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Metallic nickel nanorod arrays embedded into ordered block copolymer templates

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Abstract

We report on metallic Nickel nanorods prepared by utilizing a mask of ordered nanostructured hollow channels in a block copolymer matrix. These polymeric templates were formed by a self organized process in block copolymer supramolecular assemblies. Nickel was filled into with two different techniques, electrodeposition and washing in. We monitor the formation process of these nanorods by means of atomic force microscopy and synchrotron radiation soft X-ray based photoelectron emission microscopy. The oxidation state of the nickelrods is evaluated with X-ray absorption spectroscopy and X-ray photoelectron spectroscopy at the Ni L edges and lateral distributions of the Ni nanorods were detected with micrometer resolved X-ray absorption spectroscopy. The finding is that the Ni rods were metallic despite their preparation under ambient conditions, inside the particles no hints for NiO complexes were found. This indicates that the polymer protects Ni nanoparticles against oxidation.

Keywords: Nanostructures; Nickel; PEEM; AFM; Self assembly; Polymers

1. Introduction

Fabrication of transition metal nanoparticles is a well established field in modern surface science. A steadily growing number of publications witnesses tremendous effort stimulated by application of these compounds in future spintronic devices [1]. By downsizing transition metal (TM) clusters large localized magnetic states were found in Fe, Co, and Ni, bridging the gap between their descriptions with Hund's rules for single atoms to complex correlated many body effects in the solid state [2,3]. Normally, these effects are strong for the metallic compounds and vanish for insulating TM oxides [4]. But fabrication and storing of metallic TM nanoparticles often requires ultra high vacuum conditions, unsuitable for everyday application.

In this article we address fabrication of metallic Ni nanoparticles in the size below 10 nm by using a protective polymer matrix to prevent for oxidation. Another advantage offers the formation of long range ordered templates in the nanometer regime, allowing a nearly crystal like superstructure of the particles. By using self assembly approach (SMA) in block copolymers hollow vertically cylindrical nanostructures can be achieved [5,6]. Into these, Ni nanorods were prepared by washing or electrodeposition. The spatial distribution of the Ni is determined with synchrotron radiation based PEEM (photoelectron emission microscopy) at the Ni L edge. The electronic structure and the oxidation state is monitored by means of micrometer resolved X-ray absorption spectroscopy (XAS). XAS is considered to be an experimental technique which is well suited to probe oxidation states of nanostructures, because of its higher probing depth with respect to X-ray photoelectron spectroscopy (XPS), it is possible to resolve not only surface oxygen contamination [7]. The results show that inside the nanocylinders metallic nickel is found.

To ensure that Ni agglomerate within the nanochannels several techniques such as scattering experiments like grazing incidence small angle X-ray scattering (GISAXS) measurements were performed at the BW4 at HASYLAB (Hamburg/Germany) before. The GISAXS curves clearly signal significant differences in the scattering curves for different alignments of the Ni and it was concluded, that the Ni nanoparticles were

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perfectly embedded into the BCP template and no hints for large Ni clusters on top or below the BCP were found [6]. This interpretation is inline with the following AFM images, shown in the results section.

2. Experimental

XAS spectra were taken in the total electron yield mode with a Focus IS PEEM at the BESSY beamline U49/2 PGM 2 in Berlin /Germany. These electrons are accelerated on the phosphorous screen of the PEEM and the light emission of chosen areas is detected when the photon energy is scanned through the Ni absorption edge. These spatially resolved emission of electrons is directly associated to the absorption of the sample [9] and is therefore considered to be an X-ray absorption technique in the micrometer regime. The spectra and the PEEM data contain of original raw data, no smoothing or picture manipulations were applied.

XPS measurements were recorded with a hemispherical electron analyzer from Omicron (EA 125). X-ray photons were delivered from a commercial Mg K_α source.

Scanning probe investigations were performed by a Dimension 3100 (Digital Instruments, Inc., Santa Barbara) scanning force microscope AFM and CP (Park Scientific Instrument, Inc) in the tapping mode. The tip characteristics are: spring constant 1.5–3.7 N/m, resonant frequency 45–65 Hz, tip radius about 10 nm.

Ordered nanostructured thin polymer films have been fabricated from the SMA based on poly(styrene-block-4-vinylpyridine) (PS-PVP) and 2-(4′-hydroxybenzeneazo)-benzoic acid (HABA). They consist of cylindrical nanodomains formed by P4VP-HABA associates surrounded by PS, Fig. 1(a) and (b). The alignment of the structures was found to be out of plane [5]. The alignment of the cylindrical nanodomains is insensitive to the composition of the surface due to the self-adaptive behaviour of the supramolecular PVP-HABA assembly [5,6]. Extraction of HABA with selective solvent results in nanomembranes with hollow channels aligned perpendicular to the surface (Fig. 1(b)). The thickness of the polymer films was measured by SE400 ellipsometer (SENTECH Instruments GmbH, Germany) with 632.8 nm laser at 70° incident angle and determined to 20 nm.

Ni, purchased from Aldrich, was washed into the nanotemplate or Ni was loaded into the cylindrical channels of the membrane via electrodeposition in the galvanostatic mode using Autolab/PGSTAT30 with the Watts bath, an Ag/AgCl reference electrode and a platinum wire counter electrode.

All samples were exposed to air all the time and stored under ambient conditions and measured one to two weeks after preparation.

In this article we use several samples to verify obtained results. For PEEM, XAS and XPS we investigate samples with and without Ni nanorods always embedded into the polymer, characteristic results are presented. Their general look corresponds to Fig. 1(b), where dark grey areas are associated to Ni nanorods, the bright grey areas show the remaining nanotemplate, formed by PVP blocks. Only for AFM we use a sample, were the block copolymer matrix is removed and free standing

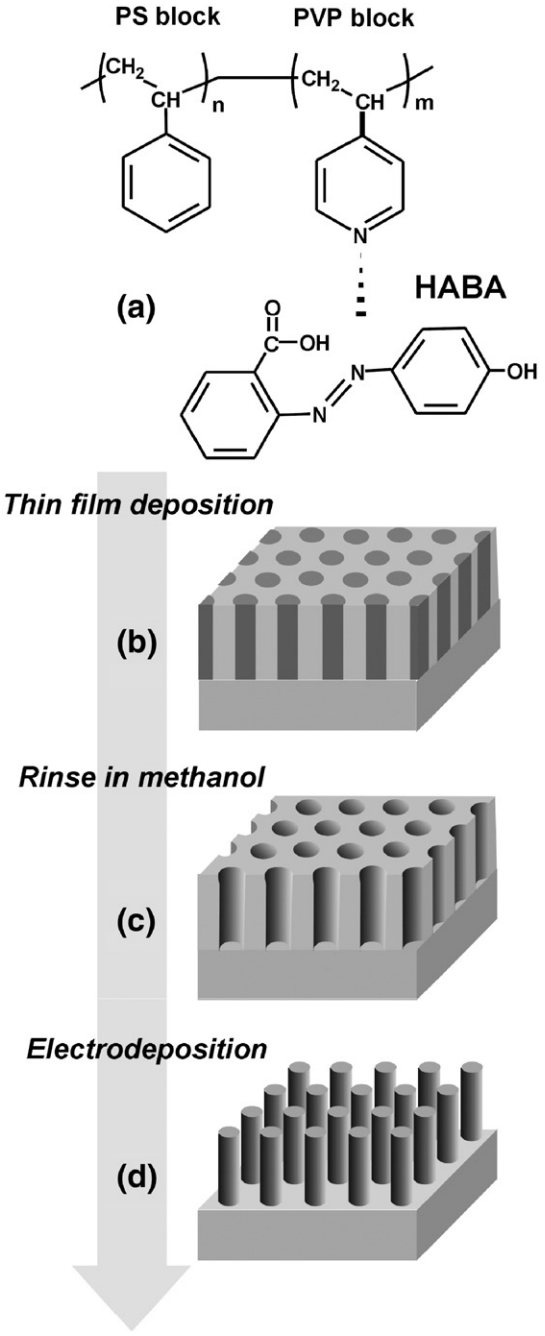

Fig. 1. The SMA based approach for metal nanorod array fabrication: chemical composition (a), microphase separation in thin films of SMA (b), nanotamplate (c), array of nanochannels/nanorods (d).

Ni nanorods are investigated (Fig. 1(d)). This becomes necessary, because the limited space inside the nanopores makes AFM scans impossible to penetrate to the top of the Ni rods.

3. Results

We studied the local geometric arrangement of the Ni nanoparticles with atomic force microscopy. In Fig. 2 an AFM image is shown for standing Ni rods to determine the lateral distribution on the submicrometer scale. The Ni nanorods were electrodeposited through a SMA mask onto a Si template and