Supporting information

Fabrication of Highly Stable and Efficient PtCu Alloy Nanoparticles on Highly Porous Carbon for Direct Methanol Fuel Cells

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Figure S1 - PXRD patterns of MOF-5 and the synthesized carbon support PC 950.

Figure S2 - PXRD patterns of the synthesized catalysts with different Pt-Cu ratios and the PXRD pattern of 30 wt.% Cu load.
Figure S3- XPS spectra of the synthesized catalysts.

Figure S4- XPS de-convoluted core line of Pt 4f in Pt/C (20%) commercial catalyst.
Figure S5- TEM micrographs of Pt/PC 950 (20%) (a-h).

Figure S6- Histograms showing particles distribution of, (a) Pt-Cu/PC 950 (15:15%) and (b) Pt/PC 950 (20%), catalysts.
**Figure S7**- CV curves of the catalysts used for the determination of EASA.

**Figure S8**- Representative ORR polarization curve showing different current regions.
**Figure S9** - LSV polarizations of commercial and synthesized catalysts with different Pt-Cu wt.% loading and LSV polarization of metal free carbon support.
Figure S10- Set of ORR polarization curves at different rotation speeds of Pt-Cu/PC 950 (15:15%).

Figure S11- Current-time response of the catalysts at 1.00 V in the presence of methanol.
**Figure S12** - Current-time response at 0.45 V vs. Ag/AgCl (a) and LSV curves at 10 mV s$^{-1}$ (b) of the catalysts in O$_2$-saturated methanol solution at 1600 rpm.

**Figure S13** - EIS response of the catalysts Pt-Cu/PC 950 (15:15%) spectrum-a, Pt/PC 950 (20%) spectrum-b and Pt/C (20%) spectrum-c (a) showing $R_{\text{elec}}$ (b) showing $R_{\text{ct}}$. 
Figure S14- TEM images of Pt-Cu/PC 950 (15:15%) before (a) and after (b) ADTs, TEM images of Pt/PC 950 (20%) before (c) and after (d) ADTs and TEM images of Pt/C (20%) (e, f) after ADTs.
**Characterization.** RIGAKU MiniFlex600 X-ray diffractometer (Cu Kα, λ = 1.544206 Å and at 40 kV and 15 mA) was used for PXRD analysis at a scan speed of 0.02 degree s⁻¹. For XPS surface analysis Kratos AXIS Ultra DLD instrument with background vacuum better than 2×10⁻⁹ mbar. The sample spot size were of 500 µm, Al Kα (energy hν = 1486.68 eV) was the radiation source and power of 164 W (10.8 mA and 15.2 kV) was used for each analysis. The adventitious carbon C 1s peak position were used as a reference. Autosorb iQ3 gas sorption analyzer (Quantachrome Instruments USA) was used for gas adsorption analysis. Each sample was degassed for 12 h at 200 °C under vacuum before analysis. The isotherms were run at liquid nitrogen temperature (77 K), BET model and DFT method were used to calculate surface area and porosity. TEM analysis were carried out using JEOL-JEM 2010F FE-TEM field-emission transmission electron microscope at a running voltage of 200 kV. Elemental analyses were performed on an ICAP 6000 Series ICP Spectrometer and 2400 Series II CHNS/O elemental analyzer.

**Electrochemical measurements.**

To perform the electrochemical measurements, electrode paste was prepared by taking 10 mg of each catalyst, suspended in 40 µL of analytical grade 2–propanol and 10 µL of Nafion 117 (binder) through sonication for 6 h to make homogenous slurry. The ink (10 µL) was applied on the surface of ring-disk electrode (RDE) properly covering the carbon disk (0.247 cm²) previously polished with alumina (0.3 µm), and the added paste was dried. The electrochemical experiments were performed using an electrochemical workstation (CH Instruments, Inc.) equipped with rotating electrode speed controller (PINE Research Instruments). Cyclic voltammetry (CV) measurements were carried out using three electrode cell assembly consist of catalyst paste coated RRDE (without rotation) as working, Ag/AgCl (3 mol L⁻¹ KCl), and Pt wire.
as reference and counter electrodes, respectively. The linear sweep voltammetric measurements (LSV) were carried out using four electrode cell assembly consist of carbon disk in RRDE with catalyst paste coated as 1st working electrode to measure the ORR, the Pt ring in RRDE as 2nd working electrode to record a voltammetric curve for H₂O₂ generation, Ag/AgCl (3 mol L⁻¹ KCl) as reference electrode, and Pt wire as counter electrode. All the potentials were converted to the reversible hydrogen electrode scale (RHE) and current densities were normalized by the surface area (0.2475 cm²) of the electrode. The electrochemical active area (EASA) of the catalysts was measured in HClO₄ solution (0.1 mol L⁻¹) at a scan rate of 50 mV s⁻¹. For ORR the electrolyte was HClO₄ solution (0.1 mol L⁻¹) saturated with O₂ at room temperature. The electrolytic cell was purged with 99.9% pure Ar for 5 min before each electrochemical experiment. The impedance measurements were carried out in the frequency range of 0.1 Hz to 10,000 Hz (at 10 mV as potential amplitude) in HClO₄ (0.1 mol L⁻¹) and methanol (1 mol L⁻¹) solution.