METAL–SEMICONDUCTOR TRANSITIONS IN NANOSCALE VANADIUM DIOXIDE—THIN FILMS, SUBWAVELENGTH HOLES, AND NANOPARTICLES

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CHAPTER III

MODULATION OF THE GOLD PARTICLE-PLASMON RESONANCE BY THE METAL-SEMICONDUCTOR TRANSITION OF A VO_2 THIN FILM

Abstract

Reported here are experimental observations of relative blue-shifts in the particle-plasmon resonance of gold nanoparticles (Au NPs) covered with a vanadium dioxide (VO_2) film as the VO_2 material undergoes a semiconductor-to-metal transition at approximately 67 °C. Although the extinction spectra of the Au NPs exhibit significant red-shifts in the presence of the surrounding VO_2 film as compared to the same particles in air, the key result of this work is the dynamically controlled blue-shift of the Au-NP dipolar plasmon resonance upon thermal switching of the VO_2 overlayer from the semiconducting to the metallic state. We also report on the size and polarization dependence of the extinction spectra in both states, and present Mie-theory calculations that confirm in a qualitative way the observed trends in the VO_2-induced modulation of the Au-NP plasmon resonance, and their origin in the VO_2 dielectric function.

3.1 Introduction

Metal nanoparticles (NPs) exhibit characteristic absorption and scattering bands in the visible range due to electromagnetic interaction of light with oscillating surface charges, the so-called localized surface-plasmon resonance or simply the particle-plasmon.[114] The existence of surface plasmons, either localized or propagating, is peculiar to the interaction of metal nanostructures with optical radiation. Similar behavior cannot be simply reproduced by scaling because the material parameters, embodied in the dielectric function, change significantly with frequency. Therefore, model experiments, say with microwaves and correspondingly larger metal structures, cannot substitute for experiments with metal nanostructures at optical frequencies. The study of the optical response of metals on subwavelength scales—and how to control it—is now often referred to as *plasmonics* or *nanoplasmonics*.[112]

3.1.1 Localized surface-plasmon resonance (LSPR)

When optical radiation encounters a small metallic sphere, the oscillating electric field sets up a coherent oscillation of the conduction-electron charge cloud, as depicted in Figure 3.1. The displacement of the electron cloud with respect to the positively charged lattice leads to the buildup of polarization charges on the NP surface, which provide a Coulombic restoring force between electrons and nuclei, thus giving rise to specific resonances in the surface charge-density oscillations. The localized surface plasmon resonance (LSPR) is distinct from the surface-plasmon polariton (SPP), in that the former is spatially confined within a particle, while the latter propagates along an extended metal-dielectric interface. The resonant electromagnetic response of noble-metal NPs is thus a consequence of the confinement of the conduction electrons to the small particle volume.[112, 113, 115] Inside the NP, a resonantly enhanced field builds up, which in turn generates a strong near-field in the immediate vicinity of the NP surface and boosts the absorption and scattering cross-sections for electromagnetic waves.

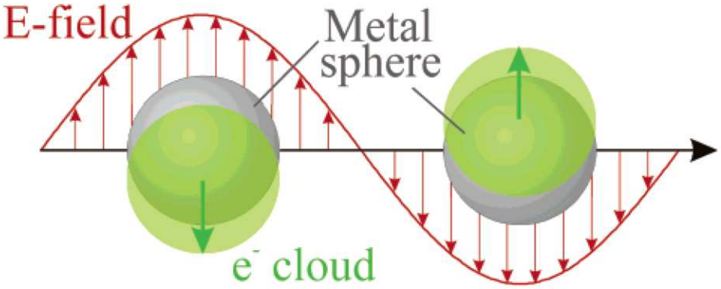

Figure 3.1: Schematic of the simplest mode of *collective* oscillation of the conduction electrons relative to the nuclei of a metal NP, the dipolar particle-plasmon. After Reference [115].

In general, the spectral position, damping, and magnitude of the plasmon resonances of individual metal NPs depend on the particle material, size, geometry, and the dielectric function of the surrounding host.[113] It is relatively straightforward to relate the lowest-order LSPR, the dipolar particle-plasmon, to the dielectric functions (permittivities) of the metal and the host medium within the framework of the so-called *quasi-static approximation*, which assumes that all points of an object respond simultaneously to the incoming light (*i.e.*, neglects retardation effects). For a small spherical NP of diameter $2a \ll \lambda$, where λ is the wavelength of the incident light in the surrounding medium, the conduction electrons inside the NP all move in phase upon plane-wave excitation, exhibiting a resonant response at a specific frequency (wavelength) where the electron motion has a phase lag of $\pi/2$ with respect to the driving field. In the small-particle limit ($2a \ll \lambda$), the field is homogeneous inside the NP and dipolar at a short distance r outside the NP surface (near-field zone: $2a \ll r \ll \lambda$), since the latter can be approximated as the electrostatic field of a point dipole of moment $\vec{\mathrm{p}}$, located at the NP center (origin) and oscillating in time with the angular frequency ω of the excitation light (hence the term *quasi*-static):[112, 116]

$$\vec{\mathrm{E}}_{\mathrm{q.s.}}(r\hat{\mathrm{n}}_r, t) = \frac{1}{4\pi\varepsilon_0}[3\hat{\mathrm{n}}_r(\hat{\mathrm{n}}_r \cdot \vec{\mathrm{p}}) - \vec{\mathrm{p}}]\frac{1}{r^3}\mathrm{e}^{\mathrm{i}\omega t} \tag{3.1}$$

where $\varepsilon_0 = 8.854 \times 10^{-12}\ \mathrm{F \cdot m^{-1}}$ is the vacuum permittivity and $\hat{\mathrm{n}}_r$ is a unit vector directed from the origin (O) to the observation point (O_1). To see how this comes about, let us place an uncharged spherical nanoparticle (radius a, relative permittivity $\varepsilon_{\mathrm{NP}}$) in a host medium (relative permittivity $\varepsilon_{\mathrm{host}}$), and apply an electric field (magnitude E_0) directed along the x-axis, $\vec{\mathrm{E}}_0 = E_0\hat{\mathrm{n}}_x$, where $\hat{\mathrm{n}}_x$ is a unit vector; refer to Figure 3.2. The task is now to find how the presence of the particle alters the applied electric field inside and immediately outside the NP. In the scalar approximation, the electric potential Φ obeys the Laplace equation of electrostatics, $\nabla^2\Phi = 0$, which in spherical coordinates becomes

$$\frac{1}{r^2 \sin\theta}\left[\sin\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin\theta}\frac{\partial^2}{\partial\varphi^2}\right]\Phi(r,\theta,\varphi) = 0 \tag{3.2}$$

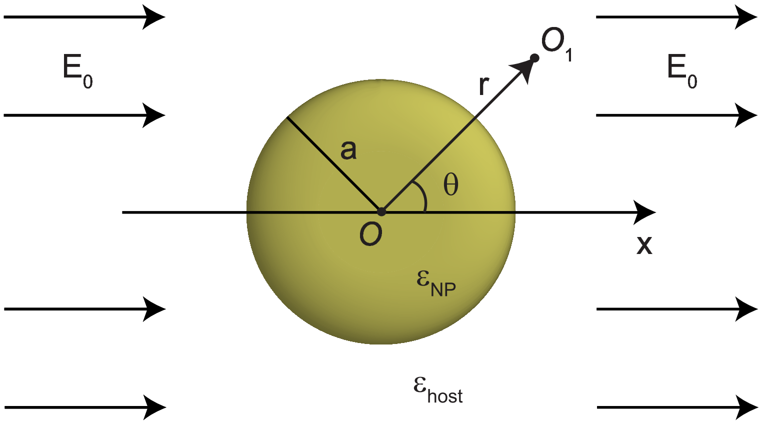

Figure 3.2: Small particle in host medium and under the applied electric field of x-polarized plane wave.

The axial symmetry of the problem suggests a solution of the type[116]

$$\textit{Inside of NP}: \qquad \Phi_{\text{in}} = \sum_{l=0}^{\infty} A_l r^l P_l(\cos\theta) \tag{3.3}$$

$$\textit{Outside of NP}: \qquad \Phi_{\text{out}} = \sum_{l=0}^{\infty} [B_l r^l + C_l r^{-(l+1)}] P_l(\cos\theta) \tag{3.4}$$

$$\begin{aligned} P_0(\cos\theta) &= 1 \\ P_1(\cos\theta) &= \cos\theta \\ P_2(\cos\theta) &= \tfrac{1}{2}(3\cos^2\theta - 1) \\ P_3(\cos\theta) &= \tfrac{1}{2}(5\cos^3\theta - 3\cos\theta) \\ P_4(\cos\theta) &= \tfrac{1}{8}(35\cos^4\theta - 30\cos^2\theta + 3) \\ &\dots \end{aligned} \tag{3.5}$$

where A_l, B_l and C_l are constant coefficients to be determined from the boundary conditions; $P_l(\cos\theta)$ is a Legendre polynomial of order l. The boundary conditions far away from the NP, where the potential must approach that of the applied field, and at the surface of the NP ($r = a$), where the "in" and "out" tangential electric fields and normal components of the electric displacements must be continuous, dictate that

$$\begin{aligned} &\textit{At infinity}: && \Phi_\infty \rightarrow \Phi_0 = -E_0 x = -E_0 r P_1(\cos\theta) = -E_0 r\cos\theta \\ &\textit{Tangential E}: && [\partial\Phi_{\text{in}}/\partial\theta]_{r=a} = [\partial\Phi_{\text{out}}/\partial\theta]_{r=a} \\ &\textit{Normal D}: && \varepsilon_{\text{NP}}\,[\partial\Phi_{\text{in}}/\partial r]_{r=a} = \varepsilon_{\text{host}}\,[\partial\Phi_{\text{out}}/\partial r]_{r=a} \end{aligned} \tag{3.6}$$

Evaluating the above boundary conditions for the series in Equations 3.3 and 3.4 yields the following solution for the potential inside (Equation 3.7) and outside (Equation 3.8) the particle:

$$\Phi_{\text{in}} = -E_0\left(\frac{3\varepsilon_{\text{host}}}{\varepsilon_{\text{NP}} + 2\varepsilon_{\text{host}}}\right) r\cos\theta \tag{3.7}$$

$$\Phi_{\text{out}} = \Phi_0 + \Phi_{\text{scatt}} = -E_0 r\cos\theta + E_0\left(\frac{\varepsilon_{\text{NP}} - \varepsilon_{\text{host}}}{\varepsilon_{\text{NP}} + 2\varepsilon_{\text{host}}}\right)\frac{a^3}{r^2}\cos\theta \tag{3.8}$$

The potential outside consists of the potentials of the incident (Φ_0) and scattered (Φ_{scatt}) fields; there is no φ-dependence owing to the azimuthal symmetry. The electric field can be calculated by taking the gradient of the potential, $\vec{\mathrm{E}} = -\nabla\Phi$, and the resulting expressions for the electric field inside (Equation 3.9) and outside (Equation 3.10) the particle are

$$\vec{\mathrm{E}}_{\text{in}} = E_0\left(\frac{3\varepsilon_{\text{host}}}{\varepsilon_{\text{NP}} + 2\varepsilon_{\text{host}}}\right)(\cos\theta\hat{\mathrm{n}}_r - \sin\theta\hat{\mathrm{n}}_\theta) = E_0\left(\frac{3\varepsilon_{\text{host}}}{\varepsilon_{\text{NP}} + 2\varepsilon_{\text{host}}}\right)\hat{\mathrm{n}}_x \tag{3.9}$$

$$\vec{\mathrm{E}}_{\text{out}} = E_0(\cos\theta\hat{\mathrm{n}}_r - \sin\theta\hat{\mathrm{n}}_\theta) + E_0\left(\frac{\varepsilon_{\text{NP}} - \varepsilon_{\text{host}}}{\varepsilon_{\text{NP}} + 2\varepsilon_{\text{host}}}\right)\frac{a^3}{r^3}(2\cos\theta\hat{\mathrm{n}}_r + \sin\theta\hat{\mathrm{n}}_\theta) \tag{3.10}$$

where the second equality for $\vec{\mathrm{E}}_{\text{in}}$ makes use of the relation between unit vectors in the spherical ($\hat{\mathrm{n}}_r$ and $\hat{\mathrm{n}}_\theta$) and Cartesian ($\hat{\mathrm{n}}_x$) bases:

$$\hat{\mathrm{n}}_x = \cos\theta\hat{\mathrm{n}}_r - \sin\theta\hat{\mathrm{n}}_\theta \tag{3.11}$$

As stated earlier, the field inside the NP is homogeneous (Equation 3.9), while the field outside consists of the incident field (first term in Equation 3.10), $E_0(\cos\theta\hat{\mathrm{n}}_r - \sin\theta\hat{\mathrm{n}}_\theta) = E_0\hat{\mathrm{n}}_x$, and the scattered near-field (second term in Equation 3.10). To show that the latter is indeed identical to the electrostatic field of an electric dipole $\vec{\mathrm{p}}$ along the x-axis, $\vec{\mathrm{p}} = |\vec{\mathrm{p}}|\,\hat{\mathrm{n}}_x = p(\cos\theta\hat{\mathrm{n}}_r - \sin\theta\hat{\mathrm{n}}_\theta)$, we expand the expression in the square brackets of Equation 3.1:

$$[3\hat{\mathrm{n}}_r(\hat{\mathrm{n}}_r \cdot \vec{\mathrm{p}}) - \vec{\mathrm{p}}] = p(2\cos\theta\hat{\mathrm{n}}_r + \sin\theta\hat{\mathrm{n}}_\theta) \tag{3.12}$$

Now, comparing Equations 3.1, 3.12 and 3.10 (second term), and expressing the dipole induced by the incident electric field as $p = \varepsilon_{\mathrm{host}}\alpha(\omega)E_0$, we finally relate the dipolar particle-plasmon resonance to the dielectric properties of the two materials involved. The link is the frequency-dependent polarizability of the induced dipole:

$$\alpha(\omega) = 4\pi\varepsilon_0 a^3 \left(\frac{\varepsilon_{\mathrm{NP}}(\omega) - \varepsilon_{\mathrm{host}}}{\varepsilon_{\mathrm{NP}}(\omega) + 2\varepsilon_{\mathrm{host}}}\right) \tag{3.13}$$

The response of the dipole becomes resonant at the oscillation frequency (ω_{res}) of the incident field where the denominator in Equation 3.13 has a minimum, limited by the imaginary part of $\varepsilon_{\mathrm{NP}}$ describing Ohmic heating losses within the particle,[113] *i.e.*:

$$\Re\mathrm{e}\left[\frac{\varepsilon_{\mathrm{NP}}(\omega_{\mathrm{res}})}{\varepsilon_{\mathrm{host}}}\right] = -2 \tag{3.14}$$

In a medium with a real-valued $\varepsilon_{\mathrm{host}}$, the cross-section ($\sigma$) and efficiency ($Q$) for scattering, absorption and extinction of the incident radiation by the particle is obtained from the polarizability (Equation 3.13) as follows:[112]

$$Q_{\mathrm{scatt}} \equiv \frac{\sigma_{\mathrm{scatt}}}{\pi a^2} = \frac{k^4}{6(\pi a\varepsilon_0)^2}\,|\alpha(\omega)|^2 \tag{3.15}$$

$$Q_{\mathrm{abs}} \equiv \frac{\sigma_{\mathrm{abs}}}{\pi a^2} = \frac{k}{\pi a^2\varepsilon_0}\Im\mathrm{m}\,[\alpha(\omega)] \tag{3.16}$$

$$Q_{\mathrm{ext}} = Q_{\mathrm{scatt}} + Q_{\mathrm{abs}} \tag{3.17}$$

where $k = 2\pi\sqrt{\varepsilon_{\mathrm{host}}}/\lambda$ is the magnitude of the incident wavevector in the host medium. The above quantities constitute the spectral response of the NP to the incident radiation, and their maxima result from the resonant condition in Equation 3.14, within the framework of the quasi-static approximation.

The polarizability in Equation 3.13 adequately describes only the near-fields and cross-sections, which nevertheless dominate the optical response of small particles when $2a \ll r \ll \lambda$. For larger particles, however, the dipolar resonance shifts to longer wavelengths (lower frequencies) and the plasmon peak broadens substantially.[113,115] The red-shift stems from retardation effects due to the finite ratio of NP size to wavelength—the conduction electrons no longer all move in phase, which reduces the depolarization field generated at the NP center by the surrounding polarized matter. Moreover, the radiative losses that were neglected in the quasi-static treatment begin to contribute to the plasmon damping (peak broadening), dominating the total damping for larger-than-100-nm Au and Ag NPs.[113] In fact, both the retardation and depolarization effects become equally important for NP sizes comparable to $\lambda/2\pi$, whereas the quasi-static treatment contains no dependence of the LSPR on NP size.[115]

Corrections can be made to the quasi-static approximation, in particular to the polarizability in Equation 3.13, that account not only for radiation damping and retardation, but also for higher-order plasmon resonances (*e.g.*, electric quadrupole oscillations where half of the electron cloud moves parallel and the other half antiparallel to the applied field[115]), as well as for particle shapes other than spherical (by including geometrical depolarization factors[113,115]). Such corrections form the basis of the so-called modified long-wavelength approximation (MLWA).[115,117] On the other hand, Maxwell's equations can be solved exactly in the case of a spherical particle of arbitrary size, as Gustav Mie[118] did in 1908, and in Section 3.3.1 we use a modified version[119] of what is now known as *Mie theory*[120] to validate the predictions of the quasi-static approximation for the shift of the Au-NP plasmon resonance with the change in $\varepsilon_{\text{host}}$ across the VO_2 phase transition.

3.1.2 Vanadium-dioxide–metal nanocomposites

As pointed out by Cortie *et al.*,[121] an important current issue in plasmonics is the possibility of a "self-regulating" LSPR of composite metallic NPs; for instance, under a sufficiently intense light irradiation, the dynamic functionality of such NPs could be used as a probe in photothermal therapy or optical sensing applications.[122,123] Vanadium-dioxide–gold (VO_2–Au) composite material is a practical candidate for enabling the modulation of plasmonic behavior, as was shown in the case of extraordinary optical transmission through subwavelength hole arrays.[124,125] VO_2 is a transition-metal oxide that exhibits a semiconductor-to-metal phase transition upon heating through a bulk critical temperature $T_c \approx 67$ °C, and the reverse transition upon cooling. The transition is accompanied by changes in the crystalline structure, large transmission contrast in the (near-)infrared range, and hysteresis. VO_2 possesses its own plasmonic resonance, albeit heavily damped, around 1.1 μm,[54,126] while Au NPs are known to have a relatively strong extinction cross-section at visible or near-infrared wavelengths.[127]

There are two recent experimental studies on metal NPs in a VO_2 matrix. In one case, Xu *et al.*[128] sputtered silver (Ag) on top of a VO_2 thin film; the resulting Ag NPs had a rather broad size distribution of particle diameters ($|\Delta(2r)| = 15$–55 nm), which generally manifests itself as a broadening of the LSPR peaks.[129] Such inhomogeneous broadening of the resonance peak was also observed by Maaza *et al.*[130] in a VO_2–Au nanocomposite made by pulsed-laser deposition (PLD), again due to the broad size distribution of the embedded Au NPs. Moreover, closely-spaced NPs—typically found in self-assembled or PLD-grown nanoparticulate films—can give rise to particle-particle interactions, and thus cause significant peak shifts[131] in addition to those due to the change in the dielectric environment.

In this report, based on our publication in Reference [132], we systematically explore the modulation of the LSPR in lithographically fabricated arrays of Au NPs by means of the reversible metal-semiconductor transition of VO_2. In particular, we demonstrate the dependence of this modulation on nanoparticle size, shape, and light polarization. The Au LSPR peaks blue-shift in the metallic state of VO_2 ($T > T_c$) with respect to the semiconducting state ($T < T_c$) by as much as 80 nm for symmetric and 200 nm for asymmetric Au NPs (including polarization effects for the latter). The relative blue-shift is qualitatively predicted by a Mie calculation, modified to take into account the imaginary part of the complex permittivity of the VO_2 medium. For the asymmetric Au NPs, we observe a strong dependence of the plasmon resonance on polarization of the incident light with respect to the major (long) and minor (short) NP axes, complemented by subtler peak shifts with varying aspect ratios at a fixed polarization.

3.2 Experimental details

Using focused-ion-beam (FIB: 30-keV Ga^+) lithography[53,133] in a layer of poly(methylmethacrylate) (PMMA: 50-nm thickness), followed by thermal evaporation of gold (Au: 15-nm thickness) and chemical lift-off, we patterned arrays of Au NPs of various sizes and shapes, ranging from elliptical cylinders (2:1 aspect ratio in the plane parallel to the substrate) to circular cylinders. In order to prevent over-exposure of the PMMA, which would have resulted in cross-linking and enhanced resistance to chemical processing,[134] the dwell time was reduced to approximately 30 μs per FIB pixel. The substrate was a glass slide coated with a transparent layer of indium-tin oxide (ITO) to reduce charging during FIB exposure.

Scanning-electron micrographs (SEMs) of typical arrays, before deposition of the vanadium-oxide overlayer, are shown in Figure 3.3a and 3.3b. Pulsed-laser deposition (PLD) and subsequent thermal oxidation were performed to make a 50-nm VO_2 layer atop the Au-NP arrays: First, the beam from a KrF excimer laser ($\lambda = 248$ nm) was focused onto a vanadium-metal target at a fluence of about 4 $J \cdot cm^{-2}$ to deposit a sub-stoichiometric vanadium oxide ($VO_{1.7}$), then the sample was annealed at 450 °C under 250 mtorr of oxygen gas for 40 minutes, in order to convert the amorphous film into stoichiometric, crystalline VO_2.

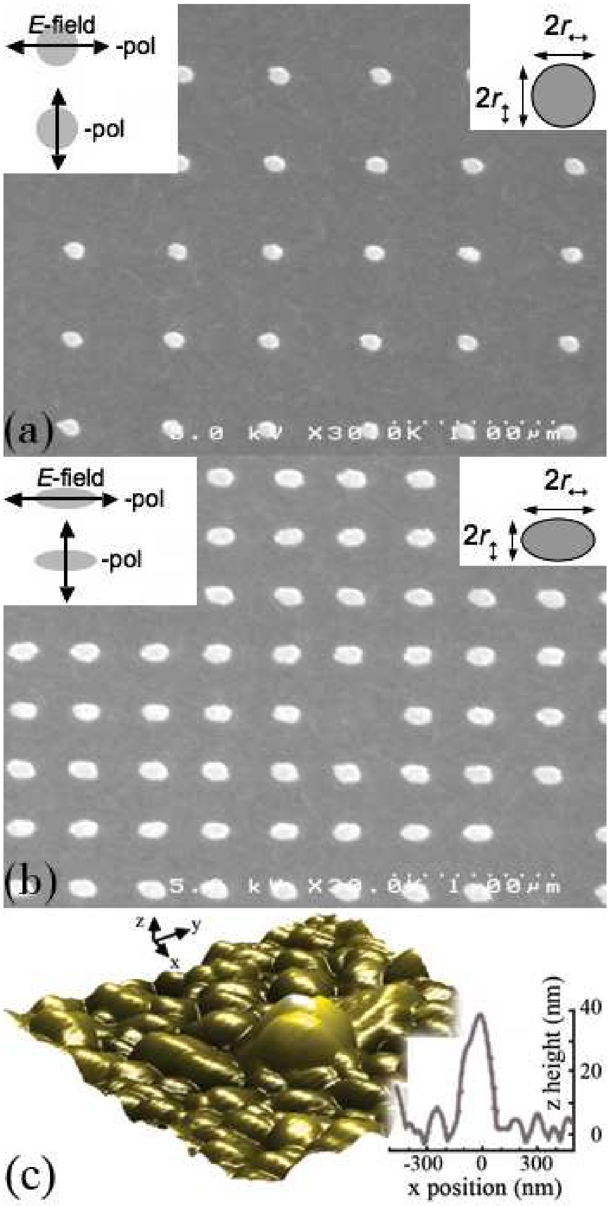

Figure 3.3: SEMs of **(a)** circular and **(b)** elliptical Au NPs on ITO-coated glass. **(c)** Atomic-force micrograph (AFM) and **(inset)** line scan of single Au NP covered with crystalline grains of PLD-grown VO_2 film. The schematic insets in **(a)** and **(b)** show the conventions used throughout the text for incident-light polarization (left) and Au-NP geometry (right).

This procedure has been demonstrated by multiple tests of stoichiometry, structure and switching properties to produce VO_2 rather than any of the multiple competing vanadium oxides.[45] Figure 3.3c shows an atomic-force micrograph (AFM) of one Au NP covered with the annealed VO_2 film. The VO_2 phase transition was confirmed by measuring the thermal hysteresis for infrared transmission ($\lambda = 1330$ nm). The sample was heated and cooled during the transmission measurement using a thermoelectric element, which was mounted on a translation-rotation stage equipped with a precision thermocouple. Optical transmission spectra of the different Au-NP arrays were acquired using linearly polarized white light at normal incidence to the sample surface. The incident-beam spot and array locations were monitored by dark-field scattering. The transmitted light was fiber-fed to a spectrometer with a cooled charge-coupled-device (CCD) detector, and normalized to transmission through the bare VO_2 film (*i.e.*, an area with no Au NPs). The resulting transmittance spectra were noise-filtered and converted to extinction spectra of the Au NPs. The optical setup is sketched in Figure 3.4.

3.3 Results and discussion

3.3.1 Qualitative predictions of environment-induced LSPR shift

The strong electric-field localization near a metal NP ensures that particle size and shape,[115, 135, 136] inter-particle spacing,[131, 137] and dielectric environment[138, 139] all have substantial effects on the extinction spectra. Therefore, the controlled geometrical parameters of lithographically fabricated NPs offer several distinct ways of modulating the particle-plasmon resonance, some of which are demonstrated below for the VO_2–Au nanocomposite.

The spectral shifts of the LSPR can be understood qualitatively within the framework of the quasi-static approximation for spherical particles. The polarizability α of a small ($r \ll \lambda$) metal sphere (here, Au NP) immersed in a host medium (here, VO_2 film) can be obtained by solving the Laplace equation;[112, 115] in the simplest case of only dipolar

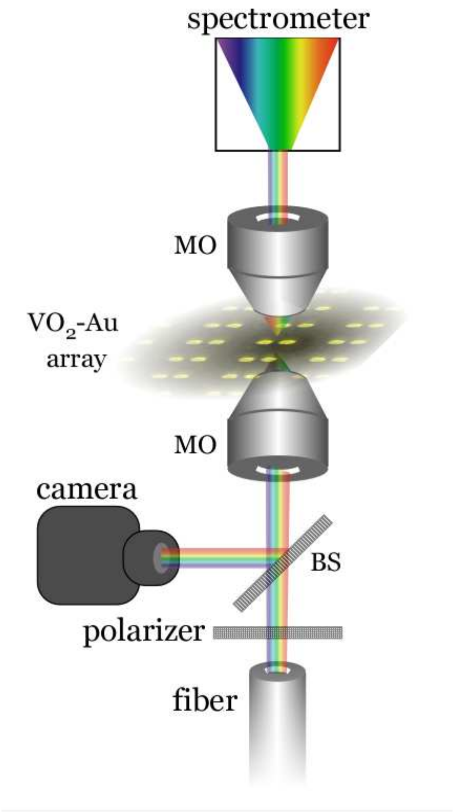

Figure 3.4: Schematic of the optical setup. *Legend*: MO ≡ micro-objective; BS ≡ beam-splitter.

excitations, α incorporates the complex-valued, wavelength-dependent permittivities $\tilde{\varepsilon}$ of the two materials as follows:

$$\alpha\,\{\text{Au sphere in VO}_2\} \propto \frac{\tilde{\varepsilon}_{\text{Au}}(\lambda) - \tilde{\varepsilon}_{\text{VO}_2}(\lambda)}{\tilde{\varepsilon}_{\text{Au}}(\lambda) + 2\tilde{\varepsilon}_{\text{VO}_2}(\lambda)} \tag{3.18}$$

The dipolar resonance condition for the Au particle requires that the real part of the denominator in Equation 3.18 vanish, *i.e.*:

$$\Re\text{e}\left[\tilde{\varepsilon}_{\text{Au}}/\tilde{\varepsilon}_{\text{VO}_2}\right] = -2 \tag{3.19}$$

Consequently, the LSPR peak occurs in the near-infrared region of the spectrum because there the real part of the Au permittivity (Figure 3.5b) becomes negative enough to cancel

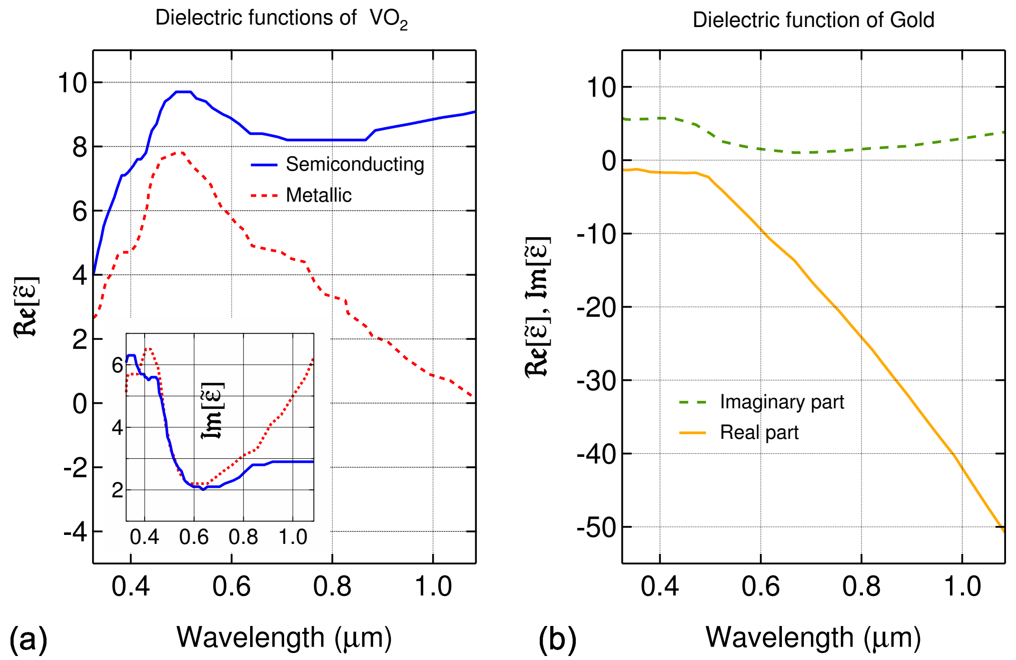

Figure 3.5: Real and imaginary parts of relative permittivities (dielectric functions) in the visible to near-infrared region for **(a)** VO_2 (data extracted from Reference [57]) and **(b)** Au (data extracted from Reference [140]).

its VO_2 counterpart in the oxide's semiconducting state, which varies between 8 and 10 at visible to near-infrared wavelengths (Figure 3.5a). In the metallic state of VO_2, however, the real part of the permittivity is considerably lower than that in the semiconducting state, which necessitates a less negative Au permittivity to satisfy the dipole resonance condition (Equation 3.19); hence, the LSPR peak should appear at shorter wavelengths when the surrounding VO_2 has switched into its metallic state. That is, the peak will be blue-shifted with respect to the semiconducting state.

Figure 3.6 shows the extinction efficiencies calculated by Mie theory for spherical Au NPs of different radii embedded in VO_2. The standard Mie formalism was amended as proposed in Reference [119], in order to account for fact that absorption in the host medium (VO_2) results in different incident intensity at different locations on the NP surface. The permittivities of VO_2 (Figure 3.5a) and Au (Figure 3.5b) were obtained from References [57] and [140], respectively; the effect of temperature on the Au permittivity is negligi-

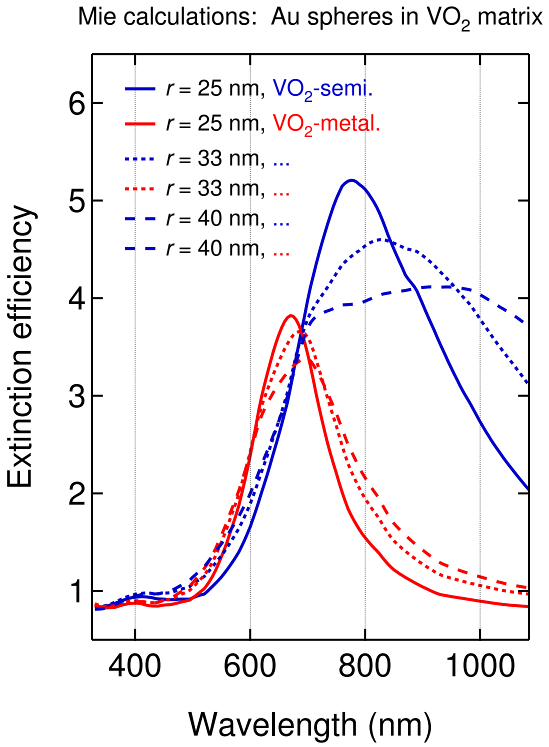

Figure 3.6: Mie calculations of extinction efficiencies for Au spheres (radii $r = 25, 33, 40$ nm) in VO$_2$ as a function of wavelength and state (semiconducting or metallic) of VO$_2$ host. Blue lines refer to the semiconducting phase, red lines to the metallic state of VO$_2$.

ble.[141] Although these Mie calculations lend support to the predictions of the quasi-static approximation for the spectral shifts of the Au LSPR, they cannot be compared directly to the experimental peak positions because of the different particle shape (*i.e.*, discs rather than spheres) and the presence of the ITO-coated glass substrate in our experiments. Crucially, however, Mie theory confirms qualitatively the observed blue-shift of the Au particle-plasmon resonance upon switching of the VO$_2$ matrix from semiconducting to metallic, as evidenced by the experimental spectra below (Figures 3.7 and 3.8).

3.3.2 Extinction spectra of symmetric Au NPs

Figure 3.7 shows extinction spectra of arrays of symmetric Au NPs of three different sizes, with inter-particle spacings of 600 nm. We first note that the Au-NP extinction peaks at room temperature (20 °C) are significantly red-shifted with respect to those taken in the absence of the VO_2 overlayer (not shown). At a high enough temperature (95 °C)—so that the VO_2 layer has already transformed into its metallic state—the spectra move by more than 60 nm towards shorter wavelengths for either polarization direction. Comparing the peak shifts in Figure 3.7a and 3.7b, we observe that the LSPRs move further to the blue with decreasing particle size, as confirmed by Mie theory. Since these Au NPs are nearly symmetrical around an axis normal to the surface, the spectra in the two polarization directions are almost identical; slight differences between the two polarizations are likely due to a small, systematic asymmetry in the particle shapes originating from stigmation misalignment of the FIB. This asymmetry is somewhat evident in the planar-view SEM in Figure 3.3a, which shows an array of nearly circular NPs slightly skewed in a common, arbitrary direction.

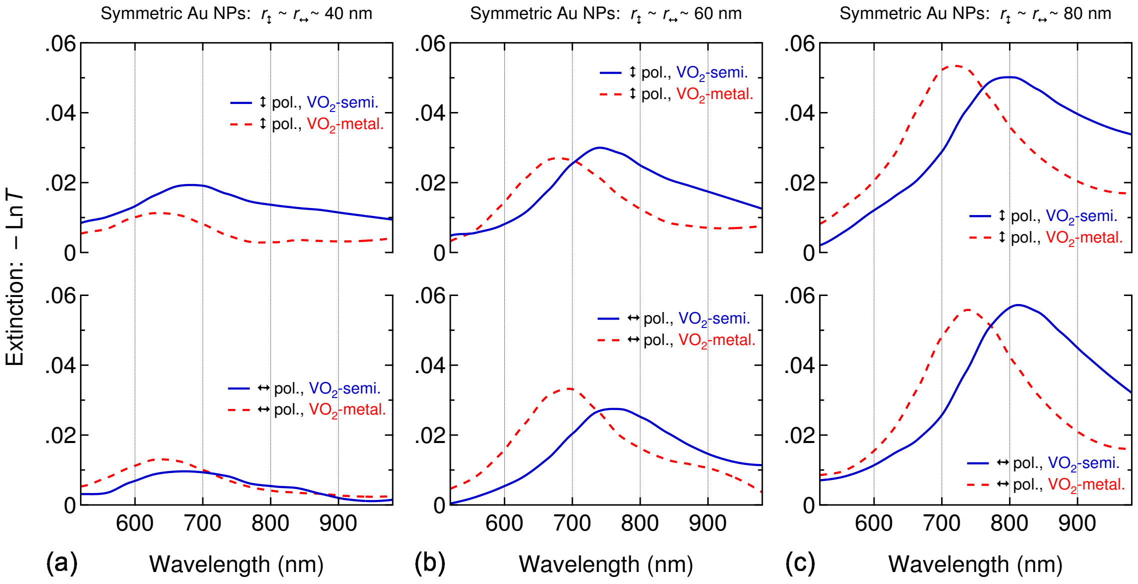

Figure 3.7: Extinction spectra as a function of wavelength, incident-light polarization, and state of the VO_2 overlayer for arrays of circular (*i.e.*, symmetric) Au NPs of three different diameters ($2r$): **(a)** 80 nm, **(b)** 120 nm, **(c)** 160 nm. *Transmittance*: $T = \mathit{Intensity}\{VO_2 + \text{Au NPs} + \text{substrate}\} \;/\; \mathit{Intensity}\{VO_2 + \text{substrate}\}$.

3.3.3 Extinction spectra of asymmetric Au NPs

The extinction spectra for three arrays of intentionally asymmetric Au NPs, covered with the same VO_2 layer, are shown in Figure 3.8. Besides LSPR shifts induced by the VO_2 phase transition and similar to those seen for the symmetric NPs, a strong dependence on polarization is also observable in the asymmetric case. When the electric field of the incident light lies parallel to the long axes of the NPs (↔-polarization), the transition-induced blue-shift of the LSPR peaks is more pronounced than when the electric field is parallel to the particles' short axes (↕-polarization). These asymmetric NPs give differences of more than 30 nm in the maximum resonant wavelength for the different polarizations, while there is hardly any shift between the two polarizations for the symmetric NPs. Thus, when compared to the LSPR position for a symmetric Au NP of $r = 60$ nm (Figure 3.7b), the resonance peaks of an asymmetric particle of $r_{\leftrightarrow} = 70$ nm and $r_{\updownarrow} = 50$ nm (Figure 3.8b) exhibit a red-shift for ↔-polarization but a blue-shift for ↕-polarization, in either state of the VO_2 overlayer.

3.3.4 Resonance shifts

Figure 3.9a summarizes our data on the shifts of the LSPR extinction peak for the symmetric Au NPs. The linear fits to the data for the semiconducting and metallic phases of VO_2 yield slightly different slopes. This divergence in resonant wavelengths stems from the permittivity difference between the two phases of the VO_2 film, which monotonically increases towards longer wavelengths (Figure 3.5a) where larger Au NPs have their resonances. For the largest of our symmetric NPs ($2r = 160$ nm), the transition-induced blue-shift of the resonant wavelength is about 80 nm (Figure 3.9a). On the other hand, our most asymmetric Au NPs ($r_{\leftrightarrow} \ / \ r_{\updownarrow} = 1.80$) can yield blue-shifts as large as 200 nm (Figure 3.9b) under the combined effects of the VO_2 phase transition and the direction of the incident electric-field vector. The red-shift in resonant wavelength with increasing aspect ratio for ↔-polarized light (see the positive-slope lines in Figure 3.9b) is brought

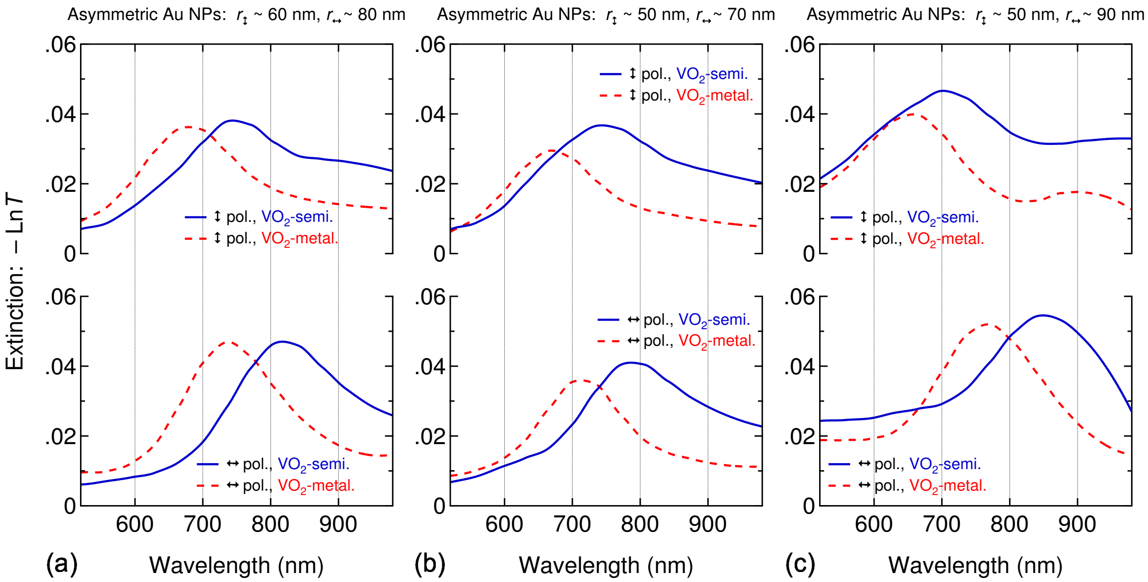

Figure 3.8: Extinction spectra as a function of wavelength, incident-light polarization, and state of theVO_2 overlayer for arrays of elliptical (*i.e.*, asymmetric) Au NPs of three different aspect ratios ($r_{\leftrightarrow}$ / $r_{\updownarrow}$): **(a)** 80 nm / 60 nm = 1.33 and **(b)** 70 nm / 50 nm = 1.40, **(c)** 90 nm / 50 nm = 1.80. *Transmittance*: T = *Intensity*{VO_2 + Au NPs + substrate} / *Intensity*{VO_2 + substrate}.

about by depolarization of the radiation across the particle surface due to the finite ratio of particle size to wavelength, as can be shown by applying electrodynamic corrections to the quasi-static treatment,[115,117] as in the modified long-wavelength approximation (MLWA) mentioned earlier (Section 3.1.1). Conversely, when the incident electric field oscillates along the short NP axes (↕-polarization), the resonance peaks blue-shift with increasing aspect ratio (see the negative-slope lines in Figure 3.9b), and the MLWA treatment also reproduces this trend.[115,117]

3.4 Summary and outlook

We have demonstrated a method to modulate the spectral features of the localized surface-plasmon resonance of Au nanoparticles by means of the metal-semiconductor transition of VO_2, by dynamically and reversibly changing the dielectric properties of the material

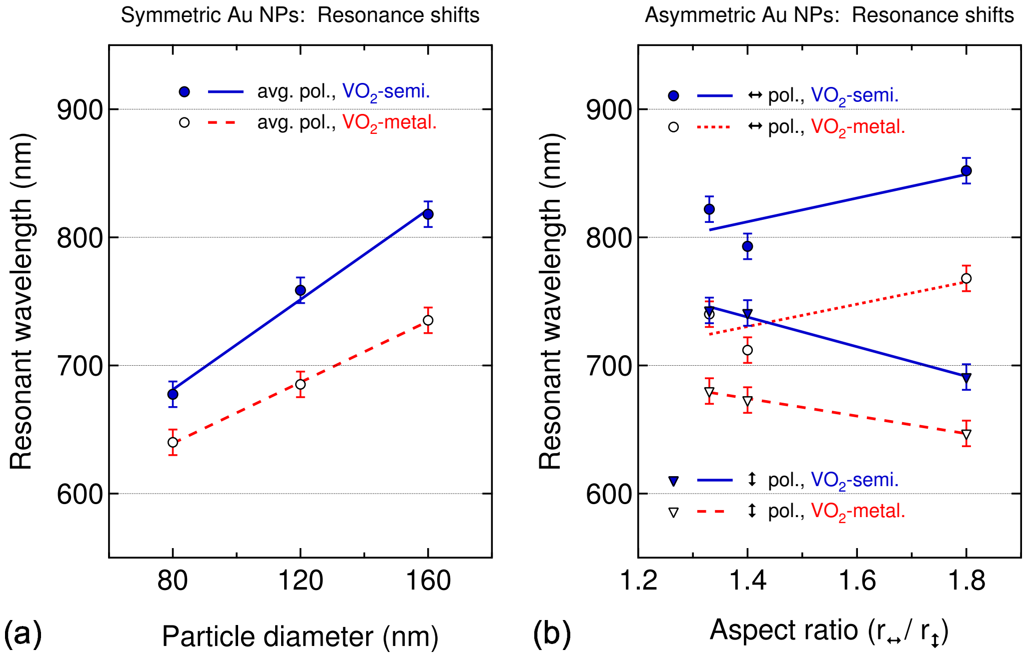

Figure 3.9: (a) Peak resonant wavelengths (from Figure 3.7), averaged over both incident-light polarizations, as a function of particle size ($2r$ = 80, 120, 160 nm) and state of the VO_2 overlayer for the circular (*i.e.*, symmetric) Au NPs. **(b)** Peak resonant wavelengths (from Figure 3.8) as a function of particle aspect ratio ($r_{\leftrightarrow}$ / $r_{\updownarrow}$ = 80 nm / 60 nm, 70 nm / 50 nm, 90 nm / 50nm), incident-light polarization, and VO_2 state for the elliptical (*i.e.*, asymmetric) Au NPs.

that covers the Au NPs. The modulation can be thermally controlled, as here, or initiated by a laser pulse on an ultrafast timescale.[54] As predicted by electromagnetic theory, the extinction spectra of the Au NPs exhibit a marked dependence on particle size and shape, incident-light polarization, and, of course, on the dielectric environment—semiconducting or metallic VO_2. The spectral shift of the Au LSPR across the VO_2 phase transition is caused by the different dielectric properties of VO_2 in each state: The transition-induced change in the VO_2 permittivity determines the spectral shift of the LSPR wavelength for the VO_2–Au nanocomposite. Invariably, a relative blue-shift of the LSPR peak follows the switching of the VO_2 host from semiconducting to metallic.

We speculate that an improved sample structure, one better suited to quantitative comparisons with Mie-theory calculations, would be an array of metal NPs fully embedded in a VO_2 matrix: for example, a “sandwich” of two 100-nm-thick VO_2 films with Au NPs in between. Another possible extension of the work presented here may involve laser switching, that is, using high-powered laser pulses to launch the LSPR of metal NPs and the metal-semiconductor transition of VO_2 simultaneously. In any case, the VO_2 phase transition emerges as a promising mechanism for dynamically controlling the plasmonic behavior of metal nanoparticles.

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