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Formation of GeO_2 nanosheets using water thin layers in lamellar phase as a confined reaction field—*in situ* measurement of SAXS by synchrotron radiation

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Highly crystallized GeO_2 nanosheets were synthesized by hydrolysis and condensation reactions of germanium alkoxide using a 2-dimensional flat thin lamellar phase water layer containing surfactant molecules at the liquid–liquid interface as a confined reaction field.

Ceramic nanosheets can invite a range of applications, particularly in the field of nanoscience and nanomaterials. One of the outstanding challenges in this area is to devise synthetic methods that will give well ordered monolayer and multiplayer thin films from inorganic precursors with specific electronic, magnetic, optical, catalytic, and other properties.[1] Towards this goal, it is important to provide wide selections of desired nanosheet crystallites. These nanosheets have been provided by the exfoliation of functional materials such as layered titanates,[2] layered manganese oxides,[3] layered niobates,[4] and layered perovskites.[1] Preparation of these layered materials, however, requires prolonged calcination at a high temperature and acid-treatment, *i.e.*, these materials are usually prepared by calcinations at 1073–1573 K for 10–20 h, followed by acid-treatment for 10 days.

Here we show a new method which facilitates preparation of highly crystallized GeO_2 nanosheets at room temperature and needs a much shorter time for formation using a flat thin lamellar phase water layer at the liquid–liquid interface. In this paper we present the processes of preparing GeO_2 nanosheets by measuring small angle X-ray scattering (SAXS) every second using strong X-rays from the synchrotron radiation source at SPring-8, and characterize the produced nanosheets by transmission electron microscope (TEM) images, X-ray diffraction (XRD), selected area electron diffraction (SAED) and SAXS.

GeO_2 nanosheets were produced by contact between distilled water and a mixed solution of laurylamine (LA) and germanium tetraethoxide $Ge(OEt)_4$ modified with equimolar amounts of acetylacetone (ACA), which was used to slow the reaction rate. No organic solvent was used. The experimental set-up is shown in Fig. 1. We used a cell for the liquid sample to measure the SAXS pattern using synchrotron radiation. The cell was made of Teflon spacer sandwiched between mylar sheets. The size was 60 mm high, 3 mm deep and 5 mm wide. The lower half of the cell was filled with water, and the location of the X-ray beam was adjusted to the surface. The X-ray beam strength was 10^{13} photons s^{-1} and both the width and height of the cross-section of the beam were less than 600 μm. A mixed solution of pure LA and $Ge(OEt)_4$–ACA was introduced upon the surface of the water using a peristaltic pump, and the formation reactions started at the liquid–liquid interface. SAXS patterns were measured at a constant interval of the order of 1 s by a CCD detector.

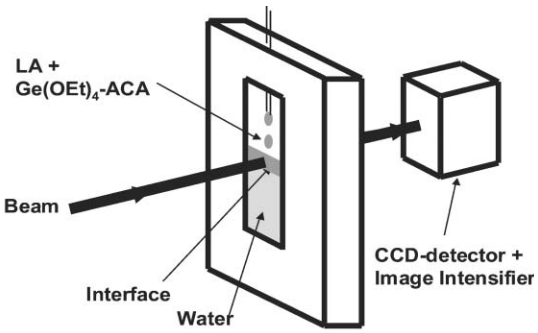

Fig. 1 Experimental set-up.

We first measured the lamellar phase formation in the system including only pure LA and water as a control experiment for GeO_2 nanosheet formation. SAXS results obtained using synchrotron radiation after LA made contact with water are shown in Fig. 2. A sharp peak at a periodical distance $d = 4.2$ nm and small peak at $d = 3.7$ nm were observed at 12 s. At 36 s, a very sharp peak at $d = 3.9$ nm, a sharp peak at $d = 3.6$ nm and a broad peak at $d = 3.0$ nm were observed. Each sharp peak indicated the formation of a lamellar phase with a uniform periodic distance corresponding to the scattering vector. The very sharp peaks obtained indicated formation of strictly ordered lamellar phases. The broad peak suggested disordered lamellar-like phase formation with various thicknesses and tilt structures. At 60 s from the contact, the peak at $d = 3.9$ nm decreased and the peak at $d = 3.6$ nm increased. The broad peak at $d = 3.0$ nm became larger. At 120 s, the peak at $d = 3.9$ nm almost disappeared and the peak at $d = 3.6$ nm became large and sharp. The broad peak became sharp and the d-value shifted to 3.2 nm. The reason for the appearance of the peak at $d = 4.2$ nm at 12 s was inferred to be that the lamellar phase included a relatively large amount of water, because the lamellar phase was very close to the interface. With the lapse of time, the lamellar phases were formed at the upper location from the interface, which might have a peak at $d = 3.6$ nm. Thus, the d-value shifted lower, finally approaching close to $d = 3.6$ nm. The product at 120 s was removed from the liquid–liquid interface as follows. First the water phase was drawn out. The surfactant molecules and non-reacted alkoxide were then washed out by alcohol. The obtained sample was dried at 313 K. SAXS of the obtained powder is shown in Fig. 3. We observed a very sharp

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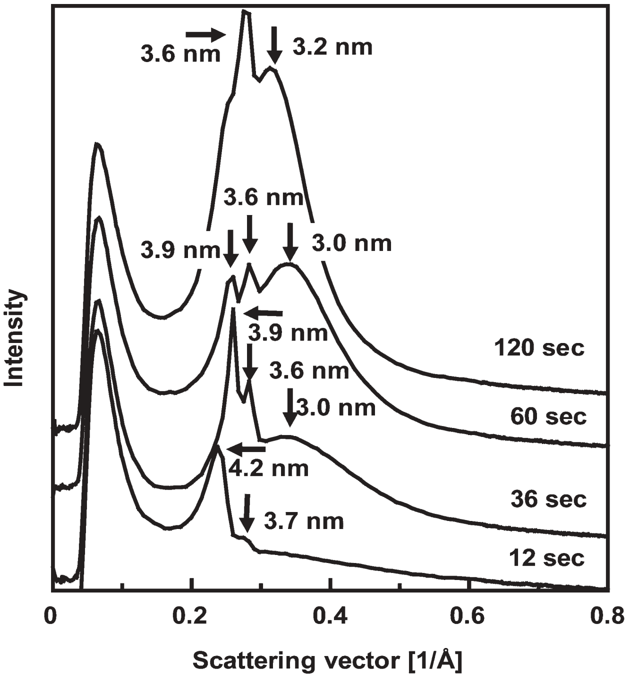

Fig. 2 SAXS findings in LA–water system at various times.

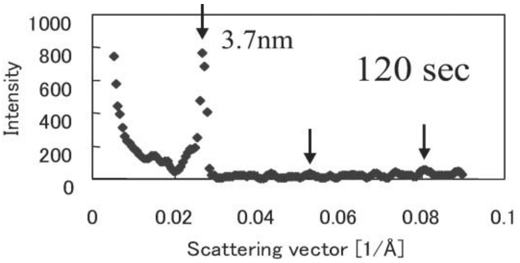

Fig. 3 SAXS findings of the dried lamellar phase taken at 120 s.

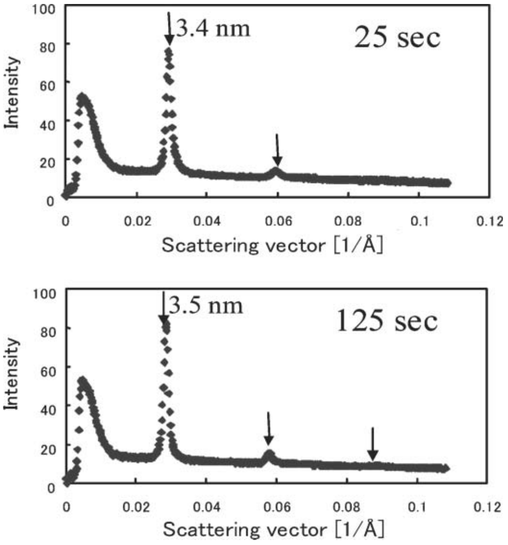

Fig. 4 Highly ordered and stable lamellar phase formation at the liquid–liquid interface under the reaction condition [Ge(OEt)$_4$]/[LA] = 0.2.

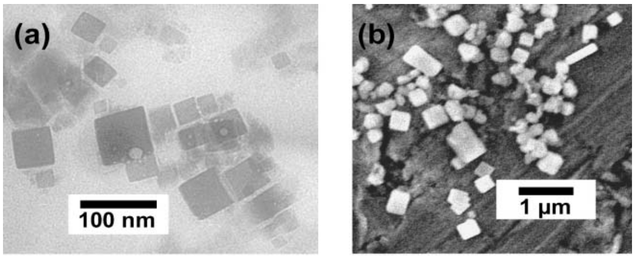

Fig. 5 (a) TEM image of the reaction products at the interface 3 min after contact; (b) SEM image of the reaction products at the interface 5 min after contact. Condition: [Ge(OEt)$_4$]/[LA] = 0.2.

peak at d = 3.7 nm, and the second and third peaks (shown by arrows) were clear, indicating that the periodic distance d becomes 3.7 nm when the lamellar phase is dried.

When germanium alkoxide with ACA was included in LA, germanium dioxide nanosheets were formed. SAXS results obtained under the condition of [Ge(OEt)$_4$]/[LA] = 0.2 are shown in Fig. 4, where [Ge(OEt)$_4$]/[LA] stands for the molar ratio of Ge(OEt)$_4$–ACA to LA. The very sharp peak of d = 3.4 nm and the second and third peaks were observed even after 125 s, indicating that a highly ordered and stable lamellar phase was formed by adding germanium alkoxide, suggesting the formation of GeO$_2$ nanosheets.

TEM and SEM preparations were made using alcohol solutions to suspend the dried samples obtained as described above. Fig. 5a shows the TEM image of the reaction products at the interface 3 min after contact under the condition [Ge(OEt)$_4$]/[LA] = 0.2. We can clearly see many square germanium nanosheets with a side length of 30–100 nm, suggesting that crystals with a tetragonal or cubic structure were formed. Fig. 5b shows the SEM image of the reaction products 5 min after contact under the same conditions as in Fig. 5a. Many cube-like shapes with a side length of 300–700 nm were observed. Since we see many squares in Fig. 5a, these cube-like shapes in Fig. 5b were inferred to be multilayers of GeO$_2$ nanosheets sandwiched between a bilayer of LA. A clear TEM image showing the layered structure of GeO$_2$ nanosheets sandwiched between bilayers of LA is shown in Fig. 6. Thus, the layered structure was confirmed. GeO$_2$ nanosheets shown in Fig. 5a at 3 min grew to large cube-like shapes in Fig. 5b. The dark- and light-colored GeO$_2$ nanosheets in Fig. 5a are inferred to be thick and thin multilayer nanosheets, respectively.

Frequently, we could not obtain SAED images of thin GeO$_2$ nanosheets, although sometimes we did obtain clear SAED images as shown in Fig. 7. These clear images might have been obtained from rather thicker GeO$_2$ nanosheets. Many spots in Fig. 7 can be

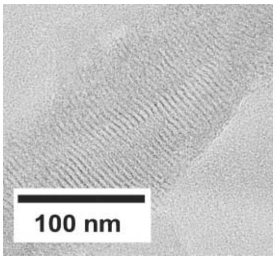

Fig. 6 TEM image of the layered structure of GeO$_2$ nanosheets sandwiched between bilayers of LA 5 min after contact.

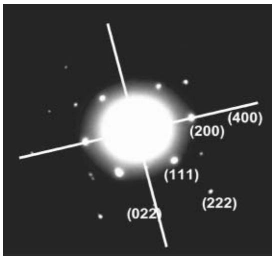

Fig. 7 SAED of GeO_2 nanosheets. $[Ge(OEt)_4]/[LA] = 0.2$.

indexed as the [011] zone axis of GeO_2 cubic phase, indicating that GeO_2 nanosheets were highly crystallized. From these observations shown in Fig. 5 and 7, we can conclude that highly crystallized GeO_2 nanosheets were prepared at room temperature within several minutes.

These crystallized GeO_2 nanosheets could be dissolved in alcohol solutions containing tetrabutylammonium hydroxide (TBAOH), *i.e.*, the multilayered structure separated into individual molecular nanosheets.

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