ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2013, Vol. 39, No. 6, pp. 427–431. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © L.A. Aslanov, V.N. Zakharov, A.V. Pavlikov, S.V. Savilov, V.Yu. Timoshenko, A.V. Yatsenko, 2013, published in Koordinatsionnaya Khimiya, 2013, Vol. 39, No. 6, pp. 323–328.

Synthesis and Properties of Nanosilicon Stabilized by Butyl and Perfluorobutyl Ligands

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Received November 14, 2012

Abstract—Nanocrystalline silicon stabilized by butyl and perfluorobutyl ligands that form improper surface states of silicon nanocrystals were synthesized. The presence of perfluorobutyl ligands on the surface of silicon nanocrystals was proved by IR spectroscopy. Nanocrystals with perfluorobutyl ligands form aggregates, which decreases the efficiency of photoluminescence. The nanocrystals with butyl ligands have smaller size but their photoluminescence can be clearly recorded.

DOI: 10.1134/S1070328413060018

INTRODUCTION

Lately, various methods for the preparation of so-called crystalline nanosilicon (nc-Si) consisting most often of 1 to 10 nm silicon nanocrystals have been developed and the physicochemical properties of nc-Si have been studied [1, 2]. Functionalization of nc-Si surface by various ligands (most often, hydrocarbon ligands) is aimed at resisting coagulation of nc-Si, preventing it from oxidation with oxygen or reaction with air moisture, imparting hydrophilic properties, and preparing for medical or biological applications [2, 3]. The effect of ligands on silicon nanoparticles is ignored, although it is known that each ligand creates extrinsic surface states of nanoparticles, which influence both photoluminescence (PL) spectra and cathodic and electroluminescence spectra [2]. For example, it was shown that one oxygen atom appearing on the silicon nanoparticle surface changes substantially the PL spectrum for particles less than 1.5 nm across [4].

The effect of surface states on the properties of solids caused by the change in the chemical composition of the surface is inherent not only in nc-Si but it is very important for adsorption, heterogeneous catalysis, electrochemistry and development of sensors. However, there are only few experimental studies of the surface state chemistry. Therefore, study of the extrinsic surface states of any item including nc-Si is of crucial interest for a broad range of specialists.

Ligands that are attached to the surface of silicon nanoparticles through carbon atom are especially important since Si–C bonds are stable against hydrolysis. The most frequently used alkyl ligands can be opposed by perfluoroalkyl ligands, which have electron-withdrawing properties, and hence the surface states they create should differ from the alkyl surface states. Therefore, we studied silicon nanoparticles functionalized by butyl and perfluorobutyl groups.

EXPERIMENTAL

The synthesis of nc-Si with surface perfluorobutyl ligands (FBu-ncSi) was performed in several stages.

First, a dispersion of nc-Si with surface bromide ligands was prepared in a Schlenk vessel with a magnetic stirrer. The vessel was purged with argon, and dried 1,2-dimethoxyethane (50 mL) and potassium metal (2.93 g, 75 mmol) were added. The mixture was heated to 85°C on a glycerol bath. Potassium was dispersed down to particles 1–3 mm in diameter. Then a solution of $SiBr_4$ (5.91 g, 17 mmol) in dimethoxyethane (10 mL) was added in an argon flow. Violet color appeared. After 1 h, a yellow-colored dispersion formed, the total reaction time being 2 h.

The concentration of bromide ions on the nc-Si surface was determined by titrating 1 mL of the resulting dispersion with a 0.04 M solution of KOH. The concentration of Si–Br bonds was 0.08 mol/L. The alkylating agent, perfluorobutyllithium, was prepared from perfluorobutyl iodide C_4F_9I (20% excess with respect to the number of bromide ligands on nc-Si) and lithium as amalgam (10% excess with respect to C_4F_9I).

Lithium amalgam was prepared in a Schlenk vessel with an air condenser fitted with a calcium chloride tube. The vessel was purged with argon, mercury (6.65 g, 33 mmol) and lithium (0.025 g, 3.6 mmol) were added, and the mixture was heated on a water bath to 200°C. The mercury and lithium were stirred in an argon flow for several seconds for homogenization and the amalgam was cooled to room temperature.

Perfluorobutyllithium was synthesized in the same Schlenk vessel in which lithium amalgam was pre-

pared. The vessel was placed in a cooling bath (NaCl/ice) at −17°C, dimethoxyethane (5 mL) and perfluorobutyl iodide (0.28 mL, 1.65 mmol) were added, and the mixture was magnetically stirred for 50 min.

The perfluorobutyl ligands were grafted on the nc-Si surface in a Schlenk vessel containing perfluorobutyllithium at −17°C. A dispersion of bromide nc-Si, which was obtained in the first stage (17 mL), was added to the vessel. The reaction time with stirring was 1 h. The dispersion was dark yellow-colored.

The resulting dispersion of perfluorobutyl nc-Si was treated with dry hydrogen chloride for 1 min to remove excess perfluorobutyllithium. A yellow dispersion of nc-Si with grafted perfluorobutyl ligands formed above mercury.

The synthesis of nc-Si with butyl ligands (Bu-ncSi) was performed under similar conditions. The use of organolithium compounds instead of usual hydrosilylation for replacement of bromide ligands by butyl ligands was chosen to ensure equal conditions of grafting of perfluorobutyl and butyl ligands on the nc-Si surface for comparability of the results.

Electron microscopic examination of nc-Si was carried out on a TITAN 80-300 high-resolution transmission electron microscope (FEI, USA) with correction of spherical aberration for the probe. The samples were examined in light- and dark-field modes at an accelerating voltage of 300 kV. In the latter case, the samples were scanned using high-angle annular dark field detector (HAADF) of scattered electrons forming so-called Z-contrast. The chemical composition of the samples was determined by energy dispersive X-ray microanalysis (EDAX, United States). The experimental data were treated and interpreted using DigitalMicrograph (Gatan) and TIA (FEI) program packages. The samples for transmission electron microscopy (TEM) examination were prepared by depositing a suspension on standard electron-microscopic copper grids with a thin carbon film.

High-resolution TEM (HR TEM) study was carried out also on a JEOL JEM 2100F/Cs instrument (JEOL Co. Ltd.) with an electron emission gun (FEG) equipped with a CEOS GmbH spherical aberration corrector (Germany), a Tridiem energy filter, and a Gatan Inc. electron energy loss spectrum alanyzer (United States). The photomicrographs were taken at a 200 kV accelerating voltage and 90 s exposure by light-field transmission microscopy.

The sample preparation procedure comprised dispersing a weighed portion of the material in a 0.2% aqueous solution of sodium dodecyl sulfate in a Sapphire ultrasonic bath (150 W, 22 kHz) for 20 min at room temperature and deposition of 100 μL of the resulting suspension on a copper grid precoated by polyvinyl formal.

The PL spectra were measured on a setup with a SOLAR TII monocromator and a Hamamatsu CCD camera. PL was excited by radiation from an Ar laser at 364 nm. The PL spectra of the dispersions were measured in a quartz tube, the solid phase was deposited on a quartz substrate. The obtained spectra were calibrated to the spectral sensitivity of the setup.

IR absorption spectra were recorded on a Bruker IFS66v/s spectrometer equipped with a multiply frustrated total internal reflection attachment.

RESULTS AND DISCUSSION

Electron-microscopic examination showed that nc-Si particles coated by butyl ligands were not larger than 3.5 nm and perfluorobutyl-stabilized particles were not larger than 6 nm (Figs. 1 and 2). The latter were mainly crystal aggregates. Possibly, they also incorporated amorphous silicon particles. These aggregates resulted from particle agglomeration during the replacement of bromide ligands by perfluorobutyl ones. The size distribution for nc-Si particles is presented in Figs. 3 and 4. The agglomeration of nc-Si during replacement of bromide ligands by butyl ligands was less pronounced.

The IR spectra (Fig. 5) exhibit absorption bands at 1458 and 1242 cm^{-1} corresponding to Si–C vibrations [5, 6]. The presence of perfluorinated ligands on the surface of nc-Si particles is indicated by the C–F absorption bands at 1369, 1200, 1101, 975, 927, and 848 cm^{-1} [7]. The weak band at 3410 cm^{-1} shows that the hydroxy groups on the nc-Si surface are few and far between, and the 1031 cm^{-1} band attests to the presence of Si–O–Si bonds on the nc-Si surface [8]. The band at about 1080 cm^{-1} could have revealed the oxygen content on the sample surface but it is covered by strong bands caused by C–F bonds. Apparently, solvent (dimethoxyethane) molecules are also present on the nc-Si surface as ligands able to form donor–acceptor bonds with vacant hybrid orbitals of the surface silicon atoms. This is indicated by C–H bands at 2988, 2932, 2882, and 2819 cm^{-1} [5, 9].

The PL spectra of nc-Si with surface butyl ligands recorded for a dispersion and for the solid are presented in Figs. 6 and 7. One can see that intensities of the PL spectra of nc-Si with surface butyl ligands decrease upon addition of an ionic liquid (IL), namely, 1,3-dimethylimidazolium iodide (mp = 83°C), to nc-Si. Unlike usual salts, which have low adhesion to nc-Si, ionic liquids are easily vitrified and are well sorbed on the nc-Si particle surface. The IL was added to reveal the extrinsic surface states of nanosilicon based on interaction with the cations and anions that constitute the IL.

A comparison of two spectra of Bu-ncSi dispersions (Fig. 6) with and without the IL show that both blue and green bands are quenched. The alkyl ligands on the nc-Si surface do not prevent the IL from reaching the nc-Si surface. Both bands in the PL spectrum are also slightly quenched in the solid phase after removal of the solvent (Fig. 7) but the quenching effi-

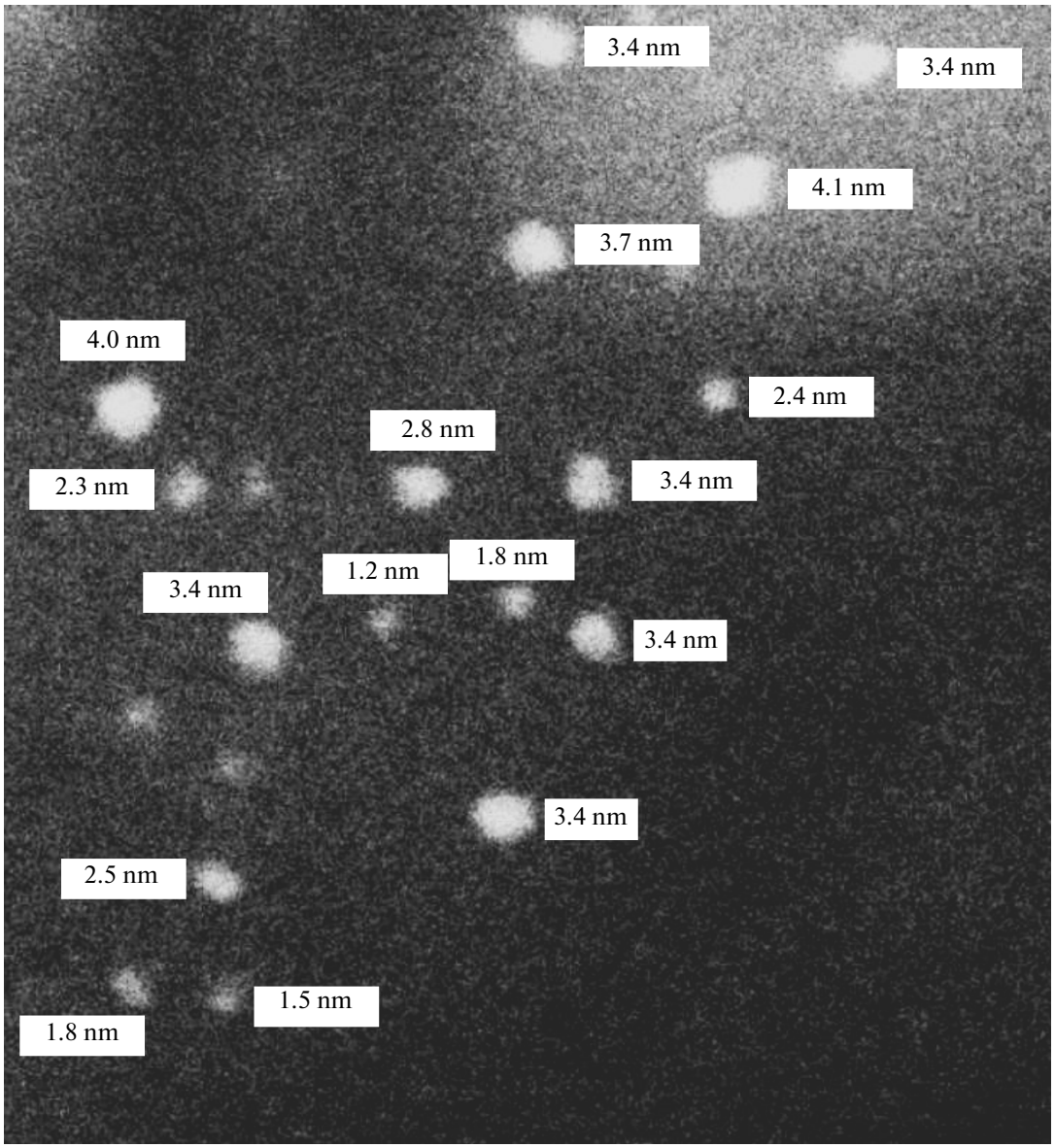

Fig. 1. Size of silicon nanoparticles with surface perfluorobutyl ligands from TEM data.

ciency is much lower. The IL is insoluble in aliphatic hydrocarbons and as long as the sample contains a diphilic solvent, i.e., dimethoxyethane, the IL ions can reach the nc-Si surface, while in the solid state, these ions are sorbed only on the sites free of butyl ligands, which reduces the efficiency of their action.

The PL intensity from nc-Si with surface perfluorobutyl ligands was very low due to the formation of aggregates by most of nanoparticles; therefore, these PL spectra are not reported. However, it was found that the intensity of the nc-Si spectrum with surface perfluorobutyl groups is higher without IL than with IL, i.e., IL quenches the PL of perfluorobutyl nc-Si. Figure 8 shows the PL spectra of solid samples. Attention is attracted by the red shift of the PL maximum for the IL-containing sample. Electron-withdrawing ligands may decrease the electron density on the nc-Si surface, and this should give rise to an unbalanced positive charge on the nc-Si surface, enhancing the sorption of anions and decreasing the sorption of cations; this may induce changes in the PL spectra, which require further investigation.

The effect of IL on the intensity of PL spectra attests to the sorption of IL on the nc-Si surface. The causes of this sorption and the mechanism of the IL effect on the intensity of the spectra of nc-Si are to be elucidated in a dedicated study.

The perfluorobutyl ligands are strong electron acceptors, while butyl groups are not; therefore, the extrinsic surface states formed by perfluorobutyl

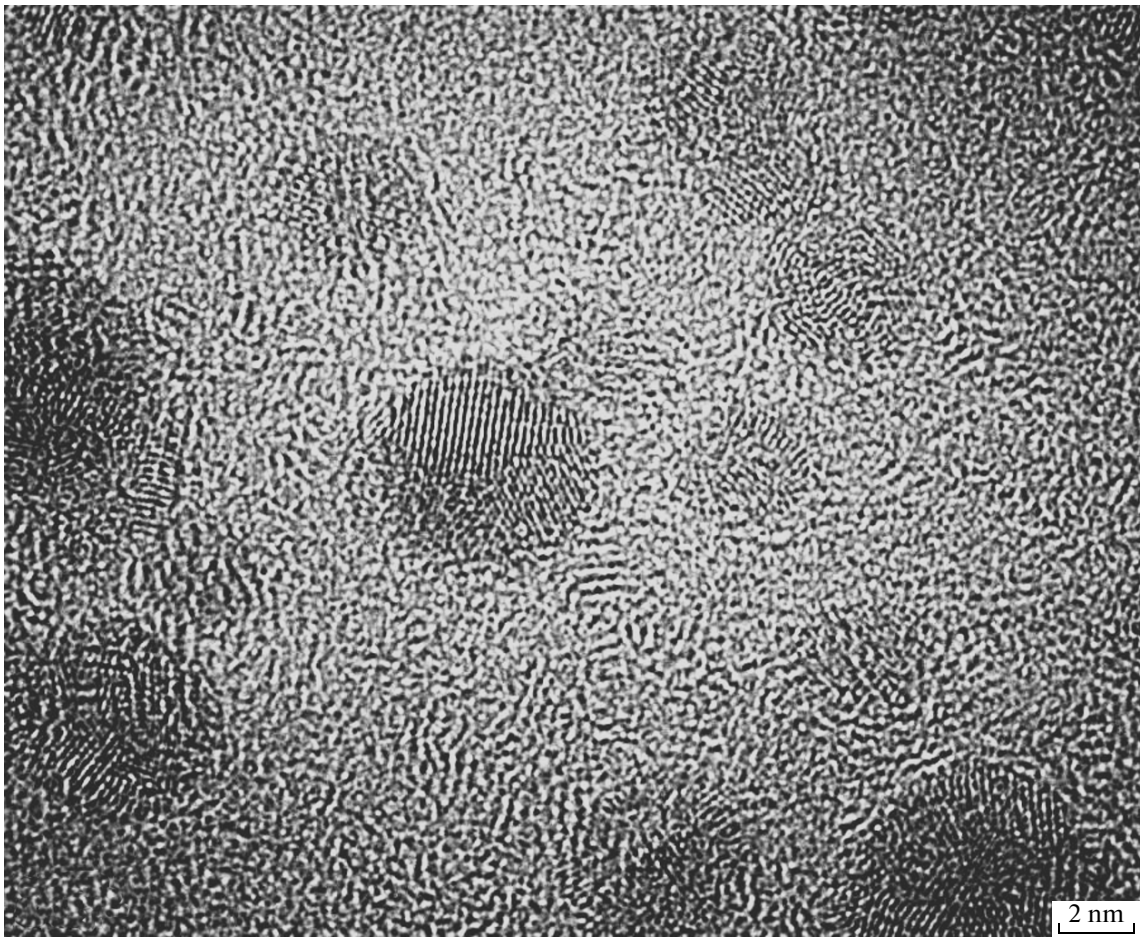

Fig. 2. HR TEM of silicon nanoparticles coated by perfluorobutyl ligands.

ligands are inevitably considerably different from those formed by butyl group; hence, the wavelengths of the maxima in the PL spectra for the two materials may also be expected to differ. However, comparison of the PL spectra of butyl and perfluorobutyl nc-Si demonstrated that the maxima nearly coincide. From

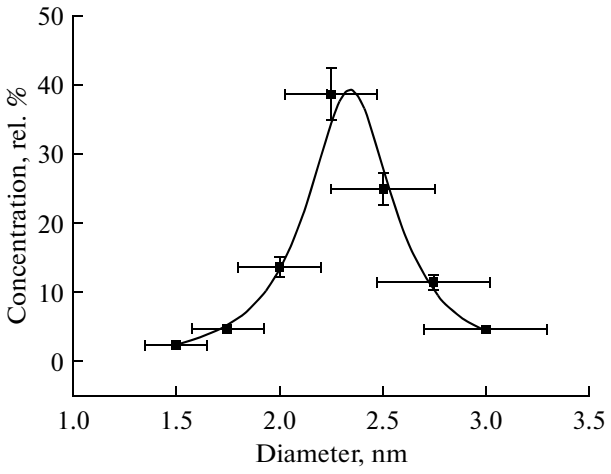

Fig. 3. Size distribution function for silicon nanoparticles coated by butyl ligands.

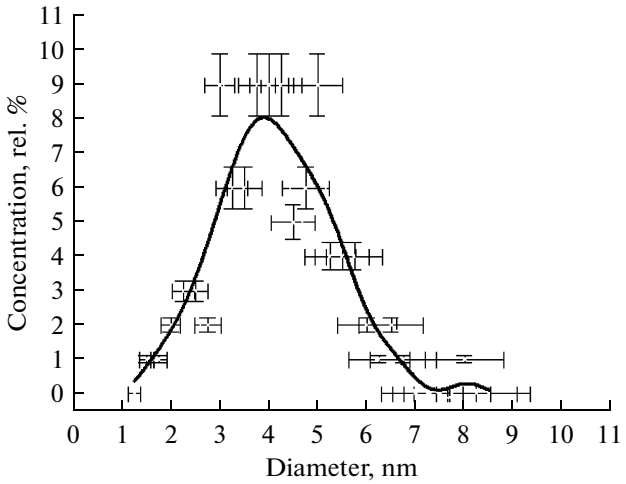

Fig. 4. Size distribution function for silicon nanoparticles with surface perfluorobutyl ligands.

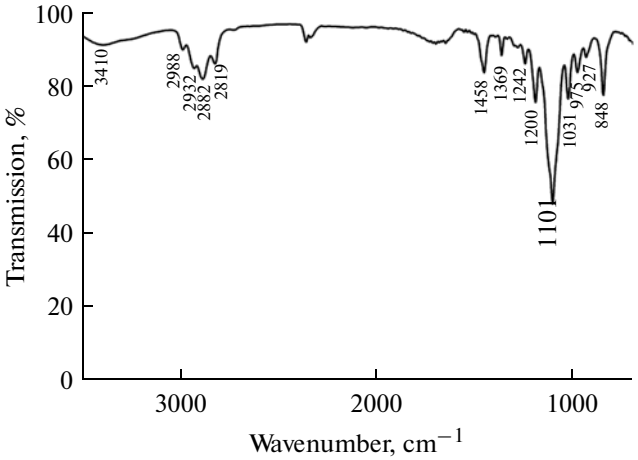

Fig. 5. IR spectrum of silicon nanoparticles functionalized by perfluorobutyl ligands.

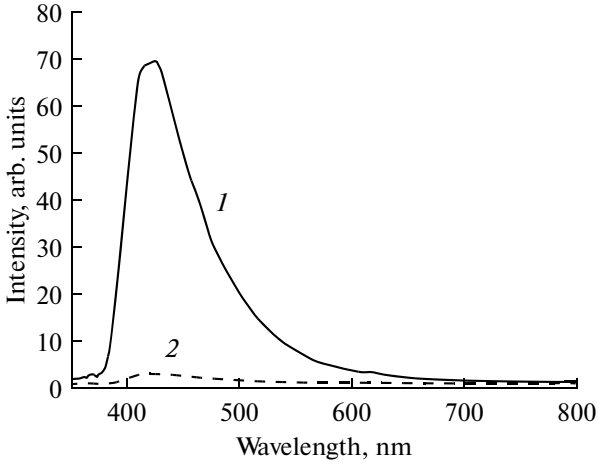

Fig. 6. PL spectrum of a glyme dispersion of silicon nanoparticles stabilized by butyl ligands: (*1*) Bu + ncSi, (*2*) Bu + ncSi + IL.

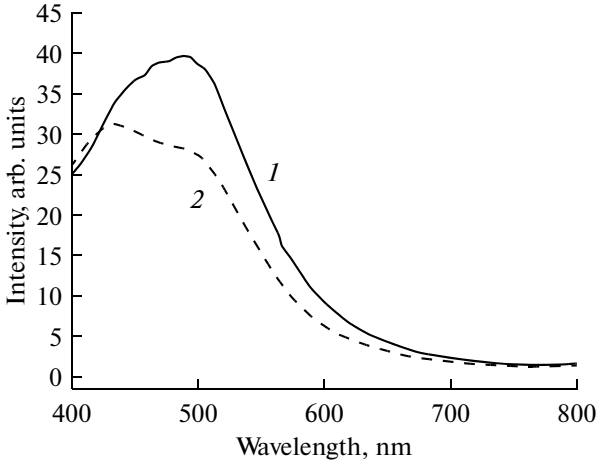

Fig. 7. Solid-state PL spectrum of silicon nanoparticles with surface butyl ligands: (*1*) Bu + ncSi, (*2*) Bu + ncSi + IL (2).

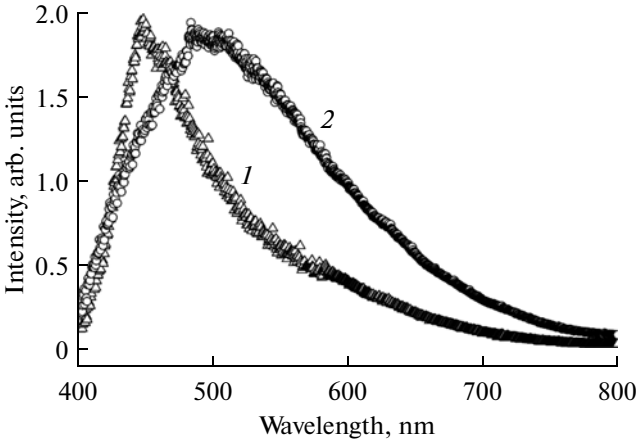

Fig. 8. Solid-state PL spectrum of silicon nanoparticles with surface perfluorobutyl ligands: (*1*) ncSi + C_4F_9, (*2*) ncSi + C_4F_9 + IL.

this it follows that the difference between the ligands in question is insufficient and it is necessary to compare electron-withdrawing perfluorinated ligands with strong donors, e.g., carbene, the use of which for stabilizing nc-Si was reported in our earlier works [10, 11].

ACKNOWLEDGMENTS

The authors are grateful to I.K. Kudryavtsev for useful discussion of the manuscript and to A.S. Orekhov for the help in electron microscopic studies.

This work was supported by the Russian Foundation for Basic Research, project no. 11-03-01071.

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Translated by Z. Svitan'ko