



Palladium modified gold nanoparticles as electrocatalysts for ethanol electrooxidation



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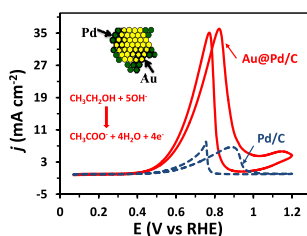
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HIGHLIGHTS

- Au@Pd core-shell catalysts consist of tiny Pd clusters with a coverage of 0.5–0.6.
- The Au@Pd is 5.4 times more active than Pd/C toward ethanol oxidation.
- The onset potential of ethanol oxidation is 100 mV lower than Pd/C.
- The larger the Au particle, the higher the ethanol oxidation current.

GRAPHICAL ABSTRACT



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ABSTRACT

Resembling core-shell electrocatalysts consisting of a Au core and Pd shell (Au@Pd) are synthesized via a Cu underpotential deposition (UPD)-Pd-displacement method. The Pd shell is non-uniform consisting of tiny Pd clusters with a coverage of 0.5–0.6. The ethanol oxidation reaction (EOR) activity of this kind of structure is much higher than Pd/C in an alkaline solution. The forward peak current density of Au@Pd is 5.4 times higher than that of Pd/C. Furthermore, the onset potential for EOR of the former is ~100 mV more negative. An interesting particle size dependent EOR activity is also observed. With increasing the Au particle size (2.9, 5.8 and 6.5 nm), the EOR activity increases. The strain and ligand effects from the Au core, together with the bifunctional reaction mechanism in the Au–Pd system may be reasons for the enhanced activity in Au@Pd catalysts.

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1. Introduction

As alternative power sources for portable electronic devices and fuel cell vehicles, direct alcohol fuel cells (DAFCs) have attracted

considerable interests [1–6]. Particularly, direct ethanol fuel cells (DEFCs) are more attractive because ethanol has less toxicity, higher theoretical energy density than methanol and can be easily produced in a large scale via the fermentation of biomass feedstock [1,6–8]. One of the main challenges for wide adoption of DEFCs is to develop more active electrocatalysts for ethanol oxidation reaction (EOR) in both acidic and alkaline media. Pd was found to be more active than Pt toward EOR in alkaline solutions [9–12]. Notable

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efforts have been made to design even more active Pd-based catalysts, such as adatom-modification [2,13–16], alloying [8,17–21], and support promotion [22–25]. Among them, Au–Pd bimetallic systems showed higher EOR activity than pure Pd in alkaline solutions [19,26–29]. On an Au–Pd surface, a bifunctional reaction mechanism has been proposed: the catalytic oxidation of CO or CO-like intermediate species was promoted on Au atoms due to their unique electron-withdrawing effect on neighboring metal atoms, releasing more Pd active sites for adsorption oxidation of ethanol molecules [30,31]. Various Au–Pd nanostructures showed 1.5–3 times of enhancement over Pd nanoparticles (NPs) [19,26,27,32–34] in terms of anodic peak current density. Core (Au)-shell (Pd) structures were also synthesized and evaluated for EOR in alkaline solutions [32,35]. It was proposed that the charge transfer between the Au core and the Pd shell was one of the main reasons for the observed high activity. The Pd shell thickness in those studies might be too thick (~2 nm) to utilize the ligand effect from the core, which is expected to disappear at ~0.9 nm [36]. Herein, we prepared the Pd atoms-modified Au/C catalysts by coating an atomic thin non-uniform Pd shell on the surface of Au NPs. The Pd layer consists of tiny Pd clusters and pinholes, where Au atoms expose to the electrolytes. In this unique structure, not only the ligand and strain effects from the Au core, but also the bifunctional reaction mechanism will be utilized efficiently.

2. Experimental section

2.1. Preparation of Au/C catalysts

Carbon-supported gold (Au/C) was prepared according to the literature [37]. Briefly, a vigorously stirred solution of tetraoctylammonium bromide (0.15 g) in 10 mL of toluene was added into 0.031 g of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Aldrich) in 5 mL of deionized water. After adding 0.046 g of dodecanethiol (Aldrich), the organic phase was isolated and the resulting solution was stirred vigorously for 10 min at room temperature. NaBH_4 (0.038 g) in 5 mL of deionized water was then added over periods of either 10 s, 2 min or 10 min, which could generate Au particles with an average particle size of 2.8, 5.6 and 6.5 nm, respectively. The mixture was further stirred at room temperature for at least another 3 h. The solvent was removed on a rotary evaporator. The black product was suspended in 10 mL of ethanol, briefly sonicated to ensure a complete dispersion. After collection, the particles were washed with at least 20 mL of ethanol and 50 mL of acetone. The as-prepared Au NPs were sonicated with carbon (Ketjen Black) in toluene to obtain the Au/C with a metal loading of ~10%. After the solvent was evaporated, the dried Au/C was heated at 280 °C in a tube furnace in air for 30 min, and then at 400 °C in H_2 for 30 min to remove the organic surfactants.

2.2. Surface modification of Au/C and electrochemical evaluation

The surface modification of Au/C with Pd atoms were carried out in a conventional three-electrode cell using a CH Instrument 627E potentiostat at room temperature. An Ag/AgCl/KCl (3 M) leak-free electrode and Pt wire were used as the reference and counter electrodes, respectively. A glassy carbon with an area of 0.196 cm^2 was used as the working electrode. The glassy carbon electrode was first polished mechanically with 0.3 μm alumina powder and cleaned thoroughly with water. Approximately 5 mg of the Au/C was dispersed in a solvent consisting of 4 mL of water, 1 mL of isopropanol, and 20 μL of 5% Nafion (Aldrich) by ultrasonic for 15 min. And 10 μL of the uniformly dispersed ink was dropped onto the surface of the glassy carbon electrode and dried under a lamp to obtain a uniform film.

Pd deposition was achieved by galvanic displacement of a Cu monolayer underpotentially deposited (UPD) on the Au surfaces. The deposition of a Cu monolayer was conducted in an Ar-saturated 50 mM H_2SO_4 (GFS Chemicals) + 50 mM CuSO_4 (Scharlau) solution. Prior to Cu UPD, the Au/C electrode was activated between 0.07 and 1.5 V for 10 cycles in a solution of 0.1 M HClO_4 (GFS Chemicals) at a scanning rate of 100 mV s^{-1} and a final cyclic voltammogram (CV) curve was recorded at 50 mV s^{-1} . All the potentials reported in this paper were referred to the reversible hydrogen electrode (RHE). The Au/C electrode, covered with a Cu monolayer was then quickly rinsed with water and immersed in a 1.0 mM Na_2PdCl_4 (99.999%, Alfa Aesar) + 50 mM H_2SO_4 solution for 2 min to displace the Cu with Pd. The as-prepared Au/C modified with Pd (denoted as Au@Pd/C) was taken out and washed multiple times with deionized water. CV of the Au@Pd/C electrode was recorded between 0.07 and 0.8 V for two cycles in a 0.1 M HClO_4 solution at a scanning rate of 50 mV s^{-1} . The upper potential limit was set to 0.8 V to minimize the dissolution of Pd [38]. All the electrolytes were purged with Ar for 30 min before conducting the electrochemical measurements.

Ethanol electrooxidation reaction measurements were conducted in a 1.0 M NaOH (ACS reagent, Sigma-Aldrich) + 1.0 M ethanol (Gradient grade for liquid chromatography, LiChrosolv) solution in the potential range between 0.07 and 1.2 V at a scanning rate of 50 mV s^{-1} . The Pd/C catalyst (30 wt%, TKK) with an average particle size of ~3.9 nm (Fig. S1) was used for comparison. Before measuring the activity for ethanol oxidation, Pd/C and Au/C were activated by potential cycling between 0.05 and 1.2 V, and 0.07–1.5 V or 1.6 V for 10 cycles, respectively.

For CO stripping experiments, CO was adsorbed on the Pd/C and Au@Pd/C by holding the potential at 0.07 V for 10 min in a CO saturated 0.1 M HClO_4 solution. The CO stripping curve was taken after extra CO in solution was removed by purging N_2 for 30 min.

All electrolytes were prepared from MilliQ UV-plus water (Millipore).

2.3. Ion chromatography analysis of products of ethanol oxidation

To check the main products during ethanol oxidation, the glassy carbon electrode covered with a thin film of Au@Pd/C catalysts (Au loading 1 mg cm^{-2} on the electrode) was kept at 0.8 V (vs RHE) for 1 h in a 1.0 M NaOH + 1.0 M ethanol solution. The electrolyte was then diluted by 20 times and immediately injected (100 μL) into an ion chromatography (Metrohm, 881compact IC Pro), which was equipped with an AS11-HC column (Dionex) for analysis. The eluent, 20 mM NaOH and 80 mM NaOH, was pumped at 1.0 mL min^{-1} . Deionized water and 100 mM H_2SO_4 were used as the regeneration agents. Acetate and carbonate calibration curves were recorded with freshly prepared standards and run immediately after the sample analysis.

2.4. Nanoparticle characterization

A drop of sample suspension was deposited on a carbon coated copper TEM grid for transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and scanning transmission electron microscopy with a high angle annular dark field (HAADF-STEM) experiments. TEM, HRTEM, STEM and the energy dispersive X-ray (EDX) characterizations were performed on an electron microscope (Tecna F30, FEI; Netherlands) with an accelerating voltage of 300 kV.

3. Results and discussion

Transmission electron microscopy (TEM) images of Au NPs with three different particle sizes supported on high surface area carbon

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