

Surface Chemistry of Luminescent Colloidal Silicon Nanoparticles

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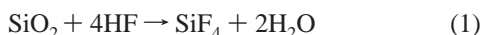
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Luminescent colloidal silicon particles are obtained by burning silane and slowly etching the product with hydrogen fluoride. Depending on their size, the particles emit red–orange or blue–green light with decay times between 28 μ s and <0.1 μ s, respectively. The quantum yield of the red luminescence is found to be 35%, i.e., much higher than the 7% previously reported, and the yield of the blue–green luminescence is 18%. The luminescence of the colloidal particles is quenched upon the attack of their surface by free radicals, oxygen-centered radicals being more efficient than carbon-centered ones. It is concluded from the dependence of the luminescence wavelength on the etching time and the dependence of the luminescence lifetime on the wavelength that the mechanism of the photoluminescence undergoes a change with decreasing particle size. The red luminescent particles exhibit amphiphilic properties, such as unusual wetting phenomena. This effect is understood in terms of the existence of few polar groups on the otherwise nonpolar surface of the particles, possibly Si–OH groups, which also act as centers of the red luminescence.

Introduction

Some years ago, we reported on the preparation and some optical properties of red–orange luminescent colloidal silicon particles.^{1,2} The particles were obtained by etching primary particles, which carried oxide structures on their surface, with hydrogen fluoride in cyclohexane suspension



As the particles obtained in this procedure can be separated from the solution, be washed, and be resuspended without noticeable loss of luminescence, one can carry out many experiments that are not amenable when they are part of a solid matrix. For example, their luminescence in various solvents has been studied, including the quenching of their luminescence by added substances.¹ As has been pointed out, the luminescent particles carry a few oxide structures on their surface, possibly Si–OH groups, which act as centers of photoluminescence and whose state of protonation strongly influences the ability of the particles to emit light.¹

In the present paper, two kinds of properties of the particles are investigated, namely, (1) optical properties, such as their luminescence spectra, lifetime, and quantum yield of luminescence, and quenching of the luminescence by free radical attack on the surface of the particles, and (2) amphiphilic properties, including agglomeration in solution, migration in media of different polarity, and unusual wetting phenomena. Those two kinds of properties appear at first sight independent of each other. However, it is proposed that the same centers on the surface of the particles play an important role in both cases.

Particle Preparation

The particles were prepared as described previously.¹ Particles with an oxide layer (which does not promote luminescence) were first obtained as a powder by combustion of silane under oxygen-deficient conditions. Ten milligrams of this powder was suspended in 30 mL of a 1:1 mixture of cyclohexane and propanol-2 in a Teflon bottle, and 5 mL of aqueous hydrofluoric acid (40%) were then added. Two phases were formed upon the addition of this reagent, an upper nonpolar phase consisting mainly of cyclohexane (with traces of water and HF) and a lower polar phase consisting mainly of propanol-2, water, and HF. During etching, the particles moved within a few hours from the polar to the nonpolar phase, where they developed luminescence upon further etching. The opalescent cyclohexane phase was treated in an ultrasonic bath every 6 h and stirred for 30 min. During all these steps, the system was in contact with air (as mentioned previously,¹ the luminescence did not develop when the etching was carried out under an atmosphere of argon).

Optical Properties

Photoluminescence Spectra and Electron Microscopy.

Figure 1 shows the luminescence spectrum upon excitation of the cyclohexane phase by 360 nm light at various times of etching. At the beginning, the luminescence band is located at 1000 nm. At longer times, it moves toward shorter wavelengths (red to orange emission). At still longer times, however, the band of the red–orange luminescence remains at about 650 nm and decays there, whereas a second band at 480 nm (blue–green emission) develops. This effect is taken as an indication of a change in the mechanism of the photoluminescence. The blue–green and red–orange luminescent particles, which are both present after 32 days of etching, can be separated by

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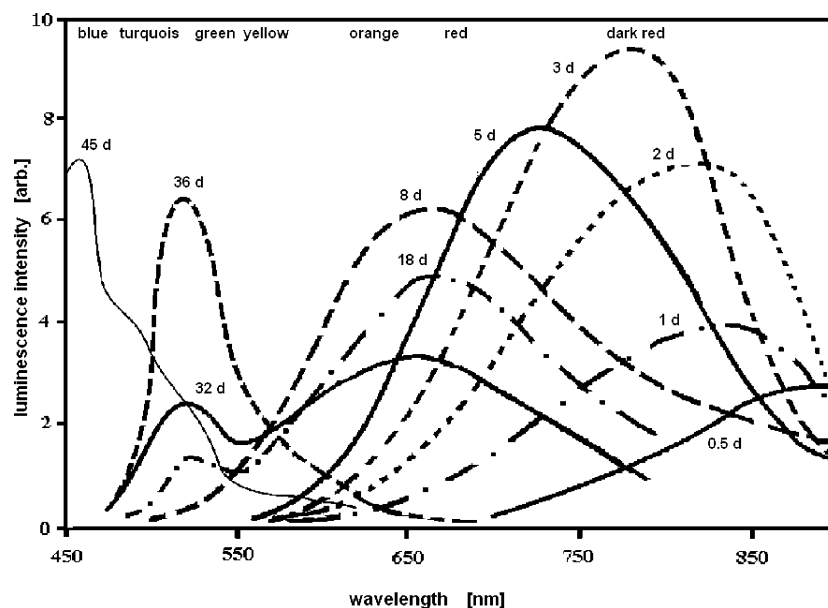


Figure 1. Luminescence spectrum at various times of aging of the cyclohexane phase under air. In the beginning, more and more polar particles lose their oxide layer; see reaction 1. They move from the lower polar phase into the upper nonpolar cyclohexane phase, where they acquire luminescence by partial reoxidation by oxygen. An equilibrium is established between surface oxidation and reduction by O_2 and HF, respectively. At longer times, the particles become smaller and smaller as silicon is consumed in reaction 1.¹

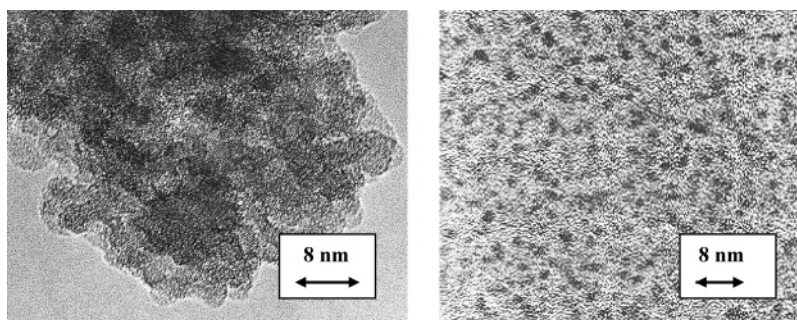


Figure 2. Electron micrographs of the red luminescent (left) and blue luminescent particles (right) which had been produced by etching for 32 days. The two types of particles were separated by centrifugation of the cyclohexane phase.

centrifugation of the cyclohexane phase (laboratory centrifuge, 4000 rot/min, $\frac{1}{2}$ hour). In the absorption spectrum of the supernatant solution, the band of the red luminescence has completely disappeared, whereas the 480 nm band is still present. It should also be noted that the blue luminescent particles tend to move from the cyclohexane phase into the aqueous phase. For this reason, the spectra in Figure 1 were taken from the cyclohexane phase after it had been separated from the aqueous phase.

Figure 2 shows electron micrographs of the particles. They have a broad size distribution, the size of the red–orange luminescent particles being about 4 nm and that of the green–blue luminescent ones being about 1.5 nm. The energy dispersive analysis revealed that only 2% oxygen was present in the red luminescent particles. This finding corroborates our previous conclusion that the predominant part of the surface of these particles consists of non-oxidized Si atoms, i.e., of a nonpolar area, with only a few polar Si–OH groups being present.

Figure 3 shows the decay of the luminescence at different wavelengths after excitation with a 308 nm laser pulse. The curves were separately recorded for each wavelength. The lifetime is shown as a function of wavelength in Figure 4. One can see that it decreases with decreasing wavelength from 28 μ s (red luminescence, 700 nm) to below 0.1 μ s (blue luminescence at 480 nm). The decrease is relatively slow at the beginning, but occurs very steeply below about 600 nm. This

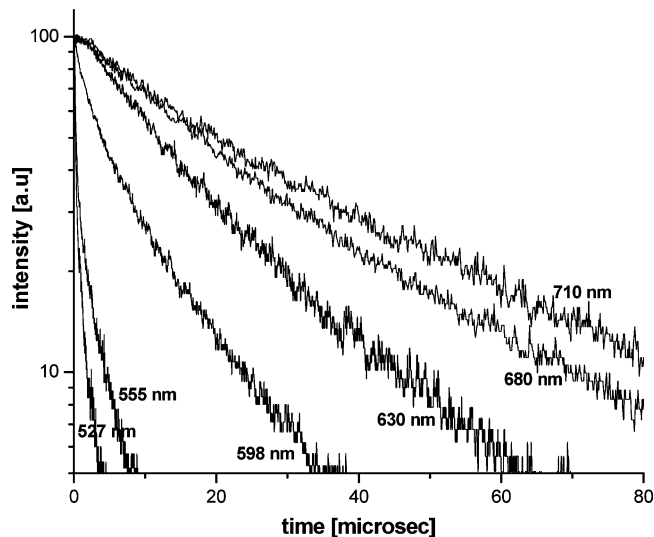


Figure 3. Decay of the luminescence at different wavelengths after excitation with a 308 nm laser pulse. (Excitation: laser XeCl, 308 nm, 30 ns, 3 mJ, focused on 1 cmsq. of quartz cuvette. Detection: 10 nm interferential filters, oscilloscope TDS 2024, photomultiplier R928).

effect also makes one suppose that a change in the mechanism of the photoluminescence takes place with changing particle size.

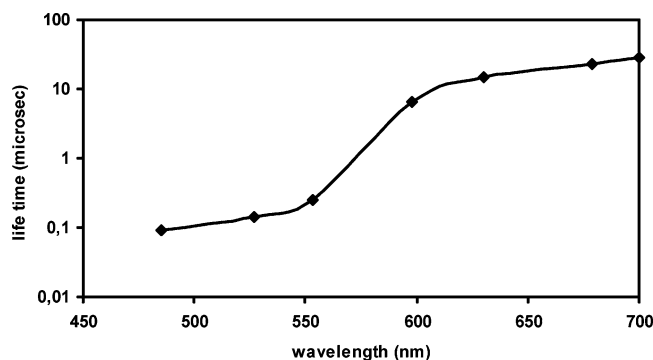


Figure 4. Lifetime of the photoluminescence as a function of wavelength. The shortest times shown in the figure are upper limits because of the relatively long resolution time of $0.07 \mu\text{s}$ of the recording system used.

Luminescence Quantum Yields. As in the earlier investigation,¹ the yield of the red luminescence was measured by comparing the area of the luminescence band with that of rhodamine G, which is known to fluoresce with a yield of 100%. In this comparison, the concentration of rhodamine G was chosen such as to achieve the same extinction of the exciting light. However, as the cyclohexane phase of the particles was opalescent, the yield of 7% reported previously was a lower limit, since the true absorbance of the solution was falsified by significant light scattering. In the present investigation, the cyclohexane solution was extracted with water to remove excess hydrofluoric acid and then diluted with dry cyclohexane by a factor of 10. When this dilute solution was aged during several hours, it became clearer, and its extinction was found to decrease by 80%, although its luminescence did not decrease. As will be described below, larger particle aggregates slowly disintegrated during aging that had caused the scattering of light. The quantum yield was now found to be 35%, which is essentially larger than the one found previously, and is comparable to the largest yields reported for luminescent silicon.^{3–5}

The quantum yield of the blue luminescence was determined as follows. One milliliter of the cyclohexane phase was diluted with 9 mL ether, and this solution was centrifuged. The red luminescent particles sedimented, whereas the supernatant liquid phase still luminesced blue–green. This supernatant phase was decanted and used for the determination of the quantum yield. A value of 18% was found, i.e., a yield comparable to the above yield of the red luminescence.

Quenching of the Luminescence. In our previous study, it was found that the red luminescence of the nanoparticles could be quenched by very small concentrations of trimethylamine in solution, and this effect was explained by a change in the protonization state of the centers of luminescence.¹ Similar experiments were now carried out with blue–green luminescing particles. It turned out that the luminescence could not be quenched by trimethylamine. This indicates that the centers which are involved in the red luminescence do not play a role in the blue–green luminescence.

The red luminescence can also be quenched, when free radicals attack the surface of dissolved particles. It has frequently been observed in radiation chemistry that chemical reactions on the surface of colloidal nanoparticles are initiated by free radicals, such as chemical bonding or electron transfer.⁶ Free radicals having a wide range of redox potentials can be produced by exposing solutions to γ -radiation.⁷

When cyclohexane is irradiated, carbon-centered radicals are produced with a yield of about 6 radicals per 100 eV absorbed radiation energy. A deaerated cyclohexane suspension containing

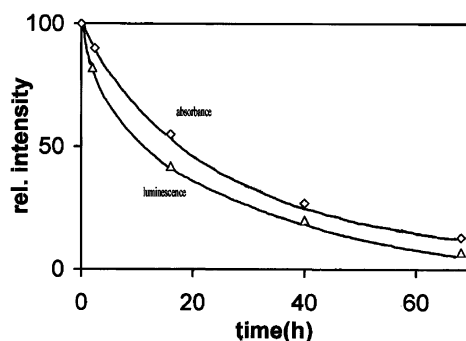


Figure 5. Luminescence and absorption of a γ -irradiated cyclohexane solution of silicon particles as functions of the irradiation time. Air had been removed from the solution by evacuating the irradiation vessel.

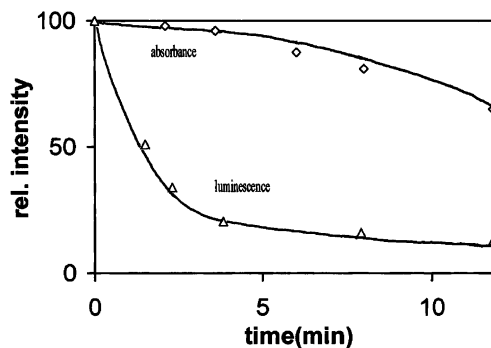


Figure 6. Luminescence and absorbance of a γ -irradiated cyclohexane solution of silicon particles as functions of time. The irradiation occurred under air. (In a comparison to Figure 5, note the different time scales.)

3×10^{-3} M red luminescent silicon particles was irradiated in the field of a Co^{60} γ source at a dose rate of 2.2×10^2 Gy/h. The dose rate was determined by chemical dosimetry ("Fricke" dosimeter⁷). At this dose rate, the rate of free radical formation is 1.5×10^{-4} M per hour. Figure 5 shows how the luminescence intensity and the absorbance of the solution change during irradiation. As the absorbance decreases and as longer irradiation times approach zero, one concludes that the silicon is dissolved. We interpret this effect as a radical attack on the surface of the colloidal particles by forming Si–C bonds and finally silicon–organic compounds. A similar effect has been observed in the case of free radical attack on dissolved elemental phosphorus.⁸ A 50% loss of silicon absorption was reached in Figure 5 after about 11 h, i.e., after about $1.5 \times 10^{-4} \times 11 = 1.7 \times 10^{-3}$ M radicals had been generated. This corresponds to about half of the concentration of silicon present in the solution. The luminescence intensity decreases upon irradiation at about the same rate as the absorbance of the particles.

Quite a different observation was made when the irradiation was carried out in the presence of air. Under these circumstances, the radicals react rapidly with O_2 to form peroxyradicals, ROO^{\bullet} , which subsequently attack the colloidal particles. ROO^{\bullet} radicals are strongly oxidizing in contrast to the C-centered radicals used in Figure 5. Figure 6 shows that the luminescence intensity rapidly decreases in a 2.0×10^{-3} M silicon solution. At 1.8 min of irradiation, when only 4.5×10^{-6} M radicals had been produced, the intensity has dropped to 50% of its original value, whereas the absorbance, which is a measure of elemental silicon still present, has almost not changed at this point. The explanation of this phenomenon is quite different from that given in Figure 5: It is not the consumption of silicon that is responsible for the decrease in luminescence, but the destruction of the luminescence centers on the surface, possibly by oxidation of the Si–OH centers to yield S=O structures on

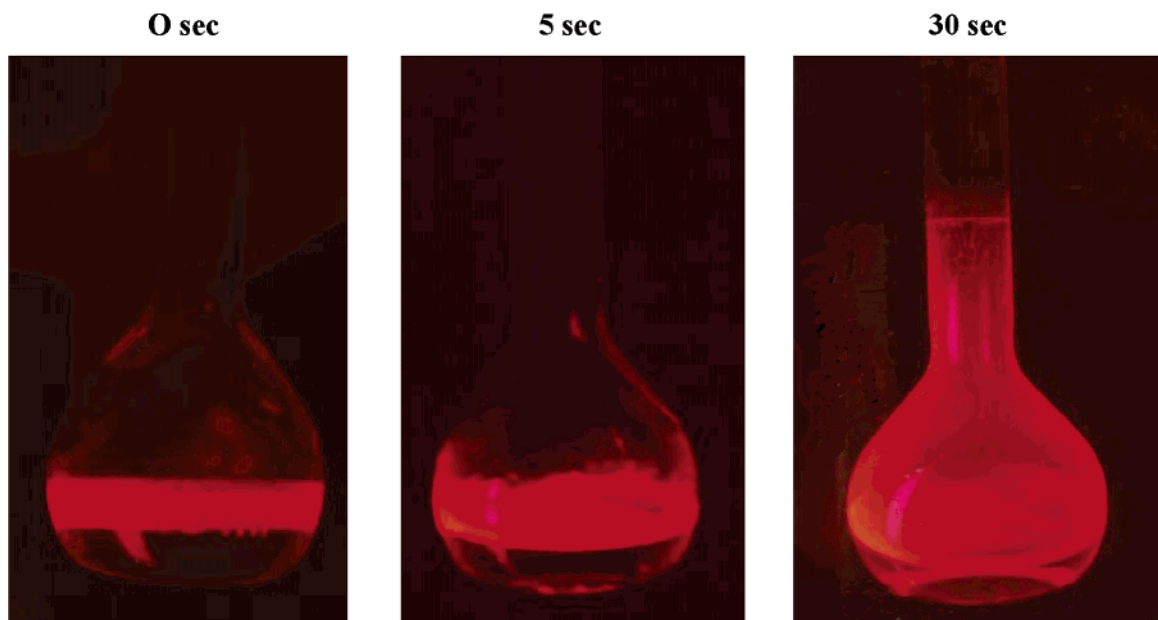


Figure 7. Demonstration of the “creep” effect: Illumination by UV light of a measuring flask containing an upper cyclohexane phase of purified luminescent particles and a lower water phase. Left: immediately after the flask was filled and shortly shaken. Middle: at 5 s; beginning of creeping. Right: at 30 s; the luminescence film has crept up the wall of the vessel and part of the tubing against the force of gravitation.

the surface. The fact that only a small number of radicals is required for efficient quenching indicates that very few centers of luminescence are present. This finding is important, as it is consistent with the above conclusions concerning the low concentration of surface centers on the particles.

Mechanism of the Photoluminescence. It has previously been suggested² that the blue–green luminescence is due to a particularly small size of the particles, where strong quantization of the electronic levels occurs, and that the red–orange luminescence is caused by larger particles which are less quantized. Our new observations, which indicate a change in the mechanism of luminescence with changing particle size, are understood in terms of two types of electron–hole recombination which occur in a competitive manner: (1) free electron plus free hole recombination and (2) free electron plus trapped hole recombination. In large particles, free electron plus free hole recombination can practically not compete because of the indirect nature of this transition. The hole is trapped near a center on the surface (which we suppose is a Si–OH group¹), and the electron then recombines with the localized hole. In small particles, however, free electron plus free hole recombination is very fast because of the quasi-direct nature of the transition, and the trapping of the hole practically takes place no longer.

Blue–green luminescent particles in colloidal systems and their separation from the red luminescent particles have recently described by Valenta et al.⁹ They adopted the model of Wolkin et al.,¹⁰ in which (similar to the above explanation) small surface centers do not significantly affect the radiative recombination of electron–hole pairs in the core of the particles.

Amphiphilic Properties

As has been pointed out previously,¹ the red luminescent particles essentially are hydrophobic, as they accumulate in the nonpolar cyclohexane phase. On the other hand, as oxygen has to be present during the process of etching, it was concluded that the luminescent particles contain a limited number of oxidized surface spots, such as Si–OH groups (as luminescence centers) which should have an affinity to a polar environment.

The presence of both polar and nonpolar surface areas may cause the particles to act as amphiphiles.

In the experiment shown in Figure 7, 30 mL of a cyclohexane solution of red luminescent particles was filled into a 50 mL measuring flask. The particles had been purified by centrifugation and washed with ether. Ten milliliters of water were added to the flask, which stayed as a polar phase below the nonpolar cyclohexane solution. The luminescence remained in the upper phase. However, a luminescent thin film rapidly crept up the glass wall of the flask and its tubing at a rate of about 4 cm per minute. This is illustrated in the figure. When the upper end of the tubing was reached, the luminescent film continued its migration by spilling over and creeping downward a few millimeters on the outer side of the glass tubing. The liquid which was transported in the luminescent film consisted of water. In fact, the creeping of the luminescence did not occur in the absence of the lower water phase in the vessel. Several “blank” experiments were made which proved that the presence of silicon particles in the system is necessary for the formation of the migrating film. No fluorescent film was formed when only cyclohexane and water were in the vessel, with each of the two liquid phases containing a fluorescent dye (pyrene in cyclohexane; methylene blue, phenosafranin, erythrosin B, or eosin Y in water). The creeping phenomenon is a complex example of the wetting of a glass surface. The driving force is thought to be a high affinity of the silicon particles to the glass surface. The fact that water is also transported in the film indicates an intricate relation between the silicon particles and water. The creep effect might be used to cover pieces of glass or quartz with a very thin layer of luminescent silicon.

In the experiment of Figure 8, the creep effect is shown in daylight, where no excitation of the luminescence occurs (the particles absorbing in the UV¹). The water phase was made visible by the red color of rubin S, a dye which is not soluble in cyclohexane. The pictures were taken versus a black and white background and at 20 s after filling the vessels. In the absence of particles, nothing of particular note happens: One recognizes the lower red-colored water phase and the colorless upper cyclohexane phase (left in Figure 8). In the presence of

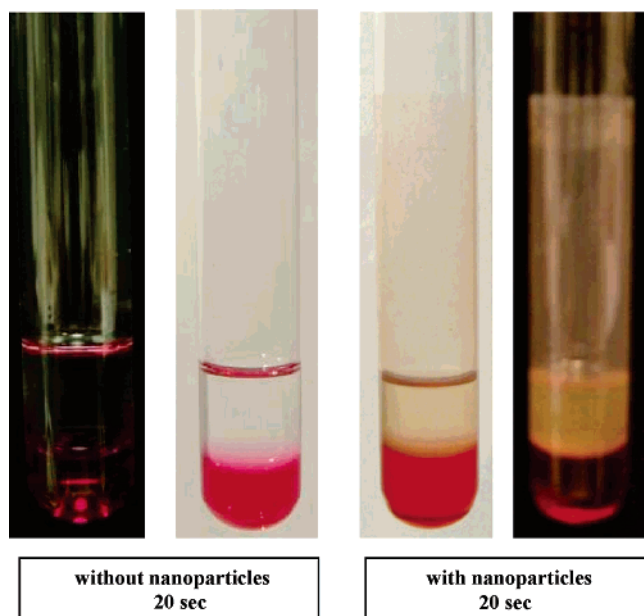


Figure 8. Creep effect in daylight. Tracing the water phase by using a water-soluble dye, Rubin S, as indicator. Left: the cyclohexane–water system without nanoparticles. Right: in the presence of nanoparticles in the cyclohexane phase.

particles in the cyclohexane phase, however, a thin weakly colored film has crept up. Its color is caused by the rubin S that is carried along with the water in the film. In similar experiments with methylene blue, a bluish film developed. We ascribe these effects to the formation of particle–water clusters in the cyclohexane phase, which can transport water-soluble dyes.

As already mentioned, the cyclohexane solution of the luminescent particles was opalescent. When it was diluted by dry cyclohexane in the ratio 1:9, the solution still was slightly opalescent in the beginning. However, it became clearer and its absorbance decreased within several hours of aging without the loss of luminescence intensity. Obviously, larger aggregates of the particles which caused the scattering of light slowly degraded into smaller ones upon the dilution of the solution. The effect did not occur when the cyclohexane solution had been diluted by wet cyclohexane (i.e., cyclohexane that had been in contact with water). The process of degradation of the large agglomerates could be accelerated by evacuation of the diluted cyclohexane solution for several seconds. All these effects are understood if one assumes that water present in a small concentration in the cyclohexane phase is favorable for the formation of agglomerates of the silicon particles. It acts as a binding material between particles, possibly through hydrogen bonds with Si–OH surface groups. A decrease of the water concentration in the solution by dilution or evacuation leads to

a slow release of water from the agglomerated particles into the solution and thus to a breakup of the agglomerates. Water may even stabilize the particles: When the water was completely removed from the cyclohexane solution by either adding a small amount of a hygroscopic substance (such as sodium sulfate or phosphorus pentoxide) or by longer evacuation, the silicon particles rapidly accumulated on the wall of the vessel. In doing so, they preferentially moved to the side of the glass vessel which was touched by the experimenter. Obviously, the complete removal of water from the agglomerates is accompanied by charging the particles and the glass surface of the vessel, an effect that is not yet understood in detail.

Final Remarks

An unusual surface chemistry of luminescent colloidal silicon particles is reported in this paper. All the optical and amphiphilic properties are explained in terms of the existence of nonpolar and polar spots on the surface of the particles, the latter being considered to be Si–OH groups. Amphiphilic properties of inorganic nanoparticles are reported for the first time. They include wetting phenomena and the agglomeration of the particles in the presence of water. A mechanism of the photoluminescence is discussed, in which two competing kinds of electron–hole recombination occur. High quantum yields of photoluminescence are found for both blue and red luminescent particles.

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