Template Fabrication of Novel Structure of Polypyrrole Nanotubules Inner-embedded with Gold Nanoparticles

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Template fabrication is a powerful method to control the shape, size, and morphology of materials on the nanoscale. A novel structure of polypyrrole (PPy) nanotubules inner-embedded with gold nanoparticles has been successfully fabricated via polymerizing the pyrrole monomer in situ in a modified porous anodic alumina (PAA) template. Their morphology and structure have been confirmed by transmission electron microscopy, selected area electron diffraction, and X-ray diffraction.

As the new type of microstructure was discovered in 1984, organic microtubules have attracted considerable attention because of their potential applications,[1] such as nanosized transistors, sensors, and molecular wires.[2] In the past decades, polypyrrole (PPy) nanotubules have become one of the most favored materials in many fields owing to their high environmental stability, biocompatibility, and good electronic conductivity.[3] Recently, composite nanostructures of metal nanoparticle–polymer have arisen many investigations because the functions of polymer materials could be further enhanced by the doping of metal nanoparticles.[4] Gold nanoparticles have been studied for many years, since it exhibits unique optical, electrical, and catalytic properties. It could be necessary to assemble the nanoparticles onto conductive PPy nanotubules to extend their applications in microelectronic and optic devices.[5] Meanwhile, PPy could provide a fast thermal-energy-transfer pathway to gold nanoparticles.[6] Recently, various Au/PPy nanostructures have been fabricated, e.g., Selvan and Nogaml have fabricated novel Au/PPy anisotropic colloids,[7] Liu and Chuang used an electrochemical pathway to prepare Au/PPy core–shell nanocomposites,[8] and the structure of the PPy nanotubules coated with gold nanocrystals have been formed by Shi and his co-workers.[9] But there is little information in the literature about the special composite structure of PPy nanotubules inner-embedded with gold nanoparticles.

Template fabrication was a typical method for preparing 1D nanostructures. The arrays of aligned nanostructures are obtained reproducibly and economically by filling the pores of the template.[10,11] Our group has fabricated the nanowires of polyaniline,[12] polydiphenylamine,[13] and metal sulfides[14] successfully by using the PAA template. The conditions of the fabrication of the nanotubules were much more stringent than that of nanowires. An efficient way was found to gain the nanotubules easily when a "molecular anchor" was first absorbed on the pore-walls of the template.[15] For example, Peng and coworkers have prepared the CdS nanotubule arrays in template by using 3-aminopropyltriethoxysilane (APS) as the "molecular anchor,"[16] In this paper, we developed this molecular anchor templating method to acquire a novel structure of Au/PPy nanotubules by the in situ oxidative polymerization of pyrrole monomer in a modified PAA template.

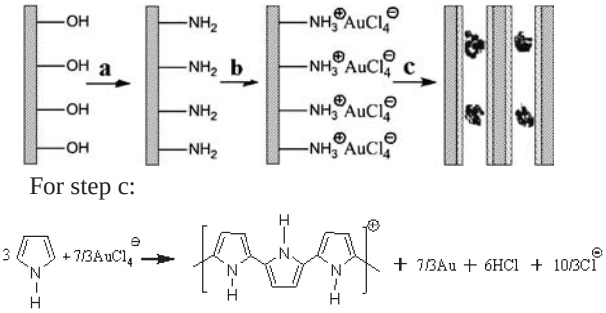

Figure 1. Schematic diagram of the preparation procedure of the Au/PPy nanotubules in the PAA template: a) Silanization with 3-aminopropyltriethoxysilane (APS); b) The absorption of $AuCl_4^-$ on the inner surface of the PAA template; c) Polymerization of the pyrrole monomer in the pores of the PAA template.[17]

The PAA template with a thickness of 20 μm and pore diameters of 60 nm in our experiment was gained by a two-step anodizing process.[18] The main preparation procedures of PPy nanotubules inner-embedded with Au nanoparticles are illustrated in Figure 1. First, the template was modified with a 10 mM anhydrous hexane solution of 3-aminopropyltriethoxysilane (APS) for 12 h. Then the amino end group-modified template was immersed into a 5 mM aqueous solution of $HAuCl_4$. After 12 h, the PAA template, containing $AuCl_4^-$, was washed by water and dried in air for further use. The PPy nanotubules were prepared by placing the oxidant-loaded template into a small vial, which was sealed in a chamber saturated with pyrrole vapor. Within 30 s, the color of the PAA template changed from orange to black, indicating the formation of PPy. The PAA template was kept to expose in the atmosphere of the pyrrole vapor for 2 h. Thus, this novel structure of the PPy nanotubules inner-embedded with gold nanoparticles was formed gradually.

The functionalization of the pore walls of the PAA template is a key step for the fabrication of the PPy nanotubules, which can change the inner surface charge of the pore walls from negative to positive. When the pore walls are positively charged, the anion like $AuCl_4^-$ could be attached on the pore walls of the template by the static attractive interaction, and the surface of the pores could be used as active sites for polymerizing vaporous pyrrole monomer to form PPy nanotubules. Under such condi-

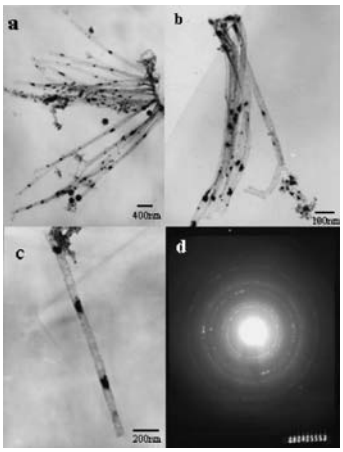

Figure 2. TEM images of uniform Au/PPy nanotubules arrays. a) and b) general view, c) magnified view and, (d) the corresponding SAED pattern.

tion, pyrrole monomer and $AuCl_4^-$ act as reducing and oxidizing agents, respectively.

TEM images in Figures 2a and 2b indicate that the typical structure of the PPy nanotubules inner-embedded with gold nanoparticles was well conformed. The PPy nanotubules are homogeneous and straight, the diameter is about 55 nm which is close to the pore size of the PAA template (60 nm). In Figure 2c, TEM image of the individual Au/PPy nanotubules shows that the gold clusters with diameter of 40 nm almost embedded at intervals in the pores of the nanotubules. When the organic monomer was polymerized in situ in the inner surface of the PPA template, the gold nanoparticles with a diameter of 10 nm which produced by reduction dispersed within the pores and then aggregated to larger clusters quickly because of the high surface energy. Some sporadic gold nanoparticles were observed out of the PPy nanotubules because of the destruction of the nanotubules. In the SAED pattern of the nanotubules (Figure 2d), several clear diffraction rings can be observed owing to the presence of gold nanoparticles, which indicated their good crystallinity.

The Au/PPy nanotubules in PAA film were analyzed by FT-IR as shown in Figure 3. In the spectrum, the appearance of C=C stretching vibration at 1621 cm^{-1} and C–N stretching vibration at 1463 cm^{-1}, which are characteristic IR absorption bands of PPy,[19] indicates the coupling of pyrrole units.

The XRD pattern of the prepared Au/PPy nanotubule arrays within the alumina template membrane is given in Figure 4. Since the most of the sample for XRD measurement is alumina membrane, the relatively peak intensity of alumina membrane is much stronger than that of Au. Despite the peak intensity of gold nanoparticles is very weak, some characteristic peaks can still be observed, which are assigned to (111), (200), and (311) planes of face-centered cubic gold crystals (cell constants $a = 4.078$ Å, JCPDS card file 04-0784). The result is consistent with the analysis of the SAED.

In conclusion, a novel structure of polypyrrole nanotubules inner-embedded with gold nanoparticles has been obtained by the in situ oxidative polymerization of the pyrrole monomer in a functionalized PAA template. It is believed that the method combining the molecular anchor-templating fabrication with in situ oxidative polymerization in a template possesses a potential

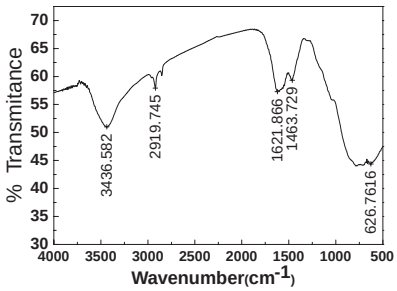

Figure 3. FT-IR spectrum of the Au/PPy nanotubules in PAA film.

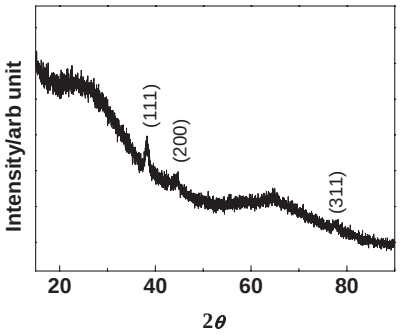

Figure 4. X-ray diffraction pattern of the Au/PPy nanotubules.

application for fabricating this structure of other metal/polymer materials.

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