



Short communication

Synthesis of highly dispersed and active palladium/carbon nanofiber catalyst for formic acid electrooxidation

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ABSTRACT

Highly dispersed and active palladium/carbon nanofiber (Pd/CNF) catalyst is synthesized by NaBH₄ reduction with trisodium citrate as the stabilizing agent. The obtained Pd/CNF catalyst is characterized by high resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD). The results show that the Pd nanoparticles with an average particle size of ca. 3.8 nm are highly dispersed on the CNF support even with a small ratio of citrate to Pd precursor, which is believed to be due to the pH adjustment of citrate stabilized colloidal Pd nanoparticles. The cyclic voltammetry and chronoamperometry techniques show that the obtained Pd/CNF catalyst exhibits good catalytic activity and stability for the electrooxidation of formic acid.

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1. Introduction

Over the past decade, the electrooxidation of formic acid has been one of the most studied subjects in fuel cell area because direct formic acid fuel cells (DFAFCs) have attracted increasing attention, which is largely due to the high theoretical open circuit voltage and small fuel crossover of DFAFCs [1]. It is generally recognized that for formic acid oxidation, Pd shows superior performance compared with Pt because Pd can catalyze the electrooxidation of formic acid with greater resistance to CO than Pt [2,3].

The morphology and size of Pd particles, which have a significant effect on the electrocatalytic activity of Pd catalyst for formic acid oxidation [4], can be tuned by selecting proper support materials and following certain synthesis procedures. Carbon nanomaterials, carbon nanotube (CNT) and nanofiber (CNF) in particular, are increasingly being used as supports for fuel cell catalysts due to their unique electrical and structural properties [5,6].

Pd nanoparticles supported on carbon materials have been synthesized mainly by the sodium borohydride (NaBH₄) reduction method and by the modified polyol reduction method in the presence of ethylene glycol and surfactants. In the case of the polyol reduction method, surfactants such as polyvinylpyrrolidone

(PVP) and sodium dodecyl sulfate (SDS) are usually employed as stabilizing agents [7,8]. Unfortunately, these stabilizers are usually strongly adsorbed on the surface of Pd nanoparticles, which may reduce the catalytic activity because of the lack of “clean”, surfactant-free Pd surface [3,9]. As to the NaBH₄ reduction method without addition of stabilizing agents, the obtained Pd particles present a broad size distribution due to difficulty in controlling the nucleation and growth steps occurring at intermediate stages of particle formation [10,11].

The synthesis of Au nanocrystals by citrate reduction could be used as a guide in the preparation of Pd particles with a narrow particle size distribution [12–15]. In 1951 Turkevich reported the synthesis of Au nanocrystals with a relatively narrow size distribution by citrate reduction method, which involves the reaction of small amount of hot chlorauric acid with small amount of trisodium citrate solution [13]. Later Turkevich reported the synthesis of Pd nanocrystals by the same method, and claimed that the size variation of the resulting Pd nanocrystals by the citrate reduction could be readily realized by simply changing the concentration of trisodium citrate [12]. In the Turkevich method, noble metal nanocrystals with a narrow particle size distribution can be synthesized because the citrate ions act as both a reducing agent, and a stabilizing agent. In the present work, a modified Turkevich method with trisodium citrate as stabilizing agent and NaBH₄ as reducing agent was employed to anchor Pd nanoparticles onto CNF support. The performance of the obtained Pd/CNF catalyst for formic acid electrooxidation was evaluated.

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2. Experimental

2.1. Synthesis of Pd/CNF catalyst

The CNFs used here were platelet type CNFs, which were synthesized and purified according to the literature [16]. Sonochemical oxidation treatment was employed to import oxygen-containing functional groups onto CNFs [11,17]. The following describes the detailed synthesis procedure for preparing the Pd/CNF catalyst. At first, 526 μL of 0.1 M PdCl_2 (in 0.1 M HCl) was added dropwise to a stirred 10 mL of 5.26 mM trisodium citrate solution kept at 10 °C. Then the solution pH was adjusted to 5.5 using 0.01 M NaOH solution. After that the above solution (Pd colloids) was added dropwise to a stirred 10 mL of 5 mg mL^{-1} CNF slurry, and stirring was continued for another 2 h at 10 °C. After that 5 mL of 0.3 M freshly prepared ice-cold NaBH_4 solution was added to the above solution in a dropwise manner. The solution was stirred for additional 3 h at 10 °C. The resulted material was filtered and washed with deionized water and then dried at 80 °C overnight. The Pd/CNF catalyst with a Pd loading of 10 wt.% was obtained.

2.2. Characterization of Pd/CNF catalyst

Morphology of the obtained Pd/CNF catalyst was examined by high resolution transmission electron microscopy (HRTEM, FEI-ecnaiG2F30 S-Twin) (HRTEM, FEI Tecnai G2F30 S-Twin). X-ray diffraction (XRD) pattern of the Pd/CNF catalyst was recorded on an X-ray diffractometer (D/MAX 2550 VB/PC, RIGAKU) at a sweep rate of 2° min^{-1} using $\text{Cu K}\alpha$ as radiation source ($\lambda = 0.154056 \text{ nm}$). Electrochemical characterization was performed on a PGSTAT 30 electrochemical workstation (Eco Chemie B.V., The Netherlands). All experiments were conducted in a conventional three-electrode system. The working electrode was prepared as follows. A suspension of Pd/CNF ink was prepared by ultrasonically dispersing 1 mg Pd/CNF in 90 μL ethanol and 10 μL Nafion (5 wt.%) solution for 30 min. A 5 μL of the above solution was pipetted onto a glassy carbon (GC) electrode (3 mm diameter) surface and dried at room temperature. The loading of Pd on the working electrode was ca. 5 μg . A Pt foil and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively.

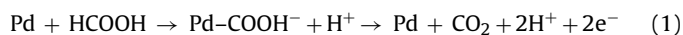
3. Results and discussion

The Turkevich method has demonstrated large advantages in colloidal chemistry because this method could enable an accurate control of the particle size and size distribution of the synthesized noble metal nanoparticles [4,12–14]. Fig. 1(a) and (b) shows the HRTEM image of the Pd/CNF catalyst prepared by NaBH_4 reduction with trisodium citrate as the stabilizing agent. For the synthesized Pd/CNF catalyst, as can be seen from the low-magnification HRTEM image (Fig. 1(a)), Pd nanoparticles are highly dispersed on the CNF support. In the higher-magnification HRTEM image (Fig. 1(b)), well-dispersed spherical Pd nanoparticles with a particle size around 4 nm can be observed. The histogram of Pd particles (Fig. 1(c)) shows that the average particle size and its standard deviation are 3.76 and 0.57 nm, respectively. More than 80% of the Pd particles have a particle size between 3 and 4.5 nm, indicating the obtained Pd particles have a relatively narrow size distribution. Previous work has proved that a large trisodium citrate/noble metal precursor ratio is beneficial to synthesize noble particles with small particle size and narrow size distribution [4,10–14]. Though the residual citrate after particle synthesis could be easily removed by washing with deionized water [4], the small amount of trisodium citrate used here may contribute to a cleaner metal surface. The trisodium citrate/ PdCl_2 ratio in this work is one, which is smaller

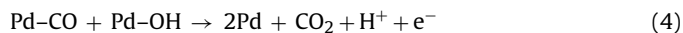
than the ratio used by Zhou and Lee [4] to obtain a comparable result. The major difference in our procedures lies in the pH adjustment of trisodium citrate stabilized PdCl_2 solution (with a pH value of ca. 3). It is believed that the stabilizing effect of trisodium citrate lies in the adsorption of citrate groups (three carboxyl acid anions) onto metal particles and corresponding steric barriers for repulsion interactions [18]. The lower the solution pH, the lower the repulsive interactions [18], which might be due to a lesser extent of protonation of citrate in a higher pH value [19]. So the adjustment of pH to a higher value could increase the stabilizing efficiency of trisodium citrate and decrease the amount of trisodium citrate used correspondingly, which may contribute to obtain a cleaner Pd surface.

The crystalline structure of the Pd/CNF catalyst was determined by the XRD technique and the result is shown in Fig. 2. The diffraction peaks at ca. 26.3, 42.5, 54.3 and 77.7 observed in the XRD pattern can be attributed to the hexagonal graphite structure of (002), (100), (004), and (110) [20,21], while the diffraction peaks at ca. 40.0, 46.5, 68.0 and 82.1 are corresponding to the 2θ values of Pd (111), (200), (220) and (311) crystal faces of face centered cubic (fcc) crystalline of the Pd particles in the Pd/CNF catalyst [22]. It can be seen from the XRD pattern that the Pd (111) plane has the largest intensity among those planes, indicating Pd catalyst mainly exhibits the (111) plane [22]. It is said that the (111)-faced Pd catalyst is more practical for fuel cell application because the (111) planes are less susceptible to oxidation [3,22]. The Pd (111) peak is used to calculate the mean size of Pd nanoparticles according to the Scherrer formula and the particle size of Pd is found to be 3.6 nm, which is consistent with the HRTEM result.

The catalytic activity of the prepared Pd/CNF toward formic acid oxidation was evaluated in deaerated 0.5 M H_2SO_4 + 0.5 M HCOOH by cyclic voltammetry with a scanning rate of 50 mV s^{-1} at room temperature, as shown in Fig. 3. It is generally recognized that the electrooxidation of formic acid can proceed through two parallel pathways, the dehydrogenation pathway (direct pathway) and the dehydration pathway (CO pathway) [23]. In the direct pathway, formic acid is directly oxidized to CO_2 and no CO intermediate is formed (Eq. (1)) [22–24].



In the CO pathway, formic acid is firstly oxidized to intermediate CO (Eq. (2)), and then CO is oxidized to CO_2 (Eq. (4)) [22–24].



The oxidation of CO intermediate needs the oxygen-containing species like OH_{ads} , which can be generated by the activation of H_2O (Eq. (3)). However, the activation of H_2O on the Pd surface is difficult and relatively high positive potentials are needed [9]. Generally, two oxidation peaks, one located at a lower potential and the other located at a higher potential, corresponding to the direct pathway and CO pathway of formic acid electrooxidation, respectively, could be observed on Pd catalyst for formic acid electrooxidation. The direct pathway is the desirable pathway, because for the direct pathway, formic acid is directly oxidized to CO_2 and no CO intermediate is formed [23]. It is worth noting that the high-potential peak is nearly undetectable in the positive-going potential scan, indicating that the formic acid electrooxidation on the synthesized Pd/CNF catalyst should proceed through the direct pathway, not involving formation of CO poisoning intermediates. The peak current density of the synthesized Pd/CNF catalyst is 40.0 mA cm^{-2} , and the corresponding mass activity is slightly higher than that of the highly dispersed and active Pd/C catalyst synthesized by Cheng et al. (0.56 A $\text{mg}_{\text{Pd}}^{-1}$ vs. 0.52 A $\text{mg}_{\text{Pd}}^{-1}$) [22]. The high catalytic

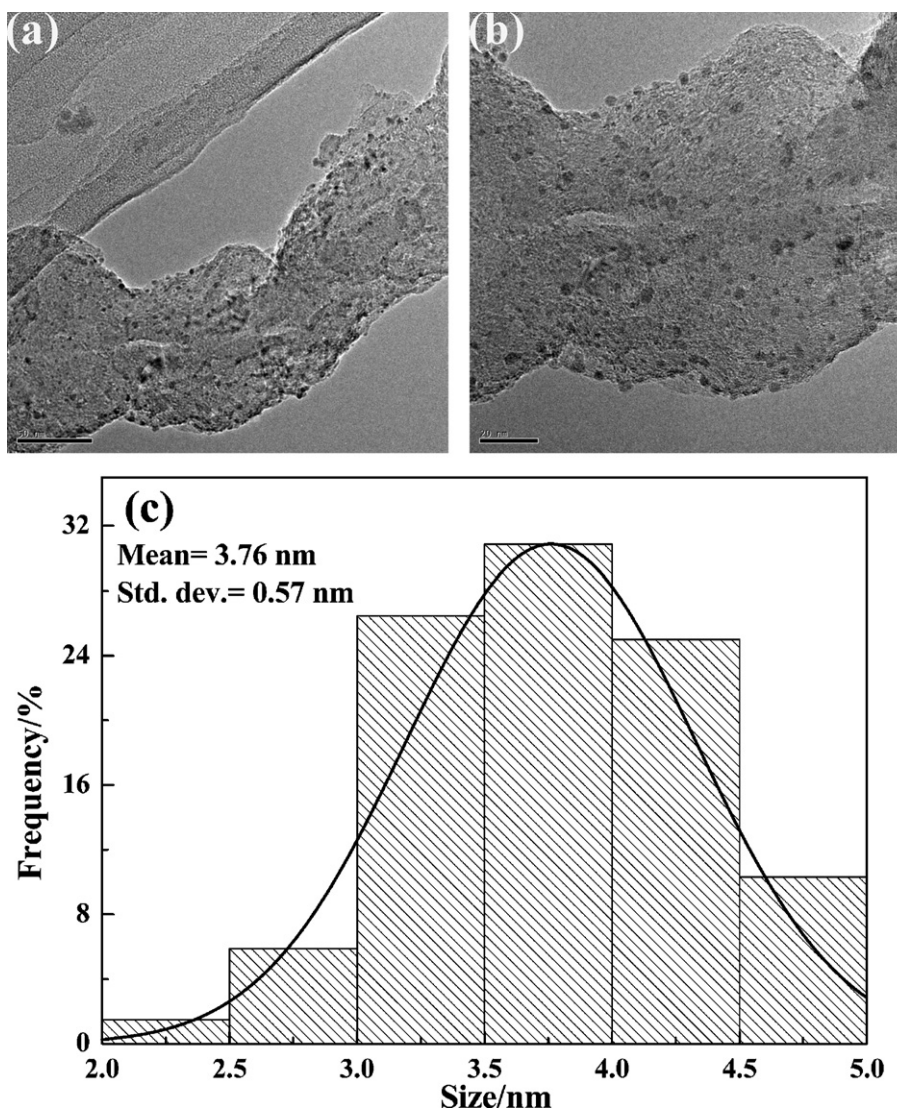


Fig. 1. HRTEM image with low magnification (a) and high magnification (b) of the synthesized Pd/CNF catalysts and the corresponding histogram of particle size distribution (c).

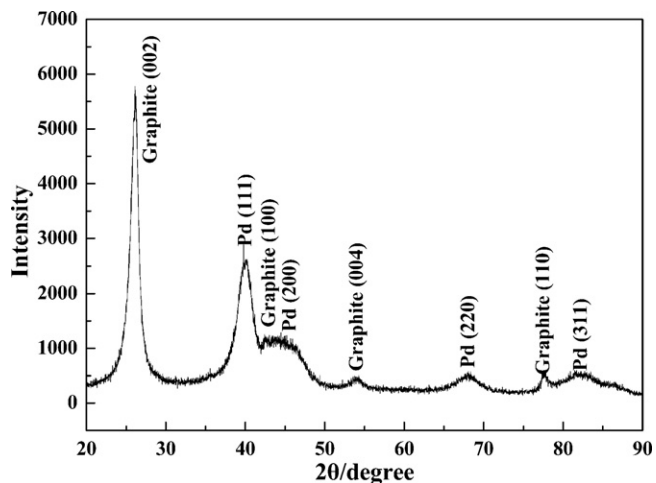


Fig. 2. XRD pattern of the synthesized Pd/CNF catalyst.

activity of the obtained Pd/CNF catalyst indicates that the stabilizing agent trisodium citrate used in the preparation process can be readily removed from the surface of Pd particles just by washing with deionized water. In the Guo's work, no catalytic activity was detected on the obtained PtRu/C catalyst if annealing had not been applied to remove the citrate acid used in the preparation of PtRu/C catalyst [25]. It is thus claimed that the annealing, heating PtRu/C catalyst at 400 °C under an N₂ atmosphere for 2 h, is essential before carrying out electrochemical measurements [25]. The easy removal of residue citrate used in our preparation process may be due to the low trisodium citrate/PdCl₂ ratio and to the relatively weak adsorption of citrate on Pd particles.

The stability test of the obtained Pd/CNF catalyst for formic acid electrooxidation has been carried out by the chronoamperometry technique at a potential of 0.1 V (vs. SCE) in 0.5 M H₂SO₄ + 0.5 M HCOOH solution and the corresponding result is shown in Fig. 4. An initial decrease in the current density with time is found for Pd/CNF catalyst, and the current density is stabilized within 500 s after application of the potential. The current density on the Pd/CNF catalyst after 3600 s is 1.21 mA cm⁻², and the corresponding mass activity is higher than that of the highly stable Pd-P/C catalyst prepared by Lu et al. [26] (17 mA mg_{Pd}⁻¹ vs. 7.1 mA mg_{Pd}⁻¹), indicating that the prepared Pd/CNF catalyst has a relatively good stability.

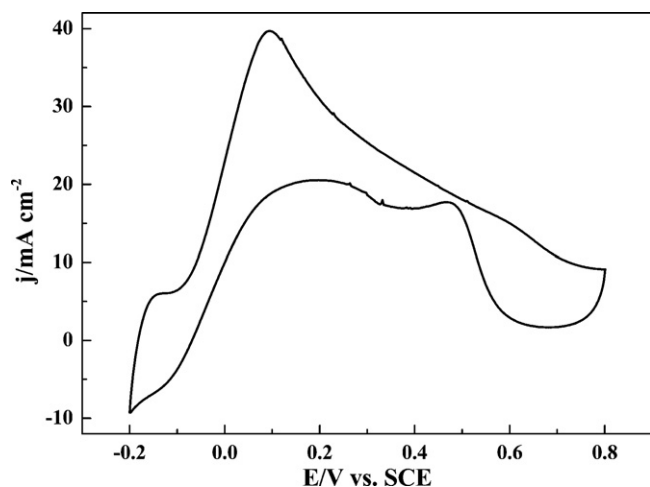


Fig. 3. Cyclic voltammogram for Pd/CNF catalyst in 0.5 M H₂SO₄ + 0.5 M HCOOH.

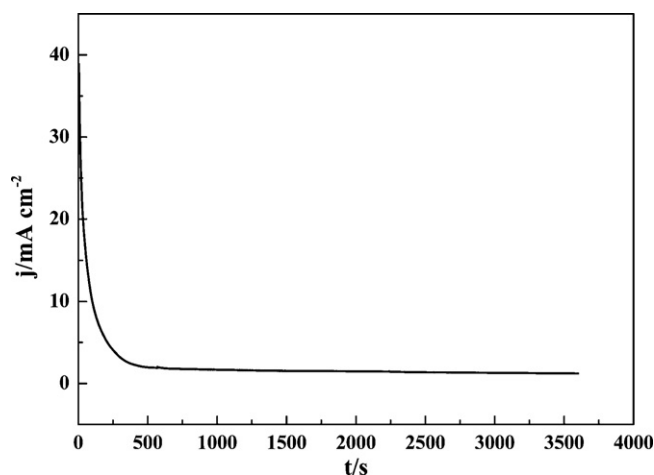


Fig. 4. Chronoamperogram of formic acid electrooxidation on Pd/CNF catalyst at 0.1 V (vs. SCE)s.

4. Conclusions

A simple process based on the Turkevich method is developed to synthesize Pd/CNF catalyst. HRTEM characterization shows the resulting Pd nanoparticles with an average particle size of ca. 3.8 nm are highly dispersed on the CNF support. XRD characterization shows the obtained Pd nanoparticles present a face-centered cubic

(fcc) structure with (1 1 1) planes as the dominant surface planes. Electrochemical characterization shows the obtained Pd/CNF catalyst has good electrocatalytic activity and stability for formic acid electrooxidation. This work may open new insights to the preparation of supported Pd nanoparticles with a narrow particle size distribution. Future work on the nucleation-growth mechanism of Pd nanoparticles in this process is under progress.

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