Deposition of Nanofilms inside a Polymer Template: Formation of Metal Nanotubes

Falk Muench, Stefan Lauterbach, Hans-Joachim Kleebe, and Wolfgang Ensinger

Department of Materials- and Geoscience, Technische Universität Darmstadt, Petersenstraße 23, 64287 Darmstadt, Germany

(Received 3 August 2012; Accepted 31 August 2012; Published 27 October 2012)

Given sufficient synthetic control, electroless plating is a suitable method for the fabrication of precisely defined nanomaterials. This study focuses on requirements which have to be met for the homogeneous and conformal electroless metal deposition within ion track etched polymer templates, allowing the fabrication of high aspect ratio metal nanotubes. Namely, the effects of (i) the seed density of the substrate, (ii) the surface-selectivity of the plating reaction and (iii) the deposition speed and the grain size of the resulting deposit are examined, and strategies to modify these characteristics in order to improve nanotube formation are illustrated. With optimized procedures, Ag, Au and Pt nanotubes were obtained. As an application example, metal nanotube membranes were utilized as flow-through microreactors, catalyzing the reduction of 4-nitrophenol with sodium borohydride. By partial exchange of Ag precursor structures with Pt, roughened Ag–Pt nanotubes with significantly improved activity were obtained. [DOI: 10.1380/ejssnt.2012.578]

Keywords: Electroless plating; Polycrystalline thin films; Nanostructure chemistry, processing and fabrication; Metal nanotubes; Catalysis

I. INTRODUCTION

Electroless plating displays a versatile route towards the deposition of polycrystalline metal films on substrates of variable composition and shape [1–5]. It is an industrially relevant reaction class which utilizes the surface-selective reduction of a dissolved metal precursor by a chemical agent. Selectivity is achieved by choosing a metastable redox pair which does not react in the bulk solution, but only on catalytically active surfaces. As the obtained metal films are active in the plating reactions, the deposition continuously carries on by autocatalysis. Key advantages of electroless plating are the possibility to cover complex shaped [4] as well as non-conductive substrates [5] and to realize very homogeneous films with excellent properties [1, 2].

Typically, this technique is used for the surface refinement of work pieces, e.g. to create electrically conducting films [1, 6] or to enhance wear and corrosion resistance [1, 2]. In these applications, besides other important issues such as bath stability and film adhesion, high deposition rates are demanded to accelerate production [3].

Electroless plating can also be used to fabricate precisely defined metal nanomaterials [4, 7–15]. Here, a shift in the synthetic requirements takes place, and nanoscale film homogeneity and highly controlled deposition kinetics become essential. Among electrolessly plated metal nanomaterials, nanotubes (NTs) [9–15] are of appreciable interest due to their special morphology and often enhanced properties. These benefits led to their manifold implementation, e.g. as permselective channels [9], flowthrough reactors [10, 11], microfluidic devices [12], heterogeneous catalysts [13, 14] or electrochemical sensors [15].

The electroless synthesis of metal NTs is usually based on the deposition on a template with channel-shaped pores, such as membranes consisting of ion track etched polymers [9–15] or anodized alumina [16]. This method combination enables extensive control over the product parameters (e.g., metal type, NT diameter, NT shape, wall thickness, NT density). However, the limited mass transport to the central channel regions causes reagent depletion within the templates, leading to varying plating rates which impede homogeneous metal deposition alongside the pore walls [11, 17, 18]. Therefore, contrary to the aforementioned case, slow reaction rates are desired as they facilitate NT formation.

In this study, we demonstrate how different reaction characteristics in electroless plating (seed density, nucleation behavior, deposition rate, particle size) can prevent NT formation and present synthetic strategies to overcome these problems. As an application example, arrays of metal NTs were used as catalysts for the reduction of 4-nitrophenol by sodium borohydride [10, 11, 16, 19].

II. EXPERIMENTAL

A. General, chemicals

Glassware was cleaned with aqua regia prior to use. All solutions were freshly prepared. Milli-Q water (> 18 MQ) was employed in all procedures. The following chemicals were applied without further purification: 4-(dimethylamino)pyridine (Fluka; puriss.); AgNO₃ (Grüssing, p.a.); CH₂Cl₂ (Sigma Aldrich, puriss. p.a.); ethanol (Brenntag, 99.5%); ethylenediamine (Fluka; puriss.); formaldehyde solution (Schütz (Fluka, puriss. p.a.); NaBH₄ (Merck, for synthesis); NaOH solution (Merck, Aldrich, 99.8%); NaBH₄ (Merck, for synthesis); NaOH solution 32% in water (Fluka, puriss. p.a.); N₂H₄ monohydrate solution 8% in water (Sigma Aldrich); methanol (Aldrich, 99.8%); NaN₄ (Merck, for synthesis); NH₃ solution 33% in water (Fluka, puriss. p.a.); (NH₄)₂SO₃ solution (Schütz

This paper was presented at the 16th International Conference on Solid Films and Surfaces (ICSFSS-16), University of Genoa, Genoa, Italy, 1-6 July, 2012.

Corresponding author: muench@ca.tu-darmstadt.de

Copyright © 2012 The Surface Science Society of Japan (http://www.sssj.org/ejssnt)
FIG. 1: NT fabrication scheme, including 1) heavy ion irradiation, 2) ion track etching, 3) activation and 4) electroless plating. Common problems in NT synthesis concerning the activation and plating steps are displayed in red: A) low seed density, B) homogeneous nucleation, C) high deposition rate and D) large size of the deposited metal particles.

Dental GmbH, 15 g Au 99.9% per liter); potassium sodium tartrate tetrahydrate (Fluka; puriss.); pyridine (Grüssing, purum); SnCl$_2$ dihydrate (Sigma-Aldrich, ACS reagent); trifluoroacetic acid (Riedel-de Haën, > 99%).

B. Nanotube synthesis

Polycarbonate foils (Makrofol® from Bayer Material Science AG, nominal thickness 30 µm) were irradiated with Au ions (energy = 11 MeV per nucleon, fluence = 1×10$^8$ ions cm$^{-2}$) at the GSI Helmholtz Centre for Heavy Ion Research. Subsequently, the foils were etched in stirred NaOH solutions (50°C, 6 mol L$^{-1}$ NaOH, time depending on desired diameter). The as-prepared templates were rinsed with water and dried. Prior to electroless plating, Ag NPs were attached to the template surface by consecutive immersion in a sensitization solution (42 mM SnCl$_2$, 71 mM trifluoroacetic acid in methanol:water = 1:1; 45 min immersion followed by thorough washing of the template with ethanol) and an activation solution (59 mM AgNO$_3$, 230 mM NH$_3$ in water; 3 min immersion followed by thorough washing of the template with ethanol and water). Subsequently, the templates were directly transferred to the plating solutions. To create Ag-Pt NTs, a membrane containing Ag NTs was attached to a membrane filtration holder (Nucleopore® sample kit for diagnostic cytology), and the hexachloroplatinic acid solution was purged through them using a glass syringe.

C. Catalysis

The reaction solution was prepared by mixing a solution containing 4-nitrophenol with a freshly prepared sodium borohydride solution. The final solution contained 8.4×10$^{-4}$ M 4-nitrophenol and a large excess of sodium borohydride (60 mM) to ensure pseudo-first order kinetics. For flow-through catalysis, 3 ml of the solution was pressed through a NT membrane using the setup described in section II.B.

D. Analysis

Scanning electron microscopy (SEM): JSM-7401F (JEOL), 5-10 kV acceleration voltage: The polymer was dissolved with dichloromethane and the metal nanostructures were collected on Si wafer pieces sputter-coated with Au. Transmission electron microscopy (TEM); CM20 microscope (FEI, Eindhoven, The Netherlands), 200 kV acceleration voltage, LaB$_6$ cathode: The NT containing templates were embedded in Araldit 502® (polymerization at 60°C for 16 h) and examined as ultrathin sections (70 nm thickness, Ultracut E ultramicrotome (Reichert-Jung) with a diamond knife (DKK)). In combination with TEM, energy dispersive X-ray spectroscopy (EDS) was performed (Oxford Model 6767 EDS system (England)). UV-Vis spectroscopy (ATi Unicam UV/vis spectrometer UV4): The UV-Vis spectra were recorded using a high scan rate of 240 nm min$^{-1}$ to evade problems caused by the formation of hydrogen bubbles. The observed range was 250-500 nm.

III. RESULTS AND DISCUSSIONS

The electroless fabrication of NTs in ion track etched polymer templates can be summarized as a sequence of redox reactions aiming to achieve conformal metal film growth on the whole template surface, especially inside the channels. Figure 1 contains a scheme of the involved synthetic steps and illustrates common problems which obstruct the formation of homogeneous NTs. First, a polymer foil (e.g. polycarbonate, polyethylene terephthalate or polyimide [20]) is irradiated with swift heavy ions. Due to their large momentum, the ions penetrate the foil on linear tracks, leaving damaged material along their paths. Second, the ion tracks are selectively etched out, leading to the evolution of channels. The shape and diameter of these channels can be adjusted by variation of the etching time and the etchant composition [20]. Third, metal nanoparticles (NPs) are attached to the polymer...
surface. As polymer substrates do not catalyze electroless plating reactions [5], this procedure is required to initiate metal deposition on the substrate surface. In the synthesis of NTs, this is mostly achieved by consecutively dipping the substrates in solutions of Sn(II) and Ag(I) [21]. During the first step (sensitization), Sn(II) ions form surface complexes with the polymer, which reduce the Ag(I) ions in the second step (activation), causing the precipitation of Ag NPs. Finally, the templates are transferred to an electroless plating bath, leading to the formation of metal NTs.

To obtain metal NTs, the activation as well as the plating reactions have to meet certain requirements. Without sufficient activation (ideally, a homogeneous and dense distribution of small, active seeds), electroless plating does not yield regular NTs [21] (see A) in Fig. 1). Several characteristics of the plating reaction can impede NT formation. Ideally, the metal film is slowly deposited only on the template surface, consists of particles of similar size (for narrow tubes, small particles are required) and is very homogeneous. If the metal reduction is not surface-selective and homogeneous nucleation occurs as a side-reaction, uncontrolled particle formation occurs in the bulk solution. The particles precipitate on the template surface and reduce the life-time of the plating bath [22] (see B) in Fig. 1). High deposition rates lead to reagent depletion in the inner template regions and cause wall thickness inhomogeneities [17] (see C) in Fig. 1). In the worst case, the pore openings are clogged before NTs can form inside the template [11]. If the plated film consists of particles which are of similar size as the desired product feature (e.g. NT wall thickness), the morphology cannot be well reproduced (see D) in Fig. 1).

In the following, the outlined obstacles in the electroless synthesis of metal NTs as well as their overcoming will be discussed on the basis of experimental examples.

A. Ensuring sufficient seed density

To evaluate the influence of the activation on NT formation, electroless Ag plating from an ethylenediamine-stabilized Ag(I)-tartrate bath [11] was chosen as this reaction leads to the formation of relatively large particles which easily allow to evaluate the nucleation density of the evolving metal films. The amount of seeds deposited on the polycarbonate template was varied by the number of activation cycles [21, 23]. Besides a regularly pretreated polymer template [17] which was sensitized and activated once, templates with three and five consecutive seeding steps were used. All templates were subjected to electroless Ag plating under identical conditions (17 mM AgNO$_3$, 100 mM ethylenediamine, 120 mM tartrate, pH 11.1, 24 h deposition at 8$^\circ$C). After metal deposition, the template was removed with dichloromethane, and the obtained nanostructures were analyzed with SEM (Fig. 2).

As can be seen, NTs were formed in all cases. However, due to the lower seed density, the walls of the NTs grown in triple (Fig. 2B) and particularly in single activated templates (Fig. 2A) remained porous, and the re-
resulting nanostructures were distinctly fragmented during the polymer dissolution. In the case of fivefold activation, many NTs were found spanning the whole template thickness of approx. 30 μm (Fig. 2C), demonstrating that high seed densities facilitate the formation of robust NTs with closed walls.

B. Suppression of homogeneous nucleation

To illustrate the effects of bath stability on the NT formation, two electroless Pt baths were prepared. The first reaction solution was adapted from the standard electroless plating bath for the synthesis of Au NTs [24] and contained 7.8 mM hexachloroplatinic acid as the metal precursor and 625 mM formaldehyde as the reducing agent. Besides heterogeneous deposition of Pt on the template surface, homogeneous nucleation occurred which was indicated by a slow change of the color of the plating solution color from initially yellow to dark brown.

SEM analysis verified the development of a thin metal film on the template (Fig. 3A, left image). However, in addition to a thin film originating from heterogeneously deposited Pt, irregular particles were formed in the solution (Fig. 3A, right image) which fell on the template and mostly blocked the pore openings (Fig. 3A, left image). Therefore, further Pt deposition inside the template was inhibited, and no well-defined NTs could be obtained.

As the Pt (IV) source is only bound to relatively weak chloro ligands, one possibility to increase the stability of the plating solution is the introduction of suitable ligands which reduce the oxidizing strength of the metal precursor [1]. In the case of Pt, ethylenediamine can be used to continuously reduce the reactivity of hexachloroplatinate by substitution of an increasing number of chloro ligands, leading to the formation of complexes of the composition \( \text{[PtCl}_{6-2x}\text{en}_x]^{(2+2-x)} \) \((x = 0-3)\) [13]. In combination with hydrazine as a reducing agent which is efficiently oxidized on Pt surfaces [25], a metastable plating solution was obtained (7.8 mM hexachloroplatinic acid, 18.7 mM ethylenediamine, 250 mM hydrazine). With homogeneous nucleation completely suppressed, free-standing Pt NTs were deposited inside the polycarbonate template (Fig. 3B).

As electroless reducing agents usually are more effective at high pH values [1, 25], pH adjustment is also an important way to modify the reactivity of plating baths. For instance, in electroless Ag plating, bath stability was increased and the plating rate was reduced by addition of acid [11]. Another important strategy to suppress homogeneous nucleation is to add trace amounts of stabilizers which interfere with the electroless plating reaction, e.g. heavy metal ions, oxo anions or chalcogenide compounds [26].

C. Reduction of the deposition speed and the particle size

For the molding of a template, it is essential that the building blocks (in electroless nanotube synthesis: metal nanoparticles) are below the size of the morphological features to be reproduced. In addition, the deposition reaction must be slow enough to enable sufficient diffusion of the reagents to badly accessible regions of the template.

As ion track etched polymer membranes have a very complex surface structure, these issues are vital for the electroless synthesis of metal NTs. To illustrate the impact of these factors, electroless Au plating from different baths with pH 10.5 was performed. First, a standard Au plating solution [27] containing 7.8 mM disulfite, 125 mM sulfite and 625 mM formaldehyde was applied to a track-etched polycarbonate template (Fig. 4A). Due to the relatively high deposition rate, only a limited amount of Au was deposited within the template, as can be seen by the morphological transition of the nanostructures which formed in the pores. At the pore openings, solid structures are found, which after few micrometers get porous and finally fragment. The fact that not even fragments of well-defined tubular shape could be found is related to the relatively large grain size of this synthesis, which impedes NT formation in narrow pores [17, 28].

To slow down electroless Au plating, additives such as 4-(dimethylamino)pyridine (DMAP) can be used which form adsorbates on the Au films and poison them to a
certain degree, leading to reduced reaction rates [10]. In addition to the effect on the deposition kinetics, the grain size of the deposit can be reduced considerably [10]. Here, we used the stem compound pyridine and its derivative DMAP. The addition of 40 mM of each pyridine to Au plating baths led to a significant and simultaneous reduction of the reaction rate and the particle size. In case of pyridine, free-standing NTs with homogeneous walls and a diameter of approx. 200 nm were easily obtained (Fig. 4B). With DMAP, a more pronounced effect on the Au plating was observed, allowing the fabrication of extremely narrow NTs with diameters of 50 nm, consisting of particles of < 10 nm size. Although these filigree structures partly collapsed upon template removal (Fig. 4C, left image), TEM proved the formation of NTs and confirmed the efficient reproduction of even very small template features in the case of sufficiently reduced particle size (Fig. 4C, right image).

Probably, the stronger interference of DMAP with the Au plating reaction is caused by the mesomeric electron shift of the dimethylamino substituent. Compared to pyridine, the basicity of the endocyclic nitrogen is increased, which enhances bonding to the Au surface and suppression of surface reactions. This reasoning is in accord with results on the phase transfer and protection of Au NPs by different pyridines [29], of which only the strongly basic DMAP led to the formation of stable aqueous colloids.

D. Application of metal NTs as microreactors

Template-embedded metal NTs can be applied as highly efficient microreactors, heterogeneously catalyzing reactions in a solution which flows through them [10, 11]. The reduction of 4-nitrophenol is frequently used as a model reaction to evaluate the performance of metal nanostructures [19]. With this reaction, it was shown that homogeneous metal deposition inside the ion track etched polymer templates is essential to achieve high activities [11].

Here, we demonstrate the addition of a second metal as another strategy to improve the performance of metal NT membranes in flow-through catalysis. First, Ag NTs were fabricated by electroless deposition from baths containing Ag(1)-ethylenediamine complexes as the oxidizing agent and tartrate as the reducing agent [11]. The product was characterized by TEM (Fig. 5A, left), showing tubes consisting of agglomerated particles of several 10 nm size. EDS proved that the nanostructures consist of Ag (Fig. 5A, right; the other elements relate to the template (C, O), the embedding resin (Si) and the TEM grid (Cu), respectively).

To introduce Pt as a second metal, one Ag NT membrane was purged with 3.9 mM hexachloroplatinic acid, leading to the cementation of the more noble Pt on the Ag nanostructures. After the exchange reaction, the membrane was cleaned with ammonia solution to remove AgCl precipitates. TEM revealed a change of the NT wall structure (Fig. 5B, left), which was rougher than in the case of the Ag NTs, consisted of smaller particles and showed some porosity. EDS confirmed the introduction of Pt, but significant amounts of Ag remained in the product (Fig. 5B, right).

Finally, nitrophenol reduction was performed with the membranes containing the Ag-Pt and the Ag NTs. Reference experiments with catalyst-free membranes confirmed that nitrophenol conversion required the presence of metal NTs. Due to the large excess of the reducing agent sodium borohydride, the reaction follows a pseudo-first order rate law, and the apparent rate constant $k_{app}$ of catalysts can be determined by the conversion of the educt over time [19]. Usually, the change of the 4-nitrophenolate concentration—in the alkaline reaction solution, 4-nitrophenol is deprotonated—is followed by UV-Vis spectroscopy [19]. Assuming Beer-Lamberts law, the educt concentration and the absorbance are linearly correlated, and $k_{app}$ can be determined according to Eq. (1):

$$\ln(A(t)/A(t = 0)) = -k_{app}t.$$ (1)

The corresponding results for the NT membranes are shown in Fig. 6. It can be seen that after the passage through the catalytic membrane, the 4-nitrophenolate caused absorbance at 400 nm is reduced, while a new peak evolves at a wavelength of 300 nm which corresponds to the product of the conversion, 4-aminophenolate. The calculated apparent rate constant of the Ag-Pt NT catalyst is $1.3 \times 10^{-2}$ s$^{-1}$, which exceeds the value of the Ag NT membrane $(8.5 \times 10^{-3}$ s$^{-1}$) by about 50%. As possible reasons for the considerable performance enhancement, the increased surface area of the roughened Ag-Pt NTs can be named aside the high intrinsic activity of Pt catalysts in the nitrophenol reduction [19].
plating reactions were investigated concerning the confor-
tions according to the apparent rate constants calculated with
at 300 nm is found. The dots mark the nitrophenolate absorp-
peak at 400 nm fades, while a growing product absorption peak
During the reaction, the educt absorption
of the reaction solution before and
IV. CONCLUSION
In this study, important characteristics of electroless plating reactions were investigated concerning the confor-
al deposition of homogeneous metal films on ion track etched polycarbonate substrates. It was shown how the
activation and plating steps can be modified to ensure a high seed density, surface-selective metal deposition, suf-
cient mass transport and low grain sizes, facilitating the
formation of metal NTs as a challenging product mor-
phology.
Due to their general nature, the discussed strategies can
be used to enhance electroless metal deposition on other
substrates with intricate shape, especially with extended
inner surfaces. However, due to the complex interaction of
the reaction conditions, the deposition kinetics and the
film structure as well as the strong dependence of these
parameters on the applied metastable redox pair, individ-
ual optimization is required.
As an application example, arrays of template-
embedded metal NTs were utilized as flow-through re-
actors, catalyzing the reduction of 4-nitrophenol. By em-
ploying Ag NTs as sacrificial templates for Pt deposition,
a possible way was illustrated how the functional prop-
erties of electrolessly plated nanomaterials can be further
improved.

Acknowledgments
We thank Prof. Dr. Christina Trautmann (GSI
Helmholtzzentrum für Schwerionenforschung GmbH, Darmstadt) for support with the irradiation experiments
and for providing access to the HRSEM and UV-Vis spec-
trometer of the materials research group. The authors
highly recognize the TEM sample preparation and mea-
urements by Ulrike Kunz. Supply of Au solution by
Schütz Dental GmbH is gratefully acknowledged.

[1] C. R. K. Rao and D. C. Trivedi, Coord. Chem. Rev. 249, 613 (2005).
[2] C. Larson and J. R. Smith, Trans. Inst. Met. Finish. 89, 333 (2011).
[3] H. O. Ali and I. R. A. Christie, Gold Bull. 20, 148 (1994).
[4] Y. Fang, J. D. Berrigan, Y. Cai, S. R. Marder, and K. H. Sandhage, J. Mater. Chem. 22, 1305 (2012).
[5] I. A. Abu-Isla, Polym.-Plast. Technol. Eng. 2, 29 (1973).
[6] G. Garcia, J. Polesel-Maris, P. Viel, S. Palacin, and T. Berthelot, Adv. Funct. Mater. 21, 2096 (2011).
[7] W. Ahn and D. K. Roper, ACS Nano 4, 4181 (2010).
[8] S. G. Jang, D.-G. Choi, C.-J. Heo, S. Y. Lee, and S.-M. Yang, Adv. Mater. 20, 4862 (2008).
[9] M. Wirtz, S. Yu, and C. R. Martin, Analyst 127, 871 (2002).
[10] F. Muench, U. Kunz, C. Neetz, S. Lauterbach, H.-J. Kleebe, and W. Ensinger, Langmuir 27, 27 (2011).
[11] F. Muench, M. Rauber, C. Stegmann, S. Lauterbach, U. Kunz, H.-J. Kleebe, and W. Ensinger, Nanotechnology 22, 415602 (2011).
[12] B. Y. Kim, C. B. Swearingen, J. A. Ho, E. V. Romanova, P. W. Bohn, and J. V. Sweedler, J. Am. Chem. Soc. 129, 7620 (2007).
[13] F. Muench, S. Kaserer, U. Kunz, I. Svoboda, J. Brotz, S. Lauterbach, H.-J. Kleebe, C. Roth, and W. Ensinger, J. Mater. Chem. 21, 6286 (2011).
[14] W. B. Kim, T. Voitl, G. J. Rodriguez-Rivera, and J. A. Dumesic, Science 305, 1280 (2004).
[15] M. Delvaux, A. Walcarius, S. Demoustier-Champagne, Anal. Chem. Acta 525, 221 (2004).
[16] Y. Yu, K. Kant, J. G. Shapter, J. Addai-Mensah, and D. Losic, Microporous Mesoporous Mater. 153, 131 (2012).
[17] R. J. Gilliam, S. J. Thorpe, and D. W. Kirk, J. Appl. Electrochem. 37, 233 (2007).
[18] S. Demoustier-Champagne and M. Delvaux, Mater. Sci. Eng C 15, 269 (2001).
[19] S. Wunder, F. Polzer, Y. Lu, Y. Mei, and M. Ballauff, J. Phys. Chem. C 114, 8814 (2010).
[20] P. Apel, Radiat. Meas. 34, 559 (2001).
[21] F. Muench, M. Uezaslan, T. Seidl, S. Lauterbach, P. Strasser, H.-J. Kleebe, and W. Ensinger, Appl. Phys. A 105, 847 (2011).
[22] M. Davenport, K. Healy, and Z. S. Siwy, Nanotechnology 22, 155301 (2011).
[23] Y. Kobayashi, V. Salgueirino-Maceira, and L. M. Liz-Marzan, Chem. Mater. 13, 1630 (2001).
[24] K. B. Jirage, J. C. Hulteen, and C. R. Martin, Science 278, 655 (1997).
[25] I. Ohno, O. Wakabayashi and S. Haruyama, J. Electrochem. Soc. 132, 2323 (1985).
[26] X. Yin, L. Hong, B.-H. Chen, and T.-M. Ko, J. Colloid Interface Sci. 262, 89 (2003).
[27] V. P. Menon and C. R. Martin, Anal. Chem. 67, 1920 (1995).
[28] M. De Leo, F. C. Pereira, L. M. Moretto, P. Scopece, S. Polizzi, and P. Ugo, Chem. Mater. 19, 5955 (2007).
[29] D. I. Gittins and F. Caruso, Angew. Chem. Int. Ed. 40, 3001 (2001).