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Platinum-Decorated Nanoporous Gold Leaf for Methanol Electrooxidation

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Extensive studies have been devoted to the development of various nanostructured catalysts for energy-related technologies such as fuel cells. Although platinum is widely studied and used as an excellent electrocatalyst in the scientific and industrial community, it is extremely susceptible to poisons such as CO-like species, which result in a dramatic decrease in efficiency. To mitigate poisoning, Pt-based bimetallic nanoparticles, such as Pt−Ru alloy, have been explored as a substitute for fuel-cell applications.[1] Meanwhile, gold nanocatalysts have attracted more and more interest since gold nanoparticles were found to be highly effective for a series of important reactions including CO oxidation.[2] In view of taking the respective advantages of platinum and gold, Pt−Au nanocatalysts have been reported to exhibit high catalytic activity in some electrocatalytic reactions.[3]On the other hand, on the basis of economic concerns, many methodologies have been exploited to enhance the utilization of Pt by dispersing Pt particles onto hollow graphitic nanoparticles,[4a] carbon nanotubes,[4b] silica aerogels,[4c] Au nanoparticles,[5] etc. However, the above strategies are involved in two common problems in practical applications, i.e., nonuniform dispersion and self-agglomeration of nanoparticles during catalyst processing, which will bury considerable Pt surface atoms and thus decrease the accessibility of the electrocatalyst.

In our research, we have been studying an alternative high-surface-area electrode material, nanoporous gold (NPG), made by a simple dealloying method.[6a] Moreover, we found that etching commercially available white gold leaf could result in a very unusual electrode material that we named NPG leaf.[6] This membrane material is only ~100 nm thick and thus has a very low gold loading of about 0.1 mg cm^{-2}. Because NPG leaf has an intrinsically uniform and conductive porous structure, the above-mentioned problems associated with nanoparticles are automatically eliminated. On the basis of this structure, an ideal electrocatalytic nanoarchitecture may be constructed by creating an atomically thin layer of Pt onto the entire surfaces of NPG leaf. Recently, we developed an interface electroless plating technique and found that Pt could be uniformly plated onto NPG leaf surfaces with near atomic precision. More interestingly, Pt overlayers were found to adopt a layer-islanding (also called Stranski−Krastanov, SK) growth mode where Pt atoms grow epitaxially on NPG surfaces.[6d] This SK growth mode implies the existence of a nearly ideal catalyst structure with a 1–2 atom thick Pt layer that completely covers the NPG surface. By employing Pt-NPG leaves as membrane electrode materials, we have indeed observed their excellent performance in hydrogen/oxygen fuel cells at an ultralow platinum loading. Considering the particular importance of direct methanol fuel cells (DMFCs),[7] in this work, we focus on their electrocatalytic activities toward methanol electrooxidation, which is of central importance in DMFCs. We will show that the synergistic effect between Pt and Au makes Pt-NPG a superior electrocatalyst with much higher activity and better poison tolerance than those of commercial catalysts.

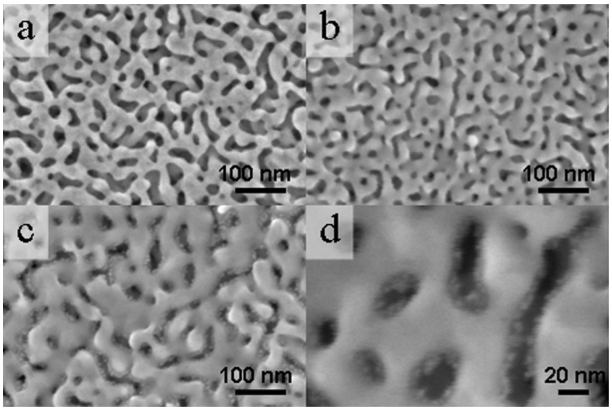

Figure 1. SEM images of (a) NPG etched in HNO_3 for 15 min; and (b−d) Pt-NPG samples that were subject to Pt plating for (b) 2 and (c, d) 128 min. The higher-magnification image in (d) illustrates the formation of Pt nanoislands on heavily plated samples.

NPG leaf samples were made by floating 12-carat white gold leaf onto concentrated HNO_3 for 15 min. Upon silver dissolution, gold atoms left behind will self-organize into an interconnected network of pores and ligaments, as featured by an SEM image in Figure 1a. One important characteristic of NPG is that its structural unit (pore/ligament size) can be tunable from a few nanometers to many micrometers by varying the starting alloy composition or etching time or by

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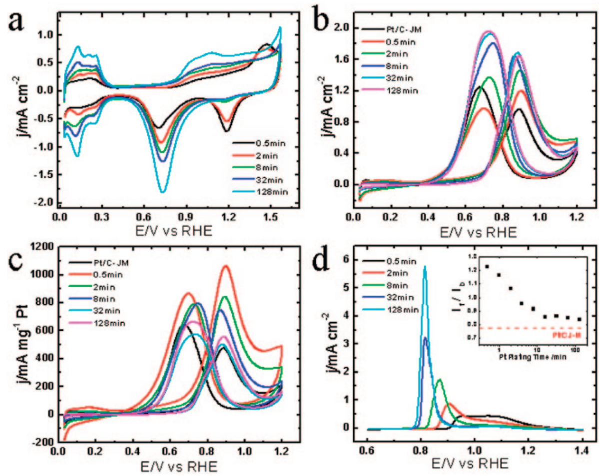

Figure 2. Electrochemical behavior of Pt-NPG samples. (a) Representative CVs in 0.5 M H_2SO_4, where currents have been normalized to the geometrical areas of electrodes; (b) ECAS-normalized and (c) mass-normalized CVs for methanol electrooxidation in 0.5 M H_2SO_4 + 1.0 M CH_3OH. CVs of commercial Pt/C catalyst (Johnson Matthey, 20 wt %) are also included for comparison; (d) CO stripping CVs of Pt-NPG as a function of plating time, where currents have been normalized to the geometrical areas of electrodes. The base lines have been subtracted for clearer demonstration. (Original curves are presented in the Supporting Information, Figure S1.) Inset in (d) profiles the I_f/I_b values of Pt-NPG samples along with that for commercial Pt/C catalyst (red line), which demonstrate the greatly enhanced resistance to carbonaceous species accumulation. Scan rate: 50 mV s^{-1}

employing thermal annealing after dealloying. This flexible porous framework is highly desirable for free transport of small molecules in all three dimensions and thus provides a sound basis for designing a new type bimetallic membrane catalysts for important reactions such as methanol or CO electrooxidation. The electrochemically active surface area (ECAS) of NPG leaf was estimated to be about 10.6 m^2 g^{-1} using Brummer's method.[8] This means that 0.05 g Pt (5 wt %) is needed to fully cover all surfaces of 1 g of NPG to form a monolayer type bimetallic Pt-NPG structure, which has an ideal surface area of about 210 m^2 g^{-1} Pt. The deposition of Pt on NPG substrate was carried out by reducing H_2PtCl_6 with hydrazine hydrate. According to the elemental analysis (EDS) results, plating for 0.5, 2, and 8 min generated Pt-NPG structures with equivalently 0.47, 0.84, and 2.4 Pt atomic layers uniformly covering the NPG substrates, respectively. Compared with NPG, Pt-plated samples exhibit a relatively smooth surface morphology (Figure 1b), suggesting a preferential growth over ligament sites with high radial curvatures. As plating time increases, isolated Pt nanoclusters start to accumulate on the surface, with a uniform size distribution around 3 nm (images c and d in Figure 1).

The success of Pt modification was further proved by a group of electrochemical cyclic voltammograms (CVs) in 0.5 M H_2SO_4 solution (Figure 2a). It is observed that after plating, the well-defined hydrogen adsorption/desorption and platinum oxides reduction peaks show up and gradually increase in intensity with the plating time, characteristic of Pt-based electrodes. Accordingly, the profiles for gold surface oxide formation and reduction markedly decrease, and plating for 8 min can suppress almost all gold signals, indicating a near complete coverage of NPG surfaces. Meanwhile, an ordered positive shift of the platinum oxide reduction peak was observed as plating time increases from 0.5 to 8 min. A further increase in the plating time to 128 min will merely result in more apparent platinum signals rather than cause any further difference in their CV profiles. This indicates that Pt island growth starts from 8 min, and samples henceforth hold very similar structures. The relatively negative potentials for low-coverage samples indicate that the strong interaction between Au substrate and Pt thin layers can strengthen the bonding between Pt and oxygen containing species, i.e., Pt becomes more active. A similar phenomenon has been observed by Pedersen and co-workers, in which they found that Au (111) substrate could surprisingly increase the reactivity of Pt overlayer because of an upshift in the Pt d-state.[9] This interaction decays quickly as the Pt overlayer gets thicker.

The catalytic activity of Pt-NPG toward methanol electrooxidation was measured by CVs in a mixed solution of 0.5 M H_2SO_4 and 1 M CH_3OH (Figure 2b). The ECAS-normalized activity of Pt, as recorded by the peak current density in the forward scan, is 1.21 (0.5 min), 1.46 (2 min), and 1.65 mA cm^{-2} (8 min). For comparison, the activity of commercial Pt/C catalyst (Johnson Matthey) was also measured to be 0.95 mA cm^{-2}. It is widely accepted that the activity of catalysts depends on the physical and chemical nature of active surface atoms, which is sensitive to the support material and the adsorbed species.[10] For example, it has been observed experimentally that Au support could provide a promotional effect on Pt overlayers for small molecule catalytic reactions.[3c] On the other hand, Du et al. reported that a certain number of neighboring Pt atoms are necessary in order for methanol electrooxidation to proceed.[11] This support effect can explain why all five Pt-NPG samples prepared can exhibit better performance than commercial Pt/C catalyst. At the same time, it is expected that the ECAS-normalized activity would continuously increase from 0.5 to 8 min plating, because the more Pt deposited, the more chance that Pt atoms can form continuous overlayers and clusters, which is essential for methanol electrooxidation. For Pt-NPG with higher platinum loadings, it is noted that 8, 32, and 128 min samples show very similar ECAS-normalized activity. This is consistent with our previous discussion that platinum plating for more than 8 min will result in an electrode structure with surfaces characterized by nano-islands. Mass-normalized current, an important parameter to evaluate the activity of surface atoms and the Pt utilization, is shown in Figure 2c. It is very apparent that the peak current in the forward scan increases with decreasing plating time and reaches 1060 mA mg^{-1} Pt for the 0.5 min sample, which is two times better than the commercial Pt/C catalyst. The values for heavily plated samples (32 and 128 min) decrease to around 500 mA mg^{-1}, which is slightly higher than that

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of Pt/C, possibly because of their similar structural features, i.e., nanoislands versus nanoparticles with similar diameter around 3 nm.

Another important factor for evaluating an electrocatalyst is its resistance to carbonaceous species accumulation. In methanol electrooxidation, the anodic peak during the reverse scan is usually attributed to the removal of intermediate carbonaceous residues formed on the catalyst during the forward scan. Therefore, the ratio of two anodic current densities, I_f/I_b, is commonly used to describe catalyst susceptibility to poisoning.[12] For commercial Pt/C, this value is 0.77, which indicates that a significant number of methanol molecules are only partially oxidized in the forward scan. However, for all Pt-NPG samples, we observed a larger I_f/I_b ratio (inset in Figure 2d), and the highest ratio (1.23) is achieved by the least-plated sample (0.5 min). Currently, the common approach to releasing Pt catalysts' poisoning effect is to alloy Pt with Ru, in view of the so-called bifunctional mechanism.[13] However, although highly successful, this strategy suffers from two drawbacks that limit the large scale commercial application of these catalysts. First, Ru itself is not catalytically active for methanol oxidation; therefore, its improvement in antipoisoning will be compromised by the degree of loss of catalytic activities because of the dilution of Pt lattices. For example, the mass-normalized activity of the most tolerant $Pt_{52}Ru_{48}$ catalyst is only half those of pure platinum, whereas $Pt_{23}Ru_{77}$ is completely inactive for methanol oxidation.[13]Second, Ru is significantly less noble as compared to Pt; therefore, it is more susceptible to corrosion, which indicates that Pt−Ru alloys are relatively unstable. However, in NPG, the unique porous morphology provides a reservoir for trapping OH^- anions, which can be strongly chemisorbed on to porous gold surfaces to form surface oxygenated species. Those chemical species are very important for onset and proceeding of methanol or CO electrooxidation reactions and can promote further oxidation of carbonaceous intermediates accumulated on Pt surface. Moreover, nanostructued gold is known to be an excellent catalyst for CO oxidation at mild conditions; therefore, constructing a novel surface alloy such as Pt-NPG may result in the unique effect of removing carbonaceous intermediates or even tuning the reaction pathway by suppressing CO formation.[14] This may also explain why Pt-NPG shows better tolerance to carbonaceous species poisoning. Finally, Au is the most noble metal, which will contribute to stabilizing the bimetallic Pt-NPG structure.

A CO stripping experiment was carried out to further characterize the surface properties of Pt-NPG (see the Supporting Information, Figure S1). The curves presented in Figure 2d have the base lines of the second cycles subtracted, so all current density information can be attributed to CO electrooxidation. The most striking observation is that the CO stripping peak for the 0.5 min sample is distinguished from other samples with a broad and flat plateau. The peak potential also shifts to a more positive value. This broad CO stripping peak at positive potential is associated with a special surface state of Pt, where (1) a majority of Pt sites do not possess enough neighboring Pt atoms[11] and (2) the alloying effect from the gold substrate is the most intense, which will significantly increase the bonding energy between Pt and CO.[9] As the Pt coverage increases, the broad peaks rapidly diminish; accordingly, a narrow peak appears at lower potentials. This peak is located at 0.9 V (vs RHE) for the 2 min sample, and as the platinum loading gets higher, it shifts to the negative direction and eventually stabilizes at ~0.8 V for the 32 and 128 min samples.

In summary, we describe an ultralow platinum loading electrocatalyst based on a novel nanoporous membrane metal, NPG leaf, and its excellent performance toward methanol and CO electrooxidation. Although it is widely accepted that the highest Pt utilization can be achieved only on monolayer (or submonolayer) type structures, to which our structures are close, the most important characteristic of Pt-NPG type structures is their easy accessibility to almost all surface precious atoms by target molecules, which the current fabrication protocol based on physical mixing of nanoparticles can never achieve. This can explain why 0.5 min Pt-NPG sample can exhibit much better performance than commercial Pt/C, although they have similar platinum utilization values (~50%, see the Supporting Information, Table S1). Considering NPG's structure flexibility and the strong synergistic effect between Pt and Au, Pt-NPG may represent an alternative ultralow precious metal loading catalyst to traditional ones with promising performance in important green-energy technologies, such as DMFCs.

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Supporting Information Available: The experimental details regarding the fabrication of NPG and Pt-NPG. The electrochemical parameters of samples, including the measured real surface area, ECAS value, Pt utilization, Pt loading, etc. The original CO stripping curves (PDF). These materials are available free of charge via the Internet at http://pubs.acs.org.

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