

One-step process to fabricate Ag–polypyrrole coaxial nanocables†

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Ag–polypyrrole nanocables were fabricated in aqueous solution at room temperature through a redox reaction between silver nitrite and pyrrole, using poly(vinyl pyrrolidone) (PVP) as assistant agent.

Metal nanowires have been the focus of many recent studies because of their potential use as active components of interconnects in fabricating electronic, photonic, and sensing devices.¹ However, the metallic nanowires are very sensitive to air and moisture, which will degrade the performance of the nanodevices.² A polymer envelope would protect metal nanowires from oxidation and corrosion, keeping good performance for a long time. Metal nanowires sheathed with conducting polymers are of particular interest for various electronic device applications, as conducting polymer nanowires and nanofibers themselves have been shown to possess the processing advantages of plastics and the optoelectronic properties of inorganic semiconductors or metals. These kinds of materials are nanocables. A nanocable is typically composed of a core nanowire sheathed by one or more outer layer similar to a coaxial cable used in signal transmission but with a diameter in the nanometre scale. They are another kind of one-dimensional nanostructured material, providing a great possibility to take advantage of different functions and properties of different materials within a single nanoscale component. Usually, the method used to fabricate these wire–sheath structured nanocables is template processing. Many existing one-dimensional nanomaterials are often used as templates to prepare nanocables. In one approach, the surface of these nanowires could be coated with conformal sheaths made of different materials by chemical, electrochemical, chemical vapor, or other means, to form coaxial nanocables.³ For instance, layer-by-layer (LBL) deposition of oppositely charged species on nickel nanorods has been reported to prepare nanocables and composite nanotubes.⁴ In addition to this, polymer nanocables can also be prepared by this approach. Polyacrylonitrile nanofibers can be easily and evenly coated with a 20–25 nm layer of conducting polypyrrole by immersion in an aqueous solution of polymerizing polypyrrole.⁵ In another approach, nanotubes were used as templates in which nanowires of different materials were fabricated. For example, polyaniline² and polythiophene nanotubes⁶ were used as templates to prepare Co–polyaniline, Ag–polythiophene and Au–polythiophene nanocables. Furthermore, block copolymers can also be used as templates to prepare these one-dimensional nanocomposites.⁷ Very recently, Yu *et al.* have reported the synthesis of silver–carbon nanocables through the hydrothermal process.⁸

In this communication, we present a simple one-step process to fabricate Ag–polypyrrole (PPy) coaxial nanocables in aqueous solution at room temperature. In this system, pyrrole monomer and silver nitrate act as reducing and oxidizing agents, respectively, and poly(vinyl pyrrolidone) (PVP) is used as assistant agent to form Ag–PPy nanocables.‡ PPy is often prepared through a redox reaction. In a chemical route, FeCl₃ is usually used as oxidizing agent.⁹ The standard reduction potential of Fe(III) to Fe(II) is 0.771 V. The standard reduction potential of Ag(I) to Ag(0) is 0.800 V. So silver nitrate has the ability to polymerize pyrrole monomer. Meanwhile, silver nitrate would be reduced to silver. PVP was often used as the coordination reagent to form Ag nanowires.^{10,11} In our system, Ag nanowires can be formed gradually with the help of PVP. At the same time, pyrrole monomer polymerizes *in situ* on the surface of silver nanowires. The growth process of silver nanowires and the polymerization of the PPy sheath will continue simultaneously. Thus, Ag–PPy nanocables with a high aspect ratio can be formed gradually. To our knowledge, this is the first time Ag–PPy coaxial nanocables have been fabricated through this one-step reaction.

Fig. 1A shows a TEM image, at lower magnification, of Ag–PPy coaxial nanocables, which indicates Ag–PPy coaxial nanocables can be achieved by this approach. A typical TEM image at

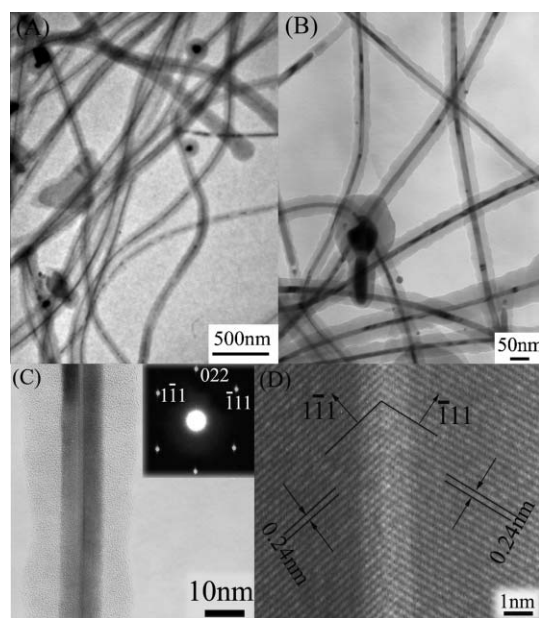


Fig. 1 (A) and (B) Low-magnification TEM image of silver–PPy nanocables. (C) High-magnification TEM image of a typical silver nanocable; inset: ED pattern of the silver nanocable. (D) HRTEM image of the silver nanocable.

† Electronic supplementary information (ESI) available: XRD and FTIR spectra of Ag–PPy nanocables. See <http://www.rsc.org/suppdata/cc/b417744d/>

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higher magnification of part of the nanocables is shown in Fig. 1B. The product displays a darker contrast core sheathed in an outer layer with a lighter contrast along the axis direction, which suggests the formation of coaxial nanocables. The outer diameter is ~ 50 nm and the diameter of the central core of the nanocables is ~ 20 nm. The lengths of these nanocables are in the range of several to several tens of micrometers. These nanocables display aspect ratios as high as 500. In Fig. 1C, the contrast in this image clearly shows that there is a twin plane. An electron diffraction (ED) pattern of this area (inset in Fig. 1C) shows the diffraction dots of Ag. The electric beam direction of this HRTEM is parallel to the [110] direction. So we can see that the twin plane is ($\bar{1}10$). The center line of this plane is [002]. The silver grows as a crystal twinned at the (111) planes, which is consistent with previous reports.^{11,12} A high-resolution TEM (HRTEM) image of the area is shown in Fig. 1D. The two planes are ($1\bar{1}1$) and ($\bar{1}11$). The dihedral angle is 107° , close to the theoretical value of 109.5° . The (111) *d*-spacing was measured to be 0.24 nm, close to the literature value of 0.236 nm. From X-ray powder diffraction (ESI†), all diffraction peaks could be indexed as the face centered cubic (fcc) phase of silver, except for the broad faint peaks at $2\theta = 18.920^\circ$, indicating that the polymer of the as-prepared sample is amorphous (there is amorphous polymer in the as-prepared sample), which is in good agreement with the results of TEM.

FTIR spectra of Ag-PPy nanocables (ESI†) showed characteristic bipolaron bands at 1200 and 925 cm^{-1} indicating the formation of PPy in its doped state.¹³ The peaks between 1650, 1540 and 1456 cm^{-1} are assigned as fundamental vibrations of pyrrole rings.¹⁴ The peak at 3400 cm^{-1} is assigned as the N–H stretching vibration. This spectrum is nearly identical to that of the PPy oxidized by FeCl_3 reported in our previous work,¹⁵ the only exception being the presence of an additional peak at 1380 cm^{-1} due to the N–O stretch of NO_3^- counterion.

Up to now, the mechanism of the fabrication of Ag-PPy coaxial nanocables in this system is not completely understood. It is believed that PVP kinetically controls the growth rates of various faces of silver through adsorption and desorption on these surfaces.^{11,16} With the help of PVP, silver grows into nanowires when they are reduced from silver ions. At the same time, PPy is polymerized *in situ* on their surfaces. In this route, polymerization and nanocrystal formation occur simultaneously. As the reaction continues, Ag-PPy nanocables with high aspect ratios are obtained. In this system, PVP plays a key role in the fabrication of the Ag-PPy nanocables. These products with a wire-like morphology are not formed under the same conditions without PVP.

In summary, we have successfully synthesized silver-PPy coaxial nanocables through only a one-step process. This synthetic route is advantageous because it simplifies the procedure to prepare nanocables with a core-sheath structure and it takes place in aqueous solution at room temperature. This technique could be

extended to the preparation of a variety of metal/conducting polymer nanocables under appropriate conditions. In addition, metal nanowires and polymer nanotubes could be obtained by removal of the sheath or core. Further studies along this direction are in progress.

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Notes and references

‡ In a typical experiment, 1.5 ml pyrrole monomer was added to a 250 ml round-bottom flask. 100 ml 0.3 M silver nitrate aqueous solution and 100 ml 0.15 M poly(vinyl pyrrolidone) ($K = 30$, $MW \approx 30\,000$) aqueous solution were then added to the flask in a dropwise manner with simultaneous vigorous stirring. After this, the reaction mixture was further stirred for 48 h. The product was washed with deionized water and alcohol by filtrating. The as-prepared sample was dried in a vacuum for two days.

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