Formation of GeO_2 Nanosheets by Surfactant-Assisted Mechanism at Liquid-Liquid Interface –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 2-dimensional flat thin water phase of lamellar structure composed of surfactant molecules and water at the liquid-liquid interface as a confined reaction space.

Lamellar phase was made by contacting water with mixed solution of surfactant (laurylamine (LA)) and germanium alkoxide ($Ge(OEt)_4$). In situ small angle X-ray scattering (SAXS) measurements were carried out every second for several minutes using strong X-rays by synchrotron radiation in the SPring 8, and the formation processes of GeO_2 nanosheet was examined. The produced GeO_2 nanosheets were characterized by transmission electron microscope (TEM) images, X-ray diffraction (XRD), selected area electron diffraction (SAED) and SAXS.

We first measured lamellar phase formation in LA/water system as control experiments for GeO_2 nanosheets formation. The lamellar phase of d=4.2 nm formed in the early stage includes large amount of water near the liquid-liquid interface. When the lamellar phase grows with time, the upper part of the lamella does not contains large amount of water, but contains rather small amount of water because the part is far from the liquid-liquid interface. When the lamellar phase is dried, we can observe very sharp peak of d=3.7 nm, and the second and the third peaks clearly, indicating that the periodical distance becomes 3.7 nm.

When germanium alkoxide $Ge(OEt)_4$ was included in LA, germanium dioxide nanosheets were formed using 2-dimensional flat thin water phase of lamellar structure. SAXS results obtained under the condition of $[Ge(OEt)_4]/[LA]=0.2$ are shown in Figure 1, where $[Ge(OEt)_4]$ and [LA] stand for the concentrations of $Ge(OEt)_4$ and LA, respectively. Very sharp peak of d=3.4 nm and the second and third peaks were observed even after 120sec, indicating that highly ordered and stable lamellar phase was formed by adding germanium alkoxide.

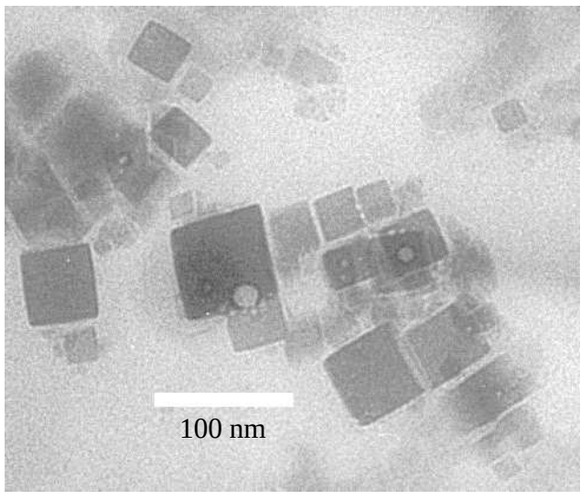

Figure 2 TEM image of the reaction products at the interface after 3min from contact under the conditions of $[Ge(OEt)_4]/[LA]=0.2$.

Figure 2 shows TEM image of the reaction products at the interface after 3 min from contact under the conditions of $[Ge(OEt)_4]/[LA]=0.2$. We can see clearly many square germanium nanosheets with a side length of 30-100 nm.

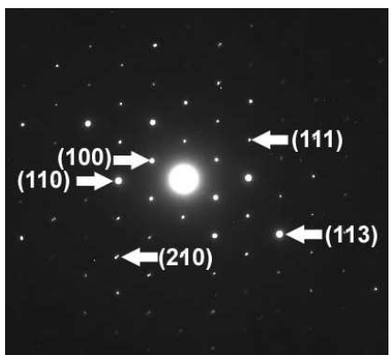

Figure 3 SAED of GeO_2 nanosheets.
$[Ge(OEt)_4]/[LA]=0.2$

Figure 3 shows SAED of GeO_2 nanosheets, which show many spots, indicating that GeO_2 nanosheets have highly ordered crystalline structure.

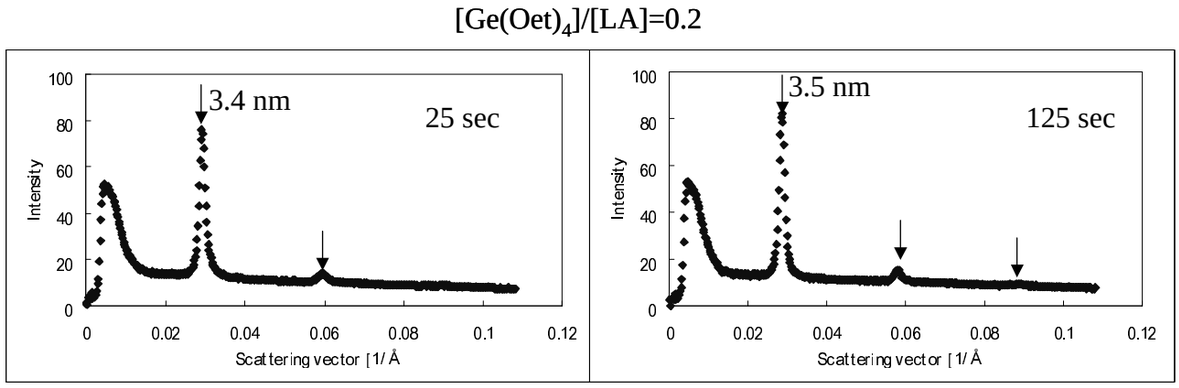

Figure 1 Highly ordered and stable lamellar phase formation at liquid-liquid interface under reaction condition of $[Ge(OEt)_4]/[LA]=0.2$.