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Communication

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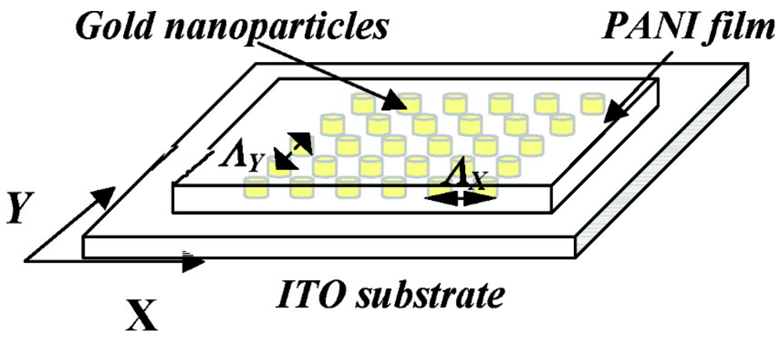

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# Conducting Polymer Electrochemical Switching as an Easy Means for Designing Active Plasmonic Devices

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Due to the continuously increasing demand for ultimate miniaturization of photonic and electronic systems, plasmonic and molecular electronics devices are currently booming as alternative technologies because of their very promising potential in writing, reading, storing, and processing information at the nanoscale.

Plasmonics is an emerging branch of photonics which uses nanostructured materials. Indeed, some metal nanoparticles are well-known to exhibit strong absorption in the visible and near-infrared range due to excitation of localized surface plasmons (LSP). The frequency of LSP mainly depends on the size, shape, and spacing of the particle and on the dielectric functions of the substrate and surrounding medium. Even though the LSP resonance can be matched to almost any desired wavelength from the visible to the near-infrared region, it cannot be easily tuned reversibly by an external physical input. Among plasmonic devices, filters,[1] waveguides,[1,2] polarizers,[3] and nanoscopic light sources[4] have been reported, but active plasmonic devices are still lacking even though first steps have been realized.[5−8]

Research efforts in molecular electronics are mainly focused on electron transport through a metal/oligomer/metal junction.[9] Conducting polymer electrochemical switching has also been demonstrated to be an easy means for controlling the electronic structure and the properties of grafted molecules.[10] This last approach is an alternative interpretation of the meaning of the two words “molecular electronic”, in which a single electron transfer on a single conducting oligomer can potentially trigger the properties of a single grafted molecule in order to write, store, or process information.

Here, we show that switching a conducting polymer electrochemically between its reduced and oxidized state makes it possible to control, switch, and modulate the LSP resonance of gold nanoparticle arrays and thus to design new active molecular plasmonic devices.

We have used polyaniline (PANI) as the conducting polymer because nanometer-thick films can be easily deposited on indium−tin oxide (ITO) and gold,[11] and because such films are known to exhibit ultrafast switching (switching time around 1 $\mu$s, RC limited) between their reduced nonconductive state and their oxidized conductive state.[12] Furthermore, PANI can be easily switched more than $10^5$ times without any degradation of the electrochemical signal.[11,12] Gold nanoparticle arrays on ITO have been fabricated by electron beam lithography (EBL).[13]

In a first attempt, we fabricated a square array of oblate gold particles, the minor axis of which is oriented normally to the ITO surface (sample A, diameter of the particles is set at 150 nm and height at 40 nm). The grating constant has been fixed to $\Lambda = 220$ nm. The spectra were recorded using X- and Y-polarized light (where X and Y are the gratings axis of the nanoparticle array). The array exhibits similar LSP under both polarizations due to minimal anisotropy.

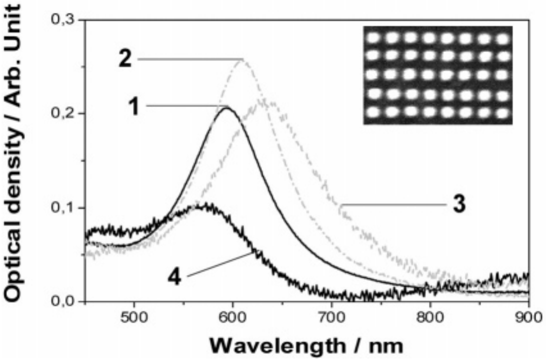

***Figure 1.*** Extinction spectra of square gold particle grating (particle diameter = 150 nm, height = 40 nm). Grating constant $\Lambda_X = \Lambda_Y = 220$ nm: (1) in air, (2) in water, (3) overcoated with a 100 nm PANI film in its reduced state, and (4) overcoated with a 100 nm PANI film in its oxidized state. Inset shows a SEM image of the grating.

Figure 1 shows the optical extinction of the gold nanoparticle array with air and water on top of the sample, prior to PANI deposition. As expected, a red shift (from 593 to 608 nm) is observed from air to water as a result of an increase in the medium dielectric function. Figure 1 also displays the response of the same gold nanoparticle array after the deposition of a 100 nm PANI film. The film was polarized at −500 mV (reduced state,) and at +500 mV (oxidized state). The voltametric response of such PANI film is shown in the Supporting Information (200 mV·s$^{-1}$ in 1 M aqueous sulfuric acid). When going from water to reduced PANI, another significant red shift is observed from $\lambda_{LSP} = 608$ nm to $\lambda_{LSP} = 633$ nm. Such effects can again be attributed to a modification of the refractive index of the nanodots' dielectric surrounding medium ($n_{air} = 1$, $n_{water} = 1.33$, $n_{PANI} > 1.33$).[11,12]

More importantly, when PANI is electrochemically switched from its reduced to its oxidized state, a dramatic blue shift is observed from $\lambda_{LSP} = 633$ nm to $\lambda_{LSP} = 571$ nm, below that of $\lambda_{LSP}$ observed in air, accompanied with a large decrease in optical density and a strong damping of LSP. This effect is reversible and has been observed repeatedly for more than 1 h while driving the electrochemical systems at 200 mV·s$^{-1}$ between −500 and +500 mV versus a pseudo-Ag reference electrode (switching time <10 s, not optimized). This experiment demonstrates that conducting polymer electrochemical switching is an easy means for modulating the maximum wavelength of nanoparticle surface plasmon resonance in a reversible way.

In a second attempt, we built an array of gold particles, which exhibits different LSP under X- and Y-polarizations due to some anisotropy.[14] The particles were arranged with different grating

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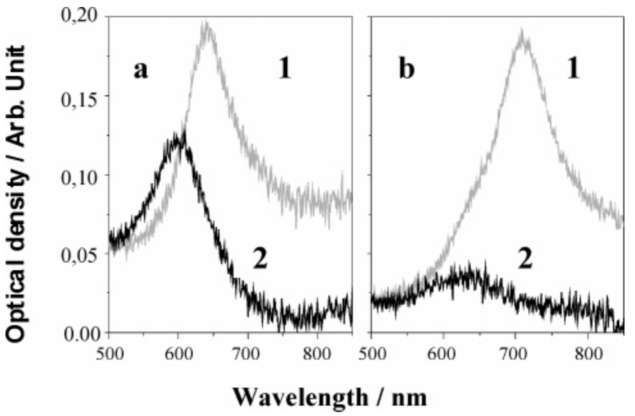

***Figure 2.*** Extinction spectra of rectangular gold particle grating overcoated with a 100 nm PANI film (particle diameter = 160 nm, height = 40 nm). Grating constants $\Lambda_X = 295$ nm and $\Lambda_Y = 315$ nm: (a) for Y-polarized light, (b) for X-polarized light. In each figure, curves 1 and 2 refer to PANI in its reduced and oxidized states, respectively.

constants: $\Lambda_X = 295$ nm and $\Lambda_Y = 315$ nm (sample B). The height of the particles is 40 nm, and the diameter is around 160 nm. As a consequence, when the extinction spectra are recorded in air, a $\Delta\lambda_{LSP}$ of 50 nm is experimentally observed between X- and Y-polarizations, which suggests that the shape of the particles is also slightly prolate. With a 100 nm PANI coating in its reduced state, the LSP resonance remains different for X- and Y-polarizations ($\Delta\lambda_{LSP} = 70$ nm), which is still attributed to grating effect and particle shape anisotropy.[14] Furthermore, for each polarization, a red shift is observed in the LSP peak when changing the superstratum medium from air to water to reduced PANI, as already observed with the square array studied previously.

Graphs a and b in Figure 2 show that the LSP resonance for X- and Y-polarization responds differently when the polymer film is switched from its reduced state to its oxidized state. Indeed, for Y-polarization (which corresponds to a weaker coupling between particles), the LSP resonance is blue-shifted compared to the spectrum when the film is in its reduced state, a result which fully reproduces the behavior observed with the square array previously studied (sample A). More importantly, for X-polarization, the LSP resonance is almost completely quenched. This effect is reversible and has been repeatedly observed for more than $10^3$ times while driving the electrochemical systems between −500 and +500 mV.

The interpretation of these results lies in the switching of the dielectric function $\epsilon$ of PANI. When PANI is in its reduced state, $\epsilon$ is real, whereas in its oxidized state, $\epsilon$ is complex ($\epsilon = \epsilon_{Re} + i\epsilon_{Im}$).[15,16] The variation of the real and imaginary parts of the dielectric function of a thin PANI film prepared in $H_2SO_4$ solution at several doping levels has been recently reported.[15] Moreover, oxidized metallic PANI samples follow a Drude-like behavior,[17−19] with a plasma frequency $\omega_p = 2$ eV, yielding a simplified expression of $\epsilon_{Re}$ given by $\epsilon_{Re} = \epsilon_\infty - (\omega_p/\omega)^2$. The imaginary part of the dielectric constant can be expressed as $\epsilon_{Im} = (2\sigma\lambda/c)$, where $\lambda$ is the vacuum wavelength of incident light, $\sigma$ the wavelength-dependent conductivity, and $c$ the speed of light.

The electrochemical switching of PANI thus generates a large change in both the real and the imaginary part of the dielectric function of the material around the nanoparticles. The large blue shift observed upon PANI oxidation can be attributed to a decrease of the real part of the dielectric constant at a wavelength around 632.8 nm, as observed by Baba et al.,[15] whereas switching in the imaginary part of the dielectric constant (from zero to a finite value) induces quenching and damping of LSP.[20]

In this context, the almost total quenching of the surface plasmon observed with sample B could be attributed either to the fact that the surface plasmon is delocalized within the polymer film (in this situation, it is no longer possible to excite LSP with incident plane light)[20] or to a dramatic decrease in the LSP lifetime due to a sharp evolution of the PANI complex dielectric function $\epsilon(\omega)$ with wavelength. These simplistic interpretations have to be taken with caution since the grating constant or the shape of the underlying nanoparticles has a clear effect on the plasmon quenching upon PANI switching. Indeed, total quenching is only observed for polarization parallel to the smaller grating constant.

Independently of the physics which governs these last experimental observations, our results clearly show that combining conducting polymers and gold nanoparticle arrays allows one to develop new active plasmonic devices, such as switches and modulators. In such an active plasmonic device, the LSP resonance can be either matched reversibly to a desired wavelength or switched off and on reversibly by changing the potential applied to the device. Conducting polymer electrochemical switching appears thus to be an easy means for designing active plasmonic devices.

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**Supporting Information Available:** Electrochemical and spectroscopic details. This material is available free of charge via the Internet at http://pubs.acs.org.

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