Improvement of the catalytic activity of PtRu bimetallic nanoparticles by a plasma treatment in their application of the ethanol electrooxidation

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Supporting Information

1. Experimental section

Materials Formaldehyde (HCHO, 37–40 wt%), hexachloroplatinic(IV) acid (H₂PtCl₆, AR), ruthenium (III) chloride (RuCl₃, GR), sodium hydroxide (NaOH, AR), ethanol were purchased from Shanghai Chemical Reagent Co. Ltd. Nafion solution DE520 (Dupont®, 5% in isopropanol and water). All the chemicals were used without further purification. The deionized (DI) water through Millipore system (Milli-Q®) with resistivity ~18.0 MΩ cm⁻¹ was used.

1.1. Preparation and purification of MWCNTs Multi-walled carbon nanotubes (MWCNTs) were prepared by chemical vapor deposition of acetylene in a hydrogen flow at 760 °C using Ni–Fe nanoparticles as catalysts.¹ These MWCNTs were then purified by a strong oxidant and calcined at 500 °C for 4 h under the argon atmosphere to remove carbon nanoparticles and carbonaceous impurities. The inductively coupled plasma-mass spectra (ICP-MS) indicated the contents of Ni and Fe used as catalyst in the synthesis of MWCNTs were less than 0.01 % and 0.03 %,
1.2. Plasma surface modification procedure The synthesis of plasma treated MWCNTs (PS-MWCNTs) was performed in a custom-built plasma generator induced by a radio frequency (RF) inductively coupled plasma (ICP) as reported in our previous work.\textsuperscript{2,3} Prior to ignition of the N\textsubscript{2} plasma, the pressure in the reactor was evacuated to 4.0 Pa. Pure N\textsubscript{2} gas was then introduced into the reactor via a gas mass flow controller (MFC) at a flow rate of 10 sccm. Plasma ignition occurred at \(~\)16 Pa with a frequency of 13.56 MHz and a supplied power of 150 W. MWCNTs were treated by N\textsubscript{2} plasma for 40 min under continuous stirring. The plasma treated MWCNTs possess a hydrophilic surface and can form a homogeneously dispersed solution in water.

1.3. Preparation of PtRu/PS-MWCNTs The PtRu/PS-MWCNTs catalysts were prepared by a HCHO reduction method as reported in ref. 4. Typically, predefined amounts of hexachloroplatinic acid (37 wt.% Pt) and ruthenium (III) chloride (40 wt.% Ru) were dissolved in deionized water. The obtained solution was adjusted to pH \(> 10\) with a 2.5 M aqueous solution of NaOH and mixed with 500 mg PS-MWCNTs, which was ultrasonicated and vigorously stirred at room temperature for 4 h, followed by adding excess HCHO (37–40 wt.%) and heating at 353 K for 1 h under constant stirring under a N\textsubscript{2} flow. The solids were then obtained by filtration, washed with excess deionized water and dried in vacuum at 353 K for 12 h.

1.4. H\textsubscript{2} plasma reduction of PtRu/PS-MWCNTs H\textsubscript{2} plasma reduction of the obtained PtRu/PS-MWCNTs catalysts synthesized above was performed in a custom-built plasma generator induced by a radio frequency (RF) inductively coupled plasma (ICP) as described in the previous section. Typically, 250 mg of the PtRu/PS-MWCNTs catalysts was introduced into the reactor. Prior to ignition of the H\textsubscript{2} plasma, the pressure in the reactor was evacuated to 4.0 Pa. Pure H\textsubscript{2} gas was then introduced into the reactor via a gas mass flow controller (MFC) at a flow rate of 10
Plasma ignition occurred at ~16 Pa with a frequency of 13.56 MHz and a supplied power of 150 W. PtRu/PS-MWCNTs catalysts were treated by H₂ plasma for 60 min under continuous stirring.

1.5. Characterization Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) investigations were carried out in a JEOL JEM-2000EX operating at 100 keV and a JEOL JEM-2011 equipped with an energy-dispersive X-ray (EDX) spectrometer using an accelerating voltage of 200 kV, respectively. The TEM samples were prepared by ultrasonic dispersion of a PtRu/PS-MWCNTs catalyst in ethanol for about 10 min, followed by dropping a small amount of the dispersion on a 400-mesh carbon-coated copper grid and letting it dry in air. X-ray diffraction (XRD) patterns were performed on a D/Max-III A X-ray diffractometer (Rigaku Co., Japan), using Cu Kα (λ_Kα1=1.5418 Å) as the radiation source to identify the crystalline structure. X-ray photoelectron spectra (XPS) of the composites were performed on a Thermo ESCALAB 250 electron spectrometer from VG Scientific using 150 W Al Kα as the exciting source. The XPS photoelectron binding energy (BE) of the adventitious carbon species, i.e., the C 1s line at 284.4 eV was used to correct the observed binding energies for surface charging. The deconvolution of the XPS spectra was by a least-square procedure to a product of Gaussian-Lorentzian functions after a background subtraction by using the software XPSPEAK.

1.6. Electrochemical measurements 1 M NaOH and 1 M NaOH + 1 M ethanol aqueous solution were selected as the electrolyte solutions for the electrochemically active surface area (ECSA) and ethanol electrooxidation measurements, respectively, and both solutions were deaerated with N₂ before measurements. The electrochemical measurements were measured at the scan rate of 50 mV s⁻¹ at 20 °C using an Autolab potentiostat/galvanostat (IM6e, Zahner, Germany) in a three electrodes and one compartment configuration cell. A Pt wire was served as the counter electrode and a KCl saturated Ag/AgCl electrode as the reference electrode. All potentials in this
work were quoted against Ag/AgCl (KCl (sat.)). A predefined amount of PtRu/PS-MWCNTs catalysts were added to 1 mL 2-propanol, which were then shaken for 30 min in an ultrasonic bath to form slurry. This slurry was brushed onto a piece of carbon paper (0.4 × 0.6 cm; HCP020P) and dried in an oven at 80 °C for 20 min to remove the solvent. The weight of the carbon paper with dried PtRu/PS-MWCNTs nanocomposites was measured and subtracted from that before coating of the slurry to obtain the loading of metal-carbon nanocomposites. Experiments were controlled so that PtRu/PS-MWCNTs catalysts were obtained the predefined amount of metal loaded on the electrode, which were later used as working electrodes for electrochemical measurements. A 100 μL amount of 5 wt% Nafion solution DE520 was spread on top of the carbon nanocomposite layer and dried at 80 °C. Nafion acted as a protective layer to prevent loss of catalyst powder into the electrolyte solution. The electrodes were activated by cycling the potential between -1.2 and 0.1 V versus Ag/AgCl for ECSA measurements and between -0.8 and 0.4 V versus Ag/AgCl for ethanol electrooxidation measurements.

2. Supplementary results

Fig. S1 Typical TEM images of the PtRu/PS-MWCNTs with higher magnifications before (a) and after (b) the H₂ plasma treatment.
Fig. S2 EDX spectrum of PtRu/PS-MWCNTs.

Fig. S3 XPS spectra for C 1s + Ru 3d in the PtRu/PS-MWCNTs before (a) and after (b) the H$_2$ plasma treatment.

The entire Ru 3d and C 1s envelopes were deconvolved, as shown in Fig. S3. The envelopes are fitted with a C 1s peak and two pairs of Ru 3d peaks, respectively, which are consistent with the results reported in literature.$^5$ The relative integration areas of the peaks indicate that metallic Ru(0) is another main species. However, the
shoulder at the low-energy side may be assigned as Ru oxide and amorphous RuO\textit{x}\textit{H}\textit{y} species.

References


