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Supporting Information

Functional Mesoporous Carbon Nanotubes and Their Integration in Situ with Metal Nanocrystals for Enhanced Electrochemical Performances

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Experimental Section

Synthesis: All the reagents used in the experiments were analytical grade (purchased from Sigma-Aldrich) and used without further purification. ZnO nanorods, which act as a template in the present work, were synthesized based on the method reported by Samulski et al. (*Chem. Commun.* **2004**, 986). For the synthesis of functional mesoporous carbon nanotubes (labeled as MCNTs in subsequent text), 150 mg of the as-synthesized ZnO nanorods, 300 mg of P123 and 182 mg of 2-amino-2-hydroxymethyl-propane-1,3-diol (Tris) were dissolved and dispersed in 150 mL deionized water by subjecting to about 10 min sonication, and then cooled down to room temperature. Subsequently, 300 mg of dopamine was added to the mixture with continuous stirring at room temperature for about 5 h. After that, the precipitates, i.e. polydopamine/ZnO, were collected by filtration, washed for several times with absolute ethanol and dried at 60 °C for 6 h. Finally, the resulting products were carbonized into mesoporous carbon/ZnO hybrid nanorods in flowing argon at 850 °C for 2 h. After the removal of ZnO nanorods in 1 M HNO_3 solution, MCNTs were obtained. For comparison, the closed carbon nanotubes (labeled as CCNTs in subsequent text) were synthesized using the same procedure only without the addition of P123.

For the synthesis of Pt/MCNTs, the above as-obtained polydopamine/ZnO hybrid nanorods were re-dispersed in ethylene glycol to form slurry. Then, chloroplatinic acid (H_2PtCl_6) was added and the slurry was then heated to approximately 140°C in a water-cooled condenser with vigorous stirring. After refluxing for 4 h, the precipitates were then centrifuged, washed, and dried overnight in air at 60 °C. Finally, the resulting products were carbonized into Pt/MCNTs/ZnO hybrid nanorods under flowing argon at 850 °C for 2 h. After the removal of ZnO nanorods in 1 M HCl solution, Pt/MCNTs were obtained.

Characterization: The as-prepared products were characterized with transmission electron microscopy (TEM; JEOL, JEM-2100F) operated at 200 kV and scanning electron microscopy (FESEM; JEOL, JSM-7600F) equipped with an energy dispersive X-ray spectrometer (EDX).

N_2 adsorption/desorption was determined by Brunauer-Emmett-Teller (BET) measurements using a Tristar-3000 surface area analyzer.

Electrochemical measurements were carried out on an Autolab PGSTAT30 potentiostat in 1 M H_2SO_4 using a three-electrode configuration. The as-synthesized carbon materials mixed with acetylene black and polytetrafluoroethylene (PTFE) binder at a mass ratio of 85:10:5 were coated onto the graphite paper (1 cm^2) as working electrodes. For a fuel cell device, a working electrode was prepared by a procedure described elsewhere.[22] Briefly, 5 mg of as-prepared Pt/MCNTs or commercially available E-TEK (Pt/C) were dispersed in 1 mL ethaol and 50 μL of 5 wt% Nafion solution by ultrasonication treatment for 10 min. Then a 10 μL catalyst ink was pipetted and spread on the glassy carbon disk. The electrolyte solution used was 1 M CH_3OH in 0.5 M H_2SO_4. In these two devices, a platinum foil was applied as a counter electrode with a standard Ag/AgCl electrode as a reference electrode.

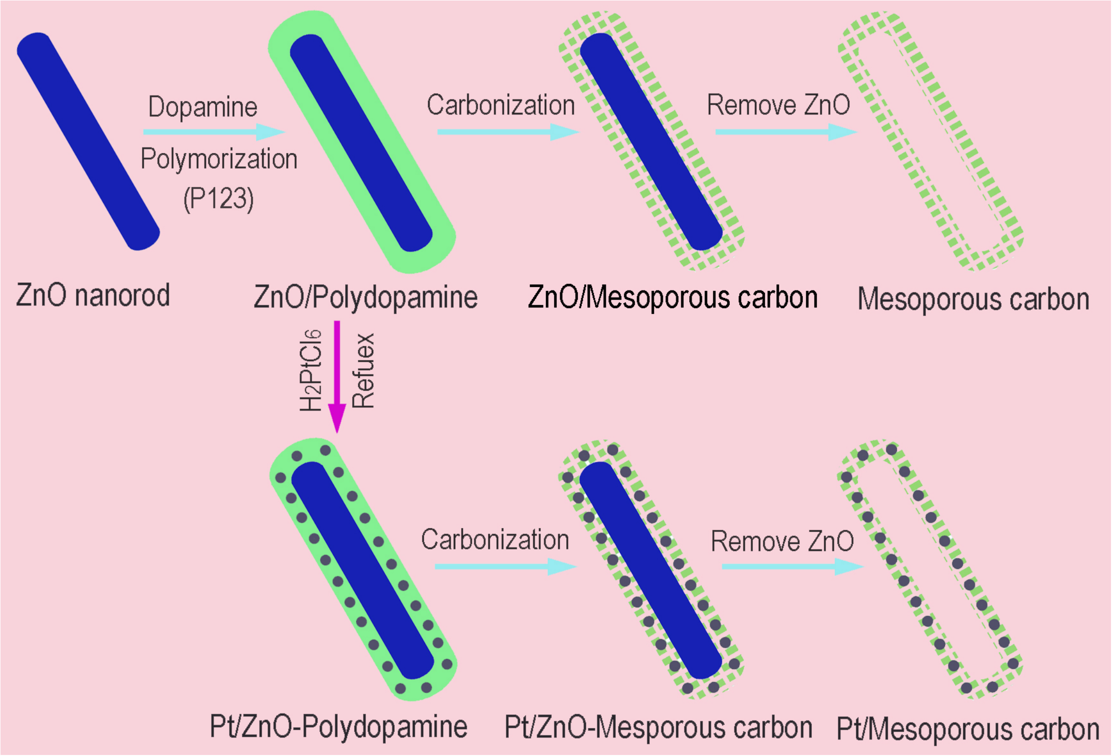

Fig. S1 Schematic diagram showing the strategy for the synthesis of functional MCNTs and their integration in situ with Pt Nanocrystals.

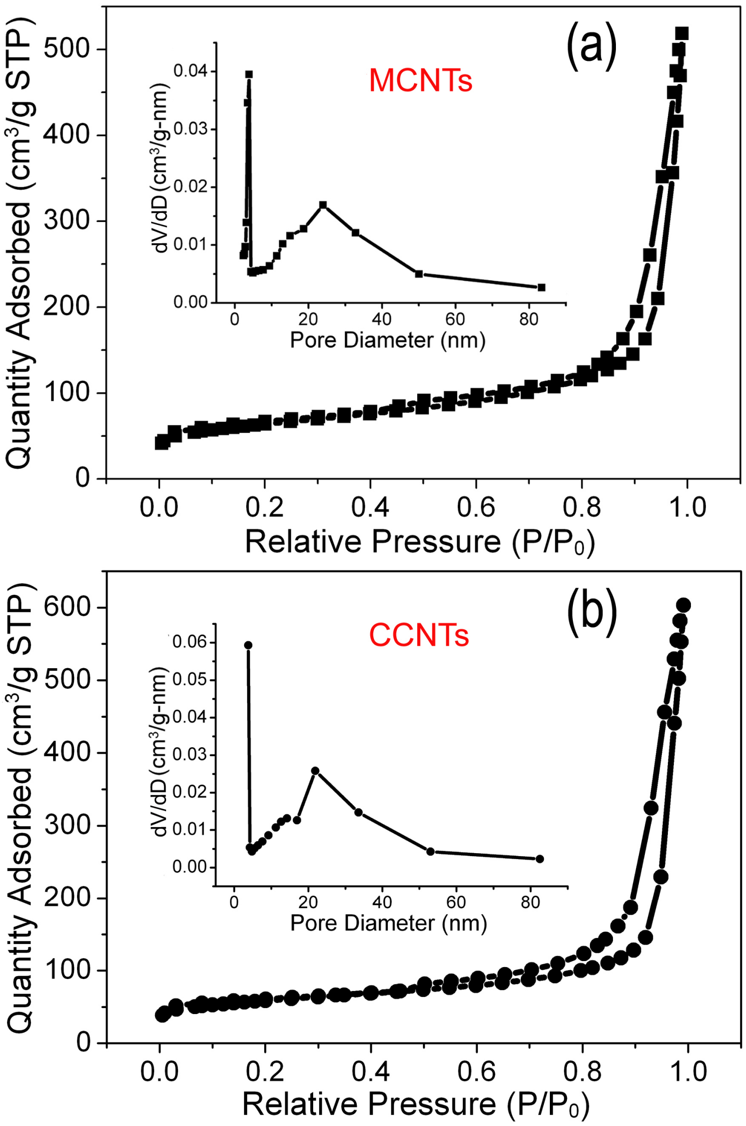

Fig. S2 Nitrogen adsorption and desorption isotherms and their corresponding pore-size distribution curves (insets) of MCNTs (a) and CCNTs (b), (Tristar-3000 surface area analyzer). The MCNTs also show a higher specific surface area of 224 m^2 g^{-1} than the CCNTs (205 m^2 g^{-1}). The isotherms show type IV characteristics with distinct hysteresis loop in the larger range of *ca.* 0.45–1.0 P/P_0, which suggests the existence of mesopores in MCNTs and CCNTs.[S1] The pore size distribution of MCNTs has mean values of 3.9 and 24 nm, respectively, and these BJH results are consistent with that of TEM observation. However, it is noted that there is no distinct mesoporous size distribution (usually 2~8 nm) observed for CCNTs. The larger pores in two samples are attributed to the tube spaces. It is expected that the MCNTs can reach a favorable balance between specific surface area and pore size distribution, which will make it excellent electrode materials and catalyst supports for high performance electrochemical energy storage and conversion applications. (S1: *Adv. Funct. Mater.* **2010**, *20*, 617.)

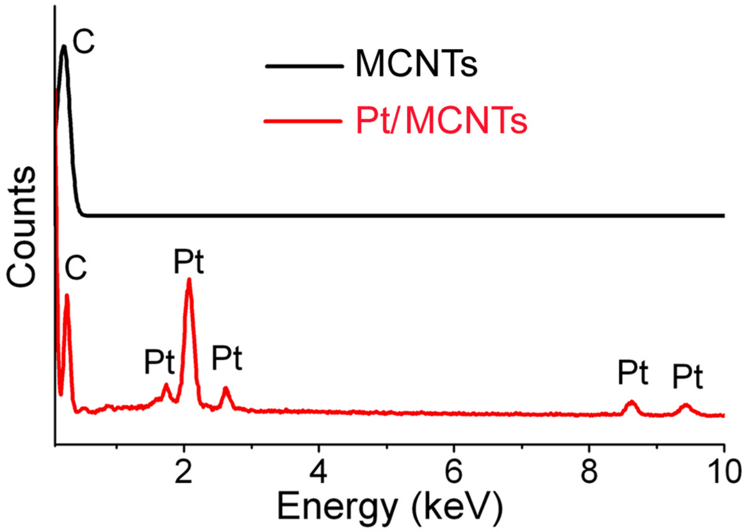

Fig. S3 EDX images of MCNTs (black line) and Pt/MCNTs (red line), respectively.

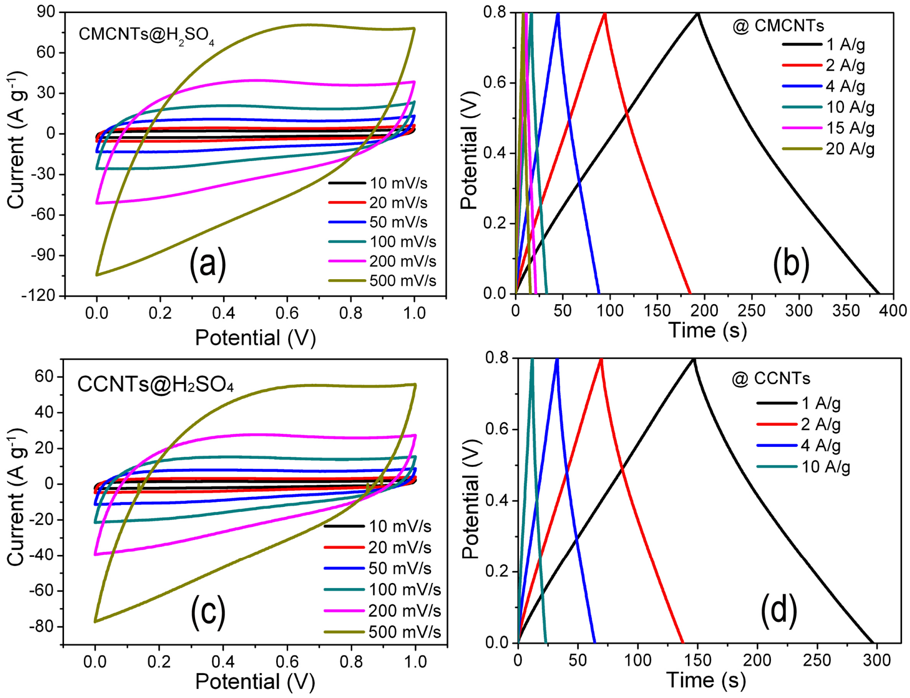

Figure S4 (a, c) CV curves of the CMCNTs and CCNTs at various scan rates from 10 to 500 mV s^{-1}. (b, d) charge/discharge curves of CMCNTs and CCNTs at different current density.

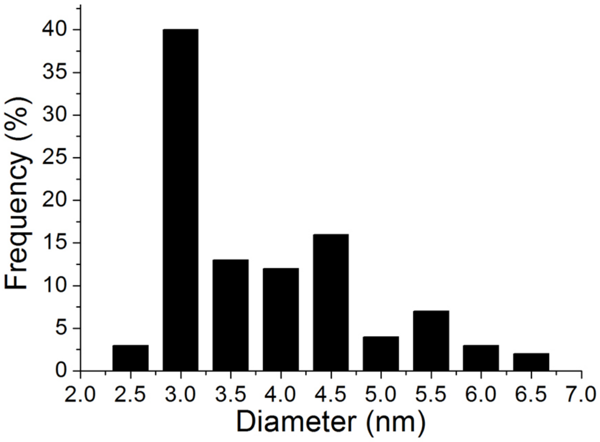

Figure S5 The diameter distribution histogram of Pt nanocrystals on the surface of MCNTs

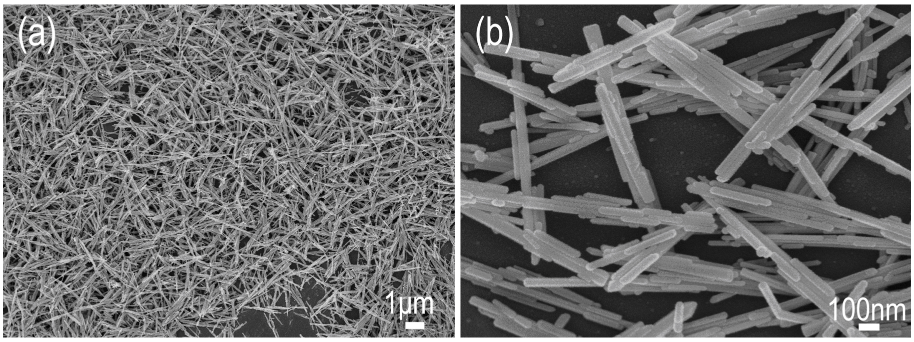

Figure S6 (a) Low magnification and (b) high magnification SEM image of ZnO nanorods, have been synthesized according to the method reported by Samulski et al. (*Chem. Commun.* **2004**, 986).