Daisy-like nanostructures for plasmonic biosensors

Hande Cavus and Mustafa M. Aslan

Successful nanofabrication of daisy-like surface topologies for development of novel plasmonic sensors was accomplished.

A surface plasmon (SP) is an optically excited electron oscillation along the interface between two media, one of which has a negative dielectric constant (i.e., gold and silver). The fundamentals of SP waves are relatively well understood. Depending on the optical properties at the boundaries, it is possible to excite SP modes guided by a thin metal film. The SP response of a medium is sensitive to both its refractive index and its absorption characteristics. Consequently, the electromagnetic wave modes of plasmonic sensors (PSs) have been extensively used in real-time diagnostic applications in both the laboratory and in industry for so-called label-free monitoring of physical and chemical molecular changes. Moreover, PSs can be quantified in real time. However, conventional PSs are not sufficiently sensitive to detect low concentrations (sub-pg/mm²) of substances with low molecular weight (here, proteins). Current research efforts are focused toward improving their sensitivity.

The catalytic, optical, and electrochemical properties of a PS can be enhanced by superficial nanostructuring, which provides more surface area, enhances the electromagnetic field, and enables efficient electron transfer. If the dimensions of the nanostructures are comparable with the wavelength of the incident light, it interacts with them in different ways. In particular, nanostructure characteristics such as size, shape, spacing, optical properties, and layer thickness may alter the spatial properties of the light (such as intensity, polarization, phase, and frequency) in a way that makes the PS more sensitive. Although we can currently tailor nanostructured films using a combination of advanced lithography methods and deposition techniques, these approaches require many steps and thus are time-consuming and expensive.

One alternative is to use porous anodized (galvanized) alumina (PA)—which is easy to work with and economical—as a template, mask, or matrix,¹ which allows fabrication of a wide range of nanostructures 10–500nm in diameter and spaced 20–1000nm apart.²,³ Different shapes are also possible. For example, gold and silver hemispherical shells can be fabricated by chemically removing PA.⁴,⁵

Here, we describe fabrication of daisy-like aluminum (Al) and gold (Au)-coated nanostructures (see Figure 1) through a much-simplified process of anodization, chemical removal, and

Table 1. Typical dimensions of the nanostructures as measured by scanning electron microscopy.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average inner diameter, (d_i) (nm)</th>
<th>Average inter-daisy distance, (l_{id}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40V Al</td>
<td>70</td>
<td>98</td>
</tr>
<tr>
<td>40V 10nm Au-coated</td>
<td>60</td>
<td>98</td>
</tr>
<tr>
<td>40V 30nm Au-coated</td>
<td>40</td>
<td>98</td>
</tr>
<tr>
<td>60V Al</td>
<td>117</td>
<td>146</td>
</tr>
<tr>
<td>60V 10nm Au-coated</td>
<td>110</td>
<td>146</td>
</tr>
<tr>
<td>60V 30nm Au-coated</td>
<td>90</td>
<td>146</td>
</tr>
</tbody>
</table>

Figure 1. Schematic of daisy-like nanostructures fabricated. \(d_o\): Outer diameter. \(d_i\): Inner diameter. \(l_{id}\): Inter-daisy distance. AFM: Atomic force microscopy.

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deposition (see Figure 2). We began by producing high-purity (99.99%) aluminum foils by melting, casting, and cold rolling. We then diced the foils onto $0.3 \times 10 \times 100$ mm plates. We annealed the plates at $400^\circ$C for 4h under flowing argon. We ultrasonically degreased the foil samples in isopropyl alcohol and

![Image](https://example.com/image1)

**Figure 2.** Nanofabrication steps. Al: Aluminum. $\text{Al}_2\text{O}_3$: Aluminum oxide. Au: Gold.

then electropolished them in a volume ratio of 1:4 perchloric acid:ethanol under a constant voltage of 20V at 5$^\circ$C for 4min. We anodized the samples at 40 and 60V in 0.3M oxalic acid at 2$^\circ$C using a stirring rate of 300rpm for 90min. Finally, we chemically removed the surface film by immersing the plates in a solution of phosphoric acid (6wt%) and chromic acid (1.8wt%) for 120min. The surface nanostructures look like daisies with three characteristic dimensions: $d_o$, outer diameter; $d_i$, inner diameter; $l_{id}$, inter-daisy distance (see Figures 1 and 2). In a finishing step, we coated the daisy-like structures with 10 and 30nm-thick gold by magnetron sputtering.

We used scanning electron microscopy images to measure the dimensions. The average inner diameter of the structures is between 40 and 117nm, and the space between them is between 98 and 146nm, depending on the anodization voltage and coating. Table 1 lists typical dimensions of the nanostructures for anodization voltages of 40 and 60V. We also used atomic force microscopy to image the daisy-like structures (see Figure 3). The figure shows uniformity of the structure, a narrow distribution of dimensions, and the proper dimensional range for localized SP excitement. These findings are all consistent with enhanced sensitivity of PSs. In addition, our ongoing

![Image](https://example.com/image2)

**Figure 3.** AFM images of Al flower-like nanostructures (anodization voltage = 40V).
investigations suggests that daisy-like nanostructures have promising optical properties as well (e.g., spectral reflectance and absorbance).

In summary, we fabricated daisy-like Al and Au nanostructures using a process of anodization, chemical removal, and deposition. The typical daisy-like surface topologies and the size range of the fabricated structures show promise for developing novel PSs in the UV-visible spectrum. Detailed results of fabrication and optical characterization have been submitted for publication.6 Our next step will be to test the nanostructured sensor performance on interactions of low-molecular-weight proteins at low concentrations.

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References