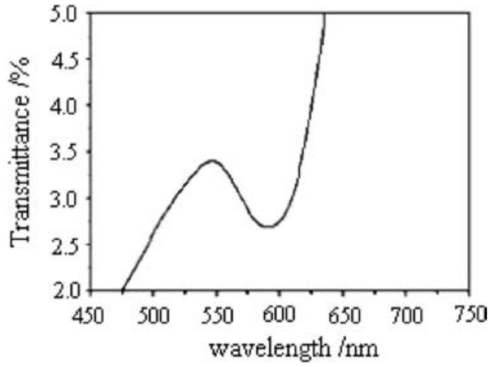

Figure 4. Transmission spectrum of the SiO_2/TiO_2 colloidal photonic crystal.

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