Cathodically-grown MnO_2 layers for pseudocapacitance and photon-electron conversion

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Birnessite, a layered manganese dioxide, has widely used an electrode material for supercapacitors due to its high redox activity and good reversibility. In addition to the anodic method [1], we have more recently found a cathodic route from aqueous permanganate to build birnessite in a thin form. The process proceeds simultaneously with the assembly of electrolyte cations toward negative charges on the just-deposited MnO_2. The thus-deposited birnessite film provides much better pseudocapacitance than the anodically-grown one even in its as-deposited state. On the other hand, MnO_2 absorbs visible light to induce the *d*-*d** transition. However, only a few papers have dealt with the photocurrent generation from MnO_2 [2]. We can find a common point among them; that is, MnO_2 nanosheet-assembled structures are utilized as the photoanode.

We report herein pseudocapacitance and visible light-driven electron transfer of cathodically-grown birnessite. As commonly employed in the capacitor application, carbon nanotubes (CNT) were combined with MnO_2 with the aim of improving ICPE (incident photon to current conversion efficiency), as well as pseudocapacitance. We are searching a possibility of solar charging as a result of their bifunctionality.

Fluorine-doped tin oxide (FTO) was used as the working electrode. Electrodeposition of birnessite was made by applying a constant potential of 0 V vs Ag/AgCl to FTO or CNT-coated FTO electrode, where the baths used consisted of 2 mM $KMnO_4$ aqueous solutions with M^+Cl^- (M^+ = Li^+, Na^+, K^+, Rb^+, Cs^+) at 50 mM. CNTs were deposited electrophoretically onto FTO substrate following the method described in the literature [3]. Pseudocapacitive properties were investigated in an aqueous electrolyte of 0.5 M Na_2SO_4. Photocurrent measurements were conducted under potentiodynamic and potentiostatic conditions. A xenon lamp was used as the excitation light source through a UV cut filter or monochromator to choose the wavelength. The transmitted light from the glass electrode was collected using an integrating sphere and measured by an illuminometer, in order to accurately estimate the amount of the absorbed light by MnO_2 layers.

First, XRD patterns were recorded for the electrodeposited MnO_2 products. Fig. 1 displays a relationship between the interlayer spacings (d_{001}) of the products prepared in the presence of different electrolyte cations on bare FTO and the ionic sizes of the cations. The vertical broken line indicates the size of water molecule. In the films grown with Rb and Cs, MnO_2 layers are supported by these cations which are larger in size than water molecule. Here, the estimated *d*-spacing reflects the sum of the thickness of a single nanosheet of MnO_2 and the diameter of cation. The optical bandgap (E_g) and flatband potential (E_{fb}) of birnessite film on FTO were determined to be 2.4 eV and +0.47 V based on the Tauc plot from UV-vis spectra and the Mott-Schottky plot from impedance measurements, respectively. In Fig. 2, CVs of birnessite/CNT/FTO electrode are depicted. Their rectangular profile, characteristic of an ideal capacitor, is maintained even at higher scan rates, due mainly to the fast electron transfer as a result of the formation of CNT/birnessite core-shell structure. Filled square plots represent the saturated values of photocurrent detected at the indicated potentials. The photocurrent starts to appear at +0.5 V, confirming n-type semiconductor behavior. The onset potential is consistent with the E_{fb} value estimated above. Fig. 3 shows *i*-*t* curves obtained at a constant potential of +1.0 V under intermittent visible light (> 400 nm) irradiation in Na_2SO_4 electrolyte with and without EtOH. The combination with CNTs enhances the photocurrent of birnessite three times, while the addition of EtOH as a hole scavenger makes it four times larger.

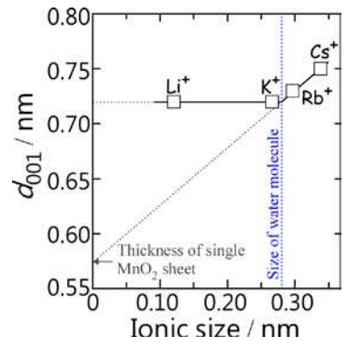

Fig. 1 The estimated d_{001} values of the films deposited at 0 V from 2 mM $KMnO_4$ solutions with 50 mM of LiCl, KCl, RbCl, and CsCl as a function of ionic size.

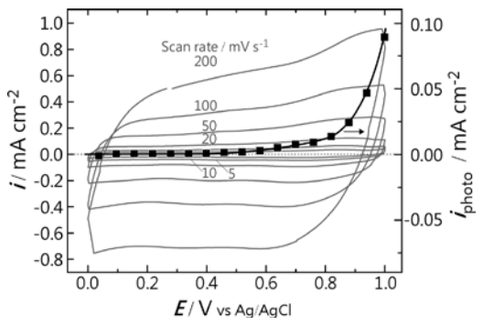

Fig. 2 CVs and plot of photocurrent taken for MnO_2/CNT/FTO electrode in an aqueous solution containing 0.5 M Na_2SO_4 and 5 M EtOH. The illumination wavelength was longer than 400 nm (and also in Fig. 3).

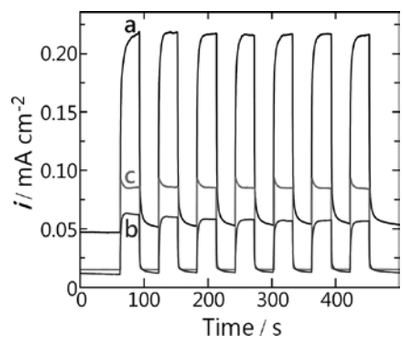

Fig. 3 *i*-*t* curves recorded at a constant potential of +1.0 V for (a, b) MnO_2/CNT- and (c) MnO_2-modified FTO electrodes in 0.5 M Na_2SO_4 electrolytes (a, c) with and (b) without 5 M EtOH.

Reference
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[3] Qin and Hu, *Appl. Surf. Sci.* **2009**, *255*, 7618.