Photoelectrochemical Behavior of the MnO_2 Nanosheet Electrodes

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We recently synthesized a new modification of nanosized oxides such as titania [1] and manganese oxide [2] by delaminating precursor layered crystals into their elementary layers. The obtained materials have been named nanosheets on the basis of their two-dimensional morphology, as depicted in Fig. 1. The crystallite has an extremely small thickness less than 1 nm and a lateral size ranging from submicrometers to several tens of micrometers. The nanosheet may provide new clues in examining various reactions at the surface and interface because nanosheet crystallite is considered to be composed entirely of surface atoms arranged two-dimensionally in a single-crystal-like order. These unusual structural features are expected to evolve novel chemical and physical properties that differ from those for granular oxides. In practice, titania nanosheets exhibit larger band gap energy than that for bulk TiO_2 due to quantum size effects [3].

The MnO_2 nanosheets were deposited on indium-tin oxide (ITO)-coated quartz glass plates (sheet resistance = 10 Ω/square) with the flat surface (R_a = 0.2 nm). The monolayer deposition was achieved via electrostatic self-assembly method. The cleaned substrate was treated with a polyethylenimine solution (2.5 g dm^{-3}, pH 9) for 20 min to introduce positive charges onto the surface, and then dipped in the colloidal suspension of MnO_2 nanosheets (0.08 g dm^{-3}, pH 9) for 20 min. UV-visible absorption spectrum for the film thus prepared shows absorption characteristic of MnO_2 nanosheets. The absorbance of ~0.03 at 380 nm is almost comparable to that for the monolayer loading of the nanosheets, which was formed in the film assembly on quartz glass substrate. In practice, AFM image revealed a dense coverage of the substrate surface with the nanosheets.

In-plane X-ray diffraction technique could detect diffraction peaks from the monolayer film of MnO_2 nanosheets. We performed the measurements using synchrotron radiation X-ray, which is effective to obtain signals from ultrathin systems. Upon self-assembly of MnO_2 nanosheets, two new peaks appeared at 2θ = 32.9 and 58.6° (λ = 0.13988 nm) in addition to many reflections from ITO substrate. These two peaks with the d-values of 2.47 and 1.43 Å are assignable to 10 and 11 reflections from two-dimensional hexagonal architecture of MnO_2 nanosheet.

The photoelectrochemical experiments were conducted in a non-aqueous electrolyte solution. An anodic photocurrent was observed when the MnO_2 nanosheet electrode was irradiated with a monochromatic light (λ = 450 nm) at 0.4 V. The photocurrent action spectrum shows the onset wavelength for the photocurrent generation of around 500 nm, indicating that the photoelectric conversion in response to visible light. The spectral profile in a wavelength range of 350-500 nm closely matches the absorption spectrum of the MnO_2 nanosheets, confirming that the observed photocurrent arises from the MnO_2 nanosheets.

References

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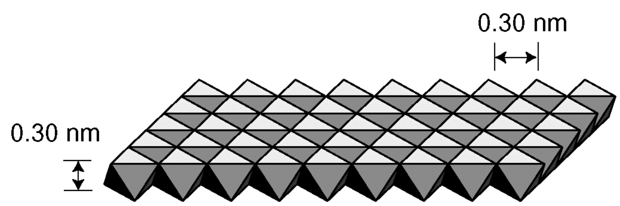

Fig. 1 Schematic representation of the crystal structure for the MnO_2 nanosheet. The MnO_2 nanosheet is composed of only of one plane of Mn ions sandwiched by two planes of oxygen atoms, giving coplanar octahedral sheet.