



Preparation of dispersible double-walled carbon nanotubes and application as catalyst support in fuel cells

Zi Ping Wu^a, Bao Yu Xia^a, Xiao Xia Wang^b, Jian Nong Wang^{b,*}

^a Shanghai Key Laboratory for Laser Processing and Materials Modification, School of Materials Science and Engineering, Shanghai Jiao Tong University, 800 Dong Chuan Road, Shanghai 200240, PR China

^b Shanghai Key Laboratory for Metallic Functional Materials, Key Laboratory for Advanced Civil Engineering Materials (Ministry of Education), School of Materials Science and Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, PR China

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ABSTRACT

Dispersion of double-walled carbon nanotubes (DWCNTs) in ethylene glycol (EG) medium by a simple ultrasonication method is investigated. Excellent dispersion of DWCNTs in EG without addition of a surfactant is found. Surface structure and crystallinity of the DWCNTs undergo little change. The dispersion state of DWCNTs is found to be very important for deposition of Pt nanoparticles on them. The Pt particles prepared in the homogenous dispersion system has a small size and uniform distribution. As a result, the electrochemical activity of the Pt catalyst is much higher than that prepared in the nondispersible system. In terms of the good dispersion in EG medium achieved by a simple method, the DWCNT solutions could also be widely used in energy, biology, medicine and other fields.

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1. Introduction

Proton exchange membrane fuel cells with high energy conversion efficiency, high energy density, low noise, and no pollution for environment, are new power sources to replace conventional ones. However, the low electrochemical efficiency of noble metal platinum (Pt) limits further industrial application. Therefore, the focus is on improving Pt catalyst electrochemical activity [1]. The electrochemical activities of Pt catalyst are also significantly affected by catalyst support. The key properties of being a suitable support for electrocatalyst include electron conductivity, surface area, and corrosion resistance. Commercial amorphous carbon black Vulcan XC-72 (VXC-72) has been most widely used as catalyst support because of its high specific surface area ($\sim 200 \text{ m}^2 \text{ g}^{-1}$) [2,3]. However, poor crystallinity of amorphous carbon black prevents further improvement in electrochemical activity.

Due to the unique structure and high crystallinity, carbon nanotubes (CNTs) have become a main focus of many recent research efforts. Especially for single-walled or double-walled carbon nanotubes (SWCNTs or DWCNTs), they have high crystallinity and surface area [4–8]. But, SWCNTs or DWCNTs tend to aggregate into bundles due to the substantial Van der Waals attraction, and these bundles are usually entangled to form larger aggregates. The entan-

gling and aggregation lead to difficult dispersion and restrictive applications of CNTs in many fields.

Surface functionalization was applied to increase the dispersion of CNTs in aqueous or organic media, including covalent and noncovalent procedures. The covalent method is a chemical modification process. This method deteriorates the unique crystallinity of CNTs by formation of new covalent bonds on CNT walls [9,10]. It is well known that noncovalent functionalization such as surface wrapping of CNTs with polymeric chains [11,12] or surface coatings using low molecular surfactants [13,14] has been shown to be useful for improving dispersion without degradation of physical properties. But, the polymers or surfactants on CNTs must be removed for many applications.

Here, we present a simple method to disperse DWCNTs in ethylene glycol (EG) medium by ultrasonication. Homogeneous solution with a concentration of 0.15 mg mL^{-1} can be obtained and the crystallinity of DWCNTs in EG is not destructed. The dispersible DWCNTs are used as a support material for depositing Pt nanoparticles. The obtained Pt/DWCNT catalyst displayed an increased electrochemical activity when compared with conventional nondispersible DWCNTs.

2. Experimental

2.1. Dispersion of DWCNTs

The DWCNTs used in this study were prepared by a spray pyrolysis method and purified by a nondestructive approach as

* Corresponding author. Tel.: +86 21 65982867; fax: +86 21 65985385.
E-mail address: jnwang@tongji.edu.cn (J.N. Wang).

reported in our previous studies [15–17]. After purification and drying, DWCNTs were added in EG or water enclosed in beakers and then ultrasonicated. Ultrasonication was performed by a bath-type ultrasonic cleaner (power: 500 W). For each experiment, the beaker was placed at the same position of ultrasonicator in which the water level was kept constant. The temperature of the ultrasonicated water typically stayed around room temperature through cycling water.

2.2. Pt deposition on DWCNTs

Pt nanoparticles were deposited on the surface of DWCNTs in EG with a good dispersion state. The EG here acted as both a reducing medium as well as a dispersion medium avoiding the conglomeration of DWCNTs and Pt particles. In a typical experiment, chloroplatinic acid (H_2PtCl_6) with an accurately known content was added into DWCNT/EG solution, and then, the mixed solution was heated to 140 °C in a reflux device for 5 h. After having been cooled to room temperature, the as-received sample was then filtered, washed with excess deionized water and dried at room temperature in a low-vacuum system. For comparison, the as-purified DWCNTs in a bad dispersion state and the commercial amorphous carbon black VXC-72 were also used as support materials in this study. The Pt loading was controlled to be 50 wt.% (weight percentage).

2.3. Characterization of the samples

The microstructure of the samples was studied using transmission electron microscopy (TEM) and high resolution TEM (HRTEM) (JEOL 2100F, accelerating voltage of 200 kV). Energy dispersive X-ray spectroscopy (EDS) was used to analyze the chemical com-

position of the selected area. Field emission scanning electronic microscopy (SEM, FEI Sirion 200) was used to evaluate distribution of purified and dispersed DWCNTs. SEM samples were prepared as follows: 2 μL DWCNTs/EG solution was dropped and spread onto a 10 mm² silicon wafer. EG was evaporized at 200 °C under the protection of Ar gas for 30 min. The chemical compositions on the surface of purified DWCNTs before and after being dispersed in EG were qualitatively analyzed by attenuated total reflection Fourier Transform Infrared (ATR-FTIR) technique using Bruker Equinox 55 equipped with DTGS detector at 4 cm⁻¹ resolution. Raman spectroscopy was carried out to examine the perfection of DWCNTs before and after dispersion using a Horiba Jobin Yvon HR 800UV with the 514.5 nm excitation wavelength laser. The crystal structure was analyzed by X-ray diffraction (XRD, D8 Advance, Bruker) using Cu K α radiation. Size of Pt particles was calculated by using the well-known Scherrer formula [18] and estimated from a number of TEM images.

2.4. Electrochemical measurements

The electrochemical activities of the catalysts were characterized by cyclic voltammetry (CV). The experiments were performed in a three-electrode cell using an EG&G potentiostat (CHI618C) at room temperature. Working electrodes were prepared by coating catalyst and 5% Nafion mixture in ethanol on a glassy carbon cylinder with a diameter of 3 mm. The Pt loading on the working electrode was controlled to 0.2 mg cm⁻². A Pt foil was used as the counter electrode, a saturated calomel electrode (SCE) was used as reference electrode, and 0.5 M H_2SO_4 was used as the electrolyte. The CV profiles were recorded at a scan rate of 100 mV s⁻¹ from the potential of -0.241 to 0.999 V vs. SCE.

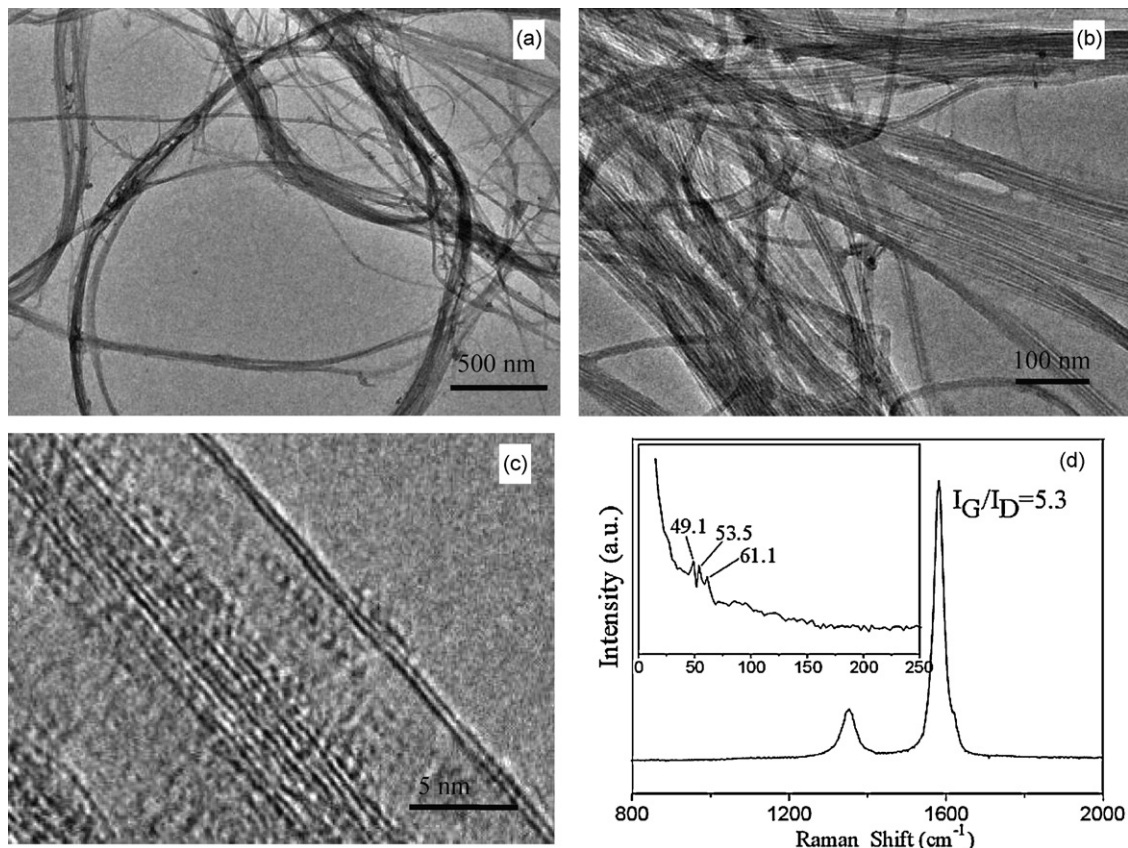


Fig. 1. Typical TEM (a and b), HRTEM images (c), and Raman spectra (d) of the as-purified DWCNTs.

3. Results

3.1. Microstructure of the purified DWCNTs

The microstructures of the purified DWCNTs were examined by TEM and HRTEM, and results are shown in Fig. 1. The bundles of DWCNTs can be seen clearly in Fig. 1a and b, whose diameter was $\sim 10\text{--}200\text{ nm}$. Fig. 1c shows a typical HRTEM image of DWCNTs. The diameter of the DWCNTs is $\sim 6\text{ nm}$. The purified DWCNTs were further characterized using Raman spectroscopy. In the high frequency region, the Raman spectrum contains two main peaks (Fig. 1d). The G-band at about 1580 cm^{-1} is associated with tangential modes in pure sp^2 hybridized graphitic carbon, while the peak of D-band at about 1350 cm^{-1} is due to disordered sp^3 type defects. The ratio of the intensities of the G- and D-bands, I_G/I_D , is a crude measure of the perfection of the graphitic structure of the nanotube. This intensity ratio for the purified DWCNTs is measured to be about 5.3, indicating that the DWCNTs have a very good graphitic structure. In the low frequency region, three main radial breathing mode (RBM) peaks can be found at $49.1, 53.5, 61.1\text{ cm}^{-1}$ (Fig. 1d, inset). It is well known that the RBM strongly depends on the tube diameter, and the tube diameter (d) can be estimated accordingly [19]. These peaks suggest that the diameter of the present DWCNTs is in the range of $3.8\text{--}6\text{ nm}$, which is consistent with the HRTEM observation. The specific surface area of the purified DWCNTs is $180\text{ m}^2\text{ g}^{-1}$ measured by nitrogen (at 77 K) adsorption and desorption, similar to that of commercial amorphous carbon black VXC-72.

3.2. Dispersion of DWCNTs in liquid media

Fig. 2a shows the dispersion characters of the DWCNTs in EG and water media after ultrasonication for 24 h. If deionized water was used as the dispersing medium, the as-purified DWCNTs could not be dispersed even by long-time ultrasonication (longer than 24 h) as shown in Fig. 2a (right). While in the case of EG, a homogeneous solution can be obtained even after standing for 72 h (Fig. 2a left). These results indicate that EG is an excellent dispersing medium for DWCNTs.

Fig. 2b shows dispersion of the DWCNTs in EG at different concentrations after ultrasonication for 24 h and then standing for 72 h ($0.15, 0.05, 0.02, 0.01\text{ mg mL}^{-1}$). In these solutions, DWCNTs dispersed homogeneously and stably in EG medium, and no agglomeration or settling can be observed. Then, the DWCNTs in the solution with a concentration of 0.15 mg mL^{-1} was filtered, washed and dried. The obtained DWCNTs were re-dispersed in EG and water media at a concentration of 0.05 mg mL^{-1} . As Fig. 2c shows, if EG was used as the dispersing medium, homogenous solution can be obtained again after slight ultrasonication. Visual inspection of this solution revealed no indication of aggregation and settling of DWCNTs after standing for 72 h (Fig. 2c left). However, when water was used as the dispersing medium, only a very small quantity of DWCNTs can be dispersed homogeneously with a very low concentration as the solution shows very light grey color (Fig. 2c right), and most DWCNTs settled at the bottom of the solution.

Fig. 3 shows SEM images of the as-purified DWCNTs and those dispersed in EG. As can be seen, the as-purified DWCNTs presented as dense bundles, and most of them had lengths of more than $5\text{ }\mu\text{m}$ (Fig. 3a). However, after ultrasonication in EG, DWCNT bundles had lengths of $1\text{--}2\text{ }\mu\text{m}$ (Fig. 3b and c). These results indicate that ultrasonication in EG solution not only made the DWCNTs dispersed but also shortened.

To further study the possible surface modification and crystallinity of the DWCNTs dispersed in EG, the ATR-FTIR technique and Raman spectroscopy were used. Fig. 4 shows ATR-FTIR spectra of the DWCNTs before and after being dispersed in EG. The two samples show the same ATR-FTIR spectra. This means that no new

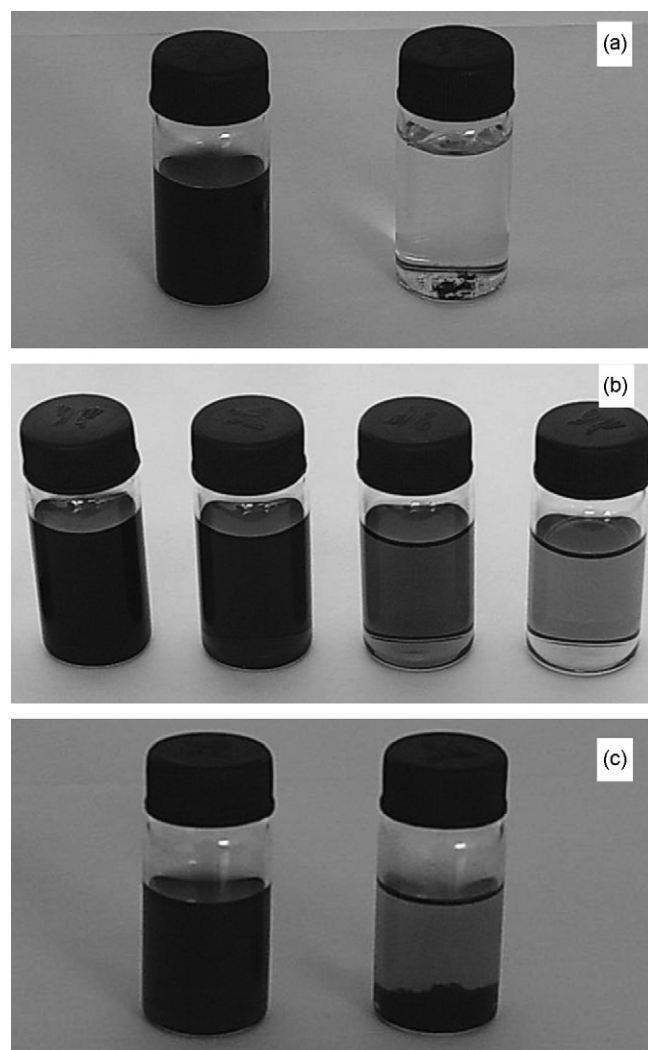


Fig. 2. (a) Dispersion of the purified DWCNTs in EG (left) and water (right) after ultrasonication for 24 h and then standing for 72 h. (b) Homogenous DWCNT/EG solutions with different concentrations, from left to right: $0.15, 0.05, 0.02, 0.01\text{ mg mL}^{-1}$. (c) DWCNTs from previous dispersion treatment and now in EG (left) and water (right) with a concentration of 0.05 mg mL^{-1} after ultrasonication for 1 h and then standing for 72 h.

functional groups were introduced on DWCNTs by the dispersion treatment. The characteristic peaks at 3550 and 3600 cm^{-1} could be attributed to O–H stretching and peaks at 1620 and 1850 cm^{-1} are attributed by $\text{C}=\text{O}$ stretching. This observation suggests that there had been some oxygenous groups on the surfaces of the DWCNTs before dispersion, which might be induced in the purification or synthesis process. Fig. 5 shows the Raman spectrum. The intensity ratio of the I_G/I_D is measured to be about 5.0, which is similar to that for the as-purified sample (5.3). The above results suggest that the surface structure and crystallinity of the DWCNTs after dispersion treatment in EG are similar to as-purified DWCNTs.

3.3. Pt nanoparticles deposited on DWCNTs

Pt nanoparticles were deposited on the DWCNTs, which was homogeneously dispersed in EG solution with different concentrations, such as 0.05 mg mL^{-1} (5DWCNT) and 0.15 mg mL^{-1} (15DWCNT). Fig. 6 shows the TEM and HRTEM images of Pt/15DWCNT catalyst prepared in homogenous DWCNT/EG systems. Pt particles were generally uniformly precipitated on the DWCNTs as displayed in Fig. 6a–d, and EDS result (Fig. 6e) indicated

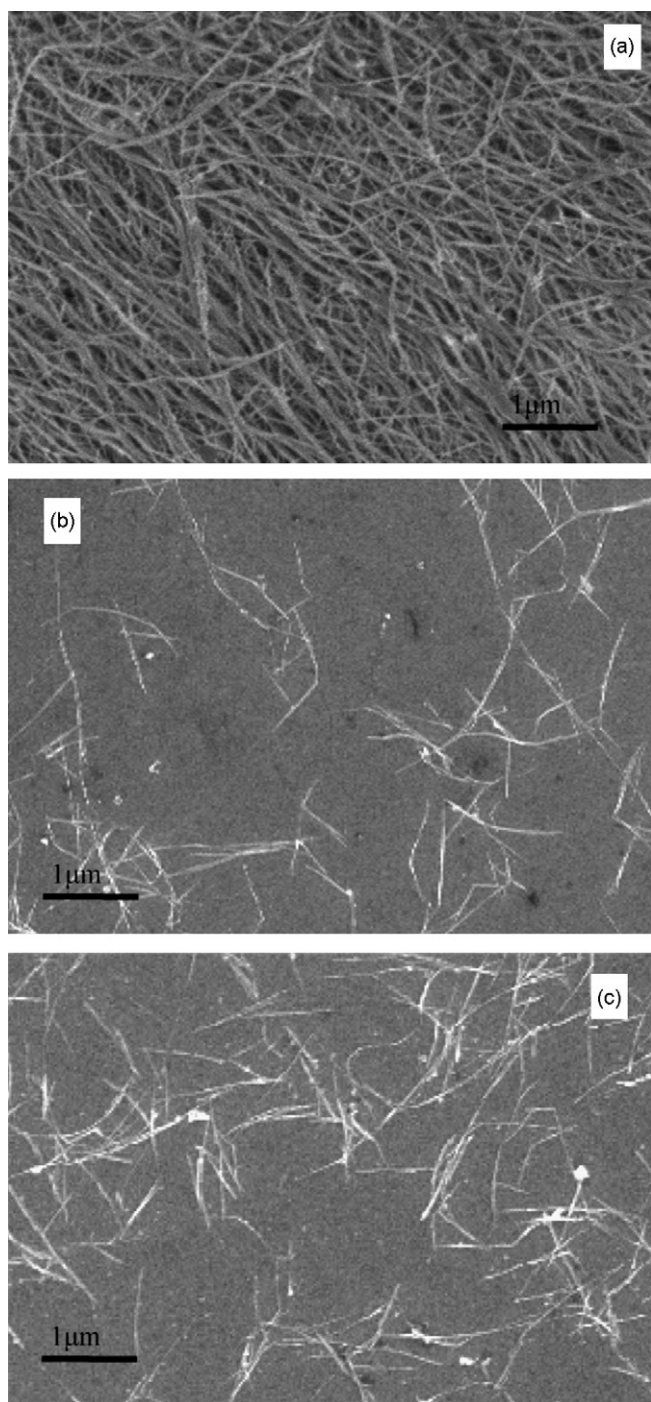


Fig. 3. SEM images of (a) as-purified DWCNTs, (b) DWCNTs deposited on Si wafers from 0.05 mg mL^{-1} DWCNT/EG solution, (c) from 0.15 mg mL^{-1} DWCNT/EG solution.

that the Pt loading is about 50 wt.% (the selected area in Fig. 6a). Statistic estimation counted from more than one hundred particles revealed that the mean size of the Pt particles was about 3.2 nm (Fig. 6f). The value is in close agreement with that estimated from the Scherrer formula based on the XRD data (3.08 nm) showed in Fig. 7. The Pt particle size of Pt/5DWCNT catalyst is similar to that of Pt/15DWCNT (not shown here), which is consistent with XRD data.

For comparison, the same amount of Pt was also deposited on the as-purified DWCNTs with low dispersion in EG ($\sim 0.15 \text{ mg mL}^{-1}$) and a commercial amorphous carbon black VXC-72 dispersed homogenous in EG with a concentration of 0.15 mg mL^{-1} . Fig. 8 illustrates the electrochemical activities of the

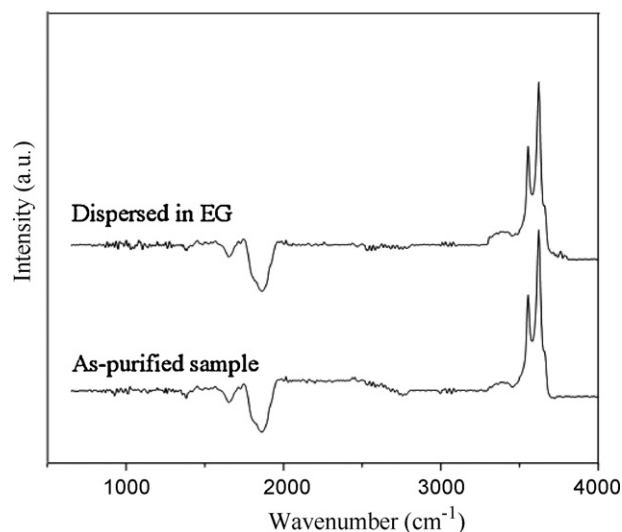


Fig. 4. ATR-FTIR spectra of DWCNTs before and after dispersion in EG.

prepared catalysts. As can be seen, the catalysts of Pt/15DWCNT and Pt/5DWCNT demonstrate apparently stronger hydrogen desorption and adsorption peaks (0.019 A cm^{-2}), and thus a higher activity than the catalyst supported on the as-purified DWCNTs (0.009 A cm^{-2}) and VXC-72 (0.013 A cm^{-2}).

4. Discussion

The present results expressly reveal that EG is a perfect dispersing medium to disperse DWCNTs. CNTs are hydrophobic materials [20,21], and thus only the liquid medium with a low surface energy can infiltrate their surfaces. But water is the material with a high surface energy (72.8 mN m^{-1}). In addition, the DWCNTs are composed of entangled bundles with long lengths. Even after some hydrophilic functional groups introduced on the surface (Fig. 4), the DWCNTs are still difficult to be dispersed in water after long-time ultrasonication (Fig. 2a right). EG was found to be a perfect dispersing medium for DWCNTs. This may be attributed to factors as follows. First, EG has a lower surface energy of 47.9 mN m^{-1} than water. With increasing the ultrasonication time, more EG liquid could be pushed into the spaces in DWCNT bundles, making the bundles inflate to a fluffy structure. This structure facilitated the

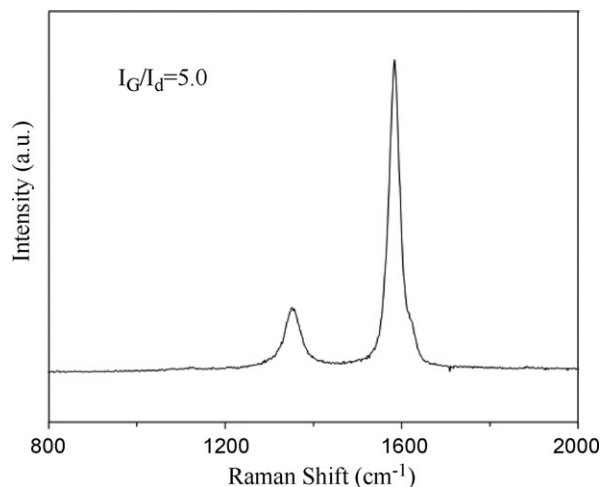


Fig. 5. Raman spectrum of the DWCNTs after dispersion in EG.

uniform distribution of mechanical stress produced by ultrasonication. As a result, bundles could be peeled or broken into smaller ones easily [17]. Comparing the TEM images of the purified DWCNTs (Fig. 1a and b) and those after Pt loading (Fig. 6a), the diameter of DWCNT bundles decreased to some extent. Meanwhile, mechanical force shortened the length of the bundles. The length change of the DWCNT bundles before and after dispersion in EG is demonstrated clearly in Fig. 3. In addition, EG has a much higher viscosity (21 mPa s) than water (1 mPa s). Therefore, the settling of finer and shorter bundles would be limited. Thus, thermodynamically stable solution could be kept for more than 72 h as Fig. 2b shows. But the exact reason for the dispersion of DWCNTs in EG but not in water needs further investigation.

The large improvement in electrochemical activity for the catalysts of Pt/5DWCNT and Pt/15DWCNT may be attributed to the small size of Pt particles and their uniform distribution on the surfaces of DWCNTs, which may be a result of the homogenous dispersion of DWCNTs in the reaction solution. This is an important requirement for uniform deposition of Pt nanoparticles on the surfaces of DWCNTs. If the deposition reaction was carried out in a nondispersible DWCNT/EG solution, Pt particles would deposit inhomogeneously and aggregate easily to form bigger particles. This is demonstrated by the much stronger diffraction peak (2 2 0) of Pt/(as-purified DWCNT) than those for Pt/5DWCNT and Pt/15DWCNT (Fig. 7). The specific surface area of DWCNTs is similar to commercial amorphous carbon black VXC-72, but HRTEM and

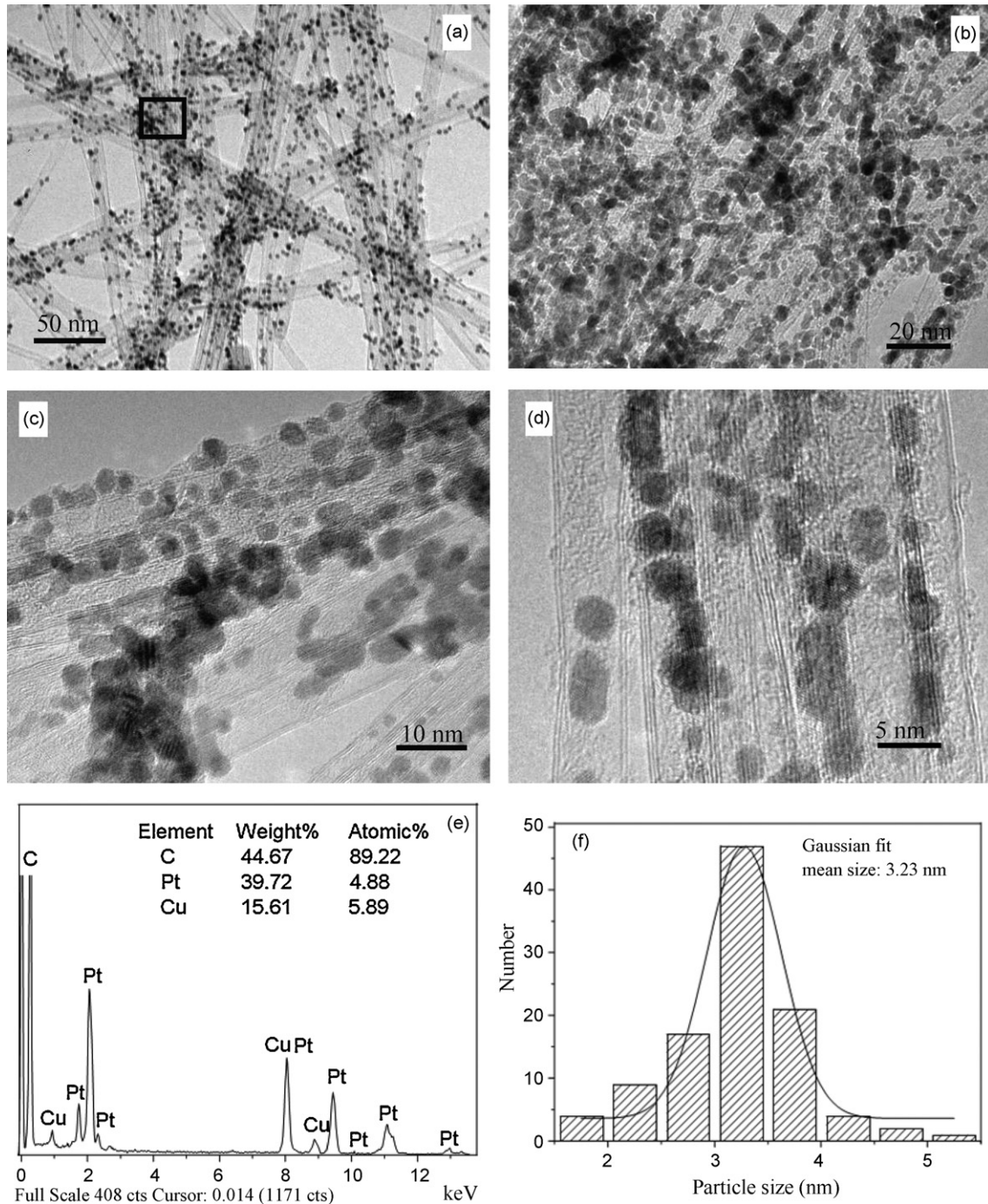


Fig. 6. TEM (a and b), HRTEM (c and d) images, EDS result of the selected area in (a) (e), and Pt particle size distribution (f) of Pt/15DWCNT catalyst.

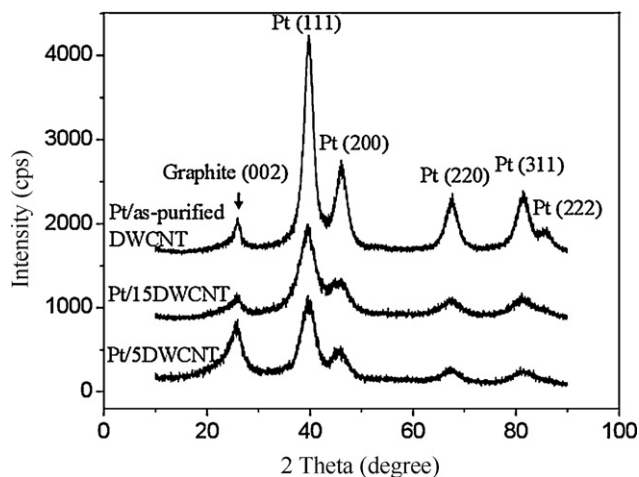


Fig. 7. XRD patterns of different Pt/DWCNT catalysts.

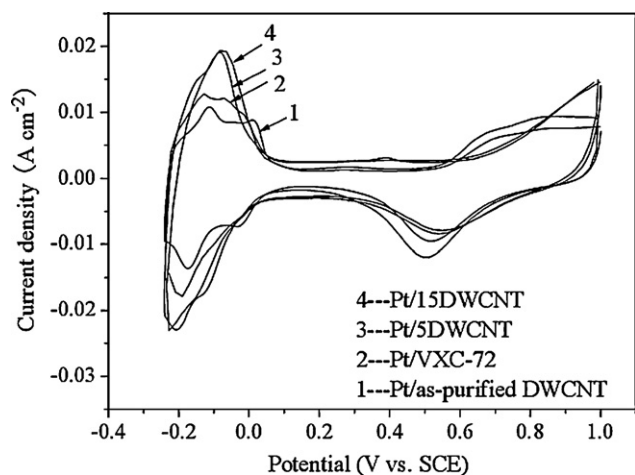


Fig. 8. CV curves of different catalysts at a scanning rate of 100 mVs^{-1} . Note: Pt loading on the working electrode was controlled to be 0.2 mg cm^{-2} .

Raman spectrum indicated that the DWCNTs had a good graphitic structure. This structure may have a better electrical conductivity than amorphous carbon black, so Pt/15DWCNT and Pt/5DWCNT catalysts exhibited a higher electrochemical activity.

5. Conclusions

EG was found to be a suitable medium to disperse DWCNTs by simple ultrasonication. During the process of ultrasonication, the

DWCNT bundles were broken and shortened into smaller ones, which were dispersible in EG without aggregation and settling. The surface structure and crystallinity of the DWCNTs were little changed after the dispersion treatment. When the Pt/DWCNT catalyst was prepared in the homogenous DWCNT/EG solution, Pt particles were deposited homogeneously, so that the electrochemical activity was apparently higher than that prepared on nondispersible DWCNTs. Such good dispersion of DWCNTs in EG medium by a simple method could be widely used in energy, biology, medicine and other fields.

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