



Templated synthesis of pure and bimetallic gold/platinum nanotubes using complementary seeding and plating reactions



Falk Muench^{a,*}, Laith Hussein^b, Tobias Stohr^a, Ulrike Kunz^a, Sevda Ayata^c, Ingeborg Gärtner^d, Hans-Joachim Kleebe^a, Wolfgang Ensinger^a

^a Technische Universität Darmstadt, Department of Materials and Earth Sciences, Alarich-Weiss-Straße 2, 64287 Darmstadt, Germany

^b Technische Universität Darmstadt, Department of Chemistry, Eduard-Zintl-Institute, Alarich-Weiss-Straße 12, 64287 Darmstadt, Germany

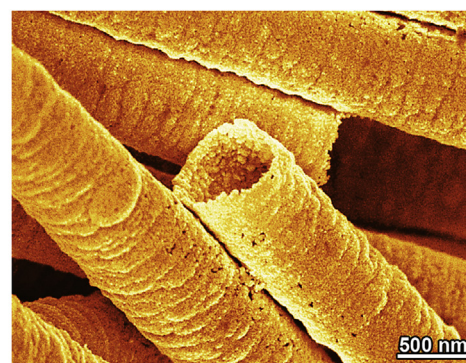
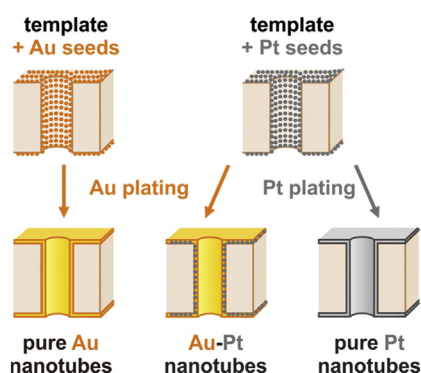
^c Dokuz Eylul University, Science Faculty, Department of Chemistry, Tinaztepe Kampusu, Buca, 35160 Izmir, Turkey

^d Technische Universität Darmstadt, MPA/IfW Darmstadt, Grafenstraße 2, 64283 Darmstadt, Germany

HIGHLIGHTS

- Electroless deposition of Au/Pt nanotubes in ion-track-etched polymer templates.
- Nanotube composition controlled akin to seed-mediated nanoparticle synthesis.
- Non-conventional sensitization and activation to avoid Sn, Ag and Pd impurities.
- Strictly monometallic Au/Pt as well as bimetallic Au-Pt nanotubes are realized.
- Nanomaterial functionality (e.g. in catalysis) can be enhanced by composition tuning.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 15 January 2016

Received in revised form 2 August 2016

Accepted 22 August 2016

Available online 23 August 2016

Keywords:

Polymer swelling

Nanoparticles

Electroless plating

Template

Metal nanotubes

Heterogeneous catalysis

ABSTRACT

The application of electroless plating to porous template membranes displays an important route towards one-dimensional metal nanostructures such as nanotubes. For this reaction class, activation pretreatments are required to introduce catalyst seeds, which initiate surface-selective metal deposition from the metastable plating baths. Hitherto, these pretreatments are performed as a means to an end to ensure reliable metal film nucleation, and introduce often undesired contaminations. In this work, we demonstrate that the seeding step can be recognized as a synthetic tool to purposefully adjust the chemical composition of electrolessly plated nanomaterials. By consecutive application of several interfacial reactions (polymer swelling, reducing agent absorption, metal nanoparticle nucleation, autocatalytic metal deposition), we fabricate gold-platinum nanotubes of well-defined composition. Aside strictly monometallic gold and platinum nanotubes, bimetallic nanotubes are produced which consist of platinum nanoparticles embedded in gold walls. As shown in the electrooxidation of formic acid, the nanotube composition has a pronounced impact on the properties of the resulting materials and can be used to enhance the catalyst performance. The outlined strategy provides a versatile route towards sets of compositionally varying metal nanostructures and allows to examine and to exploit multi-element synergies.

© 2016 Elsevier B.V. All rights reserved.

* Corresponding author.

E-mail address: muench@ma.tu-darmstadt.de (F. Muench).

1. Introduction

Metal nanotubes (NTs) display an emerging class of one-dimensional nanostructures with unique magnetic, catalytic, mechanical, optical and electrochemical properties [1–8]. These materials possess a wide range of valuable functionalities and thus can be applied in various fields, including electrochemical energy conversion [1,2,9], heterogeneous catalysis [3,10], electroanalysis [4,11], theranostics [5], selective molecular transport [12] and surface enhanced Raman spectroscopy [13]. Compared to more conventional morphologies such as nanoparticles (NPs), metal NTs can provide enhanced performance [4,9,11,14,15]. For instance, due to their one-dimensional and hollow morphology, NTs result in a more open-porous structure of a catalyst layer, and ensure the presence of continuous conduction and diffusion pathways. Also, well-defined and coherent NTs are less prone to degrading mechanisms such as particle detachment or aggregation. Accordingly, when comparing Au NTs with Au NPs in electrocatalytic applications, improved catalyst utilization, quicker response, and higher activity have been found [4,15].

The properties of nanomaterials strongly depend on their shape, size and chemical composition. Thus, flexible routes towards metal NTs of well-defined morphology and composition are sought after, enabling both the investigation of fundamental property relationships and performance optimization in given applications [5,14]. Due to the striking discrepancy between the symmetric structure of most metals and the hollow, highly anisotropic morphology of NTs, spontaneous metal NT formation is only observed in exceptional cases (e.g. with Bi, which crystallizes in a pseudolayered structure [16]). The vast majority of syntheses relies on soft [17,18], sacrificial [3,5] or hard [2,4,6] templates to induce the tubular shape. Hard templates such as porous membranes provide an exceptional degree of synthetic freedom and thus are especially important for NT fabrication. For instance, using the ion-track-etching technology, the diameter, orientation, connectivity and density of the resulting nanostructures can be independently adjusted [4].

In the templated synthesis of metal NTs, different deposition techniques such as electrodeposition [8], electroless plating [9,10] or evaporation [19,20] can be employed. Among these options, electroless plating is particularly appealing due to several reasons: (i) The method does not require complex instrumentation and is compatible with non-conducting, complex shaped and heat sensitive substrates [21]. During NT deposition, a template membrane is simply immersed in a plating solution, rendering the process facile, cost-efficient and scalable. (ii) Despite the stunning simplicity of electroless plating, it is very flexible and yields high quality products. Well-defined NTs consisting of various metals can be obtained [4], and the wall thickness can be easily adjusted by the plating time [22]. (iii) Electroless plating leads to conformal metal deposition, i.e. a metal film continuously grows on the whole template surface. In the pores of the template, this deposition mechanism favors the formation of high aspect ratio NTs. Due to the limited metal infiltration, physical vapor deposition methods tend to produce short NT stumps [19,20]. Electrodeposition often requires additional steps (e.g. the predeposition of wires in the template pores [8,23]) to obtain tubes instead of wires.

However, in order to initiate the electroless plating process, templates have to be covered with catalytic seeds by so-called activation reactions [24,25]. Conventionally, this is achieved with Ag or Pd NPs, which are deposited on the template surface by reducing Ag(I) or Pd(II) salts with Sn(II) [22,25]. The Sn, Ag and Pd species from the template activation remain in the final materials and affect their properties. For instance, Sn can negatively affect the catalytic activity of electrolessly plated Pd catalysts [26]. Moreover, the unexpected activity of Au NTs in the oxidation of CO might stem from Ag residues [27]. Often, additional etching steps are applied to

remove such contaminations from the plated nanomaterials [28]. Accordingly, it is important to provide alternative approaches for the electroless synthesis of metal NTs, in which the nanostructure composition can be freely adjusted and is not restricted by impurities that could be generated during activation.

In this study, we present a general strategy for the electroless deposition of compositionally varying sets of metal NTs, which does not rely on conventional activation. The applied seeding reaction is based on dimethylaminoborane, which is a versatile reducing agent capable of producing many types of metal NPs such as Ag, Au or Pt [24,29]. Likewise, electroless plating can be used to deposit conformal nanofilms consisting of a wide range of metals, including Rh, Cu, Ag, Au, Ni, Pd and Pt [4,30,31]. To demonstrate our approach, we chose the catalytically relevant Au/Pt system [32–39] for a systematic study. By using pure NP seeds and applying appropriate plating reactions, we show how strictly monometallic Au and Pt as well as mixed Au-Pt NTs can be prepared. This allows adjusting the catalytic activity of the NTs, which was confirmed in the electrooxidation of formic acid, a reaction highly sensitive to the surface atomic ratio and distribution of Au and Pt [36–38].

2. Materials and methods

2.1. Chemicals, general procedures

Purified water (>18 M Ω cm at room temperature) was employed in all procedures. Laboratory glassware was cleaned with *aqua regia* prior to use. The following chemicals were used as received: 4-(dimethylamino)pyridine (Fluka, puriss.), borane dimethylamine complex (Aldrich, 97%), dichloromethane (Roth, >99.8%), disulfiteaurate solution (Schütz Dental GmbH, EL-Form electroplating solution, 15 g Au L⁻¹), ethanol (Brenntag, 99.5%), ethylenediamine (Roth, >99.5%), formaldehyde solution 36.5% stabilized with methanol (Fluka, puriss. p.a.), formic acid (Merck, >99%), gold (III) chloride hydrate (~50% Au basis, Aldrich), hexachloroplatinate solution 8% in water (Fluka), hydrazine monohydrate 80% in water (Merck, for synthesis), methanol (Aldrich, 99.8%), potassium tetrachloroplatinate (II) (Aldrich, \geq 99.9%), sodium hydroxide (Grüssing, 98%), sodium sulfite (Merck, >99.9%), sulfuric acid (0.5 M standard volumetric solution, Applichem).

2.2. NT fabrication

A scheme of the complete process can be found in Fig. 1. For the template preparation, circular polymer samples (diameter: 5 cm) were punched out of commercial polycarbonate foil (Makrofol KG, nominal thickness: 10 μ m) and subsequently irradiated with swift heavy ions at the GSI Helmholtz Centre for Heavy Ion Research (Darmstadt). The irradiation was performed perpendicular to the foil surface (e.g. with Au ions, kinetic energy: 11 MeV/nucleon, fluence: 10⁸ ions/cm²). Subsequently, the latent tracks were etched out in stirred soda lye (5 M, 50 °C, 20 min etching time), resulting in the formation of continuous pores (Fig. 1, process i). The as-obtained template membranes were thoroughly washed with water, dried and coated with Au or Pt NPs using an adapted version of a two-step sensitization/activation reaction [24]. First, the polymer membranes were sensitized by immersing them in a solution of dimethylaminoborane (2 M in methanol) for 30 min. Subsequently, the templates were washed with water, and transferred to activation solutions. Depending on the desired NP type, either an aqueous solution of AuCl₃ (59 mM) or K₂PtCl₄ (59 mM) was used (reaction time: 30 min). After activation (Fig. 1, process ii or iii), the templates were stored in ethanol for 60 min to remove residual reducing agent, washed with water and subjected to electroless plating (Fig. 1, process iv or v). The plating

Download English Version:

<https://daneshyari.com/en/article/6978202>

Download Persian Version:

<https://daneshyari.com/article/6978202>

[Daneshyari.com](https://daneshyari.com)