[Supplementary Information]

Facile Synthesis of Noble Metal Nanotubes by Using ZnO Nanowires as Sacrificial Scaffolds and Their Electrocatalytic Properties

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Experimental

Chemicals and materials. Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$, 99.999%), zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, 98%), hexamethylenetetramine (99+%), polyethylenimine (PEI, $M_W = 800$), K_2PtCl_4 (98%), K_2PdCl_4 (98%), and sodium citrate dihydrate (99%) were purchased from Aldrich and used as received. Other chemicals, unless specified, were reagent grade and Milli-Q water with a resistivity of greater than 18.0 MΩ·cm was used in the preparation of aqueous solutions.

Preparation of ZnO nanowire arrays. ZnO nanowire arrays on Si wafer or ITO glass substrates were fabricated by following the literature.[S1] Prior to the growth of ZnO nanowires arrays, the substrates were cleaned by sequentially sonicating in acetone, isopropyl alcohol, ethanol, and de-ionized water, and then dried in a N_2 gas stream. The substrate were wetted with a droplet of pre-synthesized ZnO nanoparticles solution in methanol,[S2] rinsed with ethanol, and then dried with N_2 gas. This step was repeated several times for the complete coverage of seeds and the substrates were annealed afterwards at 150 °C for 10 min. Then, ZnO nanowires were grown hydrothermally by immersing the seeded substrates in aqueous solutions containing zinc nitrate (25 mM), hexamethylenetetramine (25 mM) and PEI (6 mM) at 95 °C for 2.5 hrs. The substrates were then removed from solution, washed with de-ionized water, and dried.

Synthesis of metal nanotubes. In a typical synthesis of metal nanotubes, 2 mL of an aqueous solution of metal precursor (5 mM) was added to an aqueous solution of sodium citrate dihydrate (0.05 mL, 30 mM), and then ZnO nanowire array grown on Si wafer or ITO glass was immersed into this growth solution. The reaction mixture was then heated at ~90 °C for about 1 h in a conventional drying oven.

Synthesis of Pt nanoparticles. In a typical synthesis of Pt nanoparticles, a 1 mL of 5 mM aqueous solution of K_2PtCl_4 was added to 47 mL of highly purified water. To this solution, 1 mL of 30 mM cetyltrimethylammonium bromide (CTAB) was added. After 5 sec, aqueous solution of ascorbic acid (100 mM, 1 mL) was added with vigorous stirring, and the solution was stirred further for 1 min. The solution was then heated at

~100 °C for ca. 6 min on a hot plate. The resulting Pt hydrosol was subjected to centrifugation (13,000 rpm for 5 min) to remove excess CTAB. The transmission electron microscopy (TEM) images of the products demonstrate that the majority of the sample was dendritic nanoparticles with average diameter of 19.3 ± 2 nm (see Fig. S6a).

Synthesis of Pd nanoparticles. The Pd nanoparticles were prepared by using our reported procedure.[S3] In a typical synthesis of Pd nanoparticles, 1 mL of 5 mM aqueous solution of K_2PdCl_4 was added to 47 mL deionized water and then aqueous solutions of CTAB (1 mL, 30 mM) and ascorbic acid (1 mL, 100 mM) were added to this solution with vigorous stirring. After additional stirring for 5 min, the reaction solution was stored under dark. The resultant Pd hydrosols were centrifuged (10,000 rpm) and re-dispersed in water three times to remove excess reactants in the solution. The TEM images of the products show that the majority of the sample was multi-armed nanoparticles with average particle size of 18 ± 4.5 nm (see Fig. S6b).

Characterization. Scanning electron microscopy (SEM) images of the samples were taken with a field-emission scanning electron microscope (FESEM, Phillips Model XL30 FEG). Transmission electron microscopy (TEM) images and energy-dispersive X-ray spectroscopy (EDS) data were obtained with a Phillips Tecnai F20 transmission electron microscope operating at 200 kV after placing a drop of nanotube dispersion prepared by 10 sec sonication. High-resolution TEM (HRTEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) characterizations were performed with a Phillips Tecnai G2 F30 Super-Twin transmission electron microscope operating at 300 kV. The effective electron probe size and dwell time used in HAADF-STEM-EDS mapping experiments were 1.5 nm and 200 ms per pixel, respectively. X-ray diffraction (XRD) patterns were obtained with a Bruker AXS D8 DISCOVER diffractometer using Cu Kα (0.1542 nm) radiation. The compositions of products were determined by inductively-coupled plasma-atomic emission spectrometer (ICP-AES, Spectro Ciros). Cyclic voltammetry (CV) measurements were carried out in a three-electrode cell using a CH Instrument Model 600C potentiostat. Drop-casting films of nanotubes or nanoparticles on indium tin oxide (ITO) substrates served as working electrodes. Before CV measurements, the substrates were cleaned again by sequentially washing with acetone, ethanol, and water to remove stabilizing agents on the surface of nanostructures. Pt wire and Ag/AgCl (in saturated KCl) were used as the counter and reference electrodes, respectively. All cyclic voltammograms (CVs) were obtained at room temperature. The electrolyte solutions were purged with high-purity N_2 gas before use for about 1 h.

References:

(S1) (a) L. E. Greene, M. Law, J. Goldberger, F. Kim, J. C. Johnson, Y. Zhang, R. J. Saykall and P. Yang, *Angew. Chem. Int. Ed.*, 2003, **42**, 3031; (b) M. Law, L. E. Greene, J. C. Johnson, R. Saykally and P. Yang, *Nat. Mater.*, 2005, **4**, 455.

(S2) C. Pacholski, A. Komowski and H. Weller, *Angew. Chem. Int. Ed.*, 2002, **41**, 1188.

(S3) Y. W. Lee, M. Kim and S. W. Han, *Chem. Commun.*, 2010, **46**, 1535.

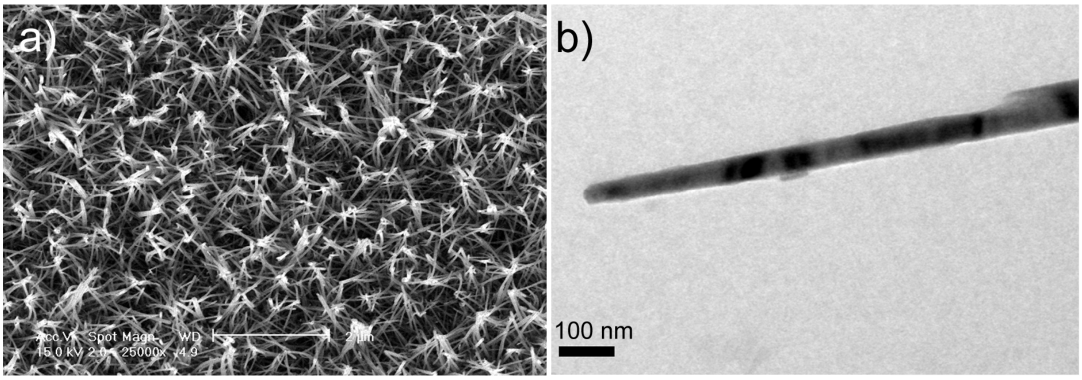

Fig. S1. (a) SEM and (b) TEM images of the ZnO nanowires grown by hydrothermal synthesis method.

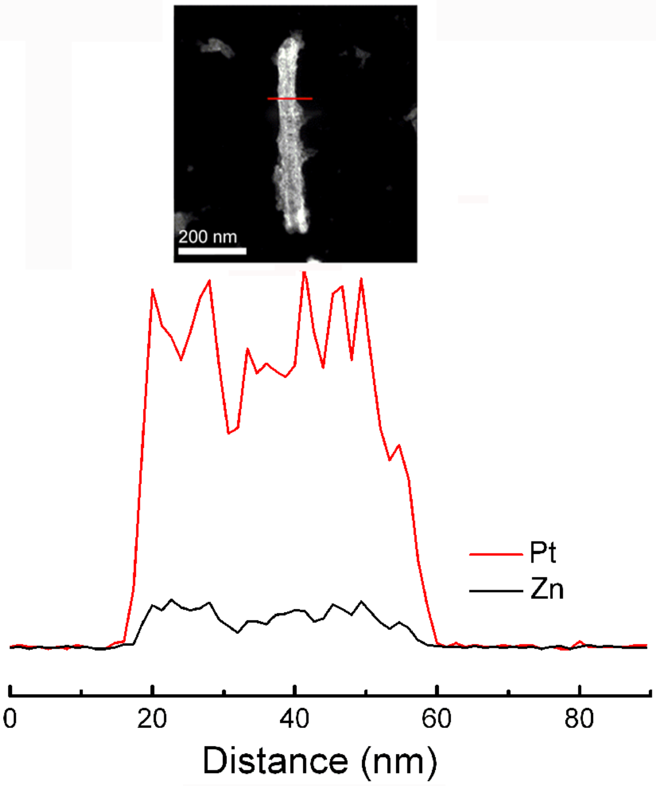

Fig. S2. HAADF-STEM image and cross-sectional compositional line profiles of a Pt nanotube.

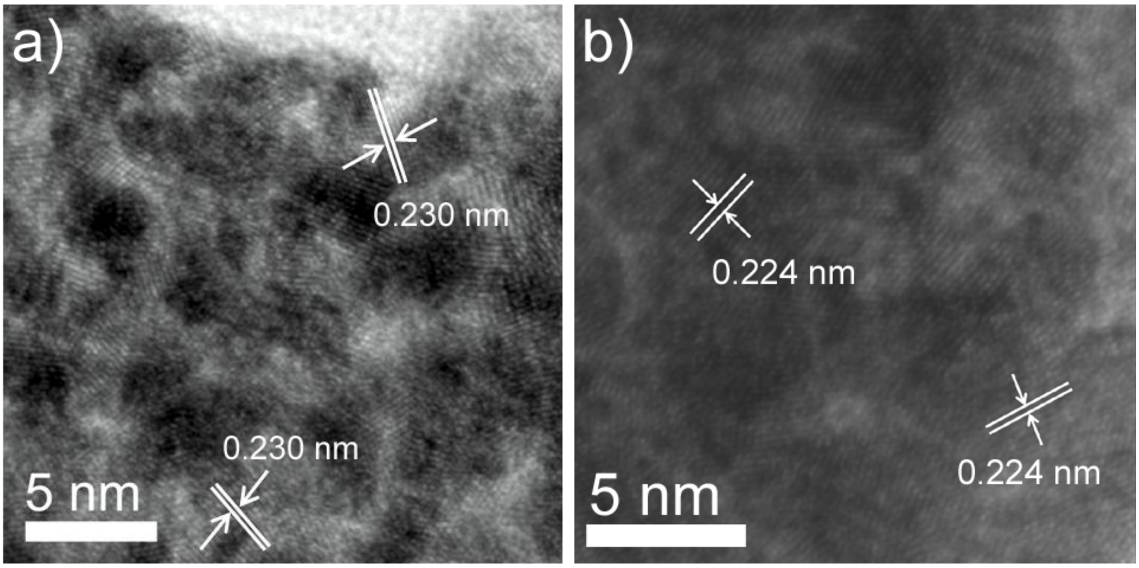

Fig. S3. HRTEM images of (a) Pt and (b) Pd nanotubes.

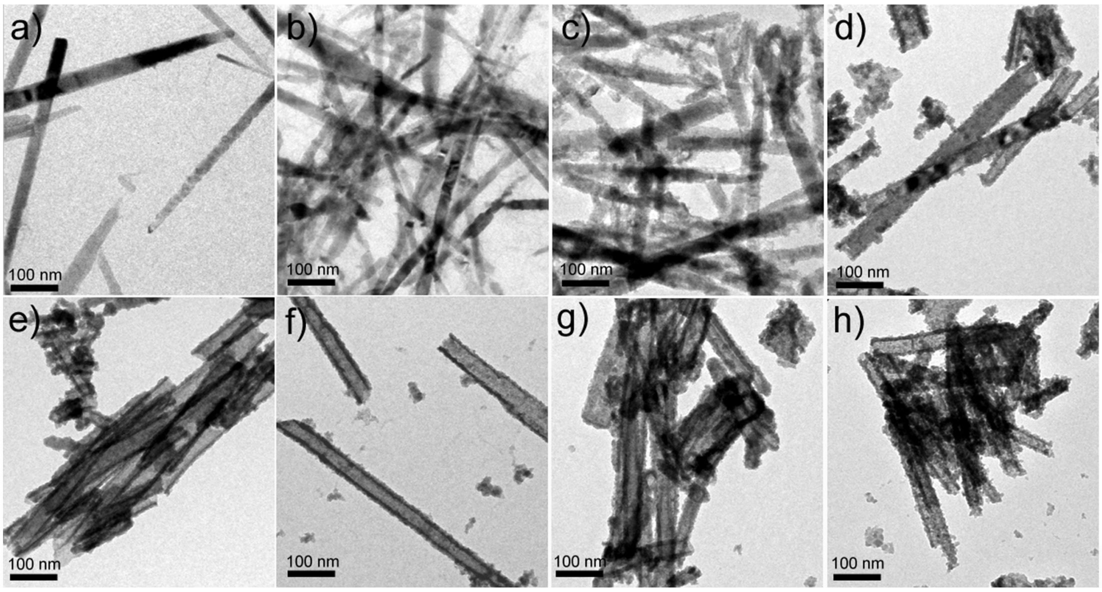

Fig. S4. TEM images of Pt/ZnO nanostructures collected at different reaction times: (a) 0, (b) 5, (c) 10, (d) 20, (e) 30, (f) 40, (g) 50, and (h) 60 min.

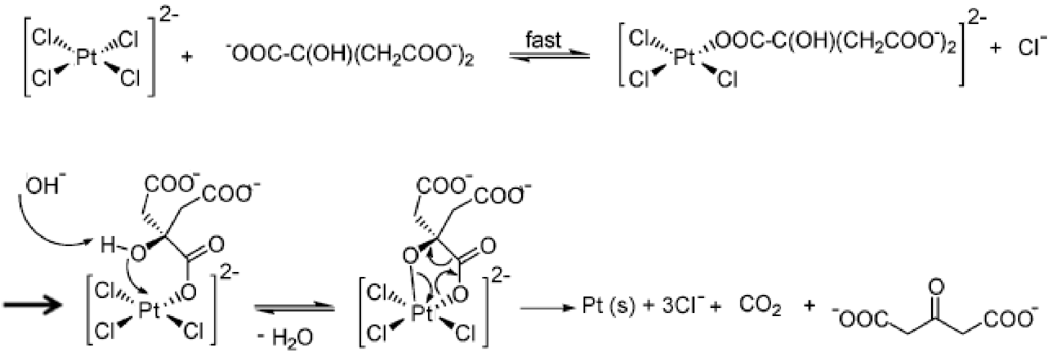

Fig. S5. Mechanism of the reduction of $PtCl_4^{2-}$ by citrate.

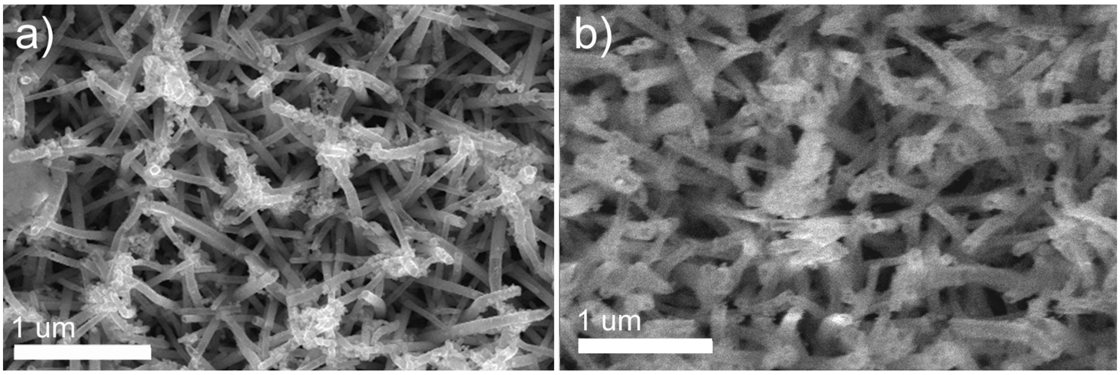

Fig. S6. SEM images of the (a) Pt and (b) Pd nanotubes grown on ITO glass.

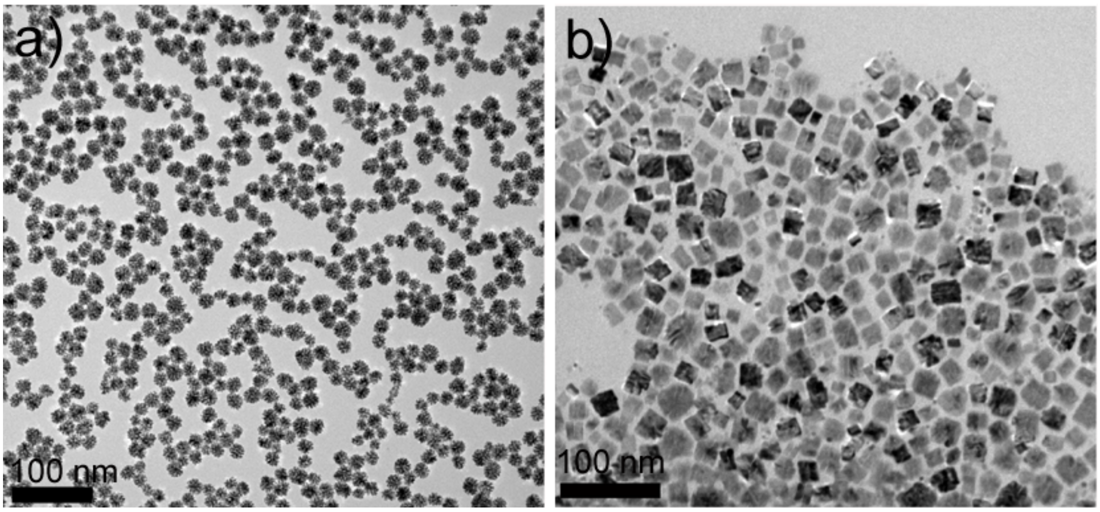

Fig. S7. TEM images of the (a) Pt and (b) Pd nanoparticles.

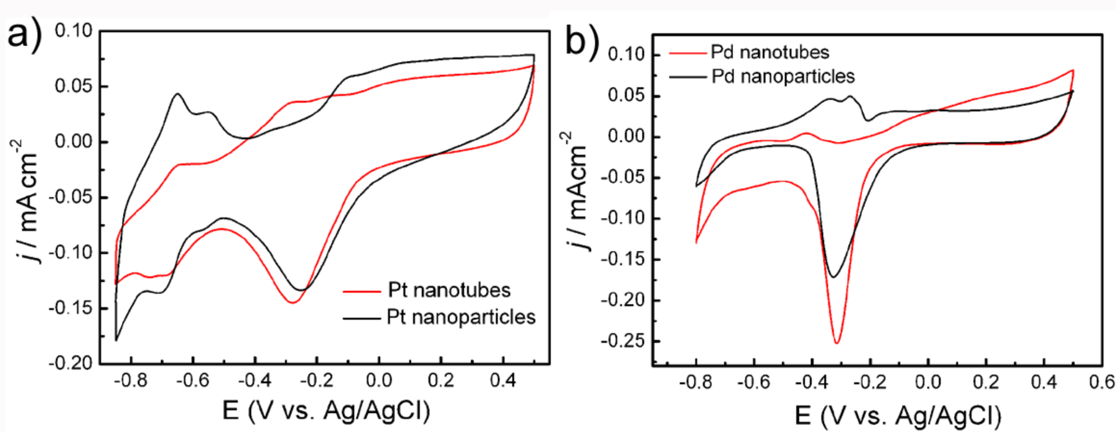

Fig. S8. (a) CVs in 0.1 M KOH for the Pt nanotubes and Pt nanoparticles on ITO electrodes. Scan rate: 50 mV s^{-1}. (b) CVs in 0.1 M KOH for the Pd nanotubes and Pd nanoparticles on ITO electrodes. Scan rate: 50 mV s^{-1}. The current values were normalized with respect to the electrochemically active surface area (ECSA), which were calculated by measuring the coulombic charges for oxygen desorption. The ECSA was estimated by the following equation; ECSA = Q_o/q_o, where Q_o is the surface charge that can be obtained from the area under the CV trace of oxygen desorption and q_o is the charge required for desorption of monolayer of oxygen on the Pt and Pd surface (420 and 424 μC/cm^2 for the Pt and Pd, respectively. Ref.: R. Woods, in *Electroanalytical Chemistry: A Series of Advances*, Vol. 9 (Ed. A. J. Bard), Marcel Dekker, New York, **1974**, pp 1-162.).

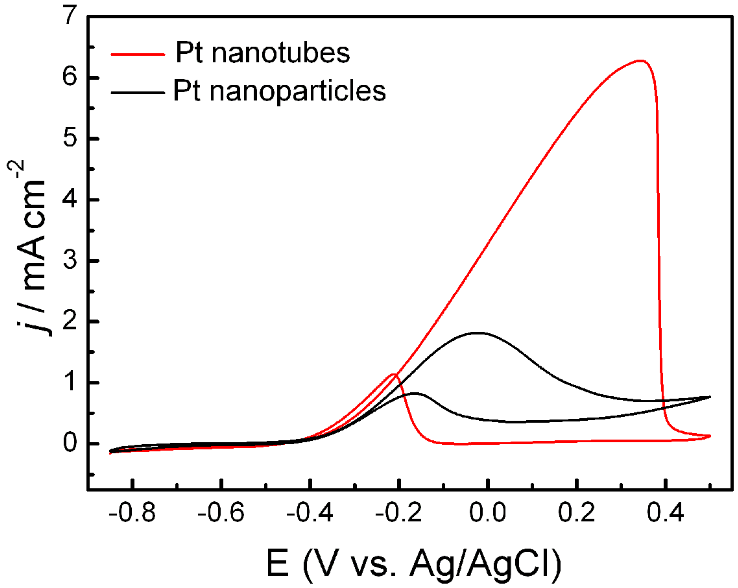

Fig. S9. CVs in 0.1 M KOH + 0.1 M methanol of the Pt nanotubes and Pt nanoparticles on ITO electrodes. Scan rate: 50 mV s^{-1}. In the case of the Pt nanotubes, the residual ZnO was completely removed by treating the nanotubes with an acidic solution (pH = 3.5 adjusted by nitric acid) for about 1 h. The absence of ZnO was confirmed by ICP-AES.