

# Tunable Electrochemical Switch of the Optical Properties of Metallic Nanoparticles

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**ABSTRACT** Control of the optical properties of oblate metallic nanoparticles (NP) is realized using an electrochemical switch consisting of a thin layer of conducting polymer (CP). Reversible modulation, moderate damping, and almost total quenching of the localized surface plasmon (LSP) resonance is achieved as a function of the thickness of the CP layer and the potential applied to the electrochemical systems, that is, the charge carrier density injected into the CP layer. These experimental results can be qualitatively reproduced using the single-particle model in the electrostatic approximation. We believe that combining an electroactive conducting polymer and NP will prove to be a general strategy for controlling the properties of various types of NP (fluorescent, magnetic, semiconducting) in many fields.

**KEYWORDS:** nanoparticle · localized surface plasmon resonance · conducting polymer · electrochemical switch

A large variety of nanometer-scale devices have been investigated in recent years because of the continuously increasing demand for ultimate miniaturization of electronic and photonic systems. Molecular electronics and plasmonic devices could overcome the physical and economic limitations of current semiconductor devices and are seen as alternative technologies because of their very great potential in writing, reading, storing, and processing information at the nanoscale.

Conducting polymers or oligomers are proposed and used as basic building blocks in molecular electronics.<sup>1–3</sup> Conducting-polymer electrochemical switching has been demonstrated to be an easy means of controlling the electronic structure and thus the properties of grafted molecules.<sup>4</sup> NPs can be considered, to some extent, as a special class of molecules and thus conducting-polymer electrochemical switching could also be used to control the properties of grafted or embedded NPs of various types on/in such materials.

Among emerging branches in photonics, plasmonics uses nanostructured materi-

als and substrates that support surface plasmons. Filters,<sup>5</sup> waveguides,<sup>5,6</sup> polarizers,<sup>7</sup> and nanoscopic light source<sup>8</sup> have been reported. In this field, metal nanoparticles (mainly gold, silver, and copper) are widely used since they exhibit strong absorption in the visible and near-infrared spectral range due to the excitation of localized surface plasmons (LSP). The LSP frequency depends mainly on the size and shape of the particle, on the substrate and surrounding medium dielectric functions, and on the particle spacing.

Active plasmonic devices, such as switches and modulators, are the subject of important research efforts. Indeed, such active systems are needed to achieve functional SP circuits. Switching SP devices using electrical input to build electro-optical devices is therefore an important issue. Chapman and Mulvaney have reported electrochemically driven plasmon shifts in Ag NP films and a moderate change of *ca.* 25% of the optical density at the wavelength of the resonance maximum.<sup>9</sup> Wang and Chumanov<sup>10</sup> have used tungsten oxide, WO<sub>3</sub>, as a matrix for the Ag NP arrays, for the electrochemical modulation of the intensity and the frequency of the cooperative plasmon resonance in a faster way than the Chapman systems.<sup>9</sup> We reported recently that conducting-polymer electrochemical switching appears to be an easy means of designing electroactive plasmonic devices.<sup>11</sup> Indeed, using oblate gold NP arrays, deposited by e-beam and overcoated by a submicrometer-thick polyaniline (PANI) layer, reversible modulation and even total switch-off of the LSP resonance have been achieved.<sup>11</sup> Similar results were obtained from colloidal gold solution in a PANI/gold-

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NP/PANI sandwich structure,<sup>12</sup> and a water-soluble gold NP/PANI composite showing the absence of the LSPR has also been recently reported.<sup>13</sup>

In this work, we show that LSPR modulation and quenching of NP arrays can be tuned by the thickness of the PANI film and by the charge carrier density injected into the PANI layer.

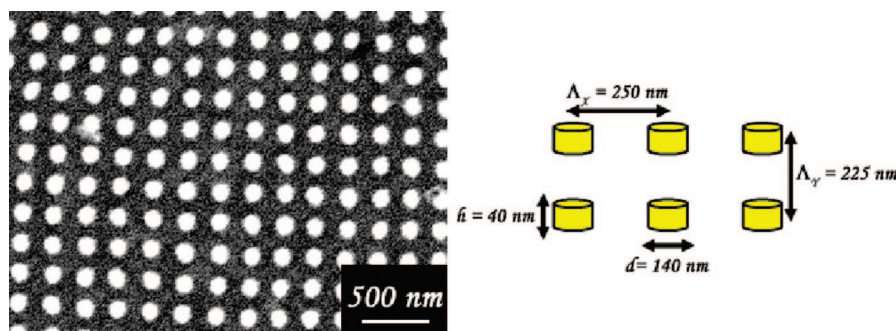


Figure 1. MEB and scheme of gold nanoparticle array (array A).

## RESULTS AND DISCUSSION

We have used PANI as the conducting polymer because thin films (20 to 100 nm) can be easily deposited on ITO and gold,<sup>14</sup> and because such films are known to exhibit an ultrafast switching (in the microsecond range) between their reduced nonconductive state and their oxidized conductive state.<sup>15</sup> Furthermore, PANI switching can be easily performed more than  $10^5$  times without any degradation of the electrochemical signal. PANI was deposited under galvanostatic conditions while the total deposition charge was monitored. Experimental conditions have been reported elsewhere.<sup>14,15</sup> Thicknesses of the generated films are calculated using the hypothesis that electrochemical growth is uniform over the whole substrate surfaces.

Figure 1 gives the general scheme of the oblate gold nanoparticle arrays used in this study. They are produced by electron beam lithography (EBL) performed on a modified scanning electron microscope (SEM). Experimental conditions for generating such substrates have been reported elsewhere.<sup>16</sup>

We have first used a gold nanoparticle array deposited on an ITO substrate consisting of oblate spheroids, with length  $d = 140$  nm, and height  $h = 40$  nm, with grating constant  $\Lambda_x = 225$  nm and  $\Lambda_y = 250$  nm (array A). Using this array A induces a small local anisotropy through far-field coupling.<sup>17,18</sup> As a consequence, when the extinction spectra are recorded in air, the maximum wavelength of the LSP peak is different when light is polarized along the X axis or the Y axis of particle. Indeed, surface plasmon resonance is observed in air at 645 nm along the X axis of the particles whereas it appears at 606 nm along the Y axis. Results observed with both polarizations are here similar, we will show only those recorded along the X axis.

Figure 2 shows the extinction spectra of the gold NP array A under X-polarized light in air and after the deposition of a 50 nm PANI film polarized at  $-500$  mV (PANI reduced state) and at  $+500$  mV (PANI oxidized state). On going from air to reduced PANI, a strong red shift is observed from  $\lambda_{LSP} = 645$  to  $\lambda_{LSP} = 682$  nm but, when PANI is electrochemically switched from its reduced to its oxidized state, a blue shift (from  $\lambda_{LSP} = 682$  to  $\lambda_{LSP} = 665$  nm) is observed and is associated with a decrease in the surface plasmon optical extinction.

These effects are reversible and have been observed repeatedly during more than 500 cycles between  $-500$  and  $+500$  mV versus a Ag/AgCl reference electrode.

In core-shell systems, gold nanoparticle LSPR is known to be highly dependent on the shell thickness.<sup>19,20</sup> Furthermore, PANI electrochemical growth is most probably not uniform on such a nanostructured electrode and a thickness of 50 nm may not be enough to fully cover the 40 nm-high gold NP. We therefore investigated the influence of PANI thickness, and deposited another 50 nm PANI film (100 nm in all) on the same gold NP array A. Figure 3 shows the influence of the PANI thickness on the LSP resonance, for X-polarized incident light. With 100 nm of reduced PANI the LSP shifts further to 693 nm. Furthermore, we observe a greater blue shift ( $\Delta\lambda_{LSPx} = 81$  and  $\Delta\lambda_{LSPx} = 17$  nm for the 100 and 50 nm PANI films, respectively) associated with a much greater decrease in the optical density (OD) when PANI is electrochemically switched from its reduced to its oxidized state.

Blue shifts have already been observed with oblate particles<sup>11</sup> and indicate that the real part of the PANI dielectric function can be triggered externally through the potential applied to the device. Indeed, in its reduced state its dielectric function ( $\epsilon$ ) is real, whereas in its oxidized state it is a complex ( $\epsilon = \epsilon' + i\epsilon''$ ).<sup>21,22</sup> Moreover, oxidized metallic PANI samples are reported to follow a Drude-like behavior<sup>23–25</sup> with a plasma fre-

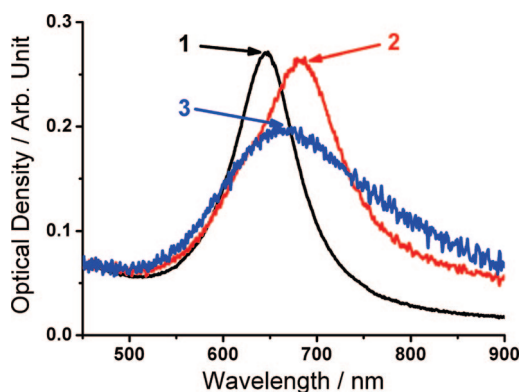
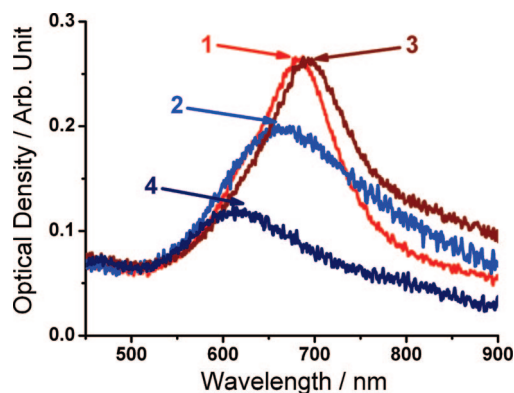


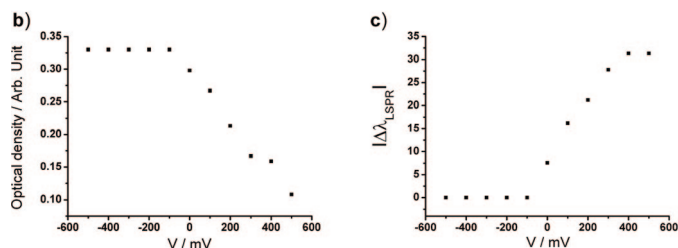
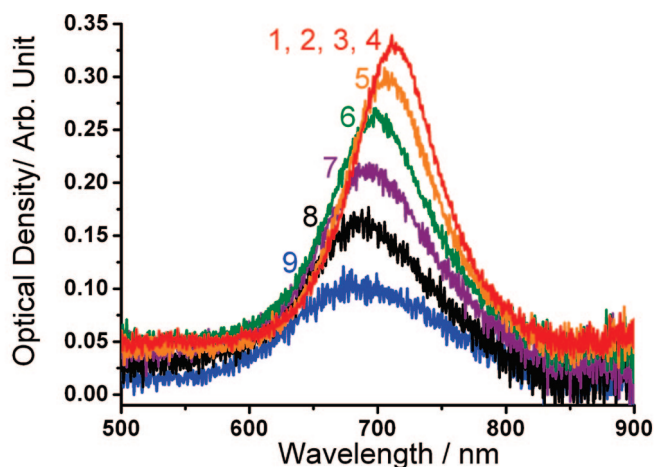
Figure 2. Extinction spectra under X-polarized light of oblate gold particle grating (array A) (1) in air, (2) overcoated with a 50 nm PANI film in its reduced state, and (3) overcoated with a 50 nm PANI film in its oxidized state.



**Figure 3.** Extinction spectra under *X*-polarized light of oblate gold particle grating (array A) (1) overcoated with a 50 nm PANI film in its reduced state, (2) overcoated with a 50 nm PANI film in its oxidized state, (3) overcoated with a 100 nm PANI film in its reduced state, and (4) overcoated with a 100 nm PANI film in its oxidized state.

quency  $\omega p = 2$  eV leading to a simplified expression of  $\varepsilon'$  given by  $\varepsilon' = \varepsilon\alpha - (\omega_p/\omega)^2$ . The electrochemical switching of PANI generates a large change in both the real and the imaginary part of its dielectric function (DF). The real part of the DF decreases upon switching (from reduced to oxidized PANI) thus explaining the observed blue shift, whereas damping of the LSPR is due to the increase in the imaginary part of PANI DF.

These experiments show that conducting polymer electrochemical switching is an easy means for modulating and damping LSPR in a reversible way and dem-



**Figure 4.** (a) Extinction spectra of prolate gold particle grating (array B) under *X* polarized light: (1 to 4) from  $-500$  to  $-100$ , (5) 0, (6)  $+100$ , (7)  $+200$ , (8)  $+300$ , (9)  $+500$  mV; (b) optical density and (c)  $|\Delta\lambda_{\text{LSPR}}|$ , plotted as a function of the applied potential. An Ag/AgCl electrode is taken as the reference electrode.

onstrate that this LSPR modulation can be tuned by varying the PANI thickness.

For a light of wavelength  $\lambda$  impinging on a material with conductivity  $\sigma$ , the imaginary part of the dielectric constant is expressed as  $\varepsilon'' = 2\sigma\lambda/c$  where  $c$  is the speed of light.<sup>22</sup> Since conducting polymer conductivity is highly dependent on the doping level, it can be predicted that LSPR in such hybrid material will exhibit a progressive damping as a function of the applied potential.

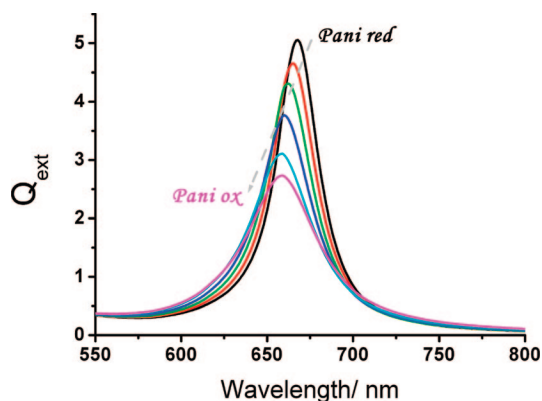
To probe this behavior, we have used a new array (array B, major axis 150 nm, minor axis 110 nm and height 40 nm, grating constant,  $\Delta x = \Delta y = 400$  nm) overcoated with a 50 nm PANI film. We have recorded (Figure 4a) the gold NP LSPR and plotted the optical density maximum (Figure 4b) and  $|\Delta\lambda_{\text{LSPR}}|$  (Figure 4c) for various potential applied to the electrode. As long as the PANI is kept in its reduced state (between  $-500$  and  $-100$  mV), no or minimal changes are seen in the optical response. However, as soon as the foot of the PANI oxidation peak (0 V) is reached, blue shift and damping of the LSPR occur. Polarizing the electrode at higher potentials, that is, increasing the PANI doping level, leads to further blue shift and LSPR damping. These results clearly show that the observed modulations of the LSPR are not due to some kind of filtering due to the PANI matrix or to electroreflectance effects observed with silver electrodes upon cathodic polarization<sup>19</sup> but are closely related to the charge carrier density injected into the conductive polymer through electrochemical doping.

We have reproduced qualitatively the LSPR experimental behavior *versus* the applied potential. For this purpose, we modeled the experimental data using the single-particle model in the electrostatic approximation,<sup>26</sup> in which the particle size is much lower than the incident wavelength  $\lambda$ . This simple mode takes especially into account the environment of the particles, corresponding in our study to a crucial parameter inducing the LSP modification. We believe that the quasi-static model remains efficient to qualitatively get a physical insight into such modification.

In this model, we first calculate the polarizability of a single particle. This is given by

$$\alpha_i = V \times \frac{\varepsilon_m - \varepsilon_{\text{surr}}}{\varepsilon_{\text{surr}} + L_i(\varepsilon_m - \varepsilon_{\text{surr}})}$$

where  $i = a, b, c$ ,  $V$  is the volume of the particle,  $\varepsilon_m$  is the frequency-dependent complex dielectric function of the metal,  $\varepsilon_{\text{surr}}$  is the DF of the surrounding medium, and  $L_i$  is the shape factor that depends on the main axes  $a, b$ , and  $c = h/2$  of the particle. Finally, we calculate the extinction cross-section using the formula  $C_{\text{ext}} = k\text{Im}(\alpha)$ . The targets we consider for the calculation are oblate gold particles, with a diameter of  $a = 10$  nm, and an aspect ratio  $r = a/c = 0.5$ . This value is taken



**Figure 5.** Extinction efficiency factor ( $Q_{\text{ext}} = C_{\text{ext}}/G$  with  $G$  being the particle cross-section) for different values of the dielectric function of the PANI film:  $\epsilon' = 4.4$  and  $\epsilon'' = 0$  (0 V, black curve);  $\epsilon' = 4.345$ ,  $\epsilon'' = 0.025$  (0.1 V, red curve);  $\epsilon' = 4.285$ ,  $\epsilon'' = 0.05$  (0.2 V, green curve);  $\epsilon' = 4.23$ ,  $\epsilon'' = 0.1$  (0.3 V, blue curve);  $\epsilon' = 4.170$ ,  $\epsilon'' = 0.18$  (0.4 V, cyan curve);  $\epsilon' = 4.170$ ,  $\epsilon'' = 0.25$  (0.5 V, magenta curve).

to have  $\lambda_{\text{LSP}}$  in air close to our experimental results. Nevertheless, this model will not reproduce quantitatively the position of the plasmon peaks since it does not take into account the size of the particles (no retardation effect). Furthermore, we introduce into the expression of the particle polarizability the effective dielectric function of the surrounding medium, to mimic the effect of the substrate (ITO). As a starting point, we roughly estimated the refractive index of the reduced PANI film on the basis of the optical studies of gold particles in different media. Using a procedure similar to that reported by McFarland *et al.*<sup>27</sup> (which introduces a linear fit in the graph representing the LSP resonance vs the refractive index) we found an effective refractive index of 2.1 for reduced PANI film + ITO substrate. This value is compatible with that reported by Baba *et al.* at 632.8 nm for reduced PANI.<sup>21</sup>

For the calculations, we introduced different values of the DF, defined in general as  $\epsilon = \epsilon' + i\epsilon''$  where  $\epsilon'$  and  $\epsilon''$  are the real and imaginary parts of the DF of the PANI film, respectively. Figure 5 simulates the influence of the potential applied to the PANI film on the LSP wavelength and damping.

We first simulated the situation of reduced PANI film, using the dielectric function  $\epsilon' = 4.4$  ( $\epsilon'' = 0$ ), (Figure 5, black curve). The LSP peak is significantly red-shifted with respect to air (not shown). We then used the  $\epsilon'$  and  $\epsilon''$  values determined by Baba *et al.* at various potentials (*i.e.*, at various doping level) at 632.8 nm wavelength.<sup>21</sup> At the beginning of PANI oxidation, the

complex value of the DF is:  $\epsilon = 4.345 + 0.025i$  (red curve) and corresponds to a small blue-shift and a moderate damping of the LSP profile). Then, by increasing  $\epsilon''$  and decreasing  $\epsilon'$  (as observed by Baba *et al.*) we were able to reproduce qualitatively the experimental LSP behavior shown in Figure 4 (see the different DF values  $\epsilon'$  and  $\epsilon''$  in the legend of Figure 5). In both cases (experiments and calculations), we observe a blue shift and a decrease in the LSP intensity, when the applied potential increases. It thus appears that the single particle model allows us, by entering in the polarizability the adequate DF values of the PANI film, to take into account the LSP spectral modifications observed experimentally (wavelength, intensity, and bandwidth) when the applied potential is changed. These simulations also confirm that the observed LSPR modifications are induced by the progressive tuning of PANI DF function with the applied potential.

## CONCLUSION

The results presented above clearly show that combining conducting polymers and gold nanoparticle arrays makes it possible to develop new active plasmonic devices such as modulators. The input of the devices is the potential applied to the electrode, which controls the state of the conductive polymer and switches its conductive properties and dielectric function. LSPR control can be achieved by controlling the PANI thickness and/or the potential applied to the system. Small variations in the potential fine-tune the LSPR, which clearly demonstrates that the observed effects are closely related to the charge carrier density injected into the PANI layer. These results can be qualitatively reproduced using a single-particle model in the electrostatic approximation.

Conducting polymer electrochemical switching has been shown to be an easy means of controlling the electronic structure and the properties of grafted molecules.<sup>4</sup> Here, we show that it is also capable of controlling the optical properties of metallic NPs exhibiting LSP resonance. If NPs can be considered as a special class of molecules, we believe that the strategy reported here will prove general and will make it possible to control the electronic structure and thus the properties of most nanoparticles (fluorescent, magnetic, semiconducting). Such hybrid systems will be useful in the design of nanosystems with various functional properties.

## EXPERIMENTAL METHODS

**Materials.** All chemical products are used without further purification. Aniline (99%) and sulfuric acid (95%) were purchased from Sigma-Aldrich and used as received.

**Characterization Techniques.** Indium–tin oxide (ITO) was used as substrate for all plasmonic devices and acted as the working

electrode. The total size of the gratings produced by EBL is limited to 100  $\mu\text{m}$  squares. The size of the electrode for PANI deposition is 1  $\text{cm}^2$ . The electrochemical cells consisted of a three-electrode arrangement with stainless steel grid counterelectrode, Ag/AgCl reference electrode. The PANI electrochemical system is known to be little affected by oxygen, so the experiments were performed without deaeration of the solu-

tion. Reversibility of observed phenomena was checked by running multiple-cycle voltammetry experiments at 200 mV s<sup>-1</sup> between -500 and +500 mV/Ag/AgCl reference electrode. Electrochemical responses of our devices were perfectly identical during cycles. Absorption measurements were carried out on an Oriol (model 74050) UV-vis spectrophotometer coupled with a fiber optic system which makes it possible to analyze an area of 100 μm × 100 μm. Prior to any PANI deposition, the substrate was repeatedly driven between -500 and +500 mV in 1 M H<sub>2</sub>SO<sub>4</sub> solution to check the LSP potential dependence and the magnitude of particle charging effects. A negligible wavelength shift was observed when the potential applied to the device was varied repeatedly. This shift is associated with a small decrease in the full-width at half-maximum (fwhm) for a grating polarized at -500 mV. These effects are in the expected range of particle charging effects for 100 nm diameter nanoparticles.<sup>9</sup> The results reported with PANI overcoating are much stronger in terms of wavelength shift, sign of shift, and LSP switch, which indicates that interpretation of our results can hardly be found in particle charging effect as observed by Chapman *et al.* for silver nanoparticle films.<sup>6</sup> A 100 nm PANI film in its reduced state does not absorb in the 500–900 nm region, whereas the oxidized film does (polaron band) with an OD of the same order of magnitude as that of the gold nanoparticles. For recording the LSP spectra, a reference was thus taken on the ITO/oxidized PANI area near the ITO/gold nanoparticle/oxidized PANI which makes it possible to extract the LSP changes. Uniformity of PANI deposition was checked by recording spectra of the film in several areas of the electrode using either ITO or ITO/PANI as reference. When the spectra of an ITO/PANI area were taken with an ITO/PANI reference in another area, the recorded optical density was null over the entire wavelength range recorded.

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## REFERENCES AND NOTES

- Aviram, A. Molecules for Memory, Logic, and Amplification. *J. Am. Chem. Soc.* **1988**, *110*, 5687–5692.
- Ratner, M. A.; Davis, B.; Kemp, M.; Mujica, V.; Roitberg, A.; Yaliraki, S. Molecular Wires: Charge Transport, Mechanisms, and Control. *Ann. N.Y. Acad. Sci.* **1998**, *852*, 22–37.
- Joachim, C.; Gimzewski, J. K.; Aviram, A. Electronics using Hybrid-Molecular and Mono-Molecular Devices. *Nature* **2000**, *408*, 541–548.
- Mangency, C.; Lacroix, J. C.; Chane-Ching, K. I.; Jouini, M.; Villain, F.; Ammar, S.; Jouini, N.; Lacaze, P. C. Conducting-Polymer Electrochemical Switching as an Easy Means for Control of the Molecular Properties of Grafted Transition Metal Complexes. *Chem. Eur. J.* **2001**, *7*, 5029–5040.
- Barnes, W. L.; Dereux, A.; Ebbesen, T. W. Surface Plasmon Subwavelength Optics. *Nature* **2003**, *424*, 824–830.
- Maier, S. A.; Kik, P. G.; Atwater, H. A.; Meltzer, S.; Harel, E.; Koel, B. E.; Requicha, A. A. G. Local Detection of Electromagnetic Energy Transport Below the Diffraction Limit in Metal Nanoparticle Plasmon Waveguides. *Nat. Mater.* **2003**, *2*, 229–232.
- Haynes, C. L.; Van Duyne, R. P. Dichroic Optical Properties of Extended Nanostructures Fabricated using Angle-Resolved Nanosphere Lithography. *Nano Lett.* **2003**, *3*, 939–943.
- Lezec, H. J.; Degiron, A.; Devaux, E.; Linke, R. A.; Martin-Moreno, L.; Garcia-Vidal, F. J.; Ebbesen, T. W. Beaming Light from a Subwavelength Aperture. *Science* **2002**, *297*, 820–822.
- Chapman, R.; Mulvaney, P. Electro-Optical Shifts in Silver Nanoparticle Films. *Chem. Phys. Lett.* **2001**, *349*, 358–362.
- Wang, Z.; Chumanov, G. WO<sub>3</sub> Sol-Gel Modified Ag Nanoparticle Arrays for Electrochemical Modulation of Surface Plasmon Resonance. *Adv. Mater.* **2003**, *15*, 1285–1289.
- Leroux, Y.; Lacroix, J. C.; Chane-Ching, K. I.; Fave, C.; Felidj, N.; Levi, G.; Aubard, J.; Krenn, J. R.; Hohenau, A. Conducting Polymer Electrochemical Switching as an Easy Means for Designing Active Plasmonic Devices. *J. Am. Chem. Soc.* **2005**, *127*, 16022–16023.
- Leroux, Y.; Eang, E.; Fave, C.; Trippe, G.; Lacroix, J. C. Conducting Polymer/Gold Nanoparticle Hybrid Materials: A Step toward Electroactive Plasmonic Devices. *Electrochem. Commun.* **2007**, *9*, 1258–1262.
- Peng, Z.; Guo, L.; Zhang, Z.; Tesche, B.; Wilke, T.; Ogermann, D.; Hu, S.; Kleinermanns, K. Micelle-Assisted One-Pot Synthesis of Water-Soluble Polyaniline-Gold Composite Particles. *Langmuir* **2006**, *22*, 10915–10918.
- Lacroix, J. C.; Diaz, A. Electrolyte Effects on the Switching Reaction of Polyaniline. *J. Electrochem. Soc.* **1988**, *135*, 1457–1463.
- Lacroix, J. C.; Kanazawa, K.; Diaz, A. Polyaniline: A Very Fast Electrochromic Material. *J. Electrochem. Soc.* **1989**, *136*, 1308–1313.
- Lamprecht, B.; Krenn, J. R.; Schider, G.; Ditzbacher, H.; Salerno, M.; Felidj, N.; Leitner, A.; Aussenegg, F. R.; Weeber, J. C. Surface Plasmon Propagation in Microscale Metal Stripes. *Appl. Phys. Lett.* **2001**, *79*, 51–53.
- Lamprecht, B.; Schider, G.; Lechner, R. T.; Ditzbacher, H.; Krenn, J. R.; Leitner, A.; Aussenegg, F. R. Metal Nanoparticle Gratings: Influence of Dipolar Particle Interaction on the Plasmon Resonance. *Phys. Rev. Lett.* **2000**, *84*, 4721–4724.
- Felidj, N.; Laurent, G.; Aubard, J.; Levi, G.; Hohenau, A.; Krenn, J. R.; Leitner, A.; Aussenegg, F. R. Grating-Induced Plasmon Mode in Gold Nanoparticle Arrays. *Chem. Phys.* **2005**, *123*, 221103/1–221103/5.
- Mulvaney, P. Surface Plasmon Spectroscopy of Nanosized Metal Particles. *Langmuir* **1996**, *12*, 788–800.
- Yan, S.; Wang, Y.; Wen, T.; Zhu, J. A. Study on the Optical Absorption Properties of Dielectric-Mediated Gold Nanoshells. *Physica E* **2006**, *33*, 139–143.
- Baba, A.; Tian, S.; Stefani, F.; Xia, C.; Wang, Z.; Advincula, R. C.; Johannsmann, D.; Knoll, W. Electropolymerization and Doping/Dedoping Properties of Polyaniline Thin Films as Studied by Electrochemical-Surface Plasmon Spectroscopy and by the Quartz Crystal Microbalance. *J. Electroanal. Chem.* **2004**, *562*, 95–103.
- Kang, X.; Jin, Y.; Cheng, G.; Dong, S. Surface Plasmon Resonance Studies on the Electrochemical Doping/Dedoping Processes of Anions on Polyaniline-Modified Electrode. *Langmuir* **2002**, *18*, 10305–10310.
- Kohlman, R. S.; Joo, J.; Min, Y. G.; MacDiarmid, A. G.; Epstein, A. J. Crossover in Electrical Frequency Response through an Insulator-Metal Transition. *Phys. Rev. Lett.* **1996**, *77*, 2766–2769.
- Tzamalidis, G.; Zaidi, N. A.; Homes, C. C.; Monkman, A. P. Doping-Dependent Studies of the Anderson-Mott Localization in Polyaniline at the Metal-Insulator Boundary. *Phys. Rev. B* **2002**, *66*, 085202/1–085202/8.
- Prigodin, V. N.; Epstein, A. J. Nature of Insulator-Metal Transition and Novel Mechanism of Charge Transport in the Metallic State of Highly Doped Electronic Polymers. *Synth. Met.* **2001**, *125*, 43–53.
- Kreibig U.; Vollmer M. In *Optical Properties of Metal Clusters*, Gonser, U., Osgood, R. M., Panish, M. B., Sakaki, H., Eds.; Springer-Verlag: Berlin, 1984; pp 23.
- McFarland, A. D.; Van Duyne, R. P. Single Silver Nanoparticles as Real-Time Optical Sensors with Zeptomole Sensitivity. *Nano Lett.* **2003**, *3*, 1057–1062.