Microwave-assisted synthesis and *in-situ* self-assembly of coaxial Ag/C nanocables†‡

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We have successfully developed a new one-pot solution-phase route, namely microwave-assisted hydrothermal reduction/ carbonization (MAHRC), for a rapid synthesis of coaxial Ag/C nanocables. The nanocables can self-assemble *in situ* in an end-to-end fashion into interconnected chains.

In recent years, one-dimensional (1-D) nanostructures such as nanowires, nanotubes and nanobelts have been extensively studied because of their great potential applications in nanoscale electronic, optoelectronic, and sensing devices.[1–6] More recently other types of 1-D nanostructure, nanocables, have begun to attract much interest because their functions may be further enhanced by fabricating core-sheath heterostructures.[7–17] Combined with possible size-related quantum confinement effects, the interface(s) between different phases along the cable's radial direction may lead to interesting properties.[9] Inspired by this, many researchers have been focusing on the synthesis of various nanocables. Up to now, a number of well-known techniques such as high-temperature chemical vapor transport,[10] physical vapor deposition[11,12] and laser ablation[13,14] have been developed to fabricate nanocables. The multistep deposition at high temperatures is inevitably time-consuming and complicated. Simple and mild routes such as solution-phase chemical methods are more promising for large-scale production. Recently, polymer-sheath nanocables have been synthesized by solution-based methods at relatively low temperatures.[15–17]

Silver (Ag) has been used extensively in catalysis, electronics, photonics and photography,[18–21] as bulk Ag exhibits the highest electrical and thermal conductivity among all metals. In this regard, 1-D Ag nanostructures seem to be particularly interesting to investigate because of their great potential for serving as important components and interconnects in nanodevices. Recently, some progress has been made with solution-phase preparation of Ag-core nanocables.[7,8] Nevertheless, these methods involved either a relatively long period of processing time or complex multi-step processes.

Microwave-induced chemical synthesis is often very efficient since it offers rapid volumetric heating, high reaction rates and selectivities, high yields of products and energy saving.[22] In this work, we demonstrate a one-pot solution-phase route, namely microwave-assisted hydrothermal reduction/ carbonization (MAHRC), for the rapid synthesis of coaxial

Ag/amorphous-carbon (*a*-C) nanocables. The as-grown Ag/C nanocables could self-assemble in an end-to-end fashion into a novel interlinked chain even in the absence of any molecular connectors. More interestingly, this route does not need any seeds, surfactants or templates. This energy-saving and environmentally friendly method is ideal for large-scale industrial production.

In a typical process, 1.5 g sucrose and 0.2 g AgNO₃ were dissolved in 30 mL deionized water. The solution was sealed in a double-walled digestion vessel. After treating at 200 °C for 20 min using a microwave digestion system (Ethos TC, Milestone), the vessel was then cooled to room temperature. The product was collected, washed with deionized water and alcohol, and dried at 60 °C for 4 h.

The crystallinity and phase of the products were examined by powder X-ray diffraction (XRD) with a Bruker D8 Advance diffractometer using Cu Kα_1 radiation (λ = 1.5406 Å). Fig. 1a shows a typical XRD pattern of the product. All the reflections can be indexed to the face-centered cubic (*fcc*) phase of Ag [space group: *Fm3m* (No. 225)], which is in good agreement with the reported data (*a* = 4.086 Å, JCPDS No. 04-0783). The morphologies and microstructures of the as-prepared products were further investigated by transmission electron microscopy (TEM) using a CM120 microscope (Philips, 120 kV). Fig. 1b shows a bright field TEM image of the same product shown in Fig. 1a. Dark/light contrast is clearly observed along the radial direction. The different contrast suggests a different phase composition, indicating the core-sheath cable structure. The dark contrast suggests Ag of larger mass thickness in the core region. Outside of the core region, the light contrast suggests that C is in the sheath layer. More TEM observations (see ESI†, Fig. S1) reveal Ag/C nanocables with an average diameter of about 100 nm and lengths ranging from 50 nm to 2 μm. Each nanocable is straight and has a uniform diameter along its entire length. The thickness ratios of core to sheath are in the range of 1–5. Energy dispersive X-ray (EDX) spectrometry was also used to examine the
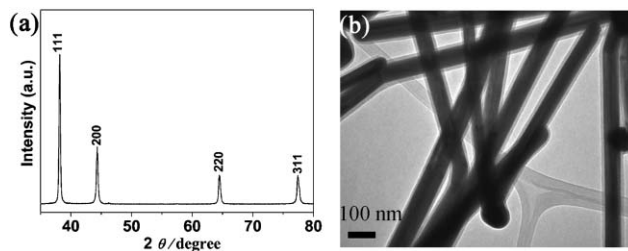
Fig. 1 (a) XRD pattern of the product synthesized *via* the MAHRC route at a controllable temperature of 200 °C; (b) TEM image of coaxial Ag/C nanocables.

local atomic composition of the nanocables. A typical EDX spectrum taken from a single nanocable confirms that the nanocables are composed of only Ag and C (see ESI†, Fig. S2).

Fig. 2a shows a bright field TEM image of an individual Ag/C nanocable having a length of about 1.3 μm. The diameter of the Ag core and the thickness of the C sheath are about 40 and 30 nm, respectively. Its corresponding electron diffraction (ED) pattern is shown in the inset of Fig. 2a which was taken by focusing the electron beam on the nanocable. There are two sets of spots in the ED pattern. Our experiments show that microdiffraction patterns on different nanocables or different positions of a single nanocable were essentially identical to that shown in Fig. 2a, indicating that the Ag core is bicrystalline. Both ends of the nanocable (Fig. 2a) are shown in Figs. 2b and 2c. The contrast in Fig. 2c clearly shows that there is a twin plane parallel to the longitudinal axis of the Ag core. The twin plane divides the Ag core into two halves, which is similar to the previous results for Ag nanowires.[23–25]

Interestingly, a novel 1-D chain topology of interconnected Ag/C nanocables can be obtained. Fig. 3 shows the low-magnification TEM images of typical examples. The Ag/C nanocables can self-assemble into chains in an end-to-end fashion. Most of the intersections between two straight segments form obtuse angles. High magnification TEM images revealing more details of each junction within an individual chain are also shown in the supplementary material (see ESI†, Fig. S3).
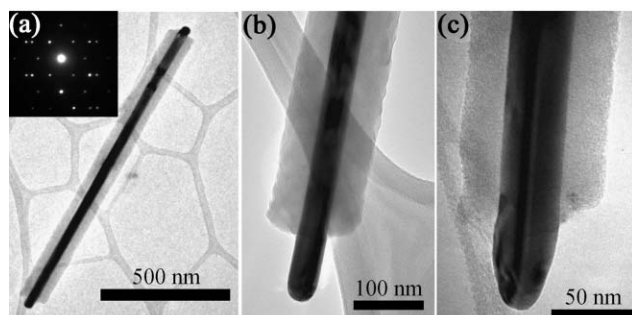
Fig. 2 (a) TEM image of an individual coaxial Ag/C nanocable. The inset gives an electron microdiffraction pattern recorded by focusing the beam on the nanocable. The diffraction pattern indicates a bicrystalline structure for the Ag core; (b) and (c) Higher magnification TEM images taken from each end of the nanocable shown in (a).
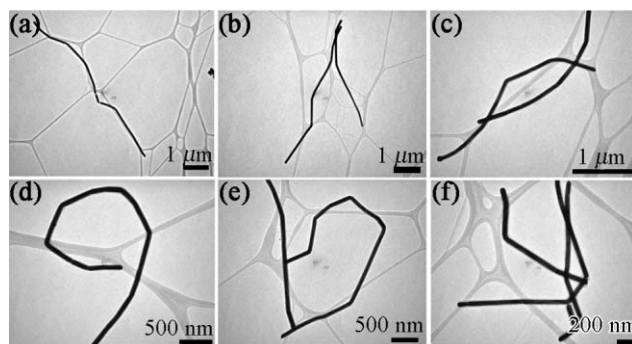
Fig. 3 Representative TEM images of interconnected chains of nanocables. Such coaxial Ag/C nanocables are self-assembled in an end-to-end fashion without using any molecular connectors.
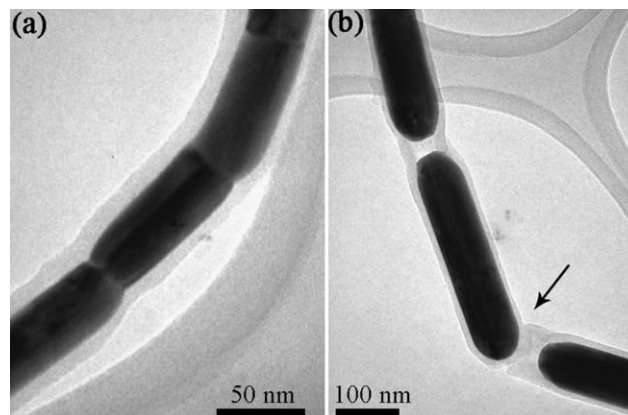
Fig. 4 (a) High magnification TEM image showing the interface between Ag nanorods in the core region; (b) TEM images showing that continuous a-C sheaths are discretely filled with Ag nanorods.

Au nanorods,[26] multisegment Au/Pt/Au nanowires[27] and TiO$_2$ nanorods[28] have been assembled preferentially in an end-to-end fashion using biotin/streptavidin or biotin/avidin as connectors. Our experimental results are quite different from these studies. The as-grown chain-like structures are probably achieved by the "oriented attachment"[29] of straight Ag/C nanocables. The presence of a-C in the sheath region may play a crucial role in the end-to-end self-assembly process. As shown in Fig. 4a, distinct contrast within the core region suggests the interfaces of the junctions are between different Ag nanorods, while no such interfaces were observed in the corresponding a-C sheath region. Furthermore, careful TEM studies reveal that some Ag/C nanocables with an open-ended sheath are continuously inter-connected through the external a-C layer (Figs. 4a and 4b) and that the tubular a-C sheaths are discretely filled with Ag nanorods. Nevertheless, if either end of an individual nanocable is closed with a-C, it cannot be interconnected perfectly with another one. A typical example (labeled by an arrow) is shown in Fig. 4b. The thermal and non-thermal effects induced by microwave irradiation probably contribute to the final morphologies and self-organizations of products.[22] The as-obtained results (especially for the self-assembly process) are significantly different from the previous work[7] using conventional hydrothermal heating. "Hot surfaces" on solid Ag as well as "hot spots" may be created under microwave irradiation. These local thermal effects may simulta-neously accelerate the reduction and carbonization reactions leading to self-organizations of Ag/C nanocables. The detailed growth mechanism for the Ag/C core-sheath nanostructures and the end-to-end self-assembly process need to be further investigated.

In summary, we have successfully developed a new MAHRC route to prepare Ag/C nanocables. Interesting interconnected nanostructures with chain-like topology can be formed. The external a-carbon layer of the core-sheath nanostructures may play a crucial role in the end-to-end self-assembly process. We believe that this MAHRC method could be extended to fabricate other metal/C core-sheath nanostructures. Coaxial nanocables consist of highly conducting metallic cores and relatively insulating sheaths may be used as components and interconnects in nanoelectronic devices.

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