Enhanced Dispersion and Durability of Pt Nanoparticles on a Thiolated CNT Support

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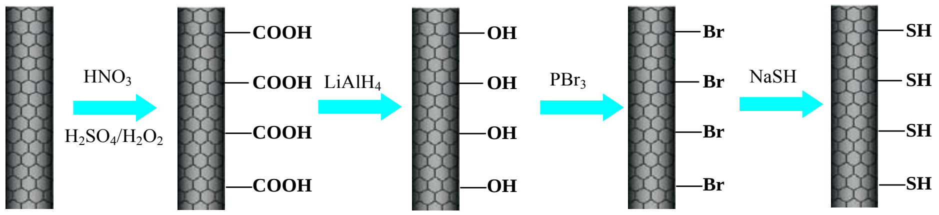
Experimental Section

(1) Preparation of SH-CNTs: The SH-CNTs sample was prepared by successive purification, carboxylation, reduction, bromination and thiolation, as shown in Scheme 1. In a typical routine, the pristine CNTs (purchased from Bill Nanotechnology, Inc.) were purified by refluxing in 14 mol/L HNO_3 for 5 h, followed by diluting, filtering, washing and vacuum drying at 80℃ overnight. The carboxylation of the purified CNTs was then carried out in H_2SO_4/H_2O_2 mixture solution (4:1 by volume) for 3 h, followed by diluting, filtering, washing and vacuum drying at 80℃ overnight. Then the COOH-CNTs were reduced to OH-CNTs by putting COOH-CNTs in excess $LiAlH_4$ dissolved in anhydrous ether in refluxing conditions for 3 h. The above suspension were filtered and washed with excess DI water and dried at 80℃. The obtained OH-CNTs were then substituted with bromide groups by refluxing the suspension in excess phosphorus tribromide dissolved in actone for 3 h at room temperature. After the suspension wasfiltered and washed with excess actone, the Br-CNTs were transferred into a 0.5M NaHS solution, which were stirred strongly at room temperature for 3 h. The **SH-CNTs** was finally obtained by filtration and washing with excess DI water and drying at 180℃for 3h to remove the residue H_2S.



Scheme 1 Schematic illustration of the Synthetic procedure for SH-CNTs

(2) Preparation of Pt/SH-CNTs, Pt/pristine-CNTs and Pt/COOH-CNTs: Pt catalysts supported on pristine CNTs, COOH-CNTs, and SH-CNTs were synthesized by the ethylene glycol (EG) reduction method. Briefly, 80 mg of CNTs support, 60 mg of sodium citrate and 1.2 mL of H_2PtCl_6 solution (20 mg/mL Pt) were mixed with 25 mL of EG, followed by stirring for 30 min and adjusting the pH to 11.0 using 1 M NaOH in EG solution. The mixture was then placed into a Teflon-lined autoclave and conditioned at 160℃ for 6 h, followed by filtering, washing and vacuum drying at 80℃. The Pt loading of all the catalysts was controlled at 20 wt%. The prepared Pt catalyst supported on pristine CNTs, COOH-CNTs, and SH-CNTs was denoted by Pt/pristine-CNTs, Pt/COOH-CNTs, and Pt/SH-CNTs, respectively.

(3) *Electrochemical measurements:* All electrochemical experiments were performed in a standard three-electrode cell at room temperature. The cell consisted of a glassy carbon working electrode (GC electrode, 3 mm in diameter, PINE: AFE3T050GC), an Ag/AgCl (saturated KCl) reference electrode, and a platinum foil counter electrode. All potentials in this study, however, are given relative to the reversible hydrogen electrode (RHE). The working electrodes were prepared by applying catalyst inks onto glassy carbon (GC) disk electrodes. In brief, the electrocatalyst was dispersed in ethanol and ultrasonicated for 10 minutes to form a uniform catalyst ink (1 mg Pt mL^{-1}). A total of 3 μL of well-dispersed catalyst ink was applied onto a prepolished GC disk. After drying at room temperature, a drop of 0.1 wt% Nafion solution was applied onto the surface of the catalyst layer to form a thin protective film. The prepared electrodes were dried overnight at room temperature before electrochemical tests.

The CV accelerating stress tests (AST) were performed at potentials between 0 and 1.2 V versus a reversible hydrogen electrode (RHE) at a scan rate of 50 mV s^{-1} in nitrogen-purged 0.5 M H_2SO_4 at room temperature. The CV curves were recorded every 50 cycles to calculate the electrochemical surface area (ECSA) of Pt in the catalysts using the following equation:

$$ECSA = \frac{Q_H}{0.21 \times [Pt]}$$

where Q_H (mC) is the charge due to the hydrogen adsorption/desorption in the hydrogen region (0.05–0.40 V) of the CVs, 0.21 mC cm^{-2} is the electrical charge associated with monolayer adsorption of hydrogen on Pt, and [Pt] is the loading of Pt on the working electrode.

All of the electrodes were pretreated by cycling the potential between 0.05 and 1.1 V at a sweep rate of 50 mV s^{-1} for 50 cycles in order to remove any surface contamination prior to ORR activity testing. The ORR polarization curves were conducted in O_2-saturated 0.5 M H_2SO_4 solution at a 2 mV s^{-1} scan rate. The rotation speed was controlled at 1,600 rpm.

(4) TEM test: Transmission electron microscopy (HRTEM) was carried out on a Zeiss LIBRA 200 FETEM instrument operating at 200 kV.

(5) XPS analysis: XPS spectra were acquired by using a PE PHI-5400 spectrometer equipped with a monochromatic Al X-ray source (Al KR, 1.4866 keV). In the data analysis, the binding energy (BE) of the core level C 1s peak was set at 284.5 eV to compensate for surface-charging effects. The Shirley background was subtracted, and satellite peaks were removed for all element peaks before curve fitting. The experimental spectra were fitted into components of Gaussian line shape. The surface elemental compositions were determined by the ratios of peak areas corrected with empirical sensitivity factors.

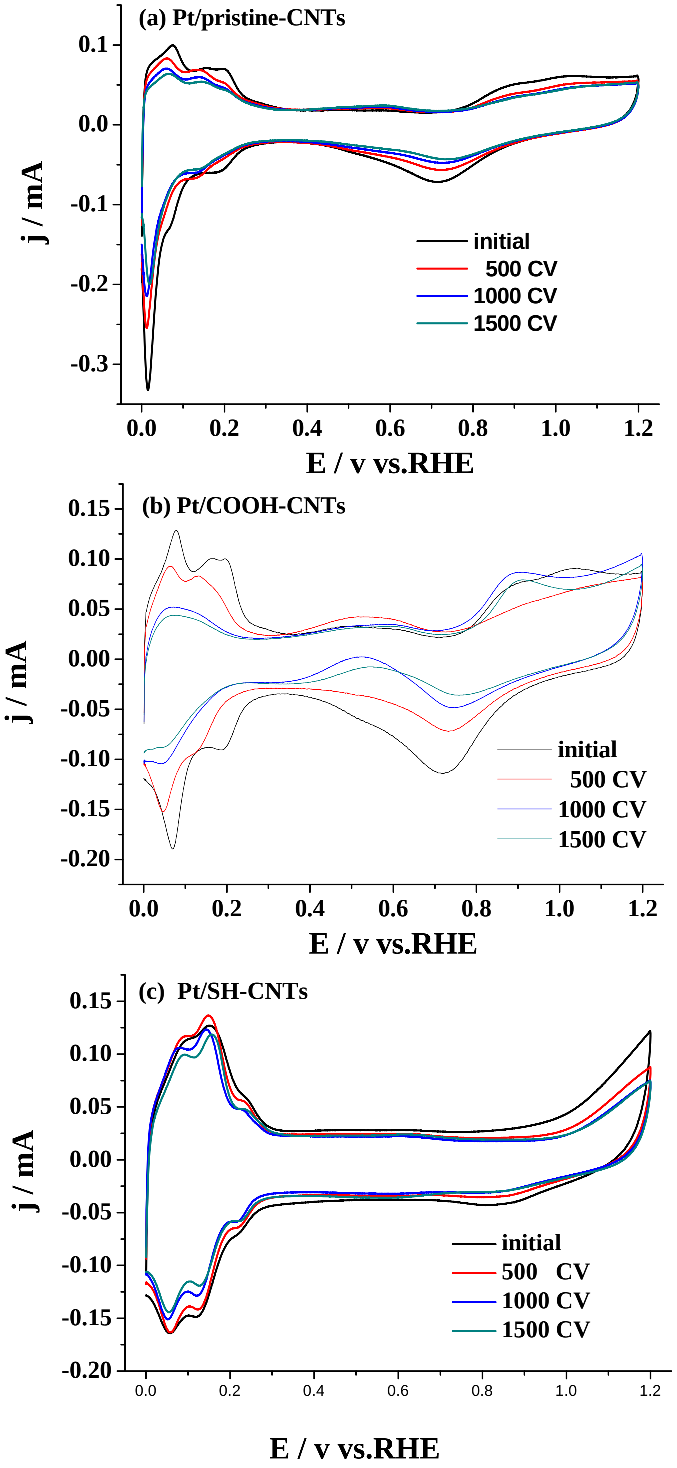


Fig. S1. CV curves of electrodes made from (a) Pt/pristine-CNTs, (b) t/COOH-CNTs and (c) Pt/SH-CNTs catalysts at different CV cycles in N_2-purged 0.5 M H_2SO_4 solution at a 50 mV s^{-1} scan rate.

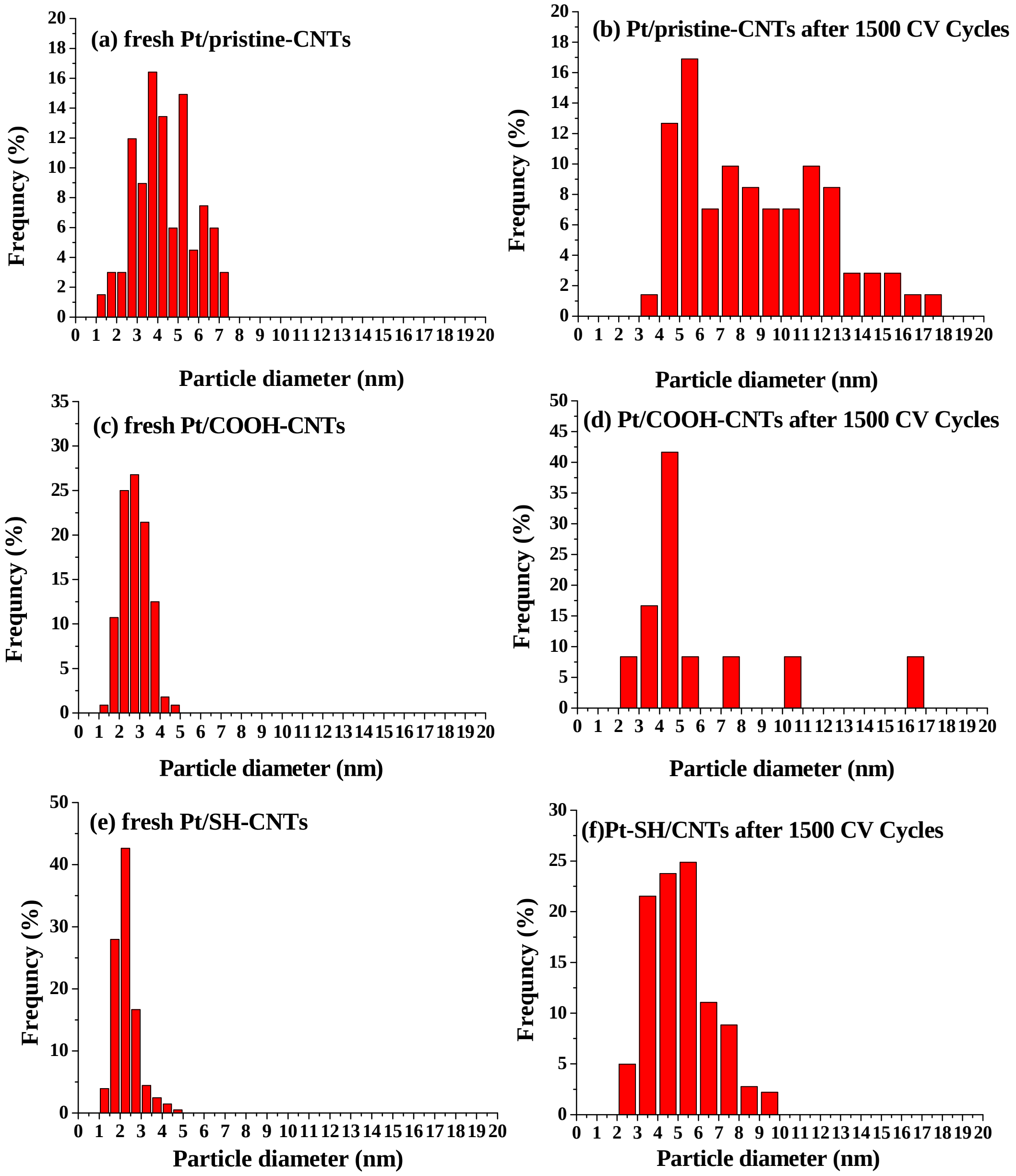


Fig. S2. Pt particle-distribution histograms of fresh (a) Pt/pristine-CNTs catalyst, (b) aged Pt/pristine-CNTs catalyst after 1,500 CV cycles, (c) Pt/COOH-CNTs catalyst, (d) aged Pt/COOH-CNTs catalyst after 1,500 CV cycles, (e) Pt/SH-CNTs catalyst, (f) aged Pt/SH-CNTs catalyst after 1,500 CV cycles.