

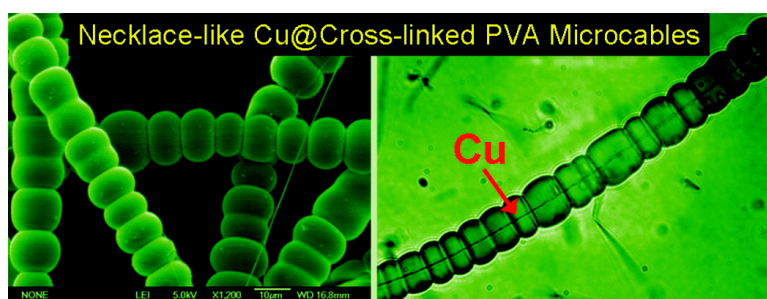
Communication

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## Necklace-Like Cu@Cross-Linked Poly(vinyl alcohol) Core–Shell Microcables by Hydrothermal Process

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Syntheses of necklace-like structures, as a unique kind of one-dimensional (1D) nanoarchitectures, have drawn much attention in recent years. Various 1D nanostructures with fluctuant diameters such as carbon,<sup>1</sup> Si,<sup>2</sup> Au,<sup>3,4</sup> Co,<sup>5</sup> CdO,<sup>6</sup> Cu<sub>2</sub>O,<sup>7</sup> SiO<sub>2</sub>,<sup>8</sup> NiFe<sub>2</sub>O<sub>4</sub>,<sup>9</sup> CdS,<sup>10</sup> CdTe,<sup>11</sup> CoSe<sub>2</sub>,<sup>12</sup> and AlN<sup>13</sup> have been produced through different routes. In high temperature chemical and physical processes,<sup>1,2,6,13</sup> the formation of such structure can be generally attributed to the non-uniformity in 1D growth. In liquid phase chemical processes, external magnetic field can arrange the preformed magnetic metal and compound nanoparticles into linear arrays.<sup>5,9</sup> Some related magnetic compounds<sup>12</sup> and even non-magnetic substitution product<sup>3</sup> can also be prepared by succeeding chemical treatment and at the same time inherit their necklace-like morphologies. In addition, polymers, surfactant micelles, amino acids, and DNA molecules have been used to guide the 1D assembly of coated or bonded nanoparticles. Electrospinning has been also used to generate 1D structures.<sup>8</sup> Most of the above 1D materials only have fluctuant diameters but do not have clear inner wire/outer bead heterogeneous structures. Organogel or polymer templates have been used for the templating synthesis of necklace-like CdS nanofibers.<sup>10</sup> Carbon nanotubes are commonly used materials acting as the axis of wires, and Co,<sup>14</sup> Co<sub>3</sub>O<sub>4</sub>,<sup>15</sup> Fe<sub>3</sub>O<sub>4</sub>,<sup>16</sup> and Ag<sup>17</sup> are the beaded nanoparticles. The potential applications of these necklaces include field-emission behavior,<sup>14</sup> heterojunction-like structures for functional nanodevices.<sup>15,16</sup> Recently, we developed a one-pot synergistic growth strategy to synthesize M@cross-linked poly(vinyl) alcohol (PVA) nano/submicrocables (M = Ag, Cu, Te).<sup>18,19</sup>

In this Communication, we report our further progress on the synthesis of unique necklace-like Cu@cross-linked poly(vinyl alcohol) (PVA) microcables that have strict wire–bead forms.

In a typical procedure, a mixture of analytically pure CuCl (0.02 g,  $2 \times 10^{-4}$  mol) and CuCl<sub>2</sub>·2H<sub>2</sub>O (0.017 g,  $10^{-4}$  mol) was added into a Teflon-lined stainless steel autoclave with a capacity of 22 mL, then the autoclave was filled with 18 mL of PVA solution (1.5 wt %, pH 9.5, modulated by NaOH solution) and kept at a filling ratio of 80% (v/v). After stirring the solution for 10 min, the autoclave was sealed, heated in an oven of 200 °C for 72 h, and then naturally cooled to room temperature, and a brownish red floccule formed, which was then collected, washed with distilled water and ethanol several times to remove ions and possible remnants, and vacuum-dried for further characterization (see details in Supporting Information).

The X-ray diffraction pattern shown in Figure 1 is in good agreement with the standard data of cubic copper with face-centered structure (JCPDS 4-836), and no other impurities are detected. The SEM images in Figure 2a,b show that the product is mainly

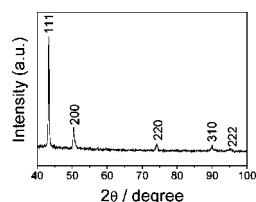


Figure 1. XRD pattern of the as-prepared sample.

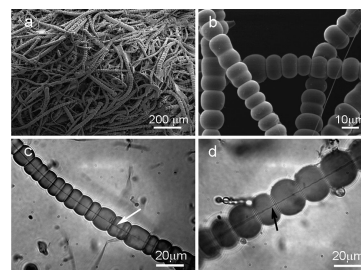
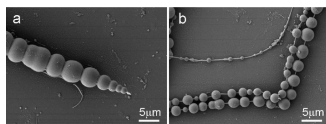


Figure 2. (a,b) SEM images of the necklace-like microcables with different magnifications. (c,d) Optical images of the necklace-like microstructures, showing the cross-linked PVA coatings on rather thin inner copper wire axes (indicated by arrows).

composed of necklace-like wires with lengths of several hundreds of micrometers to millimeters and diameters in the range from several micrometers to near 20  $\mu$ m. Generally, the linear beads with a flat sphere form compact assemblies. The inner Cu nanowires within a thinner coating can be found in optical images clearly (Figure 2c,d). Compared with the transparent coatings, each rather thin nanowire axis is found throughout the necklace-like structure.

XRD pattern and FTIR spectrum indicate the similar features as those reported previously<sup>19</sup> (see Figure S1). The XPS spectrum also shows clearly the C1s and O1s binding energies of the elements (from PVA) in obtained product at 284.6 and 532.3 eV, respectively (see Figure S2). The binding energy of Cu 2p<sub>1/2</sub> is rather weak, which can be due to the “deep” embedded Cu nanowires in this structure.

To prepare this new structure, the initial pH value of solution is kept lower and CuCl is used as a co-precursor. According to the reaction mechanism of the CuCl<sub>2</sub>–PVA reaction system,<sup>19</sup> the reducing reactions of precursor CuCl<sub>2</sub> include two stages, from CuCl<sub>2</sub> to CuCl and subsequently reduced from CuCl to Cu; HCl which appears along with CuCl (and final Cu) has the tendency to block the succeeding reaction, thus adjusting the initial pH value of solution with NaOH is essential. Herein, we propose that the intermediate CuCl can be used directly as a co-precursor to decrease the necessary dosage of NaOH to keep



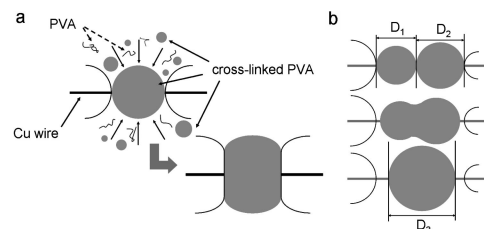
**Figure 3.** SEM images of (a) a typical tapering end of one micronecklace. (b) Strings of beads without compact arrangement.

the reducing reaction going, which has been proved by a series of experiments. The initial pH values of PVA solutions are first kept in a range from 9 to 11, then these solutions can be decreased to acidic levels of 3.5–6 after dissolution of  $\text{CuCl}_2$ , which are by far lower than the required value of 10–13 in the previous synthesis of nanocables.<sup>19</sup> However, Cu nanowires can still be reduced from the modified precursors, and the unique necklace-like morphology of cross-linked PVA coatings is due to such modulation. Apparently, lower pH value provides a more suitable condition for cross-linking of PVA and the formation of such unique microbeads, which can be verified by observation of the samples obtained from different intermediate stages (see Figures S3 and S4).

A synergistic soft–hard template mechanism (SSHM) was proposed previously to explain the formation of cable-like structures.<sup>18a,19</sup> The reduced metal copper acts as the supporting framework for the cross-linked PVA, and the cross-linking of PVA acts as the restraint to guide the growth of copper nanoparticles in reverse. Here we suppose that another independent cross-linking process of PVA exists along with the above synergistic one, which is not related directly with the reduction of copper ions. Compared with the thickness of former PVA coatings that are generally less than 100 nm, the semi-diameters of microbeads in the necklace-like structures are much larger, but the Cu nanowires still are of almost the same diameters. Thus, part of the cross-linked PVA is not involved in the reducing reaction. At a much lower pH value, on the surface of newly formed Cu@PVA nanocables, this part of cross-linked PVA with spherical shape appears and then adheres, coagulates, and grows to form initial beads or inflated structures surrounding the nanocables, which is like the coagulation of dewdrops on electric wires in winter. At the beginning, these beads distribute randomly along the nanocables. By absorbing succeeding cross-linking PVA and interfusing with neighboring existing ones, these beads will grow larger and larger, and finally make up arrays of compact flat spheres. Because of the rough homogeneity along the cables, initial random distribution still provides relative uniform arrangements. However, as shown in Figure 3a, because the ends of nanocables are finally formed, the newly formed beads have less time to grow and therefore gradual diminution sequences appear. This phenomenon actually supports our proposed growth model. When the density of PVA in solution is relatively lower, necklaces with noncompact spherical beads can also be produced (Figure 3b), without sufficient supplement of succeeding cross-linking PVA. In this case, a simple coalescence process can occur but increases the distances of neighboring beads. As illustrated in Scheme 1, the different effects of simple absorbance (newly formed cross-linked PVA from solution) and coalescence (of neighboring beads) are proposed, and the formation of necklace-like structures should be based on the combination of these effects.

In summary, we have reported here a simple one-pot route to prepare necklace-like Cu@cross-linked PVA microcables as a totally new morphology compared with the traditional cables. Under hydrothermal condition at lower pH values, the individual

**Scheme 1.** (a) Absorbing the Newly Formed Cross-Linked PVA from Solution Will Make the Beads Grow Larger and Gradually Form Compact Arrangements; (b) Simple Coalescence of Neighboring Beads with Different Diameters Gives Only a Noncompact One



process of PVA cross-linking and formation of dispersing cross-linked PVA microspheres are strengthened, which provide adhesive building blocks on the surface of synergistically formed Cu@PVA nanocables. The combination and evolution of cross-linked PVA coatings of both sources determines the final morphology of the product. Such a growth mechanism might be extended to other metal–polymer systems and has potential applications in nanofabrication of special necklace-like cables.

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**Supporting Information Available:** Characterization, and the check material procedures, FTIR, XPS spectra, and SEM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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