

Synthesis and electroactivity of carbon-nanomaterials-supported Pd nanoparticles from self-regulated reduction of sodium *n*-dodecyl sulfate

Chien-Liang Lee

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Abstract This report describes that the Pd nanoparticles are prepared and decorated successfully at the sidewalls of single-walled carbon nanotubes, multiwall carbon nanotubes, and graphite nanofibers without any surface pretreatments by self-regulated reduction of sodium *n*-dodecyl sulfate. As supported by electrochemical measurements, the newly prepared Pd-nanoparticles-decorated carbon nanomaterials are found to have the high activity for oxygen reduction.

Keywords Carbon nanotubes · Surface treatment · Electrocatalysis

Introduction

Pd nanoparticles supported on carbon nanotubes (Pd-CNTs) [1–3] are currently attracting much attention because of its unique properties on catalysis [4, 5], hydrogen storage [6, 7], sensor [8], and biosensor [9]. Of particular interest among various advanced syntheses on Pd-CNTs is the wet-chemical routes, which have advantages on cost and batch-type preparation. To deposit palladium from wet methods including chemical [10] and electrochemical deposition [11], the inner wall surface of the carbon nanotubes have to

be previously oxidized and pretreated. Accordingly, the tedious, time-consuming pretreatment is carried out necessarily for preparing Pd-CNTs. Recently, based on self-regulated reduction within pure sodium alkyl sulfate micelles, we have reported a synthetic method to simply prepare metallic nanoparticles [12, 13] and alloy nanosponges with networked nanowires [14]. The method involves the in situ generation of an alcohol reductant from sodium *n*-dodecyl sulfate, which initially serves as a protective surfactant. This is similar with the additional alcohol as a reductant for preparing metallic nanoparticles [15]. Very recently, carbon-nanotube-supported Pt nanoparticles were prepared [16]. Herein, palladium nanoparticles can be prepared in situ and concomitantly attached to the inert sidewalls of single-walled carbon nanotubes (SWCNTs), multi-wall carbon nanotubes (MWCNTs), and graphite nanofibers (GNs) without need for surface preactivation via self-regulated reduction within sodium dodecyl sulfate (SDS) micelles by the reflux of SDS solution containing SWCNTs, MWCNTs, or GNs. Sequentially, the prepared Pd-nanoparticles-supported SWCNT, MWCNT, and GN are tested to be applied as electrocatalysts for the oxygen reduction. As given by the electroanalyses, the measurement regarding the activity is thus made.

Experimental

Preparation of CNTs-supported Pd nanoparticles

In the synthetic pathway, ~5 mg raw, catalyst-free carbon nanomaterials without any surface functional group (Seed Chem Company), which is confirmed by Fourier transform infrared spectrum [16], was well dispersed in the 0.1 M

C.-L. Lee (✉)
Department of Chemical and Material Engineering,
National Kaohsiung University of Applied Science,
Kaohsiung 807 Taiwan, Republic of China
e-mail: cl_lee@url.com.tw

Present address:
C.-L. Lee
No. 415, Chien Kung Rd.,
Kaohsiung 807, Taiwan

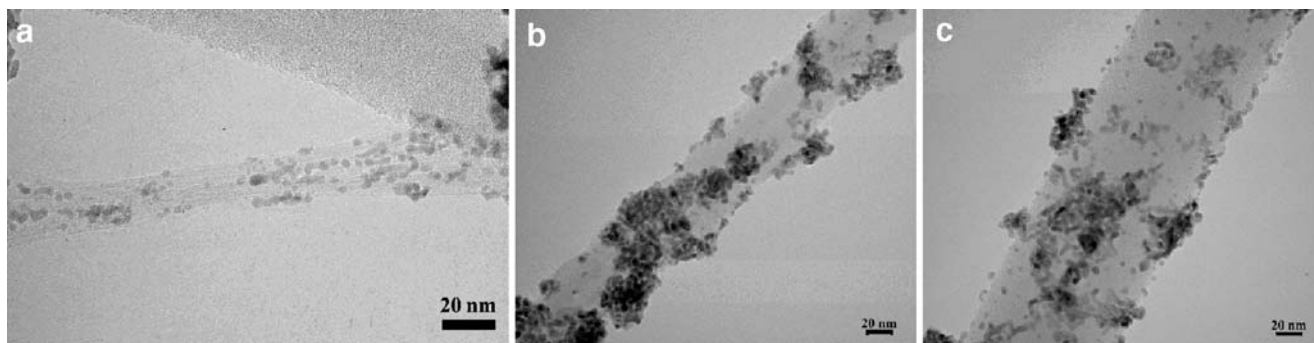


Fig. 1 The TEM images of the carbon-nanomaterials-supported Pd nanoparticles prepared via self-regulated reduction of SDS aqueous solution: **a** Pd-SWCNT; **b** Pd-MWCNT; **c** Pd-GN. Scale bar, 20 nm

50 ml SDS (Fluka) aqueous solutions by sonicator agitation for a period of ~4 h. Various fresh 1-D carbon nanomaterials without any preoxidation were used in this study, including SWCNTs (outer diameter, <2 nm), MWCNTs (outer diameter, 40–60 nm), and GNs (outer diameter, 100–200 nm). Immediately after sonication, the SDS aqueous

solution containing dispersed CNT was refluxed in an oil bath (~130 °C) for a period of ~7 h. As supported by our previous report [12], some of the sodium alkyl sulfate amphiphiles in the refluxed solution should gradually release alcohol under the refluxing temperature. Subsequently, ~0.44 mmol palladium acetate [Pd(OAc)₂;

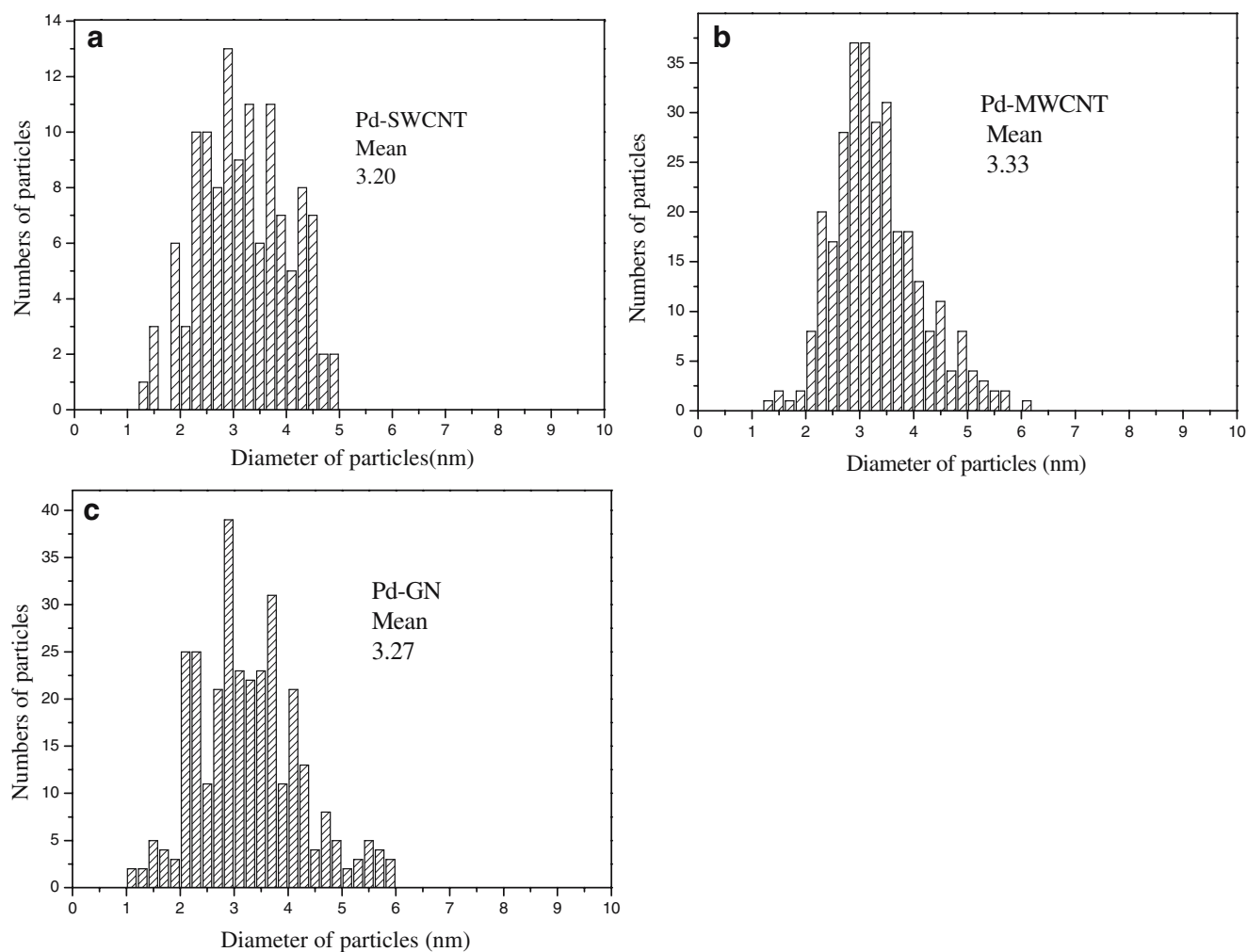
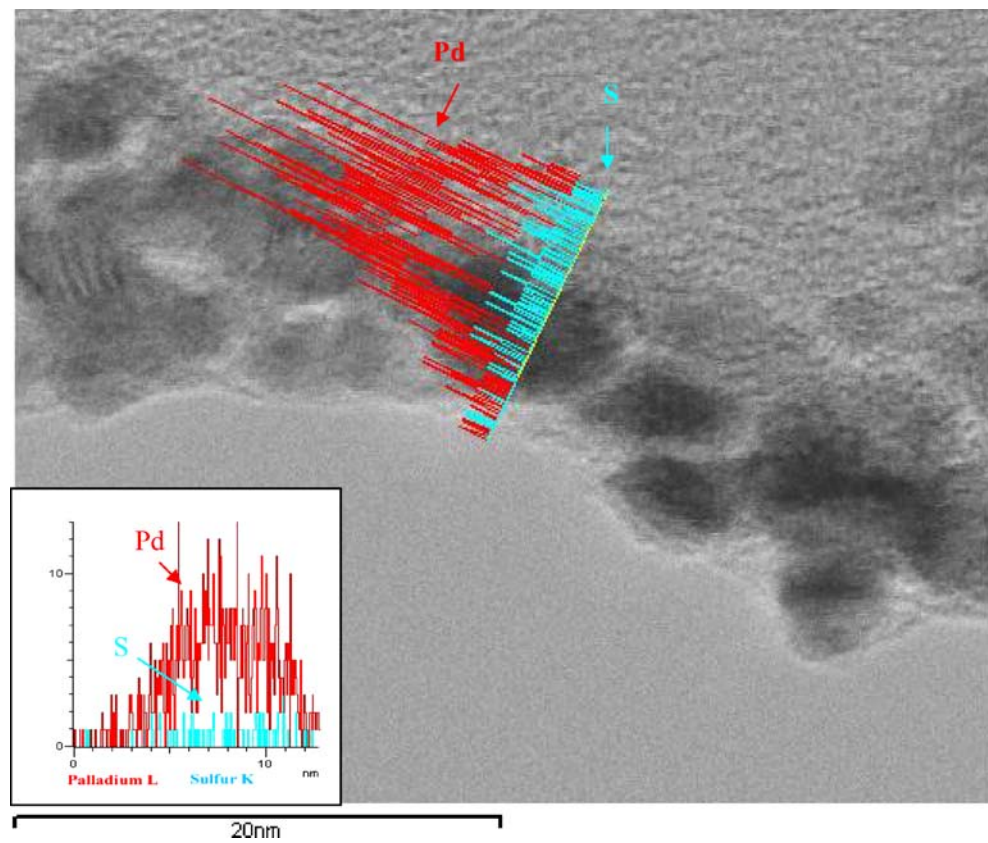


Fig. 2 The diameter calculation of the carbon-nanomaterials-supported Pd nanoparticles prepared via self-regulated reduction of SDS aqueous solution: **a** Pd-SWCNT; **b** Pd-MWCNT; **c** Pd-GN

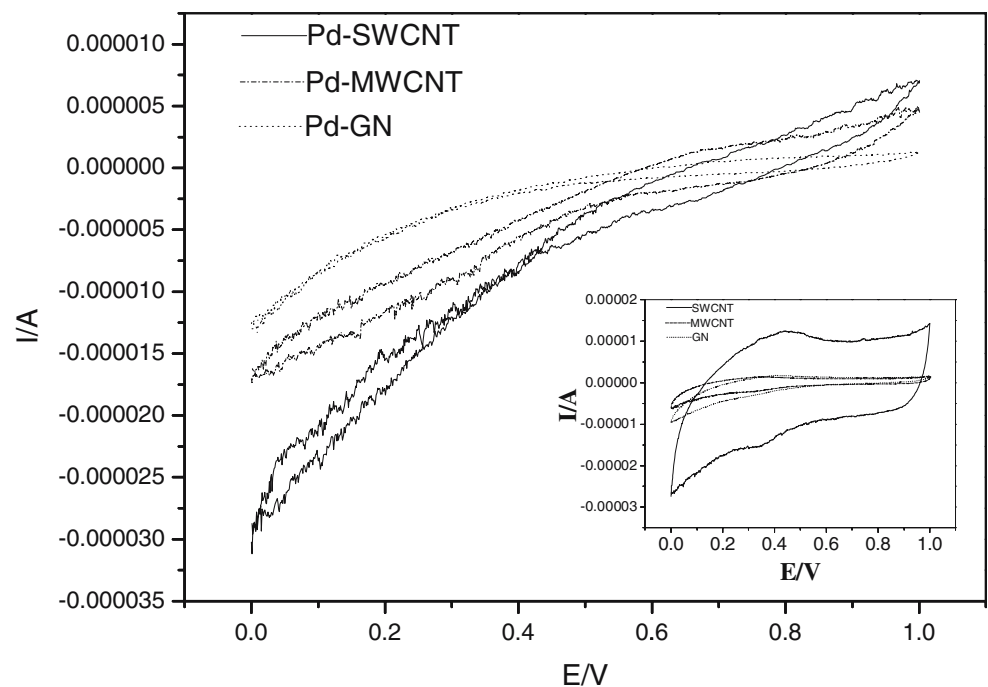
Fig. 3 The line scanning analysis of EDX for the multiwall carbon-nanotube-supported Pd nanoparticles prepared via self-regulated reduction by SDS aqueous solution



Aldrich] were added into the CNTs/SDS solution. Oxygen was not prevented because of the protection of SDS. During the reaction, Pd nanoparticles decorated at CNT were readily observed by the appearance of floatation on the

refluxing aqueous solution. This synthesized nanocomposite can be extracted with chloroform and well dispersed as a colloidal suspension. For the high-resolution transmission electron microscopy (HRTEM; JEOL, JEM-2100F) mea-

Fig. 4 The comparison on oxygen reduction for the cyclic voltammograms of the carbon-nanomaterials-supported Pd nanoparticles prepared by self-regulated reduction of SDS aqueous solution and the fresh carbon nanomaterials. The inset presents the inert electroactivities of the fresh carbon nanomaterials on oxygen reduction. Electrolyte, O₂-saturated 1 M H₂SO₄(aq); catalyst loading, 0.15 mg; electrode area, 0.07 cm²; scan rate, 5 mVs⁻¹; RDE speed: 3,600 rpm



surement, the hydrophobic nanocomposites in CHCl_3 (Aldrich) were dripped onto the copper grid with lacey film support and dried naturally.

Analyses of activity

As for the analysis of electrochemical activity, the Pd nanoparticles supported on SWCNT (Pd-SWCNT), MWCNT (Pd-MWCNT), and GN (Pd-GN) chloroform solution was percolated to form black powder and dried for 24 h before the measurement. Via ultrasonic vibration, ~ 0.015 g Pd-SWCNT, Pd-MWCNT, and Pd-GN was added and further dispersed into 5 ml aqueous solution. Thirty microliters of the resulting aqueous solution was uniformly dropped onto a $\sim 0.07\text{-cm}^2$ glassy carbon electrode (GCE) and heated at 50°C to evaporate H_2O . To prevent the catalyst from falling off the electrode, the GCE was coated with $10\ \mu\text{l}$ 5 wt.% Nafion solution (DuPont) and heated at 70°C for 20 min. Electrochemical measurement was carried out by using a potentiostat (Autolab PGSTAT30) incorporating a rotation disk electrode. A three-electrode cell, consisting of a GCE working electrode, a Pt counter electrode, and a standard hydrogen reference electrode, was used for the cyclic voltammetry (CV) measurement. The CV experiment was performed in 1 M $\text{H}_2\text{SO}_{4(\text{aq})}$ at a scan rate of 5 mV/s and a rotation speed of the working electrode at 3,600 rpm. The electrolyte was purged and saturated by O_2 gas for 20 min before the electrochemical experiment.

Results and discussion

Figure 1a–c clearly reveals HRTEM images of Pd-SWCNT, Pd-MWCNT, and Pd-GN, respectively. It can be seen that the Pd nanoparticles can be synthesized and successfully attached to the sidewall of not only GN but also CNT without the need for surface pretreatments by the present method. According to HRTEM's result, the calculation diameters of Pd nanoparticles decorated at SWCNT, MWCNT, and GN are shown in Fig. 2a–c, respectively. The mean size of the Pd nanoparticles supported on SWCNT, MWCNT, and GN are found to be ~ 3.20 , ~ 3.33 , and ~ 3.27 nm, respectively. Comparing with the mean diameter of ~ 3.36 nm for the dispersed Pd nanoparticles without any CNTs by self-regulated reduction method [12], the nanoparticle size is nearly equal. It is plausible that CNTs and GNs in the synthetic period do not involve the particle growth. On the other hand, an attaching process simply incorporating the co-deposition of Pd and CNTs upon drying the solution on the copper grid is possible. This should result in a distribution of Pd nanoparticles spread over the entire detecting area. In contrast, as supported by the HRTEM images shown in Fig. 1a–c, Pd

nanoparticles are exclusively decorated on the SWCNT, MWCNT, and GN with negligible population out of the carbon nanotube surface. The results unambiguously eliminate the possibility that the observed Pd-CNTs or Pd-GNs nanocomposites originate from the co-deposition. Additionally, for the functionalization of carbon nanotube, the surface site to be easily modified is at the cap or the end. In this study, the Pd nanoparticles can be decorated well on the sidewall. To ensure Pd nanoparticles to be on the CNT surface, energy dispersive X-ray spectroscopy (EDX) is employed. Figure 3 depicts the EDX spectrum of linear scanning for the prepared Pd-MWCNT while the image of the nanoparticles/MWCNT is detected. The strong analysis signal over black particles decorated on the carbon nanotube is detected to be palladium. This reveals the exact composition of the prepared nanocomposites. Sequentially, to test the activity of the prepared carbon-nanomaterials-supported Pd nanoparticles, the prepared Pd-SWCNT, Pd-MWCNT, and Pd-GN are applied as electrochemical catalysts for oxygen reduction. Figure 4 reveals the comparison activities of carbon-nanomaterials-supported Pd nanoparticles and catalyst-free carbon nanomaterials upon an electrochemical CV measurement in the oxygen reduction. It can be seen that the carbon nanomaterials show inert reactivity with O_2 in the acid medium. The currents of carbon-nanomaterials-supported Pd nanoparticles on reducing oxygen are clearly detected from a starting potential of ~ 0.77 V. The current intensity increases with the potential decreasing. Additionally, in this case, the activity is found to depend on the decreasing diameter of carbon nanomaterials: Pd-SWCNT > Pd-MWCNT > Pd-GN. It is probably because of the high surface area of SWCNT. It is worthy to note that, comparing with the Pd-MWCNT prepared by electrochemical method [17], the positive voltage of ~ 0.77 V toward oxygen reduction in this case is detected. This indicates that the CNT-supported Pd nanoparticles prepared by this method have high oxygen reduction activity.

Conclusion

In conclusion, Pd nanoparticles are prepared and successfully in situ attached to the inert wall of not only GN but also CNT by a simple method, the self-regulated reduction method of SDS. As supported by CV measurements, the newly prepared Pd-SWCNT, Pd-MWCNT, and GN have high activity for oxygen reduction. The positive reduction peak of Pd-CNT is measured from ~ 0.77 V. It is of great interest to note that they have the unique catalytic properties. This synthesis method brings out extraordinary physical/chemical features that are suitable for advanced applications.

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