Effect of electrochromic polymer switching on surface plasmon polaritons

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ABSTRACT

Electrochromic polymers incorporated into plasmonic systems provide a possibility to control plasmonic properties with the applied voltage. Using gold-polyaniline (PANI) bilayers, we study the effect of coloration switching on surface plasmon polaritons propagating at the PANI-gold interface. The width of the resonance, magnitude of the plasmon wave-vector and dielectric permittivity of PANI are estimated as the function of the applied voltage.

Keywords: Plasmonics, cyclic voltammetry, polyaniline, electrochromic polymers, plasmon resonance.

1. INTRODUCTION

Electrochromic materials are able to reversibly change their coloration with an applied voltage via a reversible electrochemical reaction. These materials can find use in many applications, such as optoelectronics, displays, smart windows, etc[1-6]. Polyaniline (PANI) is a good candidate for applications, since it is environmentally stable, accessible, low cost, flexible and has a relatively high electrical conductivity[7,8]. However, it has some disadvantages, such as a relatively slow speed of color switching and a requirement for a thick layer of PANI to achieve the desired color contrast.

Various approaches have been explored to improve the performance of electrochromic polymers, including recent studies exploring plasmonic substrates[9-13], which show promising results. It is found that nanostructured plasmonic systems can provide additional tools for controlling colors of the electrochromic polymer film and accelerate the speed of coloration switching. The color switching is faster in plasmonic substrates in comparison with flat metal[9]. Reducing the non-patterned electrode surface area and decreasing electrolyte resistance further decreases the switching time. Use of a gold nanomesh as a substrate leads to much brighter contrast and threshold-like color switching in comparison with flat gold substrates[13]. Changes in electrochemical switching are a general consequence of plasmonic nanostructured environments. Some of the potential factors associated with this are the alteration of the charge transport kinetics and charge transport process[14].

The electro-optic switching and electrochemical tunability of the optical properties have been investigated using plasmonic nanostructures, such as metallic nanohole arrays, plasmonic cavities and nanoparticles[9-13,15-17]. Fast-, high-contrast electrochromic switching has been achieved by enhancing the interaction of light-propagating through arrays of metallic nanoslits with a very thin layer of an electrochromic polymer on the slit sidewalls[15]. This design maintains the great optical contrast while retaining the short temporal charge-diffusion features. In a similar way, Lu et al, created an electrochemical switching device that is transparent and uses plasmonic nanocrystals with PANI coating for color displays[16]. More recently, multilayered plasmonic composites filled with dielectric spacer known as the nanoparticle-on-mirror has attracted a lot of attention. The well-defined and exceptionally small gap volumes of these plasmonic composites tighten the light inside of them allowing independent tuning of the individual nanoparticles, which serve as active nanopixels[17].

Incorporation of electrochromic polymers in the plasmonic metamaterials and metasurfaces provides a possibility for electrochemical tuning of the plasmonic resonance. While the previous research concentrates mostly on far-field optical properties of plasmonic systems with electrochromic polymers and their switching speed, in the current work we study another side of this effect and clarify the question, to which degree the plasmonic behavior of PANI-plasmonic bilayers can be controlled with applied voltage. In this work we study the effect of PANI coloration switching on surface plasmon polaritons (SPPs) propagating along an interface between a dielectric medium and a metal.

The SPP k-vector, k_{SPP}, is estimated as[18]:

$$k_{spp} = \frac{\omega}{c}\sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}}, \qquad (1)$$

where ω is the light frequency, and ε_m and ε_d are correspondingly dielectric permittivities (real parts) of metal and dielectric. Since k_{SPP} *is* higher than the optical k-vector, k_0, a matching condition is required for excitation or decoupling of SPP, which can be achieved with a grating or a prism. For this purpose, in our experiments we used structures with one-dimensional profile modulations (gratings). The SPP resonance condition reads,

$$k_{spp} = k_x + mG, \qquad (2)$$

where k_x is the projection of optical k-vector onto the grating plane, m is an integer, $G = 2\pi/T$, and T is the period of the structure. If the color switching leads to modification in ε_d, it would be associated with change in k_{spp}, and can be observed as a change in the resonance conditions (Eq.2).

2. EXPERIMENTAL

In the experiment, we used two different types of samples, flat (for comparison purposes) and profile-modulated systems. To prepare profile-modulated substrates we start with commercially available DVD-Rs (manufactured by Verbatim) by delaminating and disassembling the disk into two. We use the read/write polycarbonate side, which was initially coated with a photoreactive substance. The photo-reactive layer is removed with ethanol, and then the substrate is dried with nitrogen gas. The polycarbonate side displays a concentric periodic groove having a rectangular profile with the periodicity of 740 nm and modulation amplitude of approximately 100-120 nm. By using the thermal evaporation process, chromium and gold are deposited with a thickness of 5 and 40 nm respectively. The flat samples are prepared by depositing 5 nm of chromium and 70 nm of gold onto the glass substrates. The schematics of our samples are shown in Figure 1 (a).

The PANI films with the thickness of ~50 nm are deposited on the fabricated substrates by the electrochemical process[19]. The standard cyclic voltammetry (CV) setup is used, which is composed of three electrodes: (1) the flat gold or DVD-based substrate is the working electrode, (2) a platinum wire with a 1mm diameter is the counter electrode, and (3) a saturated Ag/AgCl calomel electrode is the reference electrode. The potential range is cycled between -0.2 and 1.2 V at a scan rate of 25 mV s^{-1} in an aqueous solution with 2 M HNO3 and 0.1 M aniline. A Biologic SP-300 potentiostat is used to record the CV curves and provide information on film deposition process. The quality of the samples and switching of colors with the voltage (from transparent yellow to dark blue) are checked visually after the deposition.

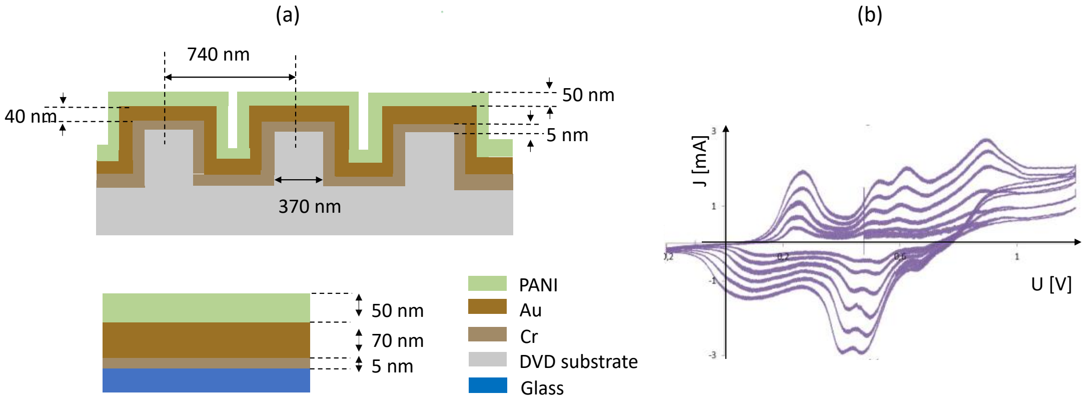

Figure 1. (a) Schematics of the DVD-based (top) and flat (bottom) structures. (b) Typical CV curve during the electrodeposition of PANI.

Plasmonic properties of DVD-based structures have been previously studied[20]. The geometry of the grating allows for a SPP excitation of the first order (m=1). It is associated with an increase in absorption at the resonance frequency and can be observed as a dip in the angular dependence of the reflection or in the spectrum of the reflectivity using a standard spectrophotometer. Since the changes in the resonance conditions due to PANI switching are expected to be small, and accuracy in measuring the angle is limited, for our experiment, we choose the spectral studies, where the sample is oriented at a certain angle, and reflectivity spectra are recorded.

However, there are certain challenges for such an experiment. Since the sample is a grating, and with a relatively high profile-modulation, in addition to reflection we expect diffraction and scattering. Thus, for correct estimation of the absorption, an integrating sphere was used which collects all reflected, transmitted, diffracted, and scattered light from the sample. To perform the color switching, the sample must be inside a cuvette with the electrolyte solution; at least two electrodes are needed for providing the voltage in the switching process. One should be able to orient the sample at a certain angle for incoming light. In addition, the setup should be safe enough for not spilling the liquid inside the spectrophotometer.

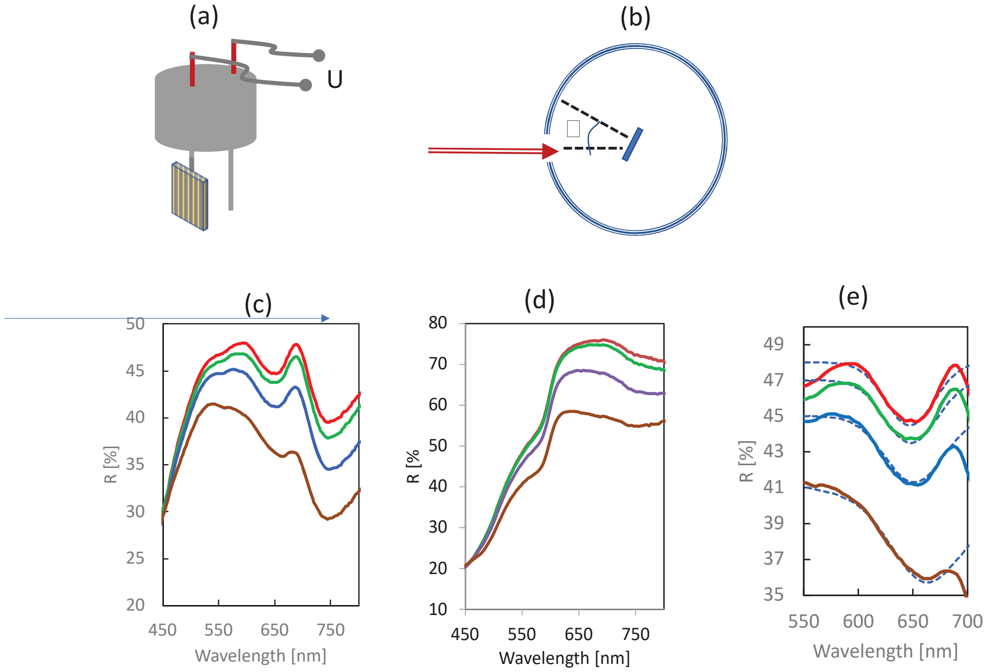

Figure 2. (a, b) Setup and sample positions in the spectrophotometer; (c, d) Reflection spectra taken at 30° in (b) grating and (c) flat systems. (e) Fitting of the dip at various voltages. Voltages are shown with color, 0 V (red), 0.1 V (green), 1.2 V (blue) and 2 V (brown).

Our approach is illustrated in Figure 2 (a, b). We use a cylindrical cuvette with a rubber cover. Two small openings are made in the rubber for electrodes. The DVD-based sample oriented with grooves vertically is connected to one electrode and placed inside the cuvette filled with the electrolyte solution of 0.1 mol/L HNO_3 and 1 mol/L $NaNO_3$. The second (counter) electrode is located behind the sample. The cuvette with the sample is placed on a goniometer stage inside the integrating sphere in the spectrophotometer. The sample is oriented corresponding to 30 deg incidence angle. We used long thin wires to connect the electrodes to an external voltage source. Horizontally polarized light is used to record the spectra. The experiment was repeated for the flat gold sample.

The data obtained for four different voltages are shown in Figs 2 (c, d). The reflectivity decreases with the applied voltage for both systems as expected manifesting the switching. The changes are gradual and start to be observed at even small voltages. The films become much darker at 1.2 V and the darkest at 2 V. The spectra obtained in the grating structure reveal two minima, around 640 nm and 740 nm. The dip around 640 nm becomes broader and shifts its position with increase in the voltage. We believe that the first dip is related to the excitation of the SPP along PANI/gold interface. The dip around the 740 nm looks the same for all voltages; it can be ascribed to the SPP along gold and polymer interface.

3. DISCUSSION

In order to analyze the results obtained in the gratings, we approximate the first spectral minimum as an increase in absorption having a Gaussian shape

$$P\ =\ Aexp(-\frac{(\omega-\omega_o)^2}{\delta^2}) \tag{3}$$

where A, w, w_0 , d are fitting parameters. This approximation is not perfect, see Fig. 2(e) but provides information on the spectral position and width, and their changes upon the applied voltage.

Table 1. Fitting parameters for the spectral dips.

Voltage [V]	**0.0**	**0.1**	**1.2**	**2.0**
A	3.45	3.5	3.45	5.15
$l_0 = 2p/w_0$ [nm]	652	652.2	655.8	670
w_0/d	22.2	21.3	17.9	11.9

The data show that with the increased voltage, the dip is broadening reducing the quality factor of the resonance and the spectral position of the dip, l_0, gradually shifts toward longer wavelengths, which can be interpreted as the change in the plasmon k-vector. The resonance condition, Eq. 2, can be rewritten as

$$k_{spp}/ k_0 = l_0 / T + n\ sin(\theta) \tag{4}$$

where $k_0 = 2p/l_0$ and n is the refractive index of the electrolyte. We assume n=1.33 as in water[21] and estimate k_{spp}/ k_0. The results are shown in Table 2. k_{spp} increases at high voltage, but the effect is small. The increase in k_{spp} can be attributed to the increase of the real part of the PANI dielectric constant. Using the Eq (1) and the values for the permittivity for gold for each resonance wavelength (extrapolated from ref.[22]), the effective dielectric constants for PANI, e'_{PANI}, are estimated, see Table 2.

Table 2. SPP wave vector and dielectric constants of metal and PANI in the resonances.

Voltage [V]	**0**	**0.1**	**1.2**	**2**
k_{SPP}/k_0	1.54	1.54	1.55	1.57
e_{gold}	-13.1	-13.15	-13.4	-14.2
e'_{PANI}	2.02	2.03	2.04	2.1

As one can see, the switching of PANI affects the SPP k-vector, and a real part of permittivity, e'_{PANI}. However, such changes are relatively small (~2% in k-vector and less of about 4% in e'_{PANI}). The strongest effect of PANI switching is observed in the losses, decreasing the Q factor twice with applying the switching voltage.

In conclusion, we explore the effect of electrochromic polymer switching on the surface plasmon polariton resonance in bilayer polyaniline-gold systems. Changes in the resonance width and position are observed upon the applied voltage, confirming the possibility to tune plasmonic effects with the electrochromic switching. However, the major effect of the switching is the decrease in the resonance Q-factor while the growth of k-vector is non-significant.

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