24

Responsive Polymer Networks and Brushes for Active Plasmonics

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24.1 Introduction

Plasmonics represents a rapidly developing research field that concerns nanoscale manipulating of light by using metallic nanostructures. Plasmonics is pursued to impact a wide range of applications including optical spectroscopy,^{1,2} optical communication technologies,^{3,4} photovoltaics,⁵ and chemical analytical technologies.⁶⁻⁹ The majority of plasmonic structures that have been developed up to now are passive, and their optical properties are fixed after they are prepared. Plasmonic structures that can be reversibly tuned are attractive materials that can advance implementation of plasmonics in areas such as miniaturized photonic circuits¹⁰ and sensors.^{11,12} Such activities lead to the establishing of a new research branch that is referred to as active plasmonics. Active plasmonics was recently subject to several reviews.^{13–15} This chapter focuses at hybrid plasmonic structures that utilize responsive polymer brushes and networks. These materials can be designed to change their refractive index, absorption, or volume in response to stimuli including temperature, pH, light intensity, or current.^{15–17} The chapter briefly introduces design rules of plasmonic structures and discusses the control of resonant coupling of light to collective charge oscillations at the metal (Section 24.2). Afterwards, Section 24.3 provides an overview of stimuli-responsive polymer architectures that can be employed for actuating plasmonic structures. Finally, the chapter presents three examples of surface plasmon actuating by responsive hydrogel gratings that were carried out at our laboratory. Sections 24.4-24.6 illustrate the preparation of hydrogel gratings by laser interference lithography, nanoimprint lithography, and contact lithography.

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24.2 Tuning Spectrum of Surface Plasmon Modes

Surface plasmons are optical waves that allow tightly confining light energy at a metallic surface. They originate from collective oscillation of electron density coupled with associated electromagnetic field. Along the surface of a metallic film, propagating surface plasmons (PSPs) can travel with the propagation constant $k_{\rm PSP}$:

$$k_{\rm PSP} = \frac{2\pi}{\lambda} \sqrt{\frac{n_m^2 n_d^2}{n_m^2 + n_d^2}},$$
(24.1)

where $k_0 = 2\pi/\lambda$ is the wavenumber of light in vacuum, n_m is complex refractive index of metal, and n_d is the refractive index of the adjacent dielectric. The coupling of a light beam to PSPs travelling on the metallic surface can be utilized by using diffraction or prism couplers. These couplers increase the momentum of a light beam in order to phase match it with PSPs at the interface. In the diffraction coupler, the metal surface is periodically corrugated (see Figure 24.1a) and the propagation constant of incident light is enhanced by the grating momentum $2\pi/\Lambda$ so it matches that of PSP:

$$\frac{2\pi}{\lambda}n_d\sin(\theta) \pm m\frac{2\pi}{\Lambda} = \pm \operatorname{Re} \{k_{\rm PSP}(\lambda)\},\tag{24.2}$$

where Λ is the period, θ is the angle of incidence, integer *m* is a diffraction order, and Re{} states for the real part of a complex number. When the condition (24.2) is fulfilled, the energy of a light beam propagating in the far field can be transferred to PSPs which typically manifests itself as a decrease in the reflectivity at resonant angle θ and wavelength λ . Another widely used means for the excitation of PSPs is based on the Kretschmann configuration of attenuated total reflection (ATR) method, which is depicted in Figure 24.1b. It shows a



Figure 24.1 Resonant excitation of PSPs by using (a) diffraction grating and (b) by the ATR method with the Kretschmann configuration.

light beam that totally internally reflects at the interface between a high refractive index (n_p) glass and a thin metal film (exhibiting refractive index n_m) with a lower refractive index (n_d) dielectric on the top. Similarly to the grating coupler, PSPs are resonantly excited and the intensity of reflected beam decreases when the following resonant condition is fulfilled at a certain angle of incidence θ and wavelength λ :

$$\frac{2\pi}{\lambda}n_p\sin(\theta) = \operatorname{Re}\{k_{\rm PSP}(\lambda)\}.$$
(24.3)

As can be seen from the phase-matching conditions (24.2) and (24.3), the resonant coupling to PSPs can be tuned by changing the propagation constant k_{PSP} , which depends on the refractive index n_d of the dielectric adjacent to the metal. Figure 24.1 illustrates that this dielectric is probed by the evanescent field of PSPs that penetrates to a distance L_p . For instance, a gold surface supports PSPs that probe the adjacent dielectric to a distance of about ~100 nm in the red part of spectrum. When changing the refractive index n_d within this depth, $\operatorname{Re}\{k_{PSP}\}\$ is altered, which leads to detuning of the resonant coupling to evanescent PSP. Figure 24.2 shows an example of the resonant coupling to PSPs that is manifested as a dip in the wavelength reflectivity spectrum. The sensitivity of the surface plasmon resonance (SPR) wavelength at which the reflectivity dip minimum occurs was investigated for both prism and grating couplers. The reflectivity spectra were simulated for a gold surface and adjacent dielectric refractive index of $n_d = 1.33, 1.345$, and 1.36. The data in Figure 24.2 reveal that a change of refractive index of $\delta n_d = 0.03$ shifts the SPR wavelength $\delta \lambda$ by about the full width of the half minimum (FWHM) of the resonance dip, which yields $\Delta \lambda = 15$ nm for the grating coupled SPR and $\Delta \lambda = 50$ for the Kretschmann



Figure 24.2 Sensitivity of surface plasmons to refractive index changes: (a) grating coupling on a sinusoidal modulated Au surface with the period $\Lambda = 440$ nm, modulation amplitude of 12.5 nm, and angle of incidence $\theta = 0^{\circ}$. (b) The coupling to surface PSPs by using a prism with $n_p = 1.845$, 50 nm thick Au layer, and angle of incidence of $\theta = 51.7^{\circ}$.

configuration. It is worth of noting that these values correspond to the figure of merit (FOM; defined as $(\delta \lambda / \Delta n_d) / \Delta \lambda$) of about 30.

An alternative option to modulate SPR offers the interaction between multiple PSP modes. This can be utilized by, for example, a dielectric grating with a period $\Lambda = \pi/\text{Re}\{k_{\text{PSP}}\}$ that diffraction couples counterpropagating PSPs. This effect relates to Bragg scattering of PSPs, and it leads to opening of a bandgap in their dispersion relation. The occurrence of the bandgap manifests itself as splitting in the SPR resonance to two branches that are associated with the excitation of ω + and ω - PSP modes. These modes exhibit standing wave nature, and the field intensity of ω - mode is confined in the grating maxima whereas that of ω + in the grating minima. The occurrence of these modes can be seen as two distinct resonances in the wavelength reflectivity spectrum as illustrated in Figure 24.3. The splitting of the resonance $\delta\lambda$ is increasing with the modulation depth of the grating as showed by series of curves (1)–(5). These data were obtained for a dielectric grating with a refractive index $n_h = 1.48$ and a dielectric with $n_d = 1.33$ on the top. They suggest that there is possible opening



(c)		<i>d</i> _{h1} (nm)	<i>d</i> _{h2} (nm)	n _h	θ(deg)	Δλ (nm)
	(1)	372	0	1.36	51.1	0
	(2)	60	25	1.48	51.4	7.4
	(3)	47	50	1.48	51.3	11.5
	(4)	37	70	1.48	51.3	17
	(5)	2	140	1.48	50.5	28

Figure 24.3 Bragg scattering of PSPs manifested as a split of SPR. (a) Assumed configuration with the refractive index of the grating of $n_h = 1.48$, $n_p = 1.845$, $n_d = 1.33$, and period of $\Lambda = 280$ nm. (b) Simulated reflectivity spectra for varied grating modulation depth d_{h1} , residual layer thickness d_{h2} , and angle of incidence θ as specified in the table (c). *Source*: Sharma et al. 2016.⁷ Reproduced with permission of Optical Society of America.



Figure 24.4 LSPs supported by (a) an individual metallic nanoparticle and (b) near-field coupling of LSPs when approaching two identical nanoparticles to close vicinity.

the bandgap that is wider than the spectral width of individual SPR $\Delta \lambda$ if the grating modulation depth d_{h1} is comparable to the penetration depth L_p .

Another type of surface plasmons can be observed on metallic nanoparticles (see Figure 24.4). These modes are referred to as localized surface plasmons (LSPs), and they allow for tighter confinement of electromagnetic field, which penetrates to a distance L_p comparable with the nanoparticle size (typically few tens of nanometers). LSPs with the dipole moment can be excited directly by an incident optical wave. This interaction manifests itself by the enhanced extinction cross-section σ_{ext} associated with increased scattering and absorption at resonant wavelength. For spherical nanoparticles with a diameter $D \ll \lambda$, the resonant wavelength can be determined analytically from Eq. (24.4). For more complex shape of nanoparticles, the spectrum of LSP modes needs to be typically simulated numerically:

$$\operatorname{Re}\{n_m\}^2 - \operatorname{Im}\{n_m\}^2 = -2n_d^2.$$
(24.4)

Similarly to PSPs, the resonant excitation of LSPs is sensitive to variations in the refractive index n_d in the vicinity to the metallic nanoparticle surface. As shown in Figure 24.5a, an order of magnitude stronger change in the refractive index of $\delta n = 0.4$ is needed in order to shift the resonance wavelength by the resonance FWHM $\Delta \lambda$. This translates to a lower FOM (of about FOM ~3) of typically used LSP-based plasmonic structures. However, localized surface plasmon resonance (LSPR) wavelength can also be efficiently modulated by the near-field coupling. As seen in Figure 24.5b, the LSPR wavelength redshifts when two identical Au nanoparticles approach to distances *d* that are shorter than the dimeter *D*. For Au nanoparticles with a diameter of D = 40 nm, the magnitude of the shift in the LSPR wavelength is similar to the resonance width when the gap reaches d = 4 nm. It is worth of mentioning that the coupling of LSP modes supported by individual nanoparticles leads to the strong confinement of light energy in the gap as indicated in Figure 24.4b.



Figure 24.5 (a) LSPR shift on a spherical Au nanoparticle of a diameter of D = 30 nm due to a change in n_d . (b) Near-field coupling between two metallic nanoparticles as a function of a distance *d* (oblate nanoparticles with radii 20 and 15 nm were assumed with electric field aligned perpendicular to the axis of symmetry).

24.3 Polymers Used for Actuating of Plasmonic Structures

Responsive polymers can be grafted to a metallic surface in order to actuate PSP and LSP modes by refractive index changes δn_d . Such systems can be designed to exploit changes in the real part of refractive index $\text{Re}\{n_d\}$ by, for example, modulating the polymer layer density. In addition, the imaginary part of the refractive index $\text{Im}\{n_d\}$ allows to strongly alter the spectrum of surface plasmon modes by, for example, the photochromic effect. Moreover, responsive polymer layers can be used as a spacer between metallic nanoparticles and their swelling and collapsing allows controlling the distance *d* between them. If the distance is comparable to the size of metallic nanoparticles, such modulation enables to strongly actuate LSP modes by the near-field coupling (see Figure 24.5b).

24.3.1 Temperature-Responsive Polymers

Poly(*N*-isopropylacrylamide) (pNIPAAm) is arguably the mostly used thermoresponsive polymer. It exhibits a lower critical solution temperature (LCST) of 32°C. pNIPAAm shows a water-swollen structure below its LCST, and above its LCST it undergoes an abrupt phase transition, which is associated with expelling of water. Highly swollen pNIPAAm-based polymer networks were investigated by the combined probing with PSPs and optical waveguide spectroscopy.^{8,9} In these works, polymer network layers with a swelling ratio (SR) above 10 and a thickness up to several micrometers were used. This material was postmodified by protein molecules in evanescent wave optical biosensors.¹⁸ As the refractive index of the pNIPAAm-based brush or networks n_d



Figure 24.6 (a) Dependence of the refractive index n_d of the pNIPAAm-based hydrogel film attached to the Au surface. (b) Structure of the polymer that can be photo-cross-linked by UV light. *Source*: Toma et al. 2013.¹⁹ Reproduced with permission of American Chemical Society.

is proportional to the density of polymer chains, it exhibits higher refractive index n_d in the collapsed state than in the swollen state. The temperaturecontrolled swelling and collapsing of the hydrogel layer in contact with water allows changing its refractive between $n_d = 1.46$ and 1.36 (see Figure 24.6). This material was employed in plasmonic amplification of fluorescence assays where the pNIPAAm-based hydrogel three-dimensional binding matrix backbone was used for modulating the excitation of long-range surface plasmons that probed the interface.¹⁹ This work utilized a Kretschmann configuration of ATR and temperature stimulus allowed for the complete switching of the plasmonically enhanced excitation. The response time of the pNIPAAm brush or hydrogel depends on its thickness as it scales with diffusion of water in and out of the structure. About millisecond time was reported for about micrometer thick pNIPAAm-based layer.¹⁹ For about 30-nm thick PNIPAAm-based brush, the response time of 150 µs was measured.²⁰

Nguyen et al. grafted pNIPAAm brushes on arrays of Au nanoparticles. They optimized the brush density and thickness in order to maximize the SPR wavelength shift $\delta\lambda$ associated with its swelling and collapsing.²¹ This work utilized a brush exhibiting the SR of about 2 and thickness up to 50 nm. Refractometric changes associated with the swelling and collapsing allowed shifting the LSPR band by $\delta\lambda = 20$ nm (the spectral width of the band was about $\Delta\lambda \sim 75$ nm). The same group employed a similar brush for surface-enhanced Raman spectroscopy (SERS).²² They used a structure that consisted of triangular Au nanoparticles prepared by nanosphere colloidal lithography with grafted pNIPAAm brushes and Au nanorods attached to the top (see Figure 24.7a). By collapsing the brush that contained the investigated analyte, the Au nanorods



Figure 24.7 (a) Schematic of thermo-responsive polymer brush system that allows tuning of near field coupling between the gold nanorods and larger gold triangular nanonoparticles. (b) Example of SERS spectra of the Nile Blue A recorded in the polymer brush swollen (I) and collapsed (II) state. *Source*: Nguyen et al. 2015.²² Reproduced with permission of American Chemical Society.

were dragged closer to Au triangular nanoparticles, which results in near-field coupling and strong field enhancement in the gap (see Figure 24.4b). This effect enables increasing the SERS signal originating from the Nile Blue analyte (see Figure 24.7b).

24.3.2 Optical Stimulus

Thermoresponsive polymers can be optically triggered by incorporating metallic nanoparticles. Upon the optical excitation of LSPs, increased temperature occurs in their vicinity due to the damping of LSPs. Such materials allow controlling LSPR, and they are pursued for thermal imaging and cancer therapy.²³

Another means for light-triggered response can be utilized by incorporating molecular switches such as azobenzene. These functional groups undergo light-induced conformational change between the cis and the trans isomerization. Exposure to UV light ($\lambda = 300-400$ nm) induces a transition to trans isomer, whereas irradiation at higher wavelengths ($\lambda > 400$ nm) triggers the inverse transition to cis isomer. These transitions are associated with a change in the distance between the para-carbon atoms from about 6 to 10 Å. This mechanical change has been exploited for the design of responsive materials.²⁴ For instance, Joshi et al. have demonstrated a photoreversible plasmonic structure with azobenzene conjugates attached to Au nanoparticles by monitoring LSPR shifts and vibrational bands by SERS (see Figure 24.8a). Conformational changes originating from the transition between cis to trans isomerization alter the thickness of a dielectric shell capping the nanoparticles, and thus they shift the LSPR peak (see Figure 24.8b). It is worth of mentioning that also other factors associated with energy transfer between the azobenzene and the gold are probably involved in the plasmonic shift.²⁵ In addition,



Figure 24.8 (a) Structure of the photoreversible conformational changes of the azobenzene-containing SAMs attached to a gold nanoprism and (b) time-dependent optical response of the monitored LSPR peaks upon constant irradiation of blue light. *Source*: Joshi et al. 2014.²⁵ Reproduced with permission of American Chemical Society.

azobenzene-based layers can be used for the modulation of near-field coupling between Au nanoparticles. The switching in isomerization allowed for changing distance between Au nanoparticles with an average size of 10 nm and shift in LSPR wavelength of 90 nm.²⁶

Shiraishi et al. reported that spiropyran moieties provide more stable photoswitchable system at room temperature than azobenzene.²⁷ This organic photochromic molecule exhibits two isomerizations (merocyanine and spirocyclic forms) that are associated with ring opening and closing upon UV–visible light exposure. The merocyanine isomer exhibits larger dipole moment. If a conjugate of spiropyran was attached to Au nanoparticles, its switching to merocyanine isomer was accompanied with reversible aggregation of the colloid and a redshift of the LSPR peak of about 50 nm.

24.3.3 Electrochemical Stimulus

Conducting polymers have been explored for actuating plasmonic response of metallic nanoparticles. Leroux et al. have reported a large blueshift of LSPR from $\lambda = 608$ to 571 nm for Au nanoparticles capped with a polyaniline (PANI) film that was switched between reduced and oxidized state.²⁸ The observed LSPR shift was associated with pronounced change in both Im{ n_d } and Re{ n_d } of the polymer.²⁹ In addition, poly(3,4-ethylenedioxythiophene) (PEDOT)-based capping layers were used for actuating LSPR.³⁰ The profound shift of the LSPR peak from $\lambda = 685$ to 877 nm was ascribed to a large change in n_d associated with oxidation and reduction of PEDOT. In a similar way, 3,4-ethylenedioxythiophene (EDOT) conjugated to polynorbornene brushes has been employed for active control of LSPR (see Figure 24.9).³¹



Figure 24.9 Extinction spectra of the EDOT conducting polymer when switched from the reduced state (dot curve) to the oxidized state (dash–dot curve) for networks with embedded Au NPs with a diameter of (a) D = 2 nm and (b) D = 7 nm. *Source*: Yavuz et al. 2009.³¹ Reproduced with permission of American Chemical Society.

24.3.4 Chemical Stimulus

Joshi et al. reported a sensing platform capable to detect glucose in physiological samples by using triangular Au nanoparticles and poly(allylamine) polymer. The protonation and deprotonation of this pH-responsive polymer causes a change of the polymer conformation inducing a shift in the LSPR peak due to associated refractive index changes.³² In addition, poly(2-vinylpyridine) polymer brushes have been employed in a multilayer structure that was sandwiched between Au nanoislands and chemically synthesized Au nanoparticles. A 50-nm blueshift was measured upon changing the pH from 5.0 to 2.0.³³ Moreover, a nanometer thick layer composed of poly(4-vinylpyridine) was deposited on Au nanoparticles. This material showed dramatic redshift of the LSPR wavelength of ~ 90 nm upon changing the pH from 2.0 to 7.0. At increased pH, the Au nanoparticles were pushed closer to each other resulting in strong near-field plasmonic coupling.³⁴

Recently, Jiang et al. have prepared Au nanorod particles capped with the PANI shell. The LSPR was actuated by changing the refractive index of the doped and undoped states of the PANI shell. The proton-doping state of the PANI polymer was controlled by using hydrochloric acid solution, which leads to the proton-doped emeraldine form with larger electrical conductivity. The reversible switching to the undoped form of PANI was achieved by neutralizing the acid with NaOH solution. As seen in Figure 24.10, this "on/off" switching from the doped to the undoped state results in a large redshift of the resonance plasmon scattering peak.³⁵



Figure 24.10 (a) Plasmonic shift and (b) switching kinetics between the doped and the undoped form of the pH responsive PANI capping a metallic nanoparticle (shell thickness of 39 nm).³⁵ *Source*: Jiang et al., 2014.³⁵ Reproduced with permission of Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

24.4 Imprinted Thermoresponsive Hydrogel Nanopillars

Among various lithography methods, nanoimprint lithography (NIL) represents an attractive technique for the preparation of nanostructures due to its high-throughput enabled by, for example, a roll-to-roll technique. The UV-NIL patterning of polymers is realized by pressing a mold against a softened or fluid polymer layer and trapping the pattern in the solid state by UV curing. This approach was used to structure the pNIPAAm-based hydrogel (see Figure 24.6b) with arrays of nanopillars. The polymer was spin-coated on top of an Au film. The pNIPAAm-based layer was dried and subsequently imprinted by using a polydimethylsiloxane (PDMS) working stamp that was soaked with ethanol. As seen in Figure 24.11a, upon the contact with a working stamp, the ethanol diffused from the PDMS working stamp and dissolved the pNIPAAm-based polymer that filled working stamp pores. Then, the surface was dried again in contact with the working stamp. Finally, the working stamp was detached and the prepared structure was UV cross-linked by irradiation dose of 10 J/cm² at wavelength $\lambda = 365$ nm.

The imprinted structure was observed by AFM *ex situ*. Figure 24.12a shows the pristine imprinted pattern of rectangular arrays of nanopillars with a period of $\Lambda = 460$ nm, height $d_{\rm hp} \sim 208$ nm, and diameter of D = 130 nm (measured at half of the maximum height). Then, the surface was brought into contact with water and the pNIPAAm structure was allowed to swell at temperature $T = 22^{\circ}$ C. Interestingly, the structure was completely erased after subsequent drying at the same temperature (see Figure 24.12b). However, when the surface was swollen again in water at $T = 22^{\circ}$ C and water evaporated at higher temperature



Figure 24.11 (a) Schematics of the imprinting procedure. (b) Optical system that was employed for the probing of swelling and collapsing of pNIPAAm-based interface by optical waveguide-enhanced diffraction.

of $T = 38^{\circ}$ C, the arrays of nanopillars were partially recovered on the surface as seen in Figure 24.12c. The erasure of the structure at $T = 22^{\circ}$ C was probably caused by the surface tension occurring upon the water evaporation on the top of the flexible hydrogel structure. However, at elevated temperature above the LCST of the polymer (see Figure 24.6a), the structure first collapsed and become a sufficiently rigid structure to withstand the subsequent water evaporation. The shape of the pillars that swelled and dried at elevated temperature (see Figure 24.12(c) changed compared to those freshly prepared, but their volume stayed approximately the same. The height of the nanopillars decreased by a factor of ~3, and they exhibit pronged shape that indicates their bending.

In order to observe temperature-induced changes in pNIPAAm nanostructures *in situ*, diffraction measurements were carried out by using the setup in Figure 24.11b. In these measurements, the intrinsically low diffraction intensity originating from highly swollen hydrogel nanopillars was amplified by the



Figure 24.12 *Ex situ* AFM observation of (a) arrays of freshly prepared pNIPAAm nanopillars in air compared to the structure that was swollen in water and dried at temperature (b) of $T = 22^{\circ}$ C below LCST and (c) of $T = 38^{\circ}$ C. *Source*: Pirani et al. 2017.³⁶ Reproduced with permission of Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.



resonantly enhanced surface plasmon and optical waveguide waves travelling along the Au surface. Their excitation enhances the electromagnetic field strength, which translates to increased diffraction efficiency. As Figure 24.13 summarizes, diffraction efficiency gradually increases with the temperature approaching LCST of pNIPAAm. It reaches its maximum at temperature of $T \sim 38^{\circ}C$, and above this value it decreases and it drops by a factor of about 6 at temperature $T = 50^{\circ}C$. The increase of the diffraction efficiency in the temperature $20-38^{\circ}C$ can be ascribed to the collapse of the polymer and formation of denser pillars. It is worth of mentioning that *in situ* measurements by AFM did not allow observing the structure. Based on a respective model, the decrease in the diffraction signal at higher temperature can be explained by the bending of nanopillars.³⁶

24.5 Thermoresponsive Hydrogel Nanogratings Fabricated by UV Laser Interference Lithography

Another means for facile structuring of polymer layers is laser interference lithography. It was employed to prepare crossed gratings by using an interference setup utilizing Llyod's mirror configuration.⁷ Photo-cross-linkable pNIPAAm-based polymer layer of thickness ~80 nm was spin coated on top of a glass substrate with 47 nm of gold film. A crossed grating with a period varying from $\Lambda = 280$ to 450 nm was recorded by double exposure to the UV interference field when the sample was rotated by 0° and 90°. The areas of the pNIPAAm-based polymer that were exposed to maximum UV interference field intensity are cross-linked, whereas those where the interference field exhibits its minimum not. Therefore, after subsequent rinsing the structure with ethanol and water, the polymer that was not exposed to UV light is washed away.



Figure 24.14 AFM images of a pNIPAAm grating with $\Lambda = 310$ nm that was dried at (a) room temperature $T = 22^{\circ}$ C and (b) at elevated temperature T > LCST. Comparison of the (c) denser grating with $\Lambda = 290$ nm and sparser grating with $\Lambda = 450$ nm observed after drying at elevated temperature. Scale bar corresponds to the length of 1 µm. *Source*: Sharma et al. 2016.⁷ Reproduced with permission of Optical Society of America.

Ex situ AFM observation of prepared gratings shows similar features as for the imprinted nanopillars (see Section 24.4). As seen in Figure 24.14a, the recorded polymer layer exhibits flat surface after washing in water and drying at room temperature. However, when the drying is performed at elevated temperature above the pNIPAAm LCST, the structure is recovered (see Figure 24.14b). In general, periodic regularity of prepared gratings that were dried at higher temperature is perturbed. This can be attributed to the process of collapsing and drying similar as discussed in Section 24.4. This effect contributed to the distortion of the periodic nanostructures when the thickness in the swollen state was comparable with the period Λ . This was confirmed when two submicrometer grating geometries with the same thickness, but a shorter period of $\Lambda = 290$ nm and a longer period $\Lambda = 450$ nm were examined where shorter (Figure 24.14c) is more perturbed than the longer period (Figure 24.14d) structure. The prepared grating structures were used for actuating of a plasmonic bandgap. The used structure resembles the geometry depicted in Figure 24.3a. The period Λ was tuned to 280 nm as was determined by a series of numerical simulations presented in Figure 24.3b. The swelling and collapsing of the hydrogel grating changes its refractive index which alters the Bragg scattering of counter-propagating PSPs. This is associated with reversible opening and closing of a plasmonic bandgap as observed by measuring angular and wavelength reflectivity at temperature $T = 22-45^{\circ}$ C. Figure 24.15 shows that



Figure 24.15 Measured reflectivity for a pNIPAAm grating with the period $\Lambda = 280$ nm and temperature (a) $T = 22^{\circ}$ C, (b) $T = 34^{\circ}$ C, (c) $T = 37^{\circ}$ C, (d) $T = 40^{\circ}$ C, and (e) $T = 45^{\circ}$ C. (f) Cross section of the reflectivity at each temperature for the indicated angle of incidence θ_{res} at which the bandgap occurs. Subsequent reflectivity curves are offset by 0.3 along the reflectivity axis. *Source*: Sharma et al. 2016.⁷ Reproduced with permission of Optical Society of America.

the resonant excitation of PSPs manifests itself as a dark band in the reflectivity spectrum, which shifts to higher angles θ when decreasing the wavelength λ . As the temperature is raised above the pNIPAAm LCST ($T > 32^{\circ}$ C), the average refractive index of the polymer structure increases and the collapse of the hydrogel leads to the occurrence of a periodic modulating on the surface. This induces splitting in the PSP dispersion relation due to the diffraction coupling of PSPs at the wavelength $\lambda \sim 800$ nm. The width of the bandgap was evaluated by plotting the cross section of SPR reflectivity as seen in Figure 24.15f. It shows that gradual collapse of the grating leads to the opening of the plasmonic bandgap and reaches its maximum of $\Delta \lambda = 12$ nm at around $T = 37^{\circ}$ C.

24.6 Electrochemically Responsive Hydrogel Microgratings Prepared by UV Photolithography

An example of the redox-responsive linear polymer is given in Figure 24.16a. Its chains are composed of thermoresponsive isopropyl acryl amide, acrylic acid conjugated with the cross-linker unit benzophenone, and vinyl-ferrocene. The copolymerization of these monomers resulted in a redox switchable system that can be cross-linked with UV light. Upon oxidation of the ferrocenes



Figure 24.16 (a) Preparing of a hydrogel grating by using contact photolithography. (b) Structure a redox-responsive polymer and (c) a microscope image of the grating structure grafted to Au surface.

to the charged ferrocenium ions, the enhanced Coulombic repulsion stabilizes the swollen state of the gel with the collapse being shifted to higher temperatures as has been shown for bulk gels with chemical control of the redox state of the ferrocene units.³⁷

The presented example concerns a thin redox-responsive hydrogel grating structure (with periodicities in the several 10- μ m range). The linear copolymer that contains all functional groups needed in the final product was spin coated onto the Au layer. Prior to the polymer deposition, the Au surface was modified with a thiol conjugated with benzophenone. Grafting of the polymer and its cross-linking was done via UV irradiation of the copolymer through a Cu grid mask with stripes generating a periodic illumination pattern on the polymer film (see Figure 24.16b). The unexposed polymer is still soluble and can easily be washed away. A light microscopic picture of such a resulting structure is shown in Figure 24.16c.

The hydrogel grating was prepared on a glass substrate with a 50-nm thick Au film. This substrate was optically matched to a glass prism in order to probe the grating with resonantly excited PSPs by using the Kretschmann configuration of ATR (see Figure 24.17). Against the Au surface with the polymer grating, a flow cell with the integrated reference electrode and counterelectrode was attached.

The angle of incidence θ of an optical wave hitting the sensor surface was tuned so PSPs were resonantly excited at the Au surface at area coated with the hydrogel. Upon a flow of phosphate-buffered saline, the potential between the Au and reference electrode was modulated in order to oxidize and reduce the ferrocene conjugate in the polymer grating. The induced variations of net charge density translate to changes in the SR and of the refractive index of the hydrogel. Since the hydrogel was prepared in a periodically patterned structure, the swelling and collapsing of the system can be observed from detuning of SPR as well as from changes in the diffraction intensity in series of reflected diffraction orders.^{23,29}

As there is shown in Figure 24.18, increasing of the potential leads to the collapse of the hydrogel which detunes the SPR and increases the zero-order reflectivity. The detuning of the SPR excitation leads to lower field strength probing the surface and accompanied decreased intensity of a diffracted light beam. This result confirms the concept of an electrically responsive gel in a grating format as a sensitive technique, complementing the classical surface plasmon spectroscopy. It can not only be used to study bioaffinity reactions³⁸ with the demonstrated advantages, for example, a reduced sensitivity to refractive index fluctuations caused by temperature or ionic strength variations³⁹; it is also very well suited to study polymeric systems per se. The fact that the periodic structure alternating between sample and reference areas in the preparation of the thin film structure offers the possibility of permanently referencing the sample signal against an internal inert standard.



Figure 24.17 Optical setup for SPR-enhanced diffraction measurement of the responsive hydrogel grating.

This "Fourier-space" approach offers additional advantages similar to holographic techniques. Although not demonstrated here explicitly, one can easily imagine to multiplex the readout scheme of this optical technique. Different grating periodicities would lead to diffraction intensities in different directions but in the same plane of incidence, easily detected by the angular discrimination of their coupling to the optical far-field. Moreover, the corresponding grating vectors do not need to be necessarily collinear: different gratings could be simply be rotated in the plane of the sample thus offering the detection of diffraction intensities propagating into different directions outside the plane of incidence. This could offer a certain "multiplexing" as it might be useful, for example, for the sensing of a variety of bioanalytes: The surface-attached ligands for various bioanalytes could be arranged in periodic structures that differ in their periodicity and/or in the direction of the grating vector. The binding events thus would lead to changes in the different diffraction intensities that can be monitored cross-talk free and completely independent from one another.

705 24.7 Conclusions



Figure 24.18 Variation of the cross-linked hydrogel grating upon potential change observed from SPR reflectivity changes (upper curve) and diffraction intensity (bottom curve).

24.7 Conclusions

Hybrid materials that comprise responsive polymer brushes and hydrogels grafted to metallic nanostructures hold particular potential in areas of sensing, optical spectroscopy, drug delivery, and therapy. These materials can be designed to provide multiple functionalities. Externally triggered change in their optical properties allows for active control of plasmonic response of the nanostructures and control of the electromagnetic field confinement. In addition, they may be postmodified with biomolecules in order to specifically respond to biological analytes. Moreover, they can protect the surface of the metallic structure from fouling in contact with complex biological fluids such as blood serum and saliva. This book chapter provides a brief introduction to plasmonic nanostructures that can be actuated by polymers responsive to wide range of stimuli including temperature, light, current, as well as specific chemicals. It discusses means of their preparation and key performance characteristics that are essential for their design in order to serve in specific application.

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References

- 1 Bauch, M.; Toma, K.; Toma, M.; Zhang, Q.; Dostalek, J. *Plasmonics* **2013**, 9 (4), 781–799.
- 2 Lee, S. J.; Guan, Z.; Xu, H.; Moskovits, M. J. Phys. Chem. C 2007, 111 (49), 17985–17988.
- **3** Ozbay, E. Science **2006**, 311 (5758), 189–193.
- 4 Engheta, N. Science 2007, 317 (5845), 1698–1702.
- 5 Hägglund, C.; Zäch, M.; Petersson, G. r.; Kasemo, B. *Appl. Phys. Lett.* **2008**, *92* (5), 053110.
- 6 Santos, G. M.; Zhao, F.; Zeng, J.; Li, M.; Shih, W. C. J. Biophoton. 2015, 8 (10), 855–863.
- 7 Sharma, N.; Petri, C.; Jonas, U.; Dostalek, J. Opt. Exp. 2016, 24 (3), 2457.
- 8 Harmon, M. E.; Jakob, T. A. M.; Knoll, W.; Frank, C. W. *Macromolecules* 2002, 35 (15), 5999-6004.
- **9** Beines, P. W.; Klosterkamp, I.; Menges, B.; Jonas, U.; Knoll, W. *Langmuir* **2007**, *23* (4), 2231–2238.
- 10 MacDonald, K. F.; Zheludev, N. I. Laser Photon. Rev. 2009, 4 (4), 562-567.
- 11 Gehan, H. I. n.; Fillaud, L.; Chehimi, M. M.; Aubard, J.; Hohenau, A.; Felidj, N.; Mangeney, C. ACS Nano 2010, 4 (11), 6491–6500.
- 12 Tokarev, I.; Minko, S. Soft Matter 2012, 8 (22), 5980.
- **13** Dong, L.; Agarwal, A. K.; Beebe, D. J.; Jiang, H. *Nature* **2006**, *442* (7102), 551–554.
- 14 Gao, W.; Vecchio, D.; Li, J.; Zhu, J.; Zhang, Q.; Fu, V.; Li, J.; Thamphiwatana, S.; Lu, D.; Zhang, L. ACS Nano 2014, 8 (3), 2900–2907.
- 15 Chen, K.; Leong, E. S. P.; Rukavina, M.; Nagao, T.; Liu, Y. J.; Zheng, Y. *Nanophotonics* 2015, 4 (1), 186–197.
- 16 Kozlovskaya, V.; Kharlampieva, E.; Khanal, B. P.; Manna, P.; Zubarev, E. R.; Tsukruk, V. V. Chem. Mater, 2008, 20 (24), 7474–7485.
- 17 Sun, Y.; Jiang, L.; Zhong, L.; Jiang, Y.; Chen, X. Nano Res. 2015, 8 (2), 406-417.
- 18 Aulasevich, A.; Roskamp, R. F.; Jonas, U.; Menges, B.; Dostalek, J.; Knoll, W. Macromol. Rapid Commun. 2009, 30, 872–877.

- 19 Toma, M.; Jonas, U.; Mateescu, A.; Knoll, W.; Dostalek, J. J. Phys. Chem. C 2013, 117 (22), 11705–11712.
- 20 Winkler, P.; Belitsch, M.; Tischler, A.; Hafele, V.; Ditlbacher, H.; Krenn, J. R.; Hohenau, A.; Nguyen, M.; Felidj, N.; Mangeney, C. *Appl. Phys. Lett.* 2015, 107 (14).
- **21** Nguyen, M.; Sun, X.; Lacaze, E.; Winkler, P. M.; Hohenau, A.; Krenn, J. R.; Bourdillon, C. l.; Lamouri, A.; Grand, J.; Levi, G.; Boubekeur-Lecaque, L. l.; Mangeney, C.; Felidj, N. *ACS Photon.* **2015**, *2* (8), 1199–1208.
- 22 Nguyen, M.; Kanaev, A.; Sun, X.; Lacaze, E.; Lau-Truong, S.; Lamouri, A.; Aubard, J.; Felidj, N.; Mangeney, C. *Langmuir* 2015, *31* (46), 12830–12837.
- 23 Rothenhaeusler, B.; Knoll, W. Appl. Phys. Lett. 1987, 51, 783-785.
- 24 Zhang, N.; Schweiss, R.; Zong, Y.; Knoll, W. *Electrochim. Acta* 2007, 52, 2869–2875.
- **25** Joshi, G. K.; Blodgett, K. N.; Muhoberac, B. B.; Johnson, M. A.; Smith, K. A.; Sardar, R. *Nano Lett.* **2014**, *14* (2), 532–540.
- 26 Sidhaye, D. S.; Kashyap, S.; Sastry, M.; Hotha, S.; Prasad, B. L. *Langmuir* 2005, 21 (17), 7979-84.
- 27 Shiraishi, Y.; Shirakawa, E.; Tanaka, K.; Sakamoto, H.; Ichikawa, S.; Hirai, T. ACS Appl. Mater. Interfaces 2014, 6 (10), 7554-62.
- 28 Leroux, Y. R.; Lacroix, J. C.; Chane-Ching, K. I.; Fave, C.; Félidj, N.; Lévi, G.; Aubard, J.; Krenn, J. R.; Hohenau, A. *J. Am. Chem. Soc.* 2005, *127* (46), 2–16023.
- 29 Rothenhäusler, B.; Knoll, W. Opt. Commun. 1987, 63, 301-304.
- **30** Stockhausen, V.; Martin, P.; Ghilane, J.; Leroux, Y.; Randriamahazaka, H.; Grand, J.; Felidj, N.; Lacroix, J. C. *J. Am. Chem. Soc.* **2010**, *132* (30), 10224–10226.
- **31** Yavuz, M. S.; Jensen, G. C.; Penaloza, D. P.; Seery, T. A.; Pendergraph, S. A.; Rusling, J. F.; Sotzing, G. A. *Langmuir* **2009**, *25* (22), 13120–13124.
- 32 Joshi, G. K.; Johnson, M. A.; Sardar, R. RSC Adv. 2014, 4 (30), 15807.
- 33 Tokareva, I.; Minko, S.; Fendler, J. H.; Hutter, E. J. Am. Chem. Soc. 2004, 126 (49), 15950–15951.
- **34** Nergiz, S. Z.; Singamaneni, S. *ACS Appl. Mater. Interfaces* **2011**, *3* (4), 945–951.
- 35 Jiang, N.; Shao, L.; Wang, J. Adv. Mater 2014, 26 (20), 3282-3289.
- 36 Pirani, F.; Sharma, N.; Moreno-Cencerrado, A.; Fossati, S.; Petri, C.; Descrovi, E.; Toca-Herrera, J. L.; Jonas, U.; Dostalek, J. *Macromol. Chem. Phys.* 2017, 218 (6), 1600400.
- 37 Saleem, M.; Yu, H.; Wang, L.; Zain-ul-Abdin; Khalid, H.; Akram, M.; Abbasi, N. M.; Huang, J. Anal. Chim. Acta 2015, 876, 9–25.
- 38 Yu, F.; Tian, S.; Yao, D.; Knoll, W. Anal. Chem. 2004, 76, 3530-3535.
- **39** Yu, F.; Yao, D.; Liu, J.; Knoll, W. Anal. Chem. **2004**, 76, 1971–1975.