# Modulation of the Gold Particle-Plasmon by the Metal-Semiconductor Transition of Vanadium Dioxide

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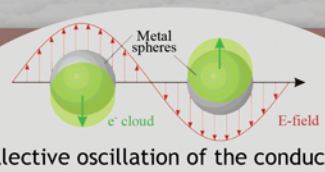


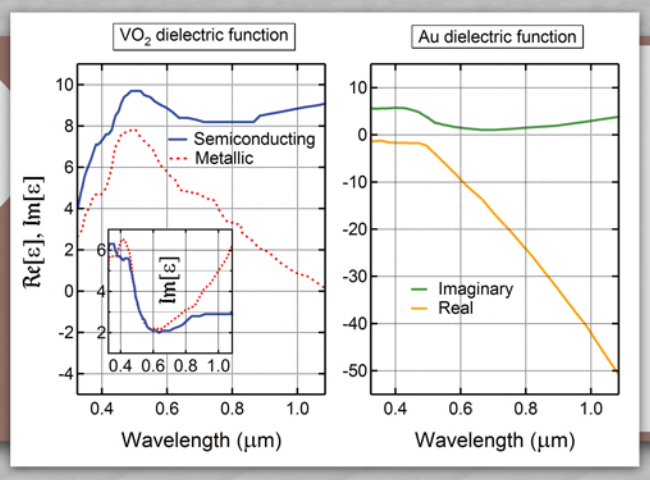

Collective oscillation of the conduction-electron cloud relative to the nuclei of a metal sphere → **"dipole particle plasmon"**

Dipole polarizability:

$$\alpha^{\text{Au sphere}}_{\text{in VO}_2} \sim \frac{\tilde{\varepsilon}_{Au}(\lambda) - \tilde{\varepsilon}_{VO_2}(\lambda)}{\tilde{\varepsilon}_{Au}(\lambda) + 2\tilde{\varepsilon}_{VO_2}(\lambda)}$$

Dipole plasmon resonance:

$$\text{Re}\left(\tilde{\varepsilon}_{Au}/\tilde{\varepsilon}_{VO_2}\right) = -2$$

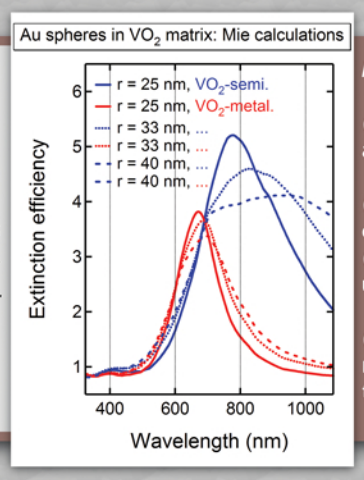



**Quasi-static Approximation:**
**($r << \lambda$, electrostatics + $e^{i\omega t}$)**

(1) Real part of $\varepsilon$-$VO_2$ is smaller in metallic than in semiconducting phase.

(2) Real part of $\varepsilon$-Au increases (less negative) as wavelength decreases.

From (1), (2), and the condition for dipole plasmon resonance → Au nanoparticle peak in metallic $VO_2$ should **blue-shift** with respect to the peak in semiconducting $VO_2$.

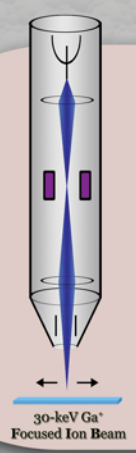


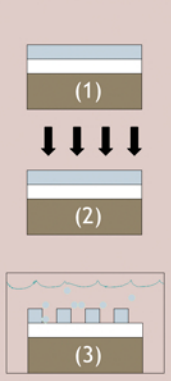

**Mie Theory:**

(1) Exact solution to Maxwell's equations for a spherical particle of arbitrary size;

(2) Assumes Au spheres (experiment: closer to disks), homogeneously immersed in $VO_2$ medium (experiment: glass substrate, indium-tin-oxide underlayer, $VO_2$ overlayer);

(3) Confirms **blue-shift** of Au particle-plasmon resonance in metallic $VO_2$, as predicted by the quasi-static approximation.




**Focused Ion Beam (FIB) Lithography:**

(1) **Spin-coat** photoresist: 50-nm PMMA on indium-tin-oxide on glass (ITO prevents charging).

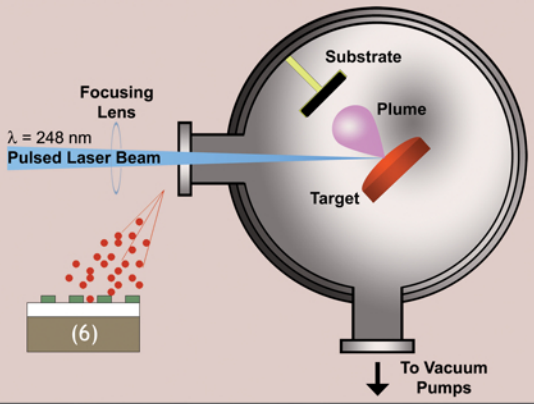
(2) **Pattern** resist with FIB: 30 μs per partcle.

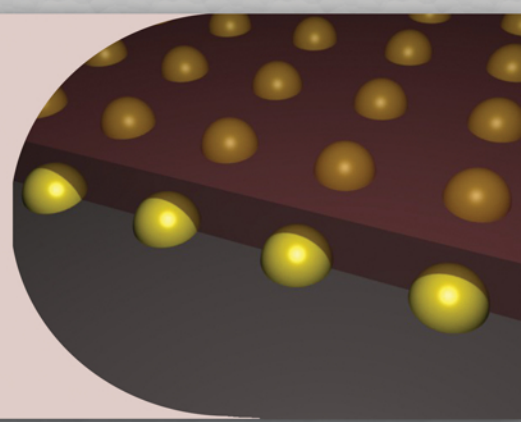
(3) Chemically **develop** patterned resist.

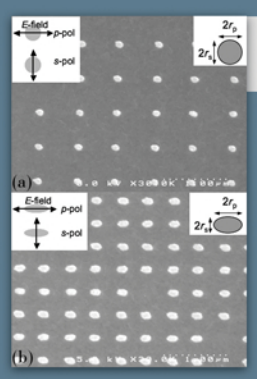
(4) **Deposit** Au film: 15 nm by thermal evaporation.

(5) Chemically **lift off** remaining resist and excess Au.

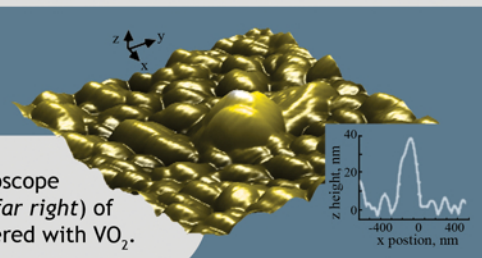
(6) **Deposit** $VO_2$ film: 50-nm amorphous $VO_{1.7}$ by pulsed-laser deposition (PLD), followed by high-temperature **anneal** in $O_2$.

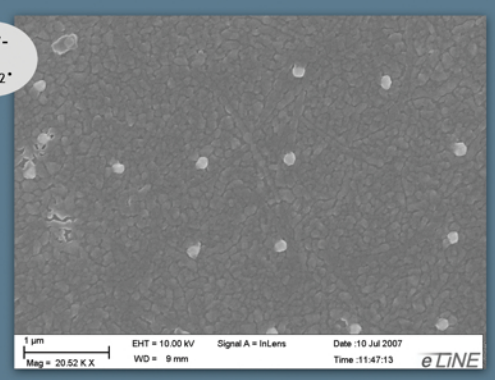



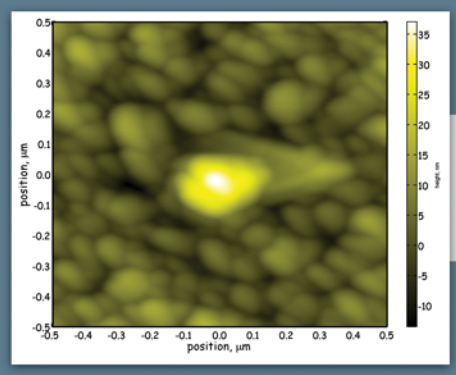



Scanning Electron Micrographs of symmetric and asymmetric Au nanoparticles (NPs), taken before (*left*) and after (*right*) covering them with $VO_2$.




Atomic Force Microscope images (*right* and *far right*) of a single Au NP covered with $VO_2$.

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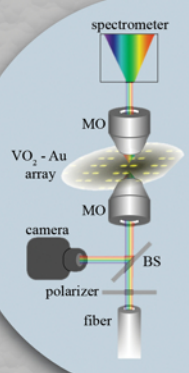


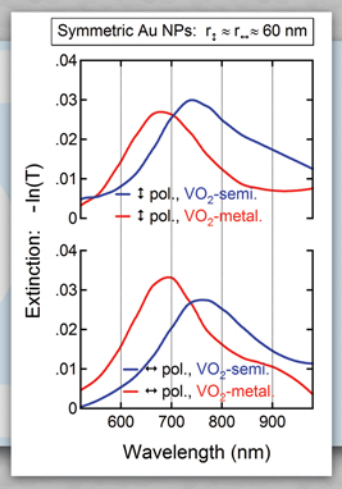

Temperature > 67 °C: $VO_2$-metal.

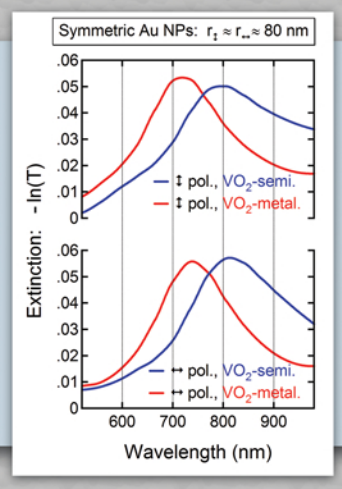
**Measured extinction spectra:**

$$-\ln(\mathbf{T}), \text{ where}$$

$$\mathbf{T} = \mathbf{I}\{Au+VO_2\} / \mathbf{I}\{VO_2\}$$

Temperature < 67 °C: $VO_2$-semi.



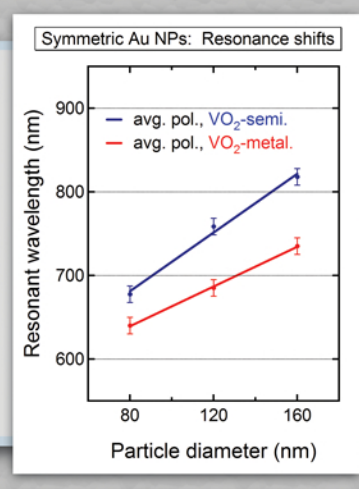



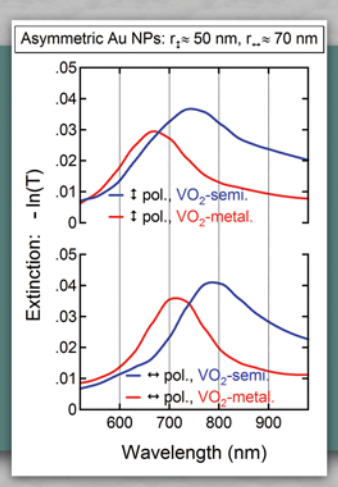

**Symmetric Au nanoparticles (NPs), covered with $VO_2$:**

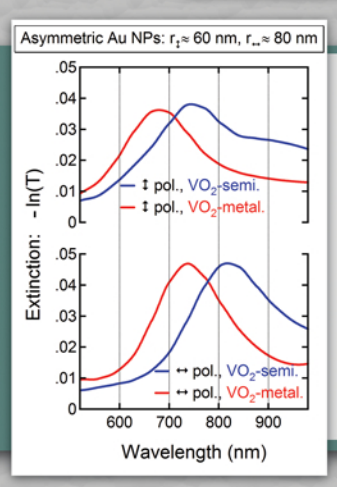
(1) Resonant wavelengths **shift little** with incident polarization, likely due to imperfect NP symmetry and array/polarizer misalignment.

(2) Resonant wavelengths **red-shift** with increasing NP size (*i.e.*, finite radius-wavelength ratio), due to dynamic depolarization of the induced-dipole radiation.

(3) Above all, correct trend in modulation of Au particle-plasmon wavelength across $VO_2$ phase transition, *i.e.*, **blue-shift** in metallic phase, as predicted by quasi-static and Mie calculations.




**Asymmetric Au nanoparticles (NPs), covered with $VO_2$:**

(1) Resonant wavelengths **shift significantly** with incident polarization, due to different size-to-wavelength ratios along NP's major and minor axes.

(2) Resonant wavelengths **shift differently** for different polarizations with increasing NP aspect ratio: **red-shift** for major-axis peaks, **blue-shift** for minor-axis peaks.

(3) Again, as $VO_2$ becomes metallic, Au plasmon resonance **blue-shifts** for both polarizations with respect to semiconducting phase.

(4) Moreover, combined effects of polarization and the $VO_2$ transition allow for much **larger resonance shifts** in these asymmetric Au NPs (up to 200 nm) than in the symmetric Au NPs (up to 100 nm).