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Synthesis and Properties of Nanosilicon Prepared by Homogeneous and Heterogeneous Reduction of Tetraethyl Orthosilicate

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Abstract—Nanocrystalline silicon was synthesized by reduction of tetraethyl orthosilicate both in homogeneous and heterogeneous processes with surface stabilization by nitrogen heterocyclic carbene (NHC) ligands. The presence of NHC ligands on the surface of silicon nanocrystals was demonstrated by IR spectroscopy. According to transmission electron microscopy data, the size of silicon nanocrystals is in the range of 2.2–8.4 nm. Photoluminescence of the samples is clearly recorded in the blue spectral region.

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INTRODUCTION

Currently, active search for methods of preparation of crystalline nanosilicon with 1 to 10 nm particle size from new types of silicon-containing raw materials is in progress. In this respect, an attempt to synthesize nanosilicon by reduction of silicon-containing intermediate products of large-scale industrial chemical processes appears quite promising.

The synthesis of nanocrystalline silicon in colloid media is usually a heterogeneous process in which the reducing agents either form a separate phase (though it is highly dispersed) or are poorly soluble in the solvent, thus decreasing the reaction rate. The search for reactions that can proceed in a homogeneous medium led us to a peculiar system consisting of tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$), sodium borohydride, an ionic liquid (IL)—1,3-dimethylimidazolim iodide ($C_5H_9N_2I$)—and diglyme as a solvent. The first two components are readily soluble in diglyme at room temperature, while IL is dissolved upon melting (at 83°C). A specific feature of reaction carried out in this system is that TEOS or IL taken separately do not react with sodium borohydride in diglyme, while when taken together, they react to form nanocrystalline silicon. Even a more potent reducing agent, sodium metal, also reacts neither with TEOS (without a solvent) nor with a solution of IL in diglyme (at 110°C). Meanwhile, the ternary mixture of the reactants (TEOS–IL–Na), which is a heterogeneous system, reacts to give nanocrystalline silicon.

We reported [1, 2] the preparation of nanocrystalline silicon by the reaction of $SiBr_4$, IL, and sodium metal in diglyme at a temperature above the sodium melting point (98°C). In this communication, we present the results of investigation of two systems, TEOS–$NaBH_4$–IL–diglyme (**I**) and TEOS–Na–IL (**II**), in one of which, silicon containing the starting reactant also does not react with molten sodium.

EXPERIMENTAL

Homogeneous synthesis (system I). Ionic liquid (2.3 mmol) and $NaBH_4$ (2.1 mmol) were dissolved in diglyme (20 mL) at 90°C. (Diglyme was chosen as the solvent because of high solubility of $NaBH_4$: 24 g in 100 g of diglyme at 25°C.) Liquid TEOS (1.0 to 1.5 mmol) was added to the mixture. The reaction was conducted in a Schlenk flask equipped with a reflux condenser and a magnetic stirrer under argon for 1.5–3 h. After 0.5 h of the reaction, the solution turned yellow. As the reaction proceeded, the color became more intense to become yellow-reddish. The reaction rate increased with increase in the $NaBH_4$ concentration. At the end of the reaction, the dispersion of nanoparticles was separated from the solid phase by a batching device. The reaction had a good reproducibility. According to transmission electron microscopy (TEM), the silicon crystal size in the dispersion was 2.2–8.4 nm.

Heterogeneous synthesis (system II). TEOS (20 mL) was mixed with Na (4 mmol) at room temperature, heated to induce sodium melting and dispersing to 1–3 mm particles. At 100°C, IL (1.8 mmol) was added. The reaction was conducted in a Schlenk flask equipped with a reflux condenser and a magnetic stirrer under argon for 2–3 h. At the end of the reaction, a crystalline precipitate was present on the bottom of the Schlenk flask. Above the precipitate, the orange layer of the excess of IL was located, and above IL, there was the yellow dispersion of nanosilicon in TEOS.

According to TEM data, the silicon crystal size in the dispersion was 2–6 nm.

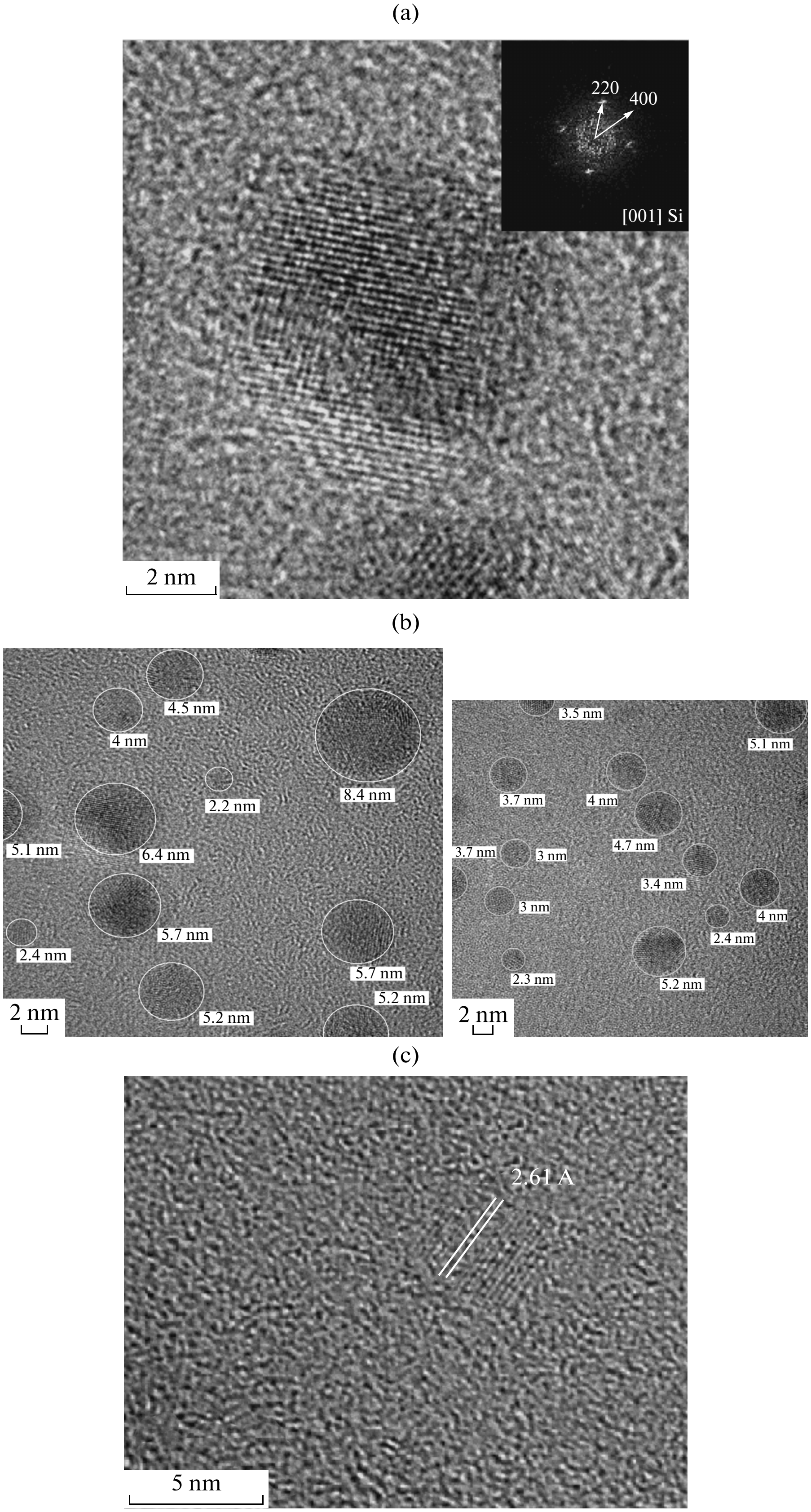

Fig. 1. (a) HR TEM image of a silicon nanoparticle and (inset) X-ray diffraction pattern of the imaged particle; (b) TEM images of silicon nanoparticles obtained by the homogeneous reaction in system **I**; (c) HR TEM image of a silicon nanoparticle obtained by the heterogeneous reaction in system **II**.

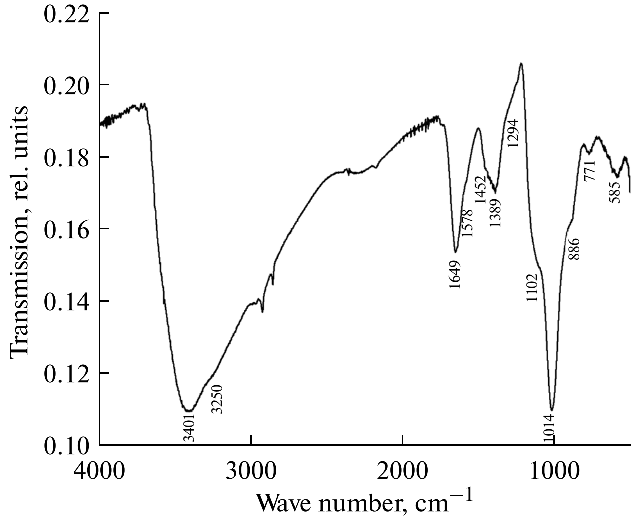

Fig. 2. IR spectrum of silicon nanoparticles obtained by the heterogeneous reaction in system **II**.

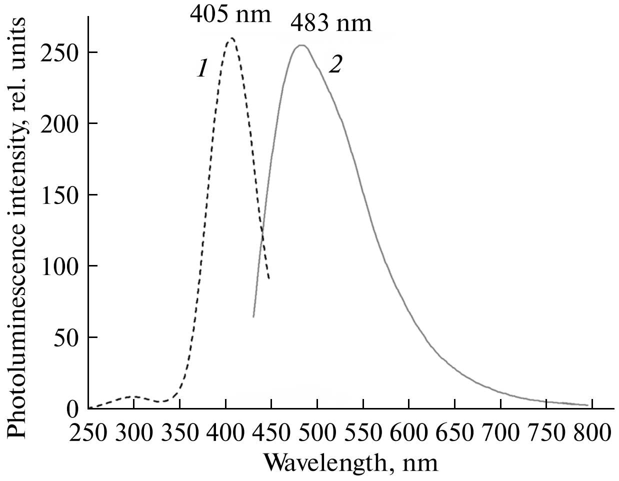

Fig. 3. PL of samples obtained in system **I**: (*1*) excitation spectrum at λ_{PL} = 464 nm; (*2*) PL spectrum at λ_{excit} = 406 nm.

The photoluminescence (PL) spectra of the dispersion of nanosilicon in diglyme were studied on a Perkin Elmer LS55 spectrometer.

IR spectra were recorded on a Tensor 27 FT-IR spectrometer (Bruker) with a resolution of 1 cm^{-1}, the signal being averaged over 32 scans. Films from solutions of the samples in 1,2-dimethoxyethane were deposited on a KBr substrate and dried in vacuum (1330 Pa) with heating to 80°C for 2 h to remove the solvent.

Electron microscopic examinations of the samples was done by high-resolution transmission electron microscopy (HR TEM) and electron diffraction on a JEOLJEM 2100F/Cs instrument (JEOLCo. Ltd., Japan) with a field-emission gun (FEG) equipped with a spherical aberration corrector, CEOS GmbH (Germany), and a Tridiem energy filter. The photomicrographs were recorded at an accelerating voltage of 200 kV and exposure time of 90 s in the bright field transmission microscopy mode. The dispersion of nanosilicon was deposited on a copper wire precoated by polyvinyl formal.

RESULTS AND DISCUSSION

In both systems, TEOS–$NaBH_4$–IL–diglyme (**I**) and TEOS–Na–IL (**II**), the formation of nanocrystalline silicon was reliably demonstrated by HR TEM. Figures 1a and 1b show HR TEM images of the silicon nanoparticles in system **I**, those for system **II** are presented in Fig. 1c. The silicon nanocrystals obtained by homogeneous synthesis have a diamond-like structure (Fig. 1a) typical of coarsely crystalline silicon. However, some nanosilicon particles detected in reaction system **II** have an interplanar spacing of 2.61 Å and Miller indices (211) typical of the polymorphic silicon phase BC8. This phase was recently prepared in a colloid system [3].

Apparently, redox reactions of TEOS with NHC (or Na) and of IL with $NaBH_4$ do not take place without complex formation of silicon with nitrogen heterocyclic carbene (NHC) ligands. Upon the complex formation between silicon and NHC ligands, redox potentials change, which is often observed in the coordination chemistry [4], and thus enable the ternary reaction to give silicon nanocrystals with the surface partly coated by NHC.

The FT-IR spectrum of silicon nanoparticle films synthesized in system **II** (Fig. 2) exhibits, first of all, strong stretching and bending modes of water molecules adsorbed on the surface at 3400 cm^{-1} (with a

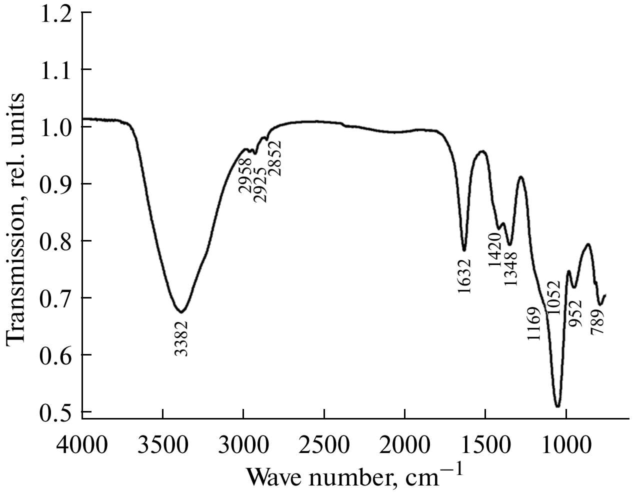

Fig. 4. IR spectrum of silicon nanoparticles stabilized by perfluorobutyl radicals.

shoulder at 3250 cm^{-1}) and 1650 cm^{-1}, respectively. Many authors [5–11] assign these bands (and also the peak at 890 cm^{-1}) to the hydroxy group bonded to the silicon atom; however, in our opinion, this needs to be additionally substantiated. One of the strongest bands in the spectrum of this sample (1014 cm^{-1}) can be assigned to Si–O vibrations, the more so, because its shoulder at 1100 cm^{-1} corresponds, most likely, to silicon dioxide vibrations [5–7].

Also, the spectra exhibit unresolved shoulders at 1452 and 1294 cm^{-1}, which, according to some authors [12, 13], can (indirectly) attest to the formation of Si–C bonds. The medium-intensity band at 1389 cm^{-1} can be assigned to HC=N stretching modes of the imidazole ring in the NHC ligands attached to silicon atoms [14].

We found that the PL spectrum of the sample obtained in system **I** shows a maximum at 483 nm (Fig. 3) only if a quarter volume of water or methanol has been added to the dispersion. The presence of silanol groups on the silicon nanocrystal surface gives rise to blue PL of the nanosilicon dispersion [15]. Since water reacts with nanosilicon to give silanol groups on the surface of silicon nanoparticles [16], it can be concluded that the PL is associated with the silanol groups formed on the surface.

Previously, we reported [17] that the IR spectrum published in [15] contains absorption bands of the solvent, which is removed only partly during drying of silicon nanoparticles formed in this solvent. The positions of the solvent bands deceptively coincided with the positions of the bands for perfluorobutyl ligands, thus distorting the positions and intensities of absorption bands.

The solvent was completely removed by heating the sample at 350°C for 3 h at reduced pressure (1330 Pa). The corrected IR spectrum of the silicon nanoparticles with perfluorobutyl ligands is shown in Fig. 4.

Thus, in this work, we developed new procedures for the synthesis of silicon nanocrystals with modified particle surface. The obtained substances were characterized by HR TEM, IR spectroscopy, and PL data.

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