δ-MnO_2 supported on carbon nanotubes for photocatalytic water splitting

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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 [1]. The common point among them is the utilization of nanosheet structure as the photoanode, which can be responsible for suppression of the recombination of excited electrons and holes in MnO_2 nanosheets. On the other hand, we have developed anodic and cathodic processes for fabricating multilayered MnO_2 as a thin film [2] and revealed its pseudocapacitive performance and the effect of conjugation with CNT on it [3]. Here, layered MnO_2 (δ-type) was deposited cathodically from aqueous permanganate onto CNT with the aim of improving the efficiency of photo catalytic water splitting through rapid electron transfer on CNT.

δ-MnO_2/CNT nanocomposite was prepared on a fluorine-doped tin oxide (FTO) substrate according to our previous paper [3]. The product was characterized by means of SEM, UV-vis, and XRD techniques. Electrochemical impedance spectroscopy and CV were conducted in 0.1 M Na_2SO_4 aqueous electrolyte. Sodium hydroxide was used for pH adjustment. Photocurrent measurements were made 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 δ-MnO_2. The potential was described with respect to the Ag/AgCl reference electrode.

The optical band gap (E_g) and flatband potential (E_{fb}) of electrodeposited δ-MnO_2 film were determined to be 2.4 eV and +0.47 V based on the Tauc plot (Fig. 1) from UV-vis spectra and the Mott-Schottky plot (Fig. 2) from impedance measurements, respectively. Fig. 3 displays the plots of satulated value of photocurrent detected when δ-MnO_2/FTO electrode was polarized at noted potentials in Na_2SO_4 solutions of pHs 6.0 (●) and 13.0 (■). The onset potential of photocurrent shifted to lower potential with an increase in pH, while the observed photocurrent obviously increased in magnitude. This demonstrates that Nernstian behavior in the oxidation of water is reproduced under visible light irradiation.

Fig. 4 shows *i*-*t* curves when the electrode was polarized at +1.0 V under intermittent visible light irradiation. Photocurrent from MnO_2 is much larger than those at FTO and CNT/FTO electrodes. This indicates that the electron transfer in MnO_2 occurs by visible light irradiation. Surprisingly, the photocurrent density of MnO_2 is enhanced nineteen times by the presence of underlying CNT. This suggests that CNT facilitates the electron transfer as a result of an increased electrochemically active area of δ-MnO_2.

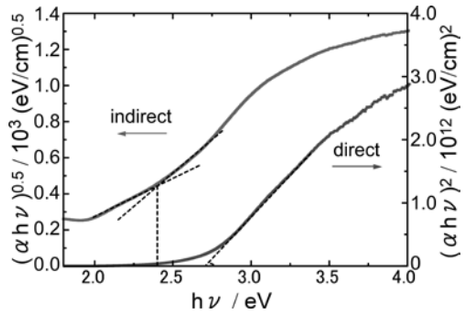

Fig. 1 Tauc plots for as-deposited δ-MnO_2 film for determining the indirect (2.4 eV) and direct (2.7 eV) band gaps.

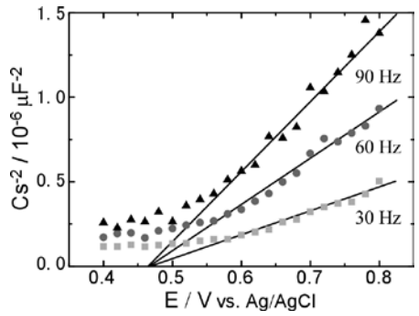

Fig. 2 Mott-Schottky plots in 0.1 M Na_2SO_4 solution under dark condition at 30 (■), 60 (●), and 90 Hz (▲) for δ-MnO_2 film.

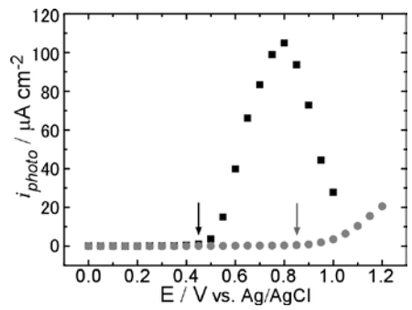

Fig. 3 Plots of satulated value of photocurrent from δ-MnO_2/FTO electrode under visible light irradiation in Na_2SO_4 solution at pH 6.0 (●), 13.0 (■).

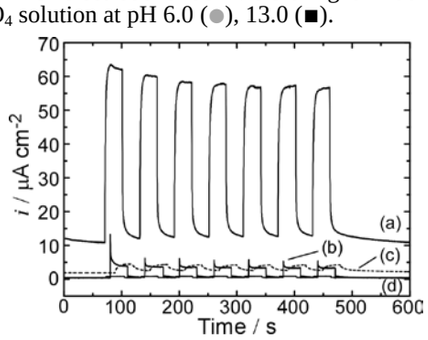

Fig. 4 *i*-*t* curves for the (a) δ-MnO_2/CNT/FTO, (b) δ-MnO_2/FTO, (c) CNT/FTO, (d) FTO in a 0.1 M Na_2SO_4 solution when the electrode was kept at +1.0 V under intermittent visible light irradiation.

Reference

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[2] Nakayama *et al.*, *Langmuir* **2005**, *21*, 354.
[3] Nakayama *et al.*, *J. Electrochem. Soc.* **2012**, *159*, A445.