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Highly Pt-like electrocatalytic activity of transition metal nitrides for dye-sensitized solar cells

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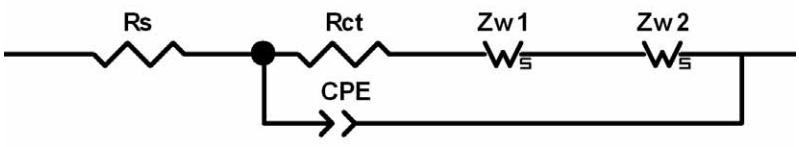
Preparation and characterization of transition metal nitrides.

All the metal nitrides were prepared by the nitridation of the metal oxide precursors in an ammonia atmosphere. The precursor (Fe_2O_3) of Fe_2N was prepared by the calcination (350 °C, 4 h) of the washed precipitate from the reaction of $Fe(NO_3)_3$ (0.2 mol L^{-1}) and $CO(NH_2)_2$ (2.4 mol L^{-1}) aqueous solution at 90 °C for 8 h. As the precursor of MoN, MoO_2 was prepared by the following procedure: KBH_4 (0.10 mol L^{-1}) aqueous solution was dropped in equal volume to the $Na_2MoO_4•2H_2O$ (0.05 mol L^{-1}) and NH_4SCN (0.25 mol L^{-1}) aqueous solution, and the resulting precipitate after the mixed solution was kept at 40 °C for 1 h was washed and dried at 60 °C for 12 h. The precursor (WO_3) of WN was prepared by the reaction between $5(NH_4)_2O•12WO_3•5H_2O$ (2.6 g, in 100 mL H_2O) and HCl (concentrated HCl:H_2O=1:1), in which the HCl solution was dropped until a clear solution was observed. After the resulting solution was kept at room temperature for 4 h, the solid product was dried and calcined at 400 °C for 2 h. The obtained oxide precursors were calcined in a tubular furnace for 2 h in an ammonia atmosphere with a flow rate of 200 sccm. In order to obtain pure-phase metal nitrides, the calcination temperature was set up at 500, 660, and 650 °C, respectively, for Fe_2N, MoN, and WN. The structure was measured by X-ray diffraction (XRD) on a Rigaku MiniFlex II diffractometer. Transmission electron microscopy (TEM) observation of metal nitrides was performed using a FEI Tecnai 20 transmission electron microscope with an acceleration voltage of 200 kV. The samples for TEM observation were prepared by ultrasonic dispersion in ethanol, and a portion was collected on a holey carbon film mounted on a specimen grid. The film thickness of all electrodes was measured with the scanning electron microscope (Hitachi S-3500N).

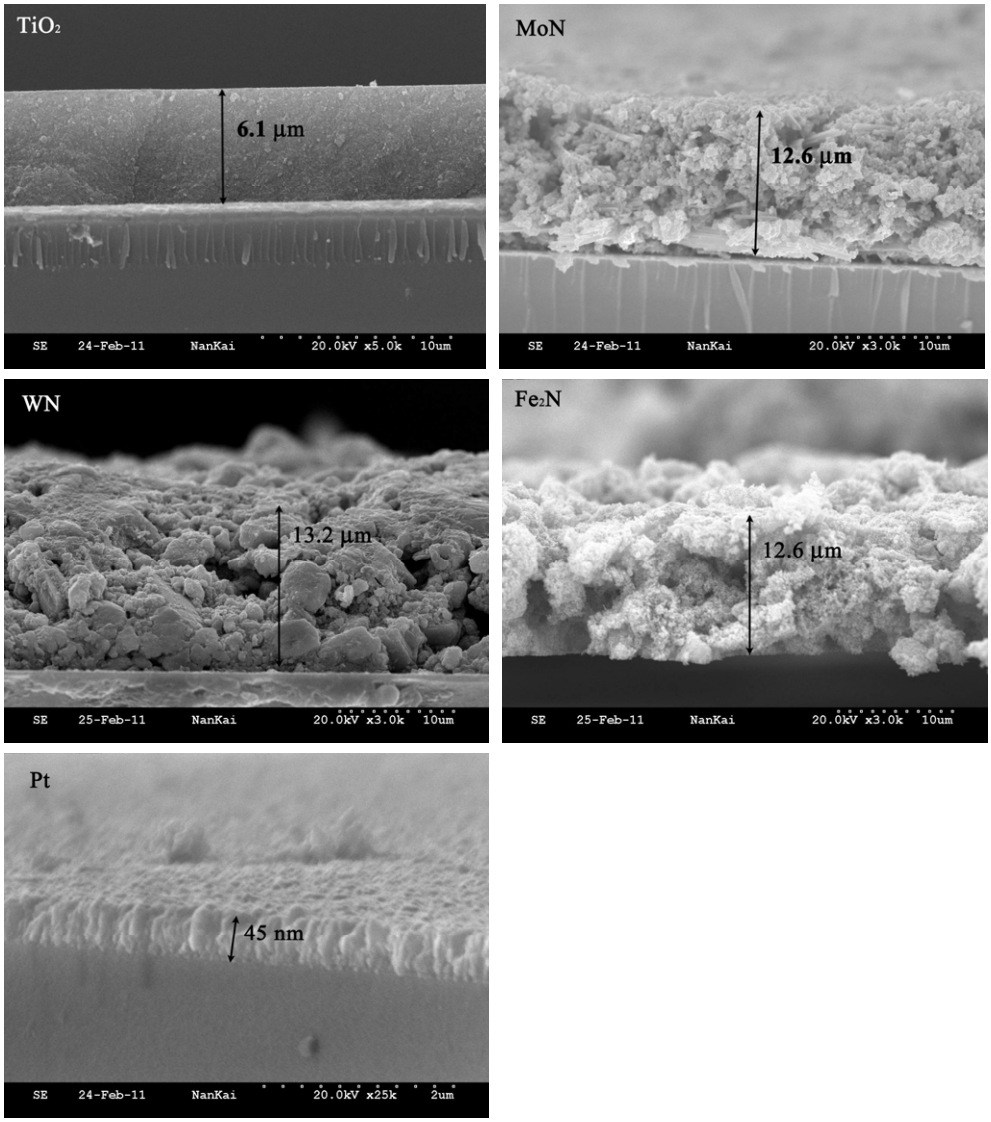
Electrochemical measurement

To prepare metal nitride counter electrode, the as-prepared metal nitride powder (0.2 g) was mixed with polyethylene glycol-20000 aqueous solution (1%, 0.5mL) and stirred until a fluid mixture formed. A film was then made by the doctor-blade method on a FTO (fluorine-doped tin oxide) conductive glass (15Ω/□, Nippon Sheet Glass). The Pt/FTO electrode was a commercial product from Dalian HeptaChroma SolarTech. In the case of the dye-sensitized TiO_2 electrode, a commercial TiO_2 sol (Solaronix, Ti-Nanoxide T/SP) was used to prepare TiO_2 film on FTO by the doctor blade method, and the film was soaked in an ethanol solution of N-719 dye for 24 h. DSSCs were assembled by clamping the TiO_2 photoanode and counter electrode together with a 50-μm-thick adhesive tape on counter electrode film to control electrolyte layer thickness and to avoid short-circuiting of the cell. The electrolyte (0.05 M I_2, 0.1 M LiI, 0.6 M 1, 2-dimethyl-3-propylimidazolium iodide (DMPII), and 0.5 M 4-tert-butyl pyridine with acetonitrile as the solvent) was injected into the aperture between the electrodes. The effective cell area was 0.25 cm^2. Both photocurrent-voltage (*J–V*) characteristic curves of DSSCs and electrochemical impedance spectra (EIS) of counter electrodes were recorded using an IM6ex (Zahner) electrochemical workstation. In *J–V* measurement, DSSCs were illuminated by a solar simulator (CHF-XM500, Beijing Trusttech) under 100 mW•cm^{-2} irradiation. EIS spectra were measured in a symmetric cell configuration with two identical counter electrodes, which was assembled by the same method as that for DSSCs. The frequency range was from 100 kHz to 100 mHz with an AC modulation signal of 10 mV and bias DC voltage of -0.60 V.

Equivalent circuit for the EIS.



Rct: charge-transfer resistance; Zw1: adsorption impedance of iodine and triiodide; Zw2: Nernst diffusion impedance; Rs: series resistance. For the Pt electrode, Zw1 is excluded in the equivalent circuit.



SEM images of electrode films on FTO substrate (cross-section), showing the film thickness.