Simple preparation method of Pd nanoparticles on an Au electrode and its catalysis for dioxygen reduction†

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A simple method for the fabrication of Pd nanoparticles is described. The three-dimensional Pd nanoparticle films are directly formed on a gold electrode surface by simple electrodeposition at −200 mV from a solution of 1 M $H_2SO_4 + 0.01$ mM K_2PdCl_4. X-Ray photoelectron spectroscopy verifies the constant composition of the Pd nanoparticle films. Atomic force microscopy proves that the as-prepared Pd nanoparticles are uniformly distributed with an average particle diameter of 45–60 nm. It is confirmed that the morphology of the Pd nanoparticle films are correlated with the electrodeposition time and the state of the Au substrate. The resulting Pd-nanoparticle-film-modified electrode possesses high catalytic activity for the reduction of dissolved oxygen in 0.1 M KCl solution. Freshly prepared Pd nanoparticles can catalyze the reduction of O_2 by a 4-electron process at −200 mV in 0.1 M KCl, but this system is not very stable. The cathodic peaks corresponding to the reduction of O_2 gradually decrease with potential cycling and at last reach a steady state. Then two well-defined reduction peaks are observed at −390 and −600 mV *vs.* Ag/AgCl/KCl (sat.). Those two peaks correspond to a 2-step process for the 4-electron reduction pathway of O_2 in this neutral medium. The former peak is ascribable to the 2-electron reduction of O_2 to H_2O_2, while the latter is assigned to the reduction of H_2O_2 to H_2O. The observed electrocatalysis for the reduction of O_2 is attributable to the extraordinary catalytic activity of the Pd nanoparticles over the bulk gold electrode.

Introduction

In recent years, the fabrication of nanostructured materials and the exploration of their properties has attracted much attention from scientists in various fields.[1–3] The continuing interest in nanosized noble metal particles has been driven by their unusual physical and chemical properties, which are quite different from those of the bulk materials.[4–6] Intensive studies have been devoted to their use as catalysts and sensors, as well as their potential applications in a new generation of optical, electronic and magnetic devices.[7–11] These applications are closely related to their size- or shape-dependent properties, such as size quantization, optical and electronic properties, surface effects, chemical reactivity, and self-assembly ability. Among these studies, some have been directed toward the synthesis of palladium nanoclusters,[12–16] partly because of the important role played by palladium in catalysis where the catalytic activity has been found to be very sensitive to the particle size, shape, surrounding media, *etc.*[17–19]

Pd colloidal particles have been prepared by a variety of techniques, including chemical liquid deposition,[20] refluxing alcohol reduction,[21–23] hydrogen reduction[24] and electrochemical deposition,[25] where, in general, the particles were formed by the reduction of metal ions in the presence of stabilizers. Moreover, most of the nanoparticles must be pre-synthesized through reduction of a metal salt by reducing agents in solution.[26,27] Often the catalyst particles are stabilized in a suitable solid matrix or by surface modification using polymers or ligands. For example, Crooks *et al.*[28,29] have prepared PAMAM dendrimer-encapsulated Pd and other metal nanoparticles that employ dendrimers as both template and stabilizer. Mayer *et al.*[30] have reported that Pd nanoparticles were prepared by reducing the metal precursors in the presence of the protective amphiphilic block copolymer polystyrene-*b*-poly(methacrylic acid). Bronstein *et al.*[23] have also reported that Pd colloids were prepared in polystyrene-poly-4-vinylpyridine (PS-*b*-P4VP) block copolymer micelles and deposited on Al_2O_3. However, a poor stability of the Pd particles under these conditions has been reported. In addition, this type of stabilization leads to the loss of catalytic activity to a great extent.[31] In this work, a direct synthetic method of three-dimensional Pd nanoparticles on a gold electrode was developed.

Oxygen reduction on an electrode surface is one of the most fundamental electrochemical reaction. This reaction is relevant to the processes occurring not only in fuel cells but also to those related to corrosion and metal-air batteries. Consequently dioxygen reduction has been well-studied. Several electrode materials with or without modification have been suggested as cathodes for the reduction of O_2 in different media.[32,33] However, it is undisputed that Pt is still the indispensable and most effective catalyst.[34] Recently, surface-modified palladium electrodes have been suggested for many electrocatalytic and electroanalytical applications in view of their superior activity.[35,36] On the other hand, the electrodeposition of highly dispersed Pd nanoparticles on an inert substrate attracts growing interest because of their extraordinarily high catalytic activity in many reactions involving small organic molecules.[16,37] But electrodes modified with Pd have been far less intensively investigated than the Pt electrode for the electrocatalysis of O_2 reduction.

In this communication, a simple preparation method of a three-dimensional Pd nanoparticle film is reported. Ideally,

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† Electronic supplementary information (ESI) available: XRD pattern of an evaporated Au electrode and CVs for the reduction of O_2 on a bare Au(111) electrode or a Pd-nanoparticle-film-modified electrode. See: http://www.rsc.org/suppdata/nj/b3/b300566f/

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well-dispersed palladium nanocrystals were deposited on a gold electrode from the electrolyte. AFM and XPS were used to characterize the Pd nanoparticles. The resulting Pd-nanoparticle-film-modified electrode possesses high catalytic activity for the reduction of dissolved oxygen.

Experimental

General procedures

Milli-Q water (18 MΩ resistivity; Millipore systems) was used for all experiments. Potassium tetrachloropalladate (K_2PdCl_4), KCl, H_2O_2 and H_2SO_4 were of analytic grade and used as received.

Analysis of the X-ray photoelectron spectra (XPS) was performed on a ESCLAB MK II using Mg as the exciting source. AFM measurements were performed with a Digital Nanoscope IIIa multimode system (DI, Santa Barbara, CA, USA). The images were acquired in the tapping mode. Measurements were made with the Si cantilever in air at room temperature. The force constant of the cantilever was 0.1–0.6 N m^{-1} with a scan rate of 1–2 Hz.

Electrochemical measurements

Cyclic voltammetry was performed with a CHI 660 electrochemical workstation (USA) in a conventional three-electrode electrochemical cell. The working electrode was an Au wire (ϕ = 3.5 mm) sealed in a Teflon jacket. The exposed geometric surface area of the electrode was 0.096 cm^2. Twisted platinum wire and Ag/AgCl/KCl (sat.) were the counter and the reference electrode, respectively. Prior to each experiment, if necessary, O_2 was bubbled directly into the cell for 30 min to obtain an O_2-saturated 0.1 M KCl solution and during the measurements O_2 was flushed over the cell solution. Electrolyte solutions were, if necessary, deaerated by bubbling N_2 for at least 30 min prior to electrochemical measurements. All the measurements were performed at room temperature.

Electrode modification procedure

The polycrystalline Au electrodes and Au plates were polished with aqueous slurries of successively finer α-Al_2O_3 powder (down to 0.05 μm) and were sonicated in water. After being washed carefully with distilled water, the Au electrodes were electrochemically pretreated in a 0.5 M H_2SO_4 solution by repeating the potential scan in the range of −0.2 to 1.5 V *vs.* Ag/AgCl/KCl (sat.) at 100 mV s^{-1} until the cyclic voltammogram (CV) characteristic for a clean Au electrode was obtained. The glass-covered gold films were purchased from Beijing (The Institute of Electronics, Chinese Academy of Sciences, China). The gold films were cleaned in a mixture of H_2SO_4–H_2O_2 (7:3; piranha solution), washed carefully with distilled water and dried in a stream of nitrogen. Then the Au films were characterized with XRD and shown to be Au (111) single crystal. (see Electronic supplementary information, ESI). Cleaned gold electrodes were modified by electrodeposition at −200 mV from a solution containing 0.01 mM $K_2PdCl_4 + 1.0$ M H_2SO_4 with magnetic stirring of the electrolyte solution. In this paper, all the modified Au electrodes used to catalyze O_2 are prepared by electrodeposition for 30 min.

Results and discussion

XPS and AFM characterization of Pd nanoparticles electrodeposited on Au electrode

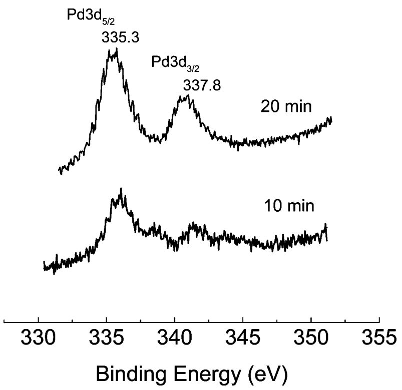

Fig. 1 X-Ray photoelectron spectra of the Pd 3d energy levels for a gold plate modified with Pd nanoparticle films by electrodeposition for 10 min and 20 min.

In order to confirm the existence of the palladium nanoparticles electrodeposited on the gold electrode surface, XPS experiments were carried out. In Fig. 1, two peaks at 335.0 and 342.5 eV, which are the characteristic $3d_{5/2}$ and $3d_{3/2}$ peaks for Pd^0, indicate the existence of Pd^0 on the Au electrode. We can see that as the electrodeposition time is prolonged, the intensity of the Pd^0peaks is increased.

Atomic force microscopy (AFM) provides further detailed information involving the surface morphology and homogeneity of the films. Fig. 2 presents the typical tapping-mode AFM images of the palladium nanoparticle films electrodeposited on gold plates at −200 mV for 10 and 30 min. After electrodeposition for 10 min [Fig. 2(B)], the Pd nanoparticles can be seen clearly. They form a densely packed film, in which each particle is in contact with adjacent ones. The Pd particles are homogeneously distributed on the electrode surface and relatively uniform with a size of 45 nm. The mean roughness (7.30 nm) is higher than that of the bare Au substrate [Fig. 2(A), 5.57 nm], but the Au electrode surface is not completely covered with Pd nanoparticles. When electrodeposition is prolonged to 30 min [Fig. 2(C)], the nanoparticles become more closely packed. In this case, the surface mean roughness is higher (9.87 nm), and the diameter (60 nm) of the Pd nanoparticles is bigger than that of the Pd nanoparticles obtained after electrodeposition for 10 min. In addition, from Fig. 2(C) we can see that the nanoparticles are arranged in lines and look to be in a very ordered arrangement. A tentative explanation might be that the bare Au substrate plate has some line terraces [Fig. 2(A)], because the metal nanoparticles tend to form at terrace zones of the surface.[38] From this point, we can infer that the morphology of the Pd nanoparticle films directly depend on the surface state of the substrate and the electrodeposition time. This interpretation is further supported by experiments in which the Pd nanoparticles are electrodeposited on an Au(111) single-crystal electrode. Fig. 2(D) and Fig. 2(E) show the AFM morphology for the bare Au(111) single-crystal surface and Pd nanoparticles electrodeposited onto an Au(111) electrode, respectively. It is clear from Fig. 2(E) that the Pd nanoparticles nicely dispersed on the surface of the Au(111) electrode and that they are very different from those shown in Fig. 2(C). This is because the surface of the bare Au(111) electrode (surface roughness: 1.63 nm) is smoother than that of the polycrystalline Au electrode (surface roughness: 5.57 nm).

The resulting Pd nanoparticle films are very stable. When immersed in 0.1 M KCl solution for one month, the morphology shows no change. This is a very valuable property for catalysts and device fabrication. It also allows one to obtain uniform charge transport throughout the whole films.

O_2 reduction by Pd nanoparticles electrodeposited on an Au electrode

Fig. 3 shows the cyclic voltamograms (CVs) obtained for the reduction of O_2 with bulk and Pd-nanoparticle-modified Au

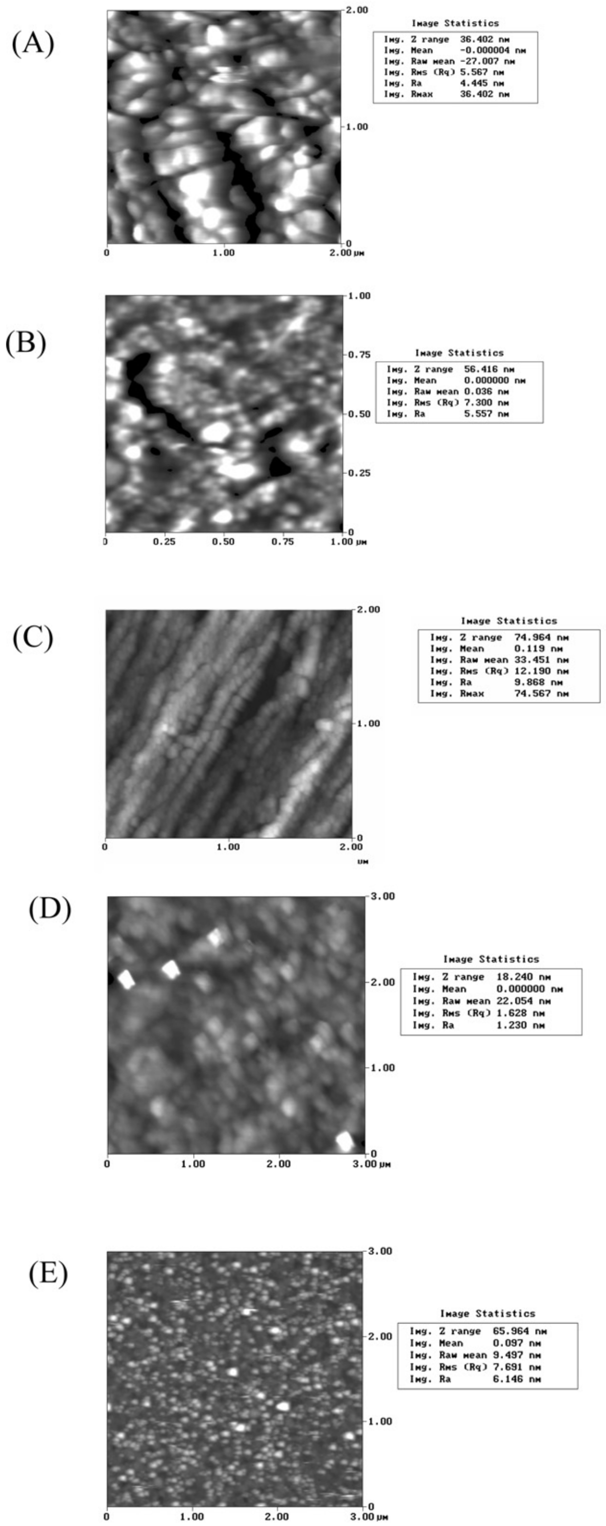

Image Statistics

Img. Z range	36.402 nm
Img. Mean	-0.000004 nm
Img. Raw mean	-27.007 nm
Img. Rms (Rq)	5.567 nm
Img. Ra	4.445 nm
Img. Rmax	36.402 nm

Image Statistics

Img. Z range	56.416 nm
Img. Mean	0.000000 nm
Img. Raw mean	0.036 nm
Img. Rms (Rq)	7.300 nm
Img. Ra	5.557 nm

Image Statistics

Img. Z range	74.964 nm
Img. Mean	0.119 nm
Img. Raw mean	33.451 nm
Img. Rms (Rq)	12.190 nm
Img. Ra	9.868 nm
Img. Rmax	74.567 nm

Image Statistics

Img. Z range	18.240 nm
Img. Mean	0.000000 nm
Img. Raw mean	22.054 nm
Img. Rms (Rq)	1.628 nm
Img. Ra	1.230 nm

Image Statistics

Img. Z range	65.964 nm
Img. Mean	0.097 nm
Img. Raw mean	9.497 nm
Img. Rms (Rq)	7.691 nm
Img. Ra	6.146 nm

Fig. 2 AFM images of Pd nanoparticle films prepared on an Au plate by electrodeposition for (A) 0; (B) 10 and (C) 30 min, respectively; (D) bare Au(111) electrode and (E) Pd nanoparticle film on an Au(111) electrode (electrodeposition for 30 min).

electrodes in air-saturated 0.1 M KCl solution. This figure reflects two important catalytic features of the Au electrode loaded with the Pd nanoparticles: (i) a significant positive shift and combination of the O_2 reduction peak from −280 and −700 mV (in the case of the bulk Au electrode) to −200 mV upon loading of the Pd nanoparticles and (ii) an increase in the peak current (compares curves a and b). At the bulk Au electrode, the reduction peaks at −280 mV and −700 mV *vs.* Ag/AgCl/KCl (sat.) are due to the 2-electron reduction of O_2 to H_2O_2 and the further reduction of H_2O_2 to H_2O, respectively.[39] The difference between the two peak potentials is very large. This means that the reduction of H_2O_2 on Au is rather slow. For the Au electrode with electrodeposited nanosized Pd particles, the single reduction peak at −200 mV is rationalyl considered the 4-electron reduction of O_2.

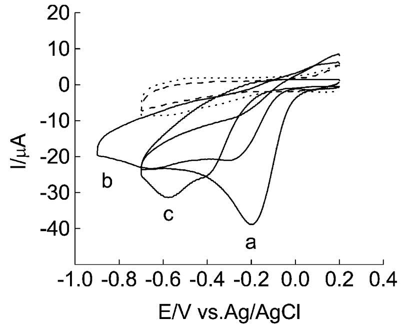

Fig. 3 CVs obtained for the O_2 reduction at: (a) freshly prepared Pd nanoparticles deposited on an Au electrode; (b) bulk Au electrode; (c) modified electrode of (a) after potential cycling for hours in air-saturated 0.1 M KCl solution. The dashed and dotted lines correspond to the bare and modified Au electrode, respectively, in N_2-saturated 0.1 M KCl solution. Potential scan rate: 100 mV s^{-1}.

In order to sustain this suggestion, the CVs were measured with a freshly prepared modified Au electrode. Fig. 4(A) shows cyclic voltammograms of the nanosized Pd particles electrodeposited on an Au electrode in the same solution saturated by O_2 at different scan rates. The peak currents vary as a linear function of the square root of the scan rate, indicating a diffusion-controlled electrochemical process. The number of electrons (n) for the catalytic reduction of dioxygen can be calculated from the slope of the plot of i_p *vs.* $v^{1/2}$.[40] The experimental results almost match the calculated peak currents for the reduction of dioxygen to water ($n = 4$), as shown in Fig. 4(B). But the situation of curve a in Fig. 3 is not very stable. The peak corresponding to the reduction of O_2 gradually decreases with potential cycling and reaches a steady state at last as shown by curve c in Fig. 3. Two well-defined reduction peaks were observed at −390 and −600 mV *vs.* Ag/AgCl/KCl (sat.). These two peaks are also ascribable to the 2-electron reduction of O_2 to H_2O_2 and the further reduction of H_2O_2 to H_2O. Compared with curve b in Fig. 3, the peak current is higher and the difference between the potentials of O_2/H_2O_2 and H_2O_2/H_2O is smaller. This indicates that the reduction of H_2O_2 by Pd nanoparticles deposited on a polycrystalline Au electrode is more rapid than on a bulk Au electrode.

To further confirm the mechanism of O_2 reduction at the modified Au electrode after potential cycling for hours, the

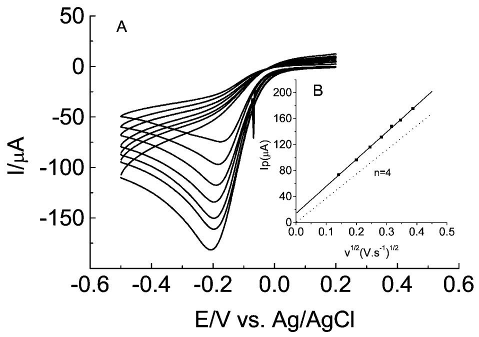

Fig. 4 (A) Cyclic voltammograms of an O_2-saturated solution at 20, 40, 60, 80, 100, 120, and 150 mV s^{-1}. (B) Plot of the electrocatalytic dioxygen reduction peak current as a function of the square root of the scan rate (solid circles and line) and the calculated curve for the reaction with $n = 4$ (dashed line). Electrolyte: 0.1 M KCl.

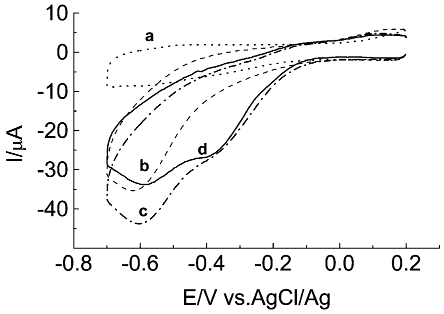

Fig. 5 Cyclic voltammograms at the Pd nanoparticles electrodeposited on an Au electrode (potential cycling for hours) in 0.1 M KCl solution saturated with N_2 (a), (b) and air (c), (d) in the absence (a), (d) and the presence (b), (c) of 2.7 mM and 2.0 mM H_2O_2, respectively. Potential scan rate: 100 mV s^{-1}.

CVs shown in Fig. 5 were conducted. Fig. 5 compares the CVs obtained at the Pd-nanoparticle-modified Au electrode after potential cycling for hours in 0.1 M KCl saturated with N_2 or air, in the absence and presence of H_2O_2. It is clear from this figure that the addition of H_2O_2 to the air-saturated 0.1 M KCl solution resulted in an increase in the reduction peak current at −600 mV, while the peak current at −390 mV was not affected (compare curves d and c). On the other hand, the addition of H_2O_2 to the N_2-saturated solution caused the appearance of a reduction peak at −600 mV and no peak was observed at −390 mV (compares curves a and b). As a conclusion of this figure, the 2-step 4-electron reduction pathway of O_2 is feasible in this neutral medium upon electrodeposition of Pd nanoparticles on Au electrode, which has been potential cycled for hours. This electrocatalytic behavior is attributed to the extraordinarily high catalytic activity of Pd nanoparticles on a bulk Au electrode.

The reduction of O_2 on Pd nanoparticles electrodeposited on an Au(111) single-crystal electrode was also investigated. It was found that the thus-prepared Pd nanoparticles still have high catalytic activity for the reduction of O_2 (see ESI).

Conclusion

In this communication, we report a simple method for the preparation of Pd nanoparticle films on an Au electrode. This method, simple and fast, is a general approach to the preparation of metal nanoparticles on solid surfaces. X-Ray photoelectron spectroscopy verifies the constant composition of the Pd nanoparticle films. Atomic force microscopy proves that the as-prepared Pd nanoparticles are uniformly distributed with an average particle diameter. It is confirmed that the morphology of the Pd nanoparticle films are correlated with the electrodeposition time and the surface state of the Au substrate. The resulting Pd-nanoparticle-film-modified electrode possesses high catalytic activity for the reduction of dissolved oxygen in 0.1 M KCl solution by a 4-electron process. Thus as-prepared Pd nanoparticle films on Au electrodes are a promising oxygen sensor, which may find uses for monitoring dissolved dioxygen (DO) in environmental analysis.

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