

Electrochemical and Photoelectrochemical Properties of the Titania Nanosheet Electrodes

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We have recently developed two-dimensional crystallites of titanium oxide by delaminating precursor layered-crystals into their elementary layers [1]. The titania nanosheet can be classified as a new nanoscale semiconductor, which is characterized by high crystallinity and well-defined chemical composition as well as extremely high anisotropy with an ultrathin thickness of ~1 nm. These unusual features result in distinctive physicochemical properties in comparison with conventional TiO₂ nanocrystallites mostly in spherical shape. In the present study, electrochemical and photoelectrochemical properties of the titania nanosheet have been examined to understand its electronic band structure, which is important for various applications such as photocatalysts and solar cells.

ITO glass plates were employed as substrates for the titania nanosheet electrodes. The substrate surface was converted to cationic by being primed with a polyethylenimine (PEI) solution. The titania nanosheets and poly(diallyldimethylammonium (PDDA) chloride) were assembled layer-by-layer from the colloidal suspension of Ti_{1.8}O₂^{4b+} and a PDDA solution, respectively. The operations for nanosheet/PDDA deposition were repeated 10 times to synthesize a multilayer assembly composed of 10 layer pairs, PEI/Ti_{1.8}O₂/(PDDA/Ti_{1.8}O₂)₉. The total thickness was estimated to be ~15 nm. The multilayer films were irradiated by UV light to remove the polymer layers, which is promoted via the photocatalytic activity of the titania nanosheet.

Electrochemical studies of the titania nanosheet electrodes were conducted in aprotic solvent. CV curves showed the insertion/extraction of the Li⁺ ion into/from the titania nanosheet galleries accompanying the reduction/oxidation of Ti⁴⁺/Ti³⁺ in the nanosheet (Figure 1). These processes caused changes in the UV-vis absorption of the titania nanosheet electrodes. Applying the negative bias at -1.2 V (vs. Ag/Ag⁺) and below brought about the reduction/enhancement of the absorption where wavelength is shorter/longer than 323 nm, respectively (Figure 2). These results indicate that the flatband

potential and the bandgap of the titania nanosheet electrodes were around -1.2 V and 3.84 eV, respectively. Photoelectrochemical measurements also gave similar values, showing the validity of these values.

References

1. T. Sasaki et al., *J. Am. Chem. Soc.*, **118**, 8329 (1996); **120**, 4682 (1998).

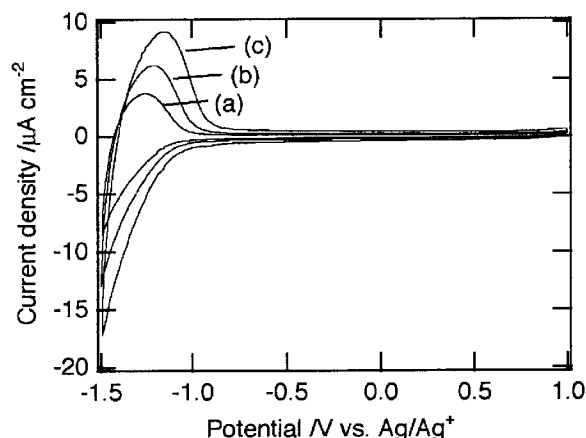


Fig. 1 Current-voltage curves for a titania nanosheet electrode in propylene carbonate containing 0.1 mol dm⁻³ LiClO₄. The sweep rate is (a) 5, (b) 10, and (c) 20 mV s⁻¹.

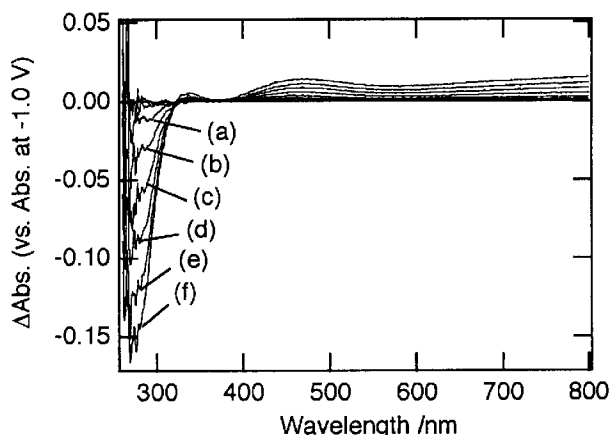


Fig. 2 Optical absorption spectra of a titania nanosheet electrode measured at the following applied potentials: (a) -1.3, (b) -1.4, (c) -1.5, (d) -1.6, (e) -1.7, (f) -1.8 V in propylene carbonate containing 0.1 mol dm⁻³ LiClO₄.