

The fabrication of inorganic nanoscale materials on colloidal particles has become the subject of intense investigation due to the potential application of these particles in the fields of electronics, photonics and catalysis, as well as nanotechnologies. One of the main challenges in these applications is to obtain uniform and controllable structures for the shells of the particles. Recently, two-dimensional nanosheets have been synthesized as a new class of nanoscale materials by exfoliation of a layered compound into constituent single layers.^{1, 2)} These nanosheets might be used as inorganic building blocks in the fabrication of core-shell composites. The nanosheets may behave like pieces of wrapping paper when covering the template surface via the layer-by-layer (LBL) self-assembly approach. We propose herein novel silicon nanosheets and silicon coated colloidal silica prepared by the LBL technique.

A starting layered-silicon material, $\text{Si}_6\text{H}_3(\text{OH})_3 \cdot \text{HCl}$, was synthesized by a topotactical reaction from CaSi_2 , which is a layered material with Si corrugated (111) layers that are linked by Ca ions. The exfoliation of $\text{Si}_6\text{H}_3(\text{OH})_3 \cdot \text{HCl}$ was carried out in aqueous sodium dodecylsulfate ($\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$) solution at room temperature for 10 days.

A tapping-mode AFM image (**Fig. 1(a)**) of the sample revealed two-dimensional objects. The

thickness of the nanosheets was evaluated to be approximately 0.7 nm, as depicted in the roughness profile (**Fig. 1(b)**). The crystallographic thickness of the $\text{Si}_6\text{H}_3(\text{OH})_3$ nanosheet was evaluated to be 0.65 nm, based Weiss siloxene single layers. This agreement means that the nanosheets are constructed with a single $\text{Si}_6\text{H}_3(\text{OH})_3$ layer.

One application of these nanosheets is synthesis of silicon-coated silica spheres for photonic crystals. In the first step of this process, the silica surface was modified with poly-sodium-4-styrenesulfonate (PSS) to create a negative charge. Next, positively charged $\text{Si}_6\text{H}_3(\text{OH})_3$ nanosheets were adsorbed onto the surface of these silica templates to form core-shell composites by the electrostatic attraction between the sheets. In order to fabricate thicker shells, PSS and the $\text{Si}_6\text{H}_3(\text{OH})_3$ nanosheets were alternatively deposited on silica spheres for a specified number of cycles. Finally, the resulting core-shell composites were heated at 950 °C under vacuum conditions to convert the nanosheets into crystalline silicon. Based on their spherical shape and uniform size, the silicon coated silica spheres could be used directly as building blocks to form three-dimensional opaline lattices (**Fig. 2**).

Research on the properties of $\text{Si}_6\text{H}_3(\text{OH})_3$ nanosheets will be interesting for nanotechnology. However, more importantly, films and nanocomposites produced using these sheets will be another step toward their application.

References

- 1) Sasaki, T., et al. : J. Am. Chem. Soc., **120**(1998), 4682
 - 2) Nakano, H., et al. : Chem. Commun., **23**(2005), 2945
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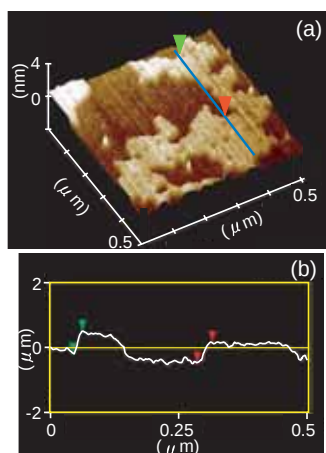


Fig. 1 (a) AFM image of silica nanosheets on a mica surface, and (b) the height profile of image (a).

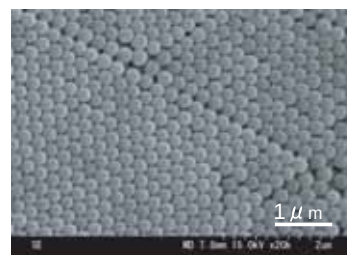


Fig. 2 SEM image of a three-dimensional crystal of silicon-coated colloidal silica.