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Synthesis of Amorphous Silica Nanosheets and Their Photoluminescence

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We demonstrate the synthesis of silica nanosheets (SiONSs) by exfoliation and oxidation with layered polysilane, $(SiH)_n$. The resulting silica was produced in the form of amorphous nanosheets with a uniform thickness of 0.68 nm, which was constructed of six-membered rings of SiO_4 tetrahedra. The thickness is an order magnitude smaller than previously reported silica nanoparticles prepared by a variety of other methods. Strong photoluminescence (PL) was observed, and the PL spectra had maxima at 2.7 and 3.1 eV. This strong emission may be because of the defect center of oxygen deficiency in the sheets. The SiONSs may have potential applications in future integrated optical devices.

I. Introduction

Nanometer-scale materials often exhibit intriguing physical and chemical properties that are rarely present in bulk materials. Two-dimensional (2D) nanostructure sheets or platelets have been synthesized as a new class of nanoscale materials, and they are ideal objects for the fabrication of nanoscale devices possessing various interesting functions.[1–3] This extremely high anisotropy and a thickness of molecular dimensions are strikingly different from nanoparticles that generally have a spherical shape.[4,5] In the past decade, much effort has been invested in realization of the 2D nanostructures by controlling the sizes and shapes.[6] Silica has also been an important subject of research for a long time. For example, the photoluminescence (PL) bands with peak energies around 1.9–4.3 eV for bulk or films forms have been reported.[7] Until now, most synthetic efforts on silica have been directed toward its nanotubes[8] and nanowires,[9] as well as their derivates earlier. These 1D nanostructures have stimulated great interest because of their peculiar physical properties and expected applications.

Compared with that of 1D silica nanostructures, a general method to synthesize 2D silica nanostructures has been lacking, which has hindered detailed experimental investigations on the properties of its 2D nanostructures. Here we demonstrate a large-scale preparation of 2D amorphous silica nanosheets (SiONSs) by the exfoliation and oxidation of layered polysilane, $(SiH)_n$. The optical properties of as-grown SiONSs were also investigated.

II. Experimental Procedure

$(SiH)_n$ was synthesized by a topotactical reaction from the Zintl phase $CaSi_2$ (Fig. 1(a)), a layered material with Si-corrugated (111) layers that are linked by the Ca ions. The structure of $(SiH)_n$ depicted in Fig. 1(b) consists of Si (111) layers terminated by H atoms. The $(SiH)_n$ was prepared according to the method described by Yamanaka *et al.*[10] About 1 g of powdered $CaSi_2$ (ca. 5–20 mesh, Aldrich, Japan) was immersed in 100 mL 37% HCl at −30°C. The mixture was continuously stirred for 7 days under Ar atmosphere. In this process, the $CaSi_2$ powder was transformed to a green–yellow solid, and no hydrogen gas bubbling was observed. SiONSs were formed by an exfoliation of $(SiH)_n$ in aqueous sodium Dodecylsulfate (S^+DS^-: $C_{12}H_{25}OSO_3Na$, Aldrich) solution at room temperature for 10 days. The $(SiH)_n$ powder (0.5 g) was added to the aqueous solution (100 mL) with molar ration of DS^- in solution/Si in $(SiH)_n = 1/6$. As-prepared suspension was a translucent and stable for 2 months without any precipitation. The sheets were characterized using transmission electron microscopy (TEM; JEOL JEM-2000 EXII, Japan) and tapping mode atomic force microscopy (AFM; Digital Instruments Nanoscope III a, Japan). Room-temperature PL of SiONSs was carried out in a JASCO FP-6600 (Japan) with an excitation wavelength of 350 nm and in a spectral range of 300–800 nm.

III. Results and Discussion

Figure 2(a) shows a scanning electron microscopy image of the as-grown $(SiH)_n$. The product consists of a sheet-like morphology with large lateral dimensions up to several micrometers. Figure 2(b) shows the X-ray diffraction patterns of $(SiH)_n$. The broad reflection peaks can be indexed on the basis of a hexagonal unit cell with $a = 0.383$ nm and $c = 0.630$ nm. The basal spacing, or the lattice constant *c*, is comparable with the value of layered polysilane reported by Dahn *et al.*[11] The in-plane hexagonal lattice constant coincides with that of $CaSi_2$ ($a = 0.385$ nm), indicating that the reaction is topotactic and the 2D silicon network of $CaSi_2$ is preserved.

The exfoliation and oxidation of the $(SiH)_n$ in the second stage resulted in a final white solution. Figure 3(a) shows a TEM image of siloxene nanosheets adsorbed on a carbon film, showing their general characteristics. The SiONSs have lateral dimensions in the range of several tens to several hundreds of nanometers, which is smaller than that of the precursor $(SiH)_n$. These sheets are almost transparent, indicating exfoliation to a high degree, although fragments were also observed in small amounts. They exhibit a uniform and homogeneous contrast, reflecting their ultra-thin nature and unit thickness. The highly diffusive ring pattern in the corresponding selected-area electron diffraction (not shown) reveals that SiONSs are of a completely amorphous state. A tapping-mode AFM image (Fig. 3(b)) of the sample adsorbed onto a mica substrate revealed structures with similar lateral dimensions as those detected by TEM. The nanosheet thickness was measured at steps between the nanosheets and the substrate surface, yielding average values of 0.68 nm, as shown in the roughness profile (Fig. 3(c)). The consistency in the thickness data and the fact that the thickness was below 1 nm clearly demonstrated that the sample was composed of nanosheets. These dimensions fell in the range of molecular species rather than small particles. The thickness is an order magnitude

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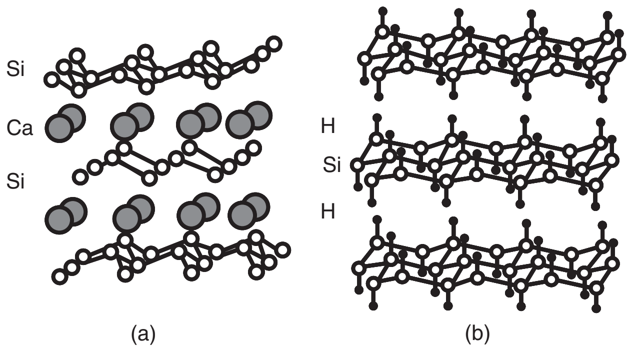

Fig. 1. Schematic illustration of (a) $CaSi_2$ and (b) layered polysilane $(SiH)_n$.

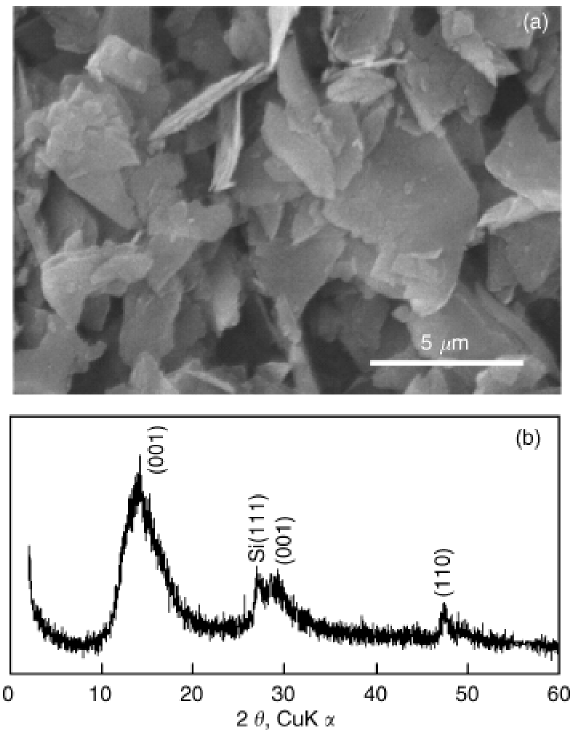

Fig. 2. (a) A scanning electron microscopy image of as-grown-layered polysilane $(SiH)_n$, (b) X-ray diffraction patterns of the $(SiH)_n$.

smaller than previously reported silica nanoparticles prepared by a variety of other methods. It is well known that the crystallographic thickness of a single layer of $NaHSi_2O_5$ is evaluated to be 0.65 nm, being based on single SiO_2 tetrahedral layers.[12] This good agreement means that the SiONSs are constructed with single SiO_2. The X-ray photoemission spectroscopy measurement reveals that the SiONSs are composed of silicon and oxygen, and quantitative analysis shows that the atomic ratio of Si:O is about 1:1.8.

The optical property of the SiONSs is that they can emit stable, high-brightness visible light at room temperature. Figure 4 displays PL spectra from 1 wt% SiONSs solutions. In this figure, two PL peaks were clearly distinguishable at energies of 2.7 and 3.1 eV. Nishikawa *et al.*[7] observed several luminescence bands in various types of high-purity silica glasses, with different peak energies ranging from 1.9 to 4.3 eV under 7.9 eV excitation. It was revealed that the 2.7 eV band was ascribed to the neutral oxygen vacancy (≡Si–Si≡), while the 3.1 eV band corresponds to some intrinsic diamagnetic defect center, such as the twofold coordinated silicon lone pair centers (O–Si–O). These defects are clearly because of high oxygen deficiency in sample preparation. These structural defects are radiative recombination centers. It is therefore reasonable for us to conclude that the light emission from the SiONSs can be attributed to the defect centers arising from oxygen deficiency.

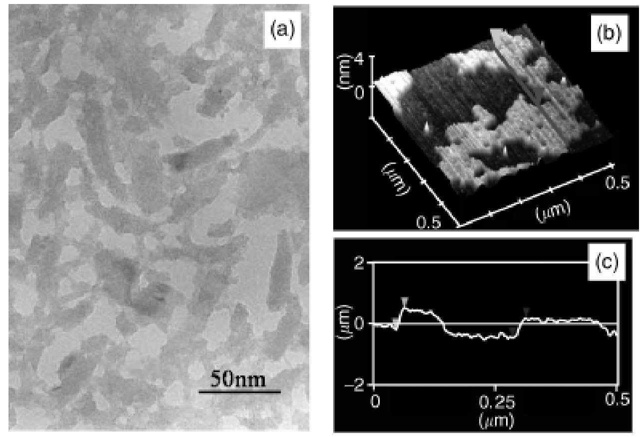

Fig. 3. (a) Transmission electron microscopy image revealing the general morphology of the silica nanosheets (SiONSs), (b) atomic force microscopy image of SiONSs on mica surface, and (c) the height profile of (b).

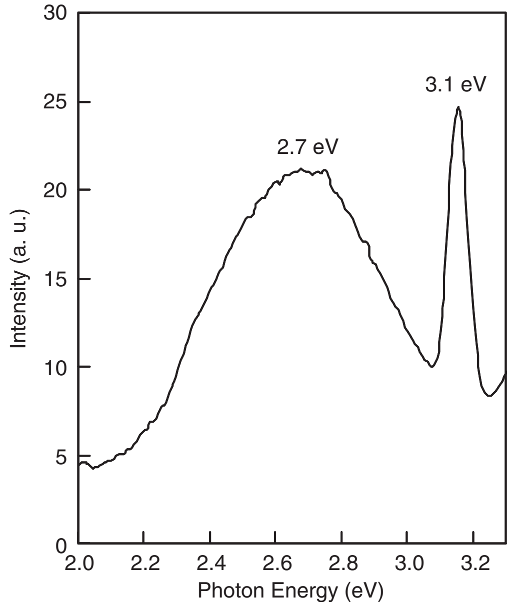

Fig. 4. Photoluminescence of the silica nanosheets blue light emission was revealed, peaking at 2.7 and 3.1 eV.

IV. Conclusions

Amorphous SiONSs with a uniform thickness of 0.68 nm was synthesized by exfoliation and oxidation with layered polysilane. A strong visible PL was observed in the SiONSs, which could be attributed to the defect center of oxygen deficiency in the sheets. Research on various properties of nanosheets themselves will be interesting for nanotechnology. More importantly, films and nanocomposites, using these sheets, will also be one of the next steps for applications.

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