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Development of a general formalism to analyze plasmonic structures using spectroscopic ellipsometry

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Abstract

Spectroscopic ellipsometry (SE) has been used to measure the full optical response of plasmonic structures. Firstly, the simple case of an anisotropic thin plasmonic layer supported on a transparent substrate is analysed by introducing a quantity named anisotropic surface excess function (ASEF). Such a quantity can be directly extracted from the experiment and simulated using either analytical or numerical methods. Afterwards, the formalism has been generalised using a transfer matrix method. In this way effects on the ellipsometric spectra of thick plasmonic films, anisotropic substrates, plasmonic structures grown on top of a multilayer system are described in terms of

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11 changes in the effective dielectric function of the system. The analysis developed here
12 has been supported by experimental evidences obtained by measuring the response of
13 anisotropic NP arrays grown at glancing angle. The agreement between theory and
14 experiment is clear, suggesting that SE can be conveniently employed to measure the
15 spectroscopic response of plasmonic structures. It is also demonstrated how the figure
16 of merit of the plasmonic resonances can be greatly improved, with particular measure-
17 ment configurations, using SE. This can increase the sensitivity of any refractive index
18 based plasmonic sensor. Finally, compared to normal transmission spectroscopies, SE
19 can easily measure the out-of-plane response of the plasmonic systems, providing a
20 much more stringent test for the suitability of certain models to simulate the far field
21 response of a plasmonic system.

22 Introduction

23 The interaction between electromagnetic waves and free electrons in a low-dimensional metal-
24 lic structure results in surface plasmon effects.^{1,2} These can be considered as the normal ex-
25 citation modes of the systems and have been the subject of tremendous interest due to their
26 application as biological sensor,³⁻⁶ enhancement effects⁷⁻⁹ and solar cell applications.¹⁰⁻¹²
27 When a metal nanoparticle (NP) is excited the electrons are highly localised and decay
28 rapidly within the structures, resulting in localised plasmon resonances (LPRs).

29 LPRs manifest themselves readily by strong absorption/reflection peaks whose positions
30 depend on the shape, size and aspect ratio of the NPs, on the property of the surround-
31 ing medium and on the relative interaction between the NPs.¹³ Their behaviour is usually
32 analysed using conventional spectroscopic methods in the far field, but recently their charge
33 distribution has been also addressed using more specific characterisation methods such as
34 cathodoluminescence,^{14,15} transmission electron microscopy¹⁶ and electron energy loss spec-
35 troscopy.¹⁷ The main limitation of conventional absorption spectroscopies is it allows one to
36 monitor only in-plane properties of the plasmonic structures due to the inherited difficulties

37 in the measurement geometry. To overcome this problem Spectroscopic Ellipsometry (SE)
38 can be utilised as it can analyse changes in the polarization state of a linearly polarized
39 beam reflected at oblique angles of incidence.^{18,19} Recently, SE analysis has been extended
40 to magnetic²⁰ or anisotropic samples²¹ using generalised ellipsometry. Scattering and depo-
41 larization properties of the samples can also be addressed and separated by normal specular
42 reflection. However, SE spectra are difficult to analyse as the response of the whole system
43 needs to be modelled and compared with experiment to address the properties of the samples
44 investigated.¹⁸ For this reason, the number of studies of plasmonic structures using SE is
45 still limited.²²⁻²⁶ Previously it was demonstrated by our group²⁷ that a quantity, named
46 Anisotropic Surface Excess Function (ASEF), could be extracted from the experiment and
47 the response of ultrathin plasmonic layer (<10 nm) directly analysed. The great advantage
48 of ASEF is it depends only on the optical properties of the plasmonic layer alone, rendering
49 easy the modelling of the nanocomposite layer alone.^{27,28} However, the hypothesis for the
50 validity of this approach appears to be limited to very specific cases.

51 At the same time many theories have been developed to describe the optical properties
52 of plasmonic structures. The first attempt dates back to the beginning of the last century,
53 when Mie calculated the absorption cross section of spherical NPs in a host matrix based on
54 the development of electromagnetic potentials in spherical harmonics.¹ For a metallic sphere,
55 with dimensions much smaller than the exciting light, the polarization of the NP leads to a
56 simple dipole behaviour placed at the centre of the sphere. However, this behaviour can be
57 strongly modified. For example, the elongation of a sphere along certain directions lowers
58 the symmetry of the system, resulting in the formation of multiple resonance peaks, cor-
59 responding to the different excitation modes of NP. Interaction with a substrate produces
60 image charge effects that modify the optical response of the system. The work by Yam-
61 aguchi^{29,30} qualitatively reproduced the experiment. However, as recently pointed out,³¹
62 more refined theories are required to quantitatively model the experimental behaviour. Also
63 electromagnetic interactions between closely spaced NPs produce a shift in the resonance

64 position and, for particular NP arrangements, Fano modes are also found which result in
65 sharp resonances.^{5,32–35} More complicated phenomena arise when irregularly shaped NPs
66 are simulated. In this case many different charge excitation patterns can be formed due
67 to changes in the susceptibility of the NP itself.³⁶ Only numerical methods, such as finite
68 element methods,^{37,38} finite-difference time-domain³⁹ or discrete dipole approximation^{40,41}
69 can reproduce the behaviour of such systems. Depending on the system analysed a suitable
70 model then needs to be applied and compared with experiment. SE can be utilised within
71 this framework to test the validity of the approach chosen. Furthermore, as the out-of-plane
72 resonances are also measured, they can no longer be treated as a free parameter and a
73 modelling of the full optical response of the system is required.

74 In this article a detailed study of LPRs with SE will be performed. The plasmonic
75 layer will be produced using an alternative self-assembled method based on glancing angle of
76 incidence on a stepped template.^{42–45} Adatoms are sent at shallow angles of just a few degrees
77 onto a faceted c-plane Al_2O_3 and part of the surface is shadowed by the presence of the steps.
78 Adatoms are only deposited in the exposed areas and spontaneously rearrange into NP arrays
(see Figure 1). The technique is simple and large homogeneous areas covering the entire

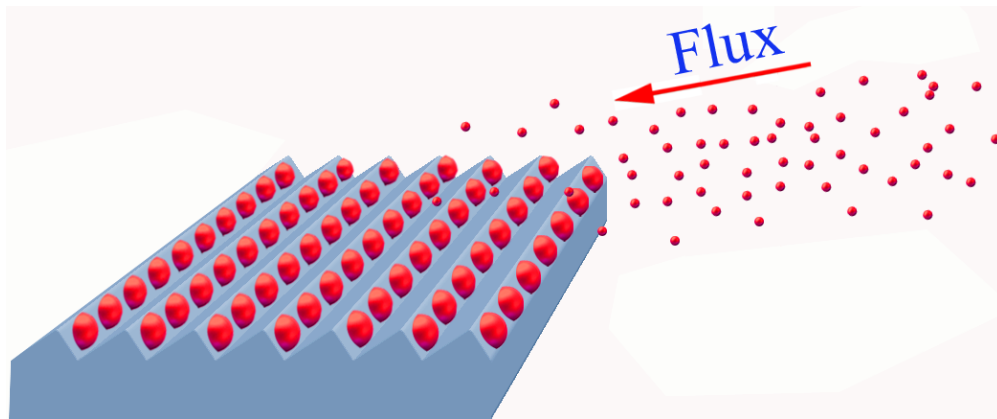


Figure 1: A schematic view of the deposition technique: a flux of collimated adatoms is sent towards the surface at a glancing angle of incidence and coalesces on the step of a patterned surface, forming NP arrays.

79

80 surface are realised. Furthermore, the technique has been shown to be largely independent
81 of the deposited metal type as NP arrays of different materials have been produced using

82 this method.⁴⁶ During the manuscript the capabilities of extracting the plasmonic response
83 of the system using the ASEF approach will be tested on the samples grown and then
84 reproduced with a dipolar method previously developed.⁴⁷ This will provide a basis for the
85 understanding of the various spectra measured. Afterwards, a more general formalism will
86 be introduced and effects which induce changes in the optical properties in the whole will be
87 systematically analysed. It will be also be demonstrated the striking advantage of using SE
88 when compared with simple absorption spectroscopy in monitoring changes in the refractive
89 index of the medium surrounding the probed NPs. Sharper resonances can be measured and
90 increases in the figure of merit (FOM) of the resonance up to 15 times have been measured.
91 This could improve the detection limit of refractive index based sensors. This study will
92 open new exciting possibilities in the analysis of the plasmonic response of structures using
93 spectroscopic ellipsometry.

94 **ASEF and plasmonic modelling**

95 In general, an analytical expression representing the properties of a single layer cannot
96 be directly extracted from SE experiment. Multiple internal reflections modify the final
97 expression of the pseudo-dielectric function $\langle \varepsilon_j \rangle$ of the system considered as a whole
98 homogeneous medium. A simple additivity of each layer hence does not hold any more. The
99 case of plasmonic nanostructure is even more complicated, as the layer is not homogeneous.
100 However, if the dimension of the structures involved (roughness and NP dimensions) are
101 much smaller than the wavelength of the exciting light, the nanocomposite layer can be
102 treated as a continuous and homogeneous layer with an effective dielectric function ε_L which
103 in turn can be anisotropic.

104 In a three phase approach (substrate, plasmonic layer and air), if the nanocomposite
105 layer is thin, the substrate response is isotropic and the optical axes are aligned with the
106 symmetry axis of the system, the picture can be incredibly simplified. In this case, the

107 additivity between the response of each layer can be assumed to hold to the first order and
 108 the ASEF can be extracted directly from the experiment as^{28,48,49}

$$\xi_j = \frac{i\lambda(\varepsilon_b - 1)}{4\pi\varepsilon_b\sqrt{\varepsilon_b - \sin^2\Theta}}(\langle \varepsilon_j \rangle - \varepsilon_b). \quad (1)$$

109 In Eq. (1) λ is the vacuum wavelength in nm, Θ is the angle of incidence, ε_b is the substrate
 110 dielectric function and air is considered as the surrounding medium.

111 Usually, ellipsometric observables are expressed in terms of the complex ratio ρ . However,
 112 the psuedo-(effective) dielectric function for the whole bulk system appearing in Eq. (1) can
 113 be extracted from the raw measurements by

$$\langle \varepsilon \rangle = \sin^2\Theta + \sin^2\Theta \tan^2\Theta \left(\frac{1-\rho}{1+\rho}\right)^2. \quad (2)$$

114 Once the substrate dielectric function is known, ASEF can hence be extracted directly from
 115 the experiment using Eq. (1).

116 The advantage of introducing the ASEF relies on its simplicity as it depends on the
 117 response of the (anisotropic) plasmonic layer alone, which can then be modelled by²⁸

$$\xi_j = d\left[(\Delta\varepsilon_j + \varepsilon_b\Delta\frac{1}{\varepsilon_z}) + \left(\frac{1}{\varepsilon_b} - \frac{\cos^2\Theta}{\sin^2\Theta}\right)(\Delta\varepsilon_j - \Delta\varepsilon_k)\right]. \quad (3)$$

118 where $j, k = (x, y)$. The coefficients in Eq. (3) are defined by

$$\Delta\varepsilon_j = \varepsilon_{L,j} - \varepsilon_b \quad \Delta\frac{1}{\varepsilon_z} = \frac{1}{\varepsilon_{L,z}} - \frac{1}{\varepsilon_b} \quad (4)$$

119 and d is the effective thickness of the homogeneous NP layer. The nanocomposite response
 120 can then be extracted by Eq. (1) and any suitable model capable of calculating the dielectric
 121 function of the plasmonic layer can be directly compared with the experiment using Eq. (3).
 122 The problem of analysing the response of the whole system has been reduced in this case to

123 the determination of the plasmonic layer dielectric function.

To compare the theory with experiment, the system investigated in this manuscript has been modelled as collection of supported identical ellipsoids placed on a rectangular lattice interacting through dipolar forces. Due to the small dimensions involved, the quasistatic approximation is assumed to be valid. Under this hypothesis an expression for ε_L reads as^{27,47}

$$\begin{aligned}\varepsilon_{L,i} &= \varepsilon_{cap} \left(1 + \frac{N\alpha_i}{1 + \alpha_i\beta_i}\right) & i = x, y \\ \frac{1}{\varepsilon_{L,z}} &= \frac{1}{\varepsilon_{cap}} \left(1 - \frac{N\alpha_z}{1 + \alpha_z\beta_z}\right)\end{aligned}\quad (5)$$

124 where ε_{cap} is the homogeneous dielectric function of the capping material, N is the number
125 of NPs per unit area and α is the polarizability of an isolated ellipsoid. The β coefficient
126 represents the interaction effects and takes into account both NP interactions and image
127 charge effects. In order to take into account the effect of the steps, the capping medium
128 dielectric function has been considered as a mixture between air and substrate in a 1:1
129 ratio.⁴⁷ In the rest of this manuscript the in-plane directions will be referred as x (along the
130 NP rows) and y (perpendicular to the rows), while the out-of-plane direction will be defined
131 as z (see Sketch in Figure 3). Using Eq. (3) and Eq. (5) the ASEF of the plasmonic layer
132 can then be modelled and directly compared with experiment. In the next section it will
133 be demonstrated the utility of the ASEF approach to model and understand the full optical
134 response of the whole system.

135 **Results and discussion**

136 The SEM of the in-plane structure deposited at glancing angle is shown in Figure 2 A.
137 The structure appears as a collection of ordered NP arrays aligned along the step edges as
138 previously reported. The in-plane semi-axes ($R_x = 12$ nm and $R_y = 10$ nm) are well below

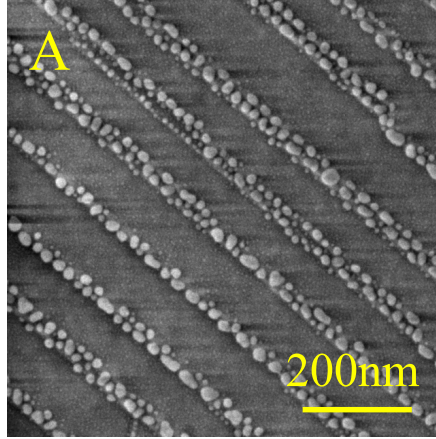


Figure 2: (A) Scanning electron micrograph of the Ag NP arrays deposited at a glancing angle of 6° . Rows of NP arrays are clearly visible along the step edge of the stepped template. Low magnification and high magnification transmission electron microscope (TEM) of a section of the same samples are shown in B and C respectively.

139 the diffraction limit and the plasmonic layer can therefore be considered as an homogeneous
 140 anisotropic layer. As the centre-to-centre distance L_x , is 27 nm the inter-particle separation
 141 (~ 3 nm) is much smaller than the average NP diameter, a strong enhancement of the electric
 142 field is expected to take place in the interstitial space between NPs. In order to fully
 143 characterize the sample, the out-of-plane morphology has been also analysed by TEM (see
 144 Figure 2 B and C (NOT YET PRESENT)), revealing the NPs appear as truncated ellipsoids
 145 of height $H = 17$ nm. Details of the exact growth mechanism of such structures can be found
 146 elsewhere.⁴⁷

147 The response of the structures grown have been first analysed by SE using the same angle
 148 of incidence $\Theta = 61^\circ$, and by changing the azimuth of the sample in the plane of incidence by
 149 an angle φ (Figure 3). This incidence angle was first chosen as it close to the Brewster angle
 150 of the Al_2O_3 substrate in the visible region. In this case, as discussed in our earlier paper on
 151 the plasmonic response of similar structures,²⁷ the ratio between the p and s components is
 152 maximised and the measurements are simplified. The measured azimuthal real and imaginary
 153 response of the structure are shown in Figure 3 A and B respectively. Superimposed onto
 154 the substrate behaviour additional features are clearly visible. The ASEF extracted from
 155 the experiment using Eq. (1) and modelled by Eq. (3) and Eq. (5) are shown in Figure 3

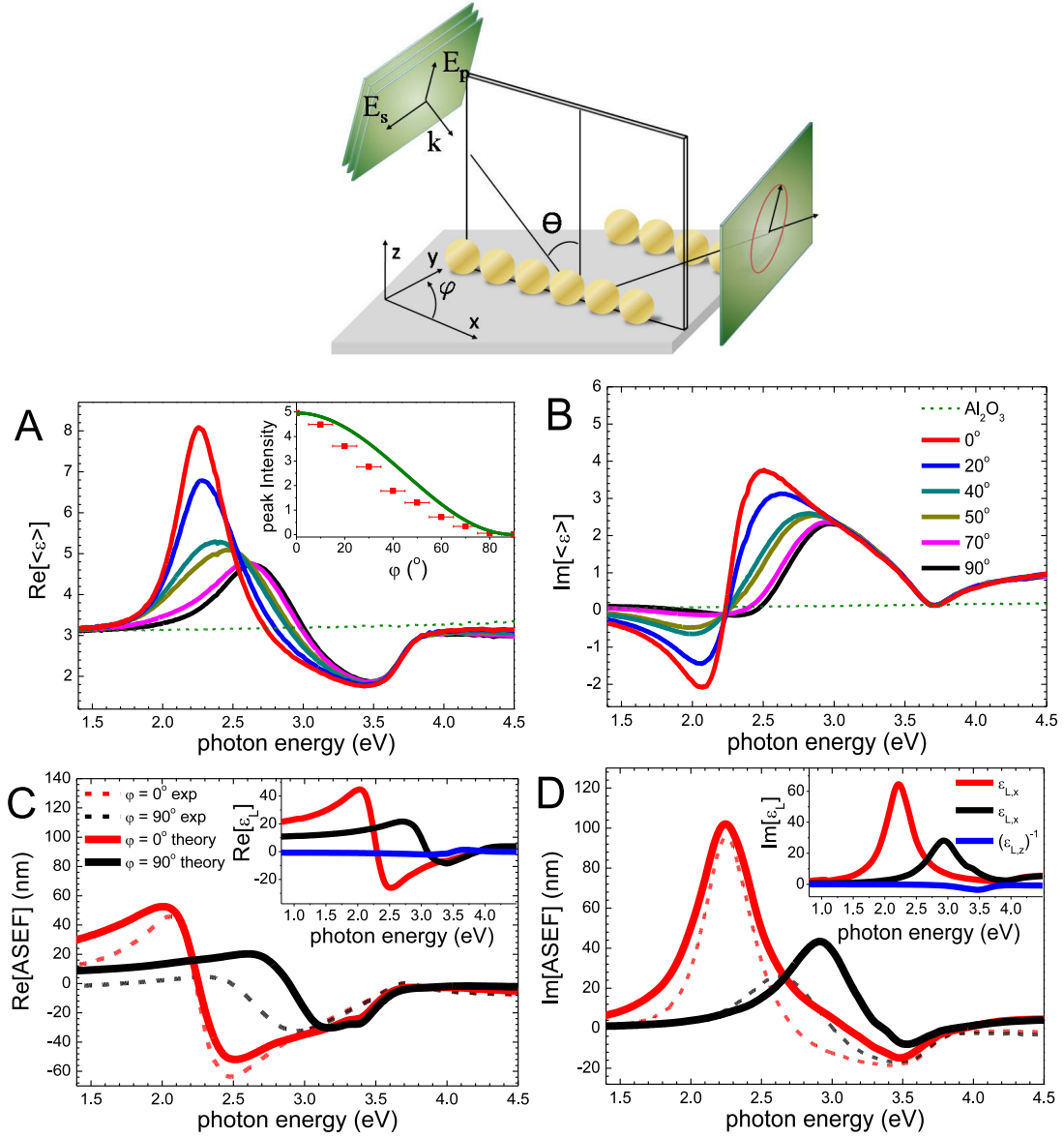


Figure 3: Real (A) and imaginary (B) parts of the pseudo-dielectric function $\langle \epsilon \rangle$ of Ag NP arrays grown at glancing angle for different azimuthal angle rotations φ . The intensity of the x resonance at 2.2 eV follows a \cos^2 dependency (inset in Fig. A). Both experimental (dotted lines) and simulated (continuous) ASEF for the parallel ($\varphi = 0^\circ$) and perpendicular ($\varphi = 90^\circ$) measurement configurations are also shown (C and D). An analysis of the ASEF suggests that the peaks observed in the real part of the pseudo-dielectric functions are related to the resonances of the plamsonic layer (see the imaginary part of ϵ_L in the inset).

156 C and D. A semi-quantitative agreement is clearly observable. The slight disagreement in
 157 the position of the y resonance could be explained by sample disorder. In the real system,
 158 double chains can be sometimes be observed and they can influence the peak position of the
 159 plasmonic response, shifting the y resonance towards the IR. Also, as the truncated NPs are
 160 modelled as ellipsoids supported on the substrate, mismatch between theory and experiment
 161 can be expected. The disagreement observed is then related to limitations in the model
 162 utilised rather than incorrect analysis of the results. However, we want to stress here that
 163 no fitting parameter has been introduced in the simulation and that the simulated spectra
 164 are obtained using only morphological parameters measured by micrographic analysis.

165 From Figure 3 A, for the measurement configuration parallel to the array ($\varphi = 0^\circ$), a
 166 positive peak can be observed at ~ 2.2 eV, together with a minima present at higher energies.
 167 As previously discussed²⁷ and suggested by the theory (see the dielectric function of the layer
 168 in the inset of Figure 3 C and D) the positive feature in the imaginary part of the ASEF is
 169 related to resonances along the x direction, while the minima at higher energy corresponds to
 170 the z resonance. The opposite sign in the out-of-plane z resonance is due to the discontinuity
 171 of the perpendicular component of the electric field in Maxwell Boundary conditions.²⁹ By
 172 rotating the sample towards the measurement configuration perpendicular to the array (φ
 173 $= 90^\circ$) the intensity of the 2.2 eV decreases monotonically following a $\sim \cos^2(\varphi)$ dependency
 174 (see inset in Figure 2 A). The behaviour can be explained by rotating the sample symmetry
 175 axis along the optical axis. In this case the rotation of the layer dielectric tensor in Eq. (5)
 176 can be expressed by the matrix

$$A(\varphi) = \begin{pmatrix} \cos \varphi & -\sin \varphi & 0 \\ \sin \varphi & \cos \varphi & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (6)$$

177 Defining now A^T as the transpose of A and remembering that the dielectric tensor of the
 178 plasmonic layer upon in-plane rotation can be expressed as $A^T \varepsilon_L A$, the \cos^2 behaviour for

179 the x resonance measured is reproduced.

180 It is important at this point to note that, comparing the normal bulk values, for thin
181 plasmonic films and transparent substrates as the one here analysed, the absorptive com-
182 ponent of the plasmonic layer is present in the real part of the pseudo-dielectric function.
183 This reversal between $Re[\langle \varepsilon \rangle]$ and $Im[\varepsilon_L]$ can be easily explained by the imaginary term
184 i present in Eq. (1). We want to stress that the validity of the ASEF approach here utilised
185 is constrained to a ultra-thin plasmonic layers and isotropic bulk responses.²⁸ However, un-
186 der these assumptions, a direct comparison between theory and experiment can be directly
187 achieved by assessing the response of the anisotropic thin plasmonic layer along the sample
188 anisotropic main axis ($\varphi=0^\circ$ and 90°) at the substrate Brewster angle. In this way it is
189 possible to minimize mixing between p and s components of the reflection coefficients (hence
190 mixing of the response of both x and y resonances) and the resonances can be immedi-
191 ately attributed to the in-plane and out-of-plane resonances along the symmetry directions
192 of the system. Clearly, the measurement for isotropic samples are further simplified as the
193 dependency on the azimuthal rotation angle is removed.

194 **Extension to a more general formalism**

195 In the previous section it was shown that the ASEF approach can be successfully applied to
196 the analysis of ultrathin plasmonic layers. It was also shown that the simulation reproduced
197 the results even when the optical axis were not aligned with the principal axis of the sys-
198 tem, provided an oportune rotation of the dielectric tensor was performed. However, the
199 validity of the ASEF approach is severely constrained to very specific cases. For example,
200 for multilayer structures or thick plasmonic layers, the formalism previously introduced is
201 no longer accurate.

202 In this section a more general formalism, based on a transfer matrix approach devel-
203 oped by Schubert is applied.^{50,51} Following his approach, an analytical expression for the

204 transmission matrix of the whole system can be obtained and the complex Fresnel reflection
205 coefficient for p and s polarized light derived. The reflection ratio $\rho = r_p/r_s$ can then be cal-
206 culated, an expression for the pseudo dielectric function obtained using Eq. (2) and compared
207 with experiment. The only input parameters required for the application of this method are
208 the dielectric function of each layer and the respective thickness. Any method which allows
209 one to model the dielectric function of the plasmonic layer can then be compared directly
210 with the response measured by SE. For example, if absorption spectra are obtained from
211 some numerical simulation, one could calculate the imaginary part of the dielectric function
212 of the plasmonic layer through the optical theorem⁵² and extract the real part through the
213 Kramers-Kronig relationship. In the following the effect of different factors on the spectra
214 as measured by SE will be discussed and a direct comparison with experiment whenever
215 possible.

216 The validity of the approach has been first verified for parallel and perpendicular con-
217 figuration by comparing the simulations with the Ag spectra measured at different angles
218 of incidence. The resonances appear in the real part of the pseudo dielectric function, so
219 the real component only for the configurations parallel and perpendicular to the arrays are
220 reported here. From Figure 4 a strong agreement between experiment and theory can be
221 noticed and a similar one was observed also for the imaginary component. First, one can
222 notice that the pseudo-dielectric function of the whole system depends heavily on the angle
223 of incidence as the optical path is changed. As the sample is anisotropic, the reflection is
224 different along the two orthogonal in-plane directions. In this case, by varying the angle of
225 incidence, different p and s components are probed, resulting in a strong change in the reflec-
226 tion ratio (and hence in the pseudo dielectric function). For the perpendicular configuration
227 (Figure 4 B and D), one can observe that the y resonance peak shift is correctly reproduced
228 for various angle of incidence but the changes in intensity are not. The disagreement is as
229 before due to a shift between the simulated y resonance and the measured one, rather than
230 an incorrect analysis of the SE results.

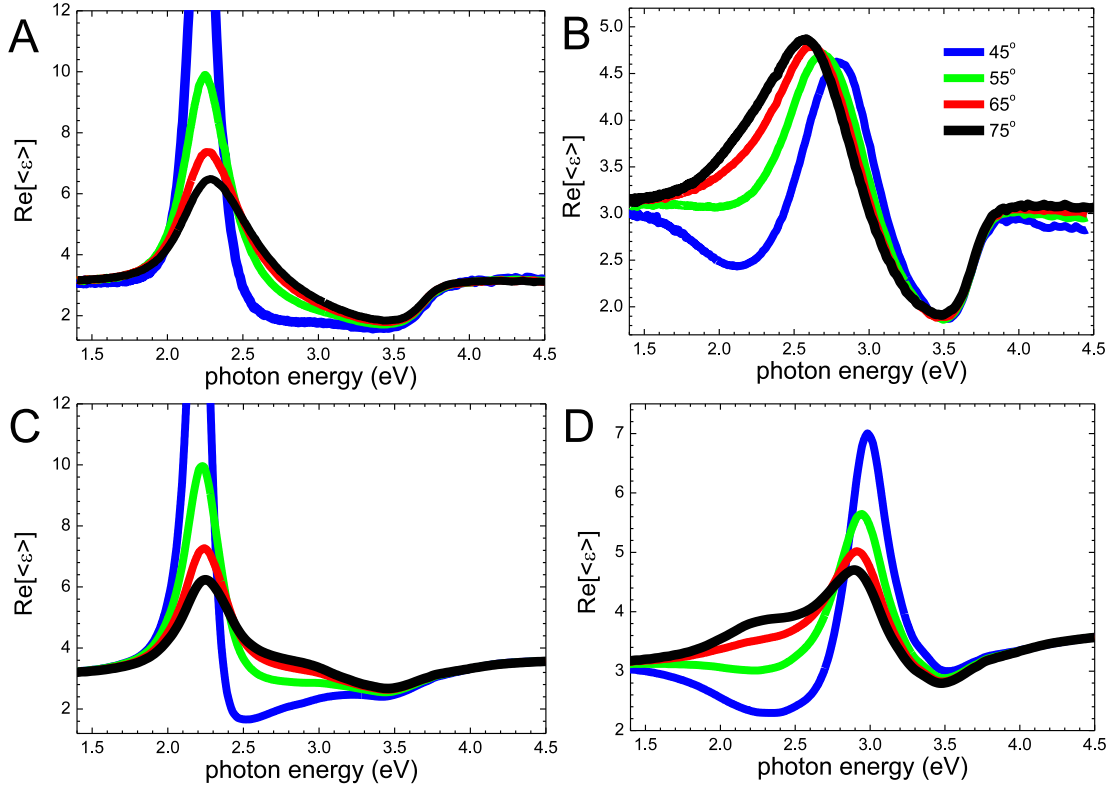


Figure 4: Real part of the pseudo-dielectric function for the measurement configuration parallel (A) and perpendicular (B) to the array at different angles of incidence. The simulated pseudo-dielectric functions for the two cases calculated using the transfer matrix formalism are shown in (C) and (D) respectively. The x resonance peak at ~ 2.2 eV observed in (A) and (C) for 45° angle of incidence has an intensity of ~ 16 .

231 Of particular interest is the fact that for $\varphi = 0^\circ$ measurement configuration (Figure 4
 232 C) the intensity of the positive peak at 2.2 eV increases by a factor of 3 when going from
 233 $\Theta = 61^\circ$ to closer $\Theta = 45^\circ$ and at the same time the resonance shows an even sharper peak.
 234 This effect is well reproduced by the simulation. The strong increase in the resonance profile
 235 is related to the presence of a singularity in the imaginary part of r_s whenever the angle of
 236 incidence is close to $\Theta \sim 35^\circ$. In case of anisotropic samples, the possibility of measuring
 237 such sharp resonances could be of great interest as the figure of merit (FOM) of the sharp
 238 resonance structure is greatly increased in this case. In particular, for $\Theta = 45^\circ$ an increase of
 239 the FOM by factor ~ 15 if compared with $\Theta = 70^\circ$ incidence angle has been realised. For this
 240 particular system, the simulations suggest that the FOM can be even further increased if the
 241 measurement angle is closer to the singularity for r_s at $\Theta \sim 35^\circ$. These results suggest that
 242 the sensitivity of any refractive index plasmon-based biosensor can be theoretically increased
 243 by choosing the appropriate incidence parameters during a SE measurements.

244 As a representative example, in Figure 5 a comparison is shown between the simu-
 245 lated absorption and SE spectra when the NP arrays are surrounded by different dielec-
 246 tric media. During the simulations the absorption profiles were obtained using the relation
 247 $A_{\text{abs},x} \propto \text{Im}[\varepsilon_{L,x}]/\lambda$.⁵² As expected, an increase in the refractive index surrounding the NPs
 248 red shifts in the x resonances position. However, a much sharper profile is obtained for the
 249 pseudo-dielectric function. This result potentially opens a new route for sensing applica-
 250 tions using SE. Furthermore, as SE is based on measurements of only relative changes in
 251 the dielectric function of the medium, a larger accuracy can be achieved if compared with
 252 standard transmission measurements. Similar enhancement have been recently reported for
 253 in-plane symmetric system once the phase of the complex ratio ρ is measured.²⁵

254 The transfer formalism developed by Schubert can be also adapted to other optical
 255 characterization method and different materials (see supporting information for reflectance
 256 anisotropy spectroscopy measurements and SE measurements on Au NP arrays). Also, the
 257 theory presented here could be extended to magnetically active systems and core-shell struc-

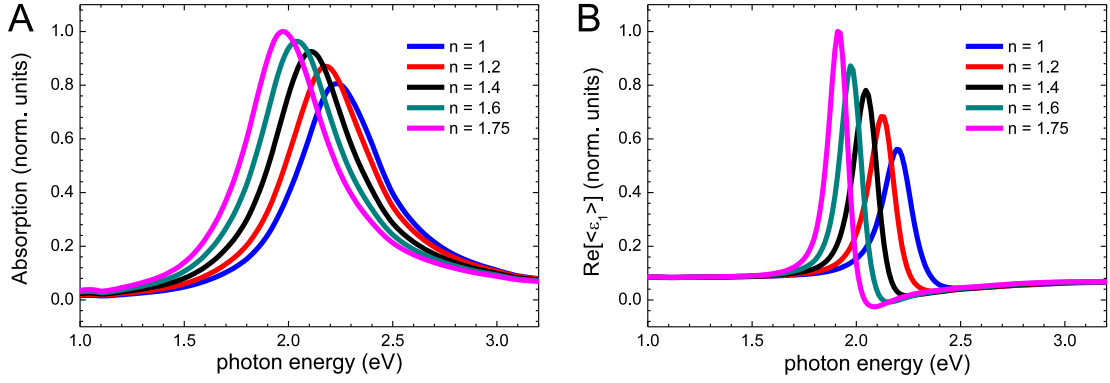


Figure 5: Simulation of the absorption along the NP arrays (A) and of the pseudo-dielectric function (B) in the parallel configuration at 45° the NP array system upon changes of the dielectric medium covering the particles. Red shift in the x resonance can be observed for increasing the dielectric medium. However, the FOM simulated using SE can be greatly increased when compared with normal absorption spectroscopy.

258 tures.^{51,53}

259 Based on the results reported so far, we believed that the transfer matrix approach here
 260 proposed is a suitable and convenient method to simulate and analyse the spectroscopic
 261 response of plasmonic structures. In the following possible additional effects which could
 262 influence the response of the system are discussed using the simulation developed. Figure 6
 263 and Figure 7 show the SE spectra for the different cases of increasing layer thickness and
 264 different substrates (Si rather than Al_2O_3) respectively. In order to facilitate the analysis,
 265 during these simulations the plasmonic layer was assumed to be in-plane isotropic ($R_x =$
 266 $R_y = 20$ nm and $R_z = 7.5$ nm) and with particles spacing large enough to disregard any
 267 inter-particle coupling ($N = 7 \times 10^{13}$ NP/m²). The self-image charge contribution produced
 268 by a the presence of a thin Al_2O_3 layer underneath the NPs is still taken into account.
 269 With these parameters, the dielectric function of the layer for the two examples is shown
 270 in Figure 6 A. As the sample is in-plane isotropic, $\langle \epsilon \rangle$ is now independent either on the
 271 azimuthal rotation angle φ and on the angle of incidence Θ . However, it can be easily seen
 272 in that changes in the plasmonic films film thickness result in a strong modification of the SE
 273 response. As previously discussed when an ASEF was introduced, for an ultra-thin structure
 274 the maximum in $\text{Re}[\langle \epsilon \rangle] \propto \text{Im}[\epsilon_L]$. The relation is valid whenever the plasmonic film d is

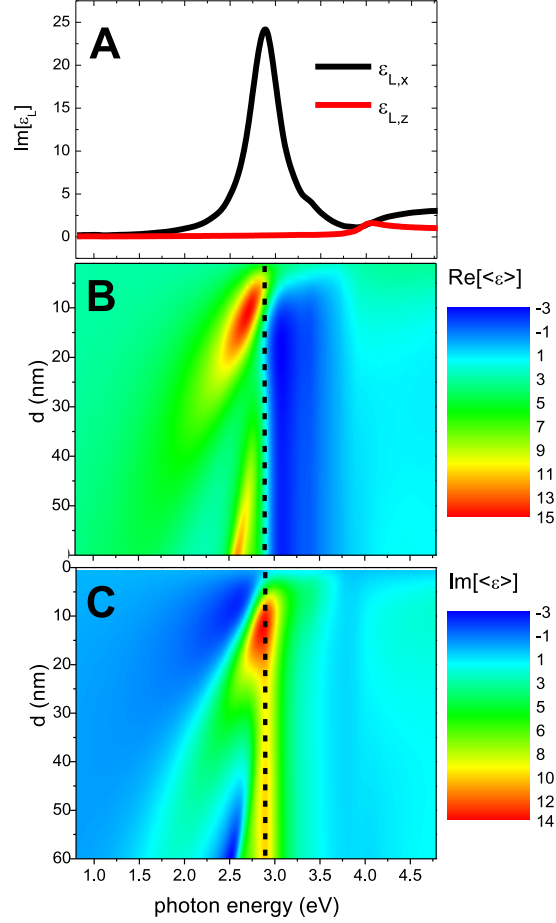


Figure 6: (A) Simulated imaginary part of the dielectric function of supported isotropic spheroids along the x and z direction. The contour plot of the real and imaginary part of the calculated psuedo-dielectric function for different plasmonic layer thickness d are shown in B and C respectively. The vertical dotted line shows the position of the x resonance and it is used as a guideline.

275 thin, i.e.

$$d \ll \frac{\lambda}{4\pi\sqrt{\varepsilon_{L,j} - \sin^2\theta}}. \quad (7)$$

276 Figure 6 now allows to a more precisely quantification of Eq. (7):even for an effective plas-
277 monic layer of 5 nm a mixture between the real and imaginary component takes place and
278 the ASEF approximation is no longer valid. Larger layer thickness results in a complex
279 behaviour which can hardly relate directly to the plasmonic features but it can be addressed
280 using our transfer matrix approach. Modifications also take place when a non transparent
281 substrate is used. For example, in the case of Si substrates, it is shown that the plasmonic
282 features of ultrathin films are hardly visible as the substrate is strongly dispersive. Further-
283 more, the overall signal lowers when larger film thicknesses are modelled. The opposite trend
284 is expected for transparent non dispersive substrates such as Al_2O_3 .

285 The results shown suggest that the SE response originated by plasmonic structures de-
286 pends on many contributing factors, such as NP morphologies, material compositions and
287 substrate dielectric function and the overall response can be heavily modified by changes in
288 any of them. However, the unknown parameters can be treated as fitting parameters and the
289 modelling achieved using self-consistent methods. Similar to standard ellipsometric results
290 of multilayer structures, an initial guess of the pseudo-dielectric function can be introduced
291 and compared with the experimental results. Then by varying the unknown parameters a
292 match with experiment can be obtained. In this case, clearly, analytical simulations such as
293 the one here introduced are much more suited for fast convergence.

294 Conclusions

295 In conclusion, we have demonstrated and developed a methodology to investigate the plas-
296 monic response of complex NP material systems. All the simulations were directly compared
297 with experiment performed by measuring the spectral response of anisotropic NP arrays
298 grown at glancing angles. First, a quantity named Anisotropic surface Excess Function

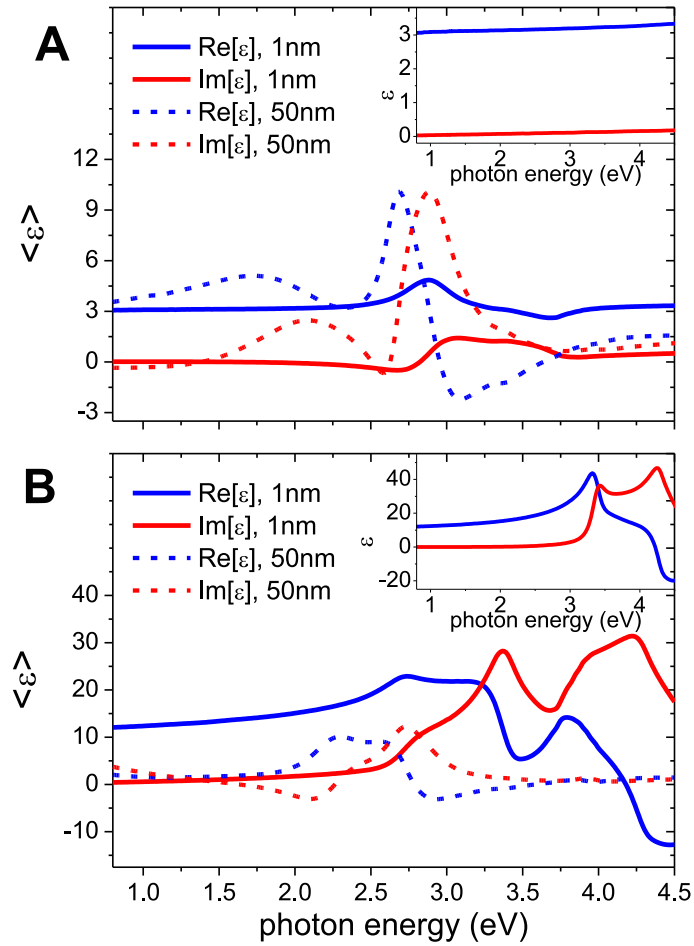


Figure 7: Pseudo dielectric function of isotropic spheroids supported on substrates Al_2O_3 (A) and Si (B) substrates for different plasmonic thickness. In the inset the bare substrate dielectric function in the two cases are shown.

299 (ASEF) is introduced and it is demonstrated how the plasmonic response of layer can be
300 directly observed.

301 Afterwards, the formalism is further developed utilising a transfer matrix method. Dif-
302 ferent effects which can lead to a modification in the response of the system are discussed
303 and a clear route for a complete analysis outlined. The approach can be adapted to thick NP
304 layers, anisotropic systems, magnetically active systems, core-shell structures and different
305 classes of material.

306 The results here show striking advantages. First, as SE can easily measure both the in-
307 plane and out-of-plane response, this technique provides a more stringent test for the validity
308 of any simulation method. Second, it is demonstrated here that in the case of anisotropic
309 layers the resonance FOM can be greatly increased at a particular angle of incidence. In this
310 way the sensitivity of any biological sensor based on the detection of changes of the dielectric
311 medium surrounding the plasmonic NPs can be incredibly improved.

312 **Methods**

313 Noble metals NP arrays have been produced by glancing angle deposition on a single crystal
314 c-plane Al_2O_3 templates. The substrates were off-cut 6° along the $[\bar{1}\bar{2}10]$ direction and
315 polished on one side. To produce the stepped surfaces^{54,55} two samples were annealed at
316 1400°C in atmosphere for 16 h. AFM analysis confirmed the texturing of the template with
317 a measured periodicity $L_y = 130$ nm. Each sample was then loaded in a ultra high vacuum
318 chamber (base pressure 2×10^{-8} mBar) and either Ag or Au was deposited at 6° with respect
319 to the normal. During the deposition a calibrated rate at normal incidence of 2.5nm/min
320 was utilised and the samples were exposed for 20 minutes. The deposition was performed at
321 room temperature.

322 The in-plane morphology was imaged by a field emission ULTRA scanning electron mi-
323 croscope (SEM) by Carl Zeiss. SE measurements were recorded with a Woollam M2000

324 variable angle spectroscopic ellipsometry system, equipped with a rotating compensator and
325 a high speed CCD camera. The measurements were performed between 245-1600 nm taking
326 670 points. The sample was aligned at each angle of incidence and rotated manually around
327 the surface normal. The estimated error in the accuracy of the rotation angle was established
328 to be $\pm 5^\circ$.

329 After measurements, Ag NP sample was capped with a 50 nm Si_3N_4 layer. The deposition
330 was performed using a Plasma Enhanced chemical vapour deposition using 5% SiH_4 and NH_3
331 as precursors (1:6 ratio). During the process a growth temperature of 300°C was utilised
332 using an RF frequency of 187.5 kHz for a total growth time of 6.15 minutes.

333 In order to analyse the out-of-plane morphology of the Ag capped sample, TEM out-
334 of-plane sections were prepared using a Carl Zeiss Auriga CrossBeam FIB-SEM as already
335 described before. Once prepared, the section was imaged by a Titan TEM operating at
336 300 kV. The substrate was aligned to the $[10\bar{1}0]$ zone axis for imaging. In all cases the
337 images were acquired in bright-field mode.

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344 **Supporting information**

345 The transfer matrix approach developed in the manuscript can be easily used also to simulate
346 the optical response measured with other spectroscopic techniques and can be utilised with
347 different materials.

348 In this section the response of Ag NP arrays measured with RAS will be compared with
 349 simulations. RAS measures the difference in reflectance (Δr) at a normal incidence between
 350 two orthogonal directions in the surface plane (x, y) normalized to the mean reflectance (r):⁵⁶

$$\frac{\Delta r}{r} = \frac{2(r_x - r_y)}{r_x + r_y}, \quad (8)$$

351 where r are the complex Fresnel reflection amplitudes. As before, the x and y indexes in
 352 Eq. (8) refer to the in-plane directions along and perpendicular to the array axes respectively.
 353 As for the complex ratio of SE, RAS can also be simulated using the same transfer matrix.
 354 During the simulations the incidence angle was considered to be close to normal incidence (3°)
 355 and the p and s components are made to coincide with the x and y ones from Eq. (8).
 356 The RAS system is a home built system which follows the 2 polarisers and photo-elastic
 357 modulator scheme.⁵⁷ The real and imaginary part of RAS has been measured immediately
 358 after exposure of the sample to atmosphere. A comparison with the theory are reproduced
 359 in Figure 8. Also in this case, the spectra appear well reproduced. The disagreement in
 360 the peak intensity is related to the non perfect matching between theory and experiment for
 the y resonance (appearing here as the negative peak). The origin of the real component

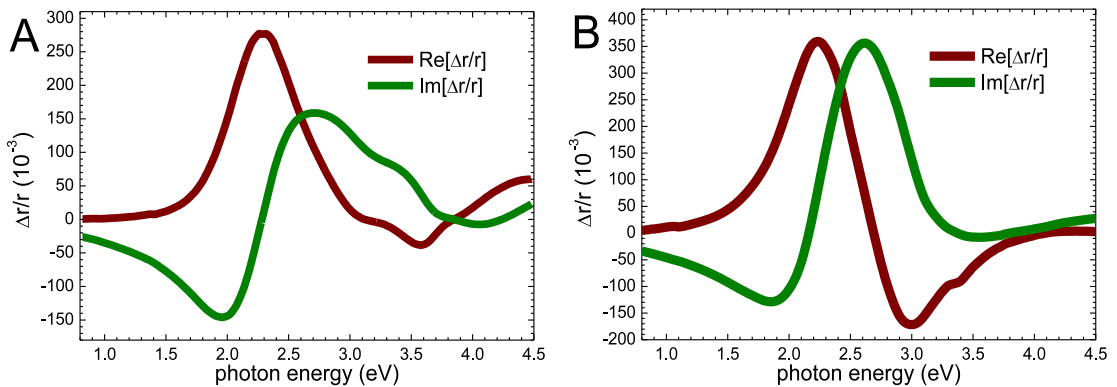


Figure 8: Experimental (A) and simulated (B) RAS spectra for the Ag NP arrays grown by glancing angle of incidence.

361
 362 of the RAS signal measured has been recently studied in our group and it was found to
 363 coincide with the difference between an intense positive (x) and a less intense negative (y)

364 peak shifted towards higher energies.⁴⁵ For the system under study it is suggested that the
365 two resonances are placed closer in the experiment if compared with the simulation (see
366 for example Figure 3 D in the text). As the peaks partially overlap, once the difference
367 between the two peaks is considered, the measured RAS peak positions appear shifted if
368 compared with the simulated ones (the same effect happens in Figure 3 D). At the same
369 time, once the difference is calculated, the relative intensity of the peaks changes. As the
370 imaginary component of the RAS is related to the real part by Kramers-Kronig relationship,
371 its intensity and position is modified in this case. Once again we would like to point out that,
372 as for the SE results, the difference between experiment and theory is then related to a non
373 perfect agreement between the real response of the plasmonic layer dielectric function and
374 the simulated effective plasmonic layer dielectric function rather than errors in the transfer
375 matrix approach used.

376 We also verified that the formalism here developed is also valid for different materials.
377 As glancing angle deposition is independent on the deposited material,⁴⁶ Au NP arrays
378 can also be produced and their response measured using SE (see Figure 9 A for a SEM
379 image of the surface after deposition). The real part of the pseudo dielectric function as
380 measured by SE in the configuration parallel and perpendicular to the array are shown in
381 Figure 9 B and C for multiple incidence angles. The optical response shows clear differences
382 if compared with Ag NPs. The main x resonance is placed further in the IR (1.77 eV) and
383 higher energy features measured for the Ag case are screened now by strong and broad
384 features related to interband transitions.⁴⁶ We have simulated also in this case the response
385 using our matrix approach. The Au dielectric function was taken from literature⁵⁸ and the
386 free electron response corrected in order to take into consideration the reduced dimensions
387 of the NPs.^{47,59} In order to simplify the discussion, the same morphological parameters as
388 the one used for Ag NPs are used during this simulations. However, the trend for different
389 deposition angles measured in the experiment coincides with the behaviour simulated with
390 our approach.

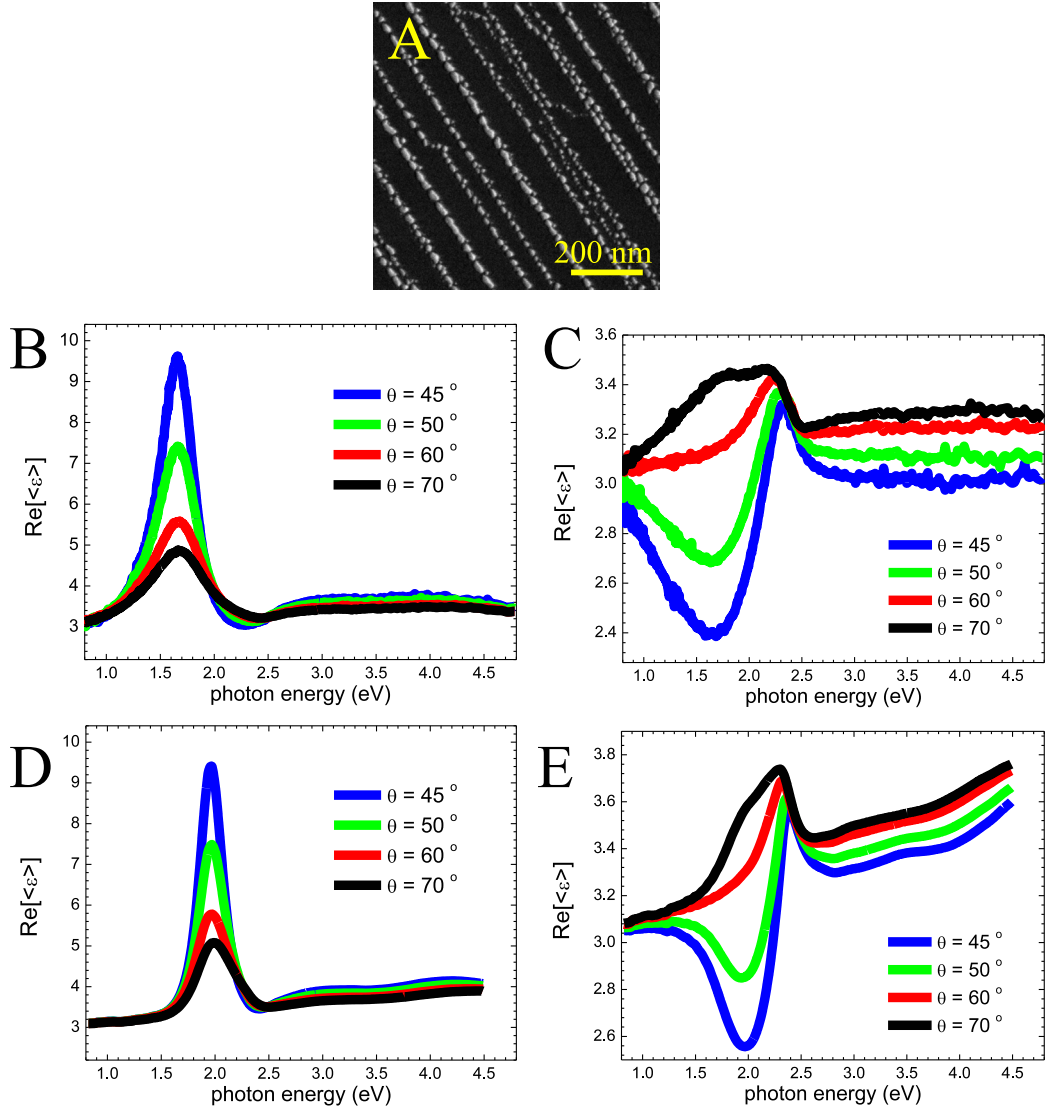


Figure 9: SE response of Au NP arrays. (A) SEM image of the in-plane morphology of the sample. Also gold NP arrays can be produced by glancing angle deposition. Measured pseudo dielectric function for the measurement configuration parallel (B) and perpendicular (C) to the array. The simulated behaviour for the two cases are shown in (C) and (D) respectively.

391 These results appear as a strong confirmation of the validity of the methodology utilised
392 even when different materials are utilised and it is verified by comparison of the RAS results
393 obtained from Ag NPs.

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