

# Large-Scale Synthesis of Flexible Gold/Cross-Linked-PVA Sub-Microcables and Cross-Linked-PVA Tubes/Fibers by Using Templating Approaches Based on Silver/Cross-Linked-PVA Sub-Microcables\*\*

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**Abstract:** Well-defined silver/cross-linked-poly(vinyl alcohol) (PVA) sub-microcables, which were synthesized from a hydrothermal reaction using AgCl and PVA as precursors, have been used as sacrificial templates to fabricate gold/cross-linked-PVA sub-microcables by etching the silver/cross-linked-PVA sub-microcables with tetrachloroaurate(III). In addition, well-

defined cross-linked-PVA sub-microtubes/sub-microfibers can also be produced by the removal of the silver cores of such sub-microcables at ambient temperature. The channel diameter

and the shell thickness could be tuned by controlling the diameter of the core sub-microfibers and the shell thickness of the precursor sub-microcables. These cross-linked-PVA-based cables, tubes, and fibers have the potential to be used in future applications such as nanodevices.

**Keywords:** etching • hydrothermal synthesis • polymers • sub-microcables • template synthesis

## Introduction

One-dimensional nanomaterials, for example, nanorods, nanowires, and nanotubes, have attracted much attention due to their potential importance to science and technology.<sup>[1–4]</sup> In particular, core-shell nanostructures have received intense attention, due to their improved physical and chemical properties over their single-component counterparts, and are of great importance to a potentially broader range of applications.<sup>[5,6]</sup> In recent years, nanocables have also attracted broad interest as a new type of one-dimensional nanostructure, because of the fact that their functions can be further enhanced by fabricating the core and sheath components from different materials.<sup>[7–11]</sup> In addition, polymer nanofibers and nanotubes have also attracted interest because they

could be used in nanoscale reinforcement, tissue engineering, specialty filters, storage or transportation of gases or fluids, fuel cells, catalysis, and drug release or encapsulation.<sup>[12]</sup> Polymer nanotubes and nanocables have usually been synthesized by using templating techniques and coating techniques. For example, polymer fibers are usually fabricated by using an electrospinning process and the polymer cables can be obtained by coating their surface by means of chemical vapor deposition. Polymer nanotubes are also fabricated by the wetting of ordered porous aluminum oxide templates.<sup>[13]</sup> Furthermore, organic nanotubes, such as those based on designed cyclic polypeptides through effective amide binding,<sup>[14]</sup> those made from porphyrin dendrimers by molding dendritic building blocks around an oligoporphyrin core,<sup>[15]</sup> and hexa-peri-hexabenzocoronene graphitic nanotubes obtained through a molecular self-assembly process, have also been reported.<sup>[16]</sup>

To date, various strategies have been developed to produce coaxial nanocables and hollow nanotubes. Bando and co-workers employed a chemical vapor deposition route to synthesize perfect SiC–SiO<sub>2</sub>–C coaxial nanocables<sup>[17]</sup> and SiO<sub>2</sub>-sheathed InS nanowires.<sup>[18]</sup> Hybrid nanostructures of SiO/SiO<sub>2</sub> have also been prepared by carbothermal reduction of silica xerogel with carbon nanoparticles.<sup>[19]</sup> Generally, these routes usually rely on rigorous conditions, for example, high energy input as well as an inert atmosphere.

Soft chemistry methods have also been explored for the synthesis of nanocables with a metal or semiconductor core

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[\*\*] PVA = poly(vinyl alcohol).

and a polymer or carbon sheath under mild conditions. CdSe/poly(vinyl acetate) hybrid nanocables can be obtained by growing semiconductor nanowires inside polymer tubules.<sup>[20]</sup> Gold nanorods have recently been coated with polystyrene or silica to form cablelike nanostructures,<sup>[21]</sup> and silver nanowires can be coated with silica to form Ag/SiO<sub>2</sub> nanocables.<sup>[22]</sup> Very recently, our group discovered a synergistic soft–hard template method to synthesize Ag, Cu, and Te/cross-linked-poly(vinyl alcohol) (PVA) coaxial nanocables,<sup>[23–25]</sup> Ag/carbon nanocables,<sup>[26]</sup> and Ag/carbon-rich composite (carbon and cross-linked PVA) sub-microcables<sup>[27]</sup> under hydrothermal conditions. Ag/polypyrrole nanocables can be synthesized by a redox reaction between silver nitrite and pyrrole in aqueous solution at room temperature with the addition of poly(vinyl pyrrolidone) used as a coordinating agent.<sup>[28]</sup>

Silver metal is an ideal material for both current and temperature conduction and these nanocables with silver cores may find potential application in future nanodevices.<sup>[29]</sup> Seeking suitable methods for fabrication of nanocables and nanotubes is still challenging.

In this paper, we present the synthesis of well-defined Au/cross-linked-poly(vinyl alcohol) (PVA) sub-microcables and cross-linked-PVA sub-microtubes/sub-microwires, by an in situ replacement reaction and a sacrificial template method at room temperature based on the well-defined Ag/cross-linked-PVA sub-microcables.

## Results and Discussion

**Synthesis of the precursor Ag/cross-linked-PVA sub-microcables:** Figure 1a shows the X-ray diffraction (XRD) pattern of the product obtained by a modified approach using AgCl instead of AgNO<sub>3</sub>.<sup>[24]</sup> All the diffraction peaks can be readily

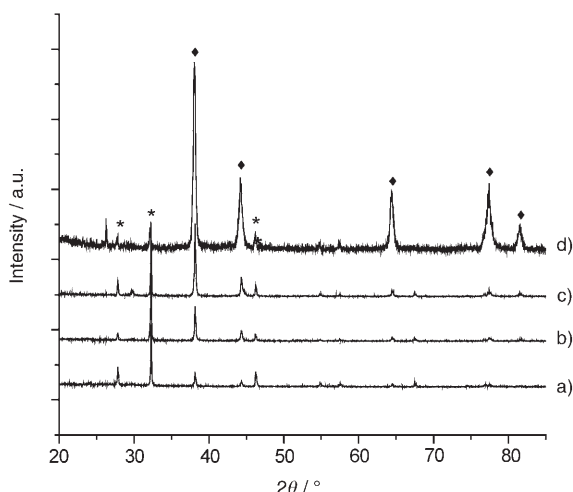


Figure 1. XRD pattern of as-synthesized Ag/cross-linked-PVA sub-microcables at 160 °C after a reaction time of a) 1, b) 2, c) 3, and d) 4 days. \* denotes the AgCl phase. ◆ denotes the newly formed Ag phase. a.u. = arbitrary units.

indexed as the *fcc* silver phase with a calculated lattice constant  $a = 4.1 \text{ \AA}$  (JCPDS no. 4-783), which is in agreement with the literature values.<sup>[30]</sup> In order to demonstrate the phase evolution of Ag from AgCl, the phase purity of the products obtained after different reaction times (1, 2, 3, or 4 days) was examined as shown in Figure 1a–d. After a reaction time of one day, diffraction peaks for the silver phase appeared. However, in the final product the amount of AgCl decreased, and the amount of Ag increased distinctly with prolonged reaction time.

The field emission scanning electron microscopy (FESEM) image in Figure 2a shows that the obtained sub-

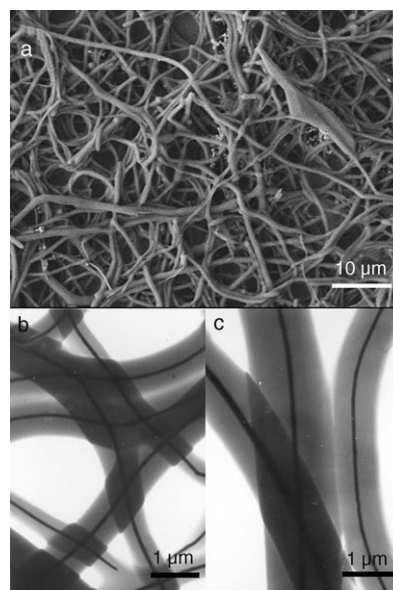


Figure 2. a) SEM image of the Ag/cross-linked sub-microcables formed by the hydrothermal process for 4 days. b), c) Typical TEM images of the sub-microcables with encapsulated silver nanowires.

microcables are several hundred micrometers long and their average diameter is about 800 nm. Transmission electron microscopy (TEM) images in Figure 2b,c show that the product is composed of uniform Ag/cross-linked-PVA sub-microcables with smooth cores of about 100–150 nm in diameter and surrounding sheaths of about 0.8 μm in thickness. The remarkable image contrast between the surrounding polymer and the inner metal wire can be clearly observed. These sub-microcables were more dispersed relative to those obtained previously.<sup>[24]</sup>

During the reaction, the pH value of the reaction solution dropped from the initial 6.8 to 2.5 after hydrothermal treatment for 96 h (Figure 3). It is suggested that the reaction process in the sealed autoclave at 160 °C occurs as follows: First, AgCl is reduced to Ag slowly to form the core, while the PVA is in turn oxidized into cross-linked PVA to wrap the core. The release of a mass of hydrogen ions into the solution from the PVA chains accounts for the sharp decrease of the pH value. In fact, a synergistic soft–hard tem-

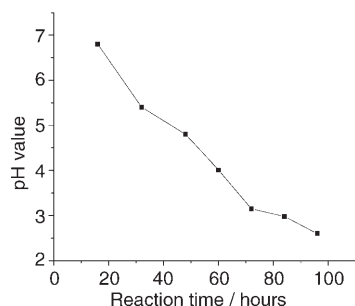
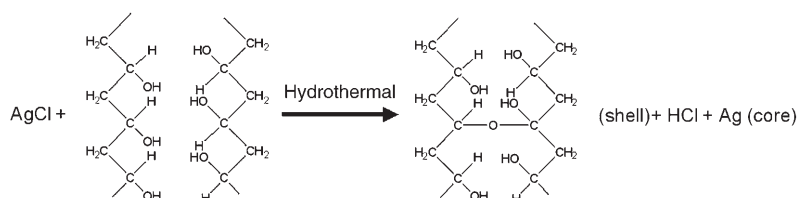


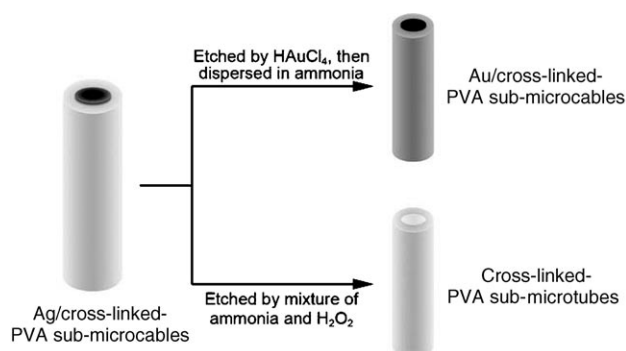
Figure 3. Time-dependent variation of the pH value during the reaction.

plate mechanism (SSHM) plays an important role in producing silver/cross-linked-PVA sub-microcables.<sup>[24]</sup> PVA acts as a soft template to direct the preferential growth of silver nanowires, and as-prepared silver nanowires offer effective sites for the deposition of insoluble cross-linked PVA, which is a vital step for forming sub-microcables. The whole reaction is similar to that of free  $\text{Ag}^+$ ,<sup>[24]</sup> which can be expressed as shown in Scheme 1.



Scheme 1.

**Synthesis of Au/cross-linked-PVA sub-microcables by an in situ templating approach:** The obtained silver/cross-linked-PVA sub-microcables can be easily transformed into gold/cross-linked-PVA sub-microcables by using an etching strategy, which has been reported previously for the preparation of gold nanoboxes.<sup>[31]</sup> In addition, cross-linked-PVA sub-microtubes can be obtained by removing the silver core by use of a solution made of ammonia and  $\text{H}_2\text{O}_2$ ,<sup>[22,32]</sup> as shown in Scheme 2.



Scheme 2. Schematic illustration of the fabrication process of Au/cross-linked-PVA sub-microcables and cross-linked-PVA sub-microtubes from Ag/cross-linked-PVA sub-microcables.

Figure 4a indicates that the product is mainly composed of wirelike sub-microstructures. Compared with the original

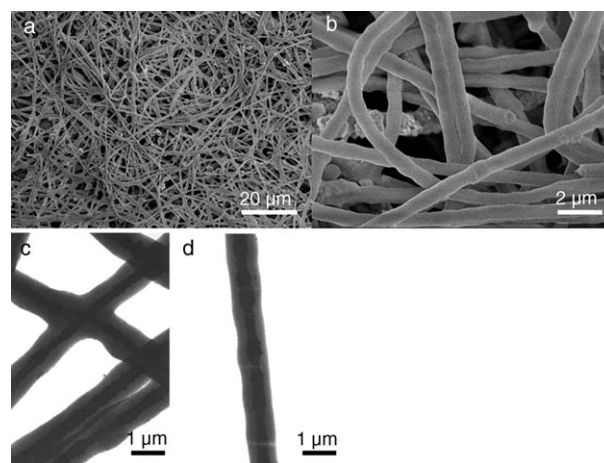


Figure 4. a),b) FESEM images and c),d) TEM images of Au/cross-linked-PVA sub-microcables.

silver/cross-linked-PVA sub-microcables, the diameter of the cables remains the same, which can be further confirmed from the TEM images shown in Figure 4c,d. As-prepared sub-microcables have a diameter of about  $1\ \mu\text{m}$  and the inner-core Au sub-microwires have an average diameter of  $250\ \text{nm}$ .

The surface of the relatively thinner gold sub-microwires is rougher than that of the Ag nanowires wrapped within cross-linked-PVA shells, which could be due to the rapid reaction rate of silver with tetrachloroaurate(III). XPS analysis of the gold/cross-linked-PVA sub-microcables (Figure 5) indicates that there is only a trace amount of gold (atomic ratio  $\text{C}/\text{O}/\text{Au} = 103:64:1$ ). Considering that XPS is a surface-analysis technique, it can be concluded that all gold nanowires are wrapped within polymer sheaths.

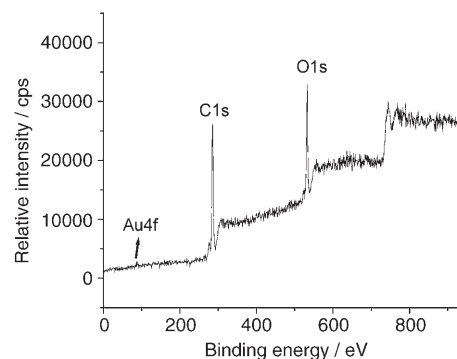


Figure 5. XPS spectrum of Au/cross-linked-PVA sub-microcables. C1s is centered at  $284.70\ \text{eV}$  (74.92 at %), O1s is centered at  $532.75\ \text{eV}$  (24.97 at %), and Au4f is centered at  $84.75\ \text{eV}$  (0.11 at %).

**Stability of Ag and Au/cross-linked-PVA microcables:** The cables obtained by the present hydrothermal treatment are very stable in distilled water (pH 7) or stored in their dry state, even when stored for a long period of time. This was confirmed by SEM and TEM observation.

The thermal stability of the samples was examined by the thermogravimetric analysis (TGA) technique in a flowing inert atmosphere. Figure 6 shows that both silver and gold/

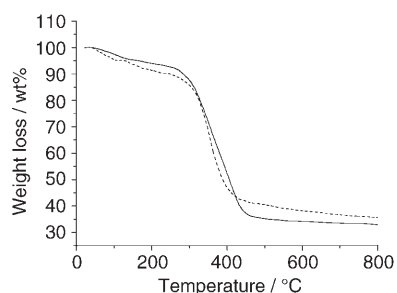


Figure 6. The thermogravimetric (TG) curve of the Ag/cross-linked-PVA microcables (—) and Au/cross-linked-PVA microcables (-----).

cross-linked-PVA microcables begin to slightly lose weight in the temperature range from 100 to 150 °C, which could be due to the loss of water in the samples. A remarkable weight loss starts at about 300 °C, which can be attributed to the decomposition of cross-linked PVA, as reported for that of the other carbohydrates.<sup>[33–35]</sup> The total weight-loss percentages for the silver and gold/cross-linked-PVA microcables are 65 and 60 %, respectively. From Figure 6, it can be concluded that the obvious weight loss occurred in the temperature range from 300 to 450 °C. After 450 °C, the weight remained unchanged.

**Synthesis of cross-linked-PVA sub-microtubes/wires by an in situ etching approach:** To produce cross-linked-PVA sub-microtubes, a mixture of aqueous ammonia (5 mL, 27 wt %) and H<sub>2</sub>O<sub>2</sub> (5 mL, 30 wt %) with a pH value of 9.0 was used to eliminate the silver cores within the cables. An FESEM image (Figure 7a) demonstrated that the majority of the samples are composed of flexible sub-microfibers. A typical TEM image showed that the thin silver core can be completely removed from its interior if the sub-microcables are kept in the solution for as long as one day (Figure 7b). If as-produced polymer sub-microtubes were dispersed in water under vigorous stirring for another day, the very thin channel structures tended to disappear, which may result from the absence of a silver-nanowire support and the extrusion of polymer walls toward the inside channel. Furthermore, H<sub>2</sub>O<sub>2</sub> played an important role in the etching process. Under vigorous stirring, H<sub>2</sub>O<sub>2</sub> in the solution will generate oxygen slowly, which will be helpful in dissolving silver as evidenced by the fact that partially etched sub-microcables are observed when H<sub>2</sub>O<sub>2</sub> was not added, as shown in Figure 7c. The main reactions can be expressed as shown in Equations (1) and (2):

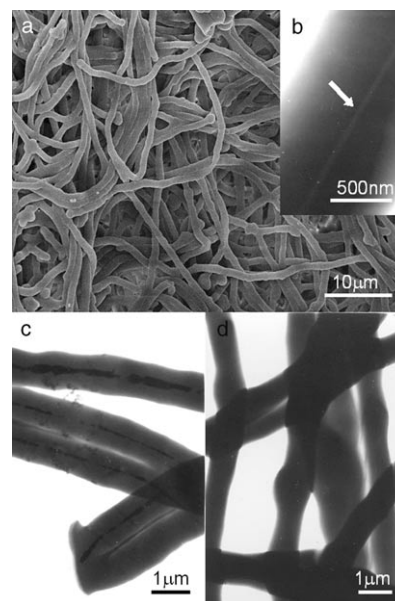
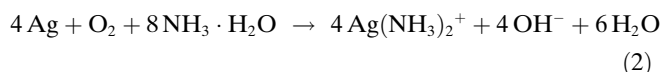
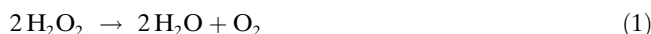


Figure 7. a) The FESEM image of cross-linked-PVA sub-microtubes after etching the Ag cores of the Ag/cross-linked-PVA cables in a mixture of aqueous ammonia solution and H<sub>2</sub>O<sub>2</sub> with pH ≈ 9 at RT for 1 day. b) A TEM image of a typical cross-linked-PVA sub-microtube with a very thin channel indicated by an arrow. c) TEM image of Ag/cross-linked-PVA sub-microcables, in which the Ag cores have only been partially attacked by the ammonia for 1 day in the absence of H<sub>2</sub>O<sub>2</sub>. d) TEM image of cross-linked sub-microfibers obtained under the same conditions as that for (a) but under vigorous stirring for another day. The core is invisible.



These approaches are being further optimized to obtain various kinds of Ag/cross-linked-PVA sub-microcables with controlled core diameter and shell thickness in order to produce Au/cross-linked-PVA sub-microcables and cross-linked-PVA sub-microtubes with tunable sizes.

## Conclusion

In summary, well-defined Ag/cross-linked-PVA sub-microcables, which are synthesized by an effective hydrothermal method using AgCl and PVA as precursors, can be used as sacrificial templates to fabricate Au/cross-linked-PVA sub-microcables by etching the Ag/cross-linked-PVA sub-microcables with tetrachloroaurate(III). In addition, cross-linked-PVA microtubes/fibers can also be produced by dissolution of the silver cores of such sub-microcables at ambient temperature. The channel diameter and the shell thickness could be tuned by controlling the diameter of the core sub-microwires and the shell thickness of the precursor sub-microcables. From the viewpoint of applications, the access of sub-microcables with noble-metal nanowires as cores could provide useful materials that require current and tempera-

ture conduction, which could be used in future nanodevices.<sup>[27]</sup> Furthermore, the cross-linked-PVA sub-microtubes obtained here may find potential application in capillary electrophoresis,<sup>[36]</sup> and colon-specific drug-delivery systems<sup>[37]</sup> as promising future building blocks.

## Experimental Section

All the reagents used in the experiment were of analytical grade and were purchased from the Shanghai Chemical Reagent Company and used without further purification.

**Synthesis of Ag/cross-linked PVA:** A modified procedure was applied for the synthesis of Ag/cross-linked-PVA sub-microcables based on our previous report.<sup>[24]</sup> In a typical procedure, AgCl ( $6 \times 10^{-4}$  mol) was precipitated by dropping an aqueous NaCl solution into an aqueous AgNO<sub>3</sub> solution. The obtained suspension was then transferred into a 34-mL Teflon-lined autoclave that contained an aqueous PVA solution (5 mL, 3 wt %) at RT under vigorous stirring for 30 min. Then the autoclave was sealed and stored in an oven at 160 °C for 4 days and allowed to cool to RT. The resulting yellow floccules were collected and washed several times with distilled water and absolute ethanol.

**Synthesis of Au/cross-linked-PVA sub-microcables:** Some Ag/cross-linked-PVA sub-microcables were transferred into a beaker under vigorous stirring. An excessive amount of HAuCl<sub>4</sub> solution was then dropped into the beaker under vigorous stirring for 1 day. Then the product was collected and further transferred into aqueous ammonia (pH ≈ 10.5) to dissolve AgCl after aging for another day under mild stirring. Finally the obtained black floccules were washed several times with distilled water and absolute ethanol.

**Synthesis of cross-linked-PVA tubes/wires:** Cross-linked-PVA sub-microtubes were obtained by etching the core of the Ag/cross-linked-PVA sub-microcables in a mixture of aqueous ammonia solution (5 mL, 26 wt %) and H<sub>2</sub>O<sub>2</sub> (5 mL, 30 wt %) at a pH ≈ 9 at RT for 1 day.

**Characterization:** The obtained samples were characterized by means of X-ray diffraction analyses, which were carried out on a (Philips X'Pert Pro Super) X-ray powder diffractometer with Cu<sub>K $\alpha$</sub>  radiation ( $\lambda = 1.541874$  Å). The size and morphology were determined with a JEOL JSM-6700F scanning electron microscope and a field emitted scanning electron microscope. Transmission electron microscopy (TEM) photographs were taken on a Hitachi (model H-800) transmission electron microscope at an accelerating voltage of 200 kV. Energy-dispersive X-ray (EDX) analyses were obtained with an EDAX detector installed on the same high-resolution transmission electron microscope. The X-ray photoelectron spectra (XPS) were collected on an ESCALab MKII X-ray photoelectron spectrometer, using non-monochromatized Mg<sub>K $\alpha$</sub>  X-ray radiation as the excitation source. Thermogravimetric analyses (TGA) were carried out on a TGA-50 thermal analyzer (Shimadzu Corporation) with a heating rate of 10 °C min<sup>-1</sup> in a flowing N<sub>2</sub> atmosphere.

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