

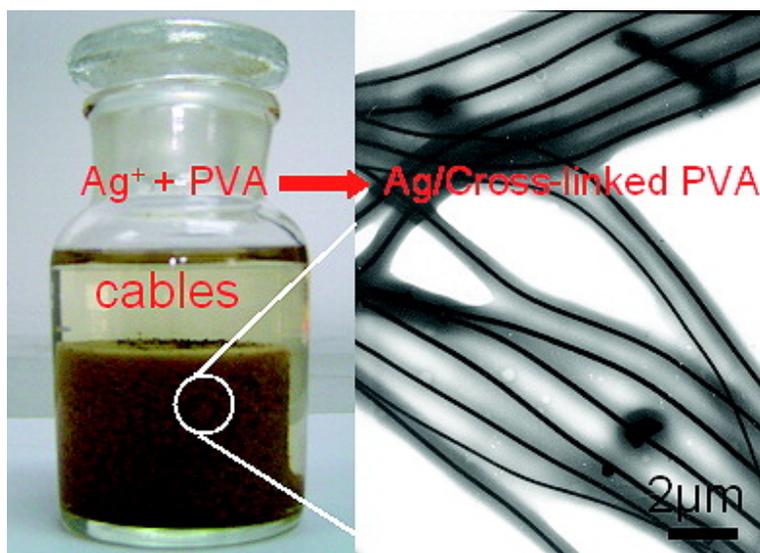
Communication

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J. Am. Chem. Soc., **2005**, 127 (9), 2822-2823 • DOI: 10.1021/ja0428154 • Publication Date (Web): 11 February 2005

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Large-Scale Fabrication of Flexible Silver/Cross-Linked Poly(vinyl alcohol) Coaxial Nanocables by a Facile Solution Approach

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Coaxial nanocables represent a new kind of nanostructures, which emerged recently and have attracted a lot of intensive investigations. New and exciting nanohybrid structures, such as coaxial nanocables with Si cores (Si/SiO₂ and Si/SiO₂/C),¹ silicon nanowires in graphitic B–C–N nanotubes,² and SiC/SiO₂,³ were just recently described. In particular, there are several methodologies for the fabrication of coaxial nanocables by high-temperature approaches, including a laser ablation method,¹ a high-temperature route,² or a carbothermal reduction method.³

In addition, several solution-based methods have emerged recently to generate polymer/polymer, semiconductor/polymer, and metal/polymer nanocables at relatively low temperatures. For instance, polypyrrole/poly(methyl methacrylate) coaxial nanocables have been synthesized through sequential polymerization of monomers within the channels of mesoporous silica, followed by dissolution of the template.⁴ Gold nanorods have recently been coated with polystyrene or silica to form cable-like structures.⁵ Layer-by-layer deposition of oppositely charged species on nickel nanorods has been adopted to prepare nickel/composite nanocable structures.⁶ CdSe/poly(vinyl acetate) hybrid nanocables have been obtained by growing the semiconductor nanowires inside polymer tubules.⁷ Ag/SiO₂ nanocables can be formed using a sol–gel method to coat Ag nanowires with amorphous silica.⁸ Recently, silver/carbon nanocables can be synthesized by a hydrothermal carbonization co-reduction (HCCR) technique.⁹

In this Communication, we report a new method to prepare flexible silver/cross-linked poly(vinyl alcohol) (PVA) nanocables for the first time via one-step in situ reduction of Ag⁺ and Ag⁺-catalyzed cross-linking of PVA chains under hydrothermal conditions.

In a typical procedure, analytically pure AgNO₃ (6×10^{-4} mol) and 5 mL of PVA (3 wt %) solution were put into distilled water at room temperature to form a clear solution, which was then stirred strongly for about 0.5 h and transferred into a 34 mL Teflon-lined stainless steel autoclave, which was sealed and maintained at 160 °C for 36 or 72 h and then air-cooled to room temperature. The resulting yellow floccule was collected and washed with distilled water and anhydrous alcohol several times to remove ions and possible remnants in the final product.

The XRD pattern in Figure 1 shows that all reflections can be readily indexed to *fcc* silver with a calculated lattice constant $a = 4.1 \text{ \AA}$, which is in good agreement with the literature values (JCPDS No. 4-783). A general overview SEM image in Figure 2a shows that the product is composed of flexible fibers with a diameter of 0.7–4 μm and length up to 100 μm. SEM and TEM images (Figure 2b–d) show that all wires are actually a composite comprised of a smooth core about 150–200 nm in diameter and a surrounding sheath about 0.5–1 μm in thickness, from which the contrast between surrounding polymer and inner core can be easily observed. Some bundles of cables are formed, and each bundle is composed of several nanocables packed in a parallel fashion (Figure 2a–d). In addition,

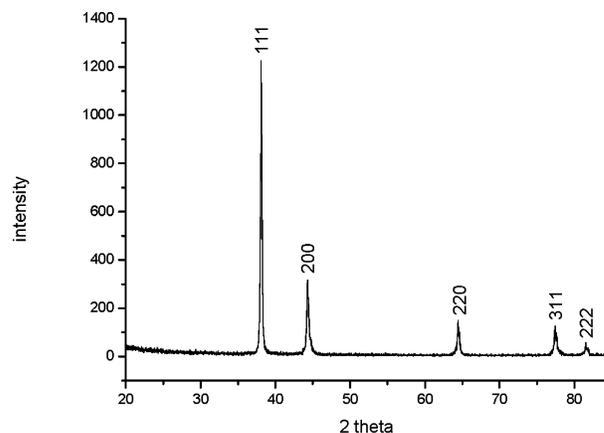


Figure 1. XRD patterns of the nanocables obtained at 160 °C for 72 h.

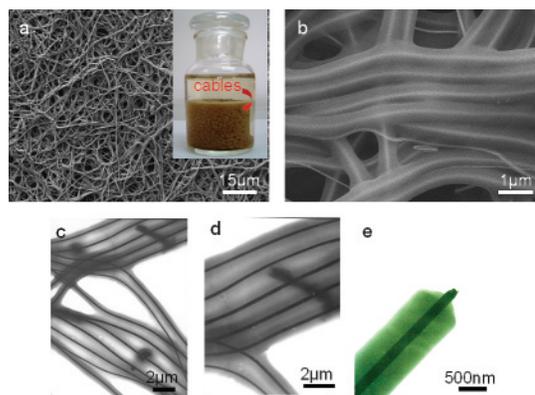


Figure 2. SEM and TEM images of the nanocables. (a) General view of the cables. Inset is the sample obtained after reaction for 72 h. (b) Magnified SEM image of the cables, clearly showing the inner core–shell structure. (c–e) TEM images of the cables.

some of the cables tend to entangle with each other. High-resolution TEM confirmed that the core Ag nanowires grew preferentially along the [110] direction (Supporting Information, Figure S1).

X-ray photoelectron spectroscopy (XPS) is used to detect the surface composition of the cables. XPS measurements indicated that C_{1s} and O_{1s} binding energies of the obtained sample are 284.60 and 532.10, respectively (Supporting Information, Figure S2). However, the binding energy at 368.10 eV for Ag_{3d} almost cannot be detected. The XPS results confirmed that all silver nanowires are confined within shells of the cross-linked PVA.

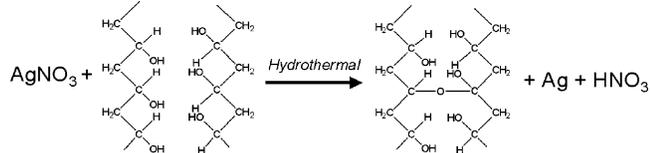
The shell thickness of the cables can be controlled. It has been found that the shell thickness of the obtained nanocables is strongly dependent on the reaction time (see Supporting Information, Figures S3–S5). The nanocables obtained at an early stage after reaction for 36 h at 160 °C are composed of straight silver nanowires with a thinner sheath (Supporting Information, Figure S3), and no

bundles are observed. Furthermore, the temperature also has a strong influence on the thickness of the shell and the uniformity of the cables (Supporting Information, Figures S6 and S7).

Either the reaction mechanism or the formation process of cables is investigated. It is well known that PVA chains will turn to cross-link after treatment at high temperature (250 °C); however, we find that hydrothermal treatment of PVA solution at 160 °C or even 200 °C cannot make it cross-linked. The cross-linked reaction that occurred at relatively low temperature in the presence of silver ions could be due to the close hydrothermal reaction conditions we adopted here. The default experiments in the absence of AgNO₃ show that PVA cannot be cross-linked, even under identical conditions. In addition, the rapid reduction of AgNO₃ into Ag nanoparticles in the same solution with an identical concentration of PVA and then hydrothermal treatment at the same temperature for the same reaction period cannot produce such cables. These results demonstrated that the presence of AgNO₃ is essential for the formation of cables, and AgNO₃ indeed plays a key role as a catalyst for oxidation–reduction reactions such as that occurring in this system. In this process, PVA can be oxidized by AgNO₃ at 160 °C into cross-linked PVA, which is insoluble in water with a deep yellow brown color (inset in Figure 2a). The detailed time-dependent experiments indicated that the Ag nanowires and irregular AgCl particles are formed in the early stage and then converted to Ag/cross-linked PVA nanocables (Supporting Information, Figures S8 and S9).

Furthermore, the pH value dropped dramatically from 5.2 for the starting initial solution to 1.8 for the residual solution after reaction, implying that the solution after reaction becomes more acidic (Supporting Information, Figure S10). The evidence of NO₃[−] absorption at 1384.5 cm^{−1} observed in the FTIR spectrum confirms the possible existence of HNO₃ in the residual solution (Supporting Information, Figure S11). The FTIR spectrum of the obtained nanocables is almost the same as that of pure PVA, which shows several absorption peaks located at about 3430, 2820, and 1600 cm^{−1} (Supporting Information, Figure S12). However, there is a wide absorption peak from 1050 to 1100 cm^{−1}, which can be assigned as the absorption peak of $\sigma_{as}(C-O-C)$ of the cross-linked PVA. It has to be pointed out that there may exist some ester in the product due to the presence of a peak at 1737 cm^{−1}.

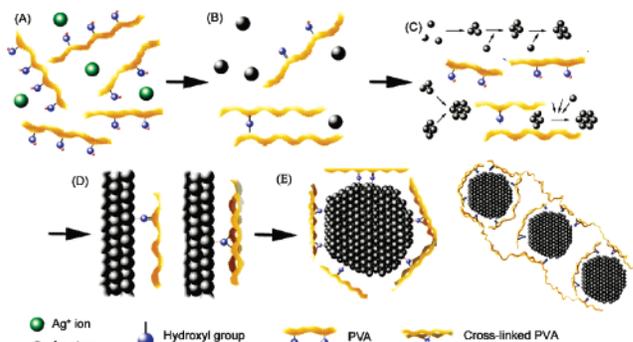
On the basis of the above analysis, the reaction that occurred under the present hydrothermal conditions can be illustrated as follows:



For comparison, the reaction of AgNO₃ (6×10^{-4} mol) with less PVA (0.5 mL) under similar hydrothermal conditions leads to the formation of only Ag nanoparticles with irregular shapes. Moreover, if less AgNO₃ (6×10^{-5} mol) was used and the amount of PVA (5 mL) was kept the same, no cables were obtained.

In fact, the formation of such elegant nanocables is controlled by a synergistic growth mechanism, which we called a synergistic soft–hard template mechanism (SSHM) (Scheme 1). It is clear that PVA is responsible for both the formation of silver nanoparticles and further oriented growth of silver nanowires stabilized by PVA; in turn, the silver wires act as a backbone on which cross-linked PVA will form. In addition, the newly formed cross-linked PVA

Scheme 1. Illustration of the Formation Mechanism of Ag/Cross-Linked PVA Nanocables^a



^a (A) The association of silver ions with PVA. (B) The formation of Ag nanoclusters stabilized by PVA. (C) The aggregation of Ag nanoclusters stabilized by PVA. (D) The formation of Ag nanowires and the entangled cross-linked PVA on the backbone of nanowires. Side view. (E) Further cross-linking of PVA results in the formation of single cables or parallel cables with bundle structure. Viewed along the cable axis.

will act as an effective bridge to connect nearby single cables to form raft-like cable bundles in a parallel fashion, as observed (Figure 2b–d).

In conclusion, we have demonstrated a simple large-scale hydrothermal synthesis of flexible nanocables with silver as cores and cross-linked PVA as shells. The in situ reduction of silver ions in the presence of PVA is possibly due to the catalysis of silver ions on the cross-linking of PVA chains under hydrothermal conditions. The synergistic effects of both the stabilization of PVA and the binding interaction of cross-linked PVA with the silver nanowires are responsible for the formation of cables and the parallel cable bundles. Since cables with metal such as copper, aluminum, or even silver as cores and some polymers, for example, poly(vinyl chloride) (PVC) or polyethylene (PE), as shells have found wide application in various fields,² the present flexible Ag/cross-linked PVA coaxial nanocables could also have potential applications in the future.

Acknowledgment. S.H.Y. acknowledges the special funding support from the Centurial Program of the CAS, the National Science Foundation of China (NSFC, Nos. 20325104, 20321101, 50372065), and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry.

Supporting Information Available: Figures S1–S12, showing SEM and TEM images of the nanocables, XPS spectrum, phases observed at different reaction times, variation of pH during the hydrothermal reaction, shape evolution process, and FTIR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA0428154