Fabrication of Large-Sized MnO_2 Nanosheets from Layered Manganese Oxide Single Crystals and Application to Sensor Materials

([1]*Graduate School of Science and Technology, Tokyo University of Science*, [2]*International Center for Materials Nanoarchitectonics, National Institute for Materials Science*)
○Hitomi Yano,[1] Akihisa Aimi,[1] Nobuyuki Sakai,[2] Takayoshi Sasaki,[2] Kenjiro Fujimoto[1]
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Nanosheets have been known to have a unique two-dimensional structure with a molecular thickness. Manganese oxide nanosheets are known to possess superior redox properties and conductivity.[1] To bring out their performance, nanosheets with large lateral size are needed. However, preparation of large-sized nanosheets was difficult because layered metal oxide crystals tend to fragment into small pieces during exfoliation process. Lateral size control of the nanosheets have been studied on such as $Ti_{0.87}O_2$.[2] On the other hand, few studies have been reported on the size control of MnO_2 nanosheets.[3] In this study, we prepared large MnO_2 nanosheets by using large-sized mother phase of layered manganese oxide single crystals and optimizing an exfoliation process, and investigated its gas sensor properties.

Single crystals of layered manganese oxide, $K_{0.3}MnO_2$, were synthesized by a flux method. K_2MoO_4 and $K_{0.45}MnO_2$ polycrystals were used as a flux agent and a crystal source, respectively. After the melting at 1000 ºC and gradual cooling, hexagonal plate-shaped single crystals of $K_{0.3}MnO_2$ with smooth surface were obtained (**Figure 1**). HCl or $(NH_4)_2S_2O_8$ was used for removal of interlayer K^+ and protonation of $K_{0.3}MnO_2$. The crystals cracked by protonating with HCl, while relatively smooth surface remained by protonating with $(NH_4)_2S_2O_8$. The reaction of the protonated crystals with delaminating agents resulted in MnO_2 nanosheets with a thickness of ~1 nm and a lateral size of up to 3 μm which is larger than conventional nanosheets derived from polycrystals (~0.3 μm) (**Figure 2**). Furthermore, MnO_2 nanosheet thin films were fabricated to evaluate hydrogen gas responsiveness based on electric resistance. The resistance changed rapidly under H_2-mixed gas exposure at 200 ºC, suggesting that the MnO_2 nanosheets have H_2 sensing abilities.

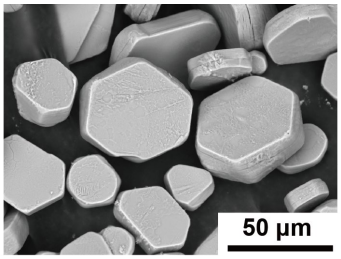

Figure 1. SEM image of $K_{0.3}MnO_2$ single crystals

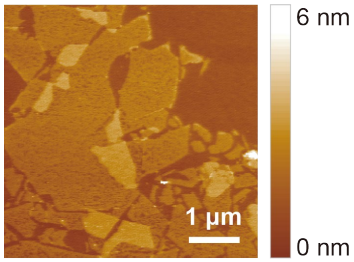

Figure 2. AFM image of MnO_2 nanosheets

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