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# One-pot Preparation of Water-soluble Blue Luminescent Silica Flakes via Microwave Heating

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Photoluminescent silica flakes were newly synthesized from silicon tetrachloride ($SiCl_4$) by reflux in *N*,*N*-dimethylformamide (DMF) without the use of any surfactants or other additives. Photoluminescence (PL) intensity was remarkably enhanced with microwave treatment. The morphology of dispersible solutes was 144 ± 16 nm flakes. It was also clarified that DMF was coordinated on the surface of the flakes and that it influences the dispersion of flakes in both aqueous and organic solvents.

Photoluminescent nanoparticles have recently been candidate nanoscopic assembled materials for numerous applications due to the unique electronic and optical properties that result from their nanometer size and the low size distribution in which they can be produced. Particularly, in the biological areas, imaging, labeling, and sensing are recent trends foreseen in the application of nanoparticles.[1,2]

Alternatively, silicon is of interest as a novel photoluminescent element because of its lower toxicity.[3] The photoluminescence of the nanoparticles is generated from quantum confinement effects and defects located at the Si–$SiO_2$ interface. Various synthetic procedures of photoluminescent nanomaterials containing silicon or silica have been proposed.[4–8] However, these procedures require specific chemicals and purification of the materials is needed.

In this study, we have explored novel synthetic methods of photoluminescent silica flakes under ambient conditions. $SiCl_4$ was used as a raw material and injected in boiling *N*,*N*-dimethylformamide (DMF). In addition, the effect of microwave heating on the formation of flakes was also clarified.

Figure 1a is a TEM picture and dynamic light-scattering (DLS) data of silica flakes prepared with microwave treatment for 8 h. The size of the flakes was 144 ± 16 nm with narrow dispersion. The DLS data corresponded with the TEM morphology of the flakes. No critical lattice fringes were observed in the flakes, indicating that the flakes were mostly formed from amorphous silica. Microwave treatment did not influence the size of the prepared flakes.

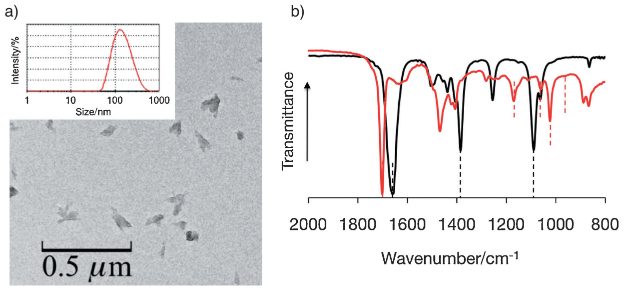

**Figure 1.** a) TEM image and DLS data of silica flakes prepared via microwave treatment for 8 h. b) ATR-FT-IR spectra of DMF (—) and silica flakes (—).

Figure 1b shows attenuated total reflectance (ATR)-FTIR spectra of DMF and silica flakes. A very strong absorption at 1655 $cm^{-1}$, mostly due to $\nu$(C=O), is the most sensitive among the DMF bands with respect to the interaction. Indeed, the band shifts toward lower wavenumbers (from 1650 to 1600 $cm^{-1}$) and broadens for the DMF-protected silica flakes, suggesting interaction of the C=O group in DMF with the silica flakes. A new, strong absorption at 1700 $cm^{-1}$ for the silica flakes might be assigned to the $\nu$(C=O) vibration mode of the carboxylic acid group. Synthesis of the DMF-protected silica flakes seems to be accompanied by the by-product of the oxidation of DMF. The 1384 $cm^{-1}$ band for DMF solvent is a coupled vibration with major contributions from $CH_3$ deformation and C–N stretching modes. It was found to shift to 1403 $cm^{-1}$ for DMF-protected silica flakes. We also see peaks at 1165, 1054, and 1022 $cm^{-1}$, which are attributed to the asymmetric stretching vibration of the Si–O–Si bonding,[9] indicating that silica-related species are indeed formed after microwave treatment. The absorption bands at 1090 and 1063 $cm^{-1}$ for DMF solvent are assigned to methyl rocking vibrations coupled with a C–N characteristic, and this band is sensitive to the formation of complexes.[10] The methyl rocking vibration bands for DMF solvent may shift and overlap the absorption of silica from 1000 to 1070 $cm^{-1}$.

We found that, after microwave treatment, the $SiCl_4$/DMF mixture solution tends to exhibit a blue PL emission peaking at ca. 450 nm. Figure 2a shows the dependence of the PL peak intensity of the mixture solution on reaction time under the excitation of a 370-nm light. The PL intensity of the solution increased with an increase in reaction time. Specifically, the PL intensity was remarkably enhanced by microwave treatment.

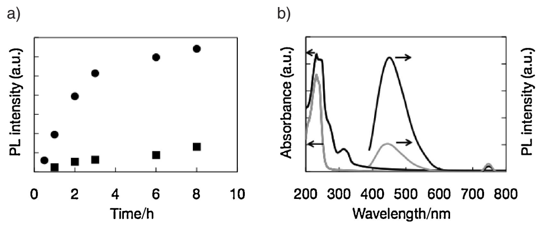

**Figure 2.** a) Time dependence of the maximum PL intensity of reacting solutions emitted at 370 nm. ●: Microwave treatment; ■: no microwave treatment (only heat treatment). b) Typical absorption and emission spectra of flakes (8-h reaction) resuspended in equivalent water. Black line: microwave treatment; gray line: no microwave treatment (only heat treatment).

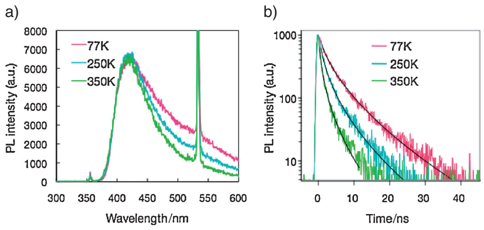

**Figure 3.** a) Steady-state photoluminescence spectra and b) PL decay curves for silica flakes measured at different temperatures. The sharp peak in a) is the second harmonic (532 nm) of the Nd:YAG laser contaminated in the incident laser beam. The solid lines in b) indicate the results of fitting to the stretched exponential function, eq 1.

The change in absorbance of the shoulder peaks at 315 nm corresponded with the manner of PL intensity; that is, the formation of the silica flakes was accelerated by microwave treatment.

Figure 2b shows typical absorption and emission spectra of silica flakes prepared with or without microwave treatment. In both cases, the reaction time was 8 h and nanoparticles were resuspended in water. The UV–visible absorption spectra of silicon flakes in water increased toward the shorter wavelengths from around 400 nm. The absorption at 240 nm is due to unreacted DMF molecules coordinated on the silica flakes, and the broad absorption band ranging from 300 to 380 nm probably results from the vibrations of Si–O-related emission centers in the silica flakes. Previously, a similar blue PL band peaking at 450 nm was observed from nanometer-sized silica particles.[11] The intensity of the blue PL band of silica flakes prepared by microwave treatment was significantly higher than those prepared by only heat treatment.

Figure 3a shows the PL peak energy of the silica flakes as a function of measuring temperature. We see that the PL peak position was almost unchanged even though the measuring temperature changes from 77 to 350 K. This result indicates that the observed PL emission does not result from the quantum confinement of silicon nanoparticles rather the PL signal is ascribed to the silica-related defect centers in the silica flakes.[12] As shown in Figure 3b, the PL decay profile was influenced by the measuring temperature, indicating that the observed emission processes compete with the thermally activated nonradiative recombination process. We found that the PL decay profile is highly nonexponential and can be fitted with the following stretched exponential function

$$I(t) = I_0 \exp[-(t/\tau)]^{\beta} \qquad (1)$$

where $I_0$ is the PL intensity at $\tau = 0$, $t$ is a characteristic decay time, and $\beta$ is the stretching parameter that represents the degree of deviation from a pure exponential decay. The stretched exponential decay can generally be found in disordered systems in which the dispersive diffusion of photoexcited electrons is possible.[13,14] It has previously been demonstrated that a number of electron-trapping sites exist on silica surfaces, resulting in highly nonexponential decay behavior.[15] Indeed, a stretched exponential PL decay in a timescale of nanoseconds was reported from luminescent silica nanoparticles as well.[11] Thus, we believe that the surface of the present silica flakes is also characterized by such electron-trapping sites, explaining the observed stretched exponential decay profiles.

A structural origin of the PL from silica-based materials has been proposed by Uchino and co-workers.[11] The dehydroxylation reaction of surface hydroxy groups results in the formation of a defect pair consisting of a dioxasilirane, $=\mathrm{Si(O_2)}$, and a silylene, $=\mathrm{Si}:$, center. One possible mechanism of PL generated from silica flakes is the defect pair produced at boiling temperature of DMF. Another possibility is the formation of defects located at Si–$SiO_2$ interface via the reduction of $SiCl_4$ with pyrolytically generated carbon monoxide from DMF.[16] The structure of the flakes consists of a small quantity of reduction species; that is, Si–Si bonds formed into a silica matrix was observed by X-ray photoelectron spectroscopy.[17]

The significant point is that the silica flakes produced in DMF were also well dispersed in water, chloroform, acetone, ethanol, etc. without any surface modification.

In summary, we explored a new process for making blue luminescent silica flakes in DMF solution. The process does not require any surfactants or other additives. With microwave treatment, the formation of silica flakes was accelerated. The silica flakes spontaneously dispersed in aqueous medium and display stable blue PL.[14] Further surface modifications of silica flakes for biorelated applications are probable because only DMF was used during the processing.

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