Supporting Information

Novel preparation of polyphosphazene-coated carbon nanotubes as a Pt catalyst support

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Experimental Materials

Hexachlorocyclotriphosphazene (HCCP, synthesized as described in the literature[1]) was recrystallized from dry hexane followed by sublimation (60 □, 0.05 mmHg) twice before use. The melting point of the purified HCCP was 113-114 □. 4,4'-(hexafluoroisopropylidene)diphenol (BPAF, purity > 99.5%) was purchased from Shanghai YiChao Chemical Co., Ltd. (Shanghai, China) and used without further purification. Multi-wall carbon nanotubes (MWCNTs, with a diameter of 15-20 nm and a length of 5-15 μm) was obtained from Beijing CNano Technology Limited (Beijing, China). Chloroplatinic acid (AR), triethylamine (TEA, AR), tetrahydrofuran (THF, AR) and absolute ethanol (AR) were purchased from Sinopharm Chemical Regent Co. Ltd. (Shanghai, China) and used directly.

Prepartion of Polyphosphazene-Coated MWCNTs

In a 100 mL round-bottomed flask, 20 mg of HCCP, 58 mg of BPAF and 5 mg of MWCNTs were dissolved into 80 mL of a mixed solvent of THF and absolute ethanol (20 : 1 by volume) and dispersed upon ultrasound (100 W, 40 KHz) for 10 min. The reaction began with the addition of 2 mL of TEA into the dispersion above and maintained in an ultrasonic bath (100 W, 40 KHz) at room temperature for 10 h. After that, the resulting precipitated product was isolated by centrifugation at 4000 rpm for 10 min, washed three times using ethanol and deionized water, respectively, and then dried at 80 ℃ to yield polyphosphazene-coated MWCNTs (PZAF/MWCNTs).

Deposition of Pt Nanoparticles on PZAF/MWCNTs with Ethylene Glycol as Reducing Agent

3 mL of the aqueous solution of 2 mg/mL chloroplatinic acid and 50 mL of ethylene glycol were added to a 100 mL round-bottomed flask. The pH value of the solution was adjusted to 10 with the ethylene glycol solution of sodium hydroxide. Then 20 mg of the PZAF/MWCNTs prepared before was dispersed into the above solution under ultrasound (100 W, 40 KHz) for 10 min. After that, the reaction was conducted at 160 □ for 6 h with magnetic stirring. When the system temperature dropped naturally to room temperature, the pH value of the dispersion was adjusted to 3-4 with sulfuric acid. Stirring continuously for 30 min and the resulting precipitated product was then isolated by centrifugation at 4000 rpm for 20 min, washed twice with ethanol and deionized water, respectively, and finally dried at 80 ℃ to yield Pt/PZAF/MWCNTs.

For comparison, Pt nanoparticles were also deposited on the pristine MWCNTs to yield Pt/MWCNTs via the same experimental procedure described above for preparing Pt/PZAF/MWCNTs, and the only difference is the replacement of PZAF/MWCNTs with MWCNTs.

Deposition of Pt Nanoparticles on PZAF/MWCNTs with Sodium Citrate as Reducing Agent

In a 150 mL round-bottomed flask, 2 mg of PZAF/MWCNTs was dispersed into 60 mL of a mixed solvent of THF and deionized water (1 : 2 by volume) under ultrasound (50 W, 40 KHz) for 10 min, following with the addition of 0.6 mL of the aqueous solution of 1.8 mg/mL chloroplatinic acid. 0.2 g of sodium citrate was dissolved into 20 mL of the mixed solvent of THF and deionized water (1 : 2 by volume), which was then slowly dropped into the above dispersion. The reaction was conducted for 10 h. After that, the resulting precipitate was isolated by centrifugation at 4000 rpm for 20 min, washed twice using ethanol and deionized water, respectively, and then dried at 80 ℃ to yield the target product.

Characterization

The high resolution transmission electron microscopy (HR-TEM) was performed with a JEM-2100 transmission electron microscope (JEOL Ltd., Japan) working at an accelerating voltage of 200 kV. The samples ultrasonically dispersed into absolute ethanol were placed a drop onto a copper grid coated with an amorphous carbon film and dried in air. The X-ray diffraction (XRD) measurements were carried out with a D/max-2200/PC X-ray powder diffractometer (Rigaku Corporation, Japan) with a Cu/Ka radiation source (40 kV, 20 mA). The diffraction patterns were recorded from 10º to 70º at a scanning rate of $5^{o}\cdot min^{-1}$. The water contact angles (CA) were measured on a Dataphysics OCA20 contact-angle system at ambient temperature. Water droplets (about

2.0 μL) were dropped carefully onto the sample surface. The contact angle value was obtained by averaging the contact angles of five different positions of the same sample. The standard deviation values were also calculated. The electrochemical performance of the as prepared Pt catalysts supported on the polyphosphazene-coated MWCNTs was measured by cyclic voltammetry (CV) at room temperature in a three electrode cell using Autolab PG302 electrochemical test system (Eco Chemie, The Netherlands). The working electrode was fabricated by casting Nafion-impregnated catalyst ink onto a glassy carbon electrode. 2.0 mg of the Pt/PZAF/MWCNTs sample was first ultrasonically dispersed into the mix of 0.5 mL of ethanol and 25 μL of ethanol containing Nafion solution (5 wt %, DuPont) for 10 min to form a catalyst ink. Then 10 μL of the catalyst ink was droped on the glassy carbon electrode and dried under infrared lamp. A platinum foil and a saturated calomel electrode (SCE) were used as the counter and the reference electrode, respectively. Electro-catalytic oxidation of methanol was carried out in the 0.5 M H_2SO_4 and 0.5 M CH_3OH aqueous electrolyte purged with high purity nitrogen gas to remove the oxygen in electrolyte with the scan rate of 50 mV/s. The electrochemical surface area of the Pt catalysts were estimated from the charges associated with hydrogen adsorption on Pt. All measurements were carried out at the room temperature.

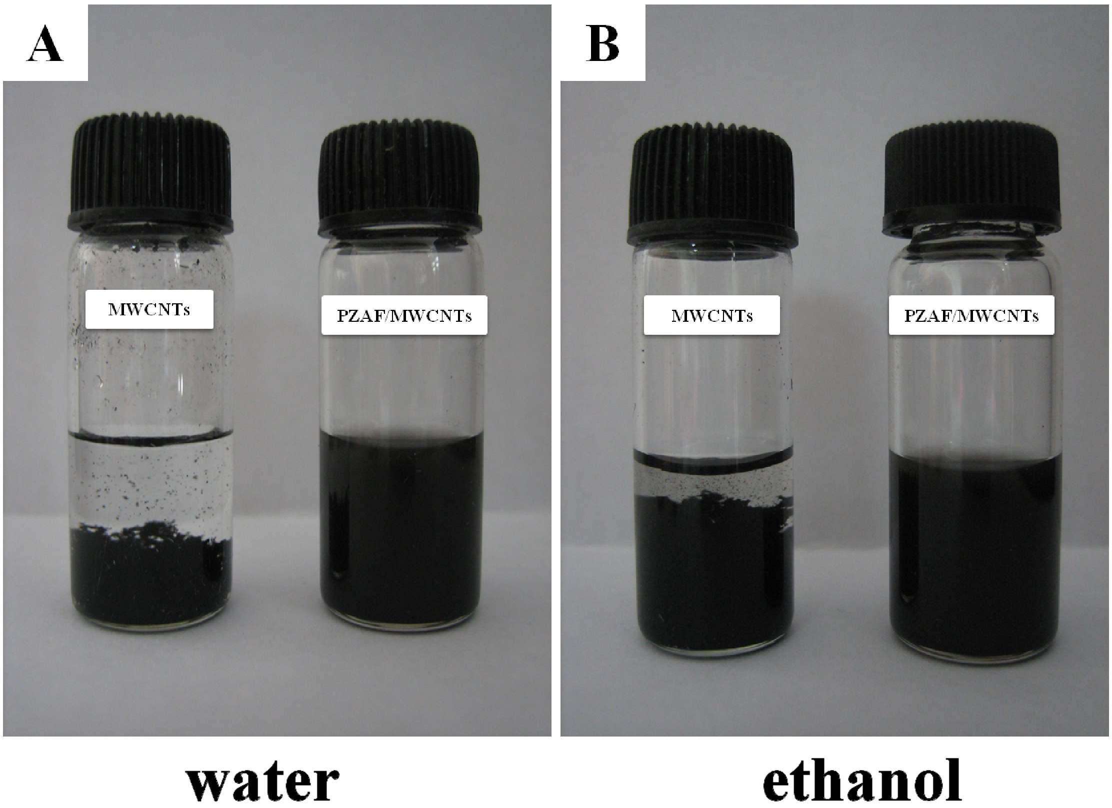

Fig. S1 Comparison of the dispersibility for PZAF/MWCNTs and MWCNTs: (A) in water, (B) in ethanol.

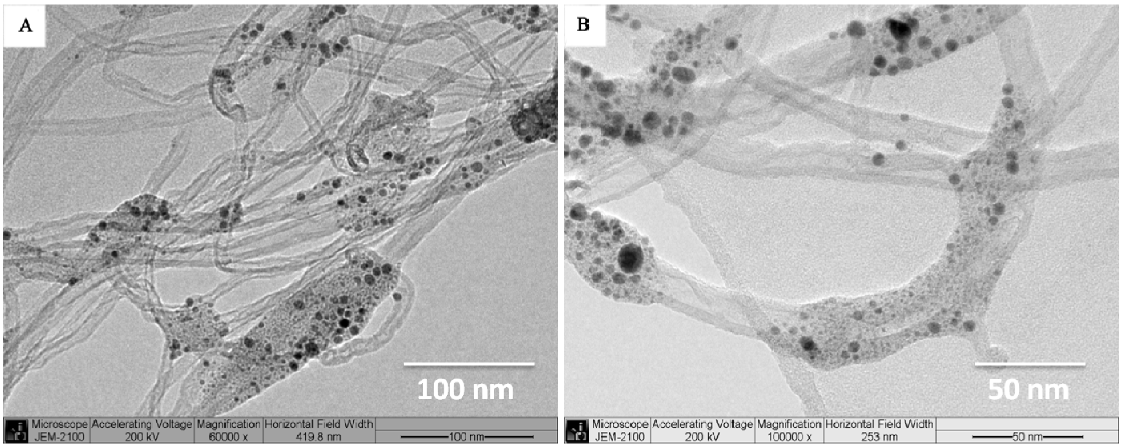

Fig. S2 TEM images of the deposition of Pt nanoparticles on PZAF/MWCNTs with sodium citrate as the reducing agent.

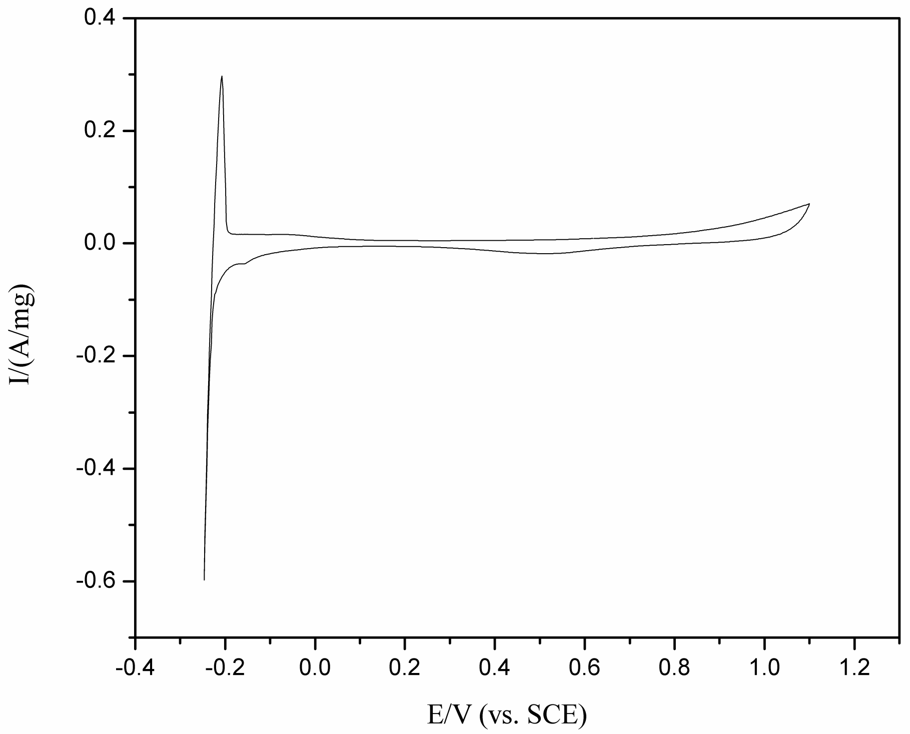

Fig. S3 Cyclic voltammogram of Pt/PZAF/MWCNTs in 0.5 M H_2SO_4 at a scan rate of 50 mV/s.

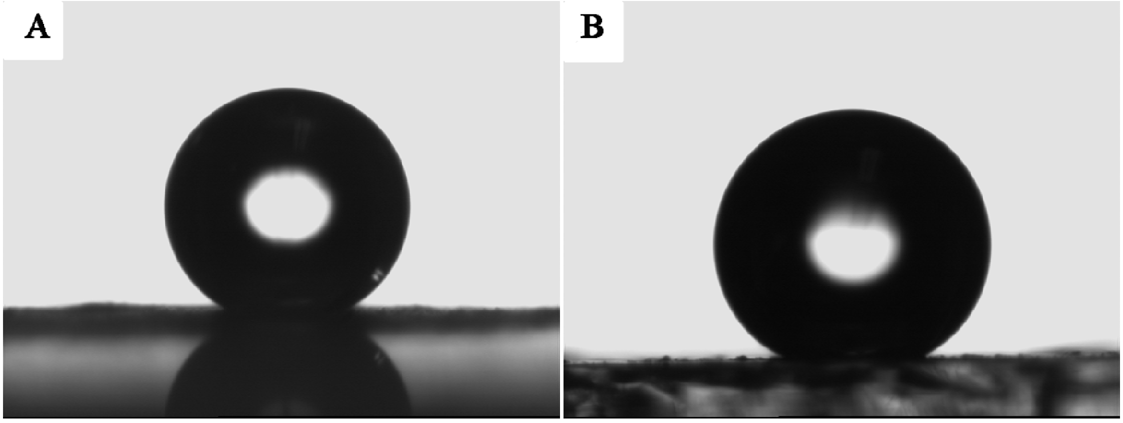

Fig. S4 The shape of a water droplet on the surface of (A) PZAF/MWCNTs and (B) pristine MWCNTs.

References

1. R. D. Jaeger, M. Gleria, *Prog. Polym. Sci.*, 1998, **23**, 179.