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Electro-deposition of platinum nanoparticles on 4-mercaptobenzene-functionalized multi-walled carbon nanotubes

Jin Shi · Xin-Sheng Li · Yu-Qi Hu · Yi-Xin Hua

Abstract A new method to electro-deposit platinum nanoparticles on the surface of multi-walled carbon nanotubes (MWNTs) functionalized with 4-mercaptobenzene has been described. X-ray photoelectron spectroscopy results reveal that 4-mercaptobenzene was attached to the surface of MWNTs. Transmission electron microscope and X-ray diffraction analysis confirm that platinum nanoparticles were highly dispersed on the surface of MWNTs, and the average size of the platinum particle is 4.2 nm. The electrocatalytic properties of the Pt/MWNT composite electrode for methanol oxidation were investigated by cyclic voltammetry, and the results show that the fabricated composites exhibit high catalytic activity and good long-term stability. The study provides a feasible approach to fabricate Pt/MWNT composite electrode for direct methanol fuel cell.

Keywords Multi-walled carbon nanotube · Platinum nanoparticles · Chemical modification · Methanol oxidation · Fuel cell

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Introduction

Direct methanol fuel cell (DMFC) has attracted great interest as a possible power source in the future for many advantages, such as high energy density of methanol, low negative impact on the environment, and ease of maintenance [1]. However, there are several unsolved technical problems that hinder the commercialization of DMFC, including high loading of noble metal electrocatalyst, slow kinetics of electrode reaction, and crossover of methanol through membrane [2–7]. Platinum and its alloy have been recognized as the most powerful electrocatalyst for methanol oxidation [8–9]. Their catalytic activity is dependent on many factors, such as particle size [10], preparation methods [11–13], supporting materials [14], etc. Among these factors, supporting materials with high surface area are essential to reduce the loading of noble metal catalyst and improve the catalytic activity [15].

Carbon nanotubes (CNTs), because of their interesting properties, nanometer size, and high surface area, have been receiving increasing attention in recent years for their application in catalyst support [16]. However, since the surface of carbon nanotube is rather inert, to explore a feasible technique to activate the surfaces of CNTs is an essential prerequisite to deposit noble metal nanoparticles on CNTs [17]. Chemical functionalization of carbon nanotubes with organic molecules is a widely used way to anchor noble metal nanoparticles to the surface of MWNTs [18–20]. Many recent literatures have reported that aryl diazonium salts could react efficiently with individual carbon nanotube to form aryl-functionalized carbon nanotubes [21–24]. Organic thiol derivatives, on the other hand, are generally well known to interact strongly with platinum surfaces [25–26]. So in this work, we have chemically attached 4-mercaptobenzene to the surface of MWNTs and

then electro-deposited platinum nanoparticles on MWNTs. Thiol end was used to tether platinum nanoparticles to the sidewall of a nanotube.

Scheme 1 illustrates the procedures to deposit platinum nanoparticles onto the surface of the chemical-modified MWNTs. The first step depicts the covalent modification of MWNT with 4-mercaptobenzene. 4-Aminothiophenol reacts with isoamyl nitrite and produces aryl diazonium salt, which further reacts with the sidewall of MWNTs and generates aryl radical by liberating N_2. These radicals attack the sidewall of the carbon nanotube and led to nanotube–radical coupling subsequently [23, 27–28]. The second step illustrates the electro-deposition of Pt nanoparticles onto the surface of the functionalized MWNTs by taking advantage of the strong thiol–Pt interaction.

It should be stressed the aryl nature of a high degree of delocalization electrons in benzene ring of mercaptobenzene, which could facilitate electron tunneling and hence reduce the electrical resistance between Pt nanoparticles and MWNTs [27–28]. This factor is very important for the obtained hybrid nanostructure for their utilization in fuel cell.

Experimental

Chemicals

MWNTs made by the CVD method were purchased from Shenzhen Nanotech Port Company (China). The average diameter was about 10–20 nm and the length 5–15 μm. 4-Aminothiophenol and isoamyl nitrite were obtained from Meryer Chemicals. K_2PtCl_6, 1,2-dichlorobenzene, and K_2SO_4 were purchased from Beijing Chemicals. All the solvents are of analytical grade.

Chemical modification of MWNTs with 4-mercaptobenzene

In a typical experiment, 32 mg of MWNTs was added to 10 mL of 1,2-dichlorobenzene in a 50-mL round-bottom flask under sonication for 10 min [29]. A 0.32 g of 4-aminothiophenol was dissolved in 5 mL of acetonitrile. The obtained solutions were added into the 50-mL round-bottom flask. The mixed suspension was bubbled with nitrogen for 10 min, and then, 0.56 mL of isoamyl nitrite was added into the vigorously stirred suspension via a syringe. The obtained mixture was continually stirred for 15 h at 60 °C in an inert atmosphere. After being cooled down to room temperature, the resultant suspension was filtered through a PTFE (0.2 μm) membrane. The collected solid was washed extensively with dimethylformamide (DMF) until the filtrate becomes colorless. Excess unreacted 4-aminothiophenol and isoamyl nitrite must be removed thoroughly. DMF was removed by washing with sufficient absolute ethanol. The obtained solid was collected and dried under vacuum at ambient temperature for 4 h.

Preparation of MWNT paste electrode

The MWNT paste electrode was prepared by mixing the 4-mercaptobenzene-functionalized MWNTs with mineral oil in the ratio of 60.0 wt.% MWNTs and 40.0 wt.% mineral oil. The paste was carefully hand mixed in a mortar and then packed into a cavity (3-mm diameter, 2-mm depth) at the end of a Teflon tube. The electrode was provided by a copper wire connected to the paste in the inner hole of the tube. The paste was kept at room temperature in a desiccator until used.

Deposition of Pt nanoparticles on the chemically modified MWNTs

Electrochemical experiments were performed on CHI760C electrochemical working station in a three-electrodes system. The MWNT paste electrode was used as working electrode. A platinum sheet (geometric surface area = 1 cm^2) and a saturated calomel electrode (SCE) were used as the counter and reference electrodes. Pt nanoparticles were electro-deposited on the functionalized MWNTs in 1 mM K_2PtCl_4+0.1 M K_2SO_4 aqueous solutions.

Scheme 1 The procedure to electro-deposit platinum nanoparticles on the surface of MWNT via sidewall covalent chemical modification of MWNTs with 4-mercaptobenzene
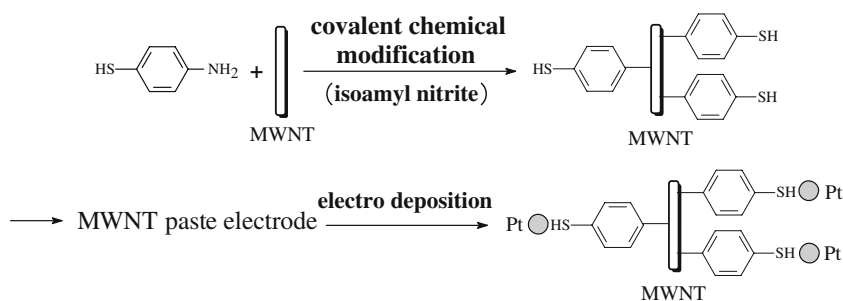
Measurements

X-ray photoelectron spectroscopy (XPS) analysis of the samples was performed on an ESCALab220i-XL electron spectrometer. The morphology of the synthesized Pt/MWNT composites was observed under transmission electron microscopy (TEM Hitachi 600) at 100 keV accelerating voltage. X-ray diffraction (XRD) data of the samples were collected using a Rigaku D/MAX 24000 diffractometer with Cu $K\alpha$ radiation.

Results and discussion

XPS analysis

Figure 1 shows the X-ray photoelectron spectroscopy (XPS) spectrum for the 4-mercaptobenzene-functionalized MWNTs. XPS results indicated that 4-mercaptobenzene was attached to MWNTs (binding energy of S 2p3/2 is 162.9 eV, with reference to C 1s at 284.6 eV) [30]. The surface elemental composition of MWNTs functionalized with 4-mercaptobenzene supplied by XPS analysis system is: C 95.18 at.% and S 4.82 at.%.

Electro-deposition of platinum nanoparticles on 4-mercaptobenzene-functionalized MWNTs

Figure 2 shows the cyclic voltammetry of the MWNT paste electrode in 1 mM K_2PtCl_4+0.1 M K_2SO_4 solution. According to the obtained results, platinum nanoparticles can be deposited on the surface of 4-mercaptobenzene-functionalized MWNTs at constant potential of 0 V, or by cyclic voltammetry [31–33]. The amount of platinum deposited on the paste electrode was calculated from the integral of the cathodic charge passed during the deposition process and estimated by assuming that reduction of Pt^{4+} to Pt^0 is 100% efficient. The obtained Pt/MWNTs paste electrode was employed as working electrode for methanol oxidation, and the maximum current density was achieved
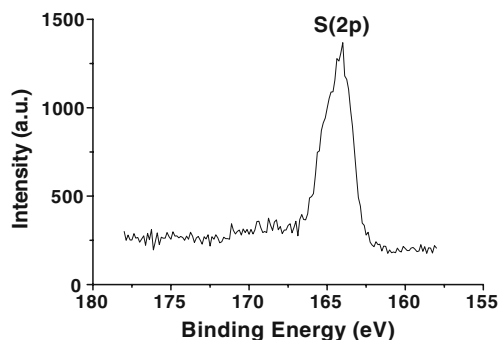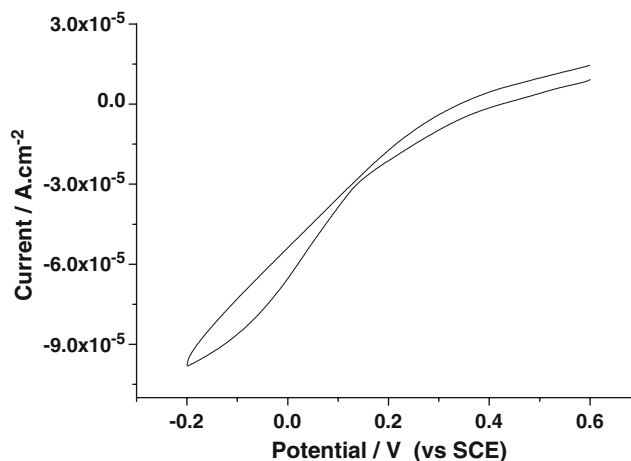
Fig. 2 Cyclic voltammogram of MWNTs paste electrode in 1 mM K_2PtCl_4+0.1 M K_2SO_4 aqueous solution. Scan rate: 50 mV/s (vs SCE)

with 18 μg/cm² of platinum deposited on the paste electrode. Hence in this work, the amount of platinum deposited on paste electrode was kept as 18 μg/cm².

TEM analysis of Pt/MWNT composites

As shown in Fig. 3, the TEM image shows that Pt nanoparticles have been well deposited on the surface of MWNTs with a diameter of 3–7 nm. It gives more evidence that 4-mercaptobenzene was attached to the surface of MWNTs.

TEM observation also shows that Pt nanoparticles remain attached to the surface of MWNTs even after sonication in water for 15 min. Adherence after sonication
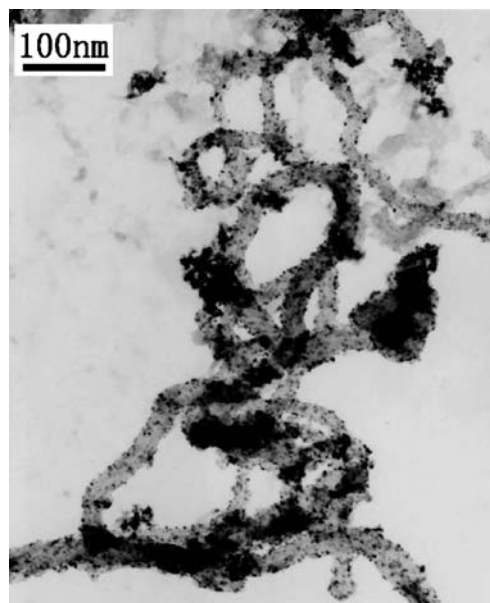
Fig. 1 XPS spectrum of the 4-mercaptobenzene-functionalized MWNTs

Fig. 3 TEM image of platinum nanoparticles electro-deposited on the surface of MWNTs functionalized with 4-mercaptobenzene
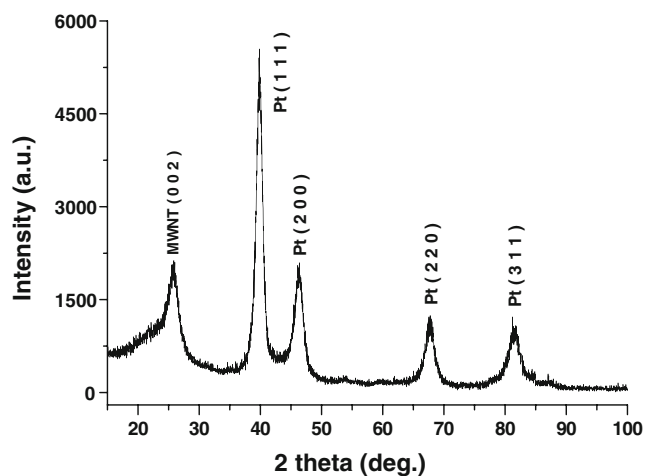
Fig. 4 X-ray diffraction (XRD) pattern of Pt/MWNT composites

supports the robust coupling of the Pt particles to MWNTs with 4-mercaptobezene acting as coupling agent.

XRD analysis of Pt/MWNT composites

The X-ray power diffraction (XRD) spectrum of Pt/MWNT composites is shown in Fig. 4. The peak at 26.2° is assigned to MWNT (002) [34]. The peaks at 39.7°, 46.2°, 67.4°, and 81.2° are assigned to Pt(111), (200), (220), and (311) crystalline plane diffraction, respectively [35].

According to the half-peak width for the Pt (220), from the Scherrer formula:

$$L = \frac{0.89\lambda}{B_{2\theta}\cos\theta_{\mathrm{B}}}$$

where L is the average particle size, λ is the X-ray wavelength (1.5418×10^{-10} m), $B_{2\theta}$ is the peak broadening,

Fig. 6 Relationship between the peak current of methanol oxidation (at 0.75 V vs SCE) and the amount of the platinum deposited on the 4-mercaptobenzene-functionalized MWNTs

and θ_{B} is the Bragg's angle of XRD peak; the mean particle size of the Pt catalyst is calculated to be 4.2 nm, which is in good agreement with the results from TEM imaging.

Electrochemical properties of Pt/MWNT composite electrode

Figure 5 shows the typical cyclic voltammograms of the obtained Pt/MWNT paste electrode in 0.5 M CH₃OH+ 0.5 M H₂SO₄ aqueous solutions. Curve (*a*) is recorded for the paste electrode which was fabricated by deposition platinum nanoparticles onto the 4-mercaptobenzene-functionalized MWNTs. The two peaks of methanol oxidation can be observed, and the peak potentials (Ep) are 0.5 and 0.75 V, respectively. The shape of the CV curves and the peak potential are in accordance with other work [36]. For comparison, we have deposited platinum on the original MWNTs without chemical modification. The fabrication process followed the same procedure as that to deposit
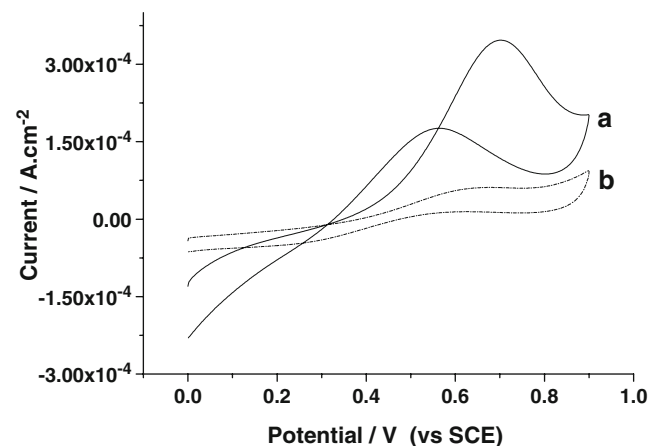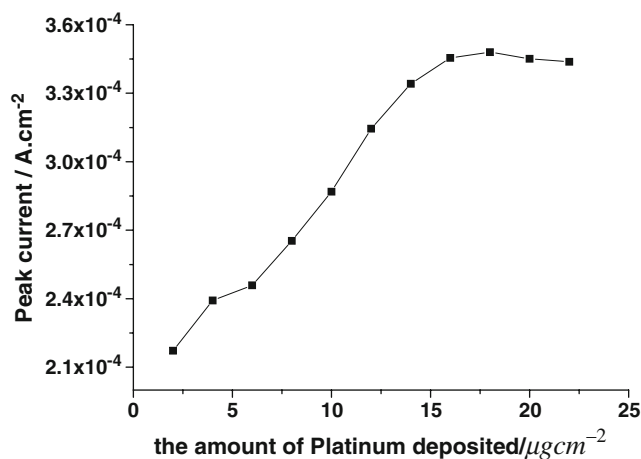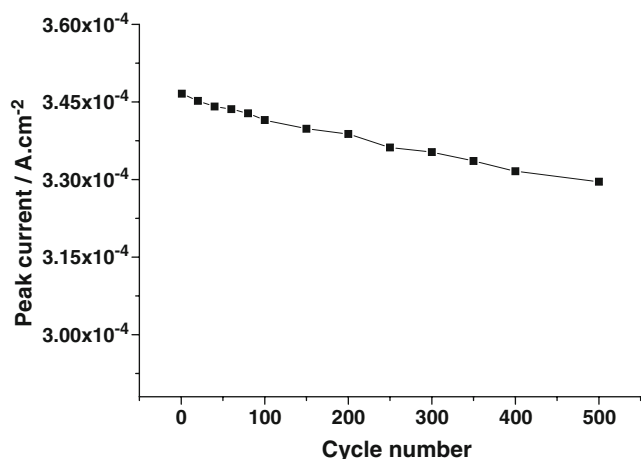

Fig. 5 Cyclic voltammogram of the Pt/MWNT paste electrodes: *a* platinum deposited on 4-mercaptobenzene-functionalized MWNTs; *b* platinum deposited on original MWNTs in 0.5 M CH₃OH+0.5 M H₂SO₄. Scan rate: 50 mV/s (vs SCE)

Fig. 7 Long-term stability of the Pt/MWNT paste electrode in 0.5 M CH₃OH+0.5 M H₂SO₄. Scan rate: 50 mV/s (vs SCE)

platinum on 4-mercaptobenzene-functionalized MWNTs. It is clearly observed that those platinum nanoparticles deposited on 4-mercaptobenzene-functionalized MWNTs exhibit significantly higher catalytic activity than that deposited on original MWNTs.

Influence of the amount of the platinum dispersed on functionalized MWNTs

The electro-activity for methanol oxidation depends on the amount of deposited platinum. Figure 6 presents the variation of the peak current density at 0.75 V as a function of the amount of platinum deposited on MWNTs. In this curve, the current density regularly increases up to 18 μg/cm^2, then reaches a plateau. After 18 μg/cm^2, the peak current density is slightly decreased. It is probably due to the formation of platinum clusters, leading to a smaller dispersion.

Long-term stability of Pt/MWNT composite electrode

The long-term stability of Pt/MWNT composite electrode was also investigated in 0.5 M CH$_3$OH+0.5 M H$_2$SO$_4$ solution. The results are shown in Fig. 7. It can be observed that the Pt/MWNT composite electrode prepared in our experiment has good long-term stability. The peak current density decreases gradually with successive scan, and the loss of the catalytic activity may result from the consumption of methanol during the CV scan. It also may be due to poisoning and the structure change of the platinum nanoparticles as a result of the perturbation of the potentials during the scanning in aqueous solutions, especially in the presence of the organic compound [37].

Conclusions

We have developed a new method to electro-deposit platinum nanoparticles on the surface of MWNTs via sidewall chemical modification of MWNTs with 4-mercaptobenzene. TEM and XRD analysis show that the platinum nanoparticles were highly dispersed on the surface of MWNTs, and the average particle size is 4.2 nm. The cyclic voltammetry results reveal that the obtained composites exhibit high electrocatalytic activity and good stability for methanol oxidation. The Pt/MWNT composites have a good potential application in direct methanol fuel cell.

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