

Giant Plasmon Resonance Shift Using Poly(3,4-ethylenedioxythiophene) Electrochemical Switching

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Abstract: Herein, we report the variation of localized surface plasmon resonance (LSPR) of gold nanoparticle (NP) arrays covered by poly(3,4-ethylenedioxythiophene) (PEDOT) as a function of the electronic state of the polymer. Giant shifts and fine-tuning of the LSPR of gold NPs surrounded by PEDOT/sodium dodecyl sulfate have been achieved. The color variations of plasmonic/conducting polymer (CP) devices are given not only by changes of the optical properties of the CP upon doping but also by a close synergy of the optical properties of CP and NP. Such systems can considerably extend the field of CP-based electrochromic devices.

Nanometer-scale devices are attracting much attention due to an increasing demand for miniaturization in photonic and electronic applications. Plasmonic and conducting polymer (CP) devices are widely investigated for writing and storing informations or for applications in sensors and photovoltaic systems. Combining these two systems leads new active plasmonic devices.¹ Promising results were obtained using polyaniline (PANI) deposited on Au nanoparticle (NP) arrays.^{2,3} Indeed, reversible modulation and damping of the localized surface plasmon resonance (LSPR) was observed upon switching PANI electrochemically between its insulating and conductive states. These effects on LSPR are attributed to the variation of dielectric function of PANI upon switching and may greatly depend on the nature of CP. Poly(3,4-ethylenedioxythiophene) (PEDOT) is another widely used CP with interesting properties. It can be electropolymerized in aqueous media containing anionic surfactants. It switches at a lower potential than PANI and becomes almost transparent in its oxidized-conductive state, whereas it is deep blue in its reduced-insulating state (isosbestic point at 720–740 nm). These advantages make PEDOT attractive for use in transparent electrodes,⁴ in electrochromic devices,⁵ and as injection layers.⁴

Herein, we report the variation of LSPR of gold NP arrays covered by PEDOT as a function of the electronic state of the polymer. Gold NP arrays were fabricated by electron beam lithography on an indium–tin oxide (ITO) substrate using a published procedure.⁶ These substrates were used as plasmonic devices and as working electrodes in our setup. They consisted of prolate particles ($d_x = 140$ nm, $d_y = 120$ nm, height = 40 nm; grating constants, $\Lambda_x = 300$ nm and $\Lambda_y = 333$ nm). Before the array was covered with PEDOT, the extinction spectra of the NP in air show two in-plane LSP resonances, associated with each of the two NP axes. The LSPR for x -polarized light (major axis) is at 760 nm (Figure 1), while that for y -polarized light (minor axis) is at 670 nm (not shown).

PEDOT was deposited under galvanostatic conditions from a solution of EDOT and sodium dodecyl sulfate (SDS) in water (see

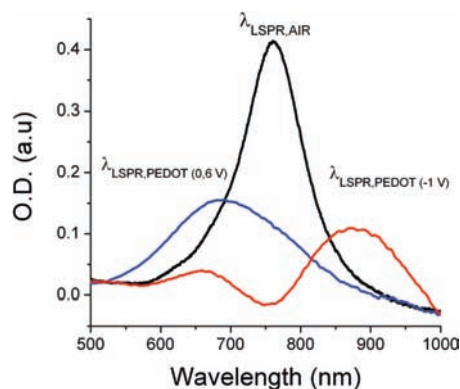


Figure 1. Extinction spectra of prolate gold particle grating (x -polarized light) in air (black curve), coated with a PEDOT/SDS film in its oxidized state (blue curve), and coated with a PEDOT/SDS film in its reduced state (red curve).

Supporting Information (SI)).⁷ The thickness measured by scanning electron microscopy is about 150 nm on the arrays and 100 nm on ITO. Extinction spectra were taken using PEDOT as reference. The transition from conductive to insulating state was performed by applying fixed potentials of 0.6 and -1 V, respectively, in an aqueous electrolyte containing 0.1 M LiClO₄; the LSPR spectra were recorded in situ simultaneously.

Figure 1 shows the optical extinction along the x -axis of PEDOT/gold arrays at 0.6 V polarization. The plasmon band is considerably blue-shifted from 760 nm in air to 685 nm and is severely damped. Under polarization at -1.0 V, a giant red-shift from 685 to 877 nm is evidenced, and damping is still observed as compared to the LSPR in air. Some minor peaks, due to incomplete subtraction of the PEDOT film absorption, are still visible. The overall shift between reduced and oxidized states is 192 nm for this PEDOT/gold NP array. It is reversible, as successive polarizations at 0.6 and -1.0 V gave similar LSPR values (incomplete reduction of PEDOT resulted in slightly smaller shifts). Compared to the shift observed with a PANI film on similar NP gratings³ or that observed using nanoscale movements within surface-bound molecular machines,⁸ such a large plasmon resonance shift, covering almost half of the visible spectrum, is unique and has never been reported elsewhere.

Such an effect can be attributed to the modification of the complex dielectric function $\epsilon'_{\text{PEDOT}} + i\epsilon''_{\text{PEDOT}}$ of PEDOT/SDS upon switching. PEDOT optical properties at several doping levels have been studied using electrochemical surface plasmon resonance spectroscopy.^{9–11} Baba et al.¹¹ gave values for a PEDOT/PF₆ film at various doping levels and at two wavelengths: $2.1 + i0.85$ and $1.8 + i0.1$ at 632.8 nm and $2.3 + i0.05$ and $1.4 + i0.55$ at 1152 nm for reduced (-1 V) and oxidized ($+0.5$ V) PEDOT, respec-

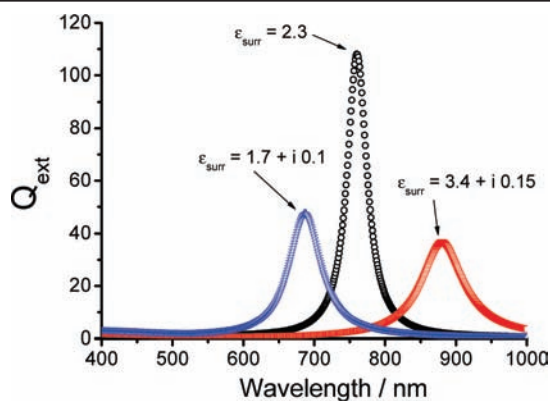


Figure 2. Extinction efficiency factor for different values of the surrounding medium effective dielectric function.

tively. The small damping observed upon switching is in agreement with these values (low variation of the imaginary part of the dielectric function from 0.1 at 632.8 nm for oxidized PEDOT to 0.05 at 1152 nm for reduced PEDOT) and can be, to some extent, attributed to the coincidence of the λ_{LSPR} in air and the isosbestic point of PEDOT. In contrast, the LSPR shifts observed here are only qualitatively consistent with these reported values (from 1.8 for oxidized PEDOT to 2.3 for reduced PEDOT). Indeed, the very large shift indicates a more pronounced variation of the real part of the dielectric function.

We have therefore modeled the experimental data using a single-particle model in the electrostatic approximation.¹² This simple model takes into account the environment of the particles and has already been successfully applied to achieve qualitative physical insight.^{2,3} The parameters are adjusted in order to have λ_{LSPR} in air close to our experimental results (760 nm), with an effective dielectric constant ($\epsilon_{\text{surr}} = 2.3$) of the surrounding medium (air/ITO) between the values of the substrate material ITO ($\epsilon = 4$, see SI) and air ($\epsilon = 1$).¹³ Figure 2 simulates the influence of the surrounding media on the LSPR wavelength.

From the simulation we found dielectric functions (ϵ_{surr}) of $3.4 + i0.15$ and $1.7 + i0.1$ when PEDOT was reduced and oxidized, respectively. These values show that the real part of the dielectric function decreases drastically upon doping PEDOT, whereas the imaginary part does not change much. The real part for reduced PEDOT/ITO ($\epsilon_{\text{surr}} = 3.4$) is compatible with ϵ'_{PEDOT} close to 2.3 as reported by Baba,¹¹ but $\epsilon_{\text{surr}} = 1.7$ for oxidized PEDOT/ITO indicates that ϵ'_{PEDOT} is below 1 at this wavelength; consequently, the LSPR is far below that observed in air. The low value of ϵ'_{PEDOT} in oxidized PEDOT compared to the values reported in other studies could be related to the use of SDS, which may enhance the metallic character of the polymer.

Similar behavior was observed for the minor axis of prolate NPs (for y -polarized light), but the shift between reduced and oxidized PEDOT/SDS is less pronounced ($\Delta\lambda_{\text{LSPR}} = 164$ nm instead of 192 nm). Several other arrays with different λ_{LSPR} in air were studied. The $\Delta\lambda_{\text{LSPR}}$ values observed upon PEDOT switching are reported in Table S11. Overall, very high plasmon resonance shifts are observed systematically, but $\Delta\lambda_{\text{LSPR}}$ increases when λ_{LSPR} goes to higher wavelength. This result is consistent with $\epsilon'(\omega)$ decreasing when ω gets closer to the PEDOT plasma frequency without reaching negative values.¹⁴

Finally, we studied extinction spectra under equilibrium conditions at various intermediate potentials (from 0.6 to -1.0 V, 3 min polarization time), i.e., at various charge carrier densities in the PEDOT film. Figure 3a shows the successive spectra, and Figure

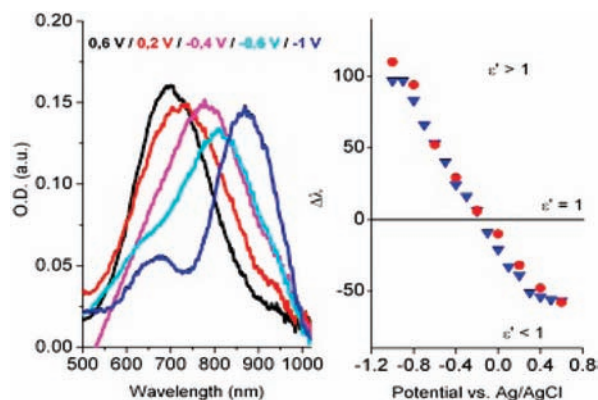


Figure 3. (a, left). Extinction spectra for prolate gold particle (x -polarized light) coated with a PEDOT/SDS film polarized at various potentials. (b, right). Variation of $\lambda_{\text{PEDOT}} - \lambda_{\text{air}} = \Delta\lambda$ versus the applied potential from -1 to 0.6 V (blue triangles) and from 0.6 to -1 V (red circles).

3b reports the variation of λ_{LSPR} maximum with the applied potential. The peak shifts smoothly from 690 nm at 0.6 V to 870 nm at -1.0 V with little damping variations. It can be fine-tuned at any intermediate value and matches the λ_{LSPR} observed in air, prior to PEDOT deposition, around -0.2 V. Little hysteresis (or memory effect) is seen in the $\lambda_{\text{LSPR}}(V)$ variations, in agreement with small hysteresis in the cyclic voltammogram of the used PEDOT film.¹⁵ Saturation is not fully observed when the potential approaches -1 V, indicating that PEDOT is not completely reduced at this potential. These results are in marked contrast to those obtained with PANI ($\lambda_{\text{LSP}}(V)$ shift of around 60 nm but with total damping of the plasmon at high wavelength), which demonstrates that tailoring the CP can yield plasmonic devices with tailored optical properties.

In conclusion, a giant shift and fine-tuning of the LSPR of gold NPs surrounded by PEDOT/SDS have been achieved. The color variations of plasmonic/CP devices are not only caused by changes in the optical properties of the CP upon doping but also by a close synergy of the optical properties of CP and NPs. Such systems can considerably extend the field of CP-based electrochromic devices¹⁶ since new colors, new electrochromic contrast, new color efficiency, and even new optical memory can be obtained using various combinations of a gold NP array and CP.

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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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