

High-Efficiency Palladium Catalysts Supported on Ppy-modified C₆₀ for Formic Acid Oxidation

1. Experimental Section

1.1 Synthesis of ppy-carbon composite. Ppy-fullerene composites were synthesized by *in situ* chemical oxidative polymerization of pyrrole monomer on fullerene (C₆₀) powders. 0.1 g C₆₀ powders was dispersed in 100 mL isopropanol aqueous solution (volume ratio=1:1) by ultrasonic treatment for 30 minutes. 3 mmol pyrrole monomer (dissolved in 10 mL ethanol) was added to the above suspension and was stirred for 30 minutes. Then 30 mL of 30% H₂O₂ aqueous solution was added slowly to the suspension with constant stirring for 4 hours at room temperature. After reaction, the resulting ppy-C₆₀ powder was filtered and rinsed with DD water and absolute ethanol until the filtrate became colorless. The obtained black powder was dried under vacuum condition at room temperature for 24 h.

1.2 Preparation of Pd/ppy-C₆₀ catalyst.

40 mg pretreated ppy-C₆₀ was added in a flask with 75 mL ethanol-water (1:2, v/v) solution, and ultrasonically treated for 30 minutes, then kept stirring for 30 min. 10 mL PdCl₂ (0.02 mol/L) aqueous solution was added slowly to the ppy-C₆₀ suspension under stirring subsequently. Freshly prepared KBH₄ solution (100 mg in 100 mL DD water) was added dropwise into the above system under stirring for 2 hours, and then the stirring was continued for another 2 hours. The whole process was operated at room temperature. Finally, the product was collected by filtration and washed several times with DD water and ethanol, then dried at 40 °C

in vacuum condition for 12 hours.

Control experiment A: Control A was done in the same conditions described as the typical experiment, except the disappearance of ppy.

Control experiment B: Control B was done in the same conditions described as the typical experiment, apart from the C₆₀ as the support.

1.3 Measurements. The morphology of catalyst was measured by JEOL-100CX high resolution transmission electron microscopy (HRTEM) operated at 200 kV. Nanoparticles were firstly immersed into ethanol and subsequently dispersed ultrasonically for 5 min. A drop of the suspension was then deposited on a lacey carbon grid and dried in air for TEM observations. X-ray diffraction (XRD) analysis was performed using D/max-2200/PC X-ray diffractometer with Cu K α radiation source. The fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Bio-Rad FTS-40 Fourier transform infrared spectrometer in the wavenumber range of 4000-400 cm⁻¹, and the thermogravimetric analysis (TGA) were performed on an NETZSCH STA 449C instrument.

The electrochemical measurements were carried out in a three-electrode cell by using Solartron 1287+1260 electrochemical test system (Solartron Analytical, England). A glassy carbon disk (3 mm o.d) coating catalyst was used as working electrode, a platinum foil (1 cm²) as counter-electrode, and an Ag/AgCl electrode as reference. 0.5 M H₂SO₄ aqueous solution was served as electrolyte for hydrogen oxidation measurements, and 1 M HCOOH in 0.5 M H₂SO₄ for formic acid

oxidation measurements, respectively. High-purity N_2 was bubbled into the electrolytes during the experiments.

Electrochemical CO stripping voltammograms were obtained by oxidizing preadsorbed CO (COad) in 0.5 M H_2SO_4 at a scan rate of $20 \text{ mV}\cdot\text{s}^{-1}$. CO was purged through 0.5 M H_2SO_4 for 30 min to allow complete adsorption of CO onto the catalyst. The working electrode was stayed at 0.1 V (*vs.* Ag/AgCl), and excess CO in the electrolyte was removed by purging with high-purity N_2 for 30 min. The amount of COad was evaluated by integrating the COad stripping peak and correcting for the capacitance of the electric double-layer. The activity of the catalysts in the oxidation of formic acid was evaluated in a solution containing 0.5 M H_2SO_4 and 1 M HCOOH, and cyclic voltammetry was performed by applying a linear potential scan at a sweep rate of $50 \text{ mV}\cdot\text{s}^{-1}$.

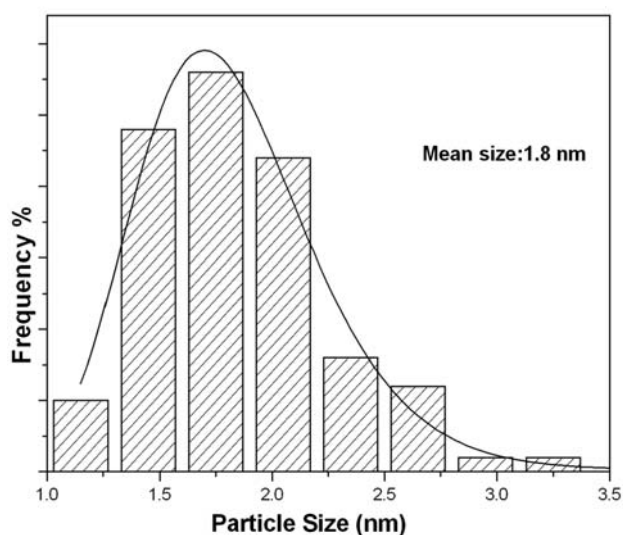


Fig.s1. The particle size distribution of Pd/ppy-C₆₀ catalyst from Fig. 1a.

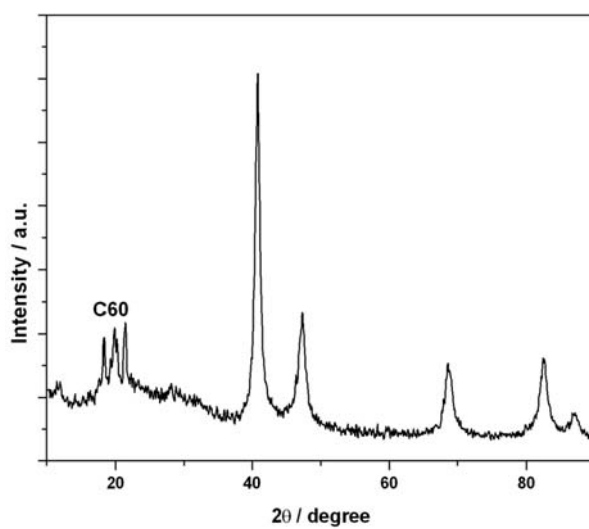


Fig. s2. the XRD patterns of the as-prepared Pd/ppy-C₆₀ catalyst.

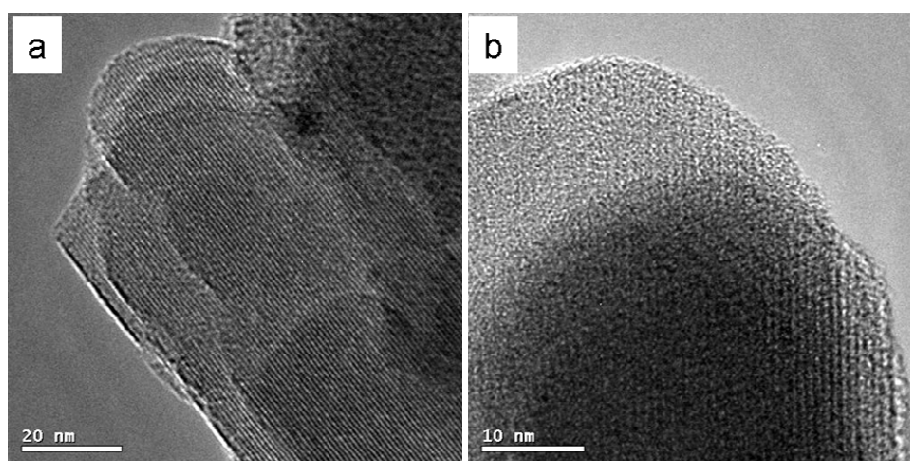


Fig. S3. HRTEM images of (a) C₆₀ nanoparticles and (b) the as-prepared ppy-C₆₀ composite.