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## COMMUNICATION

## Surface enhanced Raman scattering on aluminum using near infrared and visible excitation

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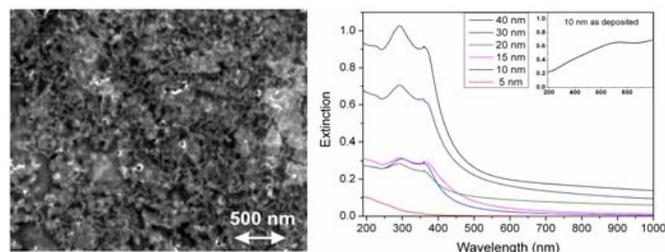
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**We observe strong surface enhanced Raman scattering on discontinuous nanostructured aluminum films using 785 nm excitation even though dielectric constants of this metal suggest plasmon supported spectroscopy in the ultraviolet range. The excitation of SERS correlates with plasmon resonances in the 1.3 – 2.5 eV range identified in electron energy loss spectra.**

Surface enhanced Raman scattering (SERS) that is, Raman scattering taking place in enhanced and highly confined local fields<sup>1</sup> is one of the most prominent plasmon supported spectroscopic effects. The creation of strong local fields depends on the dielectric constants of the metal  $\epsilon_m$  and requires a negative real part of the complex dielectric constant. Additionally, in order to achieve high enhancement levels, plasmons should exhibit small damping, i.e. the imaginary part of  $\epsilon_m$  has to be small<sup>2</sup>. Gold and silver nanospheres fulfil these requirements in the visible and violet range, respectively, and are the most common materials in plasmon supported optics and spectroscopy. In particular, surface plasmon resonances of these metals can be shifted to lower energies by variations in shape and size of the nanoparticles, and the formation of nanoshells, but also by coupling of plasmons in composites of nanoparticles, such as in aggregates and in arrays<sup>3</sup>. This enables plasmon support by silver and gold in the entire visible and near infrared (NIR) wavelength range. There is also a strong interest in the extension of SERS and other plasmon enhanced spectroscopy techniques, and plasmon supported photonics in general, to shorter wavelengths. Aluminum is considered a promising material for employing plasmonics in the ultraviolet (UV)-range<sup>4,5</sup>. UV SERS experiments using various Al nanostructures have been reported<sup>6-10</sup>. The overall potential capabilities of this metal have been discussed based on computations

and experimental characterization of its surface plasmon spectrum<sup>11-16</sup>. These studies show that Al nanostructures exhibit plasmon resonances in the UV for isolated small spherical particles. But, as for other metals, for increasing sizes and aspect ratios of Al nanoparticles<sup>12,16</sup>, and also interacting nanostructures such as arrays of Al nanostructures<sup>11</sup> or metal films with nanoholes<sup>13</sup>, plasmon resonances can shift to lower energies and appear in the visible and even in the NIR range. Additional shifts in the plasmon resonances to longer wavelengths can occur due to the formation of aluminum oxide<sup>13,16</sup>. This makes aluminum interesting for plasmonics in the entire optical range from UV to NIR.

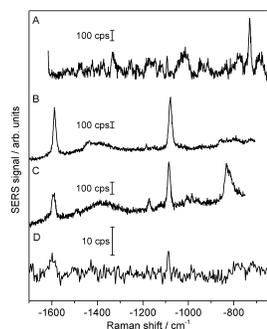
Here we study SERS of molecules on discontinuous nanostructured Al films. In particular, we want to explore SERS capabilities of these films beyond the UV range at longer wavelengths excitation. The films are prepared by evaporating aluminum at various thicknesses on glass substrates followed by annealing.



**Fig 1:** SEM image of an annealed Al film and optical extinction spectra of a smooth aluminum film (inset) and annealed films (700 °C for 10 min in forming gas) at varying thickness

Figure 1 shows SEM images of an annealed Al film along with extinction spectra of evaporated films before and after annealing. Compared to other metals, the plasma resonance of aluminum appears at relatively high energy at 15 eV. Therefore, smooth aluminum films show a strong reflectivity in the entire optical range from UV to NIR (see inset in Fig.1). The discontinuous aluminum films formed after annealing display a changed extinction spectrum. The films show now broad extinction features in the UV range. Similar changes in the extinction spectra have recently been reported for the formation of small Al nanoparticles from nanostructured aluminum films with thicknesses between 2.5 and 8 nm<sup>17</sup>. While the formation of isolated Al nanoparticles as discussed in ref<sup>17</sup> results in an absorption around 200 nm, discontinuous Al films with thicknesses between 10 and 40 nm give rise to extinction spectra up to 400 nm. Freshly prepared Al-films do not show any intrinsic Raman signature but a very thin aluminum oxide layer of a few nanometer might exist on these films. After several days, a Raman line at ~500 cm<sup>-1</sup> appears which is probably related to an oxidation of the film. The reported SERS studies have been performed on fresh films.

Figure 2 shows SERS spectra using discontinuous Al-films as enhancing nanostructures and 785 and 532 nm excitation. Molecules for the Raman experiments were applied to the film in 5  $\mu$ L droplets of 10<sup>-6</sup>-10<sup>-4</sup> M aqueous solution spread over ~10 mm<sup>2</sup>. After evaporation, spectra were collected in 180° backscattering geometry using the same objective for excitation and collection of the scattered light. Depending on the concentration of the target molecule in the droplet, 3x10<sup>5</sup> – 3x10<sup>7</sup> molecules are present in the probed ~1  $\mu$ m<sup>2</sup> area on the film. All target molecules, adenine, para-mercaptobenzoic acid (pMBA) and para-aminothiophenol (pATP) have their electronic absorption in the UV, so that there is no resonance Raman contribution to the SERS enhancement at the applied excitation.



**Fig 2:** SERS spectra measured on discontinuous aluminum films. Spectra A-C: SERS collected from 3x 10<sup>5</sup> molecules adenine, pMBA and pATP, respectively, using 785 nm excitation, spectrum D: SERS collected from ~10<sup>7</sup> molecules pATP using 532 nm excitation. Excitation 10<sup>5</sup> - 10<sup>6</sup> Wcm<sup>-2</sup>, collection time 1sec (spectra A-C) and 10 sec (spectrum D)

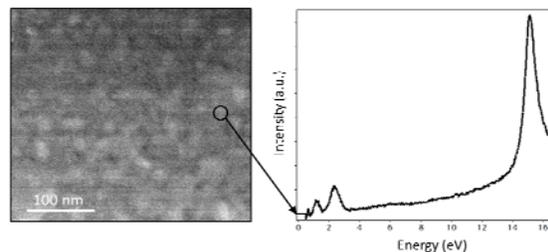
SERS spectra of all three molecules are in agreement with NIR-SERS spectra reported for these molecules on gold or silver. There is no Raman spectroscopic indication for a chemical interaction of the

molecules with aluminum or aluminum oxide. It is noteworthy that in our NIR excited non-resonant SERS experiment with adenine, the ring breathing mode at 730 cm<sup>-1</sup> is the dominating spectral feature. This is different from UV-excited and hence resonant SERS spectra of adenine on aluminum, where mainly the stretching modes of various CN bonds around 1335 cm<sup>-1</sup> were reported previously<sup>9,10</sup>.

Our experiments show that 785 nm excitation results in much stronger SERS signals than 532 nm excitation. At 532 nm excitation, only pATP at higher concentrations gives rise to a measurable SERS spectrum. This could be explained by a possible “chemical” contribution to SERS enhancement for this molecule as it has been discussed<sup>18</sup> while the electromagnetic field enhancement is only very weak at 532 nm excitation. Excitation at 405 nm did not result in any detectable SERS signal.

We can understand the strong SERS enhancement particularly at NIR excitation in the framework of the plasmonic properties of discontinuous metal films. Theory predicts intense and extremely localized fields, so-called hot spots, for aggregates formed by metal nanoparticles, fractal structures and semicontinuous random metal films related to specific plasmonic eigenmodes in these structures<sup>19-22</sup>. These hot spots have been experimentally verified for silver and gold nanostructures. For example, they enable single molecule SERS at extremely high enhancement level using non-resonant near infrared excitation<sup>23</sup>. The interesting observation here is that also discontinuous aluminum films provide hot spots in the near infrared range. This might support the hypothesis that field confinement is controlled by the geometry of the nanostructure and not by the nature of the metal or embedding medium dielectric constants<sup>24</sup>.

Plasmonic nanostructures and plasmon resonances can also be probed by electron energy loss spectroscopy (EELS)<sup>25,26</sup>. Compared to optical methods, EELS can provide three orders of magnitude better spatial resolution. Experimental evidence of the nanometer-scale confinement of plasmonic eigenmodes in random silver films has been recently provided by EELS<sup>27</sup>. EELS studies on aluminum nanoparticles performed 30 years ago have identified plasmon resonances of small isolated Al spheres at 6.7 eV and red shifted plasmon resonances around 4 eV for coupled spheres<sup>28</sup>. Here we probe the discontinuous Al films using EELS.

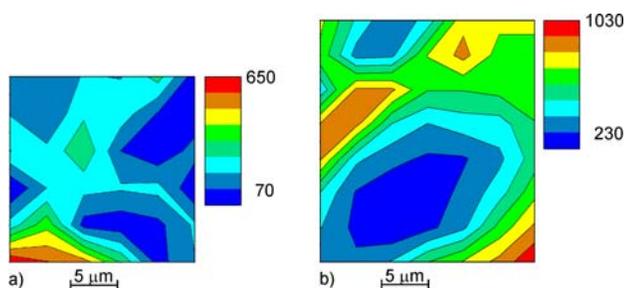


**Fig. 3:** Scanning transmission electron micrograph of the Aluminum film and electron energy loss spectrum collected from the region marked in the image

The EELS data were acquired using an FEI Titan instrument operated at 120kV, holding a subnanometer spatial resolution and

better than 0.2 eV energy resolution<sup>29</sup>. Figure 3 shows the nanostructured Al film along with a typical EELS spectrum. In addition to a strong peak at 15 eV related to bulk plasmons in aluminum, EELS spectra show resonances in the 1.3 – 2.5 eV range, i.e. in the excitation range where the strong SERS signals have been obtained (compare Fig. 2). This correlation between plasmon resonances and the excitation wavelength of SERS strongly supports the electromagnetic origin of the strong SERS effect on discontinuous Al-films. In agreement with the structure of the film shown in the STEM image that lacks indications of isolated nanoparticles, we have not observed resonances around 6.7 eV corresponding to surface plasmons of isolated small Al nanoparticles<sup>28</sup>. More studies are under way to correlate and interpret EELS data and morphology of discontinuous metal films.

Considering the large area from which the signal is collected in an optical experiment, statistically, the area on the nanostructured Al film used for collecting a SERS spectrum should support almost all possible plasmonic eigenmodes of the film. However, only excitation in the near infrared results in strong SERS enhancement, that means that only molecules in the hottest spots related to NIR excitation essentially contribute to the SERS signal.



**Fig 4:** Distribution of the SERS signal (arbitrary units) on the Al film collected with a spot size of  $1 \mu\text{m}^2$  using 785 nm excitation. Images are based on the SERS signal of the  $730 \text{ cm}^{-1}$  line of adenine and the  $1080 \text{ cm}^{-1}$  line of pMBA. The images were obtained by raster scanning a  $\sim 1 \mu\text{m}^2$  spot over a larger area.

Figure 4 displays typical images of SERS signals of two probe molecules collected by scanning a  $\sim 1 \mu\text{m}^2$  spot over a larger area using 785 nm excitation. Differences in signals are less than a factor of ten, indicating a relatively uniform mean SERS enhancement, i.e. about the same number of hottest spots related to 785 nm excitation in each  $\sim 1 \mu\text{m}^2$  sampled spot.

In conclusion, we have demonstrated strong SERS on discontinuous aluminum films using NIR excitation. EELS measurements identify plasmon modes in the visible and near infrared range for these Al structures. So far, the metal was considered as a material which supports SERS at UV excitation. Our experimental results suggests aluminum nanostructures for plasmon supported spectroscopy and photonics beyond the UV range.

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