

Short communication

Radiation induced synthesis of Pt nanoparticles supported on carbon nanotubes

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Abstract

Pt nanoparticles supported on multi-walled carbon nanotubes (MWNTs) were obtained by γ -irradiation induced synthesis and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The Pt nanoparticles, which were uniform in shape and size and well dispersed on the carbon nanotubes, were 2.5–4.0 nm in diameter. Test runs on a single stack proton exchange membrane fuel cell (PEMFC) showed that these electrocatalysts are very promising for fuel cell applications.

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1. Introduction

Carbon nanotubes (CNTs), in addition to their unique physicochemical properties for applications in biology and medicine [1–4], can be used to template the construction of nanostructured materials [5–7], such as a catalyst support for catalyst metal particles to distribute outside the walls or fill in the interior [5–12]. Pt-based electrocatalysts are usually employed in proton exchange membrane fuel cells (PEMFC) and direct methanol fuel cells (DMFC). It is well known that catalytic activity of metals is strongly dependent on shape, size and size distribution of the metal particles [13]. And it is difficult to adequately control particle shape and size with conventional preparation techniques based on wet impregnation and chemical reduction of the metal precursors [13]. These techniques, however, have been used extensively so far to distribute Pt electrocatalysts on CNTs [8–10]. CNTs-supported metal particles can also be prepared by metal vapor deposition [14] and chemical reduction deposition in liquid phase [15,16], with undesirable control of the particle size, and morphology, which is also highly influential on the catalytic activity [13]. In view of these, increasing research inter-

ests arose in using advanced techniques based on microemulsions [17], sonochemistry [18,19], and microwave irradiations [20–24] to prepare colloidal metallic particles and clusters in especially nanometer scales with improved uniformity.

Radiation chemical method for colloid preparation is advantageous in comparison to chemical reduction of metal ions. Radiolytic synthesis avails by the fact that the main reducing agent in absence of oxygen is solvated electrons, hence a very negative redox potential. This enables the reduction of metal ions to zero valent state. Besides, without property-affecting interactions between the metal and surrounding molecules (solvent, ligand and surfactant, etc.), particle products from radiolysis are pure and highly stable [25].

In this paper, we report the synthesis of Pt nanoparticles supported on carbon nanotubes by using ⁶⁰Co gamma irradiation in the presence of surfactants and a scavenger. The synthesized Pt nanoparticles supported on carbon nanotubes were characterized by XRD. Size and structure of the nanoparticles were determined by SEM and TEM. The catalytic behavior of Pt/CNTs was test in a single stack fuel cell.

2. Experimental procedures

Multi-wall carbon nanotubes (MWNTs, 95% purity) prepared by chemical vapor deposition were obtained from Shen-

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zhen Nano Particles Co. Ltd., China. The MWNTs are several tens of micrometers in length and 60–100 nm in diameter. All the reagents were of AR (99% purity) grade and were purchased from Shanghai Chemical Reagent Corporation. Hispec 4000, a commercial Pt/Vulcan carbon catalyst (platinum, nominally 40% on carbon black, typically < 1 mg Pt cm⁻²) purchased from Alfa Aesar, was used for fuel cell comparison experiment.

To an aqueous solution of chloroplatinic acid, 2-propanol was added as a hydroxyl radical scavenger and sodium salt sulfonate was added as a surfactant. After 15 min of ultrasonic dispersion, the solution was deaerated by N₂ before being irradiated in a ⁶⁰Co source at a dose rate of 2 kGy h⁻¹. The synthesized Pt nanoparticles, being stable at room temperatures, were decorated uniformly on external wall of the MWNTs.

The catalysts obtained were examined by transmission electron microscopy (TEM, JEOL JEM 2010F). Metal contents in the samples were determined by energy dispersive X-ray analysis (EDX, OXFORD 7426). For microscopic examinations, the samples were ultrasonicated in ethanol for 0.5 h before deposited them on 3 mm Cu grids covered with a carbon film. The samples were also analyzed by scanning electron microscopy (SEM, LEO 1530VP) and X-ray diffraction (XRD, AD\max-2550) using Cu K_α-rays and a graphite monochromator. A single stack fuel cell was assembled from a membrane electrode assembly, two plumbago slabs with flow manifolds on the gas and water supply sides, and two silicone rubber gaskets. The electrode was prepared from a suspension containing 0.018–0.020 g of catalyst, 0.5 mL of ethanol and 0.5 mL of distilled water. The solution, after being blended ultrasonically for 1 h, was spread uniformly across the surface of a carbon paper substrate (Toray TGPH-090) with hydrophobic treatment by a PTFE latex, followed by drying at 90 °C for 1 h. Then 0.1 mL 5% Nafion solution was spread uniformly across surface of the catalyst on the carbon paper and dried at 90 °C for 1 h.

In this paper, different MEAs were prepared for electrochemical measurements using different electrode prepared by the same method. For an electrode area of 5 cm², the amount of dried catalyst suspension applied to the electrode varied between 4.0 and 4.5 mg, the amount of dry Nafion was about 5.0 mg. A single cell assembly was prepared by sandwiching a Nafion 112 membrane (DuPont) between the anode and cathode. The Nafion 112 membrane had been cleaned by immersing in 3% H₂O₂ for 1 h at 80 °C to remove organic impurities, and in 0.5 M H₂SO₄ for 1 h at 80 °C. The residual H₂SO₄ was removed by repeated washing in boiling distilled water. The assembly of the electrodes and membrane was hot pressed for 90 s between two stainless steel plates at 130 °C and 7.5 Mpa. The MEAs obtained, with an area of 5 cm², were tested in a fuel cell in ambient conditions. The electrochemical measurements of fuel cell were carried out in an Arbin FCT system. In order to maintain high ionic conductivity of the Nafion membrane, the hydrogen and oxygen gases passed through humidifiers before feeding the anode and cathode at a flow rate of 200 mL min⁻¹.

3. Results and discussion

It is well known that radiolysis of water forms radicals, which interact with solute ions. The solvated electrons formed in radiolysis reduce the dissolved metallic ions to metal (Eq. (1)) [25]:



These metal atoms form metal particles by self-assembly in liquid phase. By optimizing the compositions and experimental conditions of pH, dose and dose-rate, etc., the size and size distribution of the particles can be under control. The method has advantages of narrow size distribution of particles and no chemical reductants.

In our study, platinum nanoparticles were prepared and directly deposited on the CNTs surface by γ -ray irradiation. Size and composition of the alloy particles were analyzed by SEM, TEM and EDX measurements. Fig. 1a and b are typical SEM and TEM images of CNTs supported catalysts, showing a remarkably uniform and high dispersion of metal particles on the CNTs surface. The Pt particle size and size distributions on the CNTs were measured with 180 particles chosen randomly in the TEM images (Fig. 1c). They were in an average diameter of 3.1 ± 0.3 nm with a relatively narrow size distribution (2–6 nm). The radiation induced synthesis facilitated evidently formation of smaller and uniform Pt particles dispersed on the CNTs support, with the Pt content being 36.8 wt.% revealed by EDX measurements (Fig. 1d).

XRD measurements (Fig. 2) show characteristic patterns of Pt fcc diffraction. The 2θ values of the Pt (1 1 1) and Pt (2 2 0) peak were 39.92° and 67.88°, respectively. The average particle size, L can also be calculated with the diffraction peaks by the Scherrer equation [26]:

$$L = \frac{0.9\lambda_{K\alpha}}{(B_{2\theta} \cos \theta_B)} \quad (2)$$

where $\lambda_{K\alpha}$ is the X-ray wavelength (1.54187 Å for Cu K_α ray), $B_{2\theta}$ the broadening of diffraction line measured at half its maximum intensity and θ_B the angle corresponding to the peak maximum. From the calculation, the average size was 3.1 ± 0.3 nm, which agrees well with the TEM measurements. In spite of a small shift to a slightly higher value, X-ray scattering from the CNTs support was detected at around $2\theta = 24\text{--}26^\circ$.

The polarization curves of the membrane electrode assembly (MEA) based on Pt/CNTs and Pt/Vulcan carbon (Hispec4000) as the cathode catalyst layers are shown in Fig. 3. Pt/CNTs and Pt/Vulcan carbon (Hispec4000) based MEA exhibits quite similar performance in the single fuel cell. The voltage decreases sharply in the low current density region of the potential–current curve. This is generally known as activation polarization because of the sluggish kinetics intrinsic to oxygen reduction reaction at the cathode surface. The slower voltage decrease in the mid-to-high current density region, or ohmic polarization region, is due to limitations to proton transport through the electrolyte membrane from the anode to cathode, and/or limitations to electron-flow in the electrode materials. The slight deviation from linearity at the high current density end of

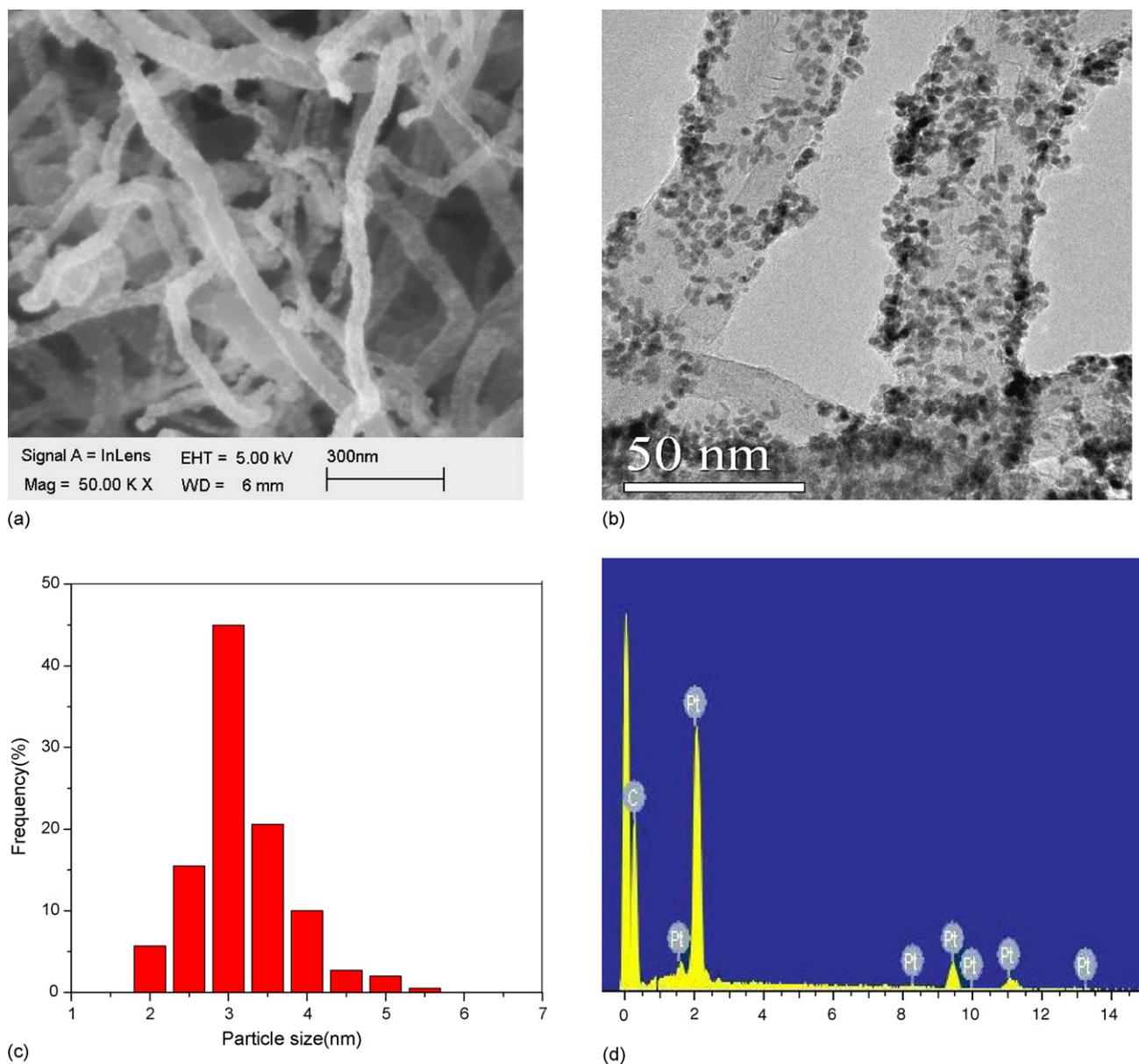


Fig. 1. Characterizations of radiation synthesized Pt nanoparticles on CNTs support. (a) SEM image, (b) TEM image, (c) the particle size distribution and (d) EDX spectra.

the polarization curves is due to intrusion of mass transfer effects.

To obtain more detailed information about the electrode kinetic parameters for the oxygen reduction in these electrodes, the experimental polarization data could be calculated by the semi-empirical equation proposed by Srinivasan and coworkers [27]:

$$E = E^0 - b \log i - Ri \quad (3)$$

$$E^0 = E_r + b \log i^0 \quad (4)$$

where E and i are experimentally measured cell voltage and current, E_r the reversible cell voltage, i^0 and b are the exchange current and the Tafel slope for oxygen reduction, respectively. R represents the total DC resistance, a summation of resistances in the polymer membrane and other electrode components

accountable for the linear variation of potential with current. The electrochemical process according to Eq. (3) is therefore only rate-limited by activation and ohmic polarizations. The experimental data were fitted to Eqs. (3) and (4) by a nonlinear least squares method. The kinetic parameters of the two electrocatalysts from regression analysis are summarized in Table 1. The two electrocatalysts have similar b values of ca. 0.06 V, which is common to most supported and unsupported Pt electrodes [28].

Table 1
Kinetic parameters from regression analysis of polarization

| Catalysts | E^0 (V) | b (V dec ⁻¹) | R (Ω cm ⁻²) |
|-------------------------------|-----------|----------------------------|-----------------------------------|
| Pt/CNTs | 0.796 | 0.050 | 0.369 |
| Pt/vulcan carbon (Hispec4000) | 0.789 | 0.074 | 0.469 |

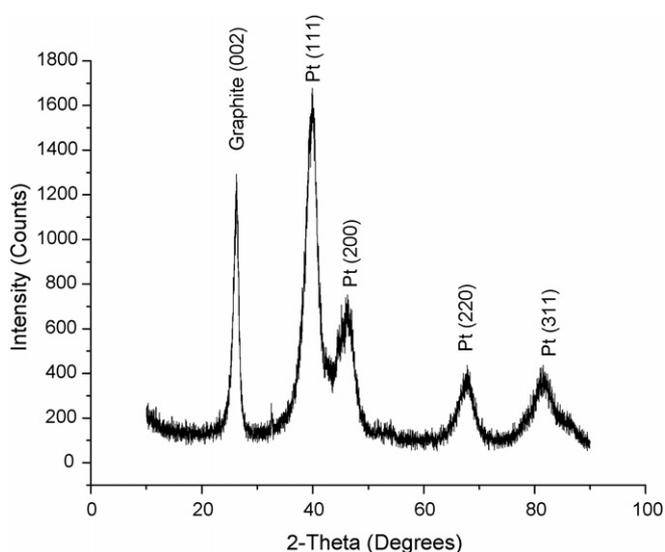


Fig. 2. XRD patterns of radiation synthesized Pt/CNT catalysts.

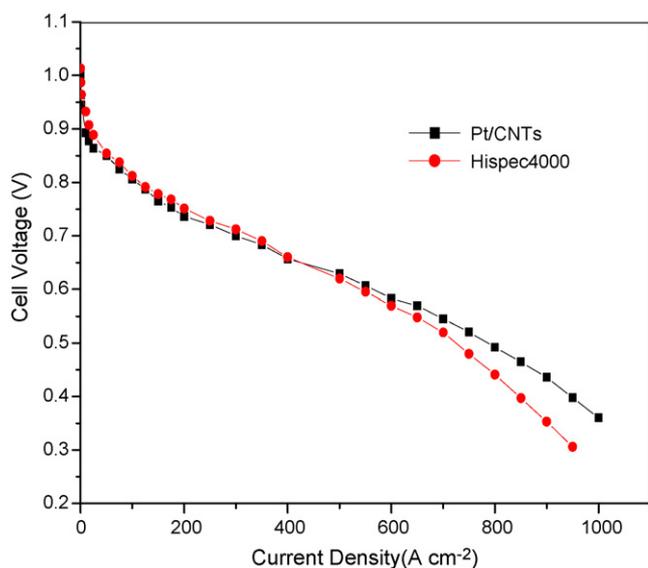


Fig. 3. Cell voltage versus current density plots of Nafion 112-coated electrodes prepared with 40 wt.% Pt/Vulcan carbon (Hispec4000) and 36.8 wt.% Pt/CNTs. $PO_2 = 15$ psi; $PH_2 = 15$ psi; $T_{cell} = 60$ °C.

4. Conclusion

In summary, we have demonstrated a simple, fast and effective method of preparing carbon-supported Pt nanoparticles as electrocatalysts for PEM fuel cell. The Pt nanoparticles, which were uniformly dispersed on CNTs, were 2.5–4.0 nm in diameters. The radiation induced synthesized catalysts showed high electrocatalytic activity tested by a single stack PEM fuel cell. And the results showed that the electrocatalysts are very promising for fuel cell applications.

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