

Supporting Information Available

Facile synthesis and electrocatalytic application of phosphonate functionalized platinum nanodendrites

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Experimental section

Materials

Ethylenediamine-tetramethylene phosphonic acid (EDTMP, shown in Scheme S1) was purchased from Shandong Taihe Water Treatment Co., Ltd. (Shandong, China). Potassium tetrachloroplatinate(II) (K_2PtCl_4) and formaldehyde solution (HCHO, 40%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Glassy carbon (GC) electrode (3 mm diameter) was purchased from Shanghai Chenghua Co (Shanghai, China). Other reagents were of analytical reagent grade and used without further purification. The solution pH was adjusted by the addition of dilute NaOH or HCl solution. All the aqueous solutions were prepared with Millipore water having a resistivity of 18.2 M Ω . Commercial Pt black was purchased from Johnson Matthey Corporation.

Preparation of phosphonate functionalized Pt nanodendrites

In a typical synthesis, EDTMP-Pt^{II} complex with DTPMP/Pt^{II} molarratio = 1:1 was achieved by heating 40 mL of an aqueous solution (pH 10.0) containing 2.5 mM potassiumtetrachloroplatinate(II) (K_2PtCl_4) and 2.5 mM EDTMP at 60 °C for 80 min.¹ Then, 0.1 mL of HCHO(40%) was rapidly added to the EDTMP-Pt^{II} complex solution and mechanically stirred for 1 h at the room temperature. After reaction, the obtained black phosphonate functionalized Pt nanodendrites were separated by centrifugation at 20000 rpm for 10 min, washed several times with water, and then dried at 50 °C for 5 h in a vacuum dryer.

Preparation of the electrode

Glassy carbon (GC) electrode was polished first with emery paper and then with aqueous slurries of fine alumina powders (0.3 and 0.05 μ m) on a polishing cloth, and was finally cleaned with ethanol and Milli-Q water under an ultrasonic bath, each for 5 min. For the preparation of working electrode, 4 mg catalyst and 5 mL H₂O were mixed and sonicated for 30 min to generate an evenly distributed suspension. Then 15.0 μ L of the resulting suspension was laid on the GC electrode surface. After drying at 40 °C, the catalyst modified working electrode was obtained. The platinum metal

loading on the electrode surface was about $169 \mu\text{g cm}^{-2}$.

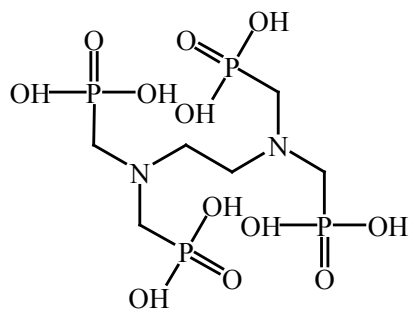
Physical characterizations

Transmission electron microscopy (TEM) measurements were made on a JEOL 2000 transmission electron microscopy operated at an accelerating voltage of 200 kV. Ultraviolet–visible (UV–vis) spectra were recorded at room temperature on a UV3600 spectrophotometer equipped with 1.0 cm quartz cells. The zeta potential measurements were performed with a Malvern Zetasizer Nano ZS90 analyzer at room temperature. X–ray diffraction (XRD) patterns were obtained with Model D/max–rC X–ray diffractometer using Cu K_a radiation source ($\lambda = 1.5406 \text{ \AA}$) and operating at 40 kV and 100 mA. X–ray photoelectron spectroscopy (XPS) measurements were performed with a Thermo VG Scientific ESCALAB 250 spectrometer with a monochromatic Al K_a X–ray source (1486.6 eV photons), and the vacuum in the analysis chamber was maintained at about 10^{-9} mbar. The binding energy was calibrated by means of the C 1s peak energy of 284.6 eV. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer thermogravimetric analyzer under N₂ atmospheres over a temperature range of 20–1000 °C with a ramp rate of $10 \text{ }^\circ\text{C min}^{-1}$.

Electrochemical measurements

All electrochemical experiments were carried out on a CHI 660 C electrochemical workstation (CH Instruments, Shanghai, Chenghua Co.). A standard three-electrode system was used for all electrochemical experiments assembled with a platinum wire as the auxiliary electrode, a saturated calomel electrode (SCE) as the reference electrode, and a catalyst modified glassy carbon (GC) electrode as the working electrode. All potentials in this study were reported with respect to the SCE. Prior to the electrochemical measurements, N₂ was bubbled through the solution for 10 min to remove dissolved O₂. During experiments, a continuous N₂ flow was maintained over the solution. All of the electrochemical measurements were carried out at $30 \pm 1 \text{ }^\circ\text{C}$.

Figures



Scheme S1. The structure of ethylenediamine-tetramethylene phosphonic acid (EDTMP).

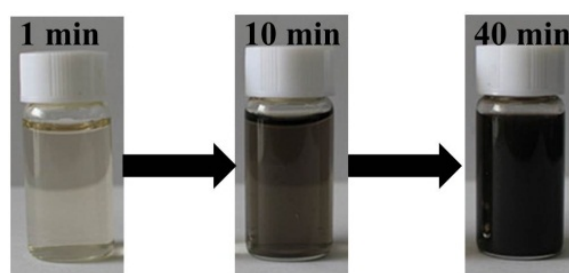


Figure S1. The photographs of colour evolution of the reaction solution.

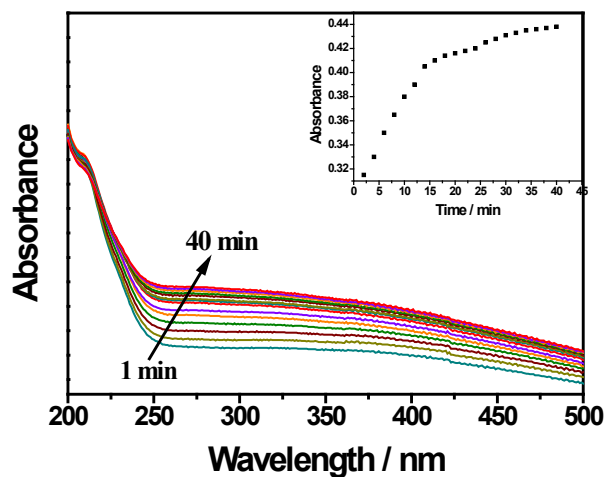


Figure S2. Time-dependent UV-vis spectra of EDTMP-Pt^{II} complex solution (pH=10.0) at the room temperature after addition of HCHO solution. The spectra are recorded at a time interval of 5 min. Inset shows dependence of the absorbance value at 300 nm on time.

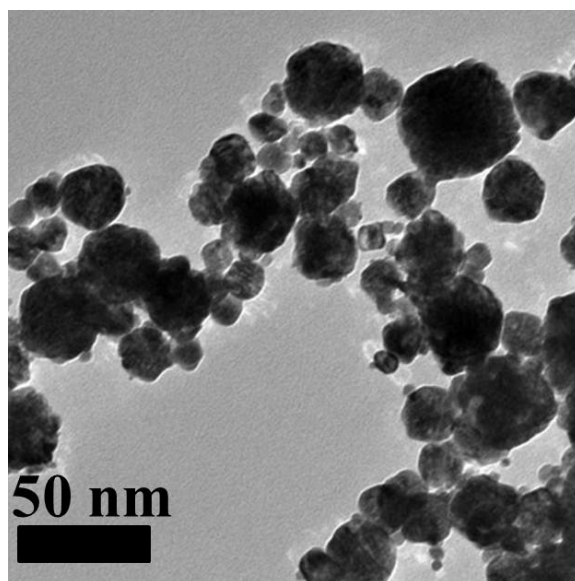


Figure S3. TEM image of the as-prepared products in the absence of EDTMP.

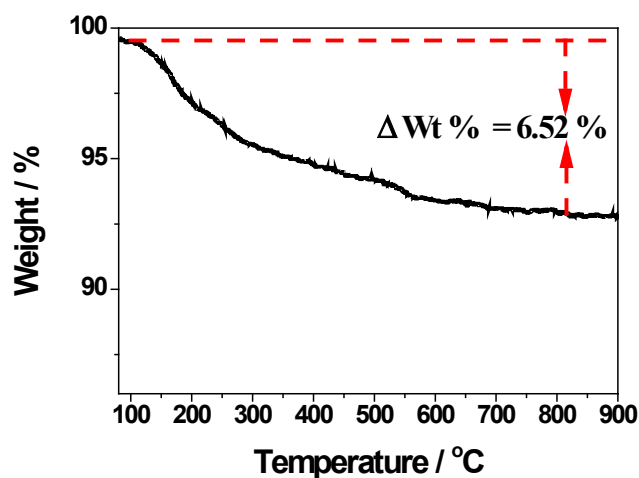


Figure S4. TGA curve of Pt nanodendrites at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ under nitrogen atmosphere.

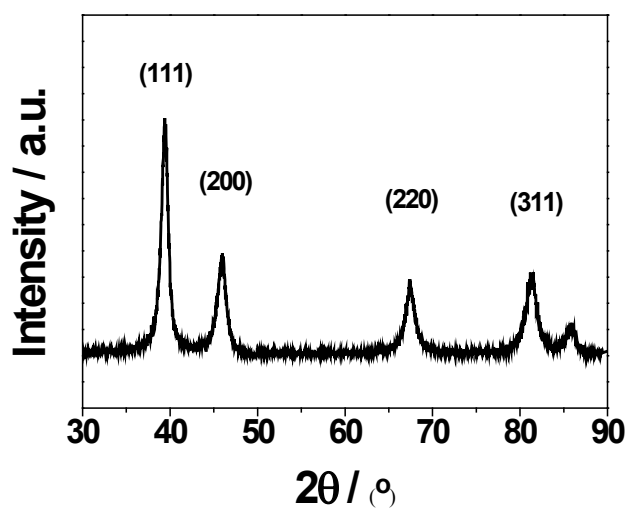


Figure S5. XRD pattern of commercial Pt black. According to Scherrer equation, the average particle size of commercial Pt black is calculated to be ca. 8.5 nm.

References

1. Chen, Y., Xu, J., Liu, X., Tang, Y. and Lu, T., *Appl. Catal. B: Environ.* 2013, **140-141**, 552-558.