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## Facile fabrication of nanoporous gold with bimodal pore structure

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## ABSTRACT

A hierarchical nanoporous gold (HNPG) membrane with a bimodal pore size distribution was fabricated by a simple one-step dehydration reaction of  $\text{H}_3\text{BO}_3$ , which is different from the complex methods of multi-cyclic electrochemical co-alloying/dealloying. The HNPG exhibits a wide pore distribution from 10 to 120 nm. The special architecture of HNPG significantly enhances the Raman signal to crystal violet and electrocatalytic activity toward the oxidation of methanol. The formation mechanism of the bimodal structure is discussed.

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## 1. Introduction

Nanoporous gold (NPG) metals, as novel functional materials, have recently attracted considerable interest in a wide variety of applications including catalysts, sensors, actuators, double-layer capacitors, and so forth [1–3]. All these special performances of NPG originate from an open bicontinuous network backbone and interconnected hollow channels in nanoscale [4,5]. Unlike uniform (single-sized) structure, a bimodal porous structure can enhance or impart novel properties because of the outstanding permeability and high surface area [6–8]. For such bimodal material, the large pores provide pathways for rapid transportations of reactants/products, while the small nano-pores simultaneously offer a large surface area to disperse the active sites [8–11]. Hence, the bimodal support has excellent advantages for improving the catalytic activity and target selectivity.

However, the preparation methods of the hierarchical nanoporous gold (HNPG) are rather complex, such as multi-cyclic electrochemical co-alloying/dealloying [4], electrodealloying-annealing-second electrodealloying [7], and dealloying-plating-annealing-dealloying [10]. The annealing was aimed at coarsening the pores for upper hierarchy channels [2,7,10], and the annealing temperature was selected at 300–500 °C. In this work, we report a novel, simple and rapid method to fabricate HNPG membrane with

bimodal porous structure by the dehydration reaction of  $\text{H}_3\text{BO}_3$ . Both the upper and lower hierarchy channels are simultaneously produced at 180–250 °C, and the formation mechanism is investigated. The HNPG provides a multifunctional platform for the improved electrocatalytic activity and surface-enhanced Raman scattering (SERS) performance. The suggested strategy is attractive for the fabrication of other bimodal porous materials.

## 2. Experiment

The  $\text{Au}_{35}\text{Ag}_{65}$  (at%) membrane of 100 nm thick was used to fabricate NPG by chemical dealloying, which was floated onto the concentrated  $\text{HNO}_3$  solution for 30 min at 23 °C and washed by distilled water. The as-prepared NPG membrane was immersed into 1 wt%  $\text{H}_3\text{BO}_3$  solution for 10 min, then annealed in muffle furnace for 30 min. The heating rate was 20 °C/min. The HNPG membranes annealed at different temperatures, were denoted as HNPG-T, where T respected the annealing temperature. The surface morphology was examined using field-emission scanning electron microscopy (FESEM, JEOL JSM-7000 F). Cyclic voltammetric (CV) measurements were performed in 0.1 M KOH containing 2 M  $\text{CH}_3\text{OH}$  at a scan rate of 100  $\text{mV s}^{-1}$  on CHI 660B electrochemical workstation. SERS was collected with a Renishaw Raman microscopy operating with a 632.8 nm He-Ne ion laser (beam size of 1  $\mu\text{m}$ ). Prior to SERS measurement, the HNPG or NPG membranes were immersed into  $10^{-6}$  M crystal violet aqueous solution for 6 h to allow sufficient adsorption.

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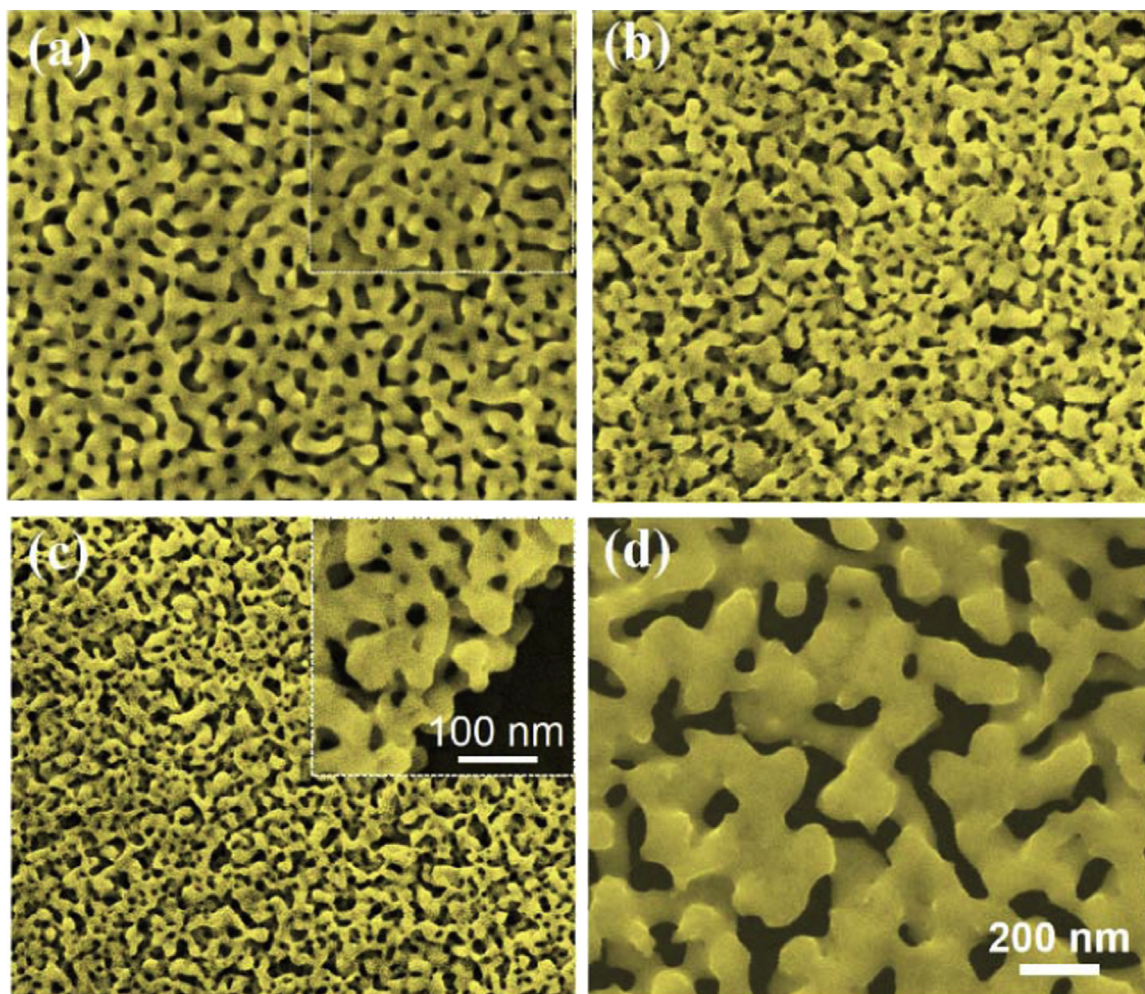
### 3. Results and discussion

The FESEM images of the typical HNPG annealed at different temperatures are shown in Fig. 1. The morphology of the NPG membrane after immersing in 1%  $\text{H}_3\text{BO}_3$  (Fig. 1a) is very similar to the original NPG (the inset in Fig. 1a), characterized by uniformly pores and ligaments in nanometer scale. Interestingly, a special hierarchical structure is observed in the HNPG-180 and HNPG-250 specimens, as shown in Fig. 1b and c. Both surfaces of the two HNPG samples exhibit two typical features of large and small pores separated by irregular ligaments. Especially, HNPG-250 displays a relatively homogeneous bimodal structure compared with HNPG-180 sample. Meanwhile, the cross-sectional SEM of the HNPG-250 shows a three-dimensional nanoporous structure (the inset in Fig. 1c). However, the HNPG-350 sample exhibits a totally different morphology from the other two HNPG samples, where an obvious pore coarsening occurs.

Fig. 2 gives the statistic distribution of pore size at different temperatures, where 300 data were counted from three SEM images. Actually, the pore size of original NPG also displays a certain distribution, mainly centralized in the range of 20–60 nm with an average size of 40 nm (in Fig. 2a). However, after heating at 180 and 250 °C, both the HNPG membranes exhibit an obviously bimodal distribution. Specifically, two peaks are observed in HNPG-180 specimen with average sizes of 20 and 80 nm, as shown in Fig. 2b. Corresponding, HNPG-250 specimen further widens the

pore distribution, where the smaller pores of 10–20 nm occupy a larger fraction, and some pores coarsen to larger sizes of 80–120 nm. The lower hierarchy pore of the HNPG-250 is much smaller than that of the reported pore size of 100 nm [4], which was fabricated in benzyl alcohol solution containing  $\text{SnCl}_2$  and  $\text{ZnCl}_2$  by multiple co-alloying/dealloying. However, the HNPG-350 exhibits a much wider pore distribution of 50–350 nm with an average pore size of 250 nm. Therefore, the formation of this hierarchical porous structure strongly depends on the annealing temperature.

The hierarchical porous structure is promising for molecular sensing application, which can be used as a SERS substrate [12,13]. The Raman scattering spectra of the HNPG using crystal violet as a labeling molecule are presented in Fig. 3a. Compared with the original NPG membrane, the HNPG obtained at 180 °C and 250 °C show more intensive SERS signals. Specifically, the observed Raman intensity of the HNPG -250 membrane at  $1620\text{ cm}^{-1}$  is 2.1 times higher than that of the original NPG membrane. This means that the SERS efficiency is correlated with the geometric effect of ligament and nanopore. Previously, it had been reported that noble metal nanomaterials with nanopores, nanogaps, and sharp tips created active sites, which were responsible for remarkable enhancement of Raman scattering signals through surface plasmon coupling and localized electromagnetic fields [13,14]. The SERS behavior of the HNPG is quite stable versus sample aging for several weeks.



**Fig. 1.** Surface morphologies of the NPG and HNPG membranes prepared at different temperatures. (a) Original NPG after immersing in 1%  $\text{H}_3\text{BO}_3$  solution; (b)–(d) HNPG prepared at 180, 250 and 350 °C, respectively. The inset in (a) is the original NPG, and that in (c) is the corresponding cross-sectional SEM. All the SEM images have the same scale bar in (d), except the inset in (c).

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