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Fabrication and characterization of a flow-through nanoporous gold nanowire/AAO composite membrane

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Abstract

The fabrication of a composite membrane of nanoporous gold nanowires and anodic aluminum oxide (AAO) is demonstrated by the electrodeposition of Au–Ag alloy nanowires into an AAO membrane, followed by selective etching of silver from the alloy nanowires. This composite membrane is advantageous for flow-through type catalytic reactions. The morphology evolution of the nanoporous gold nanowires as a function of the diameter of the Au–Ag nanowire ‘precursors’ is also investigated.

Supplementary data are available from stacks.iop.org/Nano/19/335604

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Nanoporous gold (NPG) foams have attracted considerable technological interest due to their wide range of applications in catalysis [1–6], sensing [7, 8], actuators [9, 10], electrochemical capacitors [11], surface-enhanced Raman scattering (SERS) [12, 13], low-temperature heat exchangers [14], etc. The NPG structures are usually produced by selective chemical or electrochemical dissolution of Au–Ag alloys, known as a ‘dealloying’ process in the context of corrosion technology. In terms of catalytic applications, NPG foams have at least two advantages over other catalysts or gold nanoparticles. Firstly, unlike platinum or palladium catalysts, NPG remains active at low temperature (room temperature or even lower), which is desirable for many practical applications [3, 4]. Secondly, NPG has a good thermal stability and is resistant to oxidation [3, 15], and thus can overcome the aggregation or sintering limitations from which gold nanoparticles often suffer upon the elevation of temperature or in an oxidative environment [16].

Although NPG foams have been demonstrated to show high CO oxidation activity, the catalytic reactions only occur at the surfaces of the NPG foams [3]. As a result, the high specific surface area of NPG foams can often not be utilized efficiently. Ultrathin NPG films (about 100 nm) made by dealloying white-gold leaves may overcome this limitation to a certain extent, but these ultrathin films are very fragile and exhibit brittle fracture [2, 4], which makes it difficult to find practical applications in flow-through type catalysis. Recently, Dotzauer et al reported the fabrication of catalytic membranes composed of gold nanoparticles immobilized in a porous anodic aluminum oxide (AAO) [17]. The porous membrane configuration allows flow-through catalytic reactions, and the flow (e.g. gas or liquid) through the porous membrane gives rise to a rapid convective mass transport of the reactant to the immobilized catalysts. In this case, conversions often depend on kinetics or mass flow, rather than diffusion. Therefore, flow-through type membrane supported catalysts can overcome the diffusion limitation that usually occurs in fluidized bed reactors or homogeneous solutions of catalytic beads [18]. Other groups have also pointed out the importance of mass transport on the catalytic activity when using NPG films as catalysts [3].

Here, we present a novel composite catalytic membrane which consists of an NPG nanowire (NW) array immobilized in an AAO membrane (i.e., an NPG NW/AAO composite membrane). Previously, NPG nanowires were also synthesized via a template-based approach [6, 8, 15, 19, 20], but the alumina template was usually removed before the dealloying process, thus leaving dispersed NPG nanowires, while in our case, the AAO membrane can still be retained without any...
fractures upon dealloying treatment, and it serves as a support for the NPG nanowire array. Since the AAO membrane is mechanistically stable, it is expected that the NPG NW/AAO composite membrane can be easily handled and can bear larger flow pressure compared to ultrathin NPG films.

2. Experimental details

2.1. Preparation of AAO membranes

The AAO membranes used in our experiments were prepared by a two-step anodization process as described previously [21–23]. Briefly, high purity aluminum sheets (99.999%) were first electrophosphilized in a mixture of HClO4 and C2H5OH (1:3 v/v) for 4 min. The polished Al sheets were anodized in 1 wt% H3PO4 at 195 V or 0.3 M H2C2O4 at 40 V at 1 °C. The first anodizations were usually carried out for 20 h. Subsequently, the anodized Al sheets were put into an acid mixture (6 wt% H3PO4 and 1.8 wt% CrO3) to completely remove the porous layer. Then, the second anodizations were conducted for 16 h at the same conditions as the first anodizations. Free-standing alumina membranes were obtained by etching away the underlying aluminum substrates with a mixture of CuCl2 and HCl. The barrier layers were then removed by 10 wt% H3PO4 at 45 °C for 50 min for H3PO4-anodized AAO and 5 wt% H3PO4 at 30 °C for 35 min for H2C2O4-anodized AAO, respectively.

2.2. Preparation of NPG nanowires

Figure 1 schematically illustrates the fabrication procedure of NPG NW/AAO composite membranes. Before electrodeposition, a layer of Ag was sputtered on one side of the membrane as a conductive layer. Au nanorod base electrodes were first electrodeposited into the AAO membrane at galvanostatic mode with a current density of 1 mA cm−2. Subsequently, the Au–Ag alloy NWs were electrodeposited into the AAO membrane. The electrodeposition of the Au–Ag alloy was carried out in a standard three-electrode electrochemical cell. The electrolyte was prepared by mixing commercial Au (Orotemp, major component KAu(CN)2) and Ag (Technic, major component KAg(CN)2) electroplating solutions with a molar ratio of Au+/Ag+ = 1:4. The composition of the alloy NWs can be controlled by the deposition potentials and the concentrations of [Au(CN)2]− and [Ag(CN)2]− in the precursor solution, as demonstrated by Ji et al [15, 20]. Therefore, the porosity of NPG NWs can be readily adjusted. After electrodeposition, Au–Ag alloy NWs embedded in the AAO membrane were immerse into a concentrated nitric acid solution (Fluka, 65%) at 1 °C. In this process, nitric acid can selectively etch silver in Au–Ag alloy NWs as well as the silver in the base electrode layer without affecting the AAO membrane (figure S1 (available at stacks.iop.org/Nano/19/335604)) [24], resulting in an NPG NW/AAO composite membrane.

2.3. Characterization of NPG nanowires

The morphology and structure of as-prepared NPG NWs were characterized by scanning electron microscopy (SEM, JEOL-6340F) and transmission electron microscopy (TEM, JEOL-1010 and Philips CM20T). To liberate NPG NWs from the AAO template for SEM and TEM observations, the template containing NPG NWs was immerse into 2 M NaOH solution at 45 °C for several hours. The as-obtained product was centrifuged several times and then washed with a large amount of deionized water. For SEM examination, the NPG NWs were dispersed on a silicon substrate. The silicon substrate was pasted on an SEM sample stage with conductive carbon tape. For conventional TEM investigations, a drop of suspension containing NPG NWs was placed on a carbon-coated copper grid. To further investigate the microstructure, plan-view TEM images of NPG NWs embedded within an AAO template were also taken. For this characterization, TEM specimens were prepared by first thinning down the AAO template containing NPG NWs mechanically, and then milling with Ar+ ions.

3. Results and discussion

In this study, we employed two kinds of AAO membrane with different pore sizes (Dp) and pore densities (ρ); (i) H3PO4-anodized AAO with Dp = 210 nm and ρ = 5 × 108 pores cm−2, (ii) H2C2O4-anodized AAO with Dp = 45 nm and ρ = 1 × 1010 pores cm−2. The surface and cross-sectional morphologies of these two kinds of AAO membrane are shown in figure 2.

Figure 3 represents a typical cyclic voltammetry (CV) curve for the mixed Au–Ag electrolyte used here. The deposition was carried out on a gold film and the curve was recorded at a scan rate of 20 mV s−1. It is clearly seen that the deposition peaks for silver and gold are located at −0.19 V (versus Ag/AgCl) and −1.07 V (versus Ag/AgCl), respectively, which are basically consistent with a previous report [19].
Figure 2. Top view and cross-sectional SEM images of ((a), (b)) H$_3$PO$_4$-anodized and ((c), (d)) H$_2$C$_2$O$_4$-anodized AAO membranes.

Figure 3. Cyclic voltammogram for the Au–Ag electrolyte on a gold film with a scan rate of 20 mV s$^{-1}$.

Figure 4(a) shows a representative cross-sectional SEM image of an NPG NW/AAO composite membrane prepared from H$_3$PO$_4$-anodized AAO. Most nanopores are filled with NWs. Parts of the NWs appear to be out of the nanopores and some pores (marked with white arrows) are empty due to the mechanical removal during the cross-sectioning of the sample for SEM investigation. Moreover, it can be seen that the silver base electrodes as well as the conductive silver film were removed completely. The SEM micrograph of the backside of the membrane also reveals an opening of pores due to complete removal of silver (figure 4(b)).

The morphologies of NPG NWs prepared by using two different AAO membranes are compared in figure 5. For NPG NWs prepared by using an H$_3$PO$_4$-anodized AAO template, the morphology of NPG NWs is characterized as a sponge-like structure with a three-dimensional (3D) nanoporous network, where the length of interconnecting ligaments was estimated to be 20–30 nm and the pore size to be around 20 nm (figures 5(a) and (b)). In contrast, NPG NWs obtained from an H$_2$C$_2$O$_4$-anodized AAO template exhibit a hinge-like morphology as shown in figures 5(c) and (d). These nanowires appear to be more flexible, compared to those prepared from the H$_3$PO$_4$-anodized AAO template. The length of ligaments was found to be longer than that of the sample shown in figures 5(a) and (b), while the size of pores turned out to be as small as 5 nm. Energy dispersive x-ray (EDX) analyses revealed that there was no detectable silver in the NWs, implying that the silver had been dissolved completely by concentrated nitric acid, as evidenced in the inset of figure 5(d). The Si peak in the EDX spectrum was from the Si substrate used for SEM observation.

It is also noteworthy that the removal of silver from Au–Ag alloy NWs is accompanied with a significant reduction of the wire diameter, leaving behind a gap between the outer surface of the resulting NPG NWs and the pore walls of AAO template, as shown in figures 5(a) and (b). The average diameters of NPG nanowires prepared from H$_3$PO$_4$- and H$_2$C$_2$O$_4$-anodized AAO templates were measured to be approximately 130 nm and 21 nm, respectively, which is about 38% (for the former) and 53% (for the latter) smaller than the pore diameters of the AAO membrane used. Recently, a macroscopic volume reduction during dealloying Au–Ag alloy has been reported [25]; volume shrinkage as much as 30% was observed. It was also found that the volume shrinkage of NPG nanowires is more pronounced, and is dependent on the alloy composition [8, 15]. In addition to the dissolution of
silver, other factors such as coarsening behind the dissolution front, various sources of plastic deformation, and capillary forces, may also contribute to the volume shrinkage [25]. Our results reported here are consistent with previous work. However, in our case, the volume shrinkage of resulting NPG nanowires creates a gap between the outer surface of nanowires and the pore walls of the alumina template. This gap allows the reactant molecules easily go through the membrane and diffuse into the NPG nanowires, which will greatly facilitate the mass transport of the reactants to the NPG NWs in a catalytic application of NPG NW/AAO composite membranes.

To further investigate the microstructures of as-prepared NPG NWs, TEM examinations were carried out. Figure 6(a) shows a representative TEM image of NPG NWs prepared in an H₃PO₄-anodized AAO membrane. It is clear that the structure is characterized by a 3D porous network. The nanopores form not only on the wire surface but also inside the wire. The diameter of NPG NWs is about 124 nm, much smaller than the pore diameter of the H₃PO₄-anodized AAO membrane, showing that the dealloying process greatly reduces the wire diameter. Figure 6(b) represents a plan-view TEM image of NPG NWs embedded in an H₃PO₄-anodized AAO membrane. The shrinkage in the wire diameter is evident, and the porous structure can be distinguished across the cross-section of the NWs, which is shown more clearly in the inset of figure 6(b). It is found that the cross-sectional pore size and distribution are different form wire to wire, but all NWs have multi-channels, which
would highly be desired for the applications in flow-through catalysis and micro-fluidic channels. The TEM image of NPG NWs prepared in an \( \text{H}_2\text{C}_2\text{O}_4 \)-anodized AAO membrane is presented in figure 6(c). These NWs have corrugated surface morphology and very small pores in the center of the wires, and look like hinges. The pore size is less than 10 nm. Figure 6(d) reveals a plan-view TEM image of NPG NWs embedded in an \( \text{H}_2\text{C}_2\text{O}_4 \)-anodized AAO membrane. In contrast to figure 6(b), no 3D porous structures can be observed. The magnified plan-view TEM image taken from the area marked by the square is shown in the inset of figure 6(d). The cross-sectional morphology of a very small nanopore can clearly be distinguished (in the center of the image).

As mentioned above, the NPG NWs prepared from AAO membranes with different pore diameters exhibit different morphologies. The NPG NWs prepared in \( \text{H}_3\text{PO}_4 \)-anodized AAO membranes display a 3D sponge-like porous structure, while the NPG NWs prepared in \( \text{H}_2\text{C}_2\text{O}_4 \)-anodized AAO membranes reveal non-3D hinge-like structure. We also employed \( \text{H}_2\text{SO}_4 \)-anodized AAO membranes (pore diameter about 30 nm) as templates in our experiments. It was found that there were no pores in the NWs after the dissolution of silver (figure S2 (available at stacks.iop.org/Nano/19/335604)).

At present, it has been well established that the formation of nanoporous structure of noble metal from its binary alloy is due to the rapid diffusion of noble metal atoms at alloy/solution interfaces during the dissolution of the less noble metal [26–28]. Noble metal atoms will first agglomerate into clusters to avoid highly non-equilibrium conditions in which they supersaturate the surface as adatoms. Subsequently, these clusters will coarsen to flatten and passivate the surface and finally lead to the formation of 3D porous structures. It is believed that the morphological difference of NPG NWs we report here originates from the size difference of the Au–Ag alloy NW ‘precursors’ (i.e. the difference of pore diameters of AAO membranes). As discussed above, the ligament size of the two kinds of NPG NW is about 20 nm. In \( \text{H}_2\text{C}_2\text{O}_4 \)-anodized AAO membranes (pore diameter about 45 nm), it is not possible to develop more than two ligaments radially, considering the volume shrinkage of the NWs. Thus, the ligaments can only develop longitudinally to form hinge-like structures. In contrast, although the wire diameter of NPG NWs prepared in \( \text{H}_3\text{PO}_4 \)-anodized AAO membranes
is also reduced greatly, it is still large enough to develop ligaments both radially and longitudinally so that a 3D porous network can be formed. We noted that a morphological transition in NPG ultrathin films from three dimensions to two dimensions was also reported previously [2], and was attributed to the ‘collapse’ of an original 3D structure due to the continuous coarsening associated with extended etching time in nitric acid. This morphological transition of the NPG structure is etching-time induced, while in our case, the etching time of alloy nanowire ‘precursors’ in nitric acid is constant for all samples. Therefore, the observed hinge-like NPG structure (2D-like) and non-porous gold nanowires (1D-like), which were produced from H$_2$C$_2$O$_4$-and H$_2$SO$_4$-anodized AAO respectively, are not due to the longer etching time of their ‘precursors’. Instead, they arise from the confined space in which the development of 3D network is limited.

4. Conclusions

In summary, nanoporous gold nanowire/AAO composite catalytic membranes were fabricated. By combining the porous membrane configuration of AAO and the large catalytically active surface area of nanoporous gold nanowires, this composite membrane should be useful in flow-through catalysis. Furthermore, the morphological difference of nanoporous gold nanowires prepared in AAO membranes with different pore diameters was observed. It was shown that the diameter of the Au–Ag alloy nanowire ‘precursors’, that is, the pore diameter of the AAO membrane, has a significant impact on the diffusion and rearrangement of gold atoms during the selective dissolution of silver from the alloy nanowires. This finding may facilitate further understanding of the formation mechanism of porous nanostructures during the dealloying process in confined environments.

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References