JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 11, November 2008, p. 3131 - 3134

Luminescence tuning of Si/SiO$_2$ nanoparticles in aqueous solutions

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We investigated the possibility of tuning luminescent spectra for a given Si/SiO$_2$ nanoparticle size distribution in aqueous solution. The luminescence spectra of Si/SiO$_2$ suspensions in aqueous solutions of different particle/cluster concentrations were studied. The different Si/SiO$_2$ nanoparticle/cluster concentrations were produced by both centrifugation and dilution. Depending on the centrifugal force we found a reversible shift up to 100 nm toward UV, regardless of the excitation wavelength. The shift could be reverse by sonication of the sample. A scenario based on particle and cluster size variation is also discussed.

(Received October 1, 2008; accepted October 30, 2008)

Keywords: Luminescence, Nanoparticles, Si/SiO$_2$ Quantum dots, UV effect

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1. Introduction

Luminescent materials have received much attention over the past few decades. Initially, silicon was not of great interest because it has an indirect bandgap unless it is doped with impurities. However, recent studies have shown that Si quantum dots have a quasi-direct bandgap. Thus, the luminescence of nanoporous Si [1–3] and Si quantum dots (QDs) [4, 5] has become a widely investigated area. The dependence of luminescence on the size of the quantum dots—the so-called blueshift"—is now an accepted physical phenomenon [6]. Thus, for a given particle size, a specific luminescence spectrum is obtained.

The aim of this work was to study the changes in luminescent behavior of the Si/SiO$_2$ QDs as the cluster size and concentration in aqueous solution was varied. To the best of our knowledge, our work was the first to investigate the possibility of reversibly tuning luminescence for a given particle distribution by varying the particle cluster concentration in an aqueous solution via standard dilution and centrifugation.

2. Experimental method

We created Si/SiO$_2$ nanoparticles through pulsed laser ablation (PLD) using a Nd:YAG laser with a 355-nm wavelength. The experimental details are described elsewhere [7]. The particles consisted of a crystalline Si core covered with an amorphous SiO$_2$ shell layer (1–1.5 nm thick). Their size distribution ranged from 2 to 10 nm, as estimated from transmission electron microscopy image statistics. The collected NPs were mixed by sonication in deionized water (20 mg/50 cc).

Aqueous solutions of different concentration were created by both centrifugation and dilution. For centrifugation, the following procedure was used: after several hours of sedimentation, part of the solution was carefully taken from the top of the bottle and centrifuged at relative forces of 1700 × *g*, 3700 × *g*, 7500 × *g*, and 15,000 × *g* for 30 minutes. Other parts of the solution were diluted at concentrations of 1:4, 1:16, 1:64 and 1:128. The luminescence and absorption were determined using a Perkin-Elmer LS55 spectrometer and a Cary 500 UV-Vis-Nir spectrophotometer, respectively. The size distribution of the particles in solution was determined by Dynamic Light Scattering (DLS) using a Malvern Zetasizer Nano ZS-ZEN 3600 instrument and a Philips CM120 transmission electron microscope.

3. Results and discussion

First, we investigated the cluster size distribution. We performed the measurements in aqueous solutions using a particle size analyzer based on laser diffraction. The laser analyzer could measure the sizes of the formed clusters, but not he sizes of primary particles in a cluster. The size distributions of the samples obtained by the centrifuge technique–are presented in Fig. 1. Even at the lowest centrifugal force of 1700 × *g* (half an hour of centrifugation), the cluster selection was strong: an approximately fivefold reduction was observed in the average cluster size. Further increases in the centrifugal force–only slightly reduced the average cluster size below this value.

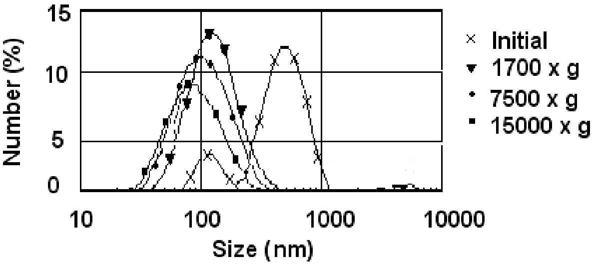

Fig. 1. Cluster size distributions for several relative centrifugal forces.

We also measured the dependence of the cluster size distribution on dilution. The variation in cluster size distribution as function of dilution is shown in Fig. 2. Note that a significant cluster size reduction could be obtained only by increasing the sample dilution. A 1:128 dilution caused a fivefold reduction in the average cluster size, suggesting that some of the bonds between clusters

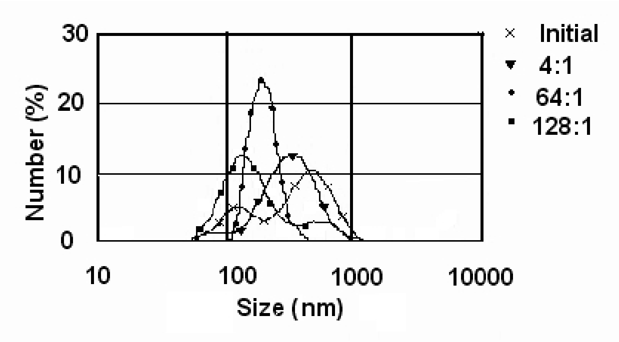

Fig.2. Size distributions for different sample dilutions.

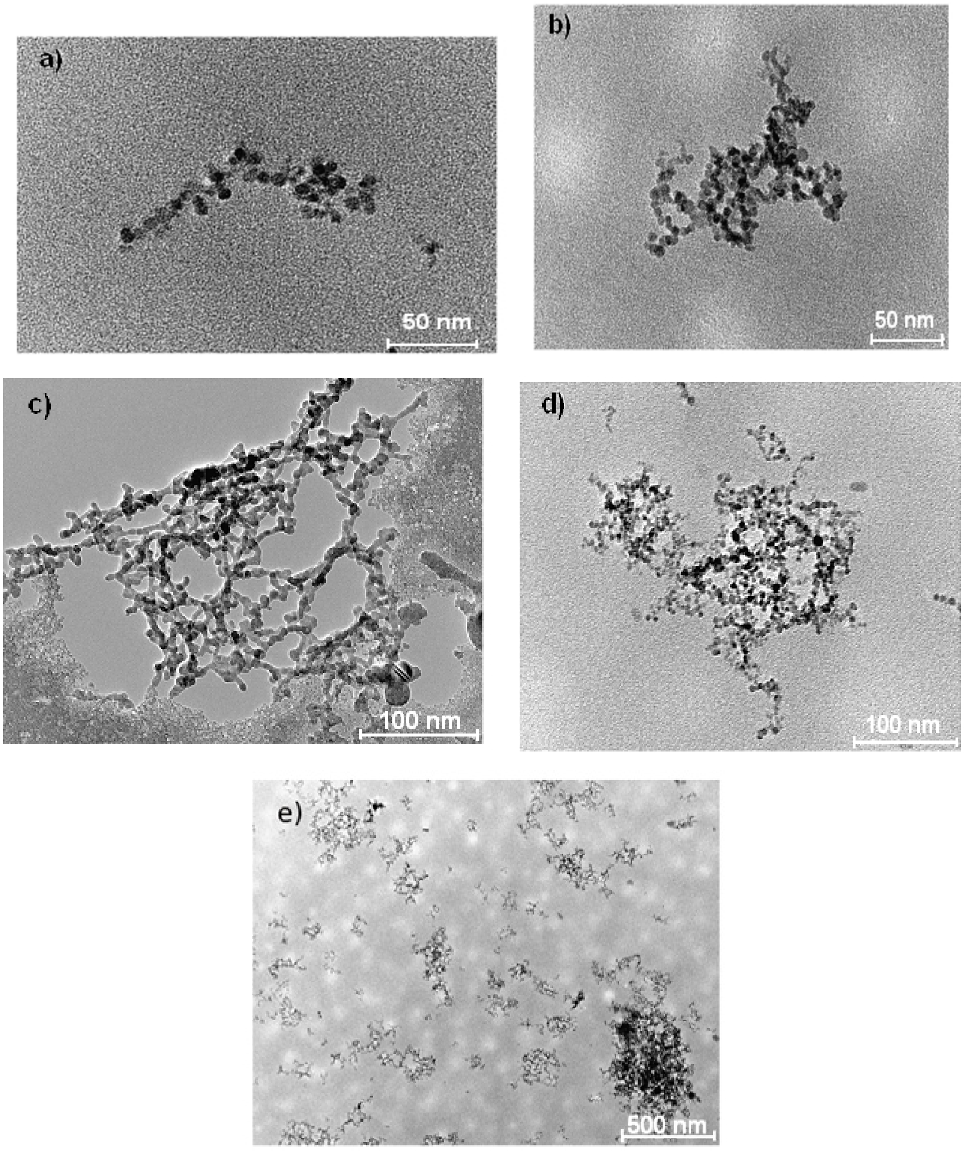

Fig. 3. TEM images of clusters after sample centrifugation for 30 min at (a) 15,000 × g, (b) 7500 × g, (c) 3700 × g, (d) 1700 × g, and (e) uncentrifuged.

were not very strong and that the clusters were not particularly stable. Brownian motion likely drove the particles agglomeration/ deagglomeration being the main process that determined the probability of separation. A 1:128 dilution produced a size distribution comparable to a 1700 × *g* relative centrifugal force applied for 30 min.

The variation in cluster size was evaluated in more detail using transmission electron microscopy (TEM). Images of the centrifuged samples are shown in Fig. 3.

When the centrifugal force was strong, the largest clusters formed contained no more than about 50 particles, but when the force was weaker, several hundred particles could be present. Thus, the main visible difference between these samples was the decrease in the maximal cluster size and the total particle number.

The luminescence results for the centrifuged solutions are shown in Fig. 4.

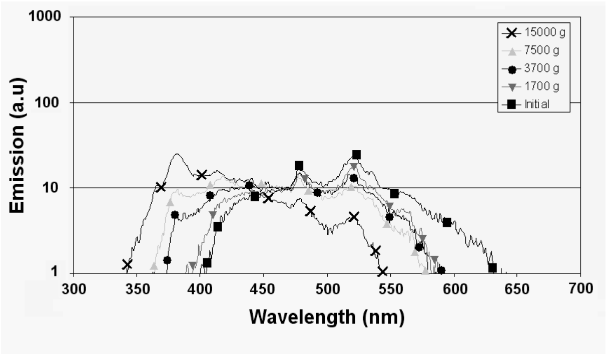

Fig. 4. Emission spectra for samples produced under different relative centrifugal forces.

The uncentrifuged sample emitted only in the 400–650 nm band, unlike the filter-collected powders measured in the air, which had two luminescence bands [8]. Since, the spectra of larger quantum dots shift to red-infrared, while those of smaller ones to visible-ultraviolet, the change in the luminescence spectra was obviously caused by the sedimentation of larger particles in the aqueous solution while preparing the solution.

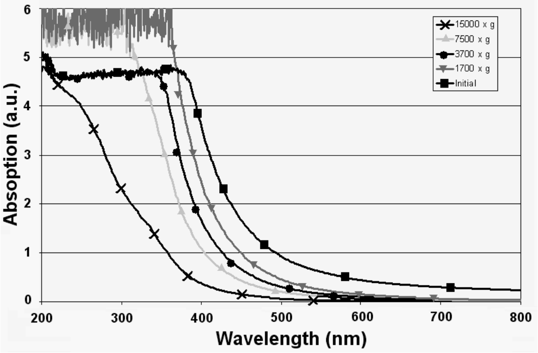

Fig. 5. Absorption spectra for samples produced under different relative centrifugal forces.

Furthermore, by increasing the centrifugal speed, we could shift the luminescence band-systematically to UV. In the 15,000 × *g* case, the total band shift was approximately 100 nm. The luminescence shift was visible for all investigated excitation wavelengths. For clarity, we chose 225 nm as the excitation wavelength because the sample absorption (Fig. 5) and emission were stronger for UV light.

In Fig. 6, the luminescence families for three centrifuged samples (initial, 3700 × *g* and 15,000 × *g*) with UV excitation wavelengths (200–300 nm) are shown.

These plots clearly show that the UV luminescence shift was directly dependent on the centrifugal force, regardless of the excitation wavelength. The shift could have been associated with the tendency for larger particles to be deposited faster than smaller ones when the centrifugal force was high. In addition, the luminescence band shift could have been correlated with the increase in dilution or decrease in cluster size.

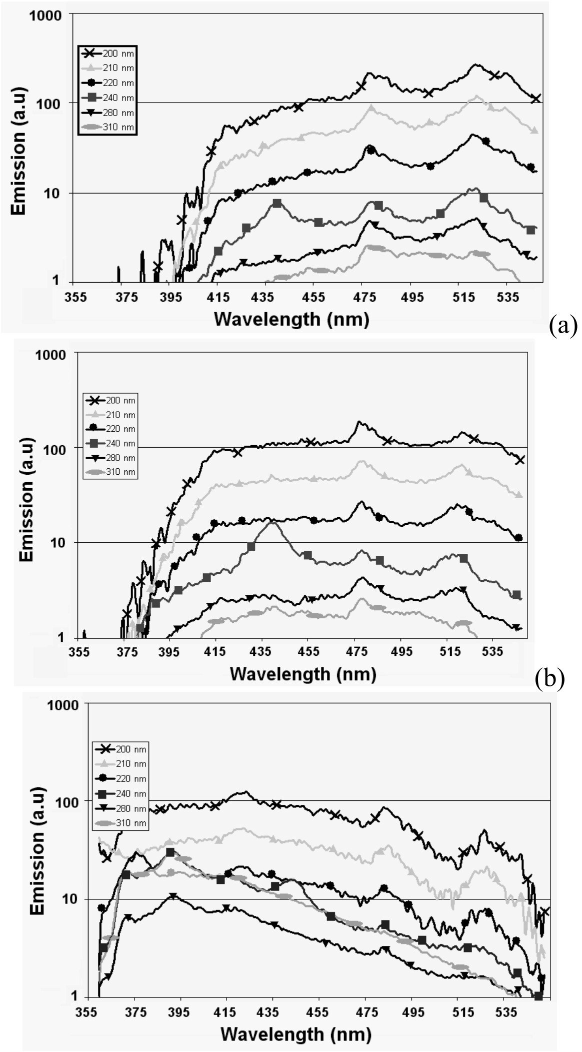

Fig. 6. Emission spectra families for samples produced under different centrifugal forces; (a) uncentrifuged, (b) centrifuged at 3700 × g for 30 min, and (c) centrifuged at 15,000 × g for 30 min, for different excitation wavelengths between 200 and 300 nm.

For this reason, we plotted the variation of luminescence with sample dilution at the same excitation wavelength (225 nm) in Fig. 7. In this case, no clear luminescence shift was observed, only a luminescence band broadening. The band broadening may have occurred because all nanoparticles were excited by the incident light, not only the largest ones. The shift could have been absent because the elementary particles size distribution was not altered by the dilution process. If this were the case, the luminescence process would have been associated only with the particle size, not the formed cluster size. By correlating cluster sizes in diluted and centrifuged samples with the emission spectra, we also confirmed that very different luminescence spectra could be obtained for the same cluster size distributions. The only factor that could explain the luminescence shift via centrifugation was therefore preferential deposition of the larger particles.

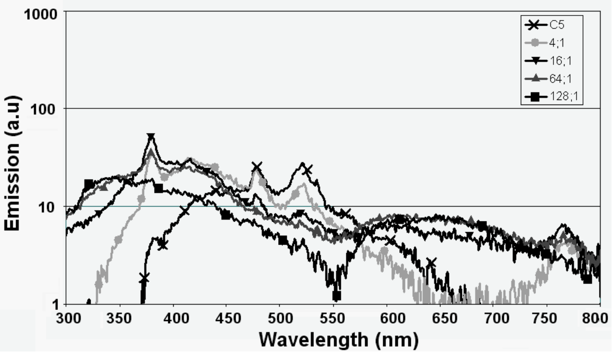

Fig. 7. Luminescence of Si/SiO_2 nanoparticles for several dilutions.

Because the bonds between clusters or larger particles are rather weak, they could be easily separated in suspension by simple agitation (sonication). If some of the particles or clusters in suspension were sedimented, after a short agitation (sonication), the luminescence spectrum would be restored to its initial form. In this way, we can tune the sample luminescence band by approximately 100 nm via centrifugation, and reverse the change by sonication.

4. Conclusions

We proposed a very simple method for tuning the luminescence of Si/SiO_2 nanoparticles in aqueous solution. Our investigations demonstrated that by centrifuging the Si/SiO_2 suspensions at different speeds, a 100 nm shift toward UV could be achieved, regardless of the excitation wavelength. The sedimentation of larger nanoparticles appeared to be the decisive feature of this process, as it affected the particle statistics and shifted the luminescence band. The shift of the spectrum could be reversed by simply agitating the solution.

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