

A facile route to fabrication of inorganic–small organic molecule cable-like nanocomposite arrays†

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A novel and facile method is reported for the preparation of silver iodide–small organic molecule (SOM) cable-like nanocomposites arrays, which involved first the fabrication of SOM nanotubes inside an anodic aluminium oxide (AAO) membrane, and then using the SOM nanotubes in AAO as secondary template to prepare the AgI nanowires in aqueous solution at room temperature.

Increasing interest has focused on the fabrication of composite nanomaterials such as nanoparticles and nanocables due to their potential for applications and as model systems to study nano-space-specific fundamental phenomena.^{1–6} Synthesis of core-shell composite nanostructures with tailored morphology and improved order is an important issue for exploring applications in nanotechnology. As a result, various nanocomposites have been prepared with properties substantially different from either the core or the shell component, which made the nanocomposite particularly attractive from both a scientific and technological viewpoint.^{7–9} The synthesis of metal–polymer (inorganic–polymer) nanocomposites by a self-assembly method,^{7a} metal oxide–metal (inorganic–inorganic) nanoparticles by iterative hydroxylamine seeding,^{8a} and polymer–polymer nanocomposites by combining layer-by-layer technique with membrane templating⁹ have been reported. Yet, little attention has so far been directed to inorganic–SOM (small organic molecule) nanocomposites. Compared to inorganic materials and polymers, the most prominent advantage of SOM is that they allow greater variety and flexibility in materials synthesis and chemical modification, which can be fully utilized in nanocomposites with enhanced performance improvement and to tailor them for prospective applications.

AgI is a well-known photosensitive material, which has been widely used in color photographic technology. AgI is only sensitive to the light around 500 nm. To extend its spectral sensitive range one of the most effective means is to resort to spectral sensitization with appropriate organic dyes.¹⁰ It can be expected that the AgI–SOM nanocomposites may exhibit better performance due to combination with the proper organic envelope.

In this communication, we report a novel and facile method for the preparation of arrays of inorganic–SOM cable-like nanocomposites. Our method uses SOM nanotubes inside the AAO membrane as secondary templates in an aqueous solution at room temperature and should be generally applicable to fabricate other inorganic–SOM nanocomposite systems. Here, as a proof of concept we use this method to prepare silver iodide–pyrene cable-like nanocomposites

Pyrene nanotubes were obtained by a simple marination method (ESI†). FESEM image in Fig. 1A shows the as-prepared SOM nanotubes were uniform, continuous arrays of tubular structures with diameters of *ca.* 100 nm and lengths up to 30 μ m. Inset in Fig. 1A is the energy-dispersive X-ray analysis (EDX) spectrum which displays only two signals ascribed to C and Au (Au was sprayed to enhance the conductivity of the samples), confirming the complete removal of Al from the AAO template.¹¹ After the sample was sonicated for 30 min SEM showed the nanotubes curled up, exhibiting the excellent flexibility of organic materials, as observed for the widely explored carbon nanotubes.^{12,13} A typical TEM image of a single nanotube is shown in Fig. 1B. From the image, the obviously unwrapped ends indicate the tubular SOM nanostructure, although the tubular stem is not transparent under TEM observation, probably due to the relatively thick wall.¹⁴ Inset of Fig. 1B reveals the electron diffraction (ED) pattern of the pyrene nanotube, which shows unambiguously the amorphous nature. The amorphous structure implies that the molecules arranged randomly (bonded by weak van der Waals force and π – π stacking force), allowing the nanotubes to swing freely. Consequently, it is reasonable to expect that the amorphous structure and the comparatively thick wall would likely be responsible for the excellent flexibility and ductility of the nanotubes.¹⁵

The aluminium membrane with the pore wall loaded with pyrene nanotubes becomes a new secondary template. It is expected that a variety of nanomaterials can be confined to grow inside the new template, and result in the formation of cable-like nanocomposites. Motivated by this idea, we attempted the fabrication of AgI nanowires within the template. In the initial effort, we introduced AgI nanowires into the nanotubes using the paired-cell method described by Kim *et al.*¹⁶ but without success. The failure of this approach might be due to the hydrophobic nature of the walls of the as-prepared nanotubes inside the AAO template, which made the hydrophilic Ag⁺ and I[–] ions difficult to enter into the channels to meet each other. Consequently, we designed a new device by using a U-tube cell where the AAO membrane separates the two different solutions as shown in Scheme 1. The silver iodide–pyrene nanocomposites can be

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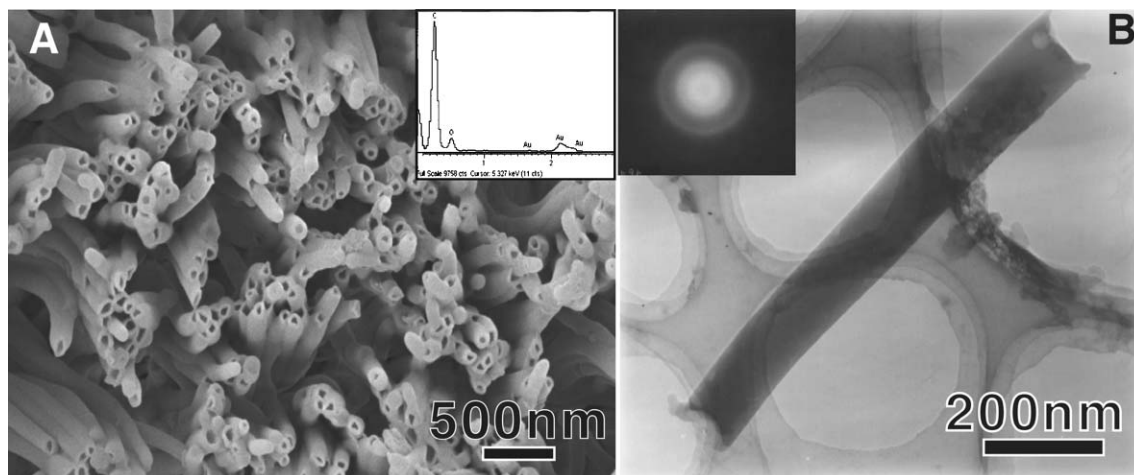
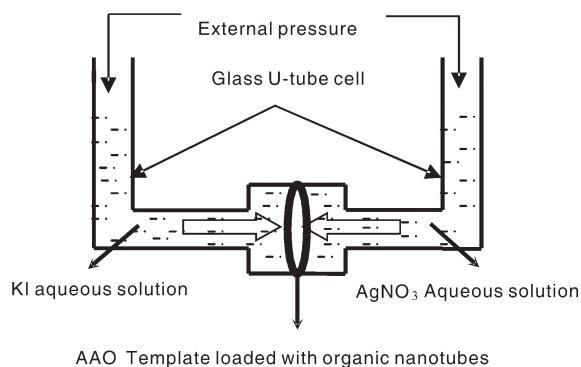


Fig. 1 (A) SEM image of pyrene nanotubes with diameters of about 100 nm and lengths up to 30 μm . Inset is the corresponding EDX. (B) TEM image of a single nanotube with ED pattern in the inset.



Scheme 1 Schematic illustration of the formation process of AgI nanowires inside the organic nanotubes.

prepared by introducing aqueous solutions of AgNO_3 (0.1 M) and KI (0.1 M) into the hollow cylinder of the as-prepared pyrene nanotubes inside the AAO membrane by exerting external pressure. The solution in the two vertical pipes can produce

partial external pressure, if necessary, additional pressure could also be introduced through the pipe by an inflator. The technique overcomes the problem of wetting by applying external pressure. The pressurized flow of different ions could enter and meet in the nanopores of the new secondary template and led to the deposition of AgI solids on the inner walls of the organic nanotubes. To ensure complete filling and formation of silver iodide–pyrene cable-like nanostructure, the experiment was continued for 2 h at ambient temperature.

After the aluminium template was removed by 6 M NaOH aqueous solution, the nanocomposites became solid nanofibrils as shown in Fig. 2A, which exhibited better rigidity compared to the initial organic nanotubes. Besides carbon, the corresponding EDX spectrum also verifies the presence of Ag and I in the product and the 1:1 ratio of silver to iodine (Fig. 2B). The TEM image shows clearly the cable-like structure of the nanocomposites (Fig. 2C), while the ED pattern (inset in Fig. 2C) shows the polycrystalline structure which is ascribed to the AgI nanowires inside the organic nanotubes. Fig. 2D shows the typical HRTEM image of the organic and inorganic layers lined out in Fig. 2C, which further

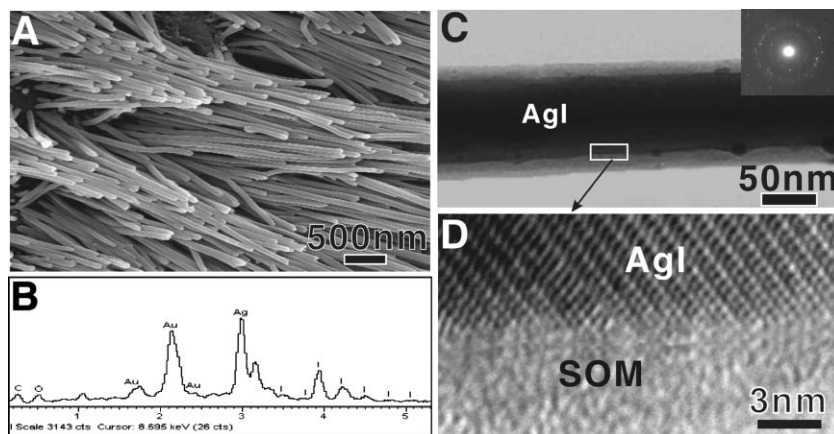


Fig. 2 (A) SEM image of the as-prepared silver iodide–pyrene nanocomposites with diameters of about 100 nm. (B) EDX spectrum of the nanocomposites in (A). (C) Typical TEM image showing the clear cable-like structure of the nanocomposite. Inset shows the corresponding ED pattern. (D) HRTEM image displaying the organic and inorganic layers as selected in (C).

confirms the cable-like structure of the nanocomposites. The HRTEM image shows clearly the two different layers of the cable. The outer layer with no lattice image reveals an amorphous structure belonging to the organic sheath layer, while the inner layer shows a typical hexagonal-close-packed lattice structure identified to be the AgI nanowire in the core. The combination of characterizations verifies definitively the successful fabrication of cable-like nanocomposites.

Based on our experiments, the vital step for the secondary template method is drawing the hydrophilic ions into the hydrophobic channel by external pressure. When no external pressure was applied, we found that very few disorderly AgI nanostructures were formed inside the organic nanotubes even after a prolong reaction time.

In summary, we developed a viable and facile approach for the preparation of arrays of inorganic–SOM cable-like nanocomposites. It takes advantage of the simplicity and effectiveness of both the physical marination method and aqueous solution chemical reaction method. The diameter and length of the nanocomposites can be readily tuned by varying the diameter and length of the channels of the templates and the sheath (or core) thickness, which can be readily controlled by the concentration of the marinating solution. Since the two processing steps are easy to realize and control and the materials used are not specific, we expect the present method can be straightforwardly extended to prepare a wide range of other cable-like inorganic–organic nanocomposites.

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