Synthesis of CoPt and $FePt_3$ Nanowires Using the Central Channel of Tobacco Mosaic Virus as a Biotemplate

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The design and assembly of a mesoscopic architecture using nanoscaled materials is of fundamental interest in the field of nanotechnology.[1] To realize such structures, it is necessary that various nanoscale components, such as nanoparticles, nanorods, nanowires, and nanotubes, be produced by simple techniques. Biological molecules have been used to produce inorganic nanomaterials in the field of biomimetic materials chemistry.[2] For example, biosupramolecular templates such as cage-shaped proteins,[3] spherical viruses,[4] and tube-shaped proteins[5] have been utilized to prepare well-defined nanoparticles and nanowires by biomineralization. Tube-shaped proteins were effectively used to produce one-dimensional nanostructured materials. Tobacco mosaic virus (TMV) is one of the ideal biological molecules for this purpose. TMV is a tube-shaped supramolecule, 300 nm in length with an outer diameter of 18 nm. It is composed of 2130 identical coat protein molecules, which are self-assembled in a helical manner together with the TMV RNA and it has a hollow central channel with a 4 nm diameter. The channel has been used to synthesize nickel and cobalt nanowires by Pd activation and electroless deposition.[5] TMV has also been used as an inorganic−organic nanotube composite,[6] as a chemoselective template for the specific attachment of ligand-linker groups,[7] and as a biological template for the controlled deposition and organization of Pt, Au, and Ag nanoparticles.[8]

Until now, all metal nanowires synthesized inside TMV have been monometallic. No bimetallic alloy nanowires have been reported, yet they could greatly expand the range of nanowire applications. CoPt is one of the most attractive bimetallic alloys. Ferromagnetic CoPt nanoparticles (NPs) biomineralized in the apoferritin cavity have been used for data storage applications.[9] CoPt and FePt nanowires[10] have the potential to be used as an ultrahigh-density magnetic recording material and as spintronics components.[11] However, it is expected to be extremely difficult to initiate and maintain the chemical reaction of two kinds of ions inside a nanometer-size channel. In this study, we devised a simple and novel technique to synthesize bimetallic Co−Pt and Fe−Pt alloy nanowires in the channel of the TMV. The nucleation and growth of Co−Pt and Fe−Pt nanowires were successfully demonstrated, and the resulting nanowires were characterized.

Our preliminary survey of Co−Pt nanowire synthesis conditions revealed that TMV has the ability to preferentially biomineralize Co−Pt bimetallic alloy (see the Supporting Information). Solutions containing 150 mM NaCl, 3 mM $(NH_4)_2Co(SO_4)_2$, and 3 mM K_2PtCl_4 with and without 0.3 mg/mL TMV were prepared, and 3 mM $NaBH_4$ was added to reduce the ions. The solution with TMVs gradually changed color and biomineralization was confirmed by transmission electron microscopy (TEM) (JEOL JEM-2200ZFS). The solution without TMV remained unchanged.

Further study revealed that the following process produced Co−Pt nanowires effectively. An aqueous solution of 0.3 mg/mL TMV in 150 mM NaCl was prepared in a microtube. $(NH_4)_2Co(SO_4)_2$ and K_2PtCl_4 were added twice, first to a final concentration of 0.5 mM and 5 min later to 1.0 mM. After 5 min, $NaBH_4$ was added twice at 5 min intervals to a final concentration of 1.0 mM. This procedure was repeated three times, i.e., the final concentration of $(NH_4)_2Co(SO_4)_2$,

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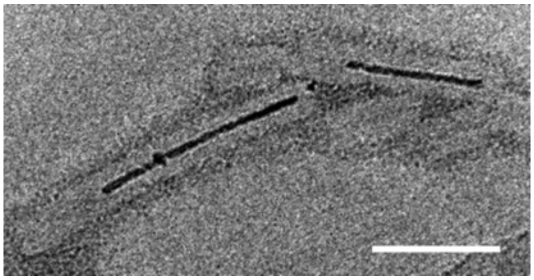

Figure 1. TEM micrograph of TMV−nanowire composites after biomineralization of Co−Pt alloy in the hollow central channel of the TMV (stained by aurothioglucose). Scale bar is 50 nm.

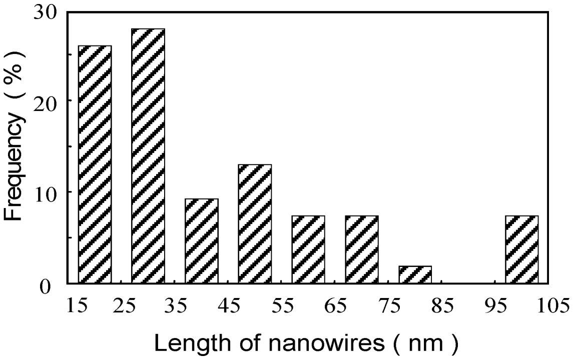

Figure 2. Distribution of the length of the Co−Pt nanowires; 54 nanowires synthesized in TMV molecules were measured.

K_2PtCl_4, and $NaBH_4$ was 3 mM each. Throughout the procedure, the reaction solution was exposed to ultrasonication with the bottom half of the microtube immersed in an ice−water bath. The sample was sonicated for 1 s at intervals of 5 s by direct immersion of the tapered microtip into the microtube (20 kHz, ∼20 W, Digital Sonifier model 450, Branson). To make Fe−Pt nanowires, we used $(NH_4)_2Fe(SO_4)_2$ instead of $(NH_4)_2Co(SO_4)_2$.

The sample solution was observed by TEM after staining with aurothioglucose, which does not stain the central hollow channel of the TMV.[3f] As shown in Figure 1, nanowires were found approximately 50−100 nm long and 4 nm in diameter. The high-resolution TEM (HR-TEM) image showed clear lattice fringes of the nanowires (data not shown). The TMV coat protein remained intact and TMV became a tube-shaped composite material with a Co−Pt nanowire.

About one-third of the TMV molecules showed a nanowire in the central channel. In most cases, the inner channels were not fully occupied, with the average Co−Pt nanowire length being 42 nm, shorter than the length of the TMV molecules. The length distribution of the nanowires is shown in Figure 2.

To investigate the mechanism of Co−Pt synthesis in the TMV channel, we first tested whether monometallic Co or Pt nanowires could be synthesized using the same process. With Co^{2+} ions alone, neither nanoparticles nor nanowires were produced. When Pt^{2+} ions were used, irregular Pt nanoparticles were formed outside the TMV, which indicated that Pt^{2+} ions were reduced to Pt but not inside the TMV channel. Therefore, both Co^{2+} and Pt^{2+} ions were necessary for nanowire synthesis inside TMV (see the Supporting Information, Figure S2).

Repeating the same process but without $NaBH_4$ addition produced neither nanowires nor nanoparticles (see the Supporting Information). Clearly, $NaBH_4$ is required for the reduction and ultrasonication alone is not sufficient to reduce ions in this system.[12]

Table 1. Nanowire Formation Results and Elemental Compositions of Co/Pt and Fe/Pt Determined by EDX Spectrum[a]

reaction conditions	NW formation	Co/Fe:Pt (at %)
Co 0 mM + Pt 3 mM	no	
Co 3 mM + Pt 6 mM	yes	10:90
Co 3 mM + Pt 3 mM	yes	17:83
Co 9 mM + Pt 3 mM	yes	45:55
Co 3 mM + Pt 0 mM	no	
Fe 3 mM + Pt 3 mM	yes	25:75

[a] The synthesis of Co−Pt or Fe−Pt nanowires was carried out using various concentrations of metal ions under the same conditions. NW formation in the TMV channel was determined by the TEM observation with aurothioglucose staining.

Without ultrasonication, the color of the reaction solution changed to dark brown, and TEM revealed a small number of short Co−Pt nanowires inside the TMV. No long Co−Pt nanowires were found (see the Supporting Information, Figure S3). The synthesized short nanowires were located at the ends of the channel in most cases, suggesting that the nucleation occurred at one end of the TMV and the nanowire grew along the channel. This suggests that the ultrasonication increased movement of the metal ions into the TMV channel, and that this was necessary for elongation.

Our results show that both Co^{2+} and Pt^{2+} ions enter the TMV channel, where $NaBH_4$ reduces them. The chemical reaction producing Co−Pt nucleus preferentially occurs inside the TMV channel. Judging from the fact that Co^{2+} ions alone could not form nanoparticles, it is plausible that Pt^{2+} ions are first reduced to form Pt nanoparticles that function catalytically to create the Co−Pt alloy. As the nanowire grows from the nucleus, ultrasonication boosts the supply of metal ions within the narrow channel, allowing the deposited Co−Pt to grow into a nanowire.

To investigate whether our process could produce Co−Pt nanowires of different composition, we next tried different concentration ratios of Co^{2+}:Pt^{2+} ions in the reaction. Nanowires could be produced with a wide range of molecular compositions as shown in Table 1. The high-resolution HR-TEM images of nanowires produced using 1:2 and 3:1 Co^{2+}:Pt^{2+} ratios showed a clear lattice fringe (see the Supporting Information, Figure S4). Figure 3a shows a typical nanowire synthesized using 9 mM Co^{2+} and 3 mM Pt^{2+}. There were domains having the same lattice direction in the crystalline nanowires. Because CoPt and $CoPt_3$ are the only intermetallic compounds composed of Co and Pt, and monometallic Co nanowires could not be produced, the observed nanowires must be composed of CoPt, $CoPt_3$, or Pt. This was supported by the HR-TEM observation that the measured lattice distance of the nanowires were from 0.21 to 0.22 nm, which is consistent with CoPt (111), $CoPt_3$ (111), and Pt (111) planes (0.21 and 0.23 nm) but larger than Co (101) planes (0.19 nm).

The EDX spectrum is shown in Figure 3b, and elemental analysis of the Co−Pt nanowire is summarized in Table 1. The presence of both Pt and Co was confirmed (the Cu signal

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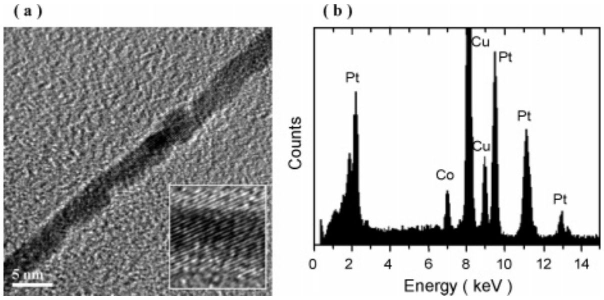

Figure 3. (a) HR-TEM micrograph of CoPt nanowire produced in the TMV central channel using 9 mM Co^{2+} and 3 mM Pt^{2+} under sonication (no staining). Scale bar is 5 nm. The inset shows a lattice image of the nanowire. (b) EDX spectrum of the nanowire showing the presence of Co and Pt as well as the ratio of Co and Pt.

arises from the TEM grid) and the composition was calculated to be $Co_{45}Pt_{55}$ (Table 1). These results suggest the nanowire is mainly composed of CoPt. The error of 5% may be due to small amounts of $CoPt_3$ or Pt. $(NH_4)_2Co(SO_4)_2$:K_2PtCl_4 molar ratios of 1:1 and 1:2 also gave nanowires with a clear lattice fringe (see the Supporting Information, Figure S4). However, the Co content was low (10−17%), suggesting these nanowires were mixtures of $CoPt_3$ and Pt. However, we could not rule out the possibility of pure Co regions mixed with Co−Pt alloy.

Nanowires synthesized using 9 mM Co^{2+} and 3 mM Pt^{2+} were subjected to magnetometry measurements using a superconducting quantum interference device (SQUID) (Quantum Design MPMS-5S) at 300 K (Figure 4). Though the nanowire solution contained small amounts of nanoparticle aggregates attached to the ends of the TMV, we used the whole solution because the aggregates could not be removed. The M−H curve (field dependence of magnetization) showed a hysteresis loop with a coercive field (Hc) of 25 Oe. This M−H loop indicated that the sample is ferromagnetic, supporting the suggestion that the nanowires mainly consist of CoPt domains.

We also tried to synthesize Fe−Pt nanowires, using $(NH_4)_2Fe(SO_4)_2$ and K_2PtCl_4 (final concentration of 3 mM each), and successfully produced a long nanowire inside the TMV central channel (see the Supporting Information, Figure S5). These nanowires showed clear lattice fringes, but the elemental ratio of Fe:Pt was 1:3, which indicates that the alloy is $FePt_3$. We hope to produce FePt (and other) nanowires using different ion concentrations and combinations.

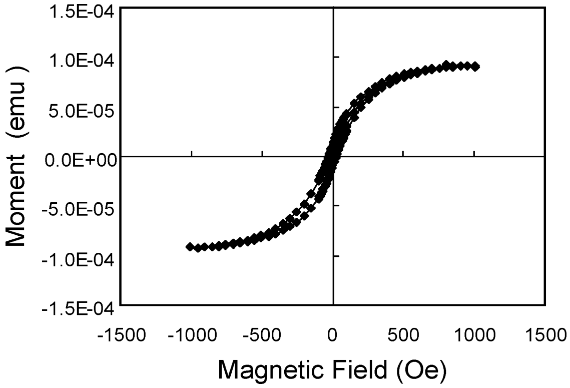

Figure 4. Magnetometry measurement of the nanowires produced in TMV central channel using 9 mM Co^{2+} and 3 mM Pt^{2+}.

In conclusion, we have demonstrated the synthesis of CoPt, $CoPt_3$, and $FePt_3$ nanowires using TMV, with a reducing agent and ultrasonication. Ultrasonication enhanced the growth of the nanowires inside the TMV central channel. To the best of our knowledge, this is the first report in which bimetallic and ferromagnetic nanowires have been produced using TMV. This method provides a convenient route to produce Co−Pt and Fe−Pt alloy nanowires of uniform diameter, which have various potential applications in nanotechnology.

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Supporting Information Available: Biominralization initiated by TMVs, control experiments of Co−Pt nanowire synthesis, Co−Pt nanowire synthesis with various Co^{2+}/Pt^{2+} ratio, Fe−Pt nanowire synthesis, and magnetometory measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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