Luminescence Property of Water Dispersed Porous Si Terminated by Carboxylic Acid Derivatives

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Si nanoparticles have been extensively studied for their potential applications in luminescent devices and nontoxic fluorescent biological probes. However, the oxidation of surface Si-H bonds of porous Si deteriorates its optical properties and hydrophobicity of porous Si makes difficult to disperse in distilled water. Surface termination by hydrophilic organic molecules such as carboxylic acid is one of the effective methods to solve these difficulties. In order to clarify the effects of the chain length of carboxylic acid on the optical properties of porous Si, we have prepared porous Si terminated with three different carboxylic acids and investigated their changes of photoluminescent properties.

Si thin films were electrochemically etched with a mixture of hydrofluoric acid and ethanol to produce hydrogen terminated porous Si. This film was crushed into small pieces to transform into powder. This Si powder was heated with acrylic acid, 4-pentenoic acid or 10-undecenoic acid under argon for 1 hour to synthesize porous Si terminated by propanoic acid, pentanoic acid or undecanoic acid, respectively. Their FT-IR spectra are consistent with the structure of Si powder terminated by carboxylic acid.

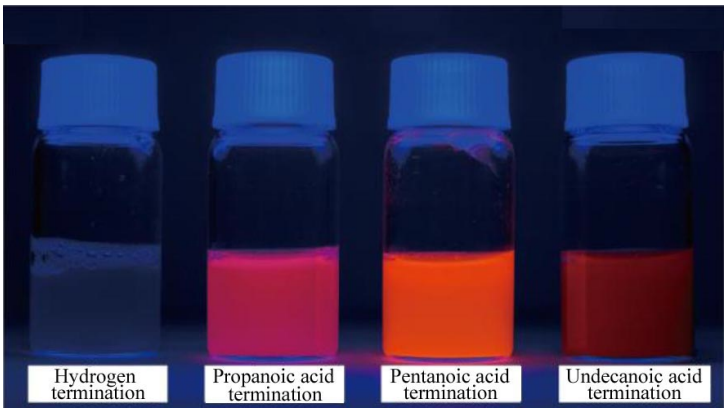

Figure 1. Photographs of porous Si powder dispersed in distilled water excited by UV light (365 nm) in a dark room.

A series of porous Si was dispersed in distilled water. All these samples were yellow suspension. Porous Si terminated by hydrogen was substantially clear and porous Si

terminated by carboxylic acid with a longer chain length was deeper in color. On the other hand, photoluminescence (PL) intensity and emission maximum wavelength excited by UV light were different in each sample as shown in Fig. 1. Moreover, the PL intensity of porous Si terminated by hydrogen decreased to approximately 0.1% after 10 days, and involved a blue shift from 770 nm to 660 nm. In contrast, the PL intensity of porous Si terminated by propanoic acid decreased slightly, and the PL maximum wavelength shifted from 760 nm to 710 nm. The PL intensity and maximum wavelength of porous Si terminated by carboxylic acid were more stable than those of porous Si terminated by hydrogen. Surface termination by organic molecules prevents the oxidation of surface Si-H bonds of porous Si. In the photodynamic measurement, substantial difference was not observed among the porous Si terminated by various carboxylic acids. [1]

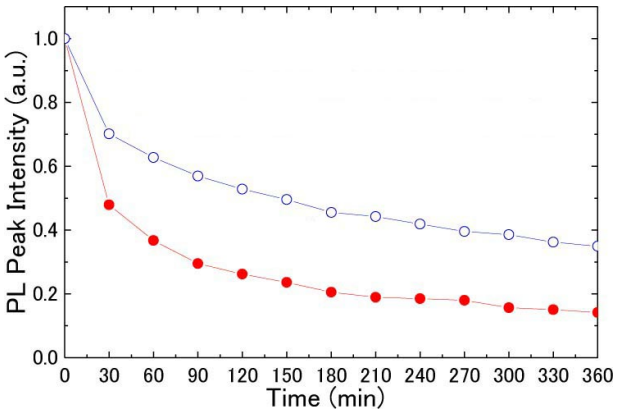

Figure 2. Time-lapse changes in the PL peak intensity of porous Si terminated by undecanoic acid (—) and undecanoate (—).

Surface termination of carboxylic acid is not sufficiently enough for hydrophilic property of porous Si. By treatment of sodium carbonate solution, carboxylic acid group is easily converted to its sodium salt. The dispersion property of porous Si in water was improved by this treatment, and better stability of PL peak intensity of porous Si was observed as shown in Fig. 2. Synthetic procedure and photodynamic property of water dispersed porous Si terminated by carboxylic acids or their sodium salt are reported.

References:

[1] M. Kamiguchi, M. Sakakibara, K. Matsumoto, K. Kamiya, T. Nomura, S. Kawabata, M. Inada, S. Suzuki, *Trans. Mat. Res. Soc. Japan,* **2016**, 41, 347