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Amino Acid Based Metal−Organic Nanofibers

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Self-assembly of small molecules and/or metal ions into nanostructures, such as spheres, tubes, rods, tapes, fibers, and crystalline particles, has evolved as an attractive strategy for fabricating materials with tunable physical and chemical properties via control of their composition, size, and shape. This versatility has opened up a broad range of potential applications in catalysis, electronics, sensing, medical diagnostics, tissue engineering, data storage, and drug delivery.[1] Recently, conventional coordination chemistry has also started to attract a great amount of interest for synthesizing these nanoscale structures. In particular, several recent studies have demonstrated that an infinite coordination polymerization of metal ions through organic ligands followed by a precipitation can generate infinite coordination polymer particles (ICPs).[2,3] Thus far, these ICPs have shown not only promising functionalities, such as magnetism,[4] porosity,[5] ion exchange[6] or optical properties,[6] but also a capacity for use as novel encapsulating matrices.[7]

Even though the latter approach, in principle, can provide interesting ICPs, nanoscale one-dimensional (1-D) coordination polymers, including rods, tubes, and fibers, are still scarce. In 2004, Martin et al. synthesized the first discrete metal−organic nanotubes by using templated layer-by-layer growth.[8] Soon after, Lin et al. prepared Gd(III)-based nanorods able to act as contrast agents through a water-in-oil microemulsion-based technique,[9] whereas Oh et al. used hydrothermal synthesis to obtain porous In(III)-based hexagonal nanorods.[10] More recently, coordination polymer-based gels and nanofibers have been described by You and Loh's groups, respectively.[11,12] These nanofibers are efficient in light harvesting, because fluorescence resonance energy transfer is favored in the 1-D structure.[12] Therefore, designing novel synthetic routes to fabricate 1-D coordination polymer nanostructures will certainly open up exciting opportunities for developing a new class of electronically, optically, and biologically active materials.

Here we report a facile template-free strategy to very long (up to one centimeter) discrete chiral coordination polymer nanofibers under ambient conditions using aqueous/organic interfacial coordinative polymerization (Figure 1). The nanofibers have diameters between 100 and 200 nm. The synthesis is based on the well-known capacity of the L- or D-aspartic acids (Asp) to generate biorelated coordination polymers when they are reacted with transition metal ions.[13] The dicarboxylate form of the Asp and Cu(II) metal ions are separated by the interface between an organic solvent containing the sodium aspartate and an aqueous phase containing the transition metal ions. The Cu(II)-Asp product, which starts to polymerize at the interface, contains exclusively long nanofibers that grow oriented along the diffusion direction. Nanofibers with shorter lengths on the order of micrometers are also produced when the phases are mixed under stirring. This observation indicates that the formation of nanofibers is not determined by the interface but more likely by the nature of the coordination polymerization of the Cu-Asp system. However, it is clear that the length of the resulting nanofibers is highly dependent on the method used for their synthesis.

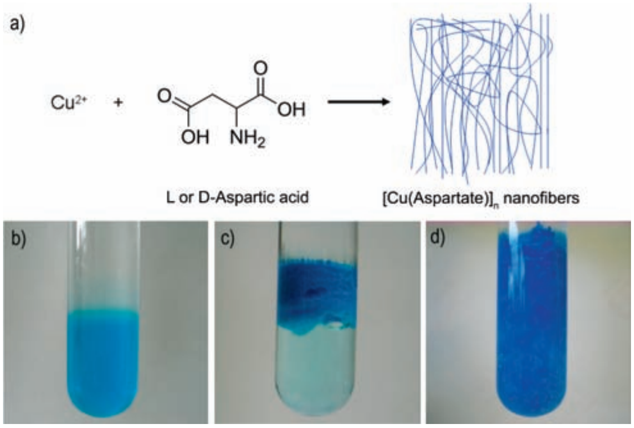

Figure 1. (a) Schematic illustration of the synthesis of Cu-Asp-based nanofibers. (b−d) Pictures taken at 0 (b), 24 (c), and 120 h (d) illustrating the aqueous/organic interfacial coordinative polymerization method used to fabricate nanofibers with lengths on the order of centimeters.

In a typical experiment, L- or D-aspartic acid and NaOH were dissolved in an ethanol/water mixture (5/1), whereas $Cu(NO_3)_2 \cdot 6H_2O$ was dissolved in water. The solutions were then transferred carefully to a test tube, generating an interface between the two layers (Figure 1b). After 3 days, dark blue fibers start to form at the liquid−liquid interface (Figure 1c). Then, as the ethanolic layer slowly diffused into the aqueous phase, these fibers gradually grew oriented along with the diffusion direction. After 2 weeks, the entire aqueous phase was filled homogeneously with dark-blue metal−organic nanofibers (Figure 1d).

Figure 2a shows a photomicrograph of bundles of these fibers, illustrating their ~1 cm length and high orientation. Transmission electron microscopy (TEM) images of these fibers show a very homogeneous sample of fibers with diameters of 100−200 nm (Figure 2c). The sample uniformity and narrow diameter distribution were also confirmed by field-emission scanning electron microscopy (FESEM). Figure 2b shows a typical FESEM image of a nanofiber thin film cast on an aluminum substrate from a colloidal suspension. The sample appears to be exclusively nanofibers, consistent with TEM images.

X-ray powder diffraction performed on the Cu-Asp nanofibers confirmed their crystalline character, but their single crystal structure determination, and therefore a detailed analysis of the structural connectivity, was not feasible due to their sub-200 nm diameter. However, some additional characterization appears to indicate that Cu(II) ions and Asp ligands are arranged in 1-D chains with the general formula $[Cu(Asp)(H_2O)_x]_n$.[14] The chemical composition of these fibers was first determined by energy dispersive X-ray (EDX) spectroscopy, which confirmed the presence of copper, oxygen,

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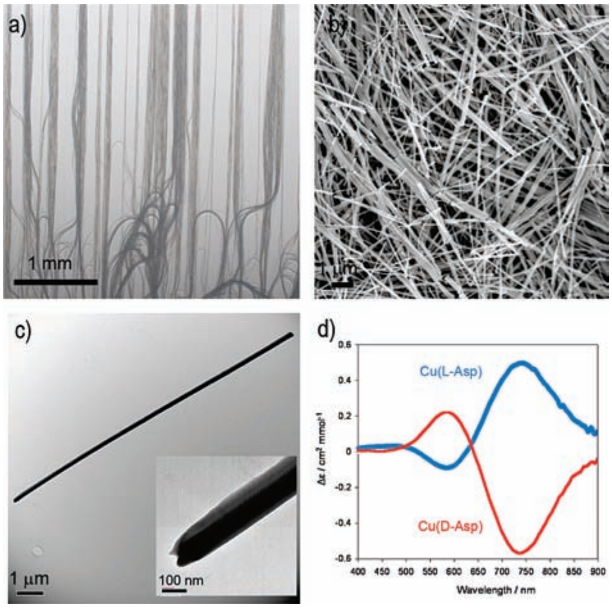

Figure 2. (a) Optical microscope, (b) FESEM, and (c) TEM images of Cu-Asp-based nanofibers. (d) Solid state CD spectra of L- (blue) and D- (red) Cu-Asp-based nanofibers.

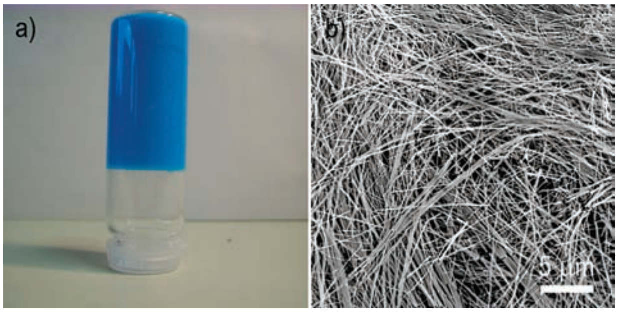

Figure 3. (a) Photograph and (b) FESEM image of the Cu-Asp-based gel.

nitrogen, and carbon. The infrared spectra show that both carboxylate groups of the Asp moieties are coordinating to the Cu(II) ions, as evidenced by the multiple characteristic asymmetric and symmetric COO^- bands centered at 1622/1586 cm^{-1} and 1403/1368 cm^{-1}, respectively.[14] A broad band in the region 2600−3600 cm^{-1} indicates the presence of water molecules and extensive hydrogen bonding. These facts, enhanced by the elemental analysis, which confirms that the ratio between Cu(II) ions and Asp is 1:1, enable us to suggest tentatively the formation of $[Cu(Asp)(H_2O)_x]$ polymeric chains.

The chirality of Cu-Asp fibers constructed from L- and D- aspartic acid was studied by Circular Dichroism (CD) spectroscopy in the solid state, using a procedure developed previously.[15] The enantiomeric nanofibers show an opposite Cotton effect (Figure 2d). The CD spectra of Cu-(D-Asp) fibers exhibit a strong Cotton effect with the crossing wavelength at 637 nm near the absorption of the Cu(II) complex. The shape and magnitude of these Cotton effects shows clearly the chiral coordination sphere of the metal ion in the nanofibers. It is noteworthy that this signal arising from d−d transitions is much clearer than those of other Cu(II) complexes.[16] The sign of the CD signal is determined by the enantiomeric form, L- or D-, of the component aspartic acid.

Cu-Asp-based nanofibers with shorter lengths on the order of micrometers were also synthesized by fast addition of an aqueous solution of $Cu(NO_3)_2 \cdot 6H_2O$ to an aqueous solution of L- or D-sodium aspartate under stirring. Interestingly, as the concentrations of both reactants were increased up to 0.07 M, homogeneous aqueous gelation was observed (Figure 3a). This opaque blue gel is stable for months at room temperature. Figure 3b shows an FESEM image of this gel, showing the characteristic interlacement of Cu-Asp-based nanofibers.

In conclusion, long chiral nanofibers can be grown using conventional coordination chemistry and biologically derived components in a diffusion controlled growth procedure. Furthermore, simple changes in the reaction strategy can induce a decrease of the fiber length or the formation of a metal−organic gel. Owing to the high flexibility of coordination polymer composition, the present strategy will certainly expand the synthesis of novel nanoscale 1D coordination polymers for future electronic, optical, drug delivery, and sensing applications.

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Supporting Information Available: Detailed synthetic procedure, IR, XRPD, TEM, EDX and FE SEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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