Synthesis of "Clean" and Well-Dispersive Pd Nanoparticles with Excellent Electrocatalytic Property on Graphene Oxide

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S *Supporting Information*

ABSTRACT: Ultrafine Pd nanoparticles monodispersed on graphene oxide (GO) surfaces were successfully prepared by the redox reaction between $PdCl_4^{2-}$ and GO. The as-made catalyst is very "clean" as a result of the surfactant-free formation process, allowing it to express high electrocatalytic ability in formic acid and ethanol oxidation relative to a commercial Pd/C catalyst. This simple and straightforward method is of significance for the facile preparation metal nanocatalysts with high catalytic activity on proper supporting materials.

Figure 1. (A−C) TEM and (D) HRTEM images of the as-synthesized PdNPs−GO.

As important catalysts, noble metals with ultrafine sizes have attracted particular interest because of their increased surface area and the number of edge and corner atoms, which greatly improve their catalytic properties.[1] For this purpose, metal particles must be produced as small as possible with a high accessible surface area. However, the surface energy increases with decreasing particle size, which usually leads to serious aggregation of the small particles in order to minimize the total surface energy.[2] To avoid the aggregation, various stabilizers, such as surfactants,[3a] polymers,[3b] and dendrimers[3c] as well as different types of ligands,[3d] have been applied as capping agents to stabilize the particles. Unfortunately, the presence of capping agents around the nanoparticles may severely limit their chemical activities. Recently, it was found that epitaxial linking of Au nanoparticles (AuNPs) with an Fe_3O_4 support greatly enhanced the AuNPs' stability and that the AuNPs kept their activity and size during catalysis.[4] Such experimental facts suggest that another solution to prevent aggregation could be anchoring of metal particles on specific supports.

Recently, Pd-based catalysts have become a hot topic of interest because of their lower cost and greater resistance to CO in comparison with Pt catalysts in polymer electrolyte membrane fuel cells.[5] Research based on first-principles calculations indicates that Pd could interact with and bind more strongly to graphene because more interaction states and transmission channels are generated between them and because Pd tends to grow into three-dimensional structures on graphene surfaces.[6] This provides a hint that graphene oxide (GO) could be an ideal substrate for growing and anchoring Pd nanoparticles (PdNPs) for high-performance electrocatalytic or electrochemical devices.
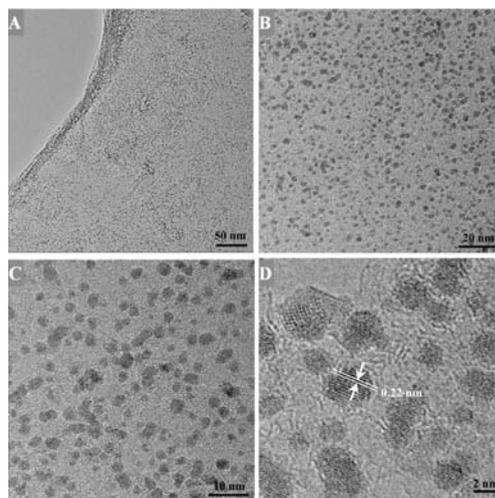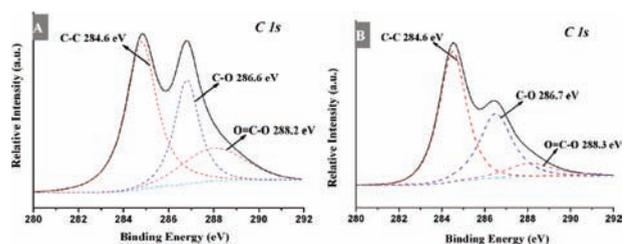
In this communication, we demonstrate that clean and well-dispersed PdNPs can be prepared by strongly anchoring the PdNPs on a GO surface, which prevents aggregation of the NPs. Moreover, in contrast to previous studies in which noble metal (e.g., Pt)-loaded GO was synthesized by applying additional reductants and surfactants,[7] GO also amazingly acted as the reductant in our synthesis. Inspired by the monodisperse, ultrafine and pristine properties of PdNPs, the PdNP-loaded GO electrocatalyst (PdNPs−GO) revealed an unusually high activity for formic acid and ethanol oxidation in acid and alkaline media, respectively.

GO was prepared from graphite spheres using the modified Hummers' method.[8] In a typical synthesis of PdNPs−GO, GO and a K_2PdCl_4 aqueous solution were mixed together in an ice bath for 30 min with vigorous stirring. The resulting products were then collected by centrifugation and washed several times with pure water. Figure 1 shows a transmission electron microscopy (TEM) image of PdNPs−GO from the synthesis. The most striking feature is that the PdNPs with a uniform size ~3.5 nm are fairly well monodispersed on the surfaces of GO. The high-resolution TEM (HRTEM) image (Figure 1D) of the

Figure 2. XPS spectra of C_{1s} on (A) GO and (B) PdNPs−GO.

Figure 3. CVs of PdNPs−GO and commercial Pd/C at 50 mV s^{-1} in (A) 0.5 M H_2SO_4 with 0.25 M formic acid and (B) 1.0 M NaOH with 0.5 M ethanol.

PdNPs shows that the interplanar spacing of the particle lattice is 0.22 nm, which agrees well with the (111) lattice spacing of face-centered cubic (fcc) Pd (0.224 nm). PdNPs−GO was further characterized by X-ray photoelectron spectroscopy to investigate the surface nature of the PdNPs and GO. The binding energy of 335.2 eV (Figure S1 in the Supporting Information) corresponds to the $3d_{5/2}$ component of the metallic Pd(0) state,[9] further testifying to the presence of metallic Pd. In addition, it is worth mentioning that the stability of the as-made PdNPs was so good that nearly no changes were observed in morphologies or sizes after the as-prepared PdNPs−GO was dispersed in aqueous solution for 2 months (Figure S2).

The driving force for Pd deposition on GO could be caused by the difference between the reduction potential of $PdCl_4^{2-}$ (0.83 V vs SCE) and the oxidation potential of GO (0.48 V vs SCE). Comparison with the binding energy of C_{1s} on a GO surface (Figure 2) clearly shows that after the reaction the peaks associated with C−C bonds (284.6 eV) became predominant while the additional peak of C−O (286.6 eV) was obviously reduced. These results indicate that the oxygenated functional groups on the GO surface may play an important part in the formation of PdNPs. Additionally, similar PdNPs−GO can be obtained under dark conditions and without ultrasonic concussion in the treatment of products, suggesting no significant light effect or other power source in the PdNPs−GO formation process. Therefore, it is rationally deduced that the spontaneous deposition of PdNPs on GO is ascribed to the redox reaction between GO and $PdCl_4^{2-}$, which is similar to the reaction mechanism between PtNPs and single-walled carbon nanotubes proposed by Dai et al.[10] It should be pointed out that the growth of PdNPs after nucleation might involve a galvanic-reaction-like process in which the reduction of Pd occurs on Pd nuclei by the electrons transferred from GO, with accompanying oxidation of GO.

To better understand the PdNPs' growth process, PdNPs−GO synthesized under different conditions was investigated by TEM. The TEM images indicated that Pd nuclei (1 nm) were formed after 5 min of reaction (Figure S3). Increasing the reaction time resulted in the growth of Pd nuclei but did not lead to an apparent increase or decrease in the density of particles, indicating that an instantaneous nucleation process occurred and that no Ostwald ripening took place following nucleation. This phenomenon also implies a strong anchoring effect between the Pd nuclei and the GO surface. However, when the reaction temperature was over 50 °C, Ostwald ripening obviously occurred, leading to a decrease in the number the nuclei and an increase in the particle size distribution (Figure S4). Such a phenomenon indicates an increase in the mobility of Pd nuclei on the GO surface due to weakening of the anchoring ability at higher temperature.

Inspired by the attractive properties (monodisperse, ultrafine, and pristine) of the PdNPs on GO, we tested our catalyst in electro-oxidation of formic acid and ethanol to study its catalytic ability. The electrochemically active surface areas (ECSAs) of both PdNPs−GO and a commercial Pd/C catalyst (Sigma-Aldrich 205699) were estimated by a calculation of the hydrogen desorption area from cyclic voltammograms (CVs) in 0.5 M H_2SO_4 solution (Figure S5). Because of the surfactant-free PdNPs surface, stable CVs of our catalyst could be easily achieved in 5 cycles. The oxidation currents were normalized to the ECSAs (0.175 cm^2 for PdNPs−GO and 0.153 cm^2 for Pd/C) for further comparison of the activities of the different catalysts. Figure 3A depicts the CVs of PdNPs−GO and commercial Pd/C in 0.5 M H_2SO_4 with 0.25 M formic acid. It can be seen that the formic acid oxidation on PdNPs−GO started at about −0.15 V, which is lower than the onset voltage for Pd/C (−0.10 V). Moreover, in the positive-going potential scan, the peak current density on PdNPs−GO was 5.2 mA cm^{-2}, ∼2.6-fold higher than that on Pd/C (2.1 mA cm^{-2}). This result implies PdNPs−GO possesses better catalytic activity than Pd/C in the oxidation of formic acid. On the other hand, PdNPs−GO also exhibited superior catalytic activity in alkaline media (Figure 3B). In the presence of 1.0 M NaOH and 0.5 M ethanol, the onsets of ethanol oxidation on PdNPs−GO were still earlier than on Pd/C. The peak current densities were ∼3- and 1.6-fold larger for our PdNPs−GO than for the commercial Pd/C catalyst in the positive- and negative-going potential scans, respectively. In addition, PdNPs−GO also exhibited high stability in electrooxidation. After 100 potential cycles, the drops were ∼4.4% (formic acid oxidation) and 6.3% (ethanol oxidation) of the initial catalytic activity in the positive-going scans on PdNPs−GO, which are much smaller than those of the Pd/C catalyst (Figure S6). This proves that our PdNPs−GO is a more active and stable catalyst in both acid and alkaline media.

In summary, we have developed a facile method for synthesizing PdNPs with a very narrow size distribution by the redox reaction between $PdCl_4^{2-}$ and GO. The resulting material, PdNPs−GO, is very "clean" because of the surfactant-free formation process, allowing it to express high electrocatalytic ability in formic acid and ethanol oxidation. We are currently carrying out a similar synthesis to prepare AuNPs−GO, AgNPs−GO, and PtNPs−GO. This simple, straightforward, and general method is of significance for the facile preparation metal nanocatalysts on proper supporting materials.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Detailed materials, instrumentation, and preparation and characterization of PdNPs−GO. This material is available free of charge via the Internet at http://pubs.acs.org.

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