Core-shell nanoparticles with self-regulating plasmonic functionality

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We propose a smart nanoparticle, a "regulatron," that exploits a cycle of dynamic plasmonic feedback to self-regulate its temperature to a fixed range. One kind of regulatron can be conceived from VO_2 and Au; the temperature of this particle when illuminated by laser irradiation of suitable intensities and wavelengths is ~340 K. We expect that regulatrons of this and other compositions will be useful in applications such as photothermal medical therapeutics.

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Morin's discovery[1] in 1959 that vanadium dioxide underwent a metal-insulator transition has stimulated much interest in this material. The semiconducting, monoclinic form of vanadium dioxide ("VO_2-M_1") transforms reversibly to a metallic, tetragonal structure ("VO_2-R") when heated above ~340 K (67 °C), a transition attended by large changes in conductivity and optical properties.[1–3] This phenomenon has inspired the development of VO_2 as the active component of "smart" window coatings that reflect sunlight when the glass gets hot, e.g., Ref. 4, as well as its use in optical switching or measurement devices, e.g., Ref. 5. However, at least one other intriguing application for this fascinating material seems to have been overlooked. Here we will show that composite Au-VO_2 nanoparticles of specific dimensions will regulate temperature through a process of dynamic feedback during illumination by a laser. We name this device a "regulatron." An optically-driven nanoscale temperature regulator will have far-reaching impact, an obvious example of which will be to prevent "run-away" heating[6] in photothermal medical therapeutics.[7–9] The conceptual Au/VO_2 regulatron to be described here is the prototype for this previously unforeseen class of mesoscale plasmonic devices, and we believe that it will be followed by regulatrons based on other materials, such as SmS, NiS, and Ga, that also have phase transitions accompanied by large changes in optical properties.

The starting point for constructing these devices are precious metal nanoparticles, which can absorb anomalously large amounts of light relative to their geometric cross-section across a relatively small wavelength region. This absorption arises through excitation of plasmon resonances on the particle.[10] For gold spheres in vacuum and with diameters of 10 to 80 nm the resonance occurs at approximately 520 nm. The overall extinction coefficient of the particle is the sum of light absorbed and light scattered, but it is only the absorbed portion that interests us here. This is converted to thermal energy, causing the phenomenon of "plasmonic heating."[6,11] Some discussion of the exploitation of plasmonic heating in nanoparticles may be found elsewhere[7,9,11–13] and it is sufficient to note here that an ability to modulate this effect would be of potential interest in both solar glazing and photothermal therapeutics, to name only two possibilities. For metals such as gold and silver the resonance of a nanosphere (and other particle shapes) is redshifted when the refractive index of the surrounding medium is increased. Several methods to produce nanoparticles of complex shape or structure have recently been developed[14] and the effect of changes in the dielectric properties of the medium are amplified with some of the new shapes.[15] Nanoshells of gold (on a dielectric core) or nanorods of gold or silver with varying aspect ratio provide a potent means to tune the plasmon resonance from the visible to near infrared.[14]

The combination of the two effects described above, metal-insulator transition and plasmonic absorption, opens a range of new possibilities for creating composite metamaterials with optical properties that are strongly temperature dependent. This possibility has been but sparsely explored, with only a few reports appearing regarding the effect of temperature on the plasmon resonance of Ag or Au nanospheres embedded in a VO_2 matrix,[16–18] of composite Au-VO_2 films[19] or of VO_2@Au (Au-on-VO_2) core-shell particles.[20] Curiously, however, the possibility of self-regulating temperature control in these structures appears to have been hitherto overlooked.

Here we examine, using computational methods, how the optical properties of various forms of composite nanoparticles of Au and VO_2 would be affected by the phase transition in VO_2, and from this field select a particular particle geometry for a more detailed analysis. Particles of spherical symmetry were modeled using the "BHCOAT" code of Bohren and Huffman,[6,10] while a less symmetrical nanorod shape was modeled with the discrete dipole approximation of Draine and Flatau.[21] Although our assertions are at this stage based only on the results of calculations, the excellent predictive capabilities[10,14] of the codes used gives us confidence in the results. The dielectric properties of VO_2-M_1 and VO_2-R were taken from Verleur *et al.*[22] and were originally determined at 300 K and 355 K, respectively. In the present work we have ignored any small variations of optical properties with temperature in the range 300 to 400 K, other than those induced by the phase transition itself, a simplification which we assert does not compromise the generality of our conclusions.

To explain the regulatron effect we consider first a simple Au nanosphere of 40 nm diameter that is coated with a 10 nm thick shell of VO_2 (a configuration designated Au@VO_2), with the composite particle surrounded by vacuum. The presence of the VO_2 shell causes the plasmon resonance to redshift by ~70 nm relative to the naked gold sphere, but if the temperature of the particle is raised above that of the $M_1 \rightarrow R$ phase transformation, there will be a sharp change in the refractive index of the VO_2, and the peak of the plasmon resonance moves back in the blue direction

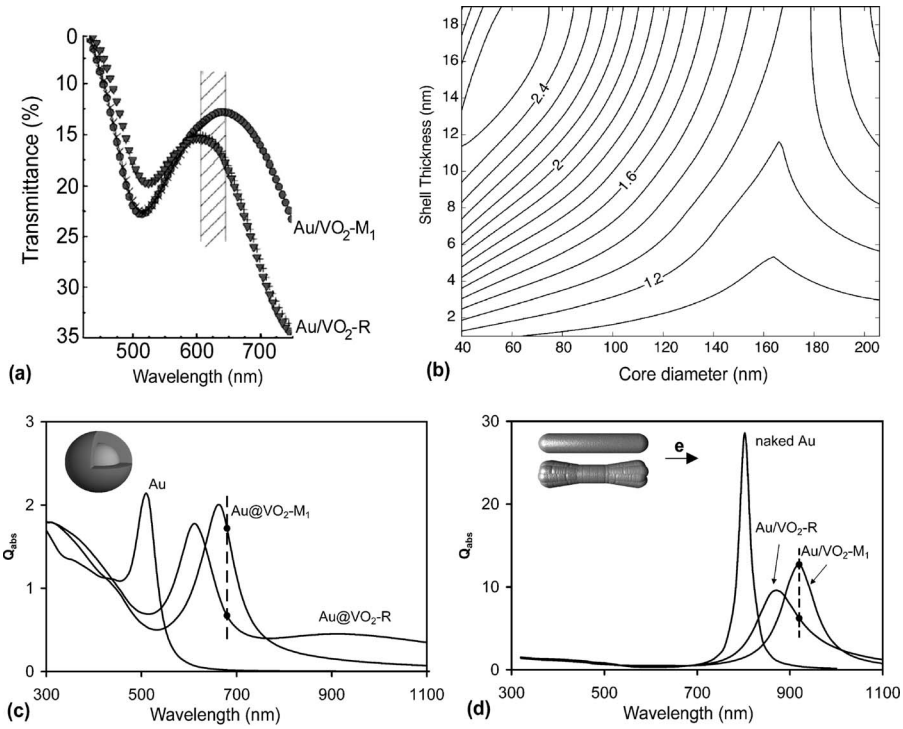

FIG. 1. Effect of the VO_2-$M_1 \leftrightarrow VO_2$-R phase transformation on the optical properties of composite Au+VO_2 nanoparticles. (a) Experimental data of Maaza,[16] redrawn with permission. The hatched region illustrates the shift in the position of peak plasmon resonance. (b) Optimization of ϕ (out-of-paper axis on figure) for Au@VO_2 particles. (c) Optimum Au@VO_2 core-shell particle with schematic of particle shown as inset. (d) Gold nanorods of 100 nm length with end caps of VO_2, compared to naked gold rod, with schematic of particles shown as inset. A numerical model of 13 000 dipoles for the plain gold rod, and 20 000 dipoles for the coated rod, was used in the calculation.

by ~20 nm. The effect will be reversible, subject only to the small hysteresis in transformation temperatures expected for the transition. This phenomenon is in itself not new having already been demonstrated for Au nanoparticles in a continuous matrix of VO_2,[16–18] e.g., Fig. 1(a).

The effect is obviously magnified for a greater difference in the optical properties of the high and low temperature forms of the structure. The maximum possible values of the ratio

$$\phi = \frac{Q_{abs}^{VO_2-M_1}}{Q_{abs}^{VO_2-R}} \tag{1}$$

for a range of Au@VO_2 particles taken over wavelengths in the interval 300 to 1800 nm are shown in Fig. 1(b). (Although this optimization could also have been performed in respect of Q_{ext}, it is the magnitude of Q_{abs} that controls plasmonic heating and hence of interest here.) The optimum value of ϕ=2.56 is achieved for these particles when the core is 58 nm in diameter and the VO_2 shell has a thickness of 16.5 nm, and this occurs at λ=680 nm, Fig. 1(c), which represents the optimum geometry for Au@VO_2 particles. A similar effect is achievable if VO_2 sheaths or end caps are overcoated on a gold nanorod, Fig. 1(d). We have not attempted to optimize this effect in this case, and the purpose in showing it here is merely to demonstrate that it will also be feasible to use nanoparticles of other than spherical shape to achieve a differential optical absorption. It is obviously also possible to apply a VO_2 outer shell on top of an existing Au nanoshell, to give for example a SiO_2@Au@VO_2 particle.

However, a solid gold nanosphere has a limited color gamut, whereas that of gold nanoshells or nanorods is more extensive and more sensitive to small variations in dielectric properties.[14] In Fig. 2(a) we show how ϕ varies as a function of wavelength for VO_2 nanospheres of 120 nm diameter, and varying thickness of Au shell. It is evident that the difference in optical properties between low temperature and high temperature particles increases as the wavelength increases, and that values of ϕ of over 12 can be achieved. The effect can be explored over a range of core radii and shell thicknesses [Fig. 2(b)].

In the case of photothermal therapeutic treatments based on plasmonic heating, laser irradiation of unhealthy tissues is applied in order to selectively destroy them while avoiding

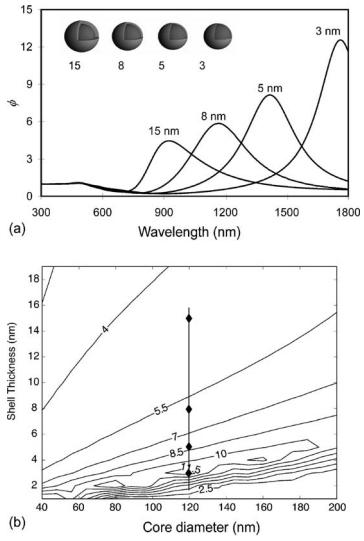

FIG. 2. Effect of the VO_2-$M_1 \leftrightarrow VO_2$-R phase transformation on the optical properties of VO_2@Au particles. (a) Variation of ϕ for a VO_2 core of 120 nm diameter and various thicknesses of Au shell. (b) Plot of ϕ_{max} for a wide range of core and shell dimensions, with the positions of the particles of (a) indicated.

collateral damage to healthy cells. Gold nanospheres, shells, or rods are concentrated in the target cells by active or passive means,[23] following which a laser with a frequency matching the plasmon resonance of the nanoparticles is used to irradiate the tissue. The optimum transparency through human skin is between 800 and 1000 nm.[24] Therefore, to optimize the selective heating effect, the plasmon resonance of the nanoparticle should also be tuned to fall in this range. An example of a suitable particle and its associated optical absorption spectrum is shown in Fig. 3(a).

The temperature and surface heat flux of a plasmonically-active nanoparticle under laser irradiation has been the subject of several investigations,[6,25–29] and we note that the assumption of adiabatic heating of the particle is only reasonable if $t \ll t_T$, where t_T, the characteristic time between particle and medium[27] provides an indication of whether transient or steady state phenomena are dominant, and is

$$t_T \approx \frac{a_0^2}{4\chi_m}, \tag{2}$$

where a_0 is the particle radius and χ_m is the thermal diffusivity of the medium which we take here as 1.53×10^{-7} m^2/s, the value for liquid water. The applicable t_T for the model system shown in Fig. 3(a) is ~6 ns, indicating that heat transfer out of these tiny particles reaches a quasi-steady state in about that time.

Here we will invoke the Pustovalov[27] model for transient heat generation and dissipation in a sphere immersed in an infinite conductor at temperature T_∞ to simulate the behavior of the VO_2 core-Au shell identified in Fig. 3(a). This solution is applicable only for time $t > t_T$. Like others[26,27] we will neglect heat transfer out of the particle by radiation. Although it is reasonable to use a conductive model for short times ($t \ll 1$ s) it should be noted that this does overestimate heat transfer rates out of the particle,[25] the error becoming significant as t approaches 1 s and convection becomes important.[6] The error is however negligible for the high speed transient phenomena considered here. With these caveats in mind, the temperature T_p in a particle subject to a laser flux I_0 while immersed in an infinite medium is[27]

$$T_p = T_\infty + \frac{I_0 Q_{abs} a_0}{4k_m}[1 - e^{-Bt}], \tag{3}$$

where k_m is the thermal conductivity of the medium, here water at 0.611 W/m/K. B is given by

$$B = \frac{3k_m}{c_p \rho_p a_0^2}, \tag{4}$$

where c_p is the particle's heat capacity (taken here to be the mass-weighted average of Au and VO_2 which is ~250 J/kg/K for this particular particle) and ρ_p is the average density of the particle (11 640 kg/m^3 in this specific case). Note that, in this geometry and provided $t \gg t_T$, T_p is effectively independent of t and hence of laser fluence, although not of laser intensity.

Although the particle shown in Fig. 3(a) has an optimum Q_{abs} in the insulating condition at $\lambda = 837$ nm, the optimum ϕ for the particle is at $\lambda = 924$ nm. At this wavelength Q_{abs} for this particle with a VO_2-M_1 core is 1.13, while for the VO_2-R core it is 0.25. We will assume continuous wave illumination for simplicity. If illuminated by a sufficiently powerful source at 924 nm, the temperature of the particle at first rises, Fig. 3(b). The details of the dynamic process that

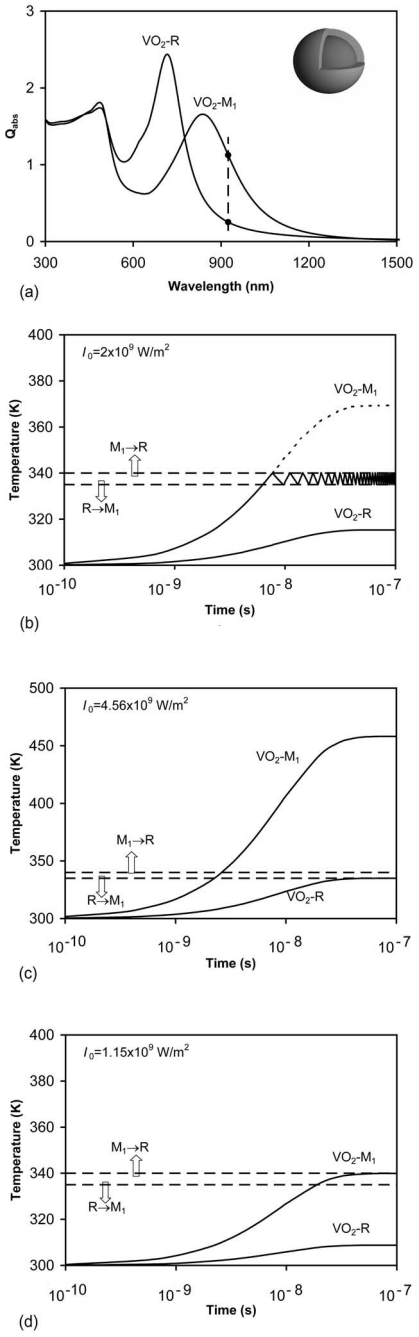

FIG. 3. Calculation of temperature in a VO_2@Au nanoparticle immersed in water and irradiated with a laser at various intensities. (a) Absorption efficiency of the particle with a 120 nm diameter core and a 15 nm thick shell which is optimized for service in the near-infrared, as a function of wavelength of light. (b) Predicted thermal behavior of particle of (a) when illuminated with 924 nm light at 2×10^9 W/m^2 showing regulatron behavior. (c) Predicted thermal behavior at upper limit of illumination intensity for regulatron behavior. (d) Predicted thermal behavior at lower limit of illumination intensity for regulatron behavior.

unfolds are influenced by magnitude of the hysteresis in phase transition temperatures which varies from as little as 1 K to as much as 50 K depending on the structure and morphology of the VO_2.[17,30,31] Here we will examine two scenarios, a 5 K hysteresis and a 50 K hysteresis. In the first case the up transformation (to VO_2-R) occurs at 340 K and the down transformation (to VO_2-M_1) at 335 K, while in the second the corresponding temperatures are taken to be 300 and 350 K.

Considering the first scenario, at 340 K the transformation of the core to VO_2-R occurs, which reduces Q_{abs} of the composite particle to only 0.25, preventing further increase (dashed line) of the temperature of the particle taking place. The available evidence indicates that this phase transition will be rapid, taking place within 1 ps.[32,33] Heat generation in the particle with the VO_2-R core is now significantly reduced, and the temperature of the particle will attempt to relax, in a few nanoseconds[25] (taken here for the purpose of our argument to be ~2 ns) to the appropriate equilibrium temperature for VO_2-R. However, once the temperature has fallen to ~335 K transformation to VO_2-M_1 occurs, the particle heats up, and the cycle would repeat, *ad infinitum*. It is evident, Fig. 3(c) however that there is a limiting upper laser intensity (4.56×10^9 W/m^2 for the present example) at which even the steady state temperature of a particle with a VO_2-R core is already 335 K. Such a particle can no longer transform back to the VO_2-M_1 phase. Similarly, no self-regulation is possible if the laser intensity is insufficient to even raise the temperature of a particle with a VO_2-M_1 core above the phase transition temperature of 340 K, Fig. 3(d), providing a lower limit (1.15×10^9 W/m^2 in the present example). The situation in the event of a 50 K hysteresis represents a further limiting case, since the transformation temperature for VO_2-$R\rightarrow VO_2$-M_1 and that of the medium would now be the same (300 K). In this case no regulatronic behavior is possible unless the medium temperature is lowered.

In this example we deliberately selected a particle where the effect would occur at ~900 nm since this could be of interest in photothermal therapeutic applications. However, the self-regulating effect would obviously operate over an even greater range of laser intensities if particles designed to operate deeper in the infrared were used [cf. Figs. 2(a) and 2(b)].

At present, no way of producing VO_2@Au core-shell particles has been demonstrated. However, we have shown elsewhere that semishells, that is, partial nanoshells, can be engineered to have similar plasmonic properties to true nanoshells.[34–36] The attraction of semishells is that they can be produced by physical vapor deposition onto a suitable template. The present VO_2@Au particles could conceivably be produced by evaporation of gold or silver onto nanospherical VO_2 template particles. The temperature of the resulting regulatrons could be verified by one of several methods already disclosed in the literature.[7,37]

In effect, these composite particles will behave as a smart metamaterials, since they will manifest both intrinsic sensing and actuating functionalities. We define regulatrons to be nano- or microparticles that can be engineered to maintain a constant temperature by means of a fast, self-adaptive and reversible transition in optical properties, even while being irradiated with a flux of varying intensity. Core-shell regulatrons may be conceptually the simplest of these new structures, but we have shown that other nanoparticle geometries could also exhibit thermal regulation properties.

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