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Preparation of Pt nanoparticles on carbon nanotubes and graphite nanofibers via self-regulated reduction of surfactants and their application as electrochemical catalyst

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Abstract

An in situ synthetic method is reported for preparing and decorating metal nanoparticles at sidewalls of sodium dodecyl sulfate micelle functionalized single wall/multiwall carbon nanotubes and graphite nanofibers. The amount and morphology of Pt nanoparticles depend on the types of carbon nanomaterials (C_{NM}). The results demonstrate for the attachment of metal nanoparticles to the carbon nanotubes' (CN) surface via non-destructed surfactant modification. These nanocomposites are successfully used as catalysts for oxidation of methanol, the results of which reveal an increase of oxidizing power of Pt/ C_{NM} upon increasing the C_{NM} diameter. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

Carbon nanotube (CN) is currently attracting much attention due to its unique physical and chemical properties [1]. Of particular interest among various advanced applications is the functionalization of the sidewalls of carbon nanotubes via either covalent or non-covalent modification [2,3]. The covalent type of CN modification is commonly applied toward biochemical [4] and catalytic [5,6] approaches, wherein most covalent methods require pre-oxidation of CN, and hence the electronic properties of the original CN might be altered [3]. As for the non-covalent functionalization, selfassembly soft materials, surfactants and polymers are often used as templates for capping carbon nanotubes so that each individual carbon nanotube can be suspended well in solution [2,3,7–11]. Recently, Smalley and coworkers [7–9] demonstrated exquisite work using an aqueous surfactant, sodium dodecyl sulfate (SDS), to trap the single wall carbon nanotube (SWCN), forming a good suspension in H₂O. The framework consists of a hydrophobic component of SDS attached to the sidewalls of carbon nanotubes via a van der Waals interaction, with the hydrophilic head solvated in aqueous solution. Subsequently, Islam et al. [10] proposed that SDS adsorbed carbon nanotubes were of a hemimicelle-like module. Mioskowski and coworkers [11] successfully imaged the striation pattern of SDS on the dry carbon nanotubes and concluded that above the critical micellar concentration (cmc), SDS can easily form a supramolecular structure on the surface of the carbon nanotubes through a self-assembly process incorporating the rolled-up half-cylinders. Conversely,

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using a cryo-transmission electron microscope (TEM), Moore et al. [9] observed some micelles decorating individual nanotubes and accordingly concluded that carbon nanotubes, to a large extent, were uniformly covered by the surfactant. While these SDS modified carbon nanotubes are becoming a focus of research, further research seems to be necessary if more insights into the mechanism of CN encapsulation are to be gained. On the other hand, in view of the catalyst for fuel cell, multiwall carbon nanotubes (MWCN) [12,13] and graphite nanofiber (GN) [14] have been exploited as high efficiency supports for Pt nanoparticles. However, up to this stage, syntheses of Pt functionalized GN, MWCN and SWCN with subsequent comparison of these three nanocomposites as catalysts in the same experiment for fuel cell are scarce.

Recently, based on self-regulated reduction within pure sodium alkyl sulfate micelles, we have reported a synthetic route to prepare Pd nanoparticles with a "spheres around sphere" structure [15] and subsequently their applications in the fabrication of electronic circuits [16]. Herein, we would like to demonstrate a novel and simple method, by which platinum nanoparticles can be prepared in situ and concomitantly attached to the sidewalls of SDS-modified SWCN, MWCN and GN, forming Pt/1-D carbon nanomaterials (C_{NM}) in a onepot reaction. Subsequently, as supported by electrochemical analyses, these Pt/GN, Pt/MWCN and Pt/ SWCN nanocomposites can be successfully applied as catalysts for the oxidation of methanol. Fair comparison regarding the oxidation power can thus be made among these three carbon nanomaterials.

2. Experimental

2.1. Preparation and materials analysis

Typically, 5 mg commercial, Pt catalyst-free C_{NM} was capped with SDS micelle and dispersed in the 0.1 M of 50 ml SDS aqueous solutions by sonicator agitation for a period of \sim 4 h. Various 1-D C_{NM} were used in this study, including graphite nanofibers (GN; outer diameter: 100–200 nm; Seedchem company), multiwall carbon nanotubes (MWCN; outer diameter: 40-60 nm; Seedchem company) and single wall carbon nanotubes (SWCN; outer diameter ≤ 2 nm; Seedchem company). Immediately after sonication, the SDS aqueous solution containing dispersed C_{NM} was refluxed in an oil bath (~130 °C) for a period of ~7 h. As supported by our previous report [15], some of the SDS amphiphiles in the C_{NM}/SDS solution should gradually release 1-dodecanol under the refluxing temperature. Subsequently, $\sim 0.061 \text{ mmol } H_2 PtCl_6$ was added into the C_{NM}/SDS solution, and was slowly reduced by 1-dodecanol to zero-valence atoms in the micellar core, forming Pt nanoparticles. During the reaction, Pt nanoparticles decorated at $C_{\rm NM}$ were readily observed by the appearance of floatation on the refluxing aqueous solution.

For the TEM (JEOL, JEM-2000EX) measurement, the hydrophobic nanocomposites (in CHCl₃) were dripped onto the copper grid with lacey film supported and dried naturally. As for the analysis of X-ray photoelectron spectroscopy (XPS, VG Microlab MK) and Fourier transform infrared spectra (FT-IR, Perkin Elmer spectrum RX-1), the Pt/C_{NM} chloroform solution was percolated to form black powder and dried for 24 h prior to the measurement.

2.2. Electrochemical measurement

Before the electrochemical measurement, black Pt/ C_{NM} powders were heated at 500 °C in a flow of N₂ gas for a period of 5 h in order to remove surfactant on the Pt/C_{NM} surface. The cooled Pt/C_{NM} (0.015 g) was added and further dispersed into 5 ml aqueous solution via ultrasonic vibration. Thirty μ l of the resulting aqueous solution was uniformly dropped onto $0.196 \, \mathrm{cm}^2$ glassy carbon electrode (GCE) (AFE2A050GC) and heated at 70 °C to evaporate H₂O. In order to prevent the catalyst from falling off the electrode, the glass carbon electrode was rinsed by 10 µl 5 of wt% Nafion solution and heated at 70 °C for 20 min. Electrochemical measurement was carried out by using a potentiostat (Autolab PGSTAT30) incorporating a rotation disk electrode (RDE, AFASR Heavy-Duty Rotator). A three-electrode cell, consisting of a GCE working electrode, a Pt counter electrode and a standard hydrogen reference electrode (NHE), was used for the CV measurement. The CV experiment was performed in 1 M H₂SO_{4(aq)} solution either with or without an addition of 2 M CH₃OH_(aq) at a scan rate of 5 mV/s and a rotation speed of working electrode of 3600 rpm. The electrolyte was purged by N₂ gas with 15 min before measuring the activity of Pt/C_{NM}.

3. Results and disscusion

The synthesized nanocomposite can be extracted with chloroform and well dispersed as a colloidal suspension. The life span of the suspension for Pt/SWCN was significantly longer than those for Pt/MWCN and Pt/GN, indicating that an increase of the C_{NM} diameter speeds up precipitation. It is noteworthy that, based on the same method, hydrophobic, C_{NM} free Pt nanoparticles could also be obtained by refluxing platinum salt and SDS in aqueous solution. Further characterization elaborated below illustrates their intriguing morphology.

Fig. 1A–C shows TEM images of Pt/GN, Pt/MWCN and Pt/SWCN, respectively. For comparison, Fig. 1D also depicts the TEM image of C_{NM} free Pt nanoparti-



Fig. 1. The TEM images of Pt nanoparticles and Pt-carbon nanomaterials via self-regulated reduction by surfactants: (A) Pt-GN; (B) Pt-MWCN; (C) Pt-SWCN; (D) Pt only.

cles prepared via the reflux of Pt salt/SDS. Fig. 1A-C clearly reveals uniform Pt nanoparticles attached to the sidewall of C_{NM} , with a narrow size distribution of particles' diameter, similar to the Pt nanoparticles prepared in Fig. 1D. Based on TEMs results, the calculation diameters of Pt nanoparticles on the GN, MWCN and SWCN are shown in Fig. 2A-C, respectively. The mean sizes of Pt nanoparticles on the C_{NM} are from \sim 1.60 to \sim 1.87 nm and closely to the Pt nanoparticles capped by SDS, as shown in Fig. 2D. It indicates that the C_{NM} do not influence the particles' growth in the preparation period and just play a role as substrates. For Fig. 1A–C, it is possible that the attaching process simply incorporates the co-deposition of Pt and C_{NM} upon drying the solution on the copper grid. However, this should result in a distribution of Pt nanoparticles spread over the entire detecting area (e.g., see Fig. 1D). In contrast, as supported by the TEM images shown in Fig. 1A-C, Pt nanoparticles are exclusively decorated on the C_{NM} with negligible population out of the C_{NM} surface. The results unambiguously eliminate the possibility that the observed Pt/C_{NM} nanocomposites originate from the co-precipitation. In order to

ensure Pt nanoparticles to be on the surface of carbon nanotubes, X-ray photoelectron spectroscopy was employed. Fig. 3 shows the XPS spectrum of Pt/MWCN. Two peaks, $4f_{7/2}$ and $4f_{5/2}$ of Pt, were obviously observed at 71.2 and 74.3 eV, respectively, supporting the dark particles adsorbed on the multiwall carbon nanotubes (see Fig. 1B) to be metallic platinum. Note that the results are also in consistence with Pt/MWCN prepared via two-step sensitization-activation method [12].

Additional information on the attachment architecture is provided by the FT-IR analysis of Pt/MWCN nanocomoposites. The IR spectra of pure MWCN and MWCN + SDS prior to reflux are shown in Fig. 4A and B, respectively. In addition, Fig. 4C depicts the IR spectrum after refluxing MWCN with SDS. In comparison, the appearance of C–H stretching frequencies in the range of 2800–3000 cm⁻¹ and a broad O–H band at 3000–3500 cm⁻¹ are obvious in Fig. 4C. We thus tentatively conclude that there is adsorption of 1-dodecanol on the surface of MWCN. In drastic contrast to Fig. 4A–C, the IR spectra of the Pt/MWCN nanocomposite resolve two new peaks at 1713 and 1748 cm⁻¹ (Fig. 4D), in which the former is more plausibly assigned to the



Fig. 2. The calculation diameter of Pt nanoparticles and Pt-carbon nanomaterials via self-regulated reduction by surfactants: (A) Pt-GN; (B) Pt-MWCN; (C) Pt-SWCN; (D) Pt only.



Fig. 3. X-ray photoelectron spectrum of Pt/MWCN prepared via self-regulated reduction by surfactants.

carbonyl stretch of a lipid acid. Note that similar lipid acid peaks were also observed on the surface of the dispersing Pt nanoparticles prepared by C_{NM-} free SDS. Previous studies [15] have concluded that 1-dodecanol released from refluxed SDS provides a driving force to reduce metal ions and consequently oxidizes to its corresponding lipid acid. It is thus plausible that the lipid acid, which is commonly treated as a bio-surfactant, could further alter the SDS-modified C_{NM} framework via the adhesion of carboxylic heads onto the C_{NM} surface [7–11]. On the other hand, the distinct 1748 cm⁻¹



Fig. 4. FTIR spectra of MWCN MWCN/SDS MWCN/SDS-refluxed and Pt/MWCN.

peak fits well with a typical ester carbonyl stretching frequency. Accordingly, it is plausible that during the phase transfer in the one-pot reaction, the co-adsorption of 1-dodecanol and uncapped lipid acids on the surface of metal (Pt) nanoparticles further undergoes esterification and links the Pt nanoparticles and $C_{\rm NM}$ inside a modified SDS template, resulting in a stable Pt/ $C_{\rm NM}$ nanocomposite observed in Fig. 1A–C.

Another point worthy of note is that the uniform distributions as well as the associated morphologies of the attached Pt nanoparticles depend strongly on the type of C_{NM} . As shown in Fig. 1, in the cases with

GN and MWCN with more defect and roughness surface than SWCN, Pt nanoparticles were found to attach uniformly on the sidewalls. The results may be rationalized by their surface morphology, which allow SDS to be encapsulated. Similar types of assembly, but lower numbers of Pt nanoparticles, were observed for the case of Pt/SWCN (Fig. 1C). In addition, as more SDSs are incorporated to stabilize the suspension of a larger diameter C_{NM} , it is reasonable to expect a higher density of Pt nanoparticles on GN than that on MWCN (see Fig. 1A and B for comparison). The observation of micellar molecules uniformly decorating the sidewall of SWCN with a distinctly narrow diameter is consistent with results reported by Smalley and coworkers [9]. As shown in the inset of Fig. 1B, this synthetic route also successfully prepared Pt nanoparticles attached to the inner wall of an open-ended MWCN. The result indicates that, to a certain extent, the deformation of micelle takes place in the SDS capped Pt/C_{NM} nanocomposite, plausibly due to the competitive carboxylic adhesion in combination with the chemical modification through esterification reaction. Future approaches to gain detailed insights into the architecture of this nanocomposite should be of great interest.

As for the catalytic potential on methanol oxidation, the activities of these Pt/1-D carbon nanomaterials are remarkable, which increase with increasing nanomaterials diameters of Pt/GN > Pt/MWCN > Pt/SWCN. Figs. 5 and 6 show results of cyclic voltammetry (CV) upon measuring the electrochemical activity of the corresponding nanomaterials in 1 M H₂SO_{4(aq)} solution without and with addition of methanol (2 M), respectively. The steepness of hydrogen areas of CV observed for Pt/GN, Pt/MWCN and Pt/SWCN (see Fig. 5) is similar with those colloidal catalysts prepared with subsequent reduction by sodium citrate on XC-72 [17]. The results

0.0015

0.0010

0.000

0.00

-0.0005

-0.0010

-0.0015

0.0

0.2

0.4

₹

Pt/GN Pt/MWCN Pt/SWCN

Fig. 5. The comparative cyclic voltammogram of Pt/C_{NM} prepared via self-regulated reduction by surfactant for hydrogen reduction: (1) Pt/GN, (2) Pt/MWCN, and (3) Pt/SWCN. Pt catalyst loading: 0.146 mg, Electrolyte: 1 M H₂SO_{4(aq)}, Scan rate: 0.005 V/s, RDE speed: 3600 rpm.

0.6

0.8

E/V

1.0

1.2

1.6

1.4

Fig. 6. The comparative cyclic voltammogram of Pt/C_{NM} prepared via self-regulated reduction by surfactant for methanol oxidation: (1) Pt/GN, (2) Pt/MWCN, and (3) Pt/SWCN. Pt catalyst loading 0.146 mg, Electrolyte: 1 M H₂SO_{4(aq)} and 2 M CH₃OH, Scan rate: 0.005 V/s, RDE speed: 3600 rpm.

clearly indicate that all nanocomposites prepared by current method can be successfully applied as electrochemical catalysts. The anodic desorption area of hydrogen in Pt/GN is apparently larger than Pt/MWCN and Pt/SWCN, indicating its higher catalytic activity. The differences in activity possibly result from the more uniform distribution of Pt nanoparticles on the graphite nanofiber, so that the active sites of whole catalysts (Pt) can adequately react with electrolyte species. Similar results have been reported for those catalysts supported on the carbon black [18]. Perhaps, the strongest support for this viewpoint is rendered by the oxidation power for methanol shown in Fig. 6, in which Pt/GN clearly shows maximum current toward oxidizing methanol.

4. Conclusion

In conclusion, we have developed a new and simple in situ approach for preparing and attaching Pt nanoparticles to the sidewall of C_{NM}. This one-pot reaction demonstrates the attachment of Pt nanoparticles to the C_{NM} surface, forming Pt/C_{NM}, via surfactant modification without the destruction, i.e., preoxidation of the CN surface structure. Our preliminary results also showed that other surfactants, such as sodium tetradecyl sulfate, could replace SDS to successfully prepare Pt nanoparticles/C_{NM} composites. As supported by CV measurements, the newly prepared Pt/C_{NM} was found to exhibit high activity toward oxidation of methanol, among which Pt/GN nanocomposites revealed maximum power. The strong coupling between CN and platinum nanoparticles in the composite may spark extraordinary physical/chemical features that are suitable for advanced applications.



0.020

0.018

- Pt/GN - Pt/MWCN

····· Pt/SWCN

C.-L. Lee et al. / Electrochemistry Communications 7 (2005) 453-458

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