Supporting Information

Catalytic System Based on Sub-2-nm Pt Particles and Its Extraordinary Activity and Durability for Oxygen Reduction

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EXPERIMENTAL SECTION

Chemicals and Materials

Selenous acid (H_2SeO_3, >99.99%), hydrazine monohydrate ($N_2H_4 \cdot H_2O$, >98%), poly(vinyl pyrrolidone) (PVP with MW≈55,000), potassium platinum(II) chloride (K_2PtCl_4, >99.99%), platinum(II)-ammonium chloride ($(NH_4)_2PtCl_4$, 99%), sodium platinum(IV) hexachloride hexahydrate ($Na_2PtCl_6 \cdot 6H_2O$, 98%), and chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, >99.99%) were all obtained from Sigma-Aldrich (St. Louis, MO) and used as received. The deionized (DI) water (18.2 MΩ·cm) obtained by purification through a Milli-Q system (Millipore, USA) was used throughout the experiments.

Synthesis of Se Nanospheres

In a standard protocol, 3.87 mg of H_2SeO_3 and 1 g of PVP were dissolved in 1 L of water, respectively. Subsequently, 11.6 mL of $N_2H_4 \cdot H_2O$ was added in one shot at room temperature under magnetic stirring. The reaction was allowed to proceed at room temperature for 3 h. The final product was collected by centrifugation, washed with water three times, and dispersed in water for further use.

Preparation of Carbon-supported Se Film (Se/C)

The suspension of Se nanospheres (1.09 mg/mL, 5 mL in total) was mixed with an aqueous suspension (15 mL) containing carbon powders (Ketjen Black EC-300J) (15 mg) to obtain a loading of approximately 25 wt% for Se nanospheres. The mixture was then sonicated in an ice-water bath for 3 h. The resultant product was collected by centrifugation, and dried at 60 °C overnight. The product was then thermally treated at different temperatures (300, 350, 400, and 450 °C) for 2 h under Ar protection. The as-obtained samples were marked as Se/C. The contents of Se in the final products were 20, 15, 12, and 7 wt% when the thermal treatment temperature was 300, 350, 400, and 450 °C, respectively, as determined by inductively coupled plasma mass spectroscopy (ICP-MS). Finally, the retrieved solid materials were re-dispersed in water for further use.

Standard Procedure for the *in situ* Growth of Pt Nanoparticles on Carbon Support

Typically, 1 mL of the aqueous suspension of Se/C (1 mg/mL, obtained after thermal treatment at 450 °C) was diluted to 10 mL by adding water and then heated to 70 °C under magnetic stirring. Once the temperature was stable, 150 μL of an aqueous solution of K_2PtCl_4

(10 mM) was added in one shot and the reaction was allowed to continue for 2 h under magnetic stirring. The solid product was collected by centrifugation, washed three times with water, and dispersed in 1 mL of water for further use. The final product was denoted standard Pt/Se/C.

Preparation of Pt Nanoparticles with Different Precursors

The procedure was the same as the standard protocol, except for the difference in precursor, such as $(NH_4)_2PtCl_4$, Na_2PtCl_6, and H_2PtCl_6. The Pt nanoparticles prepared using $(NH_4)_2PtCl_4$ shows a particle size similar to that using the standard procedure (using K_2PtCl_4 as precursor) because of the same redox potentials of $PtCl_4^{2-}$/Pt (0.755 V versus RHE) for $(NH_4)_2PtCl_4$ and K_2PtCl_4. The product prepared by Na_2PtCl_6 present bigger particle size than standard Pt/Se/C because the reduction potential of $PtCl_6^{2-}$/Pt (1.435 V versus RHE) is more positive than that of $PtCl_4^{2-}$/Pt. Na_2PtCl_6 can be reduced to Pt (0) more easily though the galvanic reaction with Se according to Eq. (S1).

$$\mathrm{Se} + \mathrm{PtCl_6^{2-}} + 3\mathrm{H_2O} \rightarrow \mathrm{SeO_3^{2-}} + \mathrm{Pt} + 6\mathrm{Cl^-} + 6\mathrm{H^+} \quad (S1)$$

However, our observations indicated that the particle size significantly decreased when H_2PtCl_6 was used. From Eq (2), we know that the addition of H^+ could depress galvanic replacement between Se and $PtCl_6^{2-}$ by shifting the equilibrium to the left side, which decreased the reaction rate and further led to small particle size.

Structural and Compositional Analyses

TEM images were taken using a Hitachi HT7700 microscope operated at 120 kV. High-resolution TEM and STEM images were acquired using an aberration-corrected FEI Titan S 80-300 STEM/TEM microscope equipped with a Gatan OneView camera at an accelerating voltage of 300 kV at Oak Ridge National Laboratory (ORNL). Energy-dispersive X-ray spectroscopy (EDX) data of Pt/Se/C was acquired using an aberration-corrected JEOL NEOARM microscope with dual large-angle EDX-SDD detectors at ORNL. Energy dispersive X-ray spectroscopy (EDS) mapping of Se/C was obtained using field emission scanning electron microscope (FE-SEM) (SU 8230, Hitachi, Japan). Elemental compositions of the nanostructures were determined by ICP-MS (NexION 300Q, PerkinElmer). Powder X-ray diffraction (XRD) patterns were obtained on a Rigaku

D/MAX-2250 V diffractometer with graphite-monochromatized Cu KR radiation. XPS was performed using a spectrometer (Thermo Scientific, KAlpha spectrometer) with Al Kα X-rays (1486.6 eV).

Preparation of the Working Electrodes

In a typical process, 1 mL of the carbon-supported catalyst (Pt/Se/C and $Pt_{2.0nm}$/Se/C) was centrifuged and re-dispersed in 1 mL of a mixture containing 0.995 mL of isopropanol and 5 μL of 5% Nafion and then sonicated in an ice bath for 40 min. The as-obtained suspension was drop-casted on a pre-cleaned glassy carbon rotating disk electrode (RDE, Pine Research Instrumentation) with a geometric area of 0.196 cm^2 and dried at room temperature. The commercial Pt/C catalyst (20 wt%, Ketjen Black EC-300J) and Se/C (obtained after thermally treated at 450 ^oC for 2 h) were used as references for comparison. The loadings of Pt and Se for each sample were 1.3 μg, as determined using ICP-MS.

Electrochemical Measurements

Electrochemical measurements were conducted in a three-electrode system using a glassy carbon rotating disk electrode (RDE, Pine Research Instrumentation) connected to a CHI 600E (CH Instruments) with a Hydroflex hydrogen reference electrode (Gaskatel) as the reference electrode, and a Pt coil as the counter electrode. The electrolyte was 0.1 M aqueous $HClO_4$ solution. The cyclic voltammograms (CVs) were recorded at room temperature in a N_2-saturated $HClO_4$ solution at a scanning rate of 50 mV s^{-1} in the potential range of 0.05-1.1 V referenced to the reversible hydrogen electrode (V_{RHE}). The specific ECSAs were calculated from the average charges associated with the adsorption and desorption of hydrogen by taking a value of 210 μC cm^{-2}. The ORR activity was measured in the potential range of 0.05-1.1 V_{RHE} in an O_2-saturated aqueous $HClO_4$ solution using the RDE method at room temperature with a scanning rate of 10 mV s^{-1} (rotating rate of 1,600 rpm). For the accelerated durability test, the CV and ORR polarization curves were measured after sweeping 5000, 10000, 15000, and 20000 cycles in the range of 0.6 and 1.1 V_{RHE} at a rate of 0.1 V s^{-1} (rotating rate of 1,600 rpm) in an O_2-saturated $HClO_4$ solution at room temperature.

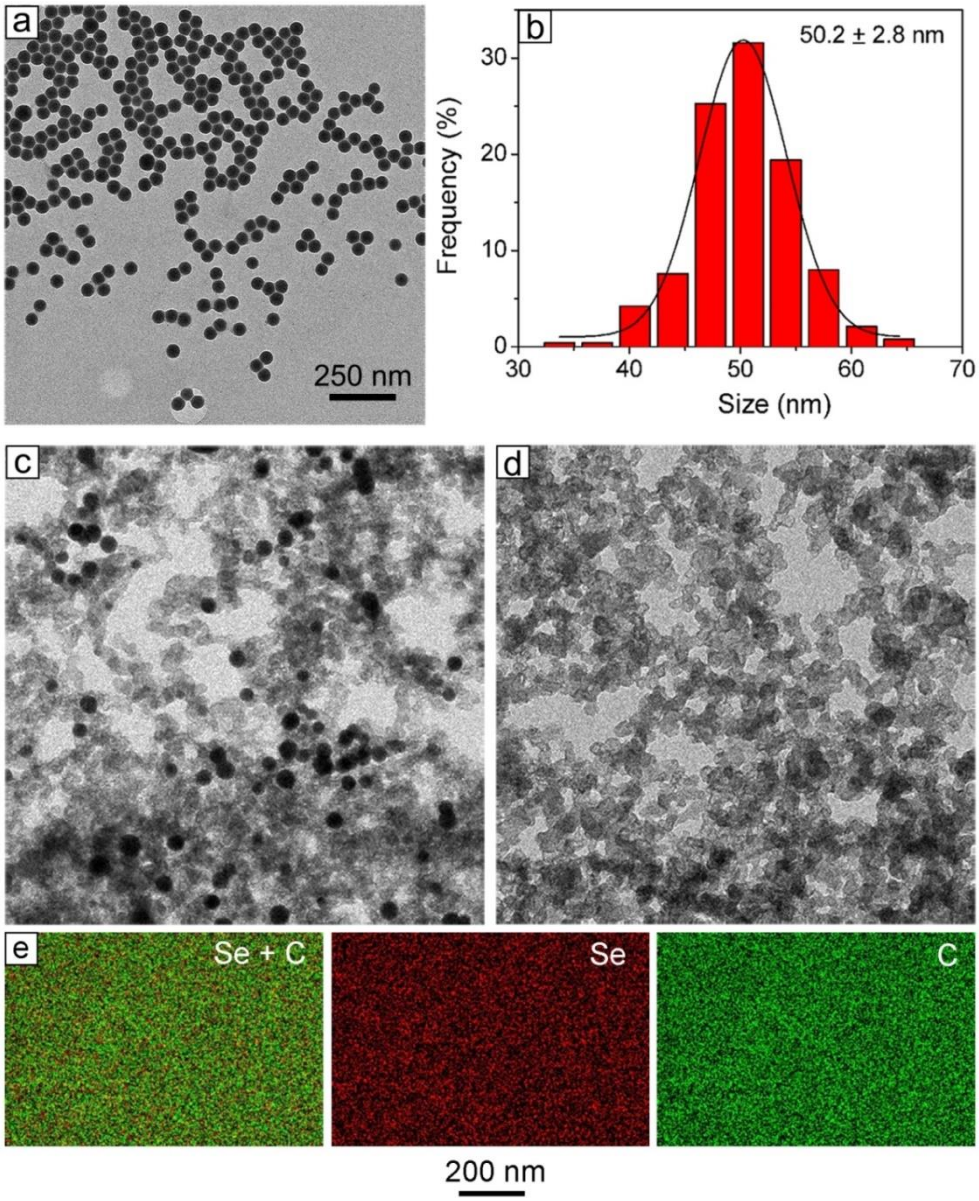

Figure S1. (a) TEM image and (b) size distribution of the Se nanospheres, which had a mean diameter of about 50 nm. (c, d) TEM images of the Se nanospheres (c) upon deposition onto a carbon support and (d) after annealing at 450 ºC and under Ar protection for 2 h. The sample is referred to as Se/C in our discussion. (e) Elemental mapping of Se and C in Se/C.

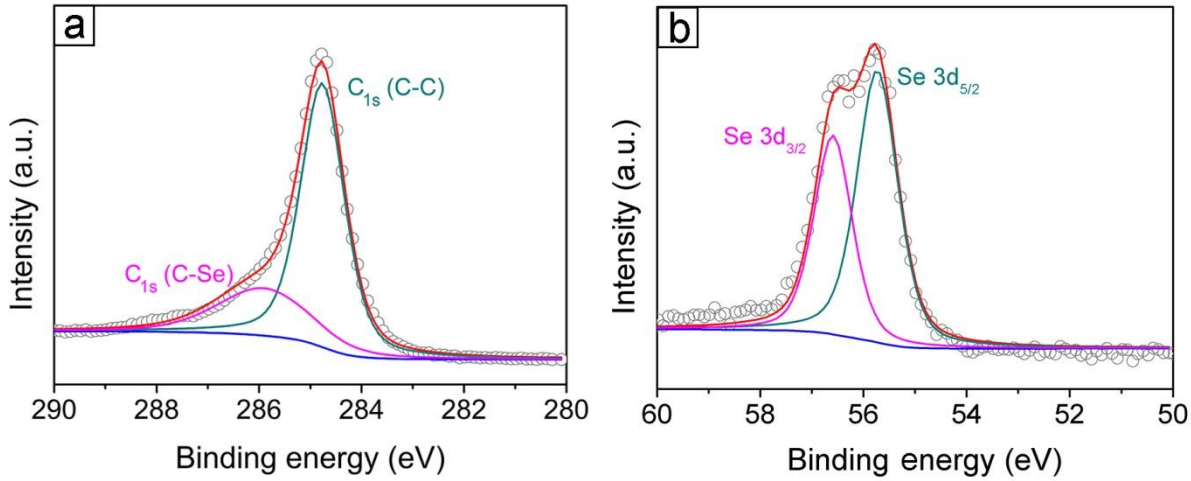

Figure S2. XPS spectra of (a) C 1s and (b) Se 3d for the Se/C sample (same as in Fig. S1d), which was prepared *via* thermal annealing at 450 ^{o}C and under Ar protection for 2 h.

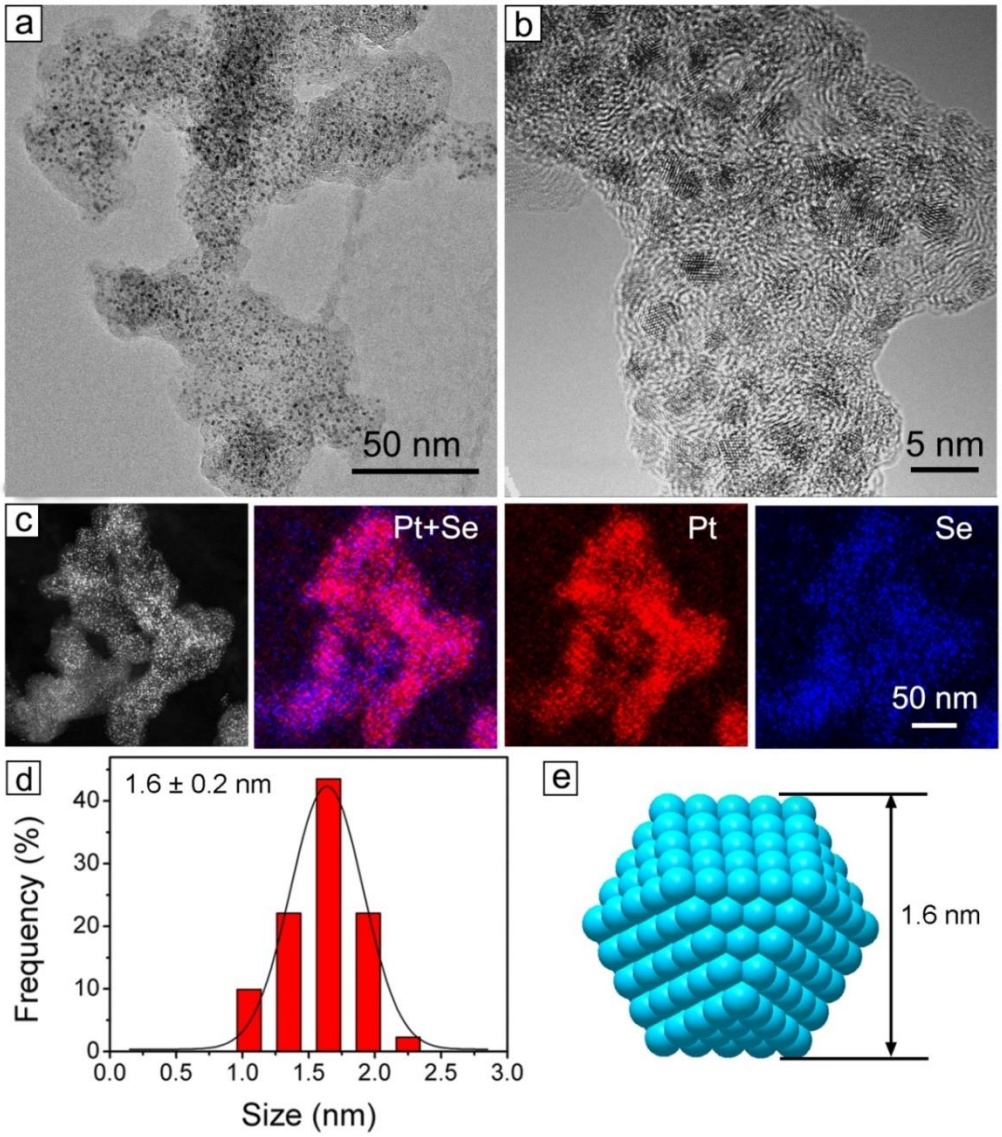

Figure S3. (a, b) TEM images, at two different magnifications, of the Pt/Se/C sample prepared using the standard protocol. (c) HAADF-STEM image and EDX mapping of Pt and Se in the Pt/Se/C. (d) Size distribution of the Pt particles. (e) An atomic model of the Pt particle typically found in the sample, together with the definition of size.

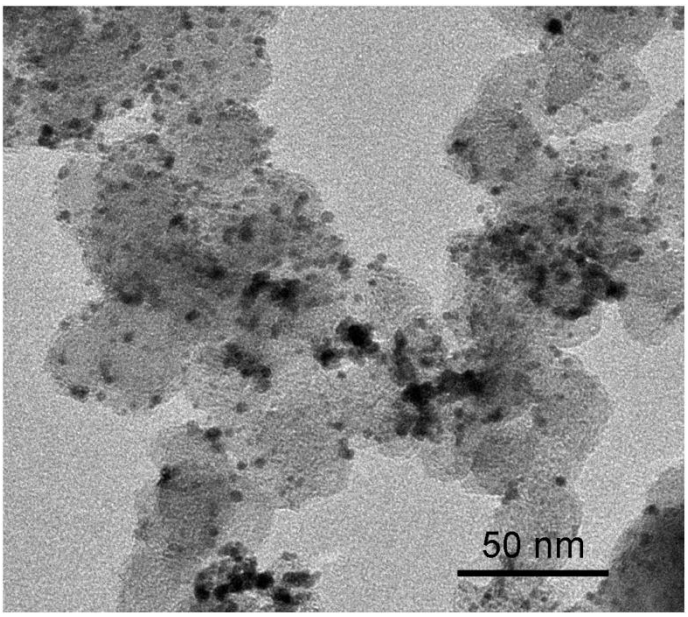

Figure S4. TEM image of a commercial Pt/C catalyst whose Pt particles had a mean diameter of 3.6±0.7 nm.

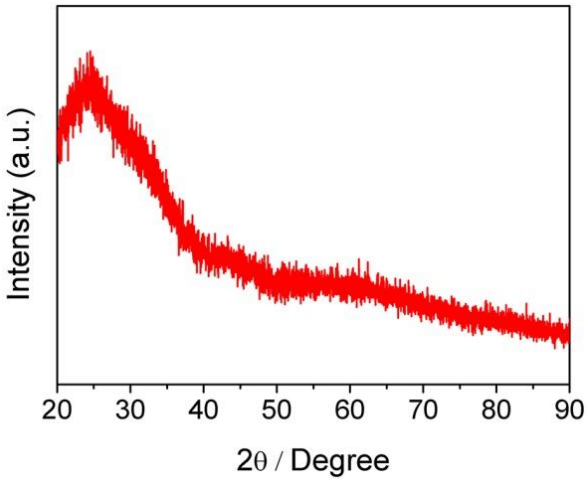

Figure S5. XRD pattern of the Pt/Se/C sample prepared using the standard protocol.

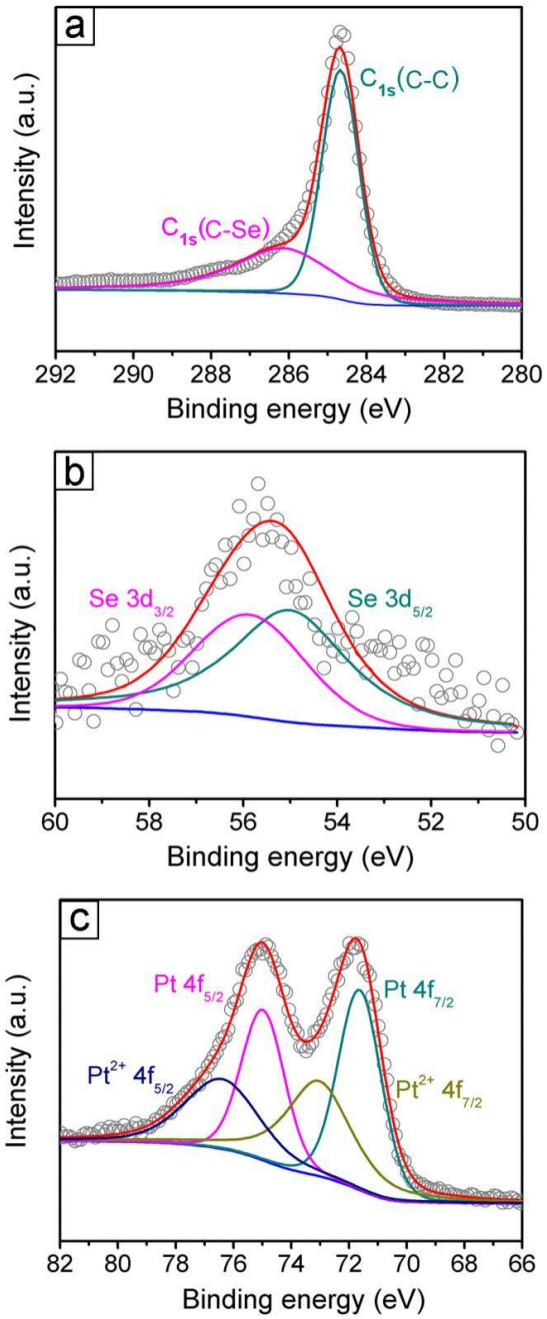

Figure S6. XPS spectra of the (a) C 1s, (b) Se 3d, and (c) Pt 4f peaks recorded from a Pt/Se/C sample prepared using the standard protocol.

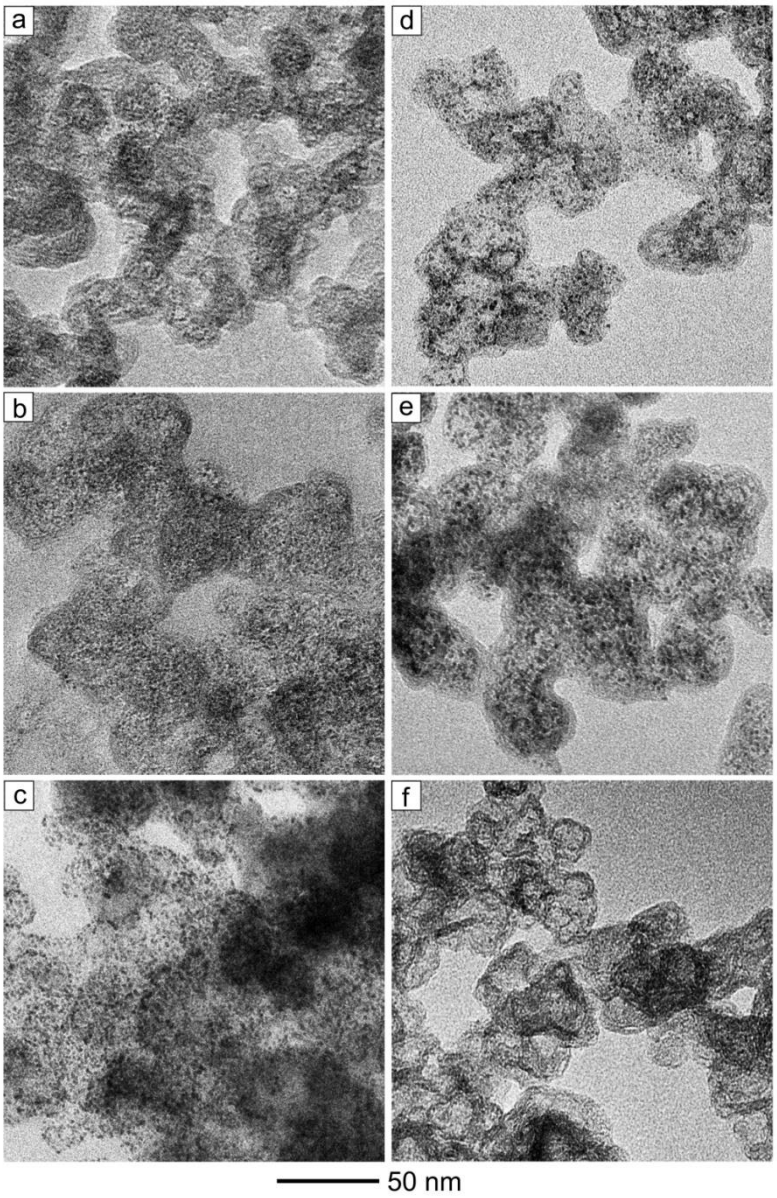

Figure S7. (a-c) TEM images of Pt/Se/C samples with different Pt loadings at (a) 11, (b) 16, and (c) 21 wt%. The samples were prepared using the standard protocol but at different temperatures for the annealing of Se/C: (a) 400, (b) 350, and (c) 300 ºC, respectively. The Pt particles were 1.6±0.2, 1.8±0.1, and 2.0±0.2 nm, respectively, in size. (d-f) TEM images of the Pt/Se/C samples prepared using the standard protocol except for the use of different precursors to Pt: (d) $(NH_4)_2PtCl_4$, (e) Na_2PtCl_6, and (f) H_2PtCl_6. The Pt particles were 1.6±0.2, 2.1±0.3, and 1.1±0.2 nm, respectively, in size.

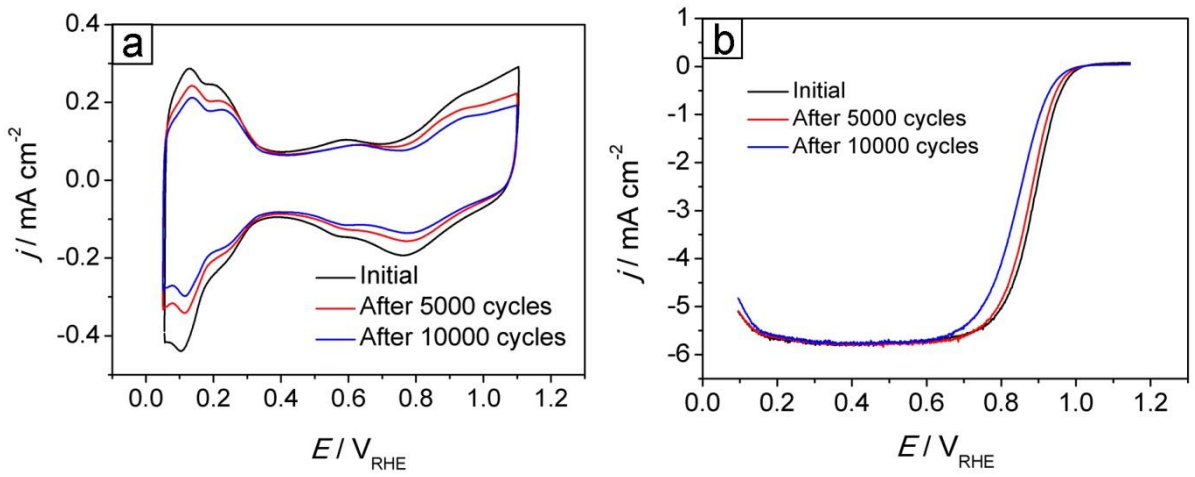

Figure S8. (a) CV and (b) ORR polarization curves recorded from the commercial Pt/C before and after different cycles of ADT. The currents were normalized to the geometric area of the rotating disk electrode.

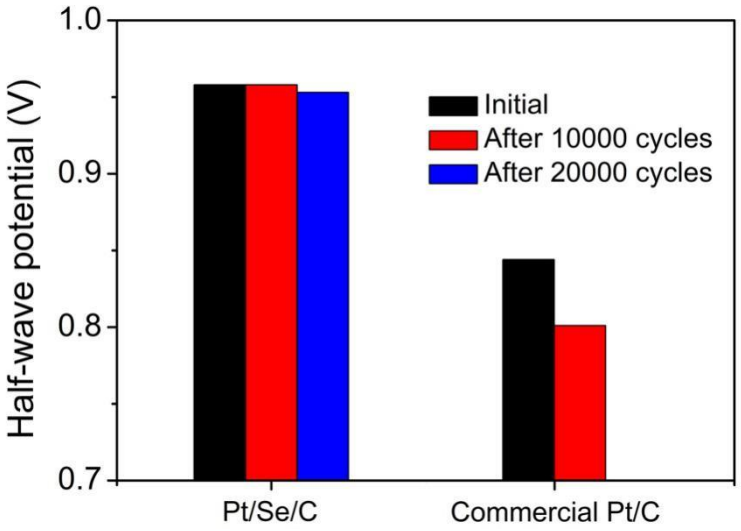

Figure S9. Comparison of the half-wave potentials of the standard Pt/Se/C and commercial Pt/C, respectively, after different cycles of ADT.

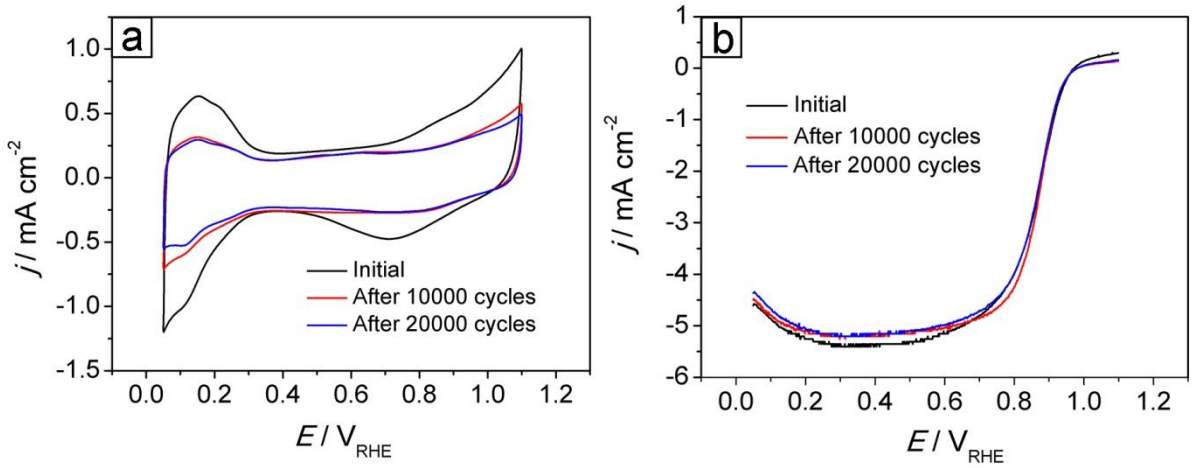

Figure S10. (a) CV and (b) ORR polarization curves recorded from the $Pt_{2.0\ nm}$/Se/C before and after different cycles of ADT. The currents were normalized to the geometric area of the rotating disk electrode.

Table S1. Electrochemically Active Surface Area (ECSA), Half-Wave Potential, Specific Activity (SA), and Mass Activity (MA) of the $Pt_{2.0\ nm}$/Se/C before and after Different Cycles of ADT.

sample	cycles	ECSA ($m^2\ g^{-1}_{Pt}$)	half-wave potential (V)	SA ($mA\ cm^{-2}$)	MA ($A\ mg^{-1}_{Pt}$)
$Pt_{2.0nm}$/Se/C	initial	133	0.86	0.17	0.29
	5 000	95	0.88	0.28	0.34
	10 000	64	0.88	0.32	0.27
	15 000	60	0.87	0.32	0.25
	20 000	54	0.86	0.36	0.25

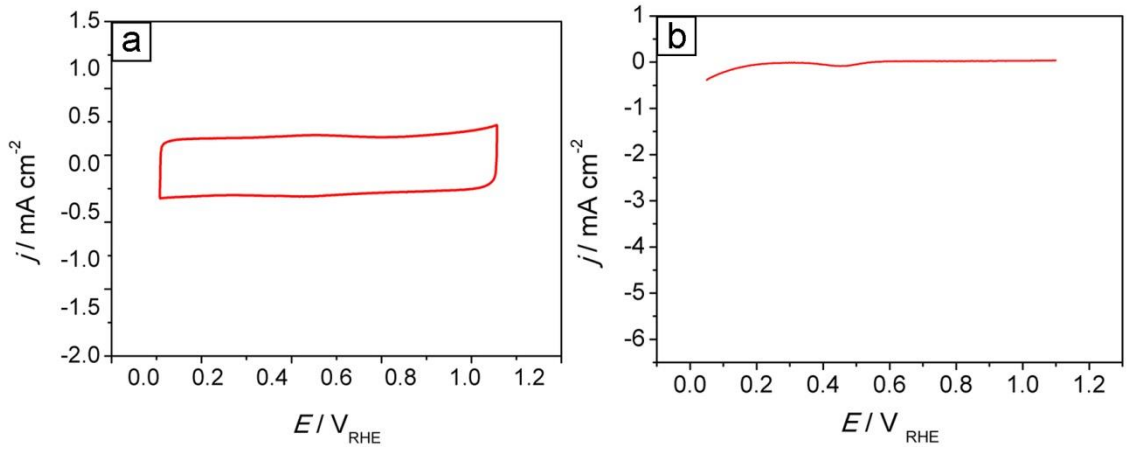

Figure S11. (a) CV and (b) ORR polarization curves recorded from the standard Se/C sample obtained by annealing at 450 ºC and under Ar for 2 h. The currents were normalized to the geometric area of the rotating disk electrode.

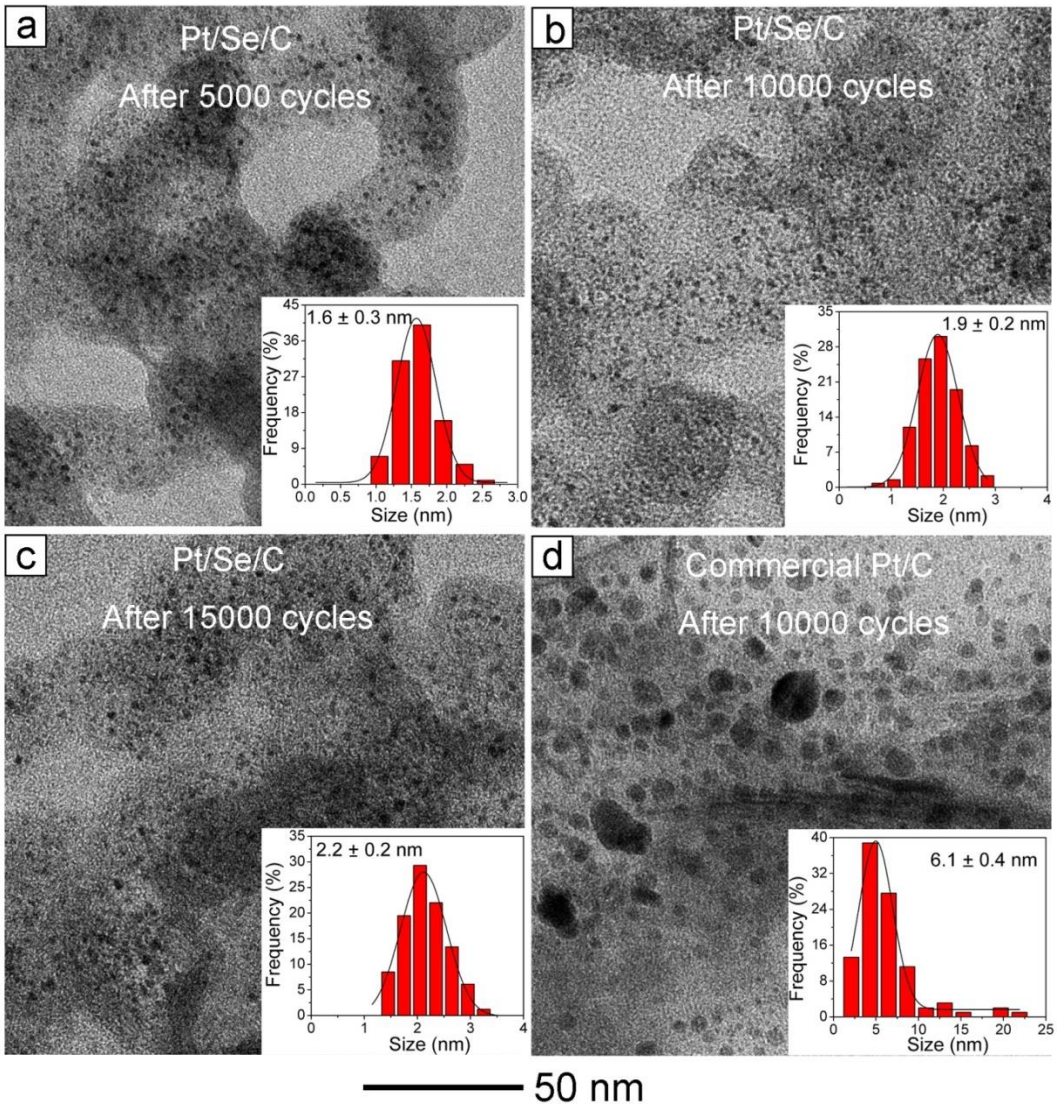

Figure S12. (a-c) TEM images of the standard Pt/Se/C catalyst after different cycles of ADT: (a) 5000, (b) 10 000, and (c) 15 000. (d) TEM image of the commercial Pt/C after 10 000 cycles of ADT. The histograms show the size distributions of the Pt particles. The average sizes of the corresponding Pt particles were (a) 1.6±0.3, (b) 1.9±0.2, (c) 2.2±0.2 and (d) 6.1±0.4 nm, respectively.

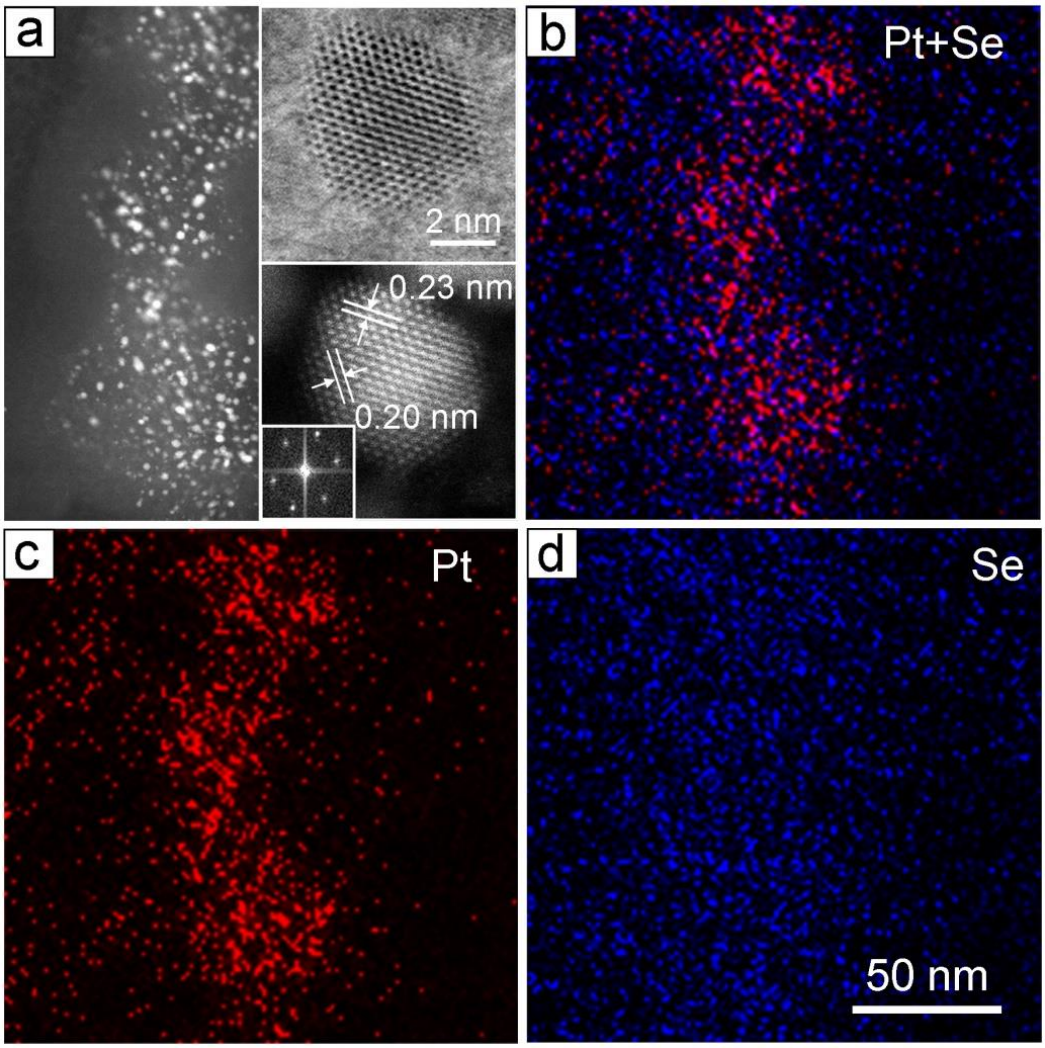

Figure S13. (a) STEM image of Pt/Se/C after 20 000 cycles of ADT and (b-d) EDX mapping of Pt and Se of the cycled Pt/Se/C. The insets are (top) bright-field, atomic-resolution STEM and (bottom) HAADF-STEM image taken from a single particle, as well as (bottom, inset) Fourier-transformed pattern.