

Facile Preparation of Network Thin Films of Pd Nanoparticles at the Air-Water Interface for Electrocatalysis

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Network-like thin films of Pd nanoparticles (NPs) at the air-water interface were facilely prepared without using any organic capping agents. Firstly, heated the respective acidic solutions of PdCl₂ and SnCl₂ to about 90 °C under stirring, and then mixed the two solutions and continued to heat the mixture to remain that temperature for about 15 min. The formation of the floating films involves the reduction of PdCl₂ by SnCl₂ into Pd NPs protected by the excessive SnCl₃⁻, the thermoaccelerated and oxygen-induced ligand replacement, and the aggregation of the Pd NPs. The films were characterized by transmission electron microscopy, atomic force microscopy and X-ray diffraction. The network films of Pd NPs display high electrocatalytic activity toward the electrooxidation of formic acid.

Keywords: Pd nanoparticles, assembly, air-water interface, network film, electrocatalysis

1. INTRODUCTION

Assemblies of metal NPs have broad applications in nanoelectronics [1], optics [2-3], sensors [4-5], catalysis [6-8], and so on. Varied methods have been developed to assemble NPs into ordered nanostructures and fractal aggregates, including evaporation [9], electrostatic attraction [10], hydrogen-bonding interaction [11], template [12] and interfacial assembly [13]. Among them, assembly of metal NPs at interfaces of oil-water [14-16] and air-water [17-19] is often employed to

prepare 2D nanostructures since these films can be easily transferred onto other solid substrates. Molecularly mediated assembly of metal NPs has been exploring to control the structure and property of nanoassemblies by modifying the NPs with specific organic and biological molecules [20-21].

In contrary, assembly of metal NPs with inorganic ligand is scarce. Talapin et al. have successfully created 2D all-inorganic conductive nanoassemblies by replacing the traditional (insulating) organic surface ligands of NPs with an inorganic cluster like $[\text{Sn}_2\text{S}_6]^{4-}$ [22]. Dong and Jin prepared 2D fractal aggregates of Ag-Au roughened core-shell NPs at the air-water interface by a thermoaccelerated electroless plating method with seeds of Ag NPs in a bath containing HAuCl_4 and NH_2OH [23]. Theoretical and experimental studies in our previous paper demonstrated that Au colloids can be stabilized for a long time with an inorganic ligand of SnCl_3^- under airproof condition. And large area ultrathin films of Au NPs can be obtained at the air-water interface of the Au colloid by oxygen-induced ligand replacement of SnCl_3^- with Cl^- [24].

In the present work, we report a facile method to prepare network-like thin films of Pd NPs at the air-water interface by heating a mixed solution of PdCl_2 and excessive SnCl_2 in an HCl medium without using any organic capping agents. To our knowledge, no such work has been reported before. The assembled film demonstrates high electrocatalytic activity toward the oxidation of formic acid.

2. EXPERIMENTAL PART

Reagents used were of analytical grade including PdCl_2 (Sinopharm Chemical Reagent Co., Ltd.), $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (Sigma-Aldrich Chemical Co.), HCl, HClO_4 , and HCOOH from different sources. All solutions of them were freshly prepared with ultra-pure water from a water purification system (Millipore Corp., USA). Weighing bottles (30×50 mm) were used as vessels for the preparation of network films of Pd NPs. Prior to use the glassware was cleaned with freshly prepared aqua regia (HNO_3 : HCl in 1 : 3 by volume) and rinsed thoroughly by ultra-pure water.

The network films of Pd NPs were prepared as follows: firstly, heated the respective acidic (with 2 mol dm^{-3} HCl) solutions of 10 cm^3 of 2 mmol dm^{-3} PdCl_2 and 10 cm^3 of 20 mmol dm^{-3} SnCl_2 to about 90°C under stirring on an electric jacket, and then mixed the two solutions and continued to heat the mixture to remain that temperature for about 15 min. A thin shiny film can be clearly seen at the air-water interface. The resulting films were transferred onto clean glass plates by Langmuir-Schäfer horizontal lifting [15], then detached from the glass plates, floating on a solution of hydrochloric acid (2 mol dm^{-3}), and rinsed for a few minutes. Subsequently, the film was transferred onto the other substrates for characterization after being dried in the air.

The film morphology of the Pd NPs was characterized either with a JEOL-1230 transmission electron microscope (TEM) or with a Veeco atomic force microscopy (AFM) in contact mode using a silicon nitride probe. X-ray diffraction (XRD) patterns were collected on a Philips PW 3040/60 powder

diffractometer using Cu K α radiation in a 2θ range from 30 to 90° with a scan rate of 0.2° s⁻¹. The working voltage of the instrument was 40 kV and the current was 40 mA.

Electrochemical measurements were performed on a CHI 660C electrochemical station (Chenhua, Shanghai, China) with a three-electrode configuration [25]. The counter electrode was a circular platinum wire (12 cm length and 1 mm diameter) and the reference electrode was saturated mercurous sulphate. The working electrode either was a pure smooth Pd disk (1 mm diameter, purity \geq 99.99%) or was the prepared thin film of Pd NPs loaded on the smooth Pd disk. Prior to use the Pd disk electrode was polished successively with emery paper and 1 μ m alumina, followed by ultrasonic cleaning in ultra-pure water.

3. RESULTS AND DISCUSSION

Inorganic species of SnCl₃⁻ is employed here acting both as a reducing agent and as a capping agent. Fig. 1 gives a schematic illustration for the preparation of the network thin film of Pd NPs at the air-water interface, similar to our previous work on the assembly of Au NPs [24]. However, heating is adopted here to speed the process and the film of Pd NPs can be obtained in 15 min, much faster than that in the assembly of Au NPs at room temperature, which took several hours [24]. By heating the mixed solution of respectively preheated solutions of PdCl₂ and SnCl₂ in the HCl medium, the solution turns to grayish black soon due to the formation of Pd NPs protected by the excessive SnCl₃⁻, which is the main species within a wide region of Cl⁻ concentrations in acidic solutions [26]. The protective ligand of SnCl₃⁻ can be oxidized by O₂ from the air and replaced by the aggressive Cl⁻ in the solution. Aggregation of Pd NPs thus occurs at the interface and they are trapped there by the surface tension, noting that the ligand replacement can only take place at the interface because of the presence of excessive Sn(II) in the bulk colloid. No such floating films can be obtained by heating a Pd colloid with a poly(*N*-vinyl-2-pyrrolidone) (PVP) capping agent prepared according to a previous report [27].

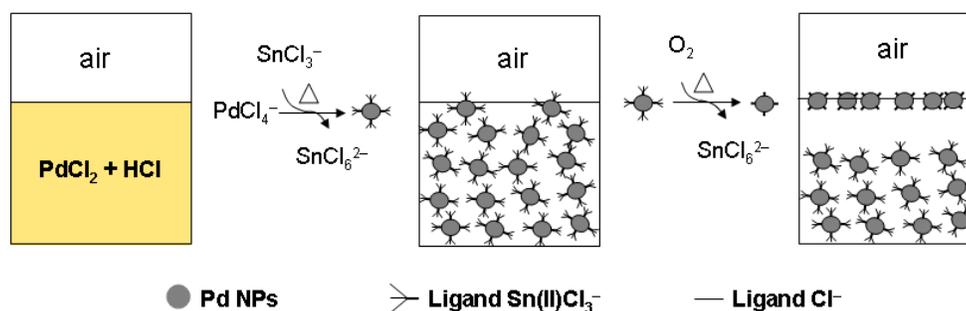


Figure 1. A schematic illustration for the preparation of the network film of Pd NPs at the air-water interface by thermoaccelerated, oxygen-induced ligand replacement and aggregation of the Pd NPs.

Fig. 2 shows the photographs of the large area floating film of aggregated Pd NPs. The thin film displays metal luster (the inset). The randomly distributed black spots in the film are the uncovered surface by the aggregated NPs due to solvent evaporation.

The XRD patterns of the thin floating film in Fig. 3 can be indexed to the diffraction of face-centered cubic structure of metallic palladium (JCPDS, card no. 87-0645). Although the peak intensity is weak, the (111) and (200) crystalline orientations are apparently distinct.

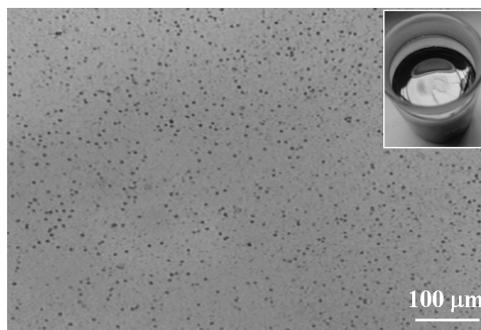


Figure 2. Photos of the large area floating film of Pd NPs.

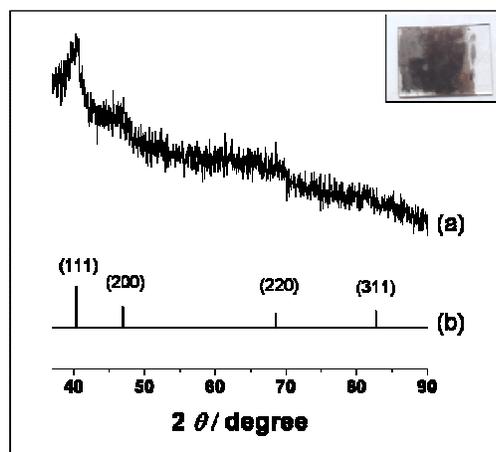


Figure 3. XRD patterns of the floating film of Pd NPs. The inset is the photograph of the sample loaded on a glass plate.

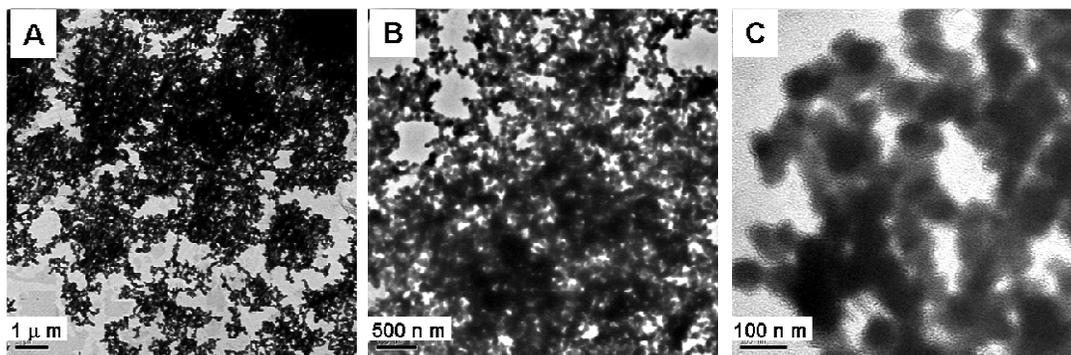


Figure 4. TEM images of the floating thin film of Pd NPs with different enlargement scales.

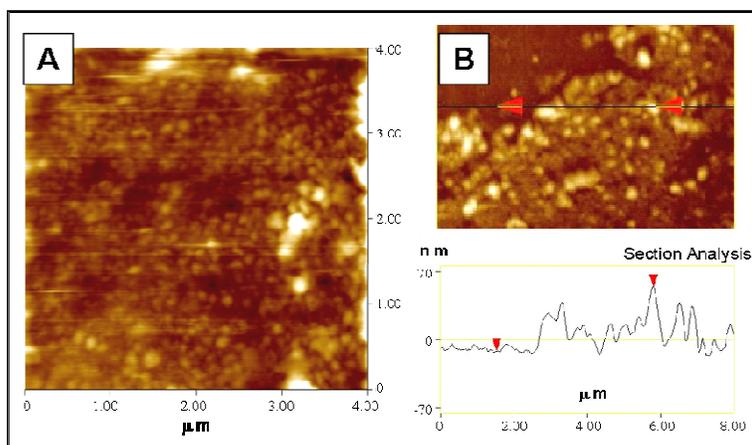


Figure 5. (A) A typical AFM image and (B) the section analysis of the thin films of Pd NPs loaded on a silicon substrate.

From the TEM image in Fig. 4, we can see clearly that the film is network-like, consisting of one or two layers of Pd NPs with a diameter about 50 nm. Fig. 5(A) shows the typical AFM image of the floating thin film of Pd NPs and the morphology is in accord with the TEM images in Fig. 4. The section analysis in Fig. 5(B) shows that the maximum thickness is about 70 nm, corresponding to a two-layer packing of Pd NPs.

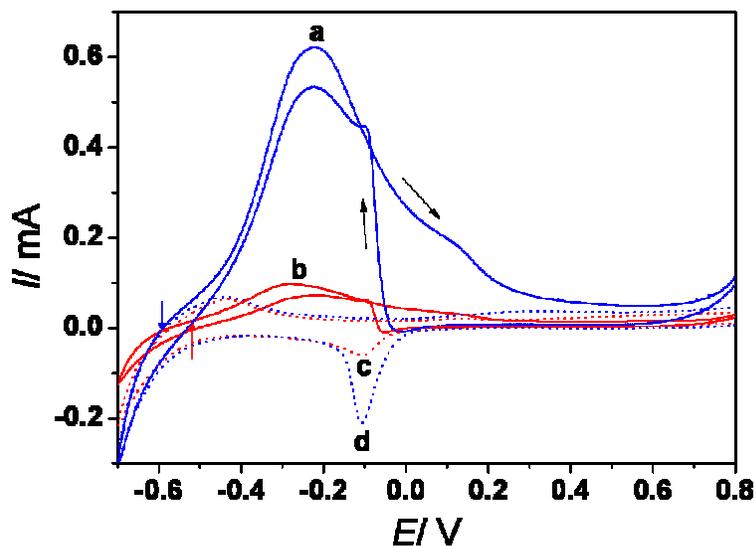


Figure 6. Cyclic voltammograms on the electrodes of (a) the thin film of the Pd NPs and (b) the smooth Pd disk in a solution of (a-b) $1 \text{ mol dm}^{-3} \text{ HClO}_4 + 1 \text{ mol dm}^{-3} \text{ HCOOH}$ or (c-d) $1 \text{ mol dm}^{-3} \text{ HClO}_4$. The thin film was loaded on the smooth Pd disk. The vertical color arrows on the left indicate the initial potentials for the oxidation of formic acid.

The network thin film of Pd NPs has much better electrocatalytic activity toward the oxidation of formic acid in an acidic solution than the smooth Pd electrode (Fig. 6). Note that the onset oxidation potential on the thin film (Fig. 6a) has a negative shift about 0.1 V and the oxidation peak current is greatly enhanced to about six times as large as that with the smooth Pd disk (Fig. 6b). It can be easily inferred from Fig. 6(c) and (d) that larger real area is not the sole reason for the high electrocatalytic activity of the network film of the Pd NPs. In the blank solution of HClO_4 , the current in the hydrogen region is only slightly larger for the thin film (the blue dotted line), which looks almost the same. In the oxygen region the peak current for the reduction of oxygen species is about two times larger for the thin film, indicating that Pd NPs are active to form adsorbed oxygen species, which might account for the high activity of the thin film of aggregated Pd NPs.

4. CONCLUSIONS

We have demonstrated that ultrathin films of Pd NPs assembly can be facilely prepared at the air-water interface by heating the mixed solutions of PdCl_2 and excessive SnCl_2 in the HCl medium. The inorganic species of SnCl_3^- can act both as the reducing agent and as the capping agent without using any organic substances. Heating can speed up the oxygen-induced ligand replacement, and the floating network thin film of aggregated Pd NPs can be obtained as quickly as in 15 min after mixing

the two solutions. The as-prepared network thin film of Pd NPs displays high electrocatalytic activity toward the electrooxidation of formic acid in acidic solution.

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