

Supporting Information

Facile synthesis of Pd-Mn₃O₄/C as High-Efficient Electrocatalyst for Oxygen Evolution Reaction

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Experimental Section

Method

All reagents used were of analytical grade purity and purchased from Sigma-Aldrich. The Mn₃O₄/C powders used in this study were prepared by a solid-state reaction by intermittent microwave heating method. The Mn(NO₃)₂ aqueous solution is mixed with dispersed carbon black (Vulcan XC-72R, Cabot Corp., USA) by dispersed by ultrasonic wave. The precipitate was dried in an oven at 373 K. The mixture was put into a homemade program-controlled microwave oven (1000 W, 2.45 GHz) for heating treatment with a 5 s on and 5 s off procedure for 20 times. The Co₃O₄/C powders were prepared with the similar method. The Pt-Mn₃O₄/C electrocatalysts were prepared by reduction of H₂PtCl₆ solution on the Mn₃O₄/C powders using an excess 0.01 mol L⁻¹ NaBH₄ solution. The ratios of Pt and Mn₃O₄ were controlled by stoichiometric calculation. The Pt/C, Mn₃O₄/C, Pt-Mn₃O₄/C or Co₃O₄/c powders were dispersed in 2-propanol with 5 wt% PTFE (polytetrafluoroethylene) under ultrasonic stirring, then, the catalyst ink was deposited on the surface of a graphite rod with the geometric area of 0.33 cm² and dried at 353 K for 30 min. The loadings of carbon black and PTFE on the electrodes were accurately controlled at 0.23 mg cm⁻² and 0.1 mg cm⁻². The sum of loading for Pt and Mn₃O₄ or Co₃O₄ on the electrodes was accurately controlled at 0.1 mg cm⁻².

Characterisation

All electrochemical measurements were tested in a three-electrode cell using the EG&GPAR283 electrochemical work station (Princeton, USA) in a temperature-controlled water-bath (Polyscience 9106,

U.S.A.) at 298 K. Solutions were freshly prepared before each experiment. A platinum foil (3.0 cm²) was used as counter electrode. All the potentials were measured versus a saturated calomel electrode (SCE, 0.241 V *versus* NHE) electrode. A salt bridge was used between the cell and the reference electrode.

XRD was carried out with a D/MAX2200 diffractometer employing Cu K α radiation ($k = 0.15418$ nm). TEM was performed with a Philips CM-300 high resolution system operating at 200 keV. Chemical-state analysis of electrocatalysts was carried out by XPS using an ESCALAB 250 X-ray photoelectron spectrometer. All XPS spectra were corrected using the C 1s line at 284.6 eV. Curve fitting and background subtraction were accomplished.

Figure S1. XRD patterns for the Mn₃O₄/C, Pd/C and Pd-Mn₃O₄(wt 2:1)/C.

X-ray diffraction (XRD) patterns for the Mn₃O₄/C, Pd/C and Pd-Mn₃O₄(wt 2:1)/C all exhibit an XRD pattern of a typical face-centered-cubic (fcc) lattice structure as shown in Figure 1S. Diffraction peaks at around 25.00° observed in all the samples are assigned to the (002) plane of the carbon. The strong diffraction peaks for manganese oxide support on carbon black at the Bragg angles of 18.04°, 28.97°, 32.43°, 36.15°, 44.42°, 50.81°, 59.98° and 64.68° correspond to the (101), (112), (103), (211), (220), (105), (224) and (400) facets of Mn₃O₄ crystal. From the XRD result, the phase of the manganese oxides is Mn₃O₄. For the pattern of Pd-Mn₃O₄(wt 2:1)/C, all of the diffraction peaks of palladium and Mn₃O₄ are observed indicating their coexistence in the catalysts. And there is no obvious shift in the diffraction peaks of palladium in these catalysts indicating that the addition of Mn₃O₄ has no effect on the crystalline lattice of palladium.

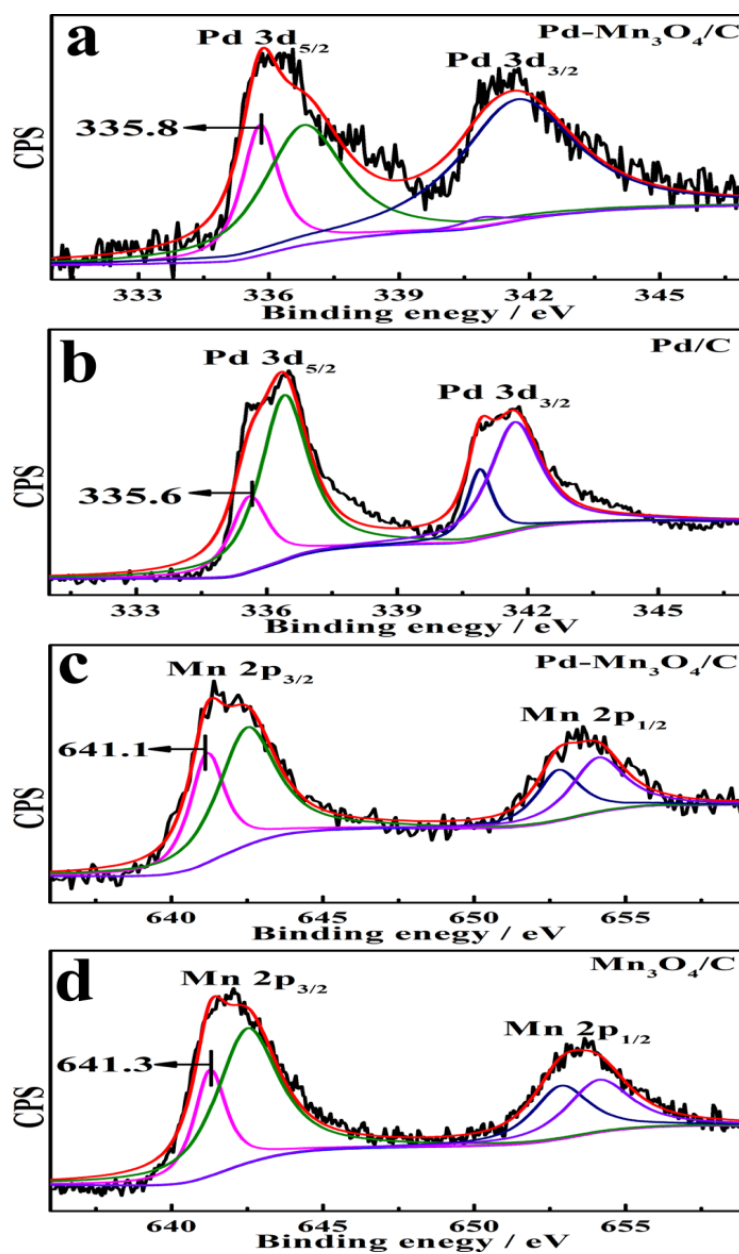


Figure S2. Comparison of core level Pd 3d XPS spectra for (a) Pd-Mn₃O₄/C and (b) Mn₃O₄/C. Comparison of core level Mn 2p XPS spectra for (c) Pd-Mn₃O₄/C, (d) pure Mn₃O₄/C.