Supporting Information

MnO₂ spontaneously coated on carbon nanotubes for enhanced water oxidation

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Experimental Details

Materials:

MWCNTs were purchased from Alpha Nano Technology Co., Ltd.(China). The specific surface area was over 200 m² g⁻¹. The purity of MWCNTs was over 95% and the outer diameter was 20–30 nm, and the length between 5 and 20 μ m. Purified water (18.2 M Ω cm) for the preparation of solutions was obtained from a Milli-Q system (Millipore, Direct-Q 3 UV), and all other chemicals and salts used were of the highest purity available from commercial sources.

Equipments and Apparatus

X-ray photoelectron spectra (XPS) were measured by ESCALAB250xi with X-Ray monochromatisation. X-ray Powder Diffraction (XRPD) data were collected with a PANalytical X'Pert Pro Diffractometer operated at 40 kV and 40 mA with Cu Ka radiation (step size: 0.017°, step time: 10.34 s). Field emission scanning electron microscopy (SEM) observations were performed on a Hitachi S-4800 microscope operated at an accelerating voltage of 5.0 kV. Transmission electron microscope (TEM) images were obtained with a TecnaiG²F30. Elemental analysis of the catalysts was performed on TJA ICP-atomic emission spectrometer (IRIS Advantage ER/S). Infrared spectra (2–4 wt% sample in KBr pellets) were recorded using a Bruker VERTEX 70v FT-IR spectrometer. Raman scattering spectra were taken using a Renishaw Invia Raman microscope; The laser light source was the 514.5 nm line radiation. UV-vis absorption spectra were recorded on a TU-1810 spectrophotometer (Beijing Purkinje General Instrument Co., Ltd.) equipped with a photomultiplier tube detector.

Kinetics of $[Ru(bpy)_3]^{3+}$ reduction.

o-MWCNTs was added to a solution of 1 mM $[Ru(bpy)_3](ClO_4)_3$ in pH 5.8 buffer (20 mM, Na₂SiF₆, NaHCO₃). At predetermined time intervals (2 min), samples were quickly collected using a membrane filter and the filtrate of absorbance of $[Ru(bpy)_3](ClO_4)_3$ was determined by spectrophotometric method at 670 nm.

Synthesis of δ-MnO₂/o-MWCNTs¹

500 mg of raw-MWCNTs were dispersed in 100 mL concentrated HNO₃ and sonicated for 1 h, and then oxidized at 120 $^{\circ}$ C for 2 h. The resulting MWCNTs were washed with deionized water and ethanol absolute, and then dried at 80 $^{\circ}$ C for 12 h. These materials were denoted as ''o-MWCNTs.''

 MnO_2 was spontaneously deposited onto the o-MWCNTs through a direct redox reaction between the o-MWCNTs and MnO_4 ⁻. 500 mg of o-MWCNTs were added to 100 mL of 0.1 M KMnO₄ solutions. The pH of the solution was about 7. During synthesis, the temperature of the solution was maintained at 70°C for 3 h using the

circulator. Delocalized π electrons on the surface of the CNTs can act as Lewis bases which are capable of complexing protons to its π structure. Both protons and electrons are needed to reduce MnO₄⁻ ions into MnO₂, as shown in the following reaction:

$$C_{\pi} + 2H_2O \rightarrow C_{\pi}H_3O^+ + OH^-$$
(1)

 $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$ ⁽²⁾

The suspension was washed using deionized water and ethanol absolute, and then dried at 60 °C for 12 h. These materials were denoted as '' δ -MnO₂/o-MWCNTs''.

Synthesis of α -MnO₂ nanotubes

In a typical experimental procedure,² 45 mL of solution containing 2.5 mmol KMnO₄ and 10 mmol concentrated HCl was placed in a Teflon-lined stainless steel autoclave. The autoclave was then treated at 140°C for 12 h. After cooling to room temperature naturally, the precipitate was filtered, washed several times with deionized water, and dried in 60°C.

Synthesis of δ -MnO₂ nanocrystalline

In a typical experimental procedure,³ 28mmol glucose was dissolved in 20 mL water and then 19 mmol KMnO₄ (50 mL) was added. A brown gel was formed and the water was periodically drained over the next 2 h. After dried at 110°C for 24 h, the product was calcined at 400°C for 2 h, and then washed several times using deionized water and dried at 90°C in air.

Synthesis of [Ru(bpy)₃](ClO₄)₃

In a typical experimental procedure,⁴ 374 mg $[Ru(bpy)_3]Cl_2$ was dissolved in 10 mL 280 μ L H₂SO₄ (0.5 M) and then a scoop of PbO₂ was added. The solution was stirred at room temperature and filtered through a fine frit. After the dropwise addition of HClO₄, and the solution was then cooled in an ice bath. The resulting $[Ru(bpy)_3](ClO_4)_3$ were recrystallized from 4 M HClO₄ at 0 °C



Fig. S1 HR-TEM images for as-prepared $\delta\text{-MnO}_2\text{/o-MWCNTs}.$



Fig. S2 FT-IR spectrum of $\delta\text{-MnO}_2\text{/o-MWCNTs}$ and o-MWCNTs.



Fig. S3 Raman spectra of $\delta\text{-MnO}_2/\text{o-MWCNTs}$ (black) and $\delta\text{-MnO}_2$ nanocrystalline (red).



Fig. S4 XRPD patterns of (a) o-MWCNTs, (b) δ -MnO₂/o-MWCNTs and (c) δ -MnO₂ nanocrystalline.



Fig. S5 XRPD patterns of α -MnO₂ nanotubes.



Element	Weight%	Atomic%
K K	18.50	24.18
Mn K	81.50	75.82
Totals	100.00	



Fig. S6 SEM image and EDX result of $\delta\text{-MnO}_2$ nanocrystalline.



Element	Weight%	Atomic%
K K	9.95	13.44
Mn K	90.05	86.56
Totals	100.00	



Fig. S7 SEM image and EDX result of $\alpha\text{-}MnO_2$ nanotubes.



Fig. S8 Time courses of O₂ evolution under photoirradiation ($\lambda > 420$ nm) of a buffer solution (Na₂SiF₆, NaHCO₃, 20 mM, pH 5.8, 10 mL) containing Na₂S₂O₈ (10.0 mM), [Ru(bpy)₃]Cl₂ (1 mM), and either 2.0 mg δ-MnO₂/o-MWCNTs (black), 1.1 mg δ-MnO₂ nanocrystalline (red) , 1.2 mg α-MnO₂ nanotubes (blue) at room temperature.



Fig. S9 Cyclic voltammogram (CV) of in a buffer solution (pH 5.8) with a carbon paste working electrode (A = 0.071 cm²) containing no catalyst (black), 1mM of [Ru(bpy)₃]Cl₂ (red) or 5% δ -MnO₂/o-MWCNTs (blue) (Ag/AgCl electrode; Pt wire counter electrode; scan rate 100 mV s⁻¹).



Fig. S10 Cyclic voltammogram (CV) of in a buffer solution (pH 5.8) with a carbon paste working electrode (A = 0.071 cm^2) containing no catalyst (black), 5% δ -MnO₂/o-MWCNTs (blue), 5% δ -MnO₂ nanocrystalline (pink) or 5% o-MWCNTs (green) (Ag/AgCl electrode; Pt wire counter electrode; scan rate 100 mV s⁻¹).



Fig. S11. XPS spectra of δ -MnO₂/o-MWCNTs before and after the reaction in the (a) the survey spectrum and (b) Mn 2p energy region. TEM images of δ -MnO₂/o-MWCNTs after photocatalytic water oxidation in the (c) and (d).

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