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A novel synthesis of ultrathin $CoPt_3$ nanowires by dealloying larger diameter $Co_{99}Pt_1$ nanowires and subsequent stress-induced crack propagation

Lifeng Liu [a,*], Ole Albrecht [b], Eckhard Pippel [a], Kornelius Nielsch [b], Ulrich Gösele [a,1]

[a] Max Planck Institute of Microstructure Physics, D06120 Halle (Saale), Germany
[b] Institute of Applied Physics, Hamburg University, Jungiusstrasse 11, D20355 Hamburg, Germany

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ABSTRACT

A novel approach to the fabrication of ultrathin $CoPt_3$ nanowires with a diameter of a few nanometers has been developed, by taking advantage of the volume shrinkage and formation of nanoporous structures upon dealloying electrodeposited $Co_{99}Pt_1$ nanowires (28 nm in diameter), followed by an ultrasonication treatment. The as-produced ultrathin $CoPt_3$ nanowires have an average diameter of 5 nm and lengths of up to 10 μm, and are found to be ferromagnetic at room temperature.

1. Introduction

Nanowires (NWs) composed of various materials such as metals, semiconductors and polymers, have been one of the most attractive research subjects in recent years because of their unique physical and chemical properties and their potential applications in future nanodevices and nanocircuits [1]. It has been well established that the physical and/or chemical properties of NWs change with decreasing diameters. For ultrathin NWs whose diameter is less than 10 nm, quantum confinement effects are expected, and surfaces or local crystal structures turn out to be important for determining the properties of the NWs [2]. Experimental studies of ultrathin NWs can help to clarify various theoretical predictions which have been made based on very thin wires [3]. In terms of device applications, the use of ultrathin NWs is conducive to the improvement of device density. A variety of methods has been developed so far to prepare ultrathin NWs, including solution phase reduction [4], oxide-assisted growth [5], vapor transport [6], and template-assisted electrodeposition [7]. More recently, several groups independently reported the synthesis of sub-5 nm Au NWs by reducing $HAuCl_4$ with oleylamine [8–12], and some review papers regarding this finding were also published [13,14]. Nevertheless, the fabrication of ultrathin NWs still remains challenging.

Here, we report on a novel approach for the fabrication of ultrathin NWs, which takes advantage of the volume shrinkage and formation of nanoporous structures upon dealloying template-assisted electrodeposited $Co_{99}Pt_1$ NWs (28 nm in diameter) [15], followed by an ultrasonication treatment during which brittle fracture occurs by cracks, propagating along the axes of the resulting nanoporous $CoPt_3$ NWs. In this way, the dealloyed nanoporous $CoPt_3$ NWs can cleave into several ultrathin components with an average diameter of 5 nm and lengths up to 10 μm.

2. Experimental

The porous anodic aluminum oxide (AAO) membranes we used were prepared by a two-step anodization process, as described previously [16]. The pore diameter and thickness of as-obtained AAO membranes were around 28 nm and 50 μm, respectively. Before electrodeposition, a Au layer was sputtered on one side of the through-hole AAO. The Au-coated AAO and a platinum mesh were used as working and counter electrodes, respectively, and a Ag/AgCl electrode was utilized as a reference. The electrodeposition was controlled by a 263A potentiostat/galvanostat (Princeton Applied Research). The electrolyte consisted of 0.5 M $CoSO_4$, 0.01 M K_2PtCl_6 and 0.485 M H_3BO_3. The deposition was conducted at −1.0 V (vs. Ag/AgCl) at room temperature.

The AAO membranes embedded with $Co_{99}Pt_1$ NWs were then immersed into 10 wt.% H_3PO_4 solution at 45 °C overnight. In this process, the AAO was completely dissolved by the acid and the $Co_{99}Pt_1$ NWs were meanwhile subjected to dealloying upon the etching of H_3PO_4, leading to the formation of nanoporous $CoPt_3$ NWs.

* Corresponding author. Tel.: +49 345 5582902; fax: +49 345 5511223.
E-mail address: liulif@mpi-halle.de (L. Liu).
[1] In memory of Prof. Ulrich Gösele.

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Afterwards, the porous NWs obtained were centrifuged and washed in deionized water and ethanol several times, and then subjected to ultrasonication treatment in an ultrasonicator (Banoelin SONOREX, 320 W, 35 kHz) for 20 ~ 40 min in order to obtain the ultrathin NWs.

To perform TEM characterization, the dealloyed $CoPt_3$ NWs, by now mostly split into ultrathin wires, were dispersed onto holey carbon-coated TEM grids. The conventional TEM investigations were carried out with a JEOL JEM-1010 microscope. The EDX and high resolution TEM analyses were performed in a FEI TITAN 80-300 microscope. To measure the magnetic properties, the powder of the ultrathin NWs was first mixed with Apiezon N Grease, and the mixture was then filled into a gelatine capsule for the measurements. Zero-field cooling and field cooling (ZFC/FC) magnetization curves (magnetic moment vs. temperature) were recorded with an applied field of 500 Oe. Magnetic hysteresis loops were measured at both 10 K and 300 K, with an applied field up to 10 kOe. The measurements were carried out in a superconducting quantum inference device magnetometer (SQUID, MPMS XL).

3. Results and discussions

The preparation of ultrathin $CoPt_3$ NWs is schematically outlined in Fig. 1. This process, in some sense, can be viewed as a nanoscale "top-down" fabrication process. The larger diameter $Co_{99}Pt_1$ NWs served as starting materials and the dealloyed nanoporous $CoPt_3$ NWs acted as "precursors" for the production of ultrathin NWs.

Fig. 2 shows a representative transmission electron microscopy (TEM) picture of the nanoporous $CoPt_3$ NWs resulted from the dealloying of $Co_{99}Pt_1$ NWs. It is evident that the NWs are characterized as porous skeletons with pore size of 1–5 nm and ligament width ranging from 2 to 8 nm. A notable feature is that the average diameter of the resulting porous NWs has been reduced to 13 nm after dealloying, compared to 28 nm of the original $Co_{99}Pt_1$ NWs. This shrinkage behavior was also observed previously in bulk nanoporous Au (NPG) and NPG films [17] as well as NPG NWs [18], and was proposed to arise from the plastic deformation by homogeneous slip in small ligaments or by climb of lattice dislocations.

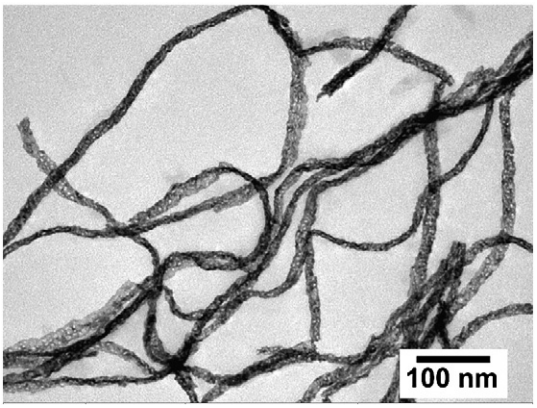

Fig. 2. Representative TEM micrograph of as-dealloyed nanoporous $CoPt_3$ nanowires.

Fig. 3a shows an overview TEM micrograph of as-produced ultrathin $CoPt_3$ NWs. It can be seen that these NWs are flexible and their lengths vary from several microns to more than ten microns. A representative single wire is displayed in the inset of Fig. 3a, the diameter of which is only 3.8 nm. The electron diffraction pattern of the ultrathin NWs only reveals a single set of diffraction rings, which can be identified as fcc $CoPt_3$ alloy. Extensive TEM observations manifested that upon 20 min ultrasonication, the yield of ultrathin NWs can reach about 85%. Unlike other solution phase synthetic methods by which thick wires, large nanoparticles and plates could also be produced [8–12], the side-products by our method are only a few uncleaved nanoporous NWs. The outer surfaces of most ultrathin NWs were found to be rugged because the ultrathin NWs were originally the ligaments of the nanoporous $CoPt_3$ NWs. Fig. 3b clearly illustrates the cleavage of the nanoporous $CoPt_3$ NWs. The selected nanoporous NWs (black circles) were observed to split into three and four continuous ultrathin NWs, respectively. Energy dispersive X-ray

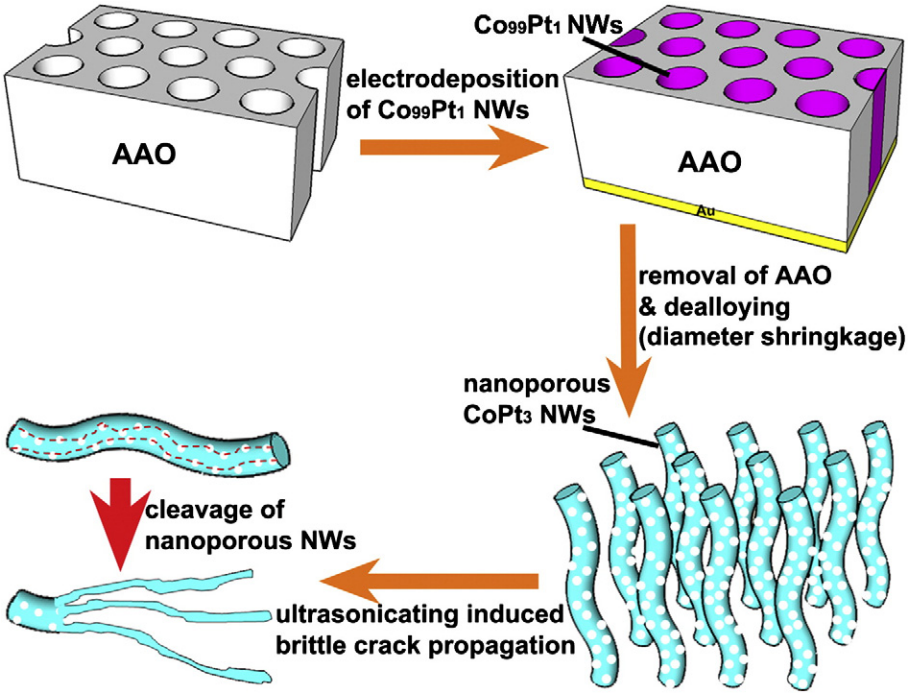

Fig. 1. Schematic illustration of the fabrication of ultrathin $CoPt_3$ nanowires.

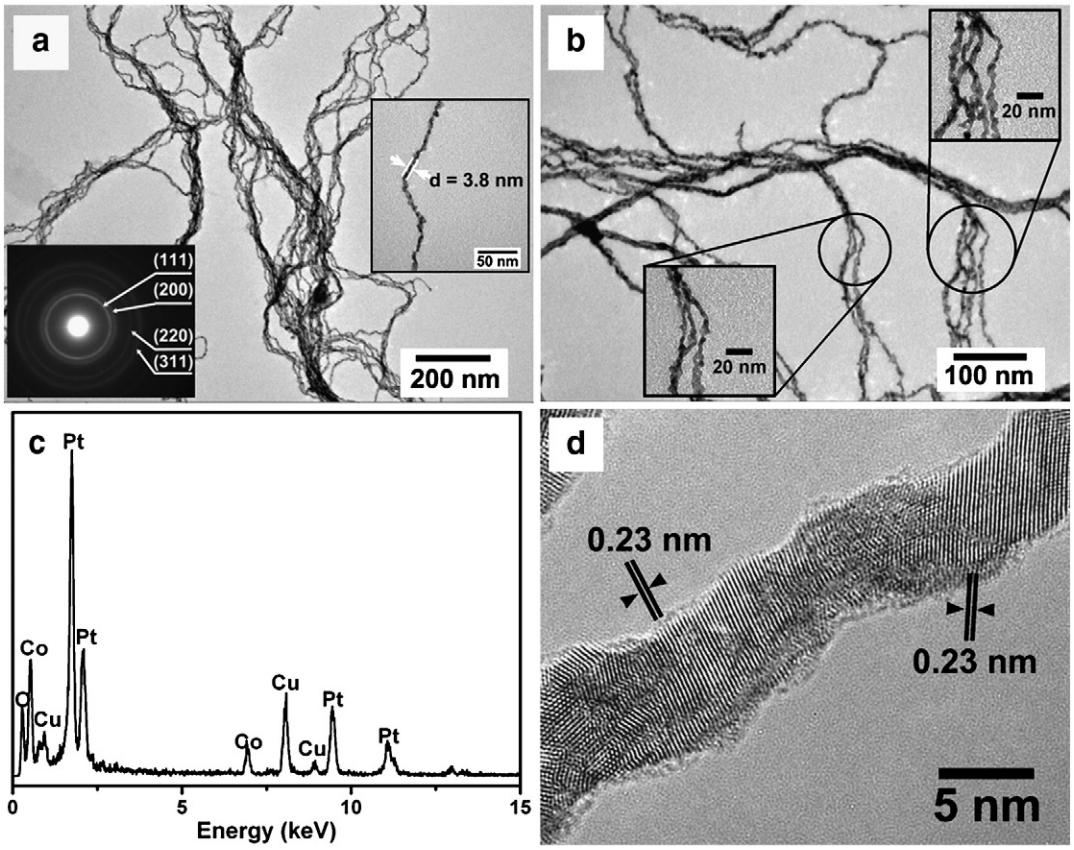

Fig. 3. TEM characterization of ultrathin $CoPt_3$ nanowires. (a) Overview TEM micrograph. Inset: a representative nanowire and a electron diffraction pattern; (b) TEM micrograph showing ultrathin nanowires resulting from the cleavage of nanoporous $CoPt_3$ nanowires; (c) EDX spectrum; (d) HRTEM micrograph.

(EDX) spectrum confirms that these ultrathin NWs, as their "parents" (i.e. nanoporous NWs), consist of Co and Pt (Fig. 3c), and their atomic ratio is 26:74 on average. Further EDX analyses indicates that the surfaces of the ultrathin $CoPt_3$ NWs are Pt-enriched, which is in accord with the dealloying model [19] and our previous study on nanoporous $CoPt_3$ NWs [15]. High resolution TEM (HRTEM) investigations manifest that the ultrathin NWs are polycrystalline (Fig. 3d). The visible interplanar spacing is about 0.23 nm, corresponding to that of the $CoPt_3$ (111) plane family (JCPDS 29-0499). Moreover, it was found that there exist many defects and dislocations inside the NWs, which may arise from the dealloying treatment and subsequent mechanical ultrasonications.

The dissolution induced cracking upon the dealloying has been studied for several decades [20–24]. In the context of corrosion protection, the generation and propagation of cracks are negative effects that may degrade the mechanical stability of the specimens, and therefore should be inhibited and avoided. However, we demonstrated here that the cracks and their propagation can be utilized positively and are favorable for the fabrication of ultrathin NWs. It is believed that the cracks may preferentially be initiated at some "pre-crack" positions with dislocations or heavily curved parts of inner pores (which may result from the volume contraction during the dealloying). Surface stress-induced compressive yielding may be the initiator of the cracks because it often exists in ligaments with diameters of several nanometers [17]. After nucleation of cracks, an external mechanical load (i.e. ultrasonication) will assist the propagation of cracks. It is assumed that the surface stress-induced cracking and the crack propagations might be more pronounced in the nanofibrous form of the dealloyed porous materials. However, the fact that the cracks propagate preferentially along the wire axes remains unclear. It is assumed that this may be related to the crystallographic orientations of the porous NWs [24], but this point needs to be further examined in future studies.

The magnetic properties of ultrathin $CoPt_3$ nanowires were studied by a superconducting quantum interference device (SQUID) magnetometer. Fig. 4a shows the zero-field cooling (ZFC) and field cooling (FC) magnetization curves of the ultrathin NWs. It is seen that the ZFC and FC curves do not overlap up to 350 K, which means that these ultrathin NWs may remain ferromagnetic up to 350 K. Fig. 4b reveals the magnetic hysteresis loops measured at 10 K and 300 K, respectively. Unambiguous hysteresis behavior is observed at 300 K, confirming the ferromagnetism of the as-prepared ultrathin $CoPt_3$ NWs. The coercivity of the ultrathin NWs is 525 Oe at 10 K and 88 Oe at 300 K, and their squareness is 0.45 at 10 K and 0.14 at 300 K, respectively. It is expected that the density of magnetic nano-devices could be greatly improved if these ultrathin $CoPt_3$ NWs are used as individual units [25]. In addition, the co-existence of magnetism and excellent electrocatalytic performance [15] in the ultrathin NWs may also potentially allow the study of interactions between magnetism and catalysis [26].

4. Conclusions

In summary, we demonstrated that surface stress-induced cracking in porous $CoPt_3$ nanowires can be used to fabricate ultrathin nanowires with a diameter of a few nanometers. These ultrathin $CoPt_3$ nanowires were found to be ferromagnetic at room temperature. Considering the universality of the dealloying behavior in binary alloys upon acid attacks and the universal existence of stress-induced cracks in the dealloyed nanoporous materials, the present method can be readily extended to prepare other ultrathin alloy nanowires, such as Ni–Pt and Co–Pd.

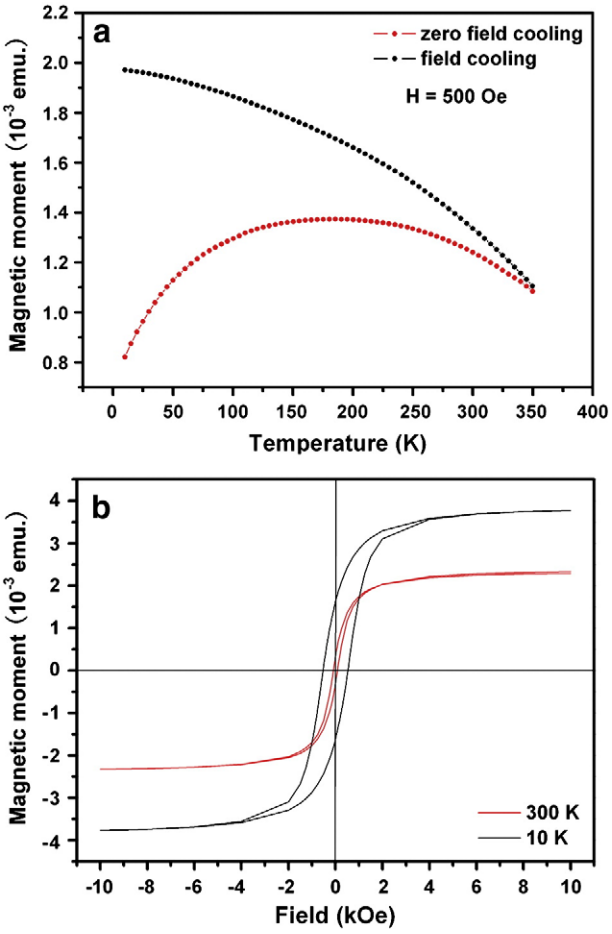

Fig. 4. Magnetic properties of ultrathin $CoPt_3$ nanowires. (a) Zero-field cooling (ZFC) and field cooling (FC) magnetization curves. (b) Magnetic hysteresis loops measured at 10 K and 300 K, respectively.

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