Contents lists available at SciVerse ScienceDirect





## Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

# Electrodeposition of long gold nanotubes in polycarbonate templates as highly sensitive 3D nanoelectrode ensembles

### Yaser Bahari Mollamahalle<sup>a</sup>, Mohammad Ghorbani<sup>a,b,\*</sup>, Abolghasem Dolati<sup>b</sup>

<sup>a</sup> Institute for Nanoscience and Nanotechnology, Sharif University of Technology, P.O. Box 11155-8639, Tehran, Iran
<sup>b</sup> Department of Materials Science and Engineering, Sharif University of Technology, P.O. Box 11155-9466, Tehran, Iran

#### ARTICLE INFO

Article history: Received 14 February 2012 Received in revised form 17 April 2012 Accepted 24 April 2012 Available online 14 May 2012

Keywords: Electrodeposited gold nanotubes Polycarbonate membranes Controlled chemical etching Nanoelectrode ensembles

#### ABSTRACT

Electrodeposition of long and well-defined gold nanotubes in polycarbonate (PC) templates is still a major concern due to pore blockage problems. In the present study, we introduce a novel method for electrode-position of long gold nanotubes within the pores of PC templates for the first time. In order to deposit gold atoms onto the pore walls preferentially, pore walls were functionalized with a coupling agent. Short and thin Ni nanotubes were then electrodeposited at the bottom of the pores. Gold nanotubes were subsequently electrodeposited at constant potentials and low solution concentrations. The morphology of nanotubes was characterized by electron microscopy and their formation mechanism was discussed in detail. Gold nanotubes were fabricated inside PC template with different lengths even as long as the template thickness which was about 6  $\mu$ m. Using controlled chemical etching of PC template, three-dimensional gold nanoelectrode ensembles (3D GNEs) were developed which show much higher sensitivity compared to their embedded GNEs counterparts in the presence of Fe<sup>2+</sup>/Fe<sup>3+</sup> redox couple. Cyclic voltammograms show that the sensitivity of 3D GNEs increases with increasing the number of etching cycle.

© 2012 Elsevier Ltd. All rights reserved.

#### 1. Introduction

Gold nanotube ensembles and arrays are of great interest because of their excellent properties such as high sensitivity in detecting different materials, and chemical and physical stability [1]. "Template Synthesis" is the most versatile method for fabrication of nanoarrays especially ensembles of gold nanotubes developed by Martin et al. [2-4]. In template synthesis, arrays of nanomaterials could be prepared inside a porous template such as polycarbonate (PC) or anodic aluminum oxide (AAO). Using template synthesis, nanowires and nanotubes of different metals [5-7], semiconductors [8–10] and polymers [11–13] could be prepared. Advantages of such templates are good control over dimensions of target and preparing wide range of materials with aligned structures [14]. Three-dimensional (3D) gold nanoelectrode ensembles (GNEs), however, show much higher sensitivity compared to their two-dimensional (2D) counterparts [15]. Zoski [16] proposed a user friendly method for developing 3D nanoelectrodes of gold nanowires using controlled chemical etching of PC templates. In

this method, a mixture of dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) and ethanol was employed and several solvent/dry wipes were used aiming to expose brushes of gold nanowires. To date, most of the activities for the fabrication of gold nanotubes in PC templates have been carried out through electroless method [2.17–21] and to best of our knowledge, there is no report using electrochemical method in these templates describing perfect long gold nanotubes [22,23]. Wang et al. [24] fabricated short gold nanotubes in PC templates through electrodeposition method which resulted in nanorods in prolonged times as one of the very few works. This may be due to problems in achieving perfect gold nanotubes through electrochemical method. In fact, gold grows both vertically and radially inside the template and the pores will be blocked soon during deposition. As a result, the fabricated gold nanotubes have to be short in length to prevent blockage of the nanotubes [24,25]. This problem, indeed, is an obstacle for developing desired length of nanotubes and also their application as 3D nanoelectrodes since nanotubes should have a length almost equal to the template thickness to ensure that gold brushes will be exposed by the controlled chemical etching of PC template. Here, we report a simple electrochemical method for preparation of long gold nanotubes in PC templates with different lengths and nearly equal to the template thickness. 3D GNEs were then prepared simply by chemical etching of PC template and their sensitivity was measured in the presence of Fe<sup>2+</sup>/Fe<sup>3+</sup> reversible couple and compared to embedded GNEs. The proposed method has an advantage over electroless method

<sup>\*</sup> Corresponding author at: Department of Materials Science & Engineering, Sharif University of Technology, P.O. Box 11155-8639, Tehran, Iran. Tel.: +98 2166165219; fax: +98 2166005717.

*E-mail addresses:* bahari@mehr.sharif.edu (Y. Bahari Mollamahalle), Ghorbani@sharif.edu (M. Ghorbani), Dolati@sharif.edu (A. Dolati).

<sup>0013-4686/\$ -</sup> see front matter © 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.electacta.2012.04.119



Fig. 1. FE-SEM images of PC template: (a) top view and (b) cross sectional view.

since in electroless deposition there is no control over the length of nanotubes except the template thickness and gold deposits all over the template including entire pore walls and both surfaces [19,20]. Moreover, deposition of gold atoms rather than the pore walls takes place on both surfaces (top and bottom) of PC template which is not suitable for sensing applications and should be removed. This needs another complementary step, usually by using a scotch tape to remove the deposited gold from the surface of PC template [4]. However, it may result in pulling out of nanotubes from the template [16]. In contrast, here, in the electrodeposition method, desired lengths of nanotubes could be prepared and deposition starts from the bottom of the pores to the top. Therefore, there is not any deposited gold on the top surface. Moreover, in contrast to the previous works with AAO template, creating 3D nanotubes is accompanied using both long gold nanotubes and PC as template since PC could be sealed around the nanotubes which results in good sensitivity.

#### 2. Experimental

All the electrodeposition experiments were performed in a glass tube cell at room temperature with a potentiostat (Autolab,

PGSTAT302N) instrument. Saturated calomel electrode (SCE) and platinum plate were used as the reference and counter electrode, respectively. Commercial PC membrane (Whatman) with nominal pore sizes of 200 nm was used as template. The inner side of the template was hydrophilic and coated with polyvinylpyrrolidone (PVP) by the vendor. The thickness and pore density of templates were 6  $\mu$ m and 3.4 × 10<sup>8</sup> pores/cm<sup>2</sup>, respectively, determined by field emission scanning electron microscopy (FE-SEM, Hitachi, S-4160) images (Fig. 1a and b). Prior to each experiment, the pore walls of the template were functionalized by 3-aminopropyltriethoxysilane (APES) as coupling agent under 30 min of ultrasonication.

To ensure a good electrical contact, a thin layer of gold with the thickness of 30 nm was sputtered on one side of the template. This layer is too thin to bridge over the pores and leaves the pores open. The template was then soaked in deionized water for 5 min under ultrasonication right before the electrodeposition test. This step is necessary for obtaining reproducible results and a homogeneous growth over the whole growing area [26]. The sputtered side of the template was attached to the working electrode and the bare side was exposed to the solution. Before the gold electrodeposition, Ni was electrodeposited at a constant potential of -900 mV



Fig. 2. Schematic illustration for fabrication of long gold nanotubes: (a) bare PC membrane; (b) modification of pore walls with molecular anchor; (c) gold sputtering on one face of the PC membrane; (d) electrodeposition of Ni nanotubes; (e) gold nanotubes electrodeposition; (f) 3D gold nanotubes after controlled chemical etching of PC membrane.



Fig. 3. Cyclic voltammogram for a 5 mM gold solution (scan rate = 20 mV/s).

from a solution containing 0.8 mol/L NiSO<sub>4</sub>· $6H_2O$ , 0.5 mol/L H<sub>3</sub>BO<sub>3</sub>, and 0.3 mol/L KCl for about 1 min. This results in short Ni nanotubes with the length of about few hundred nanometers [27]. Gold nanotubes were potentiostatically electrodeposited from different potassium gold cyanide (KAu(CN)<sub>2</sub>) solutions prepared as described previously [28]. A schematic diagram of the procedure is shown in Fig. 2. After electrodeposition, the templates rinsed totally by deionized water to remove impurities. The PC templates were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (partially by adding a few drops of CH<sub>2</sub>Cl<sub>2</sub> on PC template or completely by leaving PC template in CH<sub>2</sub>Cl<sub>2</sub> solution for 30 min) in order to be characterized by FE-SEM. For characterization by transmission electron microscopy (TEM, Philips, CM 200 operating at an accelerating voltage of 200 kV), released nanotubes were centrifuged, dispersed in ethanol solution and one drop was placed on carbon grid. In order to make 3D nanoelectrodes, a mixture of CH<sub>2</sub>Cl<sub>2</sub> and ethanol with equal volumes (50:50) was selected and several solvent/dry wipes were used according to the method proposed by Zoski [16]. For sensing experiment, GNEs embedded template was first heated at 150 °C (above the glassy transition temperature of PC membrane) for 15 min in order to seal the membrane around the GNEs. Backside of GNEs was then attached on a copper electrode by carbon paste. A hole with 3 mm diameter was punched on an insulator tape and pasted over the GNEs and whole electrode was carefully sealed. The surface of GNEs was cleaned by cycling from 0 to 1.5 V in 0.5 M sulfuric acid until reproducible results were obtained.

#### 3. Results and discussion

#### 3.1. Electrodeposition behavior of gold in PC pores

Fig. 3 represents a typical cyclic voltammetry (CV) curve for a 5 mM gold solution at a scan rate of 20 mV/s. It could be obviously observed that there are two distinct peaks at -540 mV and -1020 mV in the cathodic scan that can be interpreted in terms of Au reduction through the adsorptive decomplexing of  $Au(CN)_2^-$  to  $Au(CN)_{ads}$  and direct reduction of gold cyanide complex to metallic gold, respectively. The electrochemical reaction at the end of cathodic sweep corresponds to the hydrogen evolution reaction [28,29]. The reduction of gold could be assumed as an irreversible electrochemical reaction since there is no oxidation peak in the reverse scan close to the reduction peak potential ( $\Delta E \ge 59$  mV).

Fig. 4 shows chronoamperometric curve for a step potential of -900 mV in which the current density increases at initial stages due to the nucleation and growth process and then drops by increasing the concentration gradient of electroactive species on the surface



**Fig. 4.** *j*-*t* curve for a 5 mM gold solution at a step potential of -900 mV vs SCE. The inset shows the related *j*-*t*<sup>-1/2</sup> diagram.

(i.e. growing the diffusion layer into the solution) [30] according to Cottrell equation:

$$J(t) = \left(\frac{nFC^{\infty}D^{1/2}}{\pi^{1/2}}\right)t^{-1/2}$$
(1)

where *n*, *F*,  $C^{\infty}$ , *D* and *t* are the number of exchanged electron involved in the electrode process, Faraday constant, the solution bulk concentration, diffusion coefficient, and time respectively. The well-defined maximum peak is a result of encountering two mentioned phenomena (i.e. nucleation and growth with diffusion). Based on the linear relation of current with reverse square root of time, diffusion coefficient could be determined from the slope of the curve (the inset of Fig. 4). The calculated value for *D* was  $4.37 \times 10^{-5}$  for a 5 mM gold solution.

#### 3.2. Gold nanotubes formation inside PC pores

In this study, we applied different modifications to achieve the nanotube structure. First, the pore walls were activated and functionalized by APES. APES molecules easily adsorb to the hydrophilic pore walls by ethoxy groups while amino groups are facing to the solution. Gold ions have a strong tendency to adsorb on amino groups. This makes vertical growth rate to be much more than radial growth. In other words, formation of gold nanotubes would be facilitated using the coupling agent. Short Ni nanotubes were then fabricated at the bottom of the pores to assure that gold ions will certainly deposit inside the pores. If this step is ignored, gold would be deposited on backside of the template rather than on the pore walls which lowers the efficiency of gold deposition and results in unrepeatable data. Tian et al. [31] who fabricated different types of metal nanowires in PC template reported that during the initial 1-2 min of the electrodeposition, a more negative potential is needed to deposit metals into the pores. They believed that without this initial higher negative potential step, metal tends to grow laterally onto the conducting film instead of into the pores. However, it seems that this approach could not be applied for nanotubes since the high overpotentials result in high reduction rate of metal which in case block the pores and forms nanowires. Slow kinetic, indeed, is necessary for obtaining gold nanotubes. The other role of Ni layer is to protect backside gold sputtered of the template by preventing it from dissolution before starting the deposition test. Gold dissolution occurs because of the presence of free cyanide ions



**Fig. 5.** (a) FE-SEM micrographs of gold nanotubes prepared in 5 mM gold solution at the constant potential of -900 mV vs SCE and a deposition time of 2 h after partial dissolving the PC template and (b) EDX analysis for an individual gold nanotube.

in the electrolyte solution. During the gold deposition, gold atoms preferentially deposit onto the pore walls and as gold slowly grows inside the pores, the coupling agent makes sure that the structure would be hollow tubes. As it mentioned earlier, the electrochemical strategy for obtaining nanotubes is that the deposition rate should be slow. This implies using a dilute solution with a low deposition potential (current density). Slow kinetic makes it easy to prepare nanotubes by diffusion of gold ions from bulk solution into the pores and gold atoms are gradually deposited onto the pores walls and grow toward the bulk solution. Fig. 5a shows such conditions by using a 5 mM gold solution at the constant deposition potential of -900 mV which clearly shows that hollow gold nanotubes are formed with a wall thickness of about 40 nm. It is reported [32] that the pores in PC templates are not aligned parallel but could have a considerable angular deviation of 34° as it is clear in Fig. 1b. Therefore, even if the electrochemical deposition would proceed well, the lengths of nanotubes still vary among different pores [32] as it will be described later in this paper. In Fig. 5a, the wide angle deviations

(more than  $34^{\circ}$ ) between nanotubes are the result of etching PC by  $CH_2Cl_2$ . The solvent bends nanotubes through mechanical force. A gel-like layer seems that covers the tubes in some areas since the PC template was partially etched.

The outer diameter of nanotubes even reaches to 275 nm, which is more than the nominal diameter of the template pores. This is because the pore diameter of PC template is not the same along the thickness of the template. It is reported [26,32] that the pores in PC are not cylindrical but rather cigarlike and the pore diameter inside the template is much higher than the nominal pore size [32]. Fig. 5b shows energy dispersive X-ray (EDX) analysis for an individual gold nanotube after complete dissolution of PC template which reveals Au element with high purity (100 at.%). Taking advantage of coupling agent and deposited Ni, it was possible to prepare hollow nanotubes even in higher solution concentration and high deposition potential. Fig. 6a represents SEM micrographs of gold nanotubes prepared in 10 mM gold solution and at the potential of -1400 mV at early stages of electrodeposition. Very



**Fig. 6.** FE-SEM images of gold nanotubes: (a) gold nanotubes at initial times with; (b) thin gold nanotubes with different; and (c) long gold nanotubes. All the samples were fabricated in the same conditions (10 mM gold solution, -1400 mV deposition potential) but in different deposition times (210 s for b and 550 s for c).



**Fig. 7.** (a) FE-SEM micrographs of top surface of embedded gold nanotubes prepared in the same conditions as Fig. 6 and deposition time of 660 s; (b) the nanotubes after more deposition times; (c) the prepared nanotubes in (a) after complete etching away of PC template; (d) some broken nanotubes from (c); (e) TEM image of an individual gold nanotube; (f) *j*-*t* curve for the prepared nanotubes in (a and c).

thin nanotubes are formed due to high overpotential of deposition. With further growth, gold deposition would be proceeded along the pore walls. A careful view of these nanotubes (Fig. 6b) shows that the bottom parts of nanotubes (black arrows) are thicker than other parts (white arrows). This fact proposes that gold growth takes place much faster in vertical direction inside the pores rather than radial direction. Prolonged electrodeposition time results in longer gold nanotubes (Fig. 6c) till nanotubes reach the membrane surface (Fig. 7a). Further electrodeposition results in filling the nanotubes and tubular structure converts to wire (Fig. 7b). As described earlier, one of the most benefits of electrochemical growth compared to electroless method is that the length of nanotubes could be easily controlled.

In electroless method, gold nucleates all over the pore walls and deposition starts from the pore walls toward the center of the pores [19,20]. In comparison, in electrochemical deposition, desired length of nanotubes is easily achievable by controlling parameters such as the deposition time, deposition potential, and concentration of solution. For instance, we have prepared different lengths of nanotubes (Figs. 5a, 6a-c, and 7). Fig. 7a shows topside of the gold nanotubes before dissolving the template. Gold nanotubes are formed without any blockage with a good coverage because of good template wetting. Fig. 7c shows forest of nanotubes after complete etching away PC template in CH<sub>2</sub>Cl<sub>2</sub>. Some of the prepared gold nanotubes in Fig. 7c are broken after dissolving the template but many of them are perfect. Some of the broken gold nanotubes are shown in Fig. 7d that clearly show hollow and thin nanotubes (white arrows). Deposition time in Fig. 7c is longer (110s) than that of in Fig. 6d. It is noteworthy that the lengths of the nanotubes measured through the template, are not the same as mentioned before. TEM image of an individual gold nanotube is represented in Fig. 7e which depicts a hollow gold nanotube with a thin wall thickness less than 20 nm all over its length. The difference in size of different part of nanotubes (i.e., bottom to top) due to geometry of the pores is clear in this figure, as it noted before. There is another important factor that may be responsible for the formation of long nanotubes,



Fig. 8. FE-SEM images of 3D GNEs after: (a) 5; (b) 10; (c) 15; and (d) 20 solvent/dry wipes.

specially in high overpotentials and that is hydrogen evolution. Fukunaka et al. [33] reported that the formation of nanotubes is possible by suppression of hydrogen evolution in the nanopore. Briefly, at the very initial stage of electrodeposition, H<sup>+</sup> ions are reduced to hydrogen molecules, and simultaneously, metallic ions are reduced at the bottom of the nanopore. The concentration of dissolved hydrogen gas may initially be relatively low at the bottom of the nanopore, but within a relatively short time, the hydrogen pressure may exceed the critical value to form the nuclei of hydrogen gas bubble at the bottom of the pore. This bubble starts to grow, ends partially or completely filling all of the pore length. Finally, hydrogen dissolution into the liquid takes place and bubbles nucleates again and a relatively small but continuous flow of hydrogen out of the pore is maintained while metal forms nanotube wall. Therefore, gas bubbles are detached from the PC template surface periodically which results in an abrupt current change. Fig. 7d and f, indeed, shows these facts clearly. A big hole is formed (black arrows) at the wall of nanotube in Fig. 7d and there are some interruptions in Fig. 7f in the *j*-*t* curve which could be attributed to the formation and dissolution of bubbles. It should be noted that in the applied overpotential, defects are negligible regarding to the whole fabricated nanotubes and could be ignored. Therefore, here, hydrogen evolution could promote the formation of gold nanotubes rather than it would be a problem but in higher overpotentials it may cause serious defects and damages to the structure.

It is worth noting again that without using the modification, solid gold nanowires would be dominant structure since there is no preferential adsorption site on the pore walls and hence gold atoms tend to deposit at the bottom of the pores.

#### 3.3. Controlled template etching for developing 3D GNEs

Fig. 8 shows SEM images recorded at different solvent/dry wipes etching cycles for developing 3D GNEs. It could be clearly observed that by controlled chemical etching of the template, 3D GNEs are formed with different brush lengths in which the length of brushes increases with an increase in the number of etching cycle. After 5 etching cycles, the surfaces of gold nanotubes are exposed (Fig. 8a). 10, 15 and 20 etching cycles result in exposing brushes of gold nanotubes with an average length about 100 nm, 350 nm and 550 nm, respectively (Fig. 8b–d). However, further etching cycles could not be easily employed since it may result in curling the template, creating voids and unsealing the nanoelectrodes which are not suitable for electrochemical sensing.

#### 3.4. Electrochemical response of deposited gold nanotubes

Fig. 9 illustrates CV voltammograms for embedded and different 3D GNEs in 0.5 M sulfuric acid and at a scan rate of 100 mV/s. The peak current in the forward scan is due to stripping of gold oxide whereas the reverse scan shows a well-defined peak around 0.68 V



Fig. 9. Cyclic voltammograms for embedded and different 3D GNEs in 0.5 M sulfuric acid (scan rate = 100 mV/s).



**Fig. 10.** Cyclic voltammograms for embedded and different 3D GNEs in phosphate buffer solution containing  $5 \text{ mM K}_3\text{Fe}(\text{CN})_6$  (pH = 7, scan rate = 10 mV/s).

due to the high surface area of nanotubes exposed to the solution for the formation of gold oxide. 3D GNEs introduce a dramatic increase in the peak current compared to embedded GNEs which indicates an increase in the active surface area. The peak currents in the forward and reverse scans increase with an increase in the number of etching cycles.

The sensitivity of 3D nanotubes were examined in the presence of redox couple  $Fe^{2+}/Fe^{3+}$  in phosphate buffer solution (PBS, pH = 7) and compared with embedded GNEs. Fig. 10 depicts CV curves for both embedded and 3D GNEs. The peak shape curve for CV indicates overlapping of individual diffusion layer of each nanoelectrode because of high coverage and close spacing of nanoelectrodes so that they act like a large electrode with equal geometric surface area [16]. As expected, 3D GNEs show a higher sensitivity compared to embedded GNEs. The peak currents in both cathodic and anodic scans enhance with exposing more surface area of GNEs toward the solution. With increasing the etching steps, the geometrical shape of fabricated nanoelectrodes changes from 2D to 3D nanoelectrodes. In this process, more surface area is exposed toward the solution also radial diffusion is promoted. Therefore more sensitivity could be observed toward the electroactive species in the solution.

#### 4. Conclusions

In summary, we introduced electrodeposition of gold nanotubes inside PC templates with different desired lengths. A diffusion coefficient of  $4.37 \times 10^{-5}$  cm<sup>2</sup>/s was calculated for 5 mM gold solution at -900 mV. The FE-SEM images showed that the GNEs have a length as long as the template thickness. TEM observation revealed a well-defined hollow nanotube with a wall thickness of 20 nm.

Different parameters such as coupling agent, Ni deposition, low concentration solution, and hydrogen evolution should be carefully considered for fabrication of gold nanotubes. 3D GNEs were easily prepared by controlled chemical etching of long gold nanotubes. The CV voltammograms of 3D GNEs revealed much higher sensitivity (more than two times) compared to the embedded GNEs in response to  $Fe^{2+}/Fe^{3+}$  redox couple. The high sensitive 3D GNEs could be used in many applications such as molecular detection.

#### References

- [1] G. Yang, Y. Chen, L. Li, Y. Yang, Clinica Chimica Acta 412 (2011) 1544.
- [2] C.R. Martin, Chemistry of Materials 8 (1996) 1739.
- [3] M. Wirtz, C.R. Martin, Advanced Materials 15 (2003) 455.
- [4] V.P. Menon, C.R. Martin, Analytical Chemistry 67 (1995) 1920.
- [5] F. Nasirpouri, P. Southern, M. Ghorbani, A. Iraji zad, W. Schwarzacher, Journal of Magnetism and Magnetic Materials 308 (2007) 35.
- [6] Q. Wang, G. Wang, X. Han, X. Wang, J.G. Hou, Journal of Physical Chemistry B 109 (2005) 23326.
- [7] L. Liu, W. Zhou, S. Xie, L. Song, S. Luo, D. Liu, J. Shen, Z. Zhang, Y. Xiang, W. Ma, Y. Ren, C. Wang, G. Wang, Journal of Physical Chemistry C 112 (2008) 2256.
- [8] J. Mallet, M. Molinari, F. Martineau, F. Delavoie, P. Fricoteaux, M. Troyon, Nanoletters 8 (2008) 3468.
- [9] R. Artzi-Gerlitz, K.D. Benkstein, D.L. Lahr, J.L. Hertz, C.B. Montgomery, J.E. Bonevich, S. Semancik, M.J. Tarlov, Sensors and Actuators B: Chemical 136 (2009) 257.
- [10] L. Zhao, M. Yosef, M. Steinhart, P. Goring, H. Hofmeister, U. Gosele, S. Schlecht, Angewandte Chemie International Edition 45 (2006) 311.
- [11] S. Cho, S.B. Lee, Accounts of Chemical Research 41 (2008) 699.
- [12] M. Steinhart, J.H. Wendorff, A. Greiner, R.B. Wehrspohn, K. Nielsch, J. Schilling, J. Choi, U. Gosele, Science 296 (2002) 1997.
- [13] B. Huang, T.G.M. van de Ven, R.J. Hill, Langmuir 27 (2011) 11416.
- [14] M.S. Sander, H. Gao, Journal of the American Chemical Society 127 (2005) 12158.
- [15] L. Cao, P. Yan, K. Sun, D.W. Kirk, Electrochimica Acta 53 (2008) 8144.
- [16] K. Krishnamoorthy, C.G. Zoski, Analytical Chemistry 77 (2005) 5068.
- [17] Z. Hou, N.L. Abbott, P. Stroeve, Langmuir 16 (2000) 2401.
- [18] S. Huang, C. Sheng, Z. Yin, J. Shen, R. Li, B. Peng, Journal of Membrane Science 305 (2007) 257.
- [19] J.-R. Ku, S.-M. Lai, N. Ileri, P. Ramirez, S. Mafe, P. Stroeve, Journal of Physical Chemistry C 111 (2007) 2965.
- [20] M. De Leo, F.C. Pereira, L.M. Moretto, P. Scopece, S. Polizzi, P. Ugo, Chemistry of Materials 19 (2007) 5955.
- [21] A. Curulli, F. Valentini, G. Padeletti, A. Cusma, G.M. Ingo, S. Kaciulis, D. Caschera, G. Palleschi, Sensors and Actuators B: Chemical 111–112 (2005) 526.
- [22] X. Zhang, H. Wang, L. Bourgeois, R. Pan, D. Zhao, P.A. Webley, Journal of Materials Chemistry 18 (2008) 463.
- [23] C. Huang, Y. Hao, Nanotechnology 20 (2009) 1.
   [24] H.-W. Wang, C.-F. Shieh, H.-Y. Chen, W.-C. Shiu, B. Russo, G. Cao, Nanotechnol-
- ogy 17 (2006) 2689. [25] C.J. Brumlik, V.P. Menon, C.R. Martin, Journal of Materials Research 9 (1994) 1174.
- [26] C. Schonenberger, B.M.I. van der Zande, L.G.J. Fokkink, M. Henny, C. Schmid, M. Kruger, A. Bachtold, R. Huber, H. Birk, U. Staufer, Journal of Physical Chemistry B 101 (1997) 5497.
- [27] X. Li, Y. Wang, G. Song, Z. Peng, Y. Yu, X. She, J. Li, Nanoscale Research Letters 4 (2009) 1015.
- [28] L. Soleimani, A. Dolati, M. Ghorbani, Journal of Electroanalytical Chemistry 645 (2010) 28.
- [29] B. Bozzini, B. Busson, G.P. De Gaudenzi, L. D'Urzo, C. Mele, A. Tadjeddine, Journal of Electroanalytical Chemistry 602 (2007) 61.
- [30] A. Dolati, M. Ghorbani, M.R. Ahmadi, Journal of Electroanalytical Chemistry 577 (2005) 1.
- [31] M. Tian, J. Wang, J. Kurtz, T.E. Mallouk, M.H.W. Chan, Nanoletters 3 (2003) 919.
- [32] P. Shao, G. Ji, P. Chen, Journal of Membrane Science 255 (2005) 1.
- [33] Y. Fukunaka, M. Motoyama, Y. Konishi, R. Ishii, Electrochemical and Solid-State Letters 9 (2006) 62.