Supplementary Material (ESI) for Chemical Communications

Supporting Information

Pd/HPW-PDDA-MWCNTs as effective non-Pt electrocatalysts for oxygen reduction reaction of fuel cells

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Experimental

Self-assembly of HPW on MWCNTs: 300 mg of pristine MWCNTs were initially suspended in 20 ml DI water by ultrasonication in the presence of PDDA, which acted as the functionalization polyelectrolyte. After stirring for one night, the solution was filtered and washed with DI water for several times. The as-functionalized MWCNTs were dried at 60^{o}C and collected (denoted as PDDA-MWCNTs). The as prepared PDDA-MWCNTs were then sonicated in 20 mL of DI water containing 96 mg of HPW. After stirring, the solution was filtered and washed with DI water for several times to remove the free HPW in the solution and then dried at 60^{o}C. The collected sample of self-assembled HPW on MWCNTs is denoted as PDDA-HPW-MWCNTs. As a comparison, conventional acid-oxidized MWCNTs (denoted as Acid treated-MWCNTs) was also investigated. Acid-oxidized MWCNTs were prepared by refluxing 300 mg MWCNTs in a mixed acid (H_2SO_4:HNO_3 in 1:1 v/v ratio) solution at 140^{o}C for 4 h.

Synthesis of Pd/MWCNTs catalysts: MWCNTs-supported (with and without HPW assembled) 20wt% Pd catalysts were prepared from $PdCl_2$ aqueous solution (20mM) using the improved impregnation method.[1] An 80mg quantity of acid treated MWCNTs or HPW assembled MWCNTs was dispersed into 9.4mL $PdCl_2$ aqueous solution. After ultrasonic blending for 30 min, the suspension was heated under magnetic stirring to allow the solvent to evaporate and to form smooth thick slurry. The slurry was dried in an oven at a 60 ^{o}C. After grounding in an agate mortar, the resulting agglomerates were then heated in a tube furnace at 150 ^{o}C under flowing H_2 for 2h. Finally, the powder material was cooled to room temperature in nitrogen atmosphere. Figure S1 shows the scheme of the synthesis of Pd/HPW-PDDA-MWCNTs catalysts.

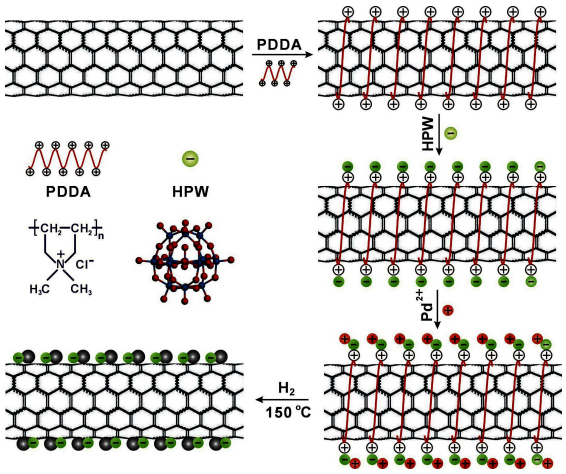

Figure S1. Scheme of self-assembly of HPW onto PDDA- functionalized MWCNTs and synthesis of Pd nanoparticles on HPW assembled PDDA-MWCNTs.

Characterization: The as-prepared Pd/MWCNTs electrocatalysts were characterized using transmission electron microscopy (TEM) with a JEOL-JEM-2010 transmission electron microscope operating at 200kV (JEOL, Japan) and X-ray diffraction (XRD) (Shimadzu XRD-6000 X-ray diffractometer) with a Cu Ka radiation. Diffraction patterns were collected at a scanning rate of 4^{o}/ min and with a step of 0.02^{o}. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Kratos XSAM-800 spectrometer with an Mg K_{α} radiator.

Electrochemical test: The oxygen reduction reaction over the prepared catalysts was studied using a rotating disk electrode. Working electrodes were prepared by mixing the catalyst powder with Nafion (0.05wt% Nafion dissolved in ethanol) solution. The mixture was sonicated before a small volume (10.0 μL) was applied onto a glassy carbon disk with a diameter 4 mm. After solvent evaporation, a thin layer of Nafion bonded powder was deposited on the GC surface to serve as the working electrode. The experimental setup involved a three-electrode arrangement connected to a potentiostat/galvanostat (Autolab model PGSTAT30). A Pt wire was used as the counter electrode, and a salt bridge connected to the reference electrode compartment was used for all electrochemical measurements. The reference electrode was a reversible hydrogen electrode (RHE) in the same electrolyte as the electrochemical cell. All potentials throughout this paper are referred to RHE. The electrochemical oxygen reduction reactions were performed in 0.5 M H_2SO_4 at room

temperature by rotating the catalyst-loaded electrodes at 2500 rpm at a scan rate of 5mVs^{-1}. The current density in the electrochemical measurements was normalized to the geometrical surface area of the working electrode.

Results

TGA and Fourier transform infrared spectra test

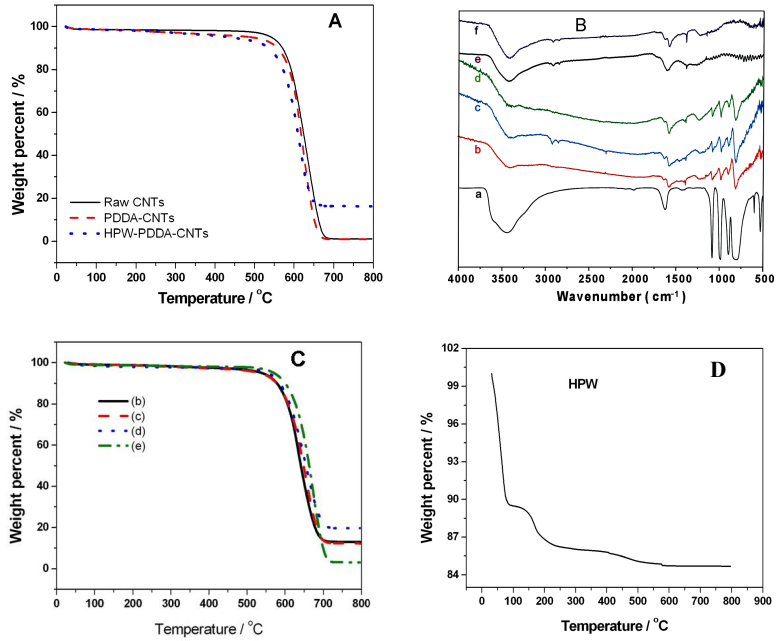

Figure S2. (A and C) TGA curves and (B) Fourier transform infrared spectra of (a) pure HPW; (b)HPW assembled on PDDA-MWCNTs; (c) HPW assembled on PDDA-MWCNTs after immersed in water for 12h; (d) HPW on pristine MWCNTs; (e) HPW on pristine MWCNTs after immersed in water for 12h; and (f) Raw MWCNTs. The TGA curve of pure HPW is shown in (D).

The weight loss for PDDA-MWCNTs and HPW-PDDA-MWCNTs in the temperature range of 200-500^{o}C is due to the decomposition of surface wrapped PDDA or the loss of water from the HPW molecule (D). The weight loss occurring in the higher temperature region of 600-800^{o}C is induced by the thermal decomposition of MWCNTs. As shown in Figure S2, the weight loss of PDDA-MWCNTs is about 4wt% and the PDDA-HPW-MWCNTs is 7wt% in the temperature region of room temperature to 500^{o}C.

CO-stripping voltammograms on Pd/Acid-treated-MWCNTs and Pd/HPW-PDDA-MWCNTs catalysts

CO-stripping voltammograms were obtained on Pd/Acid-treated-MWCNTs and Pd/HPW-PDDA-MWCNTs catalysts at a scan rate of 50mV/s in a 0.5 M H_2SO_4 solution. The electrocatalysts on the working electrode were pre-adsorbed of CO at 0.1 V vs. RHE for 10 min, followed by purging CO out of the electrochemical cell at 0.1 V for 10 min.

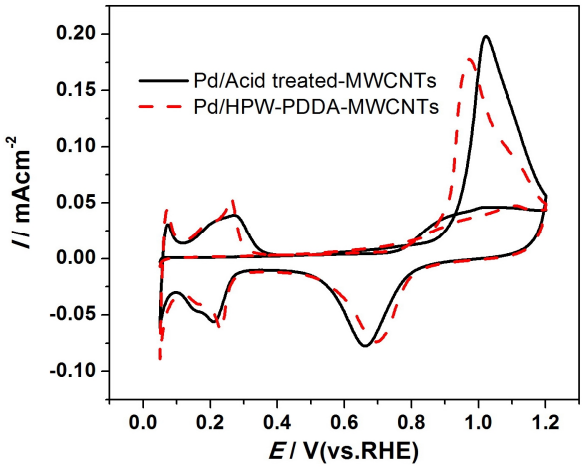

Figure S3. CO-stripping voltammograms on Pd/Acid treated-MWCNTs and Pd/HPW-PDDA-MWCNTs catalysts.

XPS spectra of the as-prepared catalyst.

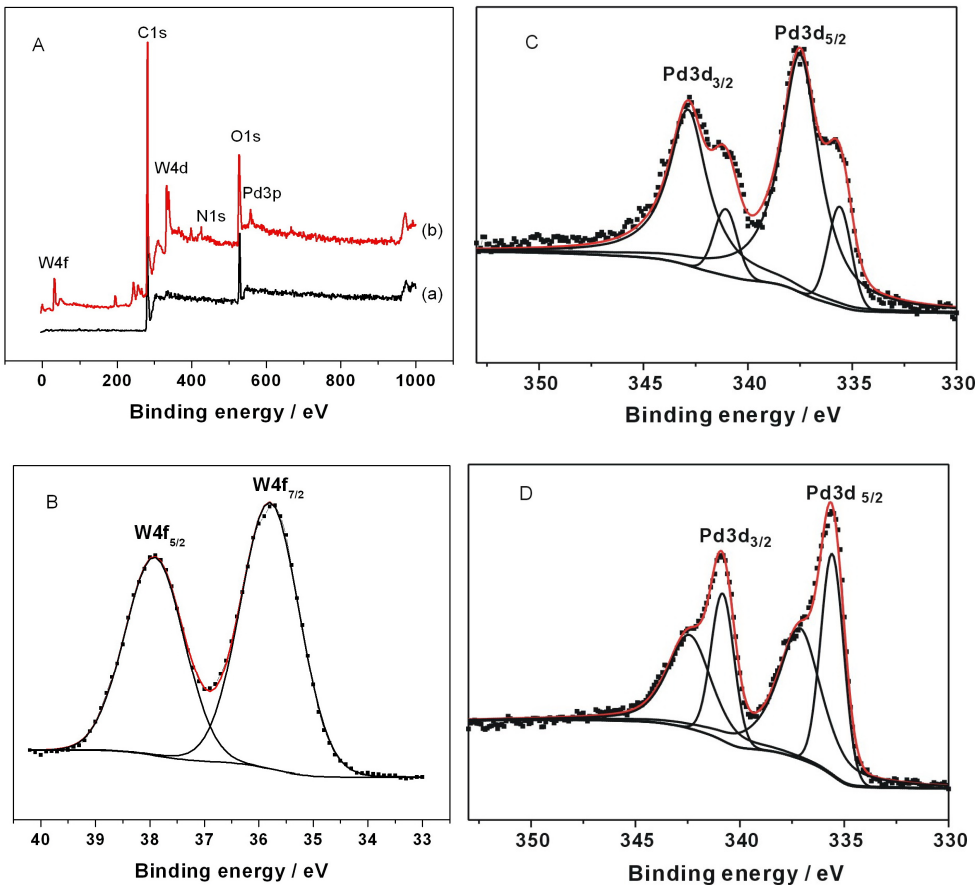

Figure S4 XPS spectra of the as-prepared catalyst. (A) the full spectrum of Pd/Acid treated-MWCNTs(a) and Pd/HPW-PDDA-MWCNTs (b); (B) W4f spectrum of Pd/HPW-PDDA-MWCNTs. (C) Pd3d spectrum of Pd/Acid treated-MWCNTs; (D) Pd3d spectrum of Pd/HP-PDDA-MWCNTs. Points: experimental data; lines: fitting curves;

Table S1. XPS results of Pd/Acid treated-MWCNTs and Pd/HPW-PDDA-MWCNTs.

Sample	Pdsurface species	Binding Energy/eV	Relative intensities
Pd/Acid treated-MWCNTs	Pd(0)	335.65	15.71%
	Pd(II)	337.55	74.29%
Pd/HPW-PDDA-MWCNTs	Pd(0)	335.57	40.47%
	Pd(II)	337.12	59.53%

References

[1] D. Wang, L. Zhuang, J. Lu, J. Phys. Chem. C **2007**, 111, 16416.

[2] B. Yang, Q. Lu, Y. Wang, L. Zhuang, J. Lu, P. Liu, Chem. Mater. **2003**, 15, 3552.