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A Tunable Polymer–Metal Based Anti-Reflective Metasurface

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Anti-reflective surfaces are of great interest for optical devices, sensing, photovoltaics, and photocatalysis. However, most of the anti-reflective surfaces lack in situ tunability of the extinction with respect to wavelength. This communication demonstrates a tunable anti-reflective surface based on colloidal particles comprising a metal core with an electrochromic polymer shell. Random deposition of these particles on a reflective surface results in a decrease in the reflectance of up to 99.8% at the localized surface plasmon resonance frequency. This narrow band feature can be tuned by varying the pH or by application of an electric potential, resulting in wavelength shifts of up to 30 nm. Electrophoretic particle deposition is shown to be an efficient method for controlling the interparticle distance and thereby further optimizing the overall efficiency of the anti-reflective metasurface.

Surfaces with very low reflectivity are of great importance for a broad range of applications, such as anti-reflective coatings,^[1,2] optical resonators (lasers),^[3] or interferometers.^[4] Broadband absorbers are of particular interest since they can facilitate efficient conversion of solar energy through photovoltaics^[5,6] or photocatalysis.^[7–9] On the other hand, narrowband optical materials have also attracted significant attention as they can be utilized in sensing applications.^[10] Plasmonic metasurfaces are highly attractive materials because the absorbed wavelength can be finely tuned by adjusting their geometric structure. They also exhibit high sensitivity toward refractive index changes in the environment, which opens up a potential avenue

for tunability.^[11,12] Giessen et al. have introduced such sensors based on metal-insulator-metal structures.^[10] By employing electron beam lithography (EBL), a gold nanodisc array featuring localized surface plasmon resonances can be fabricated on top of a gold mirror with a dielectric MgF₂ spacer sandwiched in between the nanodiscs and the mirror. The resulting plasmonic coupling enables tuning of the electric permittivity ϵ and magnetic permeability μ and leads to impedance matching between the structure and air. The device then features a minimum in the reflectance at the resonance frequency (terahertz range) that is sensitive to small refractive index changes.^[12,13]

More recently, colloidal particles have been utilized to create anti-reflective plasmonic metasurfaces.^[14,15] The colloidal approach offers scalability of the synthesis and allows different optical coatings to be incorporated, while maintaining precise control of the nanostructure and thus is especially appealing for large area applications.^[16] Mikkelsen et al. have tuned the resonance frequency of such surfaces in the visible region via random deposition of cubic silver nanoparticles onto a gold mirror.^[17] They achieved an absorbance of 99.7% at the resonance frequency, even at comparably low fill fractions of around 20% by area. Although the resonance frequency can be tailored through a variation of shape and size of the plasmonic nanoparticles, this involves strenuous preparation of different nanoparticles and in situ tuning is deemed impossible.

Contrarily, active tunability of the optical properties can be realized by integrating a switchable polymer layer as the spacer between plasmonic nanoparticles and a mirror. A change in the refractive index of such a layer can be triggered externally and used to alter both the plasmonic resonance frequency and optical impedance-matching condition. A suitable system for testing this concept has been introduced by Tsukruk et al.^[18,19] They

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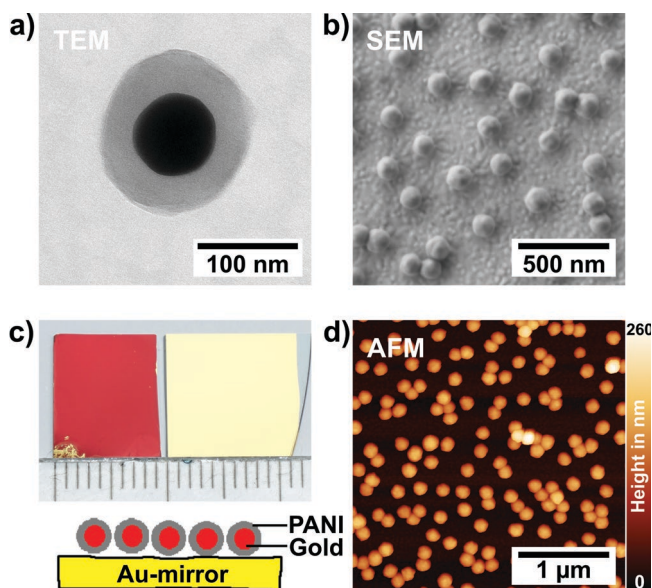


Figure 1. Surface structure of the tunable metasurface. a) TEM image of a single Au-PANI particle. b) SEM image of Au-PANI particles on a gold mirror. c) Top: photograph of the anti-reflective metasurface (consisting of Au-PANI on a gold mirror) and an Au-film reference under specular illumination (scale in mm). Bottom: a schematic cross-section of the sample. The structure is: 200 nm Au mirror, 32 nm PANI shell, 84 nm gold core. d) AFM micrograph of the surface topography.

investigated the electro-optical response of polyaniline coated silver cubes in dispersion and on transparent substrates. A strong influence of the polymer's complex refractive index on the localized surface plasmon resonance was demonstrated. Based on this system, Baumberg et al. also studied the influence of the polymer redox chemistry on (plasmonic) light scattering.^[20] Deposition of the particles on gold surfaces enabled tuning of the electrochromic properties while enhancing the plasmonic response. This is a promising route toward responsive nanoscale pixels. However, the influence of the particle layers on the reflectivity of (metallic) surfaces was outside the scope of their investigations.

Here we present a plasmonic metasurface based on polyaniline-coated gold spheres which act as a tunable, anti-reflective

coating. By combining the polymer with gold nanocrystals, we create a scalable, wet-chemically synthesized material, while providing pronounced narrowband extinction at optical frequencies. In contrast to previous works, this method provides in situ tunability of both the attenuation efficiency and the peak attenuation wavelength. This switchability is realized by utilizing the pH-responsive and electrochromic properties of the polyaniline corona. For further optimization of the anti-reflective metasurface, we discuss a facile assembly method to obtain precise control of the interparticle distance.

Our approach to making tunable metasurfaces was based on using spherical gold nanoparticles^[21] coated with polyaniline (Au-PANI).^[18] We synthesized 83.7 ± 2.8 nm gold spheres with a 31.5 ± 2.8 nm thick polyaniline shells (from TEM, see Figure 1a). The particles were deposited onto hydrophilized gold substrates via sedimentation yielding a sub-monolayer surface coverage with a homogeneous optical appearance at the macroscale as shown in Figure 1c (see Supporting Information for experimental details).

Depending on the applied concentration of the dispersed Au-PANI particles, the surface coverage was varied from $24 \pm 1\%$ (see Figure 1) to $\approx 50\%$ (see Section S1, Supporting Information). The visual appearance of the samples was strongly altered from the typical gold metallic reflection to an intense red color as displayed in the photograph in Figure 1c. The film stability toward mechanical stress (e.g., wiping) was limited but the particle adhesion was sufficient to resist gas streaming, rinsing, and immersion into aqueous solutions.

The appearance of the samples can be easily explained by comparing the resulting optical spectra in Figure 2a. For characterization of our metasurface, UV-vis spectroscopy was performed at 10° specular reflectance angle and normalized to the reflectance of a pure gold film. In addition to the low reflectance below 500 nm caused by the interband transition of gold, there is a pronounced minimum at 550 nm. It corresponds to the peak position of the localized surface plasmon resonance (LSPR) and reaches a reflectance of just 1.5% with respect to the gold mirror. This attenuation of green light results in the observed red coloration of the sample. Furthermore, there is a less pronounced band located at 800 nm which is attributed to the absorption of polyaniline in its emeraldine salt state (as synthesized).

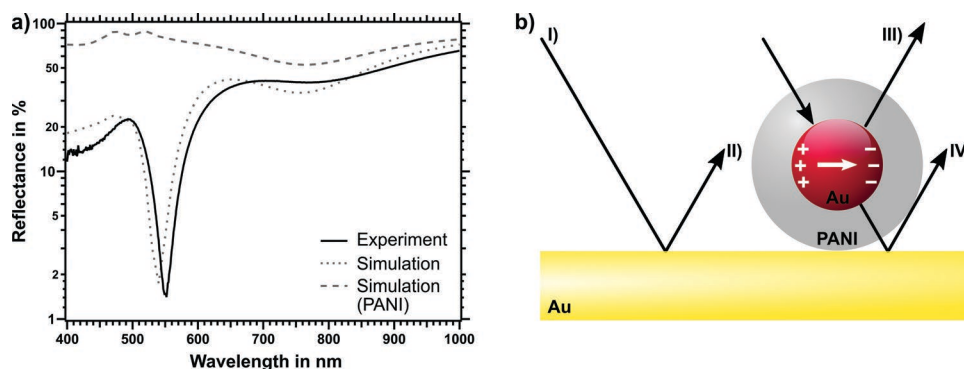


Figure 2. Optical properties of the metasurface. a) Typical specular reflectance spectrum of the anti-reflective surface (black line) together with COMSOL simulation of Au-PANI (dotted grey line) and pure PANI (dashed grey line), both normalized to the Au-film. b) Schematic of the reflection and scattering events at the mirror and the particle, showing: (I) the incident light beam, (II) the light directly reflected by the mirror, (III) the light scattered by the particle, and (IV) the light which is scattered by the particle and then reflected by the mirror.

We hypothesize that the extraordinary low reflectance exhibited by these films can be attributed to a combination of plasmonic and interference effects. Namely, the key characteristic of our system is that optical phase shifts are induced by the polymer coated particles. Similar to the mechanism proposed by Chen et al.,^[22,23] the incident light (I) (see Figure 2b) encounters various interfaces through the overall structure. The three major components are: (II) the light which is directly reflected by the gold mirror, (III) the light transmitted by the polymer and scattered by the plasmonic particle, or (IV) the light scattered by the particle and then reflected by the mirror.^[24] As a consequence of passing the polymer and interacting with the plasmonic particle, the light rays III and IV are phase-shifted with regard to the reflected light (II). The resulting destructive interference contributes to additional attenuation of light and is responsible for the performance of our metamaterial as an antireflective coating.^[22] In contrast to coupling mechanisms as discussed by Baumberg et al., we excite the particle resonance predominantly parallel to the surface (perpendicular k -vector), which results in comparably weak film-coupling at 32 nm film distance. However, alternative mechanisms based on plasmonic coupling are discussed in the Supporting Information (see Supporting Information 2).

To qualitatively interpret the described interference effects with regard to their tunability, we conducted optical simulations based on the experimental parameters. Spectroscopic ellipsometry was applied to determine the optical properties of the polyaniline corona by extracting the wavelength dependent complex refractive index (values of n and k) for our polymer (compare Supporting Information 3). Based on these optical constants, COMSOL simulations were used to calculate the reflectance of a gold mirror covered with Au-PANI particles (see Supporting Information 4 for details). The dotted graph in Figure 2a shows the simulated reflectance spectrum with an untreated PANI shell and 240 nm interparticle distance (center-to-center). The features reproduce our experimental findings, including both the reflectance minimum at ≈ 550 nm and the less-pronounced band at about 800 nm which is attributed to the absorbance of PANI as indicated by the simulation of pure polymer particles (dashed graph).

For experimental demonstration of the proposed in situ switchability, the optical properties of the anti-reflective metasurfaces were modulated using two different triggers: pH and redox reactions. As displayed in Figure 3, immersion of the substrate in either HCl- or NaOH-containing aqueous solutions altered the optical appearance of the sample. Reflection of the surface changed from reddish (initial film and after HCl immersion) to a greenish color (after NaOH immersion). This was correlated to the spectral shifts shown in Figure 3a. Alternating color changes were induced by subsequent immersion into acidic and basic solutions with reflectance spectra collected after each step. The green curves depict the spectra after immersion into HCl while blue curves correspond to the spectra after immersion into NaOH. The green spectra exhibit a pronounced minimum at 550 nm with reflectance below 2% while an additional shoulder can be observed at around 800 nm. The blue spectra feature an increased reflectance of around 10% at the peak minimum, that is, a fivefold increase. Furthermore, the band is redshifted to 570–585 nm and features a pronounced asymmetric, longer wavelength shoulder.

The optical changes are associated with the changing chemistry of the polyaniline shell around the plasmonic particles. Under acidic conditions, polyaniline is in its protonated (doped) state referred to as emeraldine salt. Following immersion into a base, the emeraldine salt is deprotonated and is converted into its emeraldine base form, shown in Figure 3b. This transition is associated with several different changes to the polymer: i) A transition from a conductor to an insulator due to deprotonation (loss of the radical cation).^[25] ii) A shift of the main absorption band from 800 to 600 nm as displayed in Figure S8, Supporting Information, because of the changes in the π -electron system.^[26] iii) A change in refractive index (see Supporting Information 3). As the localized surface plasmon peak position is strongly dependent on the refractive index of the surrounding medium, a shift is expected when the dielectric properties of the PANI layer change. Simulations based on the determined optical constants of NaOH-treated PANI are displayed in Figure S7, Supporting Information. Here, the reflectance minimum is redshifted by 20 nm as a consequence of the increased refractive index of the polymer.^[27,28] Interestingly, the minimum is less pronounced compared to that obtained for the untreated polymer, even though the emeraldine base absorbs at that wavelength. We deduce that the altered optical constants of PANI influence the phase shift of light interacting with the particle (compare the scattered light beams III and IV in Figure 2b). Consequently, destructive interference occurs to a lesser extent, which results in less attenuation of the reflected light.

The shift of the reflectance minimum was reversible over multiple cycles as displayed in Figure 3c. The slight deviations in the peak intensity and positions are attributed to chemical oxidation of the polymer, which will be discussed in the following section.

Polyaniline is known to exhibit strongly potential-dependent optical spectra.^[27] In general, three states are distinguished, each featuring a protonated (salt) and a deprotonated (base) state.^[29] In the cyclic voltammetry data shown in Figure S9, Supporting Information, two oxidation peaks can be observed at +0.05 and +0.60 V versus Ag/AgCl. We attribute the three different regions to the oxidation states Leucoemeraldine (here denoted as “Red”), Emeraldine (“Ox1”) and Pernigraniline (“Ox2”). The respective structural formulas are displayed in Figure 3b–e.

When the oxidation state is changed, the optical properties of the polymer are also altered. This can be observed in the reflectance spectra shown in Figure 3d. For this sample, the red curves (reduced state) exhibit a reflectance minimum of 0.25% at around 565 nm. When oxidized, the peak is blue-shifted by 10 nm after the first oxidation step (Ox1, green curves) and the reflectance slightly decreases to 0.15%. After the second oxidation step, the reflectance is increased by a factor of 10 (to 1.5%) and it is further redshifted by about 30 nm with respect to Ox1. At the same time, the full width half maximum (FWHM) is doubled and the peak features a pronounced shoulder at longer wavelengths. This results in visible changes to the optical appearance of the metasurface, as can be seen in the photographs in Figure 3e. The induced changes are again reversible, with only minor variations between each cycle. With regard to the performance as an anti-reflective coating, the attenuation of the reflected light is most efficient when the film is in

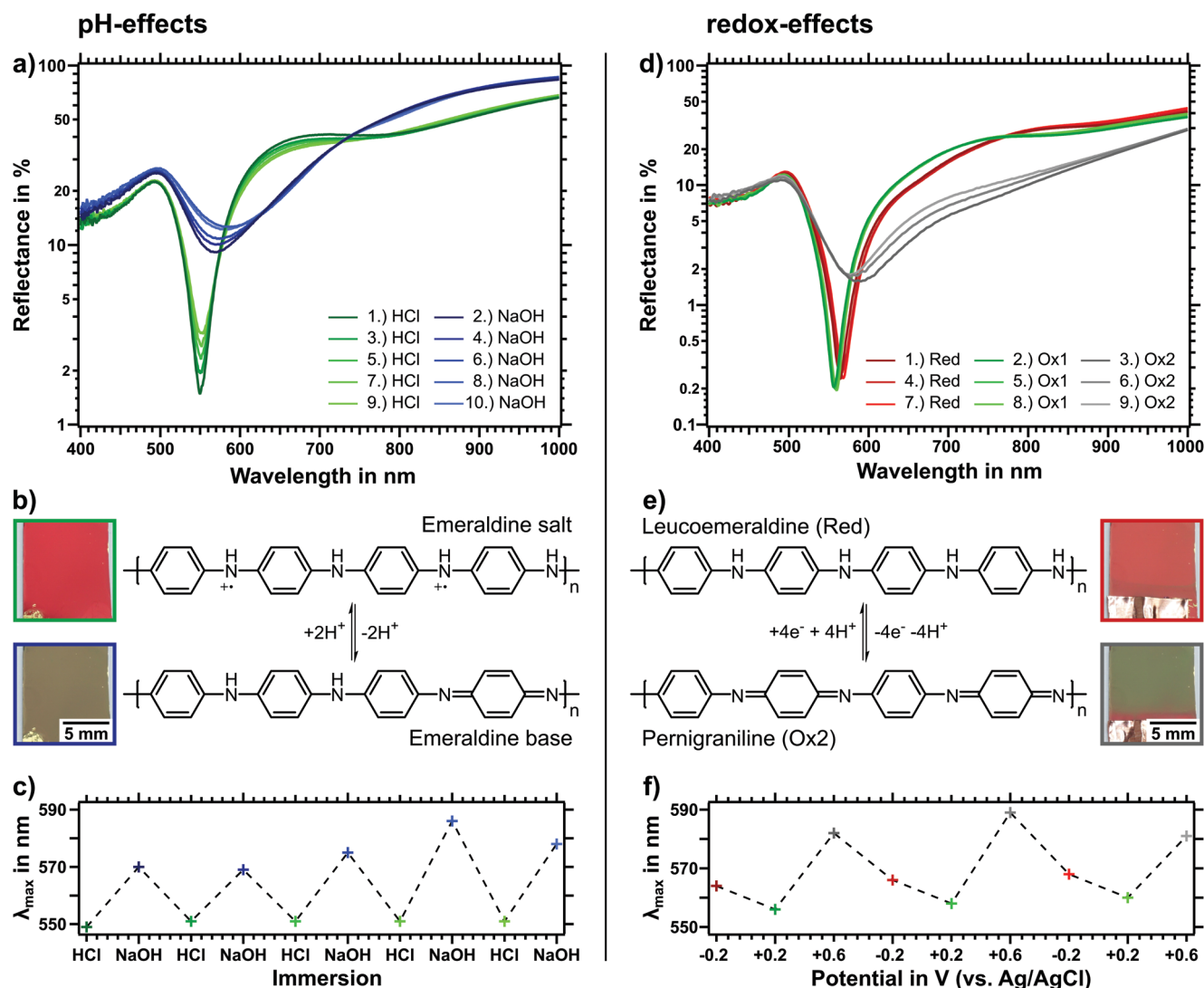


Figure 3. pH- and redox-dependent optical properties of the metasurface. a) Reflectance spectra of the surface after immersion into acidic (green) or basic (blue) solution. b) Structural formula of the protonated form (emeraldine salt) and deprotonated form (emeraldine base) of polyaniline together with respective photographs of the sample. c) Maximum peak positions of the reflectance spectra in HCl or NaOH for multiple cycles with dashed lines as a guide to the eye. d) Reflectance spectra of the tunable metasurface, after applying a reducing potential (red, -0.2 V versus Ag/AgCl), an oxidizing potential (green, $+0.2$ V), and a strong oxidizing potential (blue, $+0.6$ V). e) Structural formula of the fully reduced leucoemeraldine base and the fully oxidized pernigraniline base forms of polyaniline, together with respective photographs of the sample. f) Maximum peak positions of the reflectance spectra after applying reducing (-0.2 V) or oxidizing ($+0.6$ V) potentials with dashed lines as guide to the eye.

the emeraldine salt state (Ox1), which corresponds to the as-synthesized state.

Based on our interference-related explanation of the extraordinarily low reflectance, we assume that the number of particles per area has a major impact on the efficiency of the metasurface. More precisely, the coverage determines the ratio of light which is directly reflected by the mirror (II) or which interacts with the particle (III and IV). Thus, an optimum (minimum reflection) is expected at a certain coverage, which is not necessarily the close-packed state.^[30] To target that coverage, we conducted optical simulation with systematic variation of the interparticle distance D (see Supporting Information 8). The resulting reflectance minima with untreated PANI are displayed in Figure 4a. A global minimum is observed in this

dataset: From that point, either reducing or increasing the separation leads to a less pronounced reflectance minimum. Thus, superposition of phase-shifted light evokes the most efficient, destructive interference at a particle distance of about 190 nm. This is also accounted by the deep red color in the CIE space (see Figure 4b).

To achieve precise control of the interparticle distance, which is necessary for optimal performance of the anti-reflective metasurface, we have utilized electrophoretic particle deposition (EPD) as a route to receive well-defined nanoparticle assemblies.^[31] The mechanism displayed in Figure 4c employs the electrophoretic force between a nanostructured conductive substrate and a counter-electrode. The Au-PANI particles are attracted toward the exposed areas of the substrate. As a proof

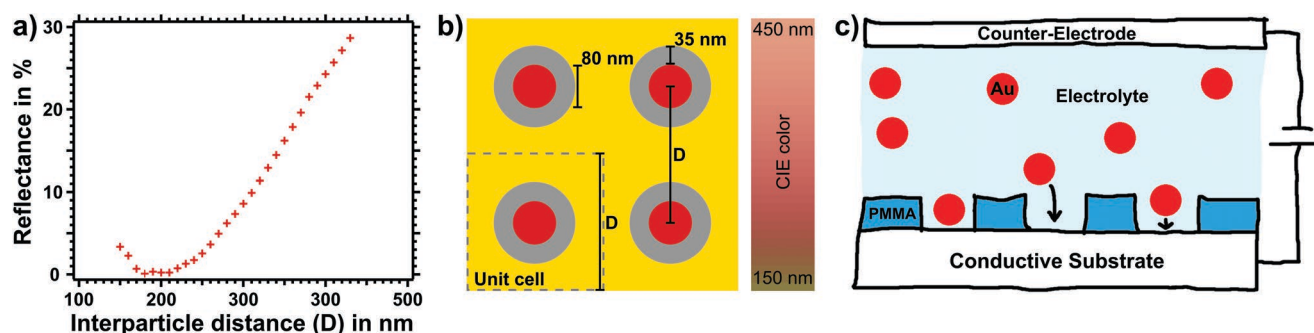


Figure 4. Optical simulations and particle assembly. a) Reflectance minima (red crosses) as a function of the particle separation, obtained from COMSOL simulations. b) Schematic of the set-up used in the optical simulations showing the interparticle distance D , the diameter of the particles (80 nm), the PANI shell thickness (35 nm), and the respective unit cell. Right: CIE color from the obtained spectra as a function of D (illuminated by standard D65 illumination). c) Schematic of the electrophoretic particle deposition (EPD) system with gold nanoparticles on a substrate that has been nanostructured with poly(methyl methacrylate) (PMMA).

of concept, we applied a positive potential to a nanostructured ITO substrate (see Supporting Information 9 for details). Due to the negative surface charge of the colloids (ξ -potential of -54 ± 7 mV), the particles were deposited in the cavities of the substrate. This resulted in assembly of Au-PANI particles in a square lattice as seen in the dark field micrograph in Figure S11, Supporting Information. For future work, utilization of nanostructured gold substrates (or other reflective surfaces) with small separation distances in the order of a few hundred nanometers will lead to significant improvements. This facile method enables the preparation of tunable metasurfaces with precise control of the interparticle separation and thereby optimization of anti-reflective properties.

We have demonstrated an active anti-reflective plasmonic metasurface. The wavelength at which anti-reflection occurs can increase by up to 30 nm as a result of an applied electric potential or a change in the pH of a surrounding solution. These spectral shifts were accompanied by an almost tenfold modulation of the reflectance of the metasurface. The observed phenomena were interpreted with the aid of finite-element simulations and a simple interference description that accounts for the interaction of the metasurface with light. These metasurfaces were constructed with a redox-sensitive polymer (PANI) which enables further studies of photo-induced charge separation in plasmonic systems: a field of study with great potential for applications in photonic energy conversion, such as photocatalysis.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

electrochromic, nanoparticles, plasmonic metasurfaces, switchable, thin-film coating

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