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Binary hydrogel nanowires of invertible core/shell phases prepared in porous alumina membranes

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Poly(*N*,*N*-dimethylacrylamide)/poly(acrylic ammonium) binary hydrogel nanowires with invertible core/shell phases were made by templated synthesis in porous alumina membranes with controlled pore wall hydrophilicity.

The study of one-dimensionally nanostructured materials including nanowires and nanotubes is of fundamental and technological importance. These materials are models for testing and understanding the fundamental concepts about the effects of dimension and size on physical properties. On the other hand, they have a wide range of potential applications in chemistry, physics, electronics, optics, materials science, and biomedical sciences. Many attempts have been propoesed to fabricate one-dimensional nanostructured materials. Among these, template synthesis is effective in controlling the shape and dimensions of the material. Well-distributed tubular and fibrillar nanostructures such as porous alumina membranes, polymer nuclearpores, or other nanoporous solids such as silica are suitable for use as templates. Porous alumina membranes possessing uniform and straight cylindrical holes with controlled aspect ratio have been extensively used as templates for preparing uniformly sized metal nanowires, polymer nanorods,[1,2] oxide nanorods,[3] and composite nanostructures.[4] Such membranes can in fact be easily fabricated, and are commercially available in different pore diameters ranging from tens of nanometers to sub-micrometers.

Hydrogels are interesting macromolecules since they are soft and can respond quickly to external stimuli with remarkable volume change.[5,6] This unique property renders the dimension, polarity and shape of hydrogels highly tunable, and enables their use in distinctive applications such as flexible connector linking objects in microelectronics.

In this study, binary poly(*N*,*N*-dimethylacrylamide) [PDMA]/poly(acrylic ammonium) [PNH$_4$AA] based hydrogel nanowires were prepared in a porous alumina membrane.[†] [‡] [§] Of the two polymers, PDMA is less polar and more insulating whereas PNH$_4$AA is polar and ionic conducting. According to Steiner *et al.*,[7,8] a change in the hydrophilicity of a substrate can induce phase inversion of an A(polar)/B(less polar) binary polymer alloy, resulting in interconversion between the substrate/A/B and substrate/B/A structures. Applying this principle to the present templating of hydrogel nanowires in porous alumina membranes, it means that one can control which of the two hydrogel phases goes into the sheath and the core of the nanowire. Without modification, the pore surface contains Al–O bonds, and hence is highly polar. This leads to preferred concentration of the polar NH$_4$AA monomers adjacent to the pore surface, and occupation of the less polar DMA monomers in the inner region of the pore. Upon polymerization, nanowires with mostly PNH$_4$AA in the sheath and PDMA in the core result. On the other hand, if the membrane is treated with hydrophobic agents such as octatrichlorosilane to form hydrophobic groups (Al–OSiC$_8$H$_{17}$) at the pore surface, distribution of the DMA and NH$_4$AA monomers inside the alumina pores will be reversed, enabling production of hydrogel nanowires with an inverted structure upon polymerization.

FTIR spectroscopy was performed to confirm the presence of Al–OSiC$_8$H$_{17}$ groups after octatrichlorosilane treatment. Two sharp methyl stretch bands at 2857 and 2928 cm^{-1} were found, indicating hindered motions of the alkylsilanes coupled to the anchoring surface, hence providing strong evidence for the presence of Al–OSiC$_8$H$_{17}$ groups.[9]

To enhance the contrast for the core–shell structure of the hydrogel nanowires under transmission electron microscopy (TEM), we employed a selective staining method. As is well known, AgNO$_3$ forms a stable complex with carboxylic groups after reduction in an aqueous phase.[10,11] When the PDMA/PNH$_4$AA hydrogel nanowires are immersed in a AgNO$_3$ solution followed by reduction by diamine hydrate, the PNH$_4$AA phase is selectively stained with the residual silver precipitate.

Fig. 1(a) shows a typical scanning electron micrograph of Ag stained PDMA/PNH$_4$AA hydrogel nanowires prepared in the unmodified porous alumina membrane.[¶] The nanowires form bundles after removal of the membrane template with an average diameter of 250 nm. The outer surface appears rather coarse due to the formation of Ag nanoparticles. In comparison, the surface of the stained hydrogel nanowires prepared in the hydrophobically modified porous alumina membrane appears smooth (Fig. 1(b)). This indicates that less silver is formed in the outer layer of the nanowires.

The bundles shown in Fig. 1 can be dispersed into individual nanowires by ultrasonication. Fig. 2(a0) shows a typical TEM micrograph of an isolated nanowire from the unmodified membrane. That the core–shell structure is not recognizable in the micrograph can be explained if the sheath layer contains such a high Ag content that all electrons impinging on the nanowire are essentially blocked by the sheath. Upon calcination at high temperature to remove the polymer, the darker (higher density) outer shell becomes more apparent (Fig. 2(a1)). This result supports the outer sheath layer to consist mainly of the PNH$_4$AA phase while the inner core is mainly the PDMA phase. This is further supported by a non-observed shrinkage in the diameter of the nanowires (*cf* Fig. 2(a0) and (a1)) even after removal of the polymer upon calcination. Most likely a dense

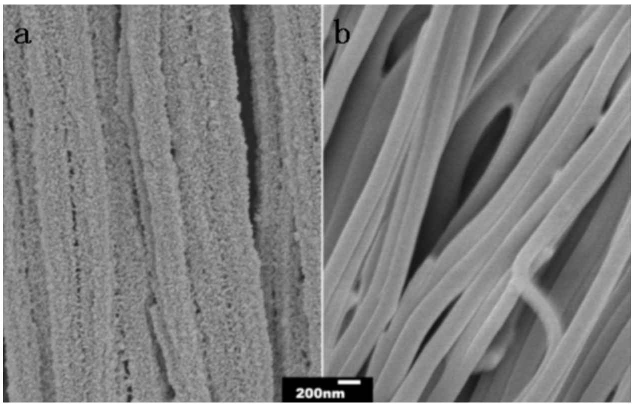

Fig. 1 Typical scanning electron micrographs of (a) Ag stained PDMA/PNH$_4$AA hydrogel nanowire prepared in the unmodified porous alumina; (b) Ag stained PDMA/PNH$_4$AA hydrogel nanowire prepared in the hydrophobically modified porous alumina.

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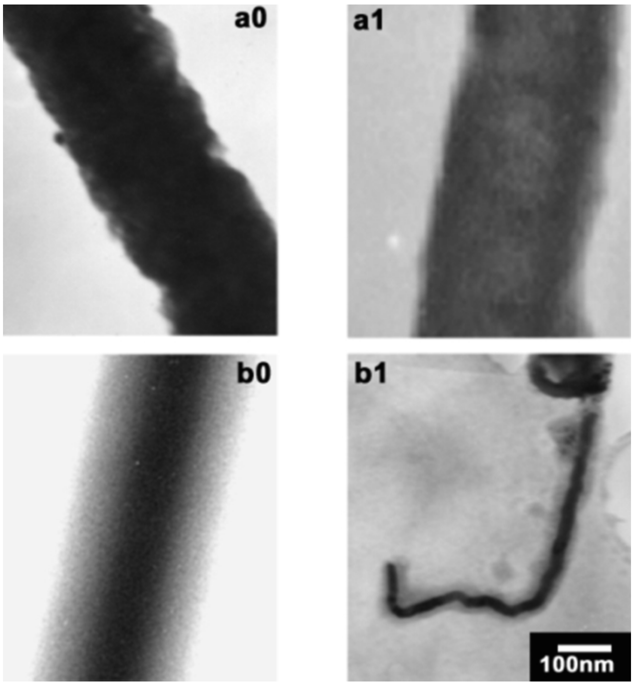

Fig. 2 Typical transmission electron micrographs of (a0) Ag stained PDMA/PNH_4AA hydrogel nanowire prepared in the unmodified porous alumina; (b0) Ag stained PDMA/PNH_4AA hydrogel nanowire prepared in the hydrophobically modified porous alumina; (a1) the sample of (a0) after calcination at 723 K for 2 h; (b1) the sample of (b0) after calcination at 723 K for 2 h (the four images have the same magnification).

packing of silver nanoparticles in the outer sheath layer aided the nanowire to withstand collapse from removal of the polymer.

When using the hydrophobically modified membrane, a dark core against a greyish shell is readily discernible (Fig. 2(b0)). This evidences that the PNH_4AA phase has been preferentially formed inside the PDMA encapsulation. After calcination, the contrast is enhanced as expected (Fig. 2(b1)). The greyish shell that seems to have survived calcination is likely due to the presence of traces of silver in the PDMA matrix. We measure the core diameter of the nanowire after calcination to be about 40 nm, which is far smaller than that before calcination (Fig. 2(b0)). This is explained by the less compact nature of the silver nanoparticles inside the nanowires as shown in Fig. 2(b0). After calcination, the silver wires are compacted, thus the diameter decreases.

The diameter and thickness of the porous alumina membranes can be controlled in a broad range, and the volume of the polymer hydrogel nanowires can be easily changed by external stimuli such as pH, temperature, composition and electric field. Therefore, the present method should allow a wide range of control on the diameter and aspect ratio of hydrogel nanowires. Conductive hydrogel nanowires can be derived by preferential staining with $AgNO_3$ followed by reduction to Ag metal. By extrusion of nanofibers through porous alumina membranes,[12] hydrogels and metal/hydrogel composite nanowires are expected to be obtained from continuous spinning.

In summary, this paper reports a simple method to prepare binary PDMA/PNH_4AA hydrogel nanowires by template synthesis in porous alumina membranes. By adjusting the hydrophilicity of the membrane pore surface, the core/shell phases of the nanowire can be controlled at will. Subsequent preferential staining and reduction of one hydrogel phase converts the binary hydrogel nanowires into metal/hydrogel composite nanowires or nanotubes.

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Notes and references

† *Materials*: the porous alumina membranes (Anodisc 47) were obtained from Whatman International Ltd (UK). In this work, the membranes had a pore diameter of 200 nm (Manufacturer's specification) and thickness of 70 μm. Acrylic acid was recrystallized twice at 253 K. *N*,*N*-Dimethylacrylamide (DMA), *N*,*N*′-methylenebisacrylamide, $AgNO_3$, reducing agent diamine hydrate, sodium hydroxide and ammonium hydroxide were purchased from Beijing Chemical Reagent Corporation and used as received. Acrylic ammonium salt (NH_4AA) was obtained by neutralization of acrylic acid with ammonium hydroxide. Ammonium peroxydisulfate was used to initiate the polymerization of the monomers.

‡ *Typical modification procedure of Anodisc 47*: the silanization process was used to modify the porous surface. The as-purchased membranes were first heated in air to 673 K at 10 K min^{-1}, then air-cooled to room temperature. Afterwards, the heat treated membranes were soaked in boiling aqueous hydrogen peroxide (30%) for 30 min followed by soaking in boiling distilled water for 30 min to hydroxylate the surface. After drying at 363 K for 30 min, the sample was reimmersed in a solution of 10% octachlorosilane in toluene to allow complete impregnation of octachlorosilane. Finally, the membranes were subjected to reflux at 333 K for 3 h under reduced pressure.

§ *Typical preparation of the samples*: the alumina membrane template was immersed in an aqueous solution of 50 wt% NH_4AA/DMA (3 : 7 wt/wt, containing 5 wt% *N*,*N*′-methylenebisacrylamide), and allowed to soak at ambient temperature for 5 h to ensure complete filling of the pores by the monomers. After bubbling with pure nitrogen, 0.1 wt% ammonium peroxydisulfate (with respect to the amount of monomers) was introduced. Then, the system was kept at 323 K for 2 h to allow free radical polymerization to form hydrogels. After the bulk hydrogel was peeled off the membrane, a hydrogel filled membrane was obtained. The hydrogel filled membrane was immersed in 10 wt% $AgNO_3$ aqueous solution for 12 h to allow the diffusion of $AgNO_3$ into the hydrogel. After the residual $AgNO_3$ was washed from the membrane with a large amount of water, an excess of 50 wt% diamine hydrate aqueous solution was added at ambient temperature to reduce the silver ions into nanoparticles. If necessary, the silver/hydrogel infilled membranes were calcined at 723 K for 2 h to obtain the corresponding Ag nanotubes or nanorods.

¶ *Typical experimental procedure for SEM and TEM*: after the alumina membranes were dissolved in 10 wt% NaOH aqueous solution, a large amount of distilled water and ethanol was used to wash the bundles of hydrogel nanowires. After drying at room temperature, the nanowires were directly observed by SEM. The bundles were ultrasonicated for 15 min, then a drop of the suspension was placed on a carbon-coated copper grid for TEM observation. A JEOL JSM-6700F field emission scanning electron microscope (SEM) and H-600A transmission electron microscope (TEM) were used.

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