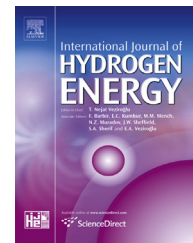




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Au–Pt core-shell electrocatalysts for oxygen reduction reaction through combining the spontaneous Pt deposition and redox replacement of underpotential-deposited Cu

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ABSTRACT

Core-shell structured Au–Pt nanoparticles are promising electrocatalysts for oxygen reduction reaction (ORR) in fuel cells due to the superior durability as well as high activity. We report the fabrication of Au–Pt core-shell nanoparticles by combining the spontaneous Pt deposition and redox replacement of underpotential-deposited (UPD) Cu. It is shown that redox replacement of UPD Cu, a commonly used approach to fabricate Pt monolayer catalysts, only can produce Pt atomic layer partially covering the Au nanoparticles, leading to insufficient Au utilization in ORR. By pre-modifying the Au nanoparticles with Pt through spontaneous deposition, which produces relatively uniformly dispersed Pt atoms on the Au nanoparticles at moderate and low Pt contents, the subsequent UPD Cu and redox replacement yield a Pt overlayer with a high coverage. The resulted core-shell nanoparticles show higher precious metal (Pt + Au) utilization than that obtained either through the single approach of the spontaneous Pt deposition or redox replacement of UPD Cu, or double redox replacement of UPD Cu.

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Introduction

Core-shell like nanoparticles with ultra-thin Pt overlayers on proper metal cores are among the best choices of electrocatalysts for oxygen reduction reaction (ORR) to overcome the recourse limitation of Pt, which currently prevents the proton exchange membrane fuel cell (PEMFC) from large scale application [1,2]. Core-shell structures also offer opportunities to improve the catalytic activity and durability in strong acidic and oxidative environment of PEMFC cathode [3–7]. Recent report by Shao et al. [8] has shown that Au, which is more

available as compared to Pt on the earth, can remarkably promote the activity of Pt for ORR in the core-shell form of Pt on Au nanoparticles. Besides, Au is also more dissolution-resistant than Pt under the conditions of PEMFC cathode [9]. It has been shown that modifying Pt nanoparticles with Au clusters can greatly improve their durability as ORR electrocatalysts in acidic media [10]. The finding of the superior ORR activity of Pt overlay on the Au nanoparticles is also an addition to the catalysis of nano-Au, which has been an area of fundamental and applied importance since Haruta's report on high CO oxidation activity of Au nanoparticles [11,12]. Earlier studies

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have showed that Pt monolayer (ML) on the bulk Au surfaces has inferior ORR activity than Pt due to the expansive lattice strain of Pt overlayer, which results in the increased oxophilicity of surface Pt atoms [13]. Shao et al.'s results have shown that the enhanced ORR activity of Pt overlay on the Au nanoparticles is a result of the lattice contraction of Au nanoparticles as compared with the bulk Au, which results in contracted Pt–Pt distance in the overlayer [8].

Redox replacement of Cu atomic layer formed through underpotential deposition (UPD) has been one of the most effective and commonly used methods to produce Pt overlayers [14–20]. The UPD Cu monolayer is formed on the surfaces of a variety of metals [21]. Uniform Pt shell on these metals is fabricated through replacing the UPD Cu atoms. However, the electrochemical and extended X-ray absorption fine structure (EXAFS) measurements by Russell and co-workers [22] have suggested that UPD may only produce a Cu atomic layer partially covering the Au nanoparticles due to the surface heterogeneity (corner, edge and facets of different reactivity). Accordingly, the subsequent redox replacement would not yield a fully covered Pt layer on the Au nanoparticles. Chemical reduction and thermal annealing have been also widely used to prepare Au–Pt core-shell nanocatalysts [23,24]. These methods usually require careful experimental control to avoid the formation of Pt island and/or dendritic branch instead of uniform Pt shell [25].

Recently, it has been shown that Pt can be deposited on the carbon supported Au nanoparticles (Au/C) through the so-called spontaneous deposition without using extraneous reducing agents [26–33]. The resulted catalysts, Au–Pt/C exhibited Pt specific and mass activities of Pt which are ca. 3.5 times higher than that of the Pt/C catalyst [26]. Although the spontaneous deposition offered a straightforward way to deposit Pt on Au/C, the catalytic activity per mass of the deposited Pt for ORR were considerably lower than that prepared through redox replacement (6–7 times higher than Pt/C), which was mainly because that Pt could form multi-layer clusters at relatively high Pt contents in the spontaneous deposition processes [26]. In this work, we show that the combination of the spontaneous deposition and redox replacement and methods can overcome the downside of each method in modifying Pt atom layer on Au/C, so that Pt atoms can be deposited on the surface of Au nanoparticles with simultaneously high coverage and dispersion. The resulting Au–Pt core-shell nanoparticles exhibited much enhanced precious metal (Pt + Au) utilization in catalyzing ORR as compared with the Au–Pt catalysts obtained either through the single approach of the spontaneous Pt deposition or redox replacement of UPD Cu, or through double redox replacement of UPD Cu.

Experimental

Chemicals and materials

20 wt % Pt/C from Johnson-Matthey (JM) was used as the reference catalyst. It will be denoted as Pt/C in the following. $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, K_2PtCl_4 , CuSO_4 , HClO_4 , H_2SO_4 were purchased from National Pharmaceutical Group Chemical Reagent Co.,

Ltd. (Shanghai, China). All chemicals are analytical grade and used directly without further purification.

Materials preparation

Deposition of Pt on Au/C through spontaneous deposition

The details for the preparation of carbon-supported Au nanoparticles (Au/C) and the spontaneous Pt deposition on Au/C have been given in a previous paper [26]. Briefly, Au nanoparticles with mean sizes of ca. 3.45 nm were first synthesized by reducing $[\text{AuCl}_4]^-$ with NaBH_4 in a mixed solution of chloroauric acid and sodium citrate, and then loaded on the surfaces of carbon black (XC-72R) [26]. The surfactant was removed by repeated centrifugation and washing with deionized water. The precipitation was then dried in vacuum overnight to obtain Au/C. The results of the inductively coupled plasma atomic emission spectroscopy (ICP-AES) indicated that the as-prepared Au/C samples possessed Au mass contents of 17.38 ± 0.5 wt%. The spontaneous Pt deposition on the Au surfaces was achieved by simply dispersing Au/C in solution containing PtCl_4^{2-} , without introducing any extraneous reducing agents or any pre-/post-treatments. The contents of Pt on the Au nanoparticles can be tuned by varying the concentration of PtCl_4^{2-} and temperatures [26]. In this study, we deposited Pt on Au/C in 6×10^{-4} M K_2PtCl_4 solution and the Pt contents were changed by varying the deposition temperatures. The obtained sample is denoted as $\text{AuPt}_x/\text{C-S}$ (x refers to the Pt/Au atomic ratio determined by the ICP-AES). Vulcan XC-72R is the most used carbon support in the preparation of the nanoparticles of noble metals because of its sufficient electronic conductivity and chemical stability under fuel cell operating conditions. It should be noticed that the relationship between carbon support and noble metals is a complex multi-variable problem which requires a very systematic approach [34]. The noble metals probably are absorbed on the defect sites of carbon surface via metal–O coordination, metal–C coordination, or Van der Waals interaction [35,36].

It should be pointed out that the exact mechanism of the spontaneous Pt deposition on Au nanoparticles remains unclear and under exploring currently. The galvanic cell mechanism proposed for the simultaneous deposition of Pt on Ru surface by Adzic et al. [37,38] should be inapplicable here because the oxidation of Au surface takes place at potential much more positive than the reduction potential of $[\text{PtCl}_4]^{2-}$. We have measured the concentrations of Au ions in solutions after the Pt deposition experiments, which were found to be negligibly small as compared with that expected for the displacement of Au by Pt. Taking the $\text{AuPt}_{0.2}/\text{C-S}$ as an example, the concentration of Au ions in the solution should be larger than 5×10^{-5} mol/L if the Pt deposition was through from the displacement mechanism; while the actual concentration of Au ions detected by ICP is less than 5×10^{-6} mol/L. In addition, the disproportionation mechanism could also be denied by the fact that the prepared $\text{AuPt}_x/\text{C-S}$ catalysts had ORR activity more than 3 times higher than Pt/C [26]. If the disproportionation of PtCl_4^{2-} occurred, considerable amounts of Pt would precipitate in bulk solution, as well as the deposition on Au surface. The resulting catalysts obtained in the subsequent centrifugation should contain unsupported Pt

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