

Combined Electrochromic and Plasmonic Optical Responses in Conducting Polymer/Metal Nanoparticle Films

Roberto Pacios¹, Rebeca Marcilla¹, Cristina Pozo-Gonzalo¹, Jose A. Pomposo¹, Hans Grande¹, Javier Aizpurua², and David Mecerreyes^{1,*}

¹New Materials Department, CIDETEC-Centre for Electrochemical Technologies and CIC NANOGUNE Consolider, Parque Tecnológico de San Sebastián, Paseo Miramón 196, E-20009 Donostia-San Sebastian, Spain

²DIPC-Donostia International Physics Center, Paseo Manuel de Lardizabal 4, E-20018 Donostia-San Sebastian, Spain

Poly(3,4-ethylenedioxythiophene)/poly(styrene sulphonate) (PEDOT/PSS) aqueous dispersions were mixed with aqueous gold nanoparticle and aqueous silver nanoparticle colloids. PEDOT/gold nanoparticles (Au NP) and PEDOT/silver nanoparticles (Ag NP) films were obtained by solvent casting the corresponding aqueous solutions. The nanocomposite films showed the optical characteristics associated with both the surface plasmon absorption resonance of the metal nanoparticles and the excitation of the bipolaron band of the conducting polymer. As an interesting application we demonstrate the use of metal nanoparticles to tune the color of PEDOT based electrochromic films from blue to violet in the case of Au NP or green in the case of Ag NP.

Keywords: Conducting Polymers, Electrochromic Displays, Metallic Nanoparticles.

Conducting polymers are versatile materials that find applications in different fields such as anti-static coatings, batteries, electrochromic devices, organic light emitting diodes, touch screens, biosensors, and plastic photovoltaics. After their discovery,¹ researchers focused on the science and applications related to their electrical conductivity. However, nowadays most of the applications derive from its subsequently discovered unique electro-optical properties.² In the case of electrochromic devices, all conducting polymers are latently electrochromic in thin film form, redox switching giving rise to new optical absorption bands in accompaniment with transfer of electrons and counter-anions.³ On the other hand, metal nanoparticles are at the center of modern research efforts due to their enormous fundamental interest and potential technical applications.⁴ Owing to the particle-geometry confinement of the conduction electrons, metal nanoparticles exhibit a characteristic plasmon resonance, which is a function of the particle nature, size, and shape.⁵ The energy and width of the surface plasmon resonances is very sensitive to the separation distance between particles and to the interaction with the surrounding medium, giving rise to detectable color change which is

of burgeoning interest for sensing in the field of biological and medical sciences. Although the combination of conducting polymers and metal nanoparticles has been previously reported,⁶ no particular attention has been paid to the potential combination of their optical responses. Only recently, Leroux et al. reported an active plasmonic device based on a gold nanoparticle (Au NP) grating by using a conducting polymer electrochemical switching.⁷ Herein we present the first report of conducting polymer/metal nanoparticle films showing electrochromic and plasmonic optical responses. As an interesting application we report the use of metal nanoparticles to tune the color of electrochromic conducting polymers.

Among conducting polymers, poly(3,4-ethylenedioxythiophene), PEDOT is probably the most successful for commercial applications.⁸ In the particular case of electrochromic devices PEDOT shows promising results due to its electrochromic switching between transparent pale blue in the oxidized state and deep blue in the neutral state.⁹ Furthermore, PEDOT/poly(styrene sulphonate) (PSS) aqueous dispersions are commercially available which allows to coat large area and flexible substrates by simple wet chemical routes. In order to investigate the combination of PEDOT with metal nanoparticles we simply mixed an aqueous dispersion of PEDOT with gold nanoparticle

*Author to whom correspondence should be addressed.

(Au NP) and silver nanoparticle (Ag NP) aqueous colloids showing typical plasmonic absorbance. At first, we selected an aqueous dispersion of 3 nm spherical Au NP as a model to demonstrate our methodology.¹⁰ Thus, this aqueous dispersion (Au 4.2×10^{-4} M) was mixed with the aqueous PEDOT (0.01 wt% dispersion) in two different concentrations, mixture 1 (1:3 vol. Au:PEDOT) and mixture 2 (2:3 vol. Au:PEDOT). Figure 1 shows the UV-Vis spectra and picture of the initial Au NP dispersion, PEDOT dispersion and mixture 1 and mixture 2. The UV-Vis absorption spectrum of the red-pink gold colloidal dispersion showed the surface plasmon resonance at around 524 nm. On the other side, the UV-Vis spectrum of aqueous PEDOT dispersion shows a pale blue color characterized by broad bipolaron absorption between 600 and 1000 nm often referred to as a "free carrier tail." The mixture solutions were violet showing different tonalities as a result of adding the pale blue PEDOT dispersion to different amounts of the red-pink gold dispersion. The UV-Vis spectra of the mixtures showed the absorption resonance peak associated to nanoparticles and the band associated to PEDOT. However, the surface plasmon absorption peak of the Au NP shifted to values of 534 nm and 548 nm, respectively as a consequence of changing the nanoparticle surrounding media due to the presence of PEDOT/PSS. Next, PEDOT/gold nanoparticle films were prepared by solvent casting of these solutions. The obtained nanocomposite films presented a similar color to the original solutions. Significantly, the UV-Vis spectra of the films showed a broader peak for the surface plasmon band with a maximum centered at 555 nm.

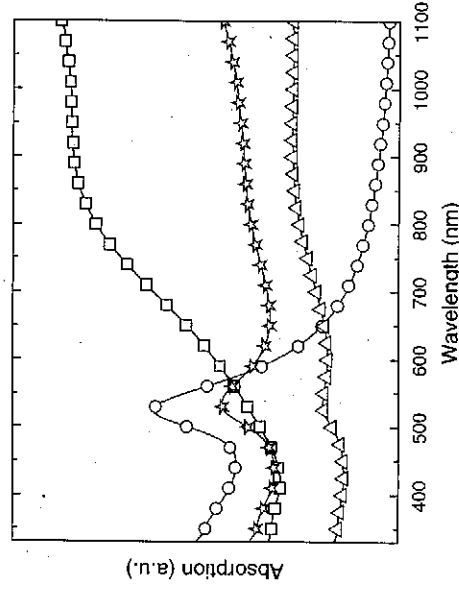
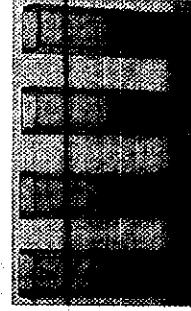


Fig. 1. UV-Vis spectra of: (□) PEDOT/PSS aqueous solution, (☆) mixture 1, (Δ) mixture 2, and (○) Au NP aqueous dispersion. At the top the photographs of the dispersions are shown, from left to right (□, ☆, Δ, ○).

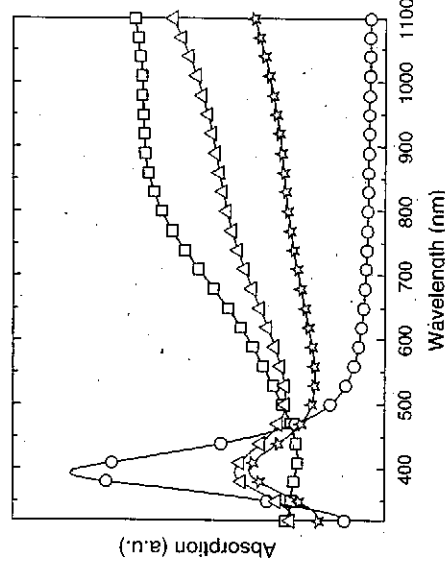
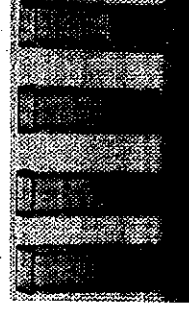


Fig. 2. UV-Vis spectra of: (□) PEDOT/PSS aqueous solution, (Δ) mixture 3, (☆) mixture 4, and (○) Ag NP aqueous dispersion. At the top the photographs of the dispersions are shown, from left to right (□, ☆, Δ, ○).

In order to extend the scope of our method, we additionally investigated the case of PEDOT and Ag NP. For this purpose, we utilized an aqueous dispersion of 7 nm spherical Ag NP. Figure 2 shows the UV-Vis spectra and picture of the initial 5.8×10^{-4} M Ag NP dispersion, PEDOT dispersion (0.01 wt%) and mixture 3 (1:3 vol. Ag:PEDOT) and mixture 4 (2:3 vol. Ag:PEDOT). The UV-Vis absorption spectrum of the yellow silver colloidal dispersion shows the particle surface plasmon peak at around 394 nm. Now, the mixture solutions were green showing different tonalities as a result of adding the pale blue PEDOT and yellow colloidal silver. UV-Vis spectra of the mixtures again showed both the absorption peaks associated to nanoparticles and the one associated to PEDOT. In this case the surface plasmon absorption peak of the Ag NP for the two different mixtures shifted only slightly to values of 396 nm and 397 nm, respectively. Next, PEDOT/silver nanoparticle films were prepared by solvent casting of these solutions. The obtained films presented a similar green color to the original solutions. As in the case of Au NP, the UV-Vis spectra of the films showed a broader peak for the surface plasmon resonance with a maximum centered at higher values 416.5 nm than in the solutions. The fact that the surface plasmon resonance is clearly seen in the composites demonstrates that Au NP and Ag NP are easily dispersed into PEDOT films by just mixing aqueous dispersions and film casting. A largest shift in the plasmon resonance in the case of Au nanoparticles is observed which is due to the closer proximity of the PEDOT absorption. Both metal nanoparticles and PEDOT maintain their

optical behavior and contribute to the optical response of the nanocomposite film.

Next, we investigated the spectroelectrochemical behaviour of PEDOT/gold and PEDOT/silver films using an optical transparent thin layer electrode cell. Cyclic voltammetry experiments of the films between -1.5 V and 0.8 V in acetonitrile using 0.1 M LiClO_4 as supporting electrolyte, led to very similar curves only showing the oxidation and reduction peaks associated to PEDOT, without any additional contribution from the metal nanoparticles (see Fig. S1). The electrochemical switching from oxidized to reduced PEDOT leads to a color change from a pale blue film to a deep blue film showing an strong absorption peak at 630 nm (Fig. 3). PEDOT/Au NP films after the electrochemical reduction step changed from violet to deep blue. The UV-Vis spectrum shows the reduced PEDOT absorption peak at 630 nm as well as a shoulder at around 546 nm associated to the surface plasmon resonance of the nanoparticles. This behavior is much pronounced in the case of Ag NP. Thus, PEDOT/Ag NP films after the electrochemical reduction step turned blue greenish from deep green. The UV-Vis spectrum shows the PEDOT absorption peak at 630 nm as well as the silver nanoparticle plasmon absorption at 426 nm. Again, due to the chemical change in the surrounding PEDOT media the surface plasmon peak moves to larger wavelengths.

In conclusion, we have demonstrated a simple combination between conducting polymers and metal nanoparticles which shows a unique optical behavior combining the plasmonic and electrochromic responses. By this method, conducting polymer films based on commercially available PEDOT/PSS with different colors such as violet and green have been easily obtained. It is worth to remark that green polymer electrochromic materials have only been recently discovered¹¹ and new research trends on electrochromic

conducting polymers pursues the search of new polymers to extend the choice of colors.¹² Our methodology has some important advantages: new monomer/polymer synthesis is not needed and the method can be extended to other conducting polymers and metal nanoparticles or nanorods showing different plasmonic bands from the visible to the near IR. This work demonstrates that metal nanoparticles can be added to the artist's palette for designing multiple color electrochromic materials and devices.

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SUPPORTING INFORMATION

Materials: $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (99.9%), NaBH_4 (99%), and poly(vinylpyrrolidone) ($M_w = 1.3000.000$ g/mol) were purchased from Aldrich and AgNO_3 (99.5%) was purchased from PANREAC S.L. BAYTRON P was purchased from Stark. All chemicals were used as received. Ultrapure water (conductivity: 0.8 S/cm) was used.

Characterization Techniques: Ultraviolet-Visible Spectroscopy (UV-Vis) was performed in a Shimadzu UV-1603 spectrophotometer. Particle sizes were measured using a Beckman Coulter N5 Submicron Particle Size Analyzer. Electrochemical characterisation was carried out on a EC-Lab MPG Bio-logic multi-potentiostat.

Synthesis of Gold Nanoparticles: A freshly prepared $10 \text{ ml } 5 \times 10^{-4}$ M solution of NaBH_4 was added dropwise under vigorous stirring to 10 ml of a 4.2×10^{-4} M gold tetrachlorauric acid solution. The solution was further stirred for 15 minutes and pink colour dispersion was obtained. A typical UV-Visible absorption spectrum shows a Surface Plasmon peak at 524 nm. Average sizes of the

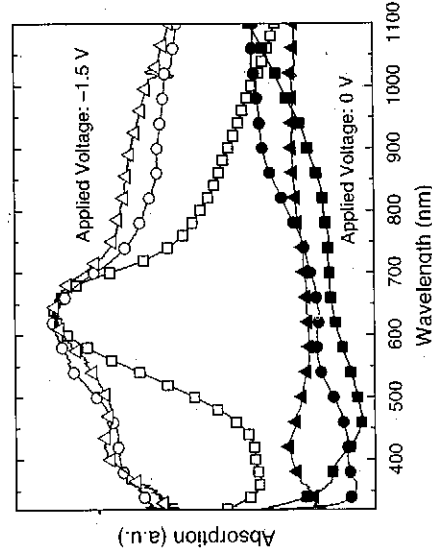


Fig. 3. Bottom part: UV-Vis spectra of PEDOT films on ITO/plastic at 0 V applied potential versus Ag/Ag^+ : (■) PEDOT; (○) PEDOT/Au NP films casted from mixture 2, and (▲) PEDOT/Ag NP casted from mixture 4. Top part: UV-Vis spectra of PEDOT films on ITO/plastic at -1.5 V applied potential versus Ag/Ag^+ : (□) PEDOT; (◊) PEDOT/Au NP film from mixture 2, and (△) PEDOT/Ag NP film from mixture 4.

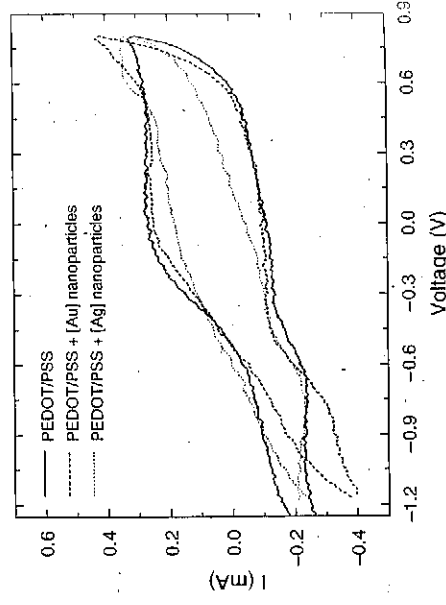


Fig. S1. Cyclic voltammogram of PEDOT films using a solution of acetonitrile with 0.1 M in LiClO_4 as supporting electrolyte, Ag/AgCl as reference electrode, and ITO as working electrode with a scan rate of 100 mV/s.

gold NP measured by Dynamic Light Scattering and TEM were 3 nm and 3.2 nm, respectively.

Synthesis of Silver Nanoparticles: A freshly prepared 10 ml 6×10^{-4} M solution of NaBH_4 was added dropwise under vigorous stirring to 10 ml of a 5.8×10^{-4} M AgNO_3 solution in the presence of 10 mg of poly(vinylpyrrolidone). The solution was further stirred for 15 minutes and yellow colour dispersion was obtained. A typical UV-Visible absorption spectrum shows a Surface Plasmon Resonance peak at 394 nm. Average sizes of the gold NP measured by Dynamic Light Scattering and TEM were 7 nm and 6.5 nm, respectively.

Cyclic Voltammetry of the Films: The redox behaviour of PEDOT nanocomposite films has been studied using cyclic voltammetry from a solution of acetonitrile with 0.1 M in LiClO_4 as supporting electrolyte, Ag/AgCl as reference electrode, and ITO as working electrode with a scan rate of 100 mV/s.

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