

## Supplementary Information

# Nano-TaO<sub>x</sub>N<sub>y</sub> Particles Synthesized from Oxy-tantalum Phthalocyanine: How to Prepare Precursors to Enhance the Oxygen Reduction Reaction Activity after Ammonia Pyrolysis?

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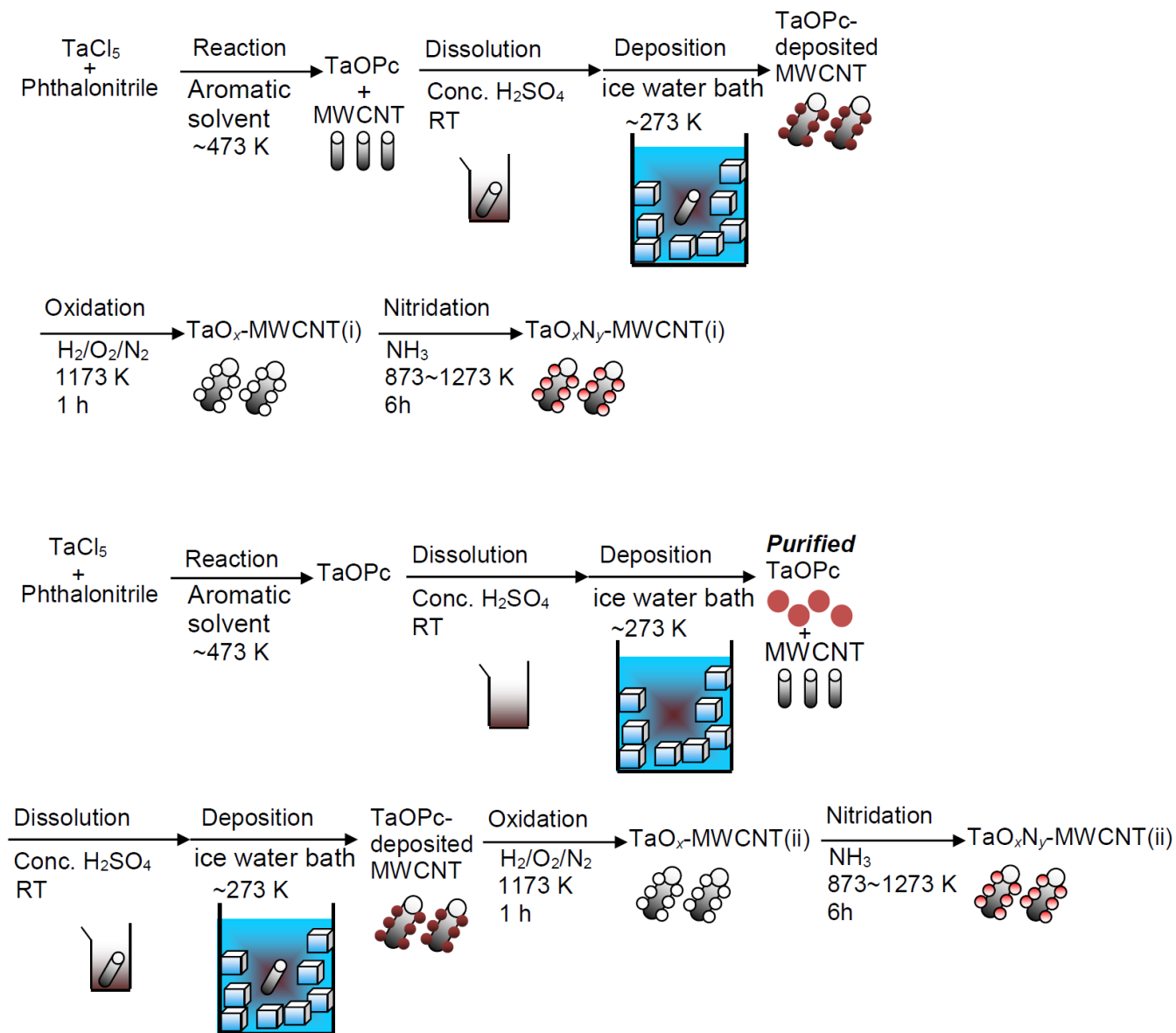
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## Synthesis of catalysts

A flow chart for the synthesis of  $TaO_xN_y$ -MWCNT(i) and  $TaO_xN_y$ -MWCNT(ii) is shown in Scheme S1.



Scheme S1. Scheme of the synthesis of (top)  $TaO_xN_y$ -MWCNT(i) and (bottom)  $TaO_xN_y$ -MWCNT(ii).

*TaO<sub>x</sub>-MWCNT(i)*: Tantalum pentachloride and phthalonitrile were put into aromatic solvents at  $\sim 473$  K to synthesize tantalum oxythophthalocyanine (TaOPc). The obtained powders and MWCNT powders (Showa Denko Co., Japan) were mixed in concentrated  $H_2SO_4$  solution to prepare TaOPc colloids-

adsorbed MWCNTs. The dispersion was quickly cooled using an ice bath to deposit TaOPc on MWCNTs. The obtained powders were washed with pure water then collected using a filter paper.

*TaO<sub>x</sub>-MWCNT(ii)*: Purified TaOPc powders were obtained using the procedure for synthesizing the precursor of TaO<sub>x</sub>-MWCNT(i) without adding MWCNTs. The TaOPc powders after being purified using a concentrated H<sub>2</sub>SO<sub>4</sub> solution were put into another concentrated H<sub>2</sub>SO<sub>4</sub> solution again then MWCNT powders were added to the dispersion. The dispersion was quickly cooled by putting them into an ice-water bath to deposit TaOPc on MWCNTs. The obtained powders were washed with pure water then collected using a filter paper.

Thus-prepared precursors were oxidized by pyrolysing them at 1173 K for 1 h under a mixed gas containing 2% H<sub>2</sub>, 0.5 % O<sub>2</sub> and 97.5% N<sub>2</sub> in a rotary quartz-tube furnace to generate TaO<sub>x</sub>-MWCNT. The gas was prepared by mixing H<sub>2</sub>/N<sub>2</sub> (4% H<sub>2</sub>) gas and O<sub>2</sub>/N<sub>2</sub> (1% O<sub>2</sub>) gas: the flow rates of both gases were 50 standard cubic centimeters per minute (sccm; 1 sccm = 1.67 × 10<sup>-8</sup> m<sup>3</sup> s<sup>-1</sup>). The mass fraction of carbon species in TaO<sub>x</sub>-MWCNT(i) and TaO<sub>x</sub>-MWCNT(ii) were determined 0.56 and 0.55, respectively using a thermogravimetric/differential thermal analyzer (Thermo plus EVO TG-DTA8120, Rigaku Co., Japan). The TaO<sub>x</sub>-MWCNT powders were placed in an alumina boat and set in a horizontal quartz-tube furnace, which was slowly evacuated and purged with N<sub>2</sub> gas. The powder samples were heated from room temperature to various temperatures, *T*, at a rate of 10 K min<sup>-1</sup>, kept at *T* for 6 h, and then cooled to room temperature at an uncontrolled rate. The flowing gases were N<sub>2</sub> at 300 sccm and NH<sub>3</sub> at 100 sccm for temperatures below and at *T*, respectively.

For simplicity, NH<sub>3</sub>-treated TaO<sub>x</sub>-MWCNT(i) and TaO<sub>x</sub>-MWCNT(ii) were denoted as TaO<sub>x</sub>N<sub>y</sub>-CNT(i) and TaO<sub>x</sub>N<sub>y</sub>-CNT(ii), respectively.

## Characterization

The morphology of TaO<sub>x</sub>-MWCNT(i) and TaO<sub>x</sub>-MWCNT(ii) were investigated using a field emission-transmission electron microscope (TecnaiG2 F20, FEI Co., U. S.). The crystal structures of the catalysts were analyzed using a X-ray diffractometer (XRD-6000, Shimadzu Co., Japan) with Cu-K $\alpha$  radiation generated at 40 kV and 30 mA in the scan range 15–85° at a scan rate of 2° min<sup>-1</sup>. The surface chemical states of the catalysts were analyzed using a X-ray photoelectron spectrometer (Quantum-2000, PHI Co., U. S.) with an Al-K $\alpha$  X-ray source (1486.6 eV).

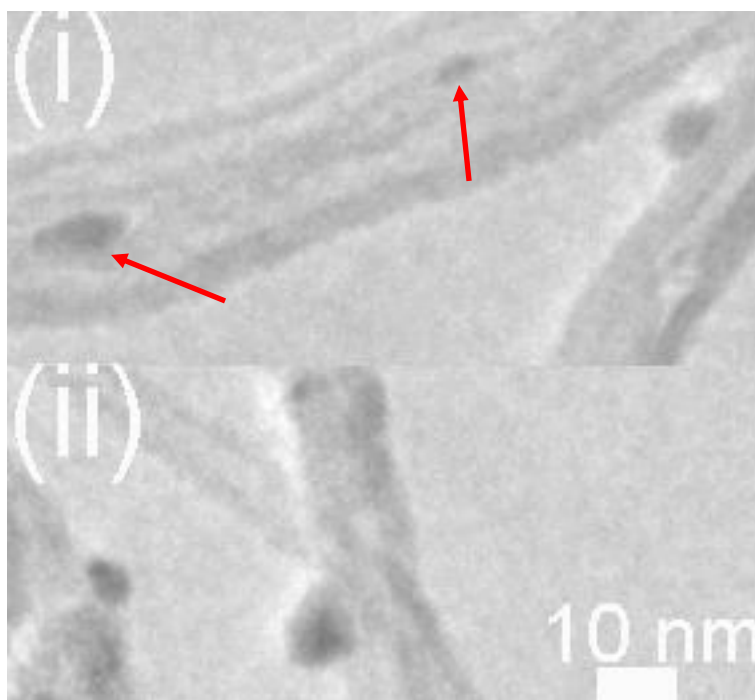
Because the CVs and rotating disk electrode voltammograms of partially oxidized tantalum carbide catalysts are almost the same at potentials in kinetically controlled region,<sup>34</sup> we obtained only CVs in this study to evaluate the ORR activity of the present catalysts. The 30 mg of catalyst powders, 1.5 cm<sup>3</sup> of a solvent consisting of ultrapure water and isopropyl alcohol, and 50 mm<sup>3</sup> of 0.5% Nafion solution [prepared by diluting a 5% (w/w) Nafion solution with ultrapure water] were sonicated for 600 s. The mass ratio of water to isopropyl alcohol in the solvent was 1. The obtained catalyst slurry was dropped onto a glassy carbon (GC) rod (5.2 mm in diameter, Tokai Carbon Co., Japan) and then dried. The mass of catalyst coated on the GC rod, *m*, was determined by measuring the mass of catalyst-coated GC rod before and after the dropping and drying procedure.

Electrochemical measurements were performed using a three-electrode cell in oxygen- or nitrogen-saturated 0.1 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> at 303 K. The catalyst-coated GC rod, a GC plate, and a reversible hydrogen electrode were used as the working, counter, and reference electrodes, respectively. Using a potentiostat (PS08, TOHO Technical Research, Japan), the working electrode surface was cleaned by repeated CV scans under oxygen at a scan rate of 150 mV s<sup>-1</sup> from 0.05 to 1.2 V with 300 cycles, to reach the steady state. After the cleaning, CVs were measured from 1.2 to 0.2 V at a scan rate of 5 mV s<sup>-1</sup> under oxygen and nitrogen. In both atmospheres, the steady state was reached within three cycles, so the data at the third cycles were used for the evaluation of ORR activity. The current obtained under

nitrogen ( $I_N$ ) subtracted from that under oxygen ( $I_O$ ) was assumed to be responsible for the ORR. In this study, the ORR current per unit mass of catalyst,  $(I_O - I_N)m^{-1}$ , was used as a measure of ORR activity.

## TEM images

Figure S1 (i) and (ii) show TEM images of TaO<sub>x</sub>-MWCNT(i) and TaO<sub>x</sub>-MWCNT(ii), respectively.



**Figure S1.** TEM images of (i) TaO<sub>x</sub>-MWCNT(i) and (ii) TaO<sub>x</sub>-MWCNT(ii).