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A novel method to fabricate nano-porous Au material through sacrifice template for N_2H_4 oxidation

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ABSTRACT

Highly ordered nano-porous gold materials were directly fabricated by dissolution of sacrificial templates of aligned Ag nanowires in a mixture solution of $HAuCl_4$. The morphology and crystal structure of the mult-materials were characterized by scanning electron microscopy (SEM), XPS respectively. The highly ordered nano-porous gold consisted of nanotubes that formed nano-void. The catalytic activity of Ag nanowires and highly ordered nano-porous gold were studied by N_2H_4 oxidation in aqueous solution. The highly ordered nano-porous gold was expected to show interesting anisotropic optical and electronic properties, and its hollow porous structures might find broad potential applications in surface plasma resonance (SPR), catalysis and chemical sensing.

KEYWORDS

Ag nanowires;
Au nano-porous;
Electrocatalytic;
N_2H_4 oxidation.

INTRODUCTION

In recent years, catalysis by gold become an intensively studied topic in research due to its promising applications in low temperature CO oxidation[1], selective oxidation of methanol[2], oxidation of alkene[3], and water gas shift reaction[4]. Metal electrodes with nano-porous structure on its surface possess great advantages in analysis and chemical reactions[2]. If nano-porous metal films (NPFs) could be directly formed on the surface of an electrode, transfer of electronic response from the surface to the substrate would be much faster than that of an electrode coated with nano-structured material by adsorbing method. Electron tomography is a technique which provides three dimensional (3-D) information on a nano-material scale[3,5], and has great potential in life sciences. Nano-porous Metal could be prepared by metal organic deposition and liquid crystal template technique[6]. Recently, de-alloying was used to fabricate nano-structured metals by selective dissolution of less noble elements from an alloy[7].

Template methods are commonly used to fabricate these materials through the replication of porous alumina or liquid-crystal templates[8,9]. These methods have the advantage of precise control over the pore size and microstructure periodicity, but normally result in materials with one-dimensional porosity, such as an array of tubes. It is generally true that the dominant length scale of the final porous structure is "burned-in", and dynamic control of the

length scale is virtually impossible.

The galvanic replacement reaction provides a simple and effective method for preparation hollow nanostructures of noble metals including Au, Pd, and Pt when Ag nanostructures are used as sacrificial templates. These hollow nanostructures are enclosed by continuous or porous walls with a tunable controllable thickness.

Here we present a novel method to fabricate nano-porous Au. This method involves four steps: fabrication of Ag nanowires, Au^{3+} reacted with Ag nanowires, dissolved AgCl with NaCl to form Au nanotubes and used Au nanotubes to form Au nanoporous materials.

EXPERIMENTAL DETAIL

Apparatus

All the electrochemical experiments were carried out at room temperature in a three-electrode cell, with Pt wire as counter electrode, Hg/HgO (1M NaOH) electrode as reference electrode, and carbon glass (GC) painting with Au nano-porous or Ag nanowires as working electrode, respectively. Voltammetry measurements were conducted by using a CHI822B electrochemical workstation (CHI China).

The surface morphology of the Ag nanowires and nano-porous Au were characterized with scanning electron microscopy (JSM- 6701F Japan). X-ray diffraction (XRD) data from the samples were collected using a Rigaku D/MAX 24000 diffractometer with Cu K radiation.

Chemical and reagents

All of the chemicals used in the experiment were of analytical grade and without purified. $AgNO_3$, $HAuCl_4$, KCl, CH_2OH-CH_2OH (EG) were pursed in china. Poly(vinyl Pyrrolidone) (PVP) came from Sigma. All chemicals were prepared with deionised water purified via Milli-Q unit. Unless otherwise stated, all measurements were performed in solutions purged with high pure nitrogen and at room temperature.

Preparation of Ag nanowires

Silver nanowires were synthesized by reducing $AgNO_3$ with EG in the presence of Pt seeds and PVP[10](detailed information in supporting information). To purify the product, the reaction mixture was diluted with water and centrifuged at 6000 rpm for 10 min.

Preparation of nano-porous Au materials

The process of fabrication of nano-porous Au can be explained by the following Progress. First the Ag nanowires were added into deionized water containing PVP. Then amount of $HAuCl_4$ solution was added into the above solution (Detailed information in supporting information). The production was centrifuged and rinsed several time to purify the production.

RESULT AND DISCUSSION

Surface characterization of Au nano-porous materials

The morphology of Ag nanowires and Au nanoporous materials were examined by SEM observation. Figure 1a presented the SEM image of the Ag nanowires prepared by the reduction of Ag ions with EG in the presence of PVP and trace amount of H_2PtCl_6. These nanowires, revealed a linear morphology with clean surface and several micrometers in length, were used as sacrificed temple to form Au nano-porous materials. Figure 1b showed high precision of Ag nanowires with diameter from 50nm to 100nm. Figure 1c showed the SEM image of Au nano-porous materials which had many void on the surface. Figure1d was the high precision SEM image of Au nano-porous materials which showed many Au nanotubes aggregated into nano-porous materials. The nano-porous materials had many highly ordered nanotubes.

Mechanism of Au nano-porous materials

The galvanic displacement reaction has been employed to synthesize nano-porous materials with Ag nanowires as sacrificial templates. Synthesizing nano-porous Au materials with high surface, which is necessary to improve the catalyst activity[11]. Herein, the driving force of the galvanic replacement reaction comes from the reduction potential gap

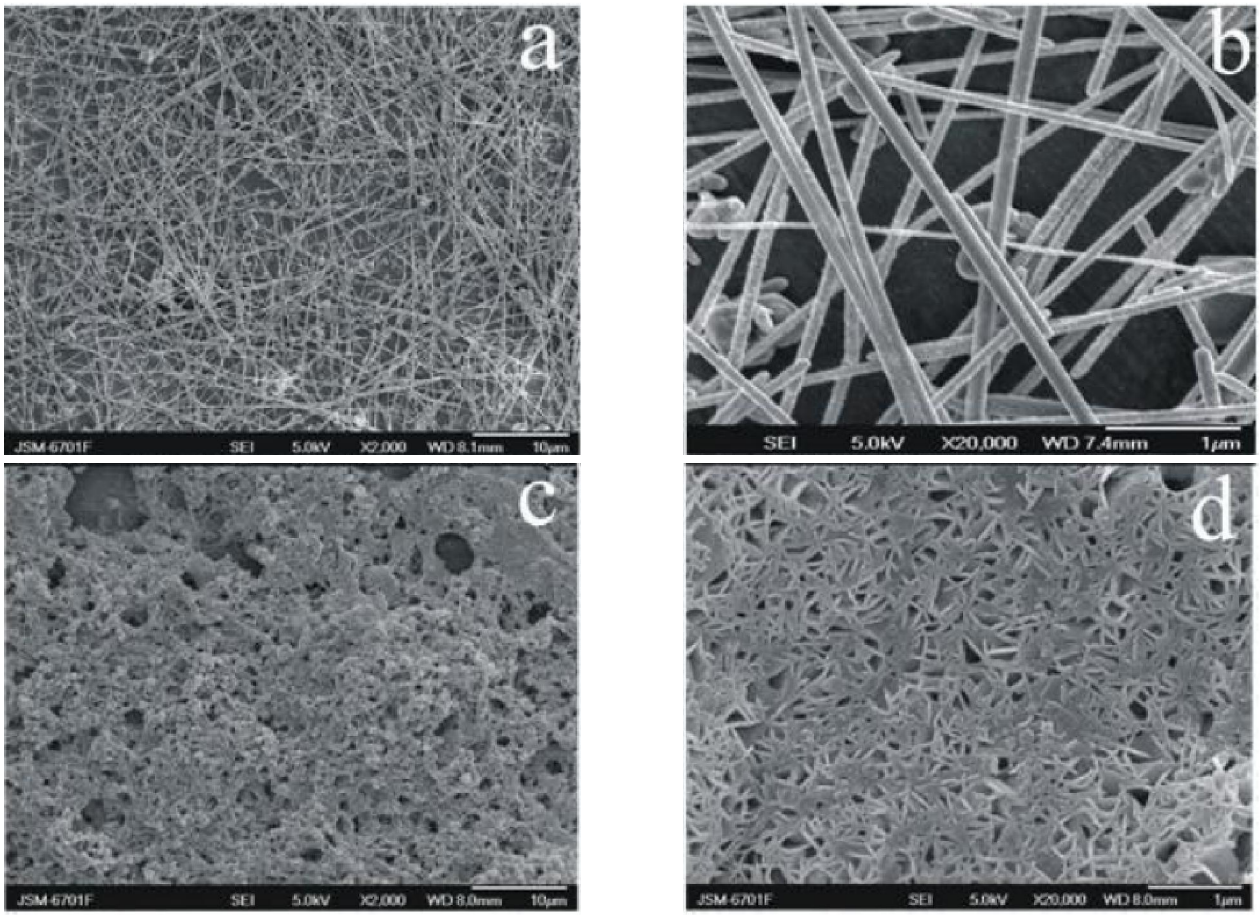

Figure 1 : (a) SEM image of the Ag nanowires used as sacrificed template;(b) High solution of Ag nanowires; (c) SEM image of the Au nano-porous materials; (d) High solution of Au nano-porous materials

between the metallic precursor (such as $AuCl_4^-$/Au) and Ag^+/Ag redox. Most importantly, heating the solution to 100°C during the galvanic replacement is very necessary for obtaining nano-porous material.

The mechanism of Au nano-porous fabrication through displacement reaction can be described as follow. First when Ag nanowires reacted with $HAuCl_4$ in boiling water. The Ag nanowires were covered by Au which was reduced by Ag nanowires. Then the Ag nanowires totally changed into AgCl. When solid NaCl was added to above production, the AgCl was dissolved in saturated concentration of NaCl solution. The above production changed to Au nanotubes. After washed with pure water and centrifuged, the solution was dropped on the glass carbon electrode. The nanotubes resembled to nano-porous materials with water evaporation which has the lowest energy.

XRD of Ag nanowires and Au nano-porous materials

The XRD pattern of the nano-porous Au is shown in Figure 2. Peaks consistent with the face-centered cubic (fcc) expected for Au are clearly observed, whereas those marked with * are assigned to the AgCl which was residual in the nano-porous Au. The four peaks (2Θ = 38.1, 44.3, 64.5 and 77.4) in XRD patterns (in Figure 2) could be indexed to (111), (200), (220), and (311) reflection lines of a face-centered cubic crystal of silver[12].

UV-vis spectral analysis of Ag nanowires and Au nano-porous materials

We could also conveniently monitor the galvanic replacement reaction between silver nanowires and the $HAuCl_4$ solution by UV-vis spectral analysis for nanostructures made of gold or silver often exhibit distinctive peaks in the UV-vis spectral. Figure 3 shows the extinction spectra recorded from aqueous dispersions of silver nanowires and the nano-porous Au after the Ag nanowires had been reacted

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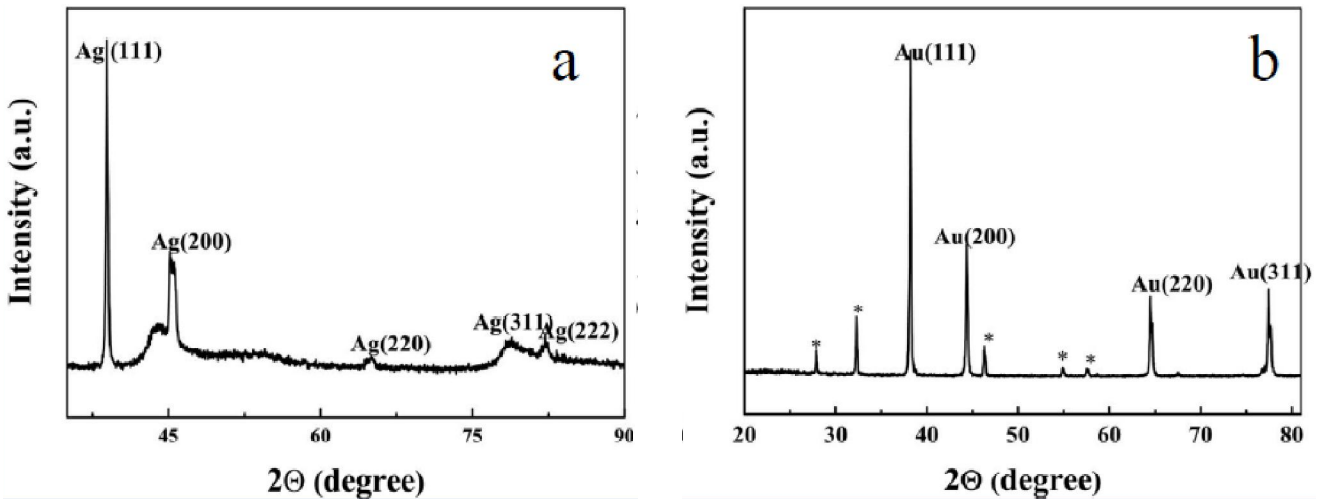

Figure 2 : X-ray powder diffraction patterns of the Ag nanowires and Au nano-porous materials

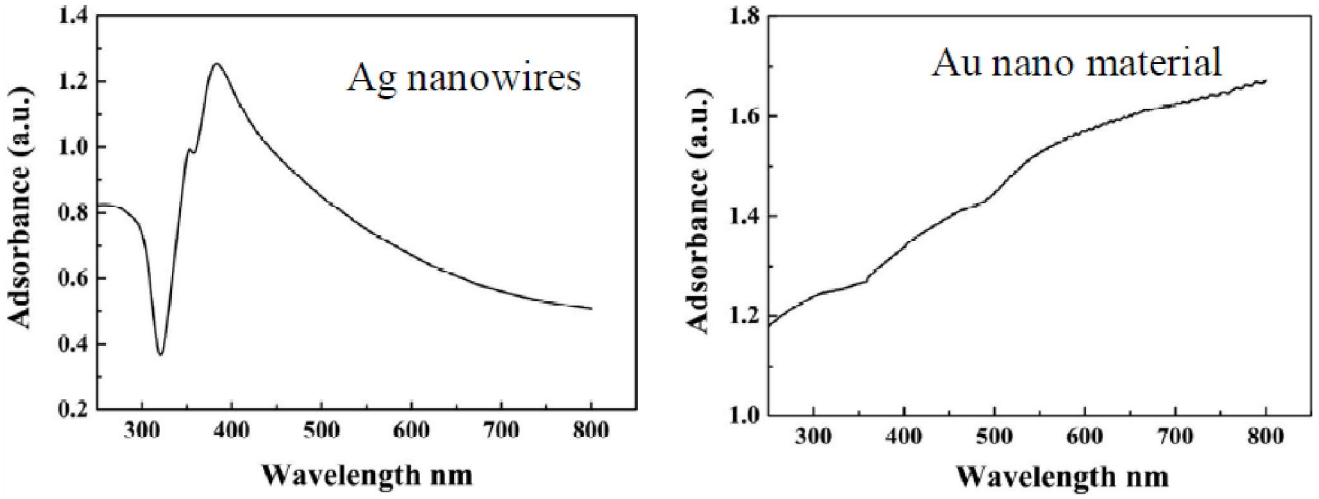

Figure 3 : UV-vi image of Ag nanowires and Au nano-porous materials

with $HAuCl_4$ and treated with NaCl solution. From the Figure 3a, the peak located at 400nm is the typical behavior of Ag nano material[13]. After the Ag nanowires reacted with $HAuCl_4$, treated with NaCl and purified with water, the peak located at 400nm (specific feature of Ag nanowires) disappeared and a new weak peak appeared located at 600nm, which was typical peak of Au nano-porous materials[14]. The experimental data further conformed that the Ag nanowires had been changed into Au nanomaterials.

XPS analysis of Ag nanoprous materials

In order to study the nano-porous Au, XPS methods was performed to identify and characterize the nano-porous Au as shown in Figure 4, two XPS bands appeared at 84 and 88eV, corresponding to the Au signal, respectively, which demonstrated the formation of Au(0) state. The peaks of Ag were confirmed to Ag^+, which was residual AgCl in Au fabrication through displacement, which has been proved by XRD.

Electrocatalytic activity of Ag nanowires and Au nano-porous materials for N_2H_4 oxidation

Cyclic voltammogram N_2H_4 Oxidation on Ag nanowires modified electrode and Au nano-porous modified electrode are compared in Figure 5. Both electrode show a similar feature: an oxidation peak in the forward scan corresponding to the N_2H_4 oxidation on the electrode. While there no backward peak appears, which means N_2H_4 reaction on electrode is irresistible reaction. The current of N_2H_4 oxidation on Ag nanowires modified electrode is 1.46mA which is 1.2 time higher than that of Au nano-

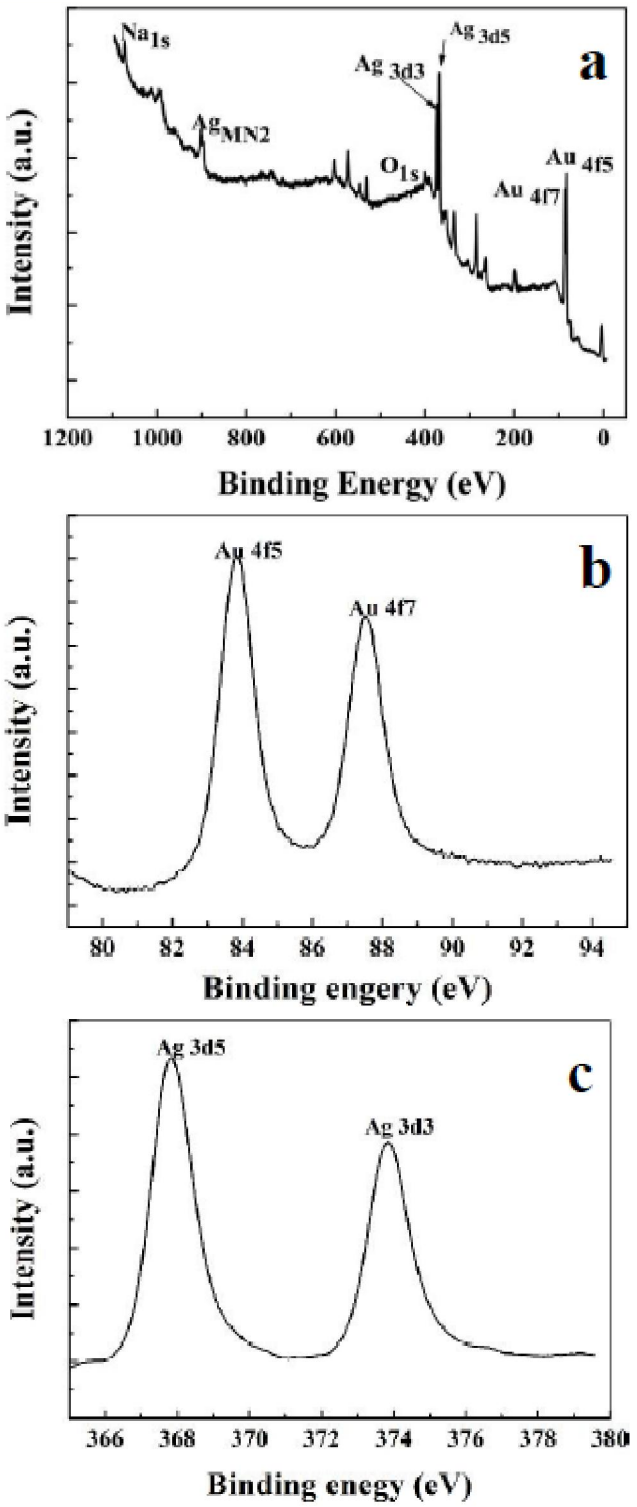

Figure 4 : XPS image of Au nano-porous materials: (a) survey image of Au nano-porous materials;(b) Ag 3d image of Au nano-porous;(c) Au 4f image of Au nano-porous materials

porous electrode. The present results indicate that Ag nanowires have higher activity than Au nano-porous. However the Ag electrode is easy poisoned

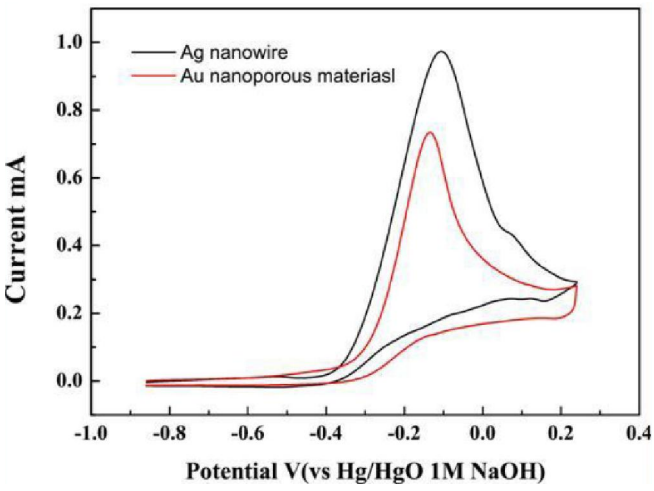

Figure 5 : Cyclic voltammetry of N_2H_4 oxidation on Ag nanowires modified GC electrode and Au nano-porous materials modified GC electrode

which limits its application[15]. Moreover the Ag electrochemical window is so narrow which confines its widely application. From the figure, it can be clearly seen that the potential of N_2H_4 oxidation on Au nano-porous electrode is more negative than that on Ag nanowires electrode. Negative potential means that N_2H_4 oxidation on Au nano-porous electrode is much easier than that on Ag nanowires electrode, which give a great potential in sensor or catalyst. The low current of Au nonaporous may be contributed to some AgCl residual in Au nano-porous materials which has been proved in XRD and XPS methods. The AgCl materials have little catalytic activity to N_2H_4 oxidation which suppresses the electrocatalytic activity of Au nano-porous materials.

CONCLUSION

We use a novel method to form Au nano-porous material. The material has high ordered structure which has highly ordered nanotubes heap up together. The Au nano-porous with particular structure shows a considerable catalytic for N_2H_4 oxidation. Au nano-porous with high order may have great potential in catalyst, sensor and so on.

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