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Luminescent Silicon Nanoparticles covered with Ionic Liquid

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ABSTRACT:

Red-, yellow- and green-luminescent silicon nanoparticles covered with ionic liquid AMImTFSI (1-Allyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide) are reported. Red luminescent silicon nanoparticles (Si-Red), yellow luminescent silicon nanoparticles (Si-Yellow) and green luminescent silicon nanoparticles (Si-Green) were prepared under the acid-etching process using hydrofluoric acid/nitric acid for 50 s, 75 s, and 90 s, respectively. Their surface protection using ionic liquid were carried out by the injection of bare silicon nanoparticles into AMImTFSI, resulting in formation of Si-Red-I, Si-Yellow-I and Si-Green-I. The Si-Red-I, Si-Yellow-I and Si-Green-I show effective luminescence after seventeen days. In this study, luminescent silicon nanoparticles covered with ionic liquid are performed for the first time.

KEYWORD: quantum dot, silicon, luminescence, surface protection, Ionic liquid

1. Introduction

Nano-scaled silicon particles are regarded as attractive luminescent materials for use in light-emitting diodes, lasers, solar cells, and bio-sensing applications [1-16]. The silicon nanoparticles are generally prepared from silicon materials or Si compounds. Koshida has reported porous silicon nanolayers prepared by the anodic oxidation of (100)-oriented boron-doped p-type Si wafer [17, 18]. Seto described the preparation of silicon nanoparticles by laser ablation of a silicon target [19]. Shirahata has reported microemulsion synthesis method of alkoxy passivated silicon nanoparticles [20]. Swihart and Kortshagen prepared silicon nano powders fabricated from SiH_4 and SiCl_4 gases using laser-induced heating and a non-thermal plasma synthesis [21, 22]. We also reported the novel synthesis and effective surface protection of air-stable luminescent silicon nanoparticles. The silicon nanoparticles are obtained by a novel elimination reaction of carbon monoxide (CO) from SiO_2 using a phenol resin at 1900 °C (Fig. 1a) [23]. Prepared silicon nanoparticles are treated using hydrofluoric acid and nitric acid (HF/HNO_3) solutions to control the particle size.

Surface protection on the silicon nanoparticles is a key factor for preparation of bright-luminescent materials, because oxidation of bare silicon surface leads to formation of non-luminescent SiO_2 compounds, quickly [24]. Various types of surface protection molecules have been reported [25-29]. We recently reported strong-luminescent silicon nanoparticles covered with styrene molecules [23]. Their silicon surface protections are based on the chemical reaction for formation of stable chemical bond between silicon atom and organic molecules, surface termination reaction [23]. The stable chemical bonds on the silicon nanoparticles, however, prevent from surface-exchange reaction for assemble formation and addition of photo-functional groups such as a photosensitizer [30-32]. The surface-exchange reaction is a key factor for development of photo-

functional materials. Stable protection on the silicon surface without formation of tight chemical bonds is required for improvement of luminescent silicon nanoparticles.

In this study, we focus on ionic liquid as a surface protector of silicon nanoparticles. Ionic liquids are ionic salt-like organic materials 100 °C. Their vapor pressures are extremely low, and they show characteristic wide electrochemical windows, high conductivity and electrolyte properties [33]. Ionic liquids as reaction and extraction solvents have been also reported [34]. Recently, Kuwabata and Torimoto have described effective surface protection performance using ionic liquids on the materials [35]. Ionic liquids have no oxygen and no water that promote oxidation of bare silicon surface. Based on their characteristic properties, we have attempted to use ionic liquids, AMImTFSI (1-Allyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide) for protection on the silicon nanoparticle surface without surface termination reaction (Fig.1b and c). Luminescence from silicon nanoparticles covered with AMIMTFSI is successfully observed for two weeks. In this study, surface protection and luminescence properties of silicon nanoparticles covered with ionic liquids are demonstrated for the first time.

2. Experimental

Materials.

Tetra-ethoxysilane ES40 as a source for silicon was purchased from COLCOAT CO.LTD. Phenol resin SR-101 as a source of carbon was obtained from AIR WATER INC. Aqueous solution of maleic acid (70 %) as a catalyst was purchased from Nippon Syokubai. Fluoric acid HF (48 %) was purchased from Tokyo Chemical Industry Co. Nitric acid HNO₃ (62%) AMImTFSI were purchased Kanto Chemical CO., INC. Polyethylene filter was obtained by Japan Entegris Inc. All other chemicals and solvents were reagent grade and were used without further purification.

Apparatus

High-speed shear shredding process is performed using Yoshida Kikai Co. LTD Nano Vita L-ES. Ultrasonic vibration was performed by AS ONE VS-100III. XRD spectra were characterized by a RIGAKU X-ray diffractometer Smart Lab Ultima U.

Preparation of silicon nanoparticle slurry

Tetraethoxysilane, phenol resin, and a 30% aqueous solution of maleic acid were mixed in the ratio of 6:3:1 to prepare the SiO₂-sol precursor and heated at 200 °C for 3 h. By-products (ethanol, water, and formaldehyde) in the SiO₂-sol were removed under the chemical reaction. The obtained precursor was subsequently heated at 900 °C for 2 h in a nitrogen atmosphere for pre-carbonization. After pre-carbonization, the precursor was heated at 1900 °C for 3 h in an argon atmosphere, which resulted in the formation of silicon nanoparticles covered with SiO_x (x = 1 and 2) and SiC (Fig. 1a).

The slurry of silicon nanoparticles with a small amount of SiO_x (8 mg) was placed into a polypropylene container with the simultaneous addition of 10 mL of 48% HF and 1 mL of 68% HNO₃ (Fig. 1b). Acid etching of the silicon nanoparticle slurry was performed under ultrasonication at 20 °C. The acid etching process was monitored by observation of the silicon nanoparticle luminescence under excitation with UV light (365 nm). The acid-etching process was stopped by the addition of methanol solution (water: methanol = 1:1 v/v, 30 ml) to the solution. Red luminescent silicon nanoparticles (Si-Red), yellow luminescent silicon nanoparticles (Si-Yellow) and green luminescent silicon nanoparticles (Si-Green) were prepared under the acid-etching process for 50 s, 75 s, and 90 s, respectively.

Treatment process using ionic liquid

After the acid etching process, solution of silicon nanoparticles in HF/HNO₃ was moved to a glove box with a high-purity nitrogen atmosphere. The solution was filtered using a polyethylene

filter (20nm mesh) and the residue (silicon nanoparticles) was washed with 10 mL of H₂O/Methanol mixture (3/1). The silicon nanoparticles were dried under vacuum at room temperature for 60 min.

Ionic liquid AMImTFSI in glass vessel 5ml was pouring into liquid nitrogen and vacuum-dried by the end of bubble disappearing and then moved into a glove box. Prepared silicon nanoparticles were poured into AMImTFSI, and were dispersed under ultra sonication (Fig. 1b). The solution of silicon nanoparticles in AMImTFSI was vacuum-thawed for removal oxygen, methanol and water.

Optical measurements

UV light source (wavelength at 365nm) was used a LED365-SPT/L (Optocode Corp.) for observation of acid-etching process. The emission spectra of silicon nanoparticles covered with ionic liquid are measured by using a Hitachi High Technologies Co. F-7000.

3. Results and discussion

We previously reported that silicon nanoparticles are obtained by the reaction of SiO₂ with phenol resins. Prepared silicon nanoparticles were identified using XRD measurements. The diffraction peaks at $2\theta = 28.43, 47.33, \text{ and } 56.12^\circ$ were assigned to the (111), (220), and (311) planes of silicon, that agree well with those of previous silicon nanoparticles [23]. The SiO₂ layers on the silicon nanoparticles are removed using hydrofluoric acid (HF), and the size of silicon nanoparticles is also controlled by acid-etching process using HF/HNO₃ (Si-Red, Si-Yellow and Si-Green). Prepared silicon nanoparticles were poured into ionic liquid (AMImTFSI), and were dispersed under ultra sonication (Si-Red-I, Si-Yellow-I and Si-Green-I).

Emission spectra of red, yellow and green luminescent silicon nanoparticles with AMImTFSI (Si-Red-I), (Si-Yellow-I) and (Si-Green-I) are shown in Fig. 2a. These emission bands

were observed at 608nm, 569nm and 545nm, respectively. Their spectra are different from that of AMImTFSI (emission band at 471nm) as shown in Fig. 2a-4. The luminescence properties of silicon nanoparticles come from the direct recombination of excited electrons and positive holes based on the wavefunction overlap in the nanometer range, which is known as the quantum confinement effect. The energy gaps of silicon nanoparticles depend on their particle sizes, indirect quantum effects of silicon nanoparticles [30].

The emission quantum yield of silicon nanoparticles with surface termination reaction using styrene was found to be 55%. Emission intensity of Si-Green-I was similar to that of silicon nanoparticles with surface termination. In contrast, that of silicon nanoparticles without surface termination was estimated to be less than 1%. In this study, we successfully observed continuous luminescence from silicon nanoparticles covered with ionic liquid.

Graphical images and their time-dependences of the emission intensities of silicon nanoparticles covered with AMImTFSI are shown in Fig. 2b. Silicon nanoparticles without any surface terminations are rapidly quenched under air. On the other hand, we can not observed the drastic decrease of the emission intensities of Si-Red-I, Si-Yellow-I and Si-Green-I for several hours. The Si-Red-I, Si-Yellow-I and Si-Green-I dispersions show effective luminescence after seventeen days. Their relative emission intensities based on the fresh-made silicon nanoparticles (100 %) are estimated to be over 20 %. We consider that ionic liquids promote effective protection from oxidation and/or impurity adsorptions of bare silicon surface. The silicon nanoparticles covered with ionic liquid can be easily exchanged using various types of functional organic molecules, which are not able to react on the silicon surface with surface protection such as styrene molecule. Dispersion of silicon nanoparticles in ionic liquid is expected to be useful as novel luminescent materials for future photonic applications.

4. Conclusions

In this study, we demonstrated effective luminescent dispersion of silicon nanoparticles covered with ionic liquid. The silicon nanoparticles with ionic liquid exhibit perfect Si-H bonds on the surface without stable chemical bonds [30]. From this point, silicon nanoparticles with ionic liquid also expected to use as not only luminescent materials, but catalysis for chemical reaction. By using TEM (transmittance electron microscope) or SEM (Scanning electron microscope) techniques [36]. We would observe directly the Si-H surface of the luminescent silicon nanoparticles with ionic liquid. Those surface observations of silicon nanoparticles are linked with study on solid-state physics of silicon nanomaterials. The silicon nanoparticles with ionic liquid are new materials for development of bright luminescent nanomaterials.

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Figure Captions

Figure 1. Systematic procedures for silicon nanoparticles covered with ionic liquid. a) Synthesis of silicon particles in SiO_x. b) Acid-etching process and preparation of silicon nanoparticles covered with ionic liquid. c) Chemical structure of ionic liquid: AMImTFSI

Figure 2 a) Emission spectra of silicon nanoparticles covered with ionic liquid, Si-Red-I (1: triangles), Si-Yellow-I (2: circles), Si-Green-I (3: squares), and AMImTFSI (4: gray). b) Time-dependence of the emission intensities of Si-Red-I (1: triangles), Si-Yellow-I (2: circles) and Si-Green-I (3: squares). Inset: graphical picture of luminescent Si-Red-I (1), Si-Yellow-I (2) and Si-Green-I (3).



