Controlled Growth of Gold Nanorod Arrays from Polyethylenimine-coated Alumina Templates

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ABSTRACT

Au nanorod arrays were grown by electrodeposition in Au-backed nanoporous alumina templates modified with polyethylenimine (PEI) as an adhesion layer. By varying the concentration and molecular weight of PEI, the length of nanorod arrays could be finely controlled. The local length distribution was extremely narrow with relative standard deviations on the order of 2% for rod lengths from 700 nm to 17 microns. The uniform growth rate appears to be determined by the adsorbed PEI matrix, which controls the growth kinetics of the grains comprising the nanorods. Templates coated with poly(acrylic acid) did not impart fine control in nanorod growth. The nanorods could also be thermally annealed within the template and released as monodisperse particles of uniform size.

INTRODUCTION

Periodic arrays of plasmonic nanostructures are candidates for the development of nanophotonic materials and devices, such as photonic band gaps [1,2] and near-field optical waveguides [2-5]. Also plasmonic nanostructures arranged in close proximity to one another often experience a strong electromagnetic coupling and become capable of generating intense but highly localized electromagnetic fields, which are desirable for enhancing a variety of nonlinear optical effects and spectroscopic sensing modalities such as surface-enhanced Raman scattering (SERS) [6-8]. Designing metal nanorod arrays for applications requires a suitable fabrication method, one which enables control over particle size, aspect ratio, and interparticle spacing [9,10]. Top-down methods such as electron-beam lithography impart excellent spatial control, but at present these are limited in sample throughput and cannot easily provide particle separations of less than 25 nm [2-5]. Self-assembly has been used successfully to organize spherical nanoparticles into close-packed 2D and 3D arrays [11-15], but organizing anisotropic particles such as nanorods into axially oriented 2D arrays is a far more challenging problem [16-20]. Size is another important factor: plasmonic responses scale roughly with particle volume but are also limited by size-dependent retardation and damping effects, so the optimal enhancements are most likely to be produced by arrays of nanorods having diameters between 40 and 100 nm, depending on the wavelength of interest [9,10].

We have recently demonstrated that nanoporous anodized aluminum oxide (AAO) membranes coated with high molecular weight polyethylenimine (PEI; M_w = 750,000) can provide significant benefits for the controlled growth of monolithic 2D arrays of Au nanorods via templated electrodeposition [21]. Here we investigate the controlled electrochemical growth of Au nanorods in AAO templates coated with PEI of different molecular weights. The electrodeposition of metal in nanoporous AAO templates is an established methodology, and is typically performed by coating one face of the substrate with a conductive layer [22]. Casting a thin coating of PEI onto nanoporous AAO provides a nonmetallic adhesion layer for Au, allowing us to circumvent issues of metal contamination. The results described here show that

the PEI-coated templates are also uniquely suited for growing pure Au nanorods of uniform length.

SAMPLE PREPARATION

Nanoporous AAO templates were prepared by a two-step anodization process [23,24]. Al foil was first anodized in a 0.3 M oxalic acid solution at 5 ºC at a constant applied voltage of 40 V for 20 h, then etched in an aqueous mixture of phosphoric acid (6 wt%) and chromic acid (1.8 wt%) at 60 ºC. A second anodization was performed for 8–11 h using the same conditions as above, followed by dissolution of the remaining Al in a saturated $HgCl_2$ solution. Pore widening and removal of the barrier oxide layer was carried out by chemical etching in 0.8 wt% phosphoric acid at 30 ºC for 60 min, to produce AAO films with highly ordered pores (average diameter = 75 nm, center-to-center distance = 105 nm).

Freshly prepared AAO templates were soaked in 1–5 wt% aqueous medium molecular weight PEI (M_w = 25,000; m-PEI) or low molecular weight PEI (M_w = 2,000; l-PEI) or poly(acrylic acid) (M_w = 2,000; PAA) solutions for 5 h at room temperature. The polyelectrolyte-coated templates were washed by soaking them six consecutive times in deionized water baths (10 min each), then dried overnight in a vacuum oven at 70 ºC. A thin film of Au (thickness ~40 nm) was thermally evaporated onto one face of the modified AAO template, and determined to be firmly adhered onto the PEI or PAA-treated substrates by visual inspection as well as by FE-SEM.

Au nanorods were elecrodeposited from the Au electroplating solution (Orotemp 24), it was obtained from Technic Inc. The electrodepositions were conducted at ambient temperatures under galvanostatic conditions at currents of 0.485 mA (current density of 1.26 mA/cm^2), using a PAR 273A potentiostat/galvanostat with a Pt wire counterelectrode and a saturated calomel electrode (SCE) as a reference. The Au-backed AAO films were placed in an electrochemical cell constructed from Teflon, with the nanopores exposed to the electrodeposition solution through a 7-mm diameter hole.

EXPERIMENTAL RESULTS AND DISCUSSION

PEI is a branched polyamine well known for its physisorption properties. For example, it can mediate the adhesion of nanomaterials onto planar substrates [25-27], or into spherical core–shell ensembles around colloidal templates [28-30]. Low molecular weight PEI is also a common additive in electroplating solutions, and often used as a brightener in the electrodeposition of metal films. These facts encouraged us to examine different molecular weight PEI coatings as an adhesion layer for Au evaporation and subsequent electrodeposition.

Au-backed AAO membranes coated with 5% m-PEI produced excellent results for the uniform electrochemical growth of Au nanorods, from 1 to 25 C at a current density of 1.26 mA/cm^2 (see Figure 1a–f). Standard deviation values were obtained for local sectors at the micron scale (σ_{local}) and also across the entire membrane at the millimeter scale (σ_{global}) to evaluate the uniformity in growth conditions provided by the m-PEI-modified AAO templates (see Table 1). The nanorods were linearly proportional to the amount of expended charge up to 25 C. The mean length (L) of the Au nanorods is nearly constant over the entire substrate, with significant deviations only at the edges of the sample (see Figure 1g).
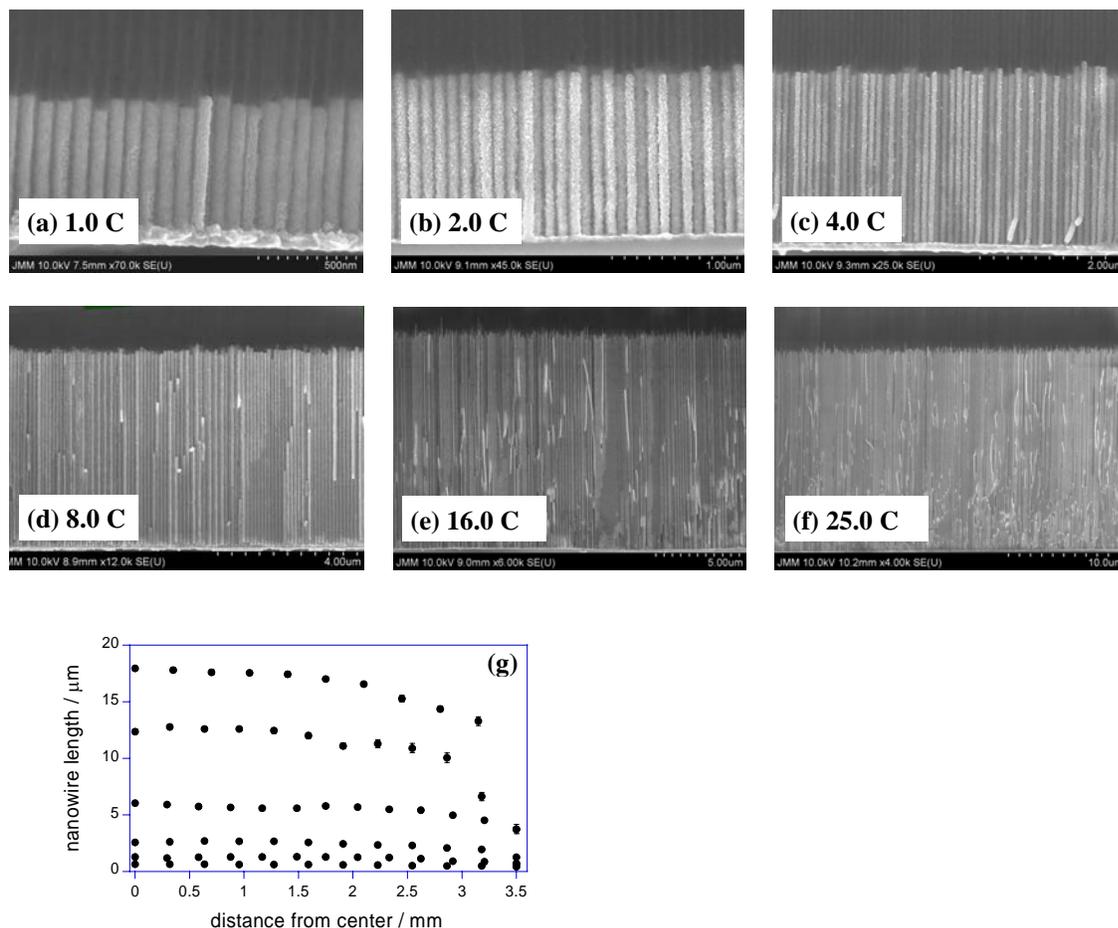
Figure 1. FE-SEM images of Au nanorods as a function of delivered charge from (a) 1.0 C; (b) 2.0 C; (c) 4.0 C; (d) 8.0 C; (e) 16.0 C; (f) 25.0 C. Nanorods were grown at a current density of 1.26 mA/cm^2, using AAO templates coated in a 5% m-PEI solution. (g) Nanorod lengths (in μm) in samples (a)−(f), measured as a function of distance from the center of the template (in mm).

Table1. Parameters obtained from TEM images using Au/m-PEI/AAO membranes

applied	mean nanorod length/μm	σ_{local}[a] /μm	σ_{global}[b] /μm
1.0	0.60	0.03	0.05
2.0	1.23	0.03	0.11
4.0	2.51	0.04	0.19
8.0	5.63	0.10	0.29
16.0	11.84	0.27	0.92
25.0	16.85	0.22	1.17

[a] σ_{local} values were measured for subsets of nanorods contained within individual SEM images

[b] σ_{global} values were performed on nanorods from center to 3-mm range, avoiding edge effects

AAO substrates modified with 1% *m*-PEI solutions produced Au nanorods of similar lengths, although with broader size distributions than the 5% *m*-PEI case (see Figure 2). The Au nanorod arrays in AAO membranes coated in 1% *m*-PEI solution were fabricated using a delivered charge of 8.84 and 13.69 C, using the same conditions as the 5% *m*-PEI case (1.26 mA/cm^2), to produce nanorods with comparable average lengths (*L* = 5.52 and 10.61 μm, respectively) and σ_{global} values (0.28 and 0.65 μm) but larger σ_{local} values (0.14 and 0.54 μm).
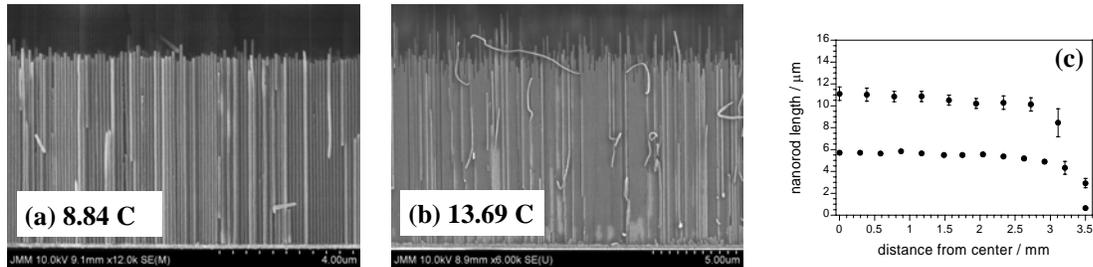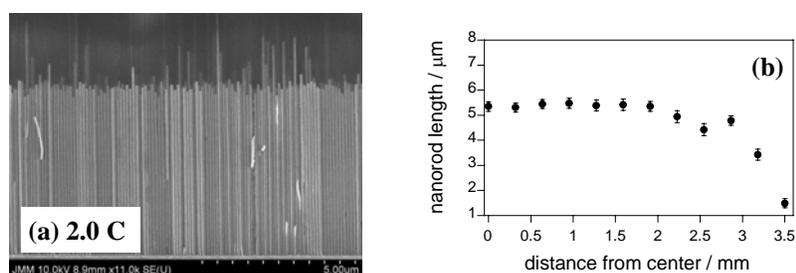

Figure 2. FE-SEM images of Au nanorods as a function of delivered charge: (a) 8.84 C (*L* = 5.52 μm; σ_{local} = 0.14 μm; σ_{global} = 0.28 μm); (b) 13.69 C (*L* = 10.61 μm; σ_{local} = 0.54 μm; σ_{global} = 0.65 μm). Nanorods were grown at a current density of 1.26 mA/cm^2, using AAO templates coated in a 1% *m*-PEI solution. (c) Nanorod lengths (in μm) measured as a function of distance from the center of the template (in mm).

Uniform Au nanorod arrays could also be grown in AAO substrates treated with 5% *l*-PEI. Nanorods were electrodeposited at 1.26 mA/cm^2 with σ_{local} and σ_{global} values similar to those of the 5% *m*-PEI solutions, for delivered charges of up to 10.8 C (see Figure 3). However, the nanorod growth rates in *l*-PEI-coated AAO templates were more retarded and less linear with delivered charge compared with those in 5% *m*-PEI solutions.
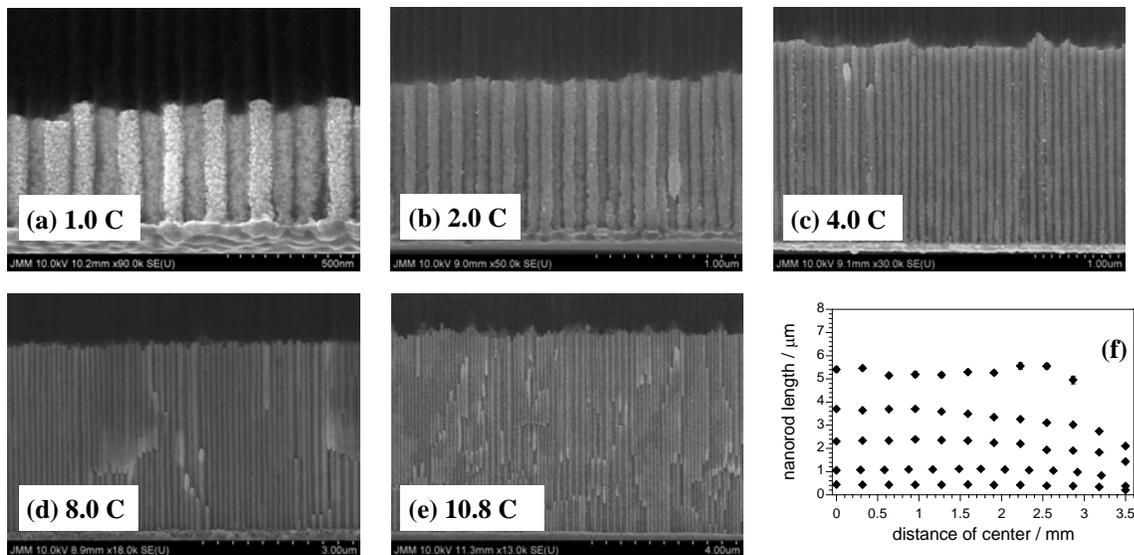
Figure 3. FE-SEM images of Au nanorods grown in AAO templates coated in a 5% *l*-PEI solution, as a function of delivered charge: (a) 1.0 C ($L = 0.42 \pm 0.03$ μm); (b) 2.0 C ($L = 1.07 \pm 0.04$ μm); (c) 4.0 C ($L = 2.24 \pm 0.17$ μm); (d) 8.0 C ($L = 3.48 \pm 0.24$ μm); (e) 10.8 C ($L = 5.29 \pm 0.21$ μm). All standard deviations are given as σ_{global}. Nanorods were grown at a current density of 1.26 mA/cm^2. (f) Nanorod lengths (in μm) measured as a function of distance from the center of the template (in mm).

The uniformity of the nanorod growth conditions provided by the PEI-modified templates is remarkable when compared with electrodepositions performed in templates modified with poly(acrylic acid) (PAA; $M_w = 2,000$). Two differences are immediately apparent with the latter substrates: (i) the local size distribution is significantly broader, and (ii) the overall lengths are much greater than those produced in the PEI-coated substrates under identical electrodeposition conditions (see Figure 4).

Figure 4. (a) FE-SEM image of Au nanorods grown in AAO template coated in a 5% PAA solution at 2.0 C, grown at a current density of 1.26 mA/cm^2. (b) Nanorod lengths (in μm) measured as a function of distance from the center of the template (in mm). Mean length $L = 5.21 \pm 0.38$ μm.

We suggest that the fine control in nanorod length imparted by PEI is due to suppression of kinetic growth processes: the PEI passivates the grains' surfaces, making grain coalescence the rate-limiting factor during electrodeposition [21]. Using medium or low molecular weight PEI provides greater penetration into the AAO channels, extending this fine growth control to many microns in length. The *m*-PEI-modified AAO membranes appear to be the most effective for controlled electrochemical growth. Those results suggest that PEI-modified alumina templates may have the capacity to produce uniform nanorods on an increased lateral scale, an issue of practical relevance for technological considerations.

In addition to fabricating 2D nanorod arrays, the PEI-coated AAO substrates can also be used to prepare aqueous dispersions of uniform Au nanorods, whose individual plasmon resonances are tunable as a function of aspect ratio in the near-to mid-infrared spectrum [31-33]. The Au nanorod arays grown in Au/*m*-PEI/AAO membranes were heated for 3 hours at 470 ºC on a commercial hotplate. Thermal annealing had two important effects: (i) the evaporated Au film was detached from the substrate with the embedded nanorods, and (ii) the nanorod aspect ratios shrank by nearly 20% (see Figure 5a). These were caused by the segregation of the PEI from Au, followed by further coalescence of the nanorod grains. The annealed nanorods remained relatively monodisperse with a relative standard deviation below 10%, and could be isolated from as dispersible particles after dissolving the AAO template in strongly basic solutions (see Figure 5b).
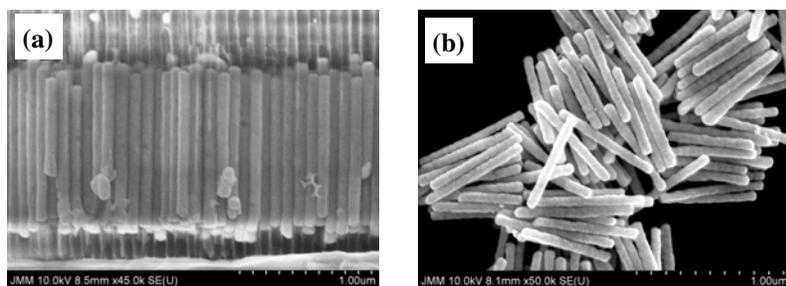
Figure 5. (a) Au nanorods (2.07 C, 0.126 mA/cm^2; $L_{initial}$ = 1.42 ± 0.02 μm) after annealing for 3 hours at 470 ºC (L_{final} = 1.15 ± 0.09 μm). The electrosynthesized nanorods are clearly separated from the evaporated Au layer (at bottom). (b) monodisperse Au nanorods (1.0 C, 1.26 mA/cm^2; L = 0.70 ± 0.07 μm) released from AAO template.

ACKNOWLEDGMENTS

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