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Mueller, Aaron David; Tobing, Landobasa Yosef Mario; Zhang, Dao Hua

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Title: Reliable fabrication of high aspect ratio plasmonic nanostructures based on seedless pulsed electrodeposition

*Aaron D. Mueller, Landobasa Y. M. Tobing, Dao Hua Zhang**

School of Electrical and Electronic Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore.

E-mail: edhzhang@ntu.edu.sg

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Strong plasmonic resonance in the visible spectrum requires high aspect ratio metallic resonators with deep subwavelength dimensions, which find applications as part of a cost-effective and practical optics-based sensing platform. Electrodeposition is a highly suitable method for fabricating such structures as it allows deposition of metals with much larger thickness and better morphology than that achieved by physical deposition. Herein, we present an in-depth study of pulsed electrodeposition of a gold film directly onto a transparent substrate without a seed layer and development of a reliable and efficient fabrication method for high aspect ratio metallic nanostructures with sub-10-nm features based on this approach. We demonstrate a low-cost fabrication of sub-100-nm metallic nanostructures based on a very high deposition rate (up to 7 nm/pulse) which nonetheless exhibit good surface morphology.

Specifically, we realized high aspect ratio rotationally symmetric plasmonic nanostructures suitable for practical sensing platform, which exhibit strong resonances in the visible spectrum with Q factors as high as 10 under unpolarized excitation.

1. Introduction

The ability to fabricate patterned metallic nanostructures over a large area on a transparent substrate is of great scientific and engineering interest for applications in plasmonic nanolithography^[1,2], imaging^[3,4], bit patterned media^[5,6], plasmon-enhanced fluorescence^[7,8], solar energy conversion^[9–11], and especially chemical and biological sensing based on surface enhanced Raman scattering (SERS) and localized surface plasmon resonance (LSPR)^[12–15]. Traditional fabrication routes for achieving such subwavelength features ($\lambda_R/2n_{eff} \sim 100$ nm or less) include focused ion beam (FIB) milling^[16] and physical deposition through template defined by electron beam lithography (EBL)^[17] or nanosphere lithography (NSL)^[18,19]. Owing to the redeposition of sputtered material, serial nature of pattern writing, and required slow writing time for high resolution features^[20], FIB milling is not suitable for large area patterns. This makes the combination of lithography, physical deposition, and lift-off remain the preferable method for the best control of structure shape, size, and periodicity^[21,22]. For a variety of applications, it is desirable to increase the interaction volume of incident radiation within the nanostructures^[23]. Recently, electrochemical deposition of metal through nanometric templates has attracted much interest due to its advantages over physical deposition^[19,24–27], such as lower material cost, better film morphology, and higher aspect ratio^[27].

Typical plasmonic metals in the UV-VIS-NIR regions are silver, gold, aluminum and copper^[28–30], all of which except aluminum can be electrodeposited using aqueous solutions.

For plasmonic applications in the visible range, silver has the lowest loss. However, gold, having slightly higher loss, especially below its interband transition at 539 nm, is often preferred due its inertness and biocompatibility ^[29,31]. It is for these reasons that gold is the metal of choice for biological and chemical sensing applications. In addition to intrinsic metal losses due to interband transitions and intraband damping, plasmonic structures can also exhibit loss due to extrinsic factors such as impurity and surface morphology. Increased surface roughness may be beneficial for SERS applications as it increases the number of local hotspots ^[32,33], but it proves detrimental to plasmonic sensing as it increases the surface resistivity and leads to mode broadening ^[34,35].

As a conductive surface is necessary for the electrodeposition process, the vast majority of electrodeposition carried out through a lithographically-defined template utilizes a metal seed layer and ends with template and seed layer removal ^[26,36–38]. In the context of LSPR applications where the discrete metal nanostructures are fabricated on a nonconductive (typically glass) substrate ^[38], the seed layer removal both adds steps to the fabrication process and risks impairing plasmonic performance due to degraded structure integrity. The wet etching process for nanoscale features is difficult to control and could entirely remove the nanostructures due to its isotropic nature. Meanwhile, dry etching of gold remains a challenge due to the low volatility and redeposition of etch byproducts ^[39]. Moreover, etching using various etchant gas recipes ^[40,41] is never completely anisotropic, even with a mask. We propose eliminating the need for these steps by depositing directly onto a glass substrate coated by a transparent conductive oxide, namely indium tin oxide (ITO). The surface conductivity of the ITO film is sufficient for electrodeposition, but not so high as to hinder plasmonic performance.

Electrodeposition is a complex electrochemical process. Factors affecting structure morphology and quality include anode and cathode geometry and materials, type of electrolyte, bath additives, temperature, electrode number, agitation, and the choice of potentiostatic (fixed voltage) vs. galvanostatic (fixed current) deposition. It is known that pulsed deposition offers a higher degree of control of the nanocrystalline structure of the deposit over direct current deposition ^[42–45]. Such a characteristic is desirable for growing metallic nanostructures for plasmonic applications. Due to the numerous factors influencing growth, the establishment of a pulsed deposition process is often implemented as a parametric study ^[45–47], with the pulse parameters themselves being the simplest to manipulate. In this work, we present an in-depth study of the role of pulse parameters in the optical properties and morphology of the electrodeposited gold film. Furthermore, we demonstrate the fabrication of high-quality well-ordered polarization-invariant gold nanostructures directly onto ITO coated glass which are suitable for sensing applications in the visible range.

2. Results and Discussion

A schematic and photograph of the electroplating setup are shown in **Figure 1**. Owing to the negligible area occupied by the nanopatterns, the patterned sample is electroplated in parallel with a sacrificial bare ITO substrate for fixing the current density in the mA/cm² range. Platinized titanium mesh is used as an anode, while a total of four copper clips are used to secure the two samples (cathode). A pair of silicon o-rings (6 mm aperture diameter) is used to prevent leakage of the plating solution. All the electrodeposition in this work is done at 3 mA/cm² current density.

Pulsed electrodeposition of nanostructures is highly dependent on two competing growth mechanisms: the nucleation rate and the growth of existing grains ^[46]. The extent to

which one process dominates over the other is influenced by cathode (sample) and holder geometry, inclusion of growth inhibitors in the plating solution, and the characteristics of the interfacial double layer between the surface and the bulk solution. When the current is on (off), the double layer capacitance is charged (discharged), affecting the diffusion of gold species to the substrate. We vary the deposition characteristics by altering the pulse parameters, which consist of four quantities, only two of which are independent. These parameters are the pulse ON time T_{ON} , pulse OFF time T_{OFF} , pulse period $T = T_{ON} + T_{OFF}$, and duty cycle $D = T_{ON}/T$, which is usually expressed as a percentage. We used a square pulse shape, illustrated schematically in **Figure 2(a)**. The various sets of pulse parameters and corresponding sample labels are shown below in Table 1, with two seconds of each pulse shape depicted in Figure 2(b).

To investigate how the pulse parameters affect the quality of gold grown directly onto ITO, with plasmonic applications in mind, we use first use optical spectroscopy and scanning electron microscopy (SEM) to respectively determine the spectral and morphological characteristics of bulk gold deposition. Representative reflection images, reflection spectra, and SEM micrographs are presented for the first three samples in **Figure 3**.

Sample S_1 , grown using DC current, was the first experiment of depositing onto an unpatterned substrate. The optical quality of the electrodeposited gold is investigated by comparing the reflection spectra from 50 representative points across the sample with the ideal reflection of gold film (dashed curve). The range of reflection spectra within one standard deviation of the mean (indicated by the shaded blue area), which we denote here as the reflection band, gauges the uniformity of the electrodeposited gold film, while the difference of the average reflection (thick blue curves) from the ideal reflection of gold film gauges the quality of the gold film. As evident from Figure 3(a), the reflection band of S_1 is

both large and spread out. Visually, the surface of sample S_1 appears opalescent in some areas and exhibits many cracks in others. From the SEM inspection in Figure 3(b), some areas appear to be solid gold (Figure 3(c)), while others are bare or have growths of dendritic structures. This is far from the ideal deposition uniformity necessary for high quality structures. Sample S_2 was electrodeposited by pulsed current with a pulse period of 1 s and a duty cycle of 50%. As shown in Figure 3(d), the reflection spectra of S_2 , while still showing a large band, have smaller range (gray shaded area) compared to that of S_1 . Moreover, the average reflection spectrum is closer to the Fresnel reflectivity calculated using refractive index data ^[48]. While the surface visually appears much more uniform, SEM inspections indicate that the deposit quality varies from smooth (Figure 3(e)) to porous (Figure 3(f)). Next, S_3 was deposited at the same duty cycle of $D = 50\%$, but with half the period ($T = 0.5$ s). The reflection band for this sample is qualitatively similar to that of S_1 , however the average reflection is closer to the calculated ideal reflection. From the SEM images (Figure 3(h)-(i)), the surface topology varies among uniformly covered areas, areas with openings and loosely connected “islands” of gold growths, and areas with holes of various size. We further investigated the effect of duty cycle with a period fixed at $T = 1$ s, with representative spectra and images of S_4 ($D=75\%$), S_5 ($D=25\%$), and S_6 ($D=10\%$) presented in **Figure 4**.

As shown in Figure 4(a), sample S_4 ($T=1$ s, $D=75\%$), has a visual appearance akin to S_2 . The reflection spectra of S_4 are more concentrated toward the middle of the range, unlike those of S_2 , which are denser toward the top of the range. The SEM images reveal that the holes in S_4 are larger and more prevalent. The difference of hole size is likely attributed to more lateral diffusion of incoming gold ions during the OFF time, which decrease the hole size for a smaller duty cycle. Based on this reason, we decrease the duty cycle further to $D = 25\%$ (S_5), and observe much narrower reflection band as shown in Figure 4(d). The spectra

all lie within a narrow range close to (and exceeding in some cases towards the near-infrared) the theoretical (ideal) value. Sample S_5 exhibits the best spectral results thus far. However, as indicated in the SEM images (Figure 4(e)-(f)), the electrodeposited gold appears to be porous in some areas and sparsely populated below the surface in others. For completeness, we investigated the case of decreasing the duty cycle even further with S_6 ($T=1$ s, $D=10\%$). As shown in Figure 4(g), the reflection band of S_6 exhibits a large range, with the average reflection far below the ideal normalized reflection. The gold film appears to have bright and dark patches (Figure 4(g), inset), corresponding to highly uneven surface (Figure 4(h)) covered by nucleated gold grains (Figure 4(i)). It is known that small duty cycle is often preferred due to the high nucleation rate and low grain growth, but under the current experimental conditions, it yields adverse results. Indeed, a balance must be maintained between two competing growth mechanisms in pulse electrodeposition. The vertical growth and the lateral diffusion are mainly dependent on ON time and OFF time, respectively. Increasing ON time (increasing duty cycle) encourages more vertical growth, which often leave behind porous film. On the other hand, increasing the OFF time encourages more lateral diffusion, which could lead to discontinuous gold film and subsequently gold nanoparticles formations. Thus, the duty cycle and period must be carefully chosen to maintain the balance between the two competing processes. For this reason, we further fix the duty cycle to $D = 25\%$ while decreasing the period to $T = 0.4$ s with S_7 . This corresponds to T_{ON} of 0.1s and T_{OFF} of 0.3s. The reflection spectra and SEM images are presented in **Figure 5(a)**.

As evident from Figure 5(a), S_7 exhibits even better optical characteristics compared to S_5 . To see the effect of longer OFF time on the quality of electrodeposited film, we also conducted electrodeposition with T_{ON} of 0.1s and T_{OFF} of 0.4s for sample S_8 , where the OFF time is 100 ms longer than for the previous sample. Although the surface of S_8 has some

areas that appear visibly smooth, there are also many areas that appear dark and patchy. The SEM inspections in Figure 5(e)-(f) reveal that the gold film of S_8 is porous. This is also indicated by the reflection band in Figure 5(d), where the average reflection is leaning towards the theoretical reflection but with a large reflection band originating from patchy areas. This confirms that lateral diffusion during off-time plays important role in the morphology of the electrodeposited film, where 100ms longer OFF time is sufficient to severely degrade the film quality. Among all the pulse schemes presented in this work, S_7 is the best plating scheme in terms of the reflection spectra and visual appearance. The proximity towards the theoretical value and the narrow reflection band indicates high uniformity of small grains with good surface coverage, as also confirmed by the SEM images in Figure 5(b)-(c). We conclude that for pulse electrodeposition of gold directly onto ITO-coated glass using our electrode and sample holder geometry, a pulse period of 0.4s with a duty cycle of 25% is optimal.

We proceeded to use this scheme for electrodeposition of various rotationally symmetric gold nanostructures, where nanopatterns with sub-20-nm features are defined by the cold sonicated development electron beam lithography process we developed previously^[5]. Rotationally symmetric nanostructures are chosen in this study because they address the requirements of a practical sensing platform such as robust mode excitation and strong optical response under unpolarized light illumination. Here, we present nanopatterns grown using either or both (in the case of dimers) of two numbers of pulses. The growth of samples using $n=10$ and $n=21$ pulses corresponds to total ON times of 1 s and 2.1 s, respectively. A selection of the fabricated nanostructures is shown in the oblique incidence SEM images in **Figure 6**, with normal incidence insets. Square dimers, having a design square side length s of 80 nm and a design gap g of 30 nm are shown in Figure 6(a) for $n=21$.

Due to the nature of the gold growth and the compliance of the resist template, the resultant nanostructures have features that are wider than the defined patterns. The square dimers were measured to have average side lengths of ~ 99 nm and ~ 103 nm ($n=10$) and ~ 106 nm and ~ 111 nm ($n=21$) in the directions parallel and perpendicular to the gap, respectively. The increased dimer square size resulted in an average gap width of about ~ 9 nm in both cases, illustrating the achievable resolution of our electrodeposition method. From the oblique SEM images, using the scale bar and adjusting for the inclination angle, the average heights of the dimer structures are estimated to be 75 ± 5 nm ($n=10$) and 84 ± 7 nm ($n=21$).

We also fabricated internally C_6 -symmetric star shapes, as shown in Figure 6(b), with a design arm length of 100 nm, feature size of 20 nm and a periodicity of 300 nm in both lateral directions, grown using $n=21$ pulses. The central region of each star appears larger at the intersection of its individual arms due to EBL proximity effects originating from overlapping e-beam exposure lines. Additionally, Figure 6(c) shows gammadion cross structures ($n=21$) with a half-arm length of 100 nm and a periodicity of 350 nm. Finally, in Figure 6(d) we fabricated arrays of ν -shaped split ring resonators ($n=10$) arranged to have four-fold rotational lattice symmetry (C_4 ν -SRR), as shown in Figure 6(d). The ν -SRRs were designed to have an arm length of 100 nm, feature size of 20 nm and an opening angle of 60° . It should be noted that ν -SRRs with opening angles ranging from 40° to 90° , and arm lengths as small as 60 nm have been successfully grown using the current method, demonstrating good angular tunability (not shown here). With the estimation as above, the heights of the C_6 stars and gammadions are approximately 64 ± 5 nm, and that of the C_4 ν -SRRs is 68 ± 8 nm.

These heights correspond to an average growth rate of 3-7 nm per pulse, or 30 – 70 nm per second of ON time. For a time rate including the pulse OFF time, this gives a growth rate of 7.5-17.5 nm/second, a much higher rate than other metallic nanostructure growth methods

based on physical or chemical vapor deposition^[36]. Several things should be noted about the growth rates. First, the height of structures grown on a given sample varies inversely with the lateral density or metal fill factor. Second, the reported growth rates are average values, and as can be inferred from the small marginal height gain achieved in the dimers by increasing from $n=10$ to $n=21$ pulses, the growth rate seems to decrease with increasing pulse number, as evidenced by the minima and maxima of the recorded voltage oscillations (see Supporting Information Figure S1), which increase for the first several pulses, and then reach steady state values. Additionally, the samples were deposited with pulses programmed with two different sampling times, causing the practical duty cycles and periods to differ slightly (Figure S1). Finally, while the $n=10$ sample was deposited using a bare ITO substrate in parallel with the patterned one, the $n=21$ sacrificial substrate was covered in gold prior to nanopattern deposition. This may also account for the difference in deposition rates.

The resonance properties of the above plasmonic nanostructures in comparison with their planar counterparts are presented in **Figure 7**, where the resonance modes (λ_{LSPR}) are indicated by the transmission dips. Unpolarized light illumination and collection was used for all structures except for the dimers, which were measured under linear polarization (parallel to the dimer gap). The electrodeposited dimers exhibit a resonance mode at 680 nm (662 nm) with Q factor ($Q = \lambda_R/\Delta\lambda$) of $Q\sim 6.37$ ($Q\sim 6.27$) for fabrication with $n=10$ ($n=21$) pulses and higher spectral contrast than their planar counterpart (Figure 7(a)). This illustrates that the structural integrity of the sub-10-nm gap of the dimer is preserved during electrodeposition. The resonance of the electrodeposited dimer is also observably narrower, which is indicative of lower damping loss due to smoother gold surface.

The properties of polarization-invariant plasmonic nanostructures such as planar gammadion and star-shaped structures and their feasibility for biosensing have been studied

previously^[49]. While the present structures are not tall enough to exhibit longitudinal resonances associated with standing wave due to Fabry-Perot (FP) reflections, we note that many of these transverse resonances are blue-shifted from those of their planar counterparts. This blue shift with increasing height, which has been experimentally observed by other groups, may be attributed to an increase in the restoring force on electrons displaced by plasmon oscillations^[50,51]. The transmission spectra of a planar and electrodeposited C_6 structures are presented in Figure 7(b), showing an observed blue shift from 962 nm to 856 nm as the thickness is increased 30 nm to 64 nm. The broad resonance of star-shaped nanostructures has been shown to originate from conductive coupling between their constituent nanorods^[49]. In our measurement, additional broadening may have originated from lower grating efficiency for wavelengths above 800 nm^[12]. The effect of increased thickness in the star-shape structure is apparent in the observation of an additional resonance mode at 590 nm (hollow arrow), which was previously absent in the planar C_6 spectrum. This mode is associated with the surface plasmon oscillations along the longitudinal direction, which is likely the transition before the FP-like longitudinal mode emerges at increasing thickness.

Figure 7(c) presents the transmission spectra of planar and electrodeposited gammadions, where, of the two modes of the planar structure, only the higher order mode around 700 nm (denoted by a hollow arrow) is observed for the electrodeposited gammadion due to the spectral limit of our Cytoviva system to wavelengths below 1000 nm. The hybrid magnetic-electric resonance properties of the gammadion have been shown to emerge from the conductive coupling of its constituent nanorods^[49]. For the planar gammadion with 30 nm thickness and 100 nm arm length, the fundamental mode (denoted by the solid arrow) and higher order mode (hollow arrow) are located at 1700 nm and 887 nm, respectively. We

observe a blue shift from 887 nm to 700 nm for the higher order mode. Additionally, we clearly observe a mode (gradient fill arrow) at 545 nm associated with the height as in the case of C_6 structure. Furthermore, on the left side main dip in the tall gammadion spectrum, we observe what appears to be a resonance at around 625 nm whose own spectral dip is overshadowed by the main dip, due to its low prominence. The resonance mode of the electrodeposited gammadion exhibits more pronounced resonance as evident from its higher resonance contrast. Finally, we present in Figure 7(d) the transmission spectra of planar and electrodeposited C_4 v-SRRs with 45° and 60° opening angles, showing the expected blue shifts and higher spectral contrasts for the resonance modes of the electrodeposited v-SRRs. The polarization-dependent optical properties of planar v-SRRs of various angles and arm lengths arranged in a square lattice have been previously investigated in detail ^[12,52]. Here, the magnetic (solid arrows) and electric (hollow arrows) modes are observed at 820 nm and 637 nm (for 45° opening angle) and 770 nm and 649 nm (for 60° opening angle). The Q factors of the magnetic and electric modes are 6.8 and 7.9 (for 45° opening angle) and 10.1 and 9.4 (for 60° opening angle), respectively.

All of the above plasmonic structures demonstrate resonance modes in the visible spectrum with high spectral contrasts under unpolarized illumination. These characteristics are in line with the requirement for practical sensing platform such as simple and cost-effective implementation, robust mode excitation, and strong optical response. Moreover, realizing these structures by electrodeposition significantly reduces the cost of fabricating plasmonic nanostructures with desired optical characteristics. In terms of sensing performance, these polarization-invariant nanostructures are expected to exhibit higher bulk sensitivities in the same way as the electrodeposited dimers have been shown to exhibit 45% higher bulk sensitivity than that of the planar dimer ^[27].

3. Conclusion

We have investigated direct pulsed electrodeposition process for realizing high aspect ratio plasmonic nanostructures which find applications in cost-effective and practical sensing platform. The role of pulse time parameters in the optical properties and morphology of the electrodeposited film has been systematically studied, from which 25% duty cycle with 400ms pulse period have been found to be the parameters for the best film quality. Using these parameters, we have successfully electrodeposited metallic nanostructures with features in the sub-10-nm regime, with their plasmonic properties consistently better than those of their planar counterparts. Specifically, we have demonstrated high aspect ratio rotationally symmetric plasmonic nanostructures that exhibit resonances in the visible spectrum and high spectral contrast under unpolarized light illumination. Coupled with the electrodeposition process, which imparts much smaller cost than that based on physical deposition, these electrodeposited polarization-invariant nanostructures address the simplicity and cost-effective requirements of a practical optics-based sensing platform.

4. Experimental Section

The EBL patterning was carried out on the Raith e_LiNE system on 120 nm thick ZEP520A e-beam resist based on 20 keV energy and 30 pA beam current. The sample was then developed in a mixture of *n*-amyl acetate and isopropanol using a sonicated cold development process with 5 s pre-sonication time, 10 s sonication time, and 20 s post-

sonication time. This process has been reported to exhibit high verticality (with $<5^\circ$ sidewall angle) and aspect ratio of ~ 10 .

For the electrodeposition process, we used a commercial (24K Pure Gold Plating Solution, Gold Plating Services, Inc.) neutral plating solution consisting of potassium aurocyanide $[\text{KAu}(\text{CN})_2]$ (0.5% wt), a cobalt complex ($\text{C}_{10}\text{H}_{12}\text{CoN}_2\text{O}_8$), a nickel complex ($\text{C}_6\text{H}_6\text{NiNO}_6\text{H}$), weak organic acid buffers, inorganic salts, and water. The current density was fixed to be $3\text{mA}/\text{cm}^2$, in line with the manufacturer's recommendation. We performed the deposition at room temperature. The recommended temperature at which to deposit was $52^\circ\text{--}66^\circ\text{C}$; however, based on prior experiments, we saw no improvement in deposit quality with increased temperature. For the current source, a Keithley 2600 Source Meter Unit was controlled using standard SCPI commands with MATLAB.

Reflection spectra of the unpatterned electrodeposited samples were obtained by normalizing the backscattering of individual samples with that of a planar silver mirror, using a Cytoviva hyperspectral imaging system, capable of measuring in the range from 400 nm to 1000 nm. The ideal reflection spectra (thick black lines) in Figures 3-5 were calculated from the experimental data of Johnson and Christy^[48], dividing air-gold reflectance by air-silver reflectance. Transmission spectra for the planar C_6 star and gammadion cross structures were measured using a spectrophotometer (Craic), in the wavelength range from 300 nm to 2000 nm, and normalized with respect to bare substrate. All other transmission spectra were obtained using the Cytoviva hyperspectral system and normalized with respect to bare substrate.

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Figure 1. Side view schematic of the dual-substrate electrodeposition holder and (b) a photograph from the front

Figure 2. (a) Illustration of current density pulse shape and parameters and (b) 2 seconds of each of the waveforms used in this work

Figure 3. Reflection spectra at various positions on samples (a) S_{DC} , (d) $S_{1/50}$, and (g) $S_{0.5/50}$, with reflection images inset, and corresponding SEM images for (b)-(c) S_{DC} , (e)-(f) $S_{1/50}$, and (h)-(i) $S_{0.5/50}$. The thick line in the spectra represents the mean of the measurements, with the shaded blue area encompassing ± 1 std. dev. The dashed curve represents the ideal normalized

reflectivity based on optical constant data. The inset images depict a square area of side 51.68 μm .

Figure 4. Reflection spectra at various positions on samples (a) $S_{1/75}$, (d) $S_{1/25}$, and (g) $S_{1/10}$ with reflection images inset and , and corresponding SEM images for (b)-(c) $S_{1/75}$, (e)-(f) $S_{1/25}$, and (h)-(i) $S_{1/10}$. The significance of the lines and shaded regions is the same as the previous figure. The inset images depict a square area of side 51.68 μm

Figure 5. Reflection spectra at various positions on samples (a) $S_{0.4/25}$ and (d) $S_{0.5/20}$ with reflection images inset, and corresponding SEM images for (b)-(c) $S_{0.4/25}$, and (e)-(f) $S_{0.5/20}$. The significance of the lines and shaded regions is the same as the previous figures. The inset images depict a square area of side 51.68 μm

Figure 6. SEM micrographs of various electrodeposited structures, all taken at 60k magnification: (a) square dimers of side length $s = 80$ nm and nominal gap $g = 30$ nm, (b) four-fold externally rotationally symmetric v -SRR ($s = 100$ nm, $\theta = 60^\circ$), (c) six-fold rotationally symmetric stars ($s = 100$ nm) and (d) four-fold internally rotationally symmetric gammadion crosses ($s = 100$ nm). All scale bars represent 400 nm.

Figure 7. Transmission spectra of (a) square dimer, (b) C_6 -symmetric star structure, (c) gammadion resonator, and (d) fourfold rotationally symmetric v -SRR array (C_4 v -SRR with $\theta = 45^\circ$ and $\theta = 60^\circ$) for planar ($h = 30$ nm) and electrodeposited ($h = 70 \pm 5$ nm) structures. The resonance modes are indicated by the solid, hollow, and gradient-fill arrows.

Table 1. Sample designations and pulse parameters. A current density of $j_{ON} = 3 \text{ mA/cm}^2$ was used for all samples

Sample	T (s)	D	T_{ON} (s)	T_{OFF} (s)
S_1	DC	100%	n/a	n/a
S_2	1.0	50%	0.50	0.50
S_3	0.5	50%	0.25	0.25
S_4	1.0	75%	0.75	0.25
S_5	1.0	25%	0.25	0.50
S_6	1.0	10%	0.10	0.90
S_7	0.4	25%	0.10	0.30
S_8	0.5	20%	0.10	0.40

Pulsed electrodeposition is used to grow gold films directly onto ITO-coated glass using various pulse parameters, and the results are compared using spectroscopy and electron microscopy. A suitable set of pulse parameters is then used to vertically grow gold nanostructures through a template, showing superior spectral characteristics to their planar conventionally-deposited counterparts.

Keyword: Nanofabrication, Electrodeposition, Plasmonics

Aaron D. Mueller, Landobasa Y. M. Tobing, Dao Hua Zhang*

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Supporting Information

Title: Reliable fabrication of high aspect ratio plasmonic nanostructures based on seedless pulsed electrodeposition

*Aaron D. Mueller, Landobasa Y. M. Tobing, Dao Hua Zhang**

Figure S1. Current (lower) and voltage (upper) waveforms used for pulsed electrodeposition for the samples with $n=10$ (solid lines) and $n=21$ (dashed lines) pulses, corresponding voltage envelopes (black solid and dashed lines) added for clarity.

Figure S1 shows the voltage and current waveforms for the two different samples. The sample with $n=10$ pulses had a signal sampling time of 0.1 s (one on sample per period), whereas the $n=21$ sample had a sampling time of 0.02 s (five ON samples per period). The total time of the first signal agrees with 10 cycles of the nominal period (0.4 s), for a total of 4 s. However, we found that there were slight delays when we decreased the signal sampling time, so that the $n=21$ waveform was about a second longer than the nominal 8.4 s. Also from the figure, with the help of the voltage envelopes added, we can see that the maxima and minima of the $n=10$ sample are respectively higher and lower than those of the $n=21$ sample after the first few pulses, from which we can infer faster charging and discharging of the capacitive double layer. This may or may not be influenced by the original surface of the sacrificial substrate.