

Surfactant-Assisted Synthesis of Uniform Titania Microspheres and Their Clusters

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In this study, we demonstrate the surfactant-assisted synthesis of uniform-sized titania microspheres and their clusters for highly responsive optical materials. Monodisperse titanium glycolate microspheres were produced by controlled hydrolysis of glycolated titanium butoxide in acetone using surfactant as a stabilizer. The diameter of as-prepared particles ranged from 230 to 650 nm and was finely controlled by changing the concentrations of titanium butoxide and surfactant. In particular, the tunable range of the particle size was at a few tens of nanometers scale by the surfactant concentration, which was much finer than that by the concentration of titanium butoxide. Then, as-prepared titanium glycolate microspheres were transformed into monodisperse titania microspheres of anatase phase by heat treatment. Pure clusters of titania microspheres with an identical configuration were obtained by encapsulating a certain number of microspheres in emulsion droplets and subsequently evaporating the emulsion phase to induce self-assembly. Dynamic and static light scattering experiments show that the pure clusters with an identical configuration were well dispersed, and the refractive index of anatase phase titania microspheres was about 2.2. In addition, monodisperse Eu-doped titanium glycolate microspheres were prepared for phosphorescence sources by adding both a soluble precursor $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and glycolated titanium butoxide in acetone. Finally, photoluminescence properties of Eu-doped titania microspheres were examined after annealing.

Introduction

Colloidal structures with a feature scale comparable to optical wavelength have been studied extensively because they have strong interaction with light.^{1,2} For example, colloidal aggregates or clusters have been proposed for strong and efficient light scatterers in flat panel display and photovoltaic devices. Recently, a high-yield synthetic route for uniform colloidal clusters has been demonstrated by evaporation-induced self-assembly of colloidal particles encapsulated in emulsion drops.^{3–5} The emulsion-assisted colloidal clusters have unique configurations which depend only on the number of the constituting particles and the pure clusters of all identical configurations can be readily fractionated by centrifugation through a density gradient medium. The structural uniformity has been confirmed by unique scattering spectra from dilute dispersions of the fractionated

clusters.⁴ However, most of colloidal particles and clusters with uniform sizes and configurations in the previous studies have used silica and polymer latexes. These materials have relatively low refractive indices and are not applicable to highly efficient light diffuser films or strong scattering materials which are required for random lasers.^{6,7} Therefore, it is still challenging to synthesize monodisperse colloidal microspheres of highly reflective materials which do not absorb visible light.

One of the potential candidates is titanium dioxide (or titania) microspheres and their clusters.^{8,9} However, it is difficult to produce uniform titania microspheres with good dispersion stability from titanium alkoxides primarily because the precursors are too reactive to separate the seed formation and growth reaction stages.^{10,11} Nevertheless, several groups have been developing the synthetic methods for titania microspheres from titanium precursors in polar solvents by

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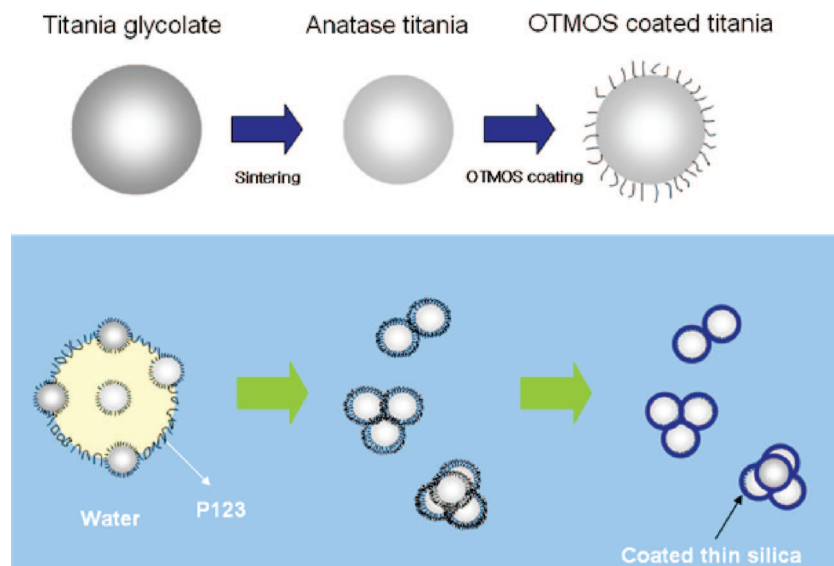
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Scheme 1. Schematic Diagram for the Fabrication of Colloidal Clusters of Titania Microspheres from Oil-in-Water Emulsion^a

^a Oil phase is hexane, and water phase contains Pluronic P123, which is used as emulsion stabilizer.

adding salts for electrostatic stabilization or polymeric stabilizers such as hydroxypropyl cellulose and block copolymers.^{10,12} The remaining issue is that these particles are still polydisperse and the uniformity does not satisfy the requirement for photonic nanostructures. Recently, Xia and his colleagues demonstrated that highly monodisperse titania particles could be produced by using a less reactive titanium precursor solution.¹³ However, the resulting particles tended to form irregular aggregates because they did not use a stabilization agent. To address this problem, we introduced a stabilizing agent into the sol-gel reaction of a titanium precursor with reduced reactivity for the synthesis of highly stable monodisperse titania microspheres. Also, the monodisperse titania microspheres were self-organized into colloidal clusters with unique configurations by using emulsion drops as confining geometries. Light scattering properties of the pure clusters with uniform configurations were characterized by a simple single-particle light scattering experiment. Fitting the scattered spectra to theoretical model simulations enabled to estimate the refractive index of titania microspheres, which is otherwise hardly measurable. Finally, highly efficient photoluminescent titania microspheres were successfully produced by doping rare-earth substances in the titania microspheres. The resulting titania microspheres are potentially useful for amplified spontaneous emitters or enhanced luminescence devices since light scattering intensity from the highly reflective particles can be strongly enhanced.^{14,15}

Experimental Section

Synthesis of Monodisperse Titanium Glycolate and Titania Microspheres. For reactivity-reduced titania precursor solutions, 0.46% (w/w) of titanium butoxide (97%, Aldrich) was chelated by

mixing with ethylene glycol in a glovebox for 10 h at room temperature, in which the moisture content was kept below 0.1 ppm. We used various types of surfactants as stabilizers including Tween 20 (polyoxyethylene (20) sobitan monolaurate, $C_{58}H_{114}O_{26}$, Aldrich), SDS (sodium dodecyl sulfate, $C_{12}H_{25}NaO_4S$, Fluka), CTAB (hexadecyltrimethylammonium bromide, $(C_{16}H_{33})N(CH_3)_3Br$, Aldrich), and Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, BASF).

Typically, for 650 nm titania microspheres, Tween 20 was dissolved in 12 mL of acetone at a concentration of 2.03 mM with rigorous stirring for 10 min. A total of 1.2 mL of the mixture of titanium butoxide and ethylene glycol was added into the acetone which contained Tween 20. Here, the concentration of titanium butoxide in acetone was kept at 1.46 mM. After agitation for 10 min, the transparent solution became milky white, and white precipitate was formed at the bottom after one day. Then, unreacted precursors and acetone were removed via solvent exchange. The white precipitate was cleaned by centrifugation at 7000 rpm for 5 min and redispersed in ethanol. The washing and redispersion processes were repeated twice. Then, the precipitates dispersed in ethanol were dried in convection oven at 70 °C. The dried samples of titanium glycolate were annealed at 500 °C for 2 h to induce phase transition to anatase phase. For titania microspheres with different sizes, we adjusted the concentrations of titanium butoxide and surfactant in acetone.

For stable dispersion of anatase titania microspheres in organic solvent, we modified the particle surface as follows: First, 1.4 mL of NH_4OH (28%, Junsei) was added into 10 mL of 8 wt % titania suspension in ethanol. Then, 2 mL of chloroform which contained 10 vol% octadecyltrimethoxysilane (OTMOS, Aldrich) was added into the ethanolic titania suspension, and the mixture was stirred for 2 h. The procedure was repeated twice for the sufficient surface coverage of OTMOS on the titania microspheres. Finally, the organically modified titania microspheres were cleaned by centrifugation to remove chloroform and unreacted precursors and redispersed in hexane.

Titania Colloidal Clusters and Fractionation. Scheme 1 shows the procedure for preparing colloidal clusters of titania microspheres. First, 500 nm titania microspheres that were treated with OTMOS were dispersed in hexane at 2 wt%. Then, 1 mL of titania microsphere suspension was added into 8 mL of water which contained 1 wt% of triblock copolymer of poly(ethylene oxide) and

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poly(propylene oxide) (Pluronic P123, BASF) as emulsion stabilizer. The two-phase mixture was emulsified in a homogenizer for 40 s at 8000 rpm. The resulting emulsion was gradually heated up to 80 °C with stirring to evaporate hexane from the drop phase. During evaporation-induced shrinkage of the hexane-in-water emulsion drops, the titania microspheres organized spontaneously into colloidal clusters. To enhance mechanical strength, the resulting clusters were coated with thin hydrophilic silica films that were formed through sol-gel reaction by adding 0.5 mL of NH_4OH and 0.25 mL of TEOS and stirring for 2 h. The clusters were fractionated according to the number of the constituent microspheres by centrifugation in density gradient medium of glycerol following the standard procedures.³ The fractionated uniform clusters were washed by centrifugation and redispersed several times to remove glycerol or any contaminants for clear microscopic image or light scattering experiment.

Synthesis of Eu-Doped Phosphorescent Microspheres. Europium (Eu)-doped phosphor titanium glycolate microspheres have been prepared by adding hydrous europium nitrate ($\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 99.9%, Aldrich) as a phosphoric precursor. First, $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 12 mL of acetone which contained Tween 20 at a concentration of 2.03 mM. The concentration of $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was in the range of 1.94–19.4 mM. Then, 1.2 mL of the mixture of titanium butoxide and ethylene glycol was added into the acetone solution and agitated for 5 min until initially transparent solution was changed into milky suspension. After aging for 3 h, the precipitate was collected and washed by centrifugation. Then, the precipitate was dried into powder in a convection oven at 70 °C. The dried sample was loaded into an alumina crucible and placed in a muffle furnace to enhance the luminescence of Eu in titania matrix. The heat treatment was carried out at 500 °C for 2 h.

Sample Characterization. Titania microspheres and their clusters in aqueous medium were observed through optical microscope (Nikon TE2000-U) equipped with an oil-immersion objective. Field-emission scanning electron microscope (FESEM, Philips FEG XL 30S) images were taken after rendering samples conductive with gold coating to avoid electric charging. The size and polydispersity of the microspheres were analyzed from the SEM images using Image Pro (ver. 4.1, Media Cybernetic). To examine the crystallinity of as-prepared particles, X-ray diffractometer (XRD, Rigaku D/MAX IIIC) with $\text{Cu K}\alpha$ radiation was used. The surface area and pore size of the titania particles were also characterized by a surface analyzer (Micromeritics).

For single particle light scattering, the fractionated cluster suspension was diluted with pure deionized water. Dynamic and static light scattering experiments were performed with Ar-ion laser of 488 nm (BI 9000AT/200SM, Brookhaven). The angle-dependent scattering intensity was calculated using a T-Matrix Solver for Maxwell equation programmed by Mackowski.¹⁶ Photoluminescence spectra of Eu-doped titania microspheres were measured on a high resolution mapping system (LabRam HR, Sci-Tech) with the excitation wavelength of 325 nm (He-Cd laser). Zeta potential of as-prepared particles in aqueous solution was examined by a particle size analyzer (Zetasizer Nano ZS, Malvern) to check the phase stability in aqueous medium.

Results and Discussion

Surfactant-Assisted Synthesis of Monodisperse Titanium Glycolate and Titania Microspheres. In Figure 1, the SEM images show that as-prepared titanium glycolate

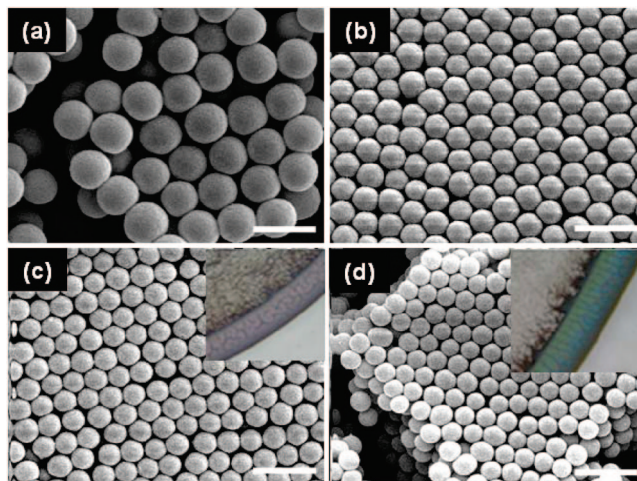


Figure 1. SEM images of the spherical colloids of titanium glycolates with different diameters that were prepared from the mixture of titanium butoxide and ethylene glycol in acetone: (a) 650 nm, (b) 460 nm, (c) 330 nm, and (d) 300 nm. The concentrations of titanium butoxide and Tween 20 in acetone were (a) 1.46 mM and 2.03 mM, (b) 1.34 mM and 2.03 mM, (c) 0.974 mM and 2.03 mM, and (d) 0.731 mM and 0.34 mM, respectively. Scale bars are 1 μm .

microspheres in the presence of Tween 20 surfactant are highly monodisperse ranging from 300 to 650 nm. The monodisperse titanium glycolate microspheres were cast into colloidal crystal films of several tens of stacking layers, which reflected incident light selectively in a specific range of wavelength. Insets of Figure 1c,d showed the images of the specific reflected colors under the optical microscope.

In our synthetic strategy, the particle size was changed with the concentrations of titania precursor and Tween 20 surfactant. As shown in Figure 2a, the particle size became larger as the concentration of titanium butoxide in acetone was increased from 0.61 to 1.46 mM at a fixed surfactant concentration of 2.03 mM. On the other hand, the particle size was a slightly decreasing function of the surfactant concentration. As shown in Figure 2b, 330 nm titanium glycolate microspheres were produced by titanium butoxide in acetone at a concentration of 0.731 mM without surfactant. Then, as the concentration of Tween 20 was increased stepwise from 0 to 1.70 mM in the titania precursor solution, the particle size was decreased monotonically to about 225 nm. Further increase in the concentration of Tween 20 above 1.70 mM did not induce the size change. It is noteworthy that the degree of change in the particle size induced by the variation of the surfactant concentration was small as compared with the size change by the concentration of titanium butoxide. Consequently, our method can control the particle size precisely by adjusting both the concentrations of titania precursor and surfactant.

By annealing the titanium glycolate particles at 500 °C, anatase titania microspheres were produced as shown in the SEM image of Figure 3b. Compared with titanium glycolate microspheres in Figure 3a, the surface of titania microspheres was slightly roughened because the removal of ethylene glycol left behind mesopores during heat treatment. Their crystalline structures were confirmed from XRD peaks in

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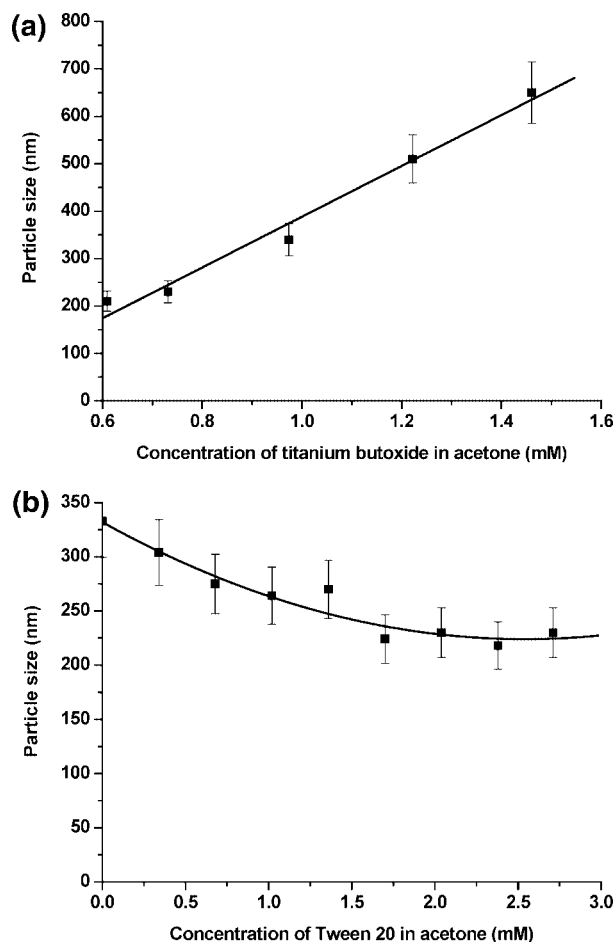


Figure 2. Average particle sizes of titanium glycolate colloids as a function of (a) the concentration of titanium butoxide in acetone with 2.03 mM of Tween 20 and (b) the concentration of Tween 20 in acetone with 0.731 mM of titanium butoxide.

Figure 3c, and the average crystallite size was about 9 nm as estimated from Scherer equation. We observed small grains of anatase phase titania particles, which were less than 10 nm as shown in the TEM images of Figure S1 of Supporting Information. During heat treatment, the surface area, which was measured by N_2 adsorption, increased from 11.4 m^2/g for as-prepared titanium glycolate particles to 87.2 m^2/g for annealed titania.

We have also studied the effect of types of surfactant on the morphology of as-prepared titanium glycolate particles using anionic surfactant SDS, cationic surfactant CTAB and nonionic surfactant Pluronic P123. Here, the concentrations of surfactants in acetone were fixed at 2.03 mM and the concentrations of titanium butoxide in acetone were changed from 0.73 to 1.46 mM. As shown in Figure 4a and b, when ionic surfactants SDS and CTAB were used instead of Tween 20, spherical particles were also produced. However, their size distribution was broadened and most of the particles were agglomerated because the stabilizing effects of ionic surfactants in acetone were not good enough as compared with nonionic surfactant Tween 20. In the presence of SDS, the primary particle sizes were not changed by the concentration of titanium butoxide. In case of CTAB, the primary particle sizes gradually increased from 200 to 460 nm, when the concentrations of titanium butoxide were changed from

0.73 mM to 1.46 mM (See Figure S2 of Supporting Information).

When triblock copolymer Pluronic P123 was used as surfactant, titania microspheres were produced together with rod-like particles as shown in Figure 4c. The formation of rod-like particles was due to the templating micelles of the triblock copolymer. With increase in the concentration of titania precursor in acetone from 0.73 to 1.46 mM, the size of titania microspheres was increased from 50 to 300 nm. The rod-like particles were 1 to 10 μm long with transversal length scale ranging from 100 to 500 nm. Since the number density of the templating micelles for rod-like particles was fixed at a constant surfactant concentration, the fraction of rod-like particles was gradually increased as the concentration of titanium butoxide decreased. In particular, most of titania particles were rod-like when the titanium butoxide concentration was as low as 0.73 mM (see Figure S3 of Supporting Information).

Cluster Formation of Titania Microspheres. Colloidal clusters of titania microspheres were produced from hexane-in-water emulsion drops which contained a certain number of titania microspheres. The clusters of titania microspheres in water were successfully produced when hexane was completely removed by evaporation. The aqueous dispersion of titania clusters was highly stable because triblock copolymers tethered at the cluster surface prevented cluster-cluster aggregation. During cluster formation, three distinctive forces act on the emulsion droplets which encapsulate titania particles: namely, capillary force that pushes the particles together in shrinking oil droplets, short-range repulsive force that keeps them apart, and van der Waals attraction that ultimately binds them together. From previous reports, the ultimate cluster configurations are nearly identical for a given number (n) of the constituting microspheres when n is not large. For example, the cluster configuration of silica or polymer latex particles with polydispersity as small as 0.005 is insensitive to the precise nature of interaction forces up to $n = 7$. In this paper, we could observe all identical configurations up to $n = 6$. For $n > 7$, a number of different packing structures were observed due to relatively high polydispersity (~ 0.1) of titania microspheres. It should be noted that the polydispersity we obtained is very low considering the highly reactive nature of titania precursor. To get pure titania clusters with uniform configurations, as-prepared titania clusters were redispersed in water and fractionated by centrifugation at 600 times of gravity for 15 min in linear density gradient of glycerol medium. The result is reproduced in Figure 5 which shows that the pure clusters were successfully fractionated into isolated bands. The optical and SEM images show that each band contains pure clusters with an identical configuration. In our previous report, we demonstrated that the density gradient centrifugation was capable of producing a massively large number of pure clusters of polystyrene latex spheres in laboratory-scale experiments.⁴ The same levels of productivity and purity can be expected from the density-gradient centrifugal fractionation of titania clusters because the densities and diameters of polystyrene latex and titania particles were not significantly different. Indeed, each fractionated band contained

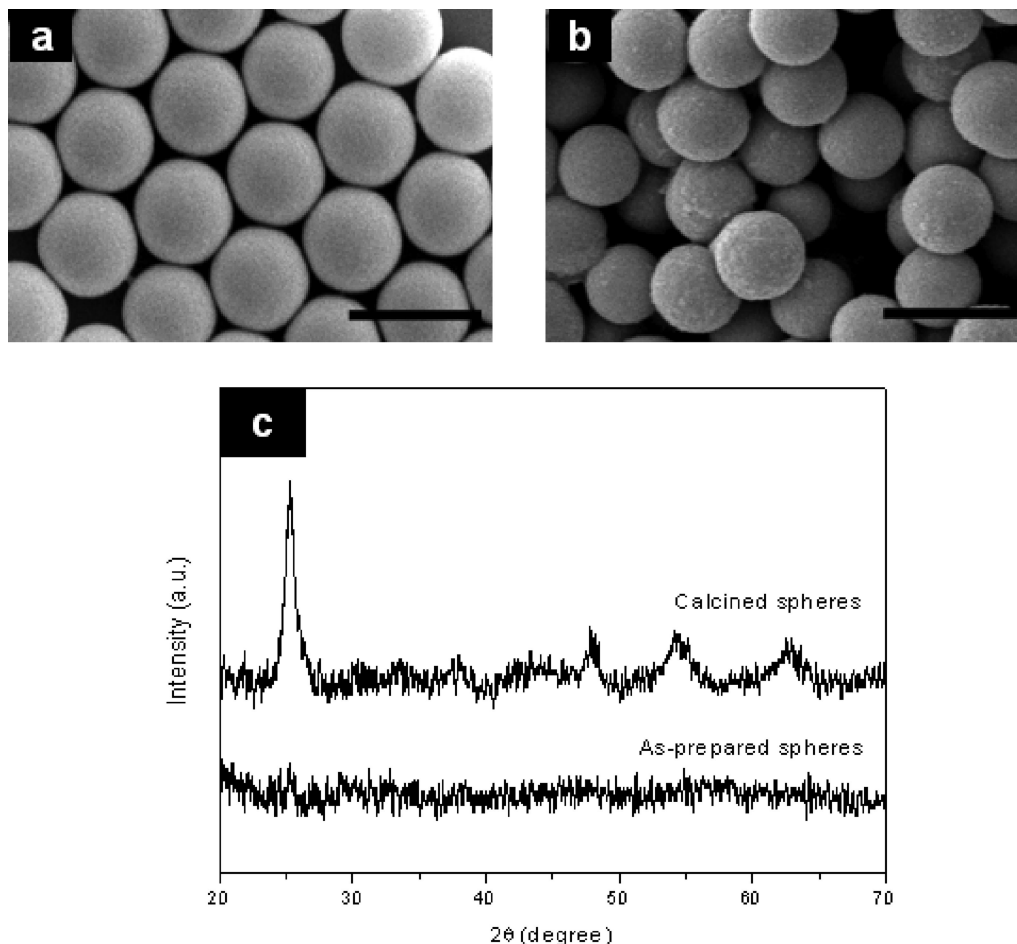


Figure 3. SEM images of (a) titanium glycolate and (b) titania microspheres before and after sintering. Scale bars are 1 μm. (c) X-ray diffraction patterns of titanium glycolate and titania microspheres before and after sintering.

billions of titania clusters which were all uniform in their configuration for $n = 2-6$. This indicates clearly that breakup or aggregation of clusters did not occur during centrifugal sedimentation in density gradient medium.

As we mentioned earlier, titania with high refractive indices causes strong scattering compared to polymer latexes or silica, which is potentially useful for optical applications. For example, when the structured clusters are randomly embedded in optical films, the strong localization of light will be achieved by strong multiple scattering.

Static Light Scattering of Colloidal Titania Clusters.

Single isolate spheres (singlets), two-sphere clusters (doublets), and three-sphere clusters in triangular coordination (triplets) were extremely diluted in water and static light scattering experiment was performed. To do this, we used Ar-ion laser with wavelength of 488 nm as a light source and the colloidal clusters of 520 nm titania microspheres. In Figure 6, the scattered intensities are plotted as a function of the scattering angle for singlets, doublets and triplets. Also included for comparison are the corresponding theoretical results from T-Matrix simulation that is one of the powerful methods to compute the electromagnetic scattering of isolated spheres or clusters of spheres by solving Maxwell equation for the multiple spherical boundary domains.¹⁶ For uniform colloidal clusters which consist of a few identical spheres, the required parameters for T-matrix simulation are the configuration, size and refractive index of the constituting

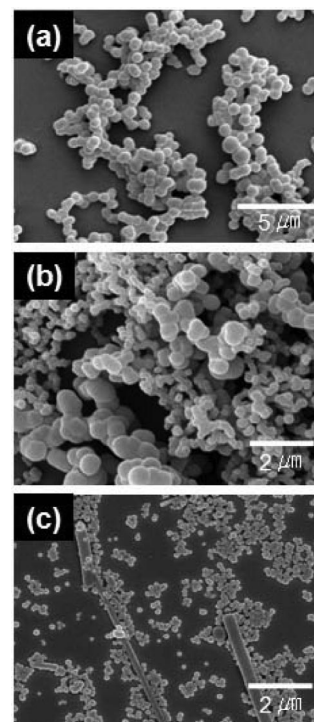


Figure 4. SEM images of titanium glycolate microspheres produced using (a) SDS, (b) CTAB, and (c) Pluronic P123 as stabilizers. The concentrations of titanium butoxide and surfactants were fixed at 1.46 mM and 2.03 mM in acetone, respectively.

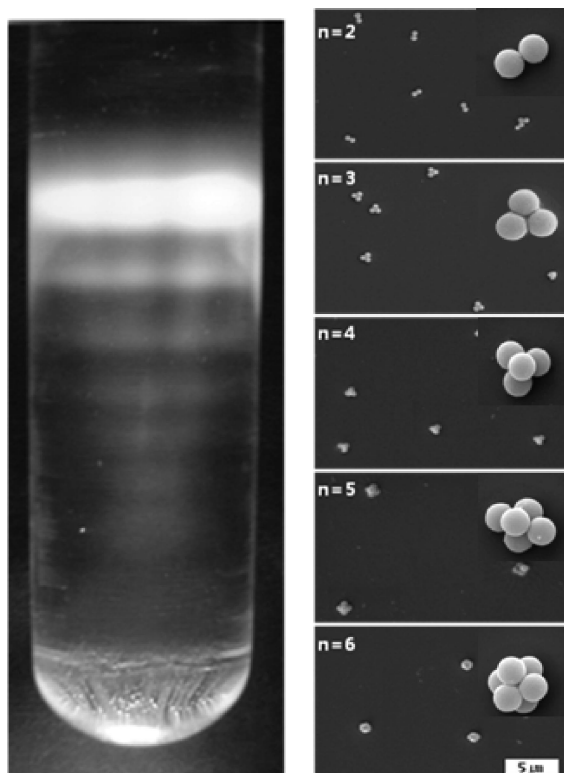


Figure 5. Test tube containing a cluster suspension of 520 nm titania microspheres separated by density gradient centrifugation and SEM images of colloidal clusters extracted from the corresponding bands.

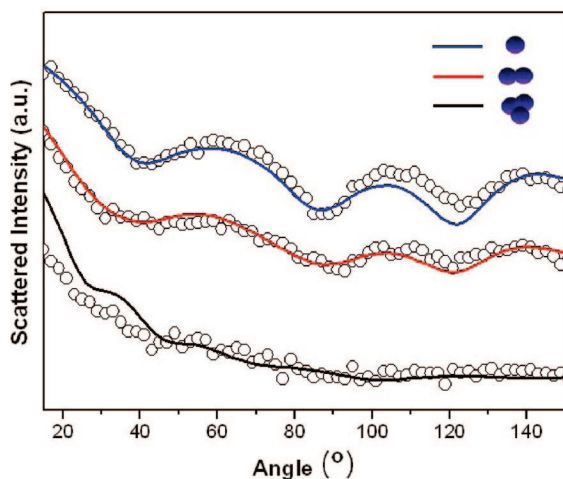


Figure 6. Scattered intensity as a function of the scattering angle of thin-silica coated titania singlets, doublets and triplets. Solid lines are the simulated scattered intensities. The wavelengths of incident and scattered light were 488 nm and the diameter of titania microspheres was 520 nm.

spheres. Here, we considered only real part of the refractive index, assuming that titania particles do not absorb light. Then, the scattered field in T-matrix became spherical transverse wave, and finally the scattered intensity of clusters was given as a function of the scattering angle. In the scattering experiment, the standard deviation of the measured intensities was kept below 10% for all measured angles. Experimental data are in good agreement with the simulation results for all uniform clusters. By matching the experimental light scattering data with T-Matrix simulation, the average refractive index of the prepared titania microspheres was estimated as about 2.2, which was numerically accurate for

a given set of free parameters. This is slightly lower than the refractive index of 2.4 for single-crystal anatase phase titania because the titania microspheres are polycrystalline with pores among granules as shown in the TEM images of Figure S1 of Supporting Information.

Eu-Doped Luminescent Titania Microspheres. Eu-doped luminescent microspheres were also prepared by adding $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ as a doping agent in titanium glycolate matrix. The SEM images in Figure 7a–c showed Eu-doped titania microspheres that were synthesized for three different $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ concentrations of 1.94, 9.7, and 19.4 mM in acetone with fixed concentrations of titanium butoxide and Tween 20 at 1.46 mM and 2.03 mM, respectively. The particle sizes were decreased with increase in the concentration of $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. Specifically, the average particle size, which was 650 nm in the absence of Eu-dopant, was decreased to 500 nm in the presence of $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ at 1.94 mM. Further increase in the dopant concentration to 9.7 mM and 19.4 mM reduced the average particle size to 380 and 330 nm, respectively. Also, the particle size distribution was slightly broadened in the presence of $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ with polydispersity of 0.13–2.0 due to weak aggregation. Although Eu-doped titania nanoparticles were slightly polydisperse as compared with undoped titania, the size distribution is still narrow enough to make uniform clusters of Eu-doped titania particles up to the fourth-order ($n = 4$). Recently, clusters of spherical particles, which were coated with light emitting substances such as semiconductor nanocrystals, have been prepared to explore the resonance mode of light among the neighboring spherical particles for their potential applications as coupled resonators and whispering gallery mode sensors.¹⁷ The Eu-doped titania particles prepared here can be used directly as light emitting cluster structures without any additional coatings of light emitting substances.

After Eu-doped microspheres were annealed at 500 °C for dense phosphor materials, we observed photoluminescence intensities depending on the doping concentration as shown in Figure 7d.¹⁷ The maximum PL intensity was observed for 9.7 mM of $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. From the spectrum, the energy transition of Eu^{3+} from $^5\text{D}_0$ to $^7\text{F}_n$ was observed as indicated in Figure 7d. The main peak at 615 nm was indicative of the energy transition from $^5\text{D}_0$ to $^7\text{F}_2$. The low intensities for 1.94 and 19.4 mM of $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ as compared with that of 9.7 mM of $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were due to either the lack of Eu ions inside titania matrix or the deactivation between excess Eu^{3+} ions.

Eu-doped microspheres had negative zeta potential of ca. –30 mV so that they were easily dispersed in water without forming aggregates. Therefore, luminescent particles embedded in titania matrix can be used as phosphorescent material with high scattering intensities in either solution or dried state.

Conclusions

Monodisperse colloidal titania microspheres were successfully synthesized with controlled hydrolysis of the

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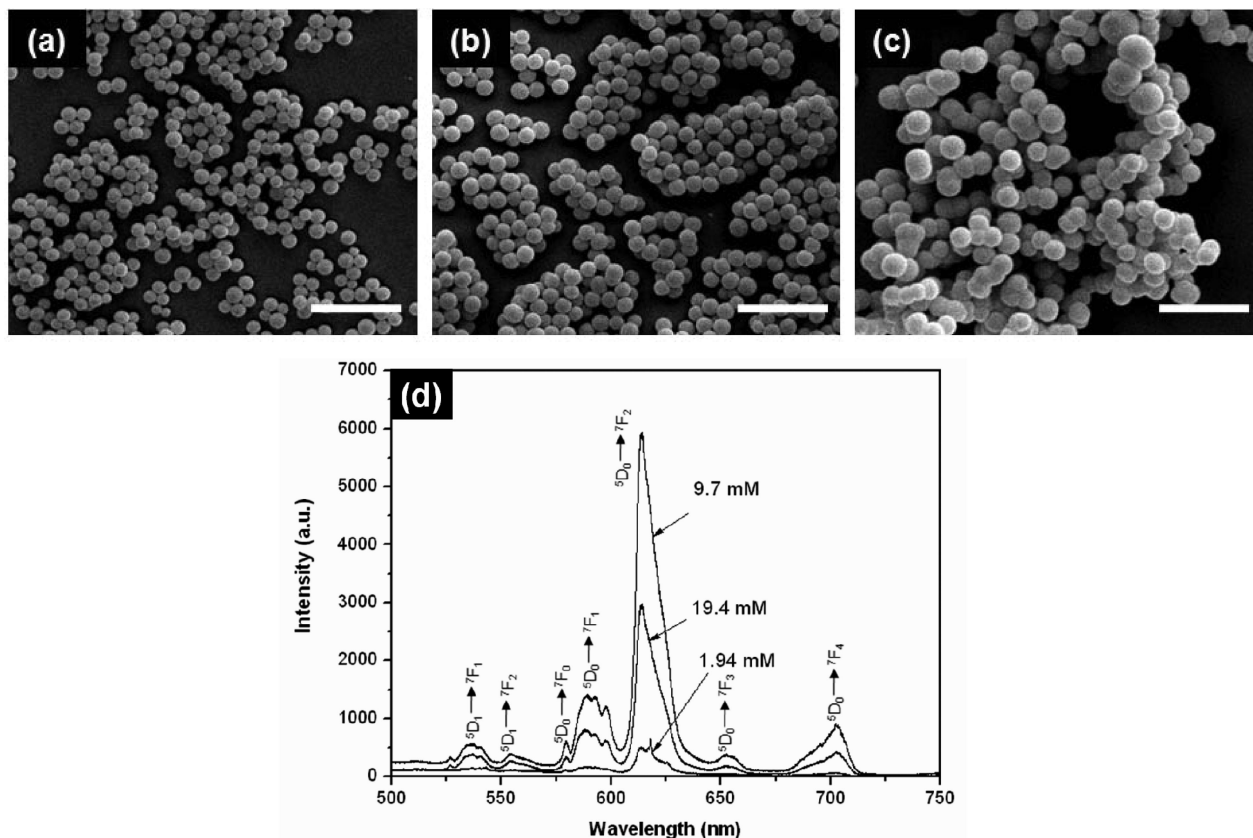


Figure 7. SEM images of titanium glycolate microspheres doped with different concentrations of $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ of (a) 19.4 mM, (b) 9.7 mM, and (c) 1.94 mM. Scale bars are 2 μm . (d) Emission spectra of annealed Eu-doped phosphor microspheres prepared by different doping concentrations.

reactivity-reduced titania precursor in acetone in the presence of Tween 20, in which precursor solutions were titanium butoxide chelated with ethylene glycol. By changing the concentrations of titanium precursor and surfactant, the particle size was controlled with fine-tunability. Obtained particles were transformed into crystalline titania microspheres of anatase phase by heat treatment. The anatase titania microspheres were encapsulated in hexane-in-water emulsion and aggregated with unique configuration according to the number of constituent particles as hexane was evaporated. Then, the titania clusters were readily fractionated into pure clusters with uniform configurations by density gradient centrifugation. Finally, uniform sized Eu-doped luminescent titania microspheres were successfully synthe-

sized. The resulting particles can be used as phosphorescent materials with highly scattering matrices.

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Supporting Information Available: TEM images of anatase titania spheres and SEM images of titanium glycolate microspheres prepared with different surfactants and concentrations (PDF). This information is available free of charge via the Internet at <http://pubs.acs.org>.

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