

Gold tubes membrane with novel morphology replicated from ZnO template

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Abstract

Gold tubes membrane with novel morphology was fabricated on glass substrate by electroless plating gold on ZnO crystals array, and then annealing and removing the ZnO template by acid erosion. The morphology and size of the gold tubes membrane were decided by ZnO template. Hexagonal gold tubes membrane and double-wall gold tubes membrane were obtained, which enjoys some potential usage in electrode modification or chemical separation due to their huge surface area and unique geometric structure. SEM images show that those gold tubes in membrane are hollowed hexagonal columns with a closed head and an open bottom. Further researches found that two main factors determined the success of replication: the gold seeds (4–5 nm in diameter) immobilized on ZnO surface through APTMS (3-Aminopropyl-trimethoxysilane) before gold electroless plating and the annealing condition after electroless plating.

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1. Introduction

One-dimensional (1D) arrays with various morphologies such as wire, rod, belt and tube have stimulated wide interests due to their great potential in the fundamental studies of the effects of morphology, dimensionality, and size on their physical and chemical properties as well as for their application in optoelectronic devices [1–4]. As for gold, considerable attention has been paid to the preparation of nanoparticles [5,6], nanorods [7,8], nanowires [8] and their assemble on solid substrate [9–11] because of their unusual properties different from those of the bulk state and potential applications in optical, electronic and catalytic materials.

Martin and co-workers have developed a general approach—template synthesis to make nanomaterial membranes [12–14], and they have prepared gold

nanowires and nanotubes membranes by electroless deposition process within the cylindrical pores of nanopore polycarbonate template membranes. The outside diameter of the obtained gold nanotubes is determined by the pore diameter of the template, and the inside diameter is determined by the electroless deposition time. The inside diameter can be controlled from tens of nanometers down to less than 1 nm [15–18]. Recently, these unique nanotubes membranes have been used as nanoscopic or microscopic electrodes [19,20], chemical separation membranes [21–25], and catalyst for oxidation of CO with O₂ ($\text{CO} + 1/2\text{O}_2 = \text{CO}_2$) at room temperature [26].

Recently, 1D nano/microcrystalline ZnO has attracted much attention due to its special properties and large-scale arrays of ZnO crystals with good orientation and different morphologies, such as tower-like rods and tubes, have been prepared [27]. In this paper, we utilized ZnO rods array with tower-like hexagonal structure as templates and got the membrane

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of closed hexagonal gold tubes by electroless deposition. Different from Martin's method, gold was deposited on the wall of ZnO rods, so the inside diameter of tubes was decided by the ZnO template. Longer deposition time can increase the outside diameter of tubes. In order to keep the hexagonal morphology replicated from ZnO templates, HAuCl₄/hydroxylamine hydrochloride was selected as plating solution because the thickness of tubes wall must be uniform and far smaller than the diameter of ZnO hexagonal rods. In this autocatalytic redox process [28], gold deposits only on the catalytic surface in a gentle way [29]. In our work, gold nanoparticles (4–5 nm in diameter) serving as catalyst were first immobilized on the surface of ZnO hexagonal rods through APTMS before electroless plating. ZnO template was removed by acid after gold plating, and gold tubes membrane was obtained. Losing the support of ZnO rods, the thin wall of gold tubes was in a great risk of collapse when removing the ZnO template. Research found that slowly removing ZnO with diluted acid and proper annealing condition were two main factors to avoid this kind of collapse. The unique character of the obtained membrane is the morphology of tubes, which is only decided by the morphology of ZnO templates. Besides the hexagonal gold tubes membrane, we also fabricated the membranes of double-wall tubes using ZnO tubes array as template by the same method. Those kinds of tubes membranes with novel morphologies may enjoy a potential use in chemical separation since the novel shape of the tubes may influence the transfer of some particles or molecules such as protein.

2. Experimental

2.1. Chemicals

All chemicals are analytical-grade reagents and used without further purification. Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O), thiourea, ammonium chloride, ammonia (25%), hydroxylamine hydrochloride, sodium citrate, tetrahydrofuran (THF), and polycarbonate were purchased from Shanghai Chemical Reagent Corp. HAuCl₄, APTMS and NaBH₄ were obtained from Sigma-Aldrich, Fisher (Acros).

2.2. Preparation of ZnO template

1D ZnO array with different morphologies was prepared according to the literature [27]. In a typical process to prepare towel-like ZnO crystals, well-cleared glass slides were immersed in reaction solution containing 0.01 mol zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O), 0.01 mol thiourea, 0.002 mol ammonium chloride, 5.0 ml ammonia and 95 ml distilled water for 1 h at 95 °C in a

Teflon vessel. After reaction, thin ZnO films with a pure white color formed on glass surface. The morphology of ZnO films was decided by the method to prepare reaction solution. In our previous work, we found ultrasonic pretreatment could generate a suitable amount of ZnO cluster nuclei for subsequent growth. Ultrasonic pretreatment can also enhance the activity of ZnO nuclei. Thus, after an appropriate ultrasonic pretreatment time, ZnO nuclei assemble in a hexagonal circle on the substrates and grow into tube-like arrays. To obtain tube-like ZnO crystals, reaction solution was pretreated for 35 s before reaction to increase the amount of active nuclei.

2.3. Preparation of gold seeds

Gold seeds were prepared by reduction of HAuCl₄ with sodium borohydride in the presence of sodium citrate as a capping agent [30]. To a 250 ml flask filled with 100 ml sodium citrate solution (5.0×10^{-5} M), 0.5 ml HAuCl₄ (0.01 M) was added under vigorous stirring. Then 0.5 ml NaBH₄ (0.01 M) was added all at once. A faint color change occurred immediately, indicating the production of gold nanoparticles.

2.4. Preparation of gold tubes membrane

In order to enhance the affinity of ZnO to gold seeds, the ZnO film was first immersed in 1% APTMS aqueous solution for 30 min to form a monolayer of amido on ZnO. After being rinsed with deionized water and dried in nitrogen atmosphere at 70 °C, the obtained sample was immersed in prepared gold seeds solution for 5 h and finally high-coverage monolayer of gold nanoparticles was formed on amido modified ZnO surface.

The gold shells on ZnO rods array were formed by reduction of Au³⁺ (in the form of HAuCl₄) on ZnO rods surface with gold seeds as catalyst, using Brown and Natan's iterative hydroxylamine seeding procedure. In a typical experiment, ZnO film with gold nanoparticles (seeds) was immersed in 30 ml aqueous solution containing 0.01% HAuCl₄ and 0.4 mM hydroxylamine hydrochloride for 15 min for the reduction of Au³⁺. After repeating this process for three times and rinsing well, the sample was annealed at 250 °C for 3 h under nitrogen protection. During this process, a distinctive change in color can be observed from pure white to dark gray. Then this film was immersed in 0.05 M HCl solution for 2 h to thoroughly remove ZnO template. Finally a transparent gold film with a black color remained on glass slide.

2.5. Instrumentation

The morphologies of gold tubes membrane and their template were observed with scanning electron microscope

(SEM) (HITACHI S-2150). The crystal structure of the ZnO template and gold tubes membrane were analyzed using XRD (SHIMADZU XRD-6000) with $\text{CuK}\alpha$ radiation and Energy dispersive X-ray (EDX) spectrum (EDAX FALCON) linked with JSM-6360VL SEM. Transmission electron microscope (TEM JEOL JEM-100CX) was used to research the morphology of gold seeds nanoparticles in aqueous solution.

3. Results and discussion

3.1. Morphology of hexagonal gold tubes membrane

SEM was used to observe the morphologies of hexagonal gold tubes membrane and ZnO rods array template. Fig. 1A, C shows the SEM images of original ZnO template with different magnification, while B, D are the corresponding images of hexagonal gold tubes membrane after the ZnO template being removed. Comparing the two group photos, we can find the hexagonal morphology of ZnO template was successfully duplicated by seed-induced electroless gold deposition, and hexagonal gold membrane was obtained. From this we can also find that the diameter of gold

rods and its template-ZnO rods are both 600 nm and no distinctive increase, which indicated that the gold layer coated on ZnO template is very thin and its thickness can be neglected compared with the diameter of ZnO rods.

Single gold tube was selected to further investigate the morphology of gold tubes membrane (Fig. 2). Results show that the gold tube has an hexagonal structure with a small head (about 600 nm) and big bottom (about 1000 nm). The top surface was a hexagon, seemingly a little thicker than other surfaces, which may be caused by the unsymmetrical deposition of gold on ZnO surface. Because it is difficult for plating solution to infiltrate into the space between ZnO columns, the gold layer was thicker on the top surface of ZnO columns. After the ZnO being removed, the difference in thickness remained. As to the thickness of gold tubes, it was 50–100 nm according our estimate. In fact, Farid Bensebaa and coworkers [31] have prepared continuous gold film on a poly (diallyldimethylammonium chloride)-modified glass slide by the same electroless gold deposition method. The gold film they prepared on modified glass slide was 50–60 nm in thickness measured by AFM. Further more, they found that there was a linear relationship between the thickness of gold film

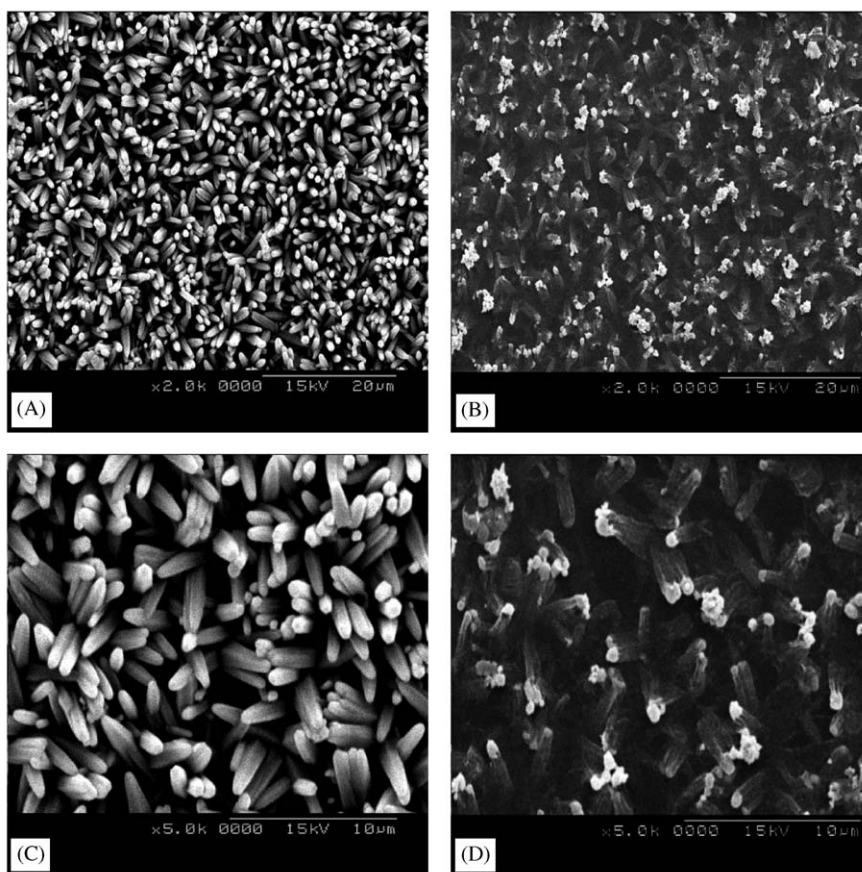


Fig. 1. The morphology of hexagonal gold tubes membrane (B, D) and its corresponding tower-like ZnO array template (A, C) with different magnification.

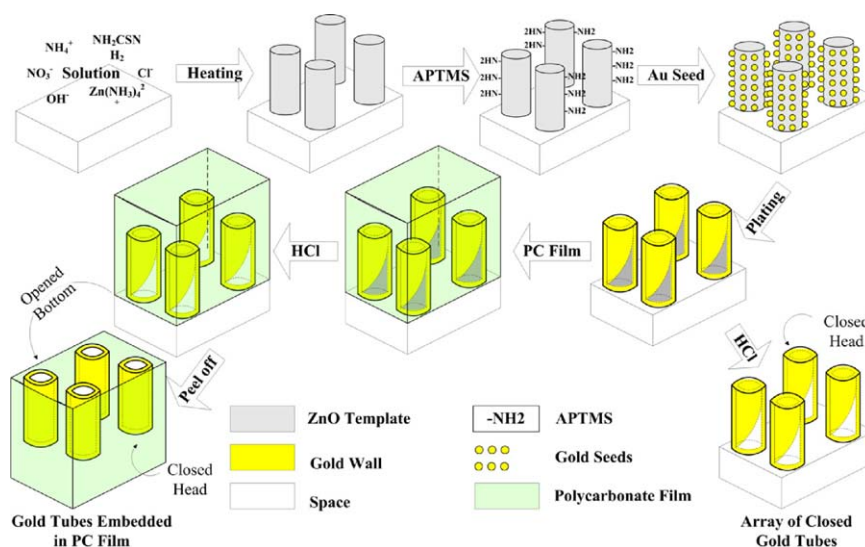
and electroless deposition time. Because we repeated the deposition process for three times, the gold tube wall was supposed to be theoretically 150–180 nm in thickness. But in view of the difficulty for plating solution to infiltrate to the space between ZnO columns, the thickness of gold tube wall should be far more less than this value.

According to our preparing strategy (Scheme 1), the thin gold layer should be evenly coated on the surfaces of hexagonal ZnO rods. After removing the ZnO rods by diluted HCl, gold layer would remain as hexagonal structure with the same size of ZnO rods. There was no gold deposition process after removing the ZnO template and no new stuff can occupy those cavums, so the hexagonal gold rods (Fig. 2) should be hollowed hexagonal columns with a closed head and an open



Fig. 2. SEM image of a single hollowed hexagonal gold tube on membrane.

bottom. The wall of gold tubes is very thin, especially at the bottom, and those tubes are not strong enough to keep their original structure when we try to scrape them off the slides, so it is very difficult to directly observe the internal structure of those closed cavums. In order to get the direct evidence that the ZnO is thoroughly removed and the remained gold are in tube structure, we strengthened those gold tubes with polymer (Scheme 1). In a typical experiment, 5% polycarbonate solution in THF was spin coated on the gold tubes array with ZnO rods in them. After being dried at 70 °C for 2 h, the polycarbonate film occupied the space between gold tubes and greatly reinforced them. Removing ZnO in the gold tubes by acid, we got the gold tubes array embedded in polycarbonate film. This film is strong enough to be peeled off from glass slide, and from the undersides of this film we can observe the bottom of the embedded tubes array, which should be opened according to our strategy. From Fig. 3, we find that those gold columns are really hollowed hexagonal tubes as expected. Because those tubes are embedded in polycarbonate film, the thickness of gold tubes cannot be distinguished from the surrounding polycarbonate. In Fig. 3 we can only observe the hexagonal holes of those tubes which should be occupied by the ZnO hexagonal columns before acid treatment. Those holes are about 1 µm in diameter agreeing well with the size of the bottom of the hexagonal tubes shown in Fig. 2, which indicates that the ZnO template has been thoroughly removed by acid and that gold tubes remained under the protection of the surrounding polycarbonate. From the above discussion, we think the hexagonal columns shown in Fig. 1 are hollowed hexagonal tubes with a closed head and an open bottom, and their internal structure is also a hexagonal vacuum with the same size as that of the ZnO template.



Scheme 1. Preparation process of gold tubes membrane.

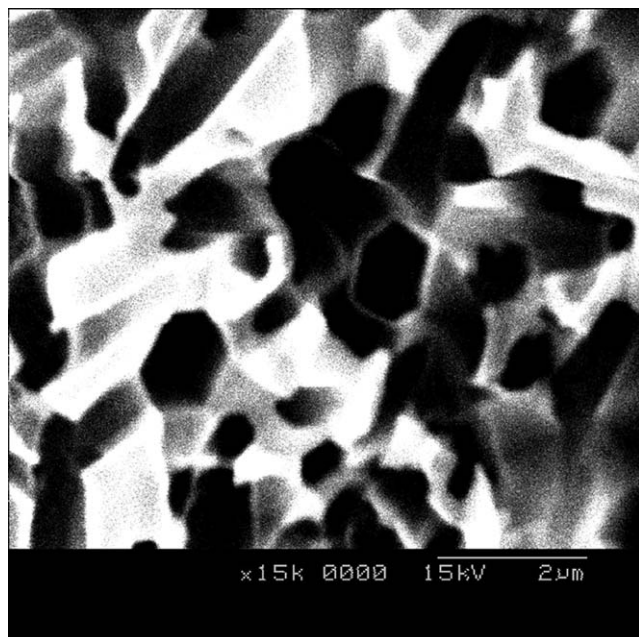


Fig. 3. Gold tubes array embedded in polycarbonate film.

3.2. XRD and EDX analysis

XRD was used to study the component of the film in different stages. Fig. 4A is the XRD pattern of ZnO template. ZnO crystals are of wurtzite structure, and the diffraction peaks can be indexed to a hexagonal structure with cell constants of $a = 3.24 \text{ \AA}$ and $b = 5.19 \text{ \AA}$ (JCPDS card No. 36-1451). After gold deposition and annealing, several new peaks appear in Fig. 4B besides those peaks of ZnO. Those new peaks are the diffraction results of synthetic gold (JCPDS card No. 4-784). After being eroded with diluted HCl, all the diffraction peaks of ZnO disappear and the remained peaks can be attributed to the patterns of synthetic gold (Fig. 4C).

EDX spectrum, linked with SEM, was used to analyze the element of ZnO rods (Fig. 5A) and hexagonal gold tubes after being eroded with diluted HCl (Fig. 5B). In this analysis, the electronic beam is focused only on the head of one upright ZnO rod or gold tube, so the results can represent the real composition of a single ZnO rod and gold tube shown in Fig. 1. No peak for Zn is found in Fig. 5B, which also indicates that ZnO has been thoroughly removed by HCl. From Fig. 5B, the peaks for other elements (Si, Al, Mg, Ca, Na, and O), besides that of gold, are also found. This is because the wall of hollowed gold columns is very thin and the electronic beam can easily penetrate it and reach the substrate of glass. This is also a collateral evidence that the hexagonal columns showed in Fig. 5B,D were hollowed since the electronic beam cannot pierce the solid gold columns from head to bottom.

In general, both XRD and EDX results prove that the ZnO template has been thoroughly removed by

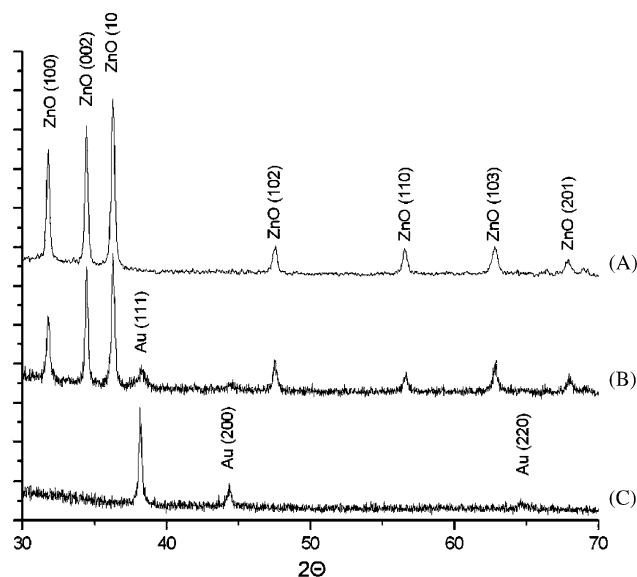


Fig. 4. XRD pattern of sample in different stages: (A) pure ZnO template; (B) after gold deposition and annealing; (C) final hexagonal gold tubes membrane.

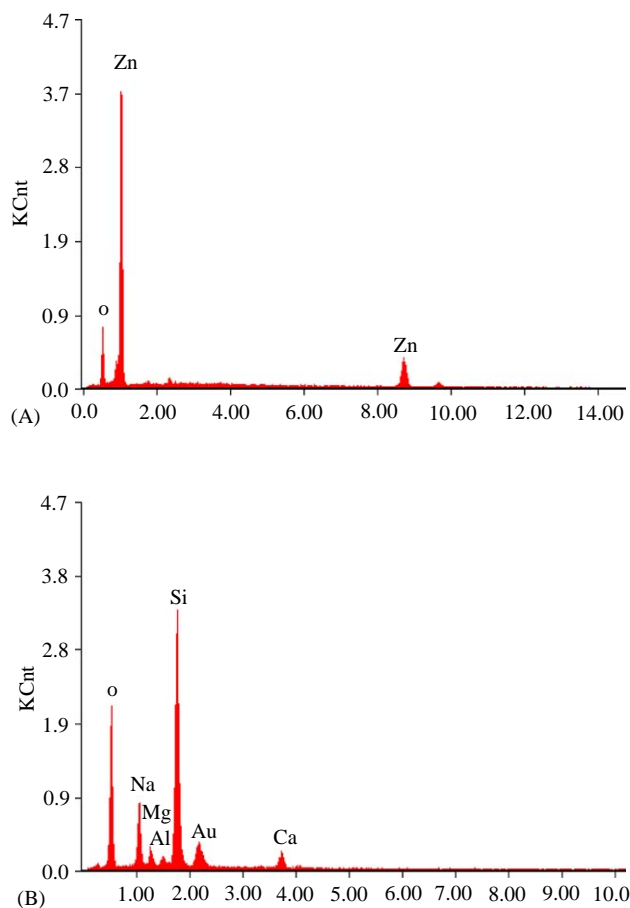


Fig. 5. EDS analysis of (A) ZnO rods and (B) final hexagonal gold tubes.

acid and the hollowed hexagonal columns membrane is pure gold.

3.3. Several factors decided the success of replication

Just as being demonstrated in previous sections, the basic building blocks for the gold tubes membrane are hollowed gold hexagonal columns whose walls are very thin compared to their cavums size. So replication condition must be precisely controlled in order to avoid the collapse of those hollowed columns. We found electroless deposition condition and annealing temperature were two key factors that determined the success of replication.

3.3.1. Influence of gold seeds

HAuCl_4 /hydroxylamine hydrochloride is an autocatalytic redox process, and gold deposits only on the catalytic surface. Gold nanoparticles (4–5 nm in diameter, Fig. 6), serving as catalyst, were first immobilized on the surface of ZnO hexagonal rods through APTMS before electroless plating, then gold can be evenly deposited on the surface of ZnO hexagonal rods through electroless plating process. In parallel experiments, almost no gold can be deposited on the non-seeds ZnO template in the first 20 min. Some gold can be deposited on those non-seeds ZnO template (judging by color change) increasing the deposition time to 60 min, but it can be easily rinsed out due to its poor adhesion.

Farid Bensebaa and coworkers [31] have studied the mechanism of HAuCl_4 /hydroxylamine hydrochloride autocatalytic redox process. They found gold seeds surface-catalyzed reduction exhibited very fast kinetics. Au^{3+} was reduced on those gold seeds and made them larger and larger. In our work, gold seeds were firstly immobilized on ZnO template by APTMS, so the gold film still enjoyed a good adhesion even after electroless plating. On the other hand, the reduction of Au^{3+} is

very slow without catalyst. In fact, some gold colloids can also be formed on the non-seeds ZnO template giving an ultra-long plating time. Those colloids formed at first stage can serve as catalyst to the further reduction of Au^{3+} . Finally, some gold particles formed in solution deposited on ZnO template by gravity. So the adhesion of gold particles on ZnO template is weak and gold tubes cannot be obtained after the ZnO template was removed.

3.3.2. Influence of annealing temperature

A proper annealing as post-treatment can enhance the strength of gold wall. The annealing process was taken at 250 °C for 3 h under nitrogen protection. After this process, the particles on gold wall coalesced and became bigger with noticeably rounded shapes [31], which made the hollowed gold hexagonal more strong. Other annealing temperatures, such as 100, 200, 300, 400 and 500 °C, were also used, but 250–300 °C were found to be the best annealing temperature arrange to keep morphology. We think gold particles partially melted and grown together under this temperature. While lower temperature cannot melt those particles, too high temperature will thoroughly fuse those particles and destroy their overall arrangement (Fig. 7).

3.4. Morphology of double-wall gold tubes membrane

With the same method to fabricate hexagonal gold tubes membrane, the membranes with double-wall tubes using ZnO tubes array as template can be obtained. The section illustration (Scheme 2) shows the structure difference between hexagonal gold tubes membrane and double-wall gold tubes membrane. Since gold can deposit on both outside wall and inside wall of ZnO

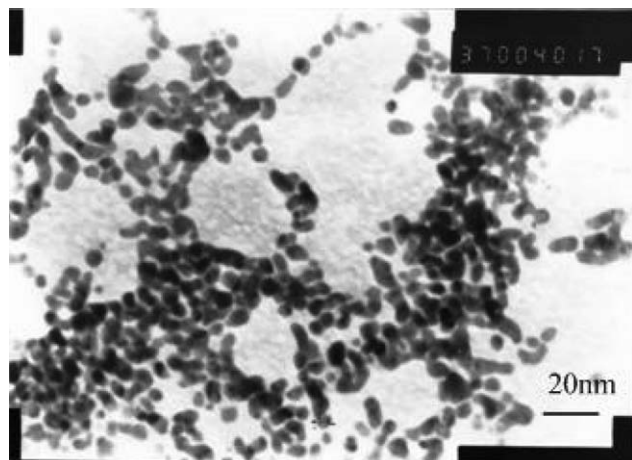


Fig. 6. TEM image of gold seeds serving as catalyst in our method.

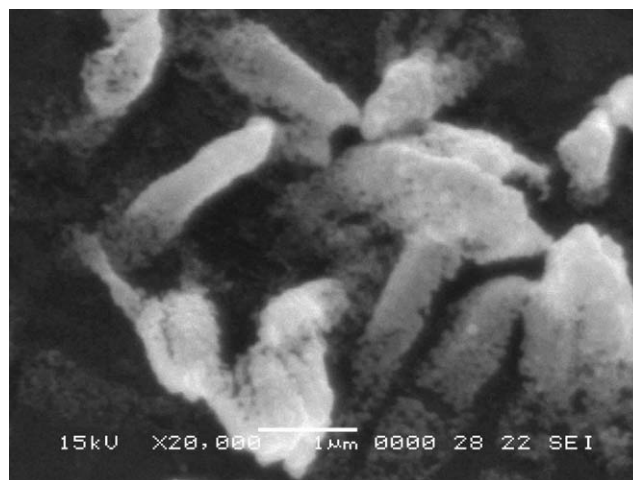
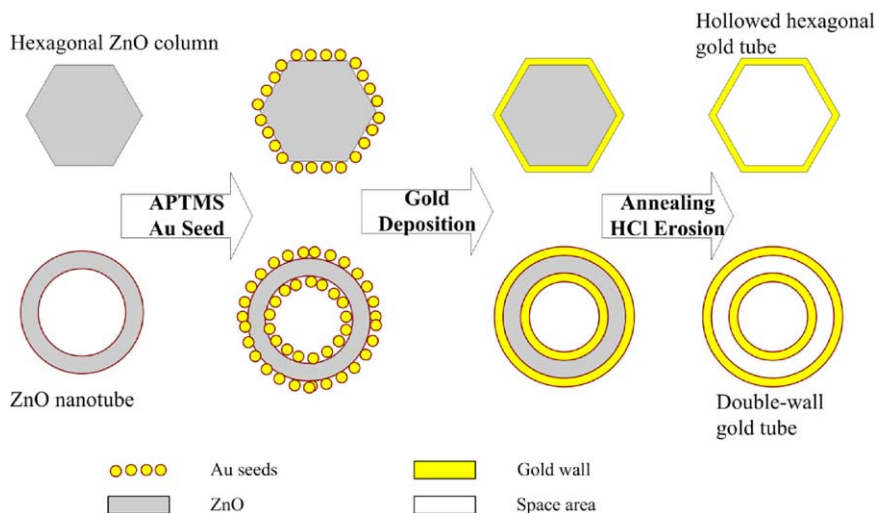


Fig. 7. SEM image of gold tubes membrane annealed at 500 °C. The too high temperature destroyed their hexagonal morphology compared to Fig. 2.



Scheme 2. Section illustration of the structure difference between hexagonal gold tubes membrane and double-wall gold tubes membrane in every fabrication stage.

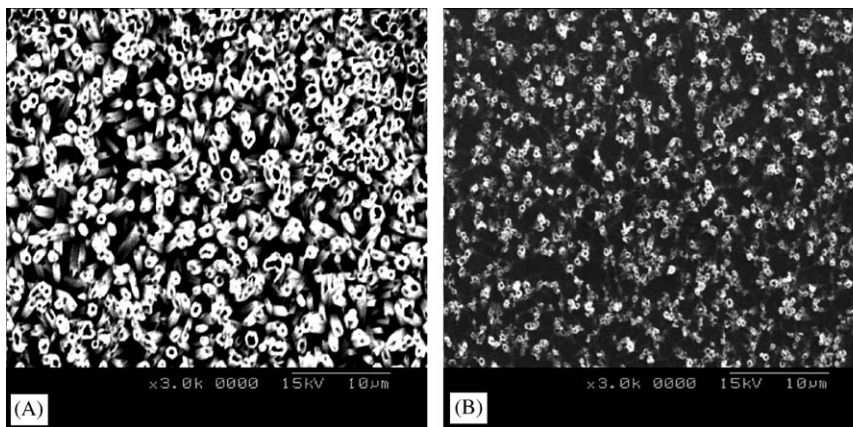


Fig. 8. Morphology of double-wall gold tubes membrane (B) and its corresponding ZnO tubes array template (A).

tubes template, there forms a double-wall tubes structure when removing the ZnO between the two gold layers. Fig. 8 shows the SEM images of ZnO tubes array (A) and the corresponding gold tubes (B). For the same reason mentioned above, we cannot directly observe the double wall, but we think our speculation is reasonable.

4. Conclusion

The paper presents a simple method to fabricate a gold tubes membrane based on the self-assembly of a gold seeds layer on a ZnO template surface pretreated with APTMS, followed by electroless gold plating, annealing and removing the ZnO template. Results show that the morphology of ZnO template can be precisely replicated by controlling the plating and annealing conditions. Utilizing different ZnO templates, we got the hexagonal tubes membrane and double-wall tubes membrane which

enjoy a potential usage as electrodes material or chemical separation membrane due to their novel geometrical shape or huge surface area.

Acknowledgments

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