Supplementary Information

Pt Nanoparticle Netlike-Assembly as Highly Durable and Highly Active Electrocatalyst for Oxygen Reduction Reaction

Hong-Hui Wang[a], Zhi-You Zhou[a]*, Qiang Yuan[b], Na Tian[a], Shi-Gang Sun[a]*

[a] State Key Lab of Physical Chemistry of Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China.
[b] Department of Chemistry, Guizhou University, Guiyang, Guizhou province 550025, China

**Corresponding author Email: zhouzy@xmu.edu.cn; sgsun@xmu.edu.cn*

1. Reagents and materials

K_2PtCl_6 (99.99%, A.R.), NaBr (99.9%, A.R.), sodium citrate (99.9%, A.R.), poly(vinylpyrrolidone) (PVP, MW 40,000), sodium lauryl sulfate (SLS, A.R.), and $HClO_4$ (G.R.) were purchased from China Medicine Shanghai Chemical Reagent Corp. A commercial Pt black catalyst was purchased from Alfa Aesar (HiSPEC 1000, Johnson Matthey Inc.)

2. Synthesis of Pt nanoparticle netlike-assembly (Pt-NNA)

K_2PtCl_6 (21 mg), sodium citrate (203 mg), NaBr (103 mg), PVP (102 mg) and SLS (291 mg) were added into 8 mL water with stirred for 5 minutes. The resulting homogeneous solution was transferred to a 20 mL Teflon-lined stainless-steel autoclave. The sealed vessel was heated at 200°C for 2 h, and cooled to room temperature. The products were separated via centrifugation at 12000 rpm for 30 minutes, and further washed with deionized water, 2 M NaOH ethanol solution, acetone solution (acetone : water = 1 : 4 V/V), and ethanol in sequence for several times to remove the residual surfactants (i.e., PVP and SLS) and salts (i.e., sodium citrate, NaBr). Finally, the purified products were dispersed with ethanol for further use. The real Pt concentration (Some Pt was lost after the above washing process) in the final ethanol solution was determined by an UV-Vis spectrophotometric method proposed by Ayres et al.[s1] In this method, Pt samples were dissolved in aqua regia, and the resulting $PtCl_6^{2-}$ ions were then reacted with $SnCl_2$ in hydrochloric acid solution, yielding a yellow color solution with a maximal absorptive wavelength at 406 nm.

3. Electrochemical test

Electrochemical experiments were carried out in a standard three-electrode cell at a water bath (30 ± 0.5 ºC). The electrode potential was controlled by a PAR 263A potentiostat/galvanostat (EG&G). The counter electrode was a Pt foil, and the reference electrode was a reversible hydrogen electrode (RHE). All potentials reported in this paper are referred to the RHE scale. The working electrode is a glassy carbon (GC, ϕ=5 mm) electrode embedded into a Teflon holder. Prior to the electrochemical test, the GC electrode was mechanically polished using successively alumina powder of size 5, 1, and 0.3 μm. It was then cleaned in an ultrasonic bath. The suspension of Pt-NNA or Pt black was spread on the GC electrode. As soon as the electrode was dried under infrared lamp, 10 μL Nafion diluents (0.05 wt.%

Nafion® solution) was coated onto the electrode surface.

The 0.1 M $HClO_4$ solutions were prepared with Millipore water (18 MΩ cm) provided by a Milli-Q Labo apparatus (Nihon Millipore Ltd.). The solutions were deaerated by bubbling high-purity N_2 (99.999%), and then steady-state cyclic voltammograms were recorded to obtain the electrochemical active area (ESA) of Pt, calculated from the electric charge of hydrogen adsorption/desorption (210 μC cm^{-2}). The electrocatalytic activity for oxygen reduction reaction (ORR) was tested in an O_2-saturated 0.1 M $HClO_4$ in a rotating disk electrode system (Pine Inc., USA) at a rotation rate of 900 rpm. Electrode potential was scanned from 0.05 to 1.1 V at 10 mV s^{-1}, and the solution ohmic drop (i.e., IR drop) was compensated.

3 Effect of Pt loading on durability test

The loading of Pt catalysts exhibit little effect on stability test results. For example, if the loading of Pt black on GC electrode was decreased from 8.26 to 2.01 μg, similar loss in electroactive surface area (ESA) was observed (-37 *vs* -34%) after 20,000 potential cycles, as shown in Fig. A2.

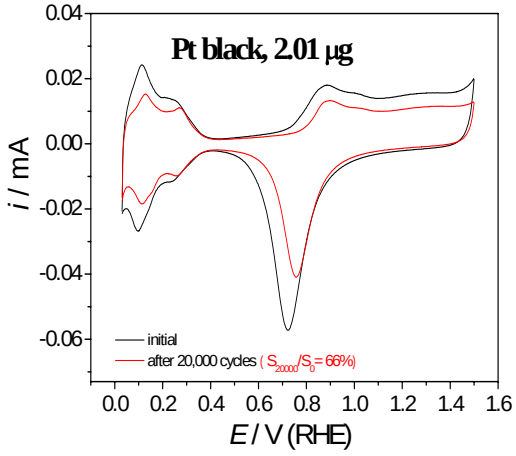

Fig. S1 The electrochemical durability of commercial Pt black with lower loading (2.01 μg). Other conditions are same with those in Fig. 3b.

4 TEM images and histogram of particle sizes of Pt/C before and after the durability test

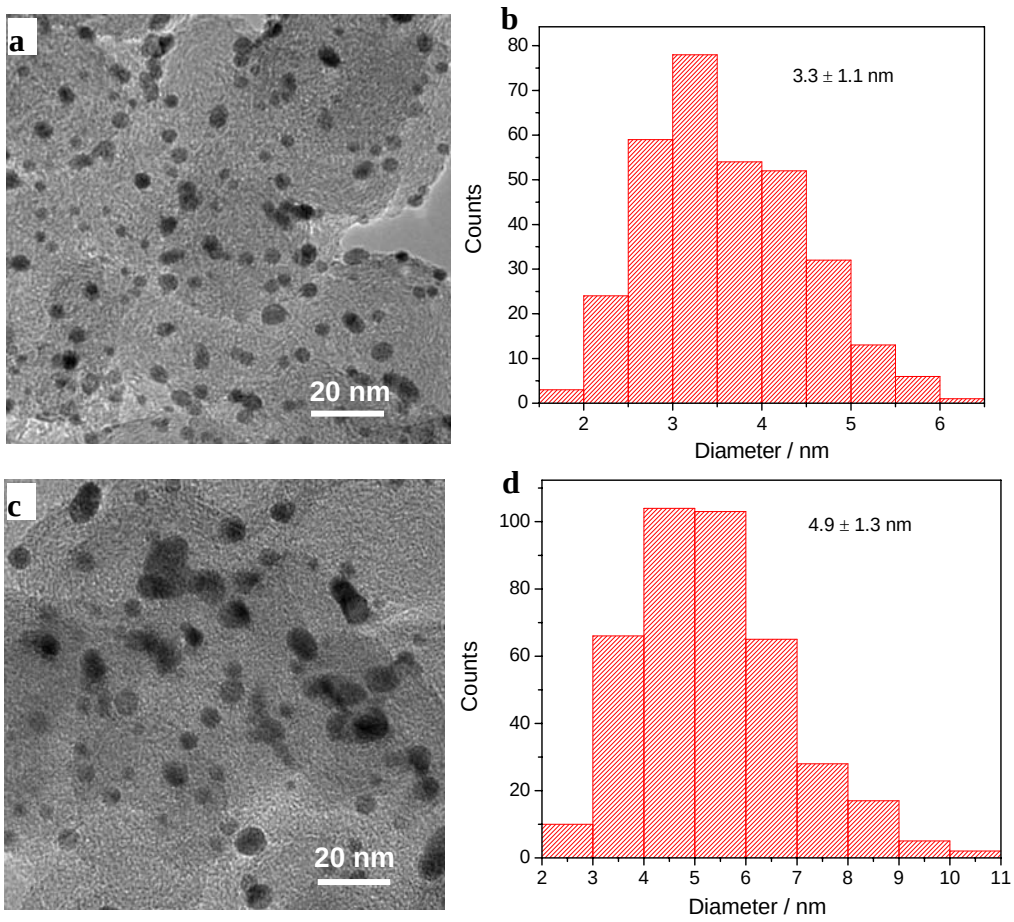

Fig. S2 TEM images and histogram of particle sizes of Pt/C catalyst before (a, b) and after (c, d) the durability test of 20,000 potential cycles. After the stability test, the average particle size of Pt/C significantly increases from 3.3 to 4.9 nm.

5 TEM images of Pt black before and after the durability test

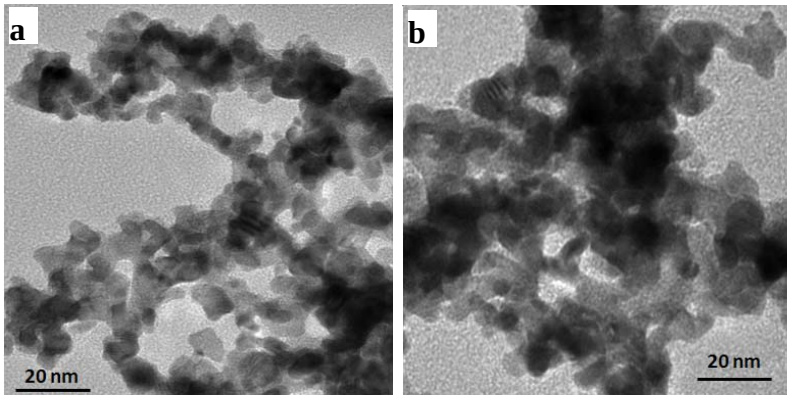

Fig. S3. TEM images of Pt black catalysts before (a) and after (b) the durability test of 20,000 potential cycles. After the stability test, the degree of agglomeration becomes greater.

References

(S1) G. H. Ayres and A. S. Rieyek, *Anal. Chem.*, 1953, **16**, 299-304