

Supporting Information:

Preparation of Pd-decorated Fullerenols on Carbon Nanotubes with Excellent Electrocatalytic Properties in Alkaline Media

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Experimental Details:

Materials: All chemical reagents used in this experiment were of analytical grade. H₂SO₄, HNO₃, NaOH, H₂PdCl₄, methanol, ethanol, ethylene glycol and tetrabutylammonium hydroxide (TBAH) were procured commercially and were used as received without further purification. The Raw-CNTs were purchased from Shenzhen Nanotechnologies Port Co. Ltd. (Shenzhen, China) with the diameters of 20-40 nm, lengths of 5-15 μm, and purity of 95%.

Preparation of acid-treated CNTs: In this treatment, the Raw-CNTs were first dispersed in a concentrated H₂SO₄-HNO₃ mixture (8.0 M for each acid) and then placed in an ultrasonic bath for treatment at a bath temperature of 60 °C with duration of 2 h. The acid-treated CNTs was filtered using a PTFE membrane with 0.22 μm pore-size and washed with double-distilled water and ethanol several times and dried in a vacuum oven at 70 °C for about 12 h for further use.

Preparation of C₆₀ fullerenols: The C₆₀ fullerenols were prepared by using the C₆₀(toluene)/NaOH_(aq)/TBAH method described elsewhere.¹ 36 mg of C₆₀ fullerene was dissolved into 20 mL of toluene with magnetic stirring at room temperature. 20 mL of NaOH solution (50 wt%) and then 1 mL of tetrabutylammonium hydroxide (TBAH,

10 wt%) were added into the mixture with vigorous magnetic stirring at room temperature. After 10 minutes, the stirring was stopped, and the water and toluene phase were allowed to settle to form a black solution at the water/toluene interface. The nearly colorless toluene layer was carefully removed and the remaining aqueous layer was stirred vigorously at room temperature for about 12 h. Then 200 mL of methanol was added to the reaction flask, resulting in the precipitation of C₆₀ fullerenols material. The brown precipitate was collected by centrifugation and washed several times using the mixture solution of deionized water and methanol. The prepared samples were dried in a vacuum oven at 70 °C for about 12 h for further use.

Preparation of Pd@F/CNTs catalyst: To make a uniform deposition of Pd-modified C₆₀ fullerenols on the walls of the acid-treated CNTs (20 wt% metal content), H₂PdCl₄ (1.67 mL, 56.4 mM) and C₆₀ fullerenols (2 mg) were first dissolved in ethylene glycol-water solution (30 mL, v/v ratio 2:1). Firstly, the mixture was ultrasonic treatment for 5 min, and then refluxed at 120 °C for 10 min with continuous magnetic stirring. After that, 38 mg of acid-treated CNTs dissolved in 30 mL ethylene glycol-water solution was added. After another 2 hours refluxing with continuous magnetic stirring, the mixture was filtered through a PTFE membrane and washed with double-distilled water and ethanol several times. The obtained Pd@F/CNTs was dried in a vacuum oven at 70 °C for 12 h for further use. As contrast catalysts, different mass contents of C₆₀ fullerenols with 0, 0.5, 1.0, 1.5, 2.5 and 3.0 mg were added, which were prepared using similar

procedures as described above.

Characterization: Fourier transform infrared spectrometry (FT-IR) (Thermo Fisher Scientific, America) was employed to analyze the surface chemical composition of the purified C₆₀ fullerenols. UV-visible spectroscopy (Shimadzu UV-2550) was used to analyze the samples at room temperature from 200 to 800 nm. Raman spectrometry (DXR Raman Microscope, America) was used to study the integrity and electronic structure of the samples. X-ray photoelectron spectroscopy (XPS) data was recorded with an ESCALab220i-XL electron spectrometer from VG Scientific using 300W Al K α radiation, in which the binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. The morphology and microstructure of the synthesized materials were investigated by TEM (JEM-2010, Japan). The amount of Pd in each catalyst was determined by inductively coupled plasma-optical emission spectroscopy (Shimadzu ICPE-9000), and prior to analysis, the catalysts were digested in aqua regia for 24 h, and then diluted to a certain concentration. The electrochemical studies experiments were performed with a CHI 660D electrochemical analyzer (CH Instruments, Chen hua Co., Shanghai, China).

Electrochemical Measurement: The electrochemical activity of Pd@F/CNTs and Pd/CNTs electrocatalysts was measured for the electro-oxidation of methanol in alkaline media. As a typical process, 2.0 mg of electrocatalysts sample was ultrasonically mixed in 400 μ L of ethanol-water solution (1:1, v/v ratio) to form a homogeneous ink followed by dropping 5 μ L of the electrocatalysts ink onto the surface of a glassy carbon electrode (GCE, with a diameter of 3 mm). Then, 7 μ L of Nafion solution of 1.0% in ethanol was added to fix the electrocatalysts on the GCE

surface. Pt sheet and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. All potentials in the present study were given versus SCE reference electrode. The electrochemical active surface area (EAS) was measured in 0.5 M NaOH solution. The electrocatalytic activity and stability for the methanol oxidation reaction was measured in 0.5 M NaOH + 1.0 M CH₃OH solution at a scan rate of 50 mV·s⁻¹. Several activation scans were performed until reproducible voltammograms were obtained, and only the last cycles were used for comparison of the catalytic activity. The Pd metal loading was kept at 5 μg for Pd, all tests were conducted at ambient temperature (25±0.5 °C).

References

- 1 F. Niu, J. Wu, L. Zhang, P. Li, J. Zhu, Z. Wu, C. Wang and W. Song, *ACS Catal*, 2011, **1**, 1158-1161.