



Synthesis of Pd nanowire networks by a simple template-free and surfactant-free method and their application in formic acid electrooxidation

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ABSTRACT

A large volume of Pd nanowire networks with lengths of a few tens of nanometers are synthesized successfully by the inherent self-assembly process with the stabilizing effect of sodium citrate. The Pd nanowire networks exhibit a superior electrocatalytic activity for formic acid oxidation. The specific area activities of Pd nanowire at 0.1 V calculated from the forward-scan currents were 1.38 mA cm^{-2} , which is 97% higher than that obtained from Pd nanoparticle or peanut-like structures (0.70 mA cm^{-2}). The mechanism of the significant enhancement of the catalytic activity of Pd nanowire network can be due to the unique surface characteristics and effective electronic conduction path within the Pd nanowire networks.

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1. Introduction

Recently, direct formic acid fuel cells are receiving much attention as one of the most attractive energy sources [1,2]. As one of the noble metals, Pd was found to show superior catalytic activity for formic acid oxidation reaction compared with Pt catalysts [3]. Considerable efforts were therefore made to synthesize and develop novel Pd catalysts.

Since the electrocatalytic activity strongly depends on the shape of metal nanomaterials [4,5], morphology-controlled synthesis of Pd nanostructures with tailored shape and size is highly desirable [6,7]. Pd nanowires have attracted more attention for their excellent properties. Up to now, most of research has focused on synthesis of Pd nanowires by template methods [7–9]. Specific hard templates can be used to obtain ordered Pd nanowire arrays [7], but the diameter of nanowire is usually too big, resulting in low Pd specific surface area. In contrast, various soft templates have been widely used for synthesis of Pd nanowires with smaller diameter. In the case of this soft template method [8,9], some complicated chemicals such as organic surfactants, polymers, and biomacromolecules are required for the formation of a soft template. On one hand, the control of the synthesis process is not easy and requires sophisticated equipment. On the other hand, the remaining soft template may have a negative effect on the performance of Pd nanowire, especially for electrochemical applications. Therefore, developing a simple and straightforward templateless

method to prepare Pd nanowires is critical. Although Wang et al. [10] reported a templateless method using a large molecule polymer, the key point in that work is still that the polymer provides a framework for formation of Pd nanowire. Furthermore, the remaining polymer on Pd nanowires is not easily removed.

Herein, we report the synthesis of Pd nanowire networks using a simple template-free and surfactant-free method. The Pd nanowire networks were fabricated by a spontaneous self-assembly process in solution. The key strategy in this method is making full use of inherent self-assembly behavior of Pd and tight control of the experimental parameters. This method is simple and environmental friendly. Most importantly, it can produce a large volume of Pd nanowire networks with nearly clean surface. The obtained Pd nanowire networks exhibit a high electrochemical activity for formic acid oxidation. The formation mechanism of Pd nanowire networks is also discussed in this communication.

2. Experimental

In the experiment, trisodium citrate and KBH_4 serve as the stabilizer and reducing agent respectively. A typical preparation of Pd nanowire (defined as Pd NW) consists of the following steps. An aqueous solution (0.075 ml) of 200 mM Na_2PdCl_4 was mixed with 20 ml H_2O in a beaker, followed by the addition of 6 mg trisodium citrate. After 5 min, a 3 ml aqueous solution including 6 mg trisodium citrate and 3 mg KBH_4 was injected into the beaker at a low flow rate. The reaction lasted for 30 min with constant stirring. The products were centrifuged, washed and then ultrasonically dispersed in distilled water.

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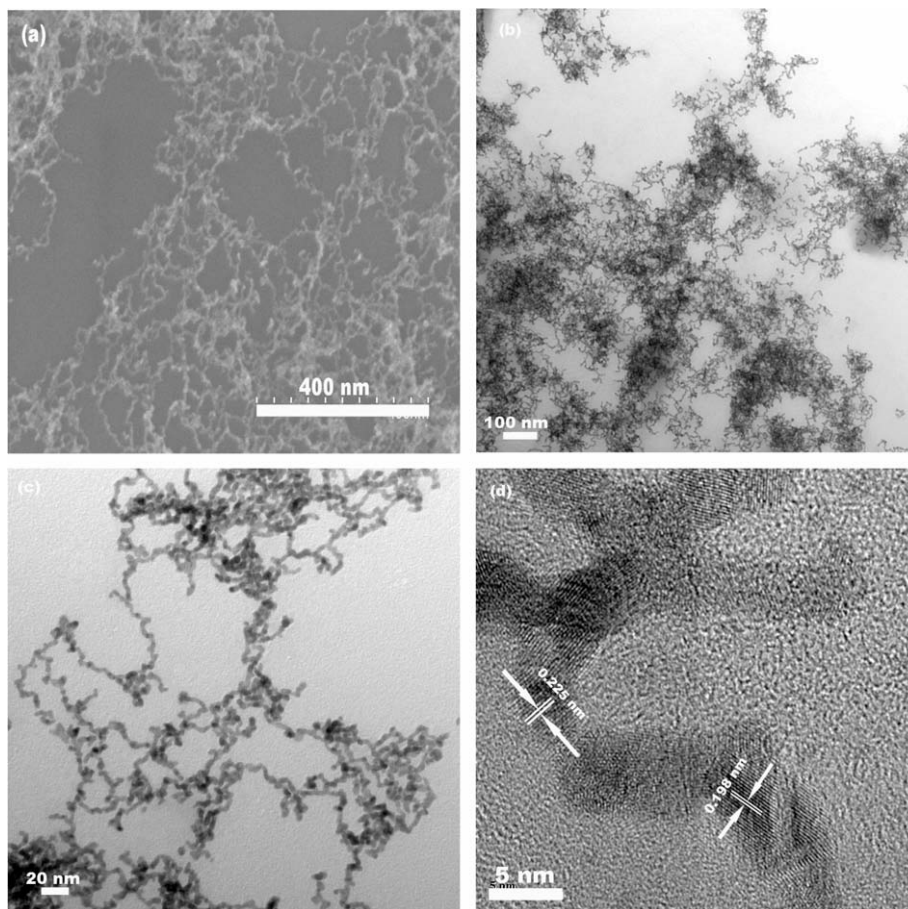


Fig. 1. SEM image (a), TEM images (b, c), and HRTEM image (d) of the Pd nanowire network.

For comparison, Pd nanoparticles or “peanuts” (defined as Pd NP) were also prepared by the same method. The preparation method is similar to that of Pd nanowires, the only difference being the use of a lower Pd precursor concentration. Of 0.045 ml an aqueous solution of 200 mM Na_2PdCl_4 was mixed with 20 ml H_2O in a beaker. Other parameters were kept the same as for Pd NW above.

Electrochemical measurements were performed using a standard three-electrode electrochemical cell on a CHI 600 C electrochemical working station. A polished glass-carbon disk electrode was used as the substrate. An amount of Pd nanostructure solution

was pipetted onto the surface of the electrode and dried in air at room temperature. Then, a drop of Nafion solution (5 wt.%) was pipetted on it and the working electrode was thus obtained. A conventional three-electrode cell was used, including a Ag/AgCl (saturated KCl) electrode as reference electrode, a platinum wire as the counter electrode, and the as-prepared Pd electrodes as the working electrodes. Cyclic voltammeter (CV) with a scan rate of 20 mV s^{-1} and chronoamperometry (CA) experiments at 0.1 V were conducted in N_2 purged in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 0.5 \text{ mol L}^{-1} \text{ HCOOH}$ solutions at 25°C .

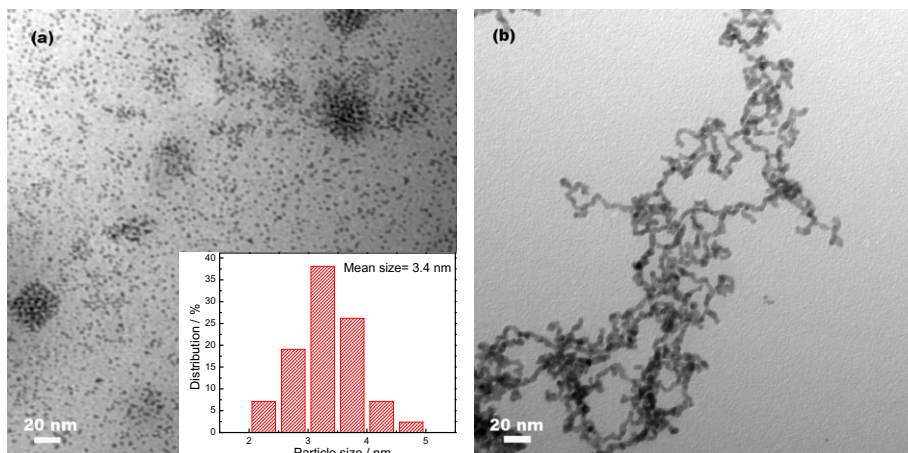


Fig. 2. TEM images of Pd nanoparticle or peanuts-like shape (a) and Pd nanowire network (b) prepared with different Pd precursor concentration.

The electrochemical active surface areas are determined from CO stripping voltammograms in 0.5 mol L⁻¹ H₂SO₄ according to Ref. [11]. The electrochemical specific surface areas of the Pd NP and NW are estimated as being 615.2 and 585.4 cm² mg⁻¹ from the integration of the stripping charge. The current densities in this study were obtained by normalizing the current to the electrochemical active surface area.

The morphologies and structures of the catalysts were characterized by a field emission scanning electron microscope (Hitachi S-4800), transmission electron microscopy (TEM) (Philips CM 10) and high-resolution transmission electron microscopy (HRTEM) (JEOL 2010 FEG).

3. Results and discussion

Fig. 1 shows the morphologies of Pd NW network. As shown in Fig 1a, the SEM images show that a three-dimensional Pd NW network is formed. The low-magnification TEM image in Fig 1b reveals the presence of abundant Pd NW, and the Pd NW are a few tens of nanometers long. Sometimes individual Pd nanoparticles can be observed in the NW network, which also appeared in other literature [8,10]. From the higher magnification in Fig 1c, it can be seen that Pd NW is highly interconnected and formed into an extended nanowire network. The HRTEM image shows Pd NW with a diameter of around 4 nm. Meanwhile, the interplanar distances obtained by HRTEM were mainly 0.225 and 0.198 nm, corresponding to the predominant (1 1 1) and (2 0 0) *d*-spacing of cubic Pd [12–14], which confirmed the presence of polycrystalline Pd.

Fig. 2 compares the different Pd nanostructures synthesized by the same method but with different volume (0.045 ml for Fig. 2a and 0.075 ml for Fig. 2b) of 200 mM Na₂PdCl₄ aqueous solution diluted in 20 ml distilled water. As shown in Fig 2a, with the low Pd precursor concentration, uniform Pd NP were obtained, and some of them assembled into a peanut-like structure, but no long Pd nanowires were found. The Pd NP exhibits a narrow size distribution and the mean size is 3.4 nm. In contrast, three-dimensional Pd NW networks were well formed by the appropriate increase of Pd concentration in the self-assembly process (Fig. 2b).

Fig. 3 illustrates the possible formation process of Pd nanostructures with the effect of citrate. It is well known that the size of metal nanoparticles can be controlled in solutions by the strong electrostatic repulsion from the adsorbed stabilizer on the nanoparticles [15]. In general, the strong repulsion between nanoparticles may also inhibit self-assembly process. In particular, when Pd concentration is low, excess amount of stabilizer absorbed on Pd

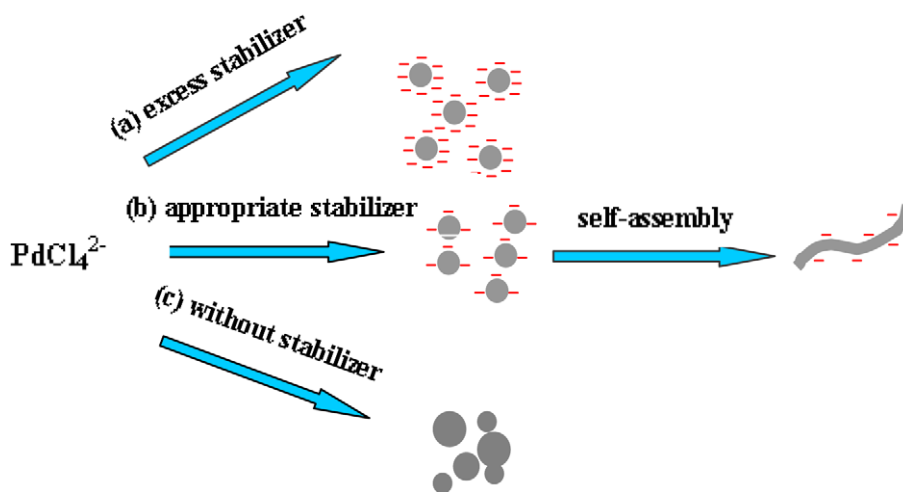


Fig. 3. A schematic illustration of trisodium citrate-mediated self-assembly of Pd nanowire and Pd nanoparticle.

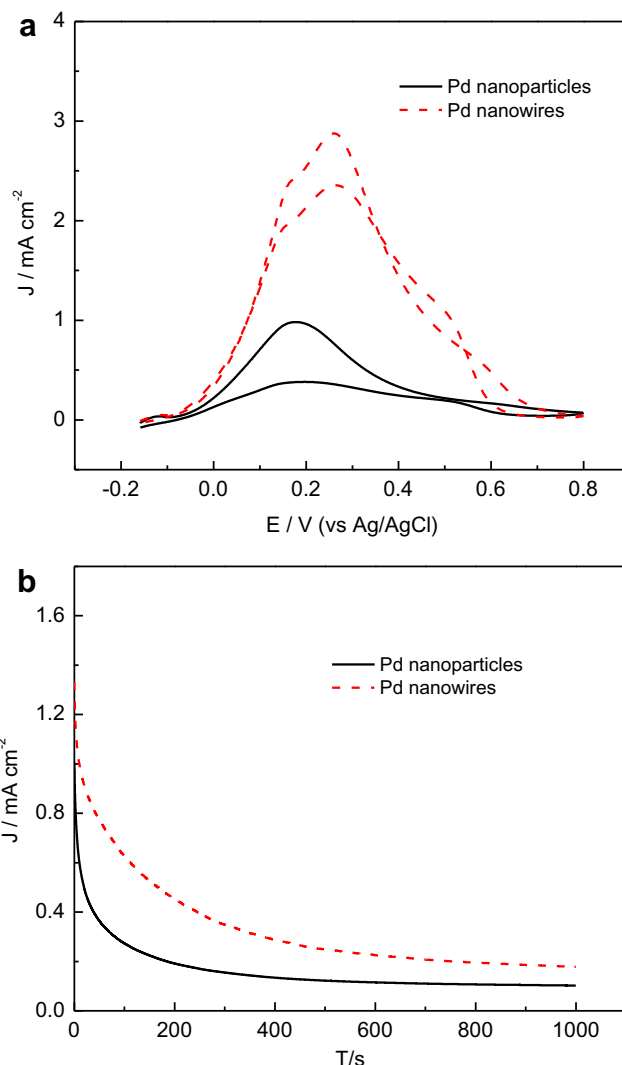


Fig. 4. Cyclic voltammograms with a scan rate of 20 mV s⁻¹ (a) and chronoamperometric curves at 0.1 V (b) of Pd nanoparticle or peanut-like shapes and Pd nanowire network in 0.5 M HCOOH + 0.5 M H₂SO₄ solution. The current density was obtained by normalizing the current to the electroactive surface area.

nanoparticles will result in formation of uniform Pd nanoparticles with small size, and no nanowires are self-assembled (see Fig. 3a

and Fig. 2a). However, a proper decrease of the electrostatic repulsion by using a higher Pd concentration or a small amount of stabilizer cannot restrict remarkably the self-assembly process (see Fig. 3b and Fig. 2b) [16]. Therefore, uniform Pd nanowires will be formed. In contrast, with the absence of citrate, the resulting Pd nanostructures are large nanoparticles as well as a few nanowires with large diameter (see Fig 3c, and TEM image not shown here). Thus, Pd may possess superior inherent self-assembly behavior, which is the main reason for formation of Pd nanowires in this study. Here, trisodium citrate is only a stabilizer, controlling the increase of Pd nanowire size.

To study the electrocatalytic activity of Pd NW for formic acid oxidation, Fig. 4 compares the formic acid oxidation activities on the Pd NW and Pd NP. The specific area activities of Pd NW at 0.1 V calculated from the forward-scan currents were $1.38 \text{ mA cm}^{-2} \text{ Pd}$, which is 97% higher than that obtained from Pd NP structures ($0.70 \text{ mA cm}^{-2} \text{ Pd}$). The forward peak current for formic acid oxidation on Pd NW is $2.86 \text{ mA cm}^{-2} \text{ Pd}$, which is significantly higher than $0.97 \text{ mA cm}^{-2} \text{ Pd}$ of that on Pd NP structure.

The electrochemical stability of the Pd NW and Pd NP structures for formic acid oxidation was also investigated by the chronoamperometric curves. A decrease in the current density with time is found in each electrode sample, which is attributed to the intermediate poisoning species formed by formic acid oxidation. After the application of the set potential for 1000 s, the area-normalized current densities for the Pd NW and Pd NP structures were 0.18 and 0.10 mA cm^{-2} , respectively. The results further demonstrate that the Pd NW catalyst exhibited the better performance. Wang et al. indicated that the superior activity of Pd NW network can be attributed to the effective electronic conduction and passage through the highly interconnected networks [10]. Park also support the explanation based on their Pt nanowire work [17]. Recently, Ksar et al. explained the improved activity of Pd nanowire in terms of the electronic states of the surface atoms on nanowires [8]. In our work, both the effective electronic conduction path and unique surface characteristics may contribute to the enhanced electrocatalytic activity of the Pd NW networks.

4. Conclusions

In summary, Pd nanowires with small diameter were formed in solutions by a simple template-free and surfactant-free method. The concentration of Pd precursor is the major factor for formation of Pd nanowires. Trisodium citrate was used as the stabilizer and the control of the stabilizer influences the formation of uniform Pd nanowires with small diameter. The as-prepared Pd nanowires exhibit a superior catalytic activity for formic acid oxidation. The template-free and environmentally friendly method is a very attractive way to produce Pd nanowires for use in formic acid fuel cells.

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