Active control of the optical properties of nanoscale coatings using 'smart' nanoparticles

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ABSTRACT

Coatings that can self-modulate their optical properties as a function of an external stimulus are of significant technological interest. In this regard, the possibilities for thermo- or electrochromic materials such as VO_2 and WO_3 are already comparatively well-known. Here, however, we explore a new kind of 'smart' coating, based on the active control of a plasmon resonance in nanoparticles. One possible system is based on the modulation of the plasmon resonance of a precious metal nanorod or nanosphere by an active dielectric shell. The active dielectric undergoes an insulator-to-metal transition on increase of temperature which modulates the plasmon resonance of the underlying precious metal nanoparticle, thereby changing the wavelength at which its optical extinction is maximum. In the case of nanorods, the absorption maximum of the longitudinal plasmon is particularly sensitive to the aspect ratio of the nanoparticle and the dielectric properties of the environment, and may be readily tuned across the visible and near-infrared portions of the spectrum. In addition, nanoparticles of certain thermochromic dielectrics, such as VO_2, are expected to have a plasmon resonance of their own which can be switched on or off by control of the temperature. We consider some of the possibilities, using both the discrete dipole approximation and the exact analytical solution due to Mie to calculate the optical properties.

Keywords : nanorods, gold, silver, plasmon resonance, thermochromic, vanadium dioxide, active plasmonic control

1. INTRODUCTION

Nanoparticles of certain compounds and elements undergo a plasmon resonance with light. This phenomenon has been particularly well studied in the coinage metals (Cu, Ag, Au) for at least two reasons : (i) these nanoparticles are relatively stable under ambient conditions and, (ii) their resonances occur in, or near to, the visible part of the spectrum[1-3]. The single dipole plasmon resonance of spherical nanoparticles splits into a transverse and a longitudinal mode as the particle becomes elongated into rod-like shapes. The absorption maximum of the longitudinal plasmon is particularly sensitive to the aspect ratio of the nanoparticle, and may be readily tuned between 450 and 700 nm for Ag, or 550 to 1500 nm for Au. There has been some interest in using such precious-metal particles for chemical sensing, e.g.[4], and medical applications, e.g.[5,6], however these are not the topics that we will address here. Rather, the present paper is focused on the exploitation of the optical properties of coatings of precious metal nanorods to produce a 'smart', spectrally-selective coating. In this scheme the optical properties of the coating are modulated using a concept that we term 'active plasmonic control'. The idea builds on the previous work of Malik Maaza and co-workers[7] in 2005, in which the complex optical response of a composite Au/VO_2 nanocoating was examined.

Coatings of nanospheres on transparent substrates are of interest even without active plasmonic control because they can be configured to give spectral selectivity on transmission[8,9], while angular selectivity is additionally possible with nanorods[3] or nanocaps[10]. In the case of nanorods this is because the intensity of the longitudinal plasmon resonance also

depends closely on the polarization and orientation of the incoming light. In principle or in practice these coatings can be configured to block the infrared radiation of sunlight (for windows)[11], used as dichroic filters[3], or used as the basis for a color-change device[12]. However, we show here that further functionality can be imparted to the coatings by surrounding the nanoparticles with an active dielectric matrix capable of undergoing an externally stimulated change in optical properties. This is because the position and intensity of a plasmon resonance are also dependent on the dielectric constants of the medium in the immediate vicinity of the nanoparticle. The effect is significantly more pronounced for nanoshells or nanorods than for nanospheres[13]. Electrochromic, thermochromic or other systems based on this phenomenon can be envisaged.

Vanadium dioxide (VO_2) is a particularly attractive candidate material for the role as 'active dielectric' in a nanoscale coating system. The material undergoes a reversible transition between a semiconductor phase (VO_2-M) to a conducting phase (VO_2-R) at about 68°C [14,15]. In the transition from semiconductor to metal both the electrical conductivity and optical reflectivity of the VO_2 change dramatically. The transition is most commonly induced by a change in temperature but is actually electronic in nature. Therefore, it can also be induced isothermally by an injection of photo-carriers or by subjecting the VO_2 to a strong electric field [15,16]. The phase change is exceptionally rapid in the latter instances, occurring in less than a picosecond[15]. Several interesting applications of these phenomena in VO_2 have been identified, including thermochromic windows, e.g.[17], optical fiber switching devices[16,18], holographic storage systems[19], switchable photonic crystals[20], and infrared bolometers[21]. Here, however, we will concentrate on showing how the transition in VO_2 could be used to modulate a plasmonic response.

2. CALCULATIONS

The simulations of the nanorods described here were carried out with the DDSCAT code of Draine and Flatau [22,23], while those of the spherical core-shell particles used BHCOAT, a code originally from the textbook of Bohren and Huffman that invokes the analytical solution of Mie[24]. Both programs calculate the extinction, absorption and scattering efficiencies for a nanoparticle, but DDSCAT uses the discrete dipole approximation (DDA), in terms of which the particle is rendered as a 3-D array of dipoles which are then processed numerically. Convergence in materials (such as gold) with high refractive indices (n and k) is slow and the dipole volume must be small in order to produce a stable numerical result. In the present work electron scattering off the surfaces has been neglected and bulk dielectric properties have been used. This is considered acceptable if the rods are longer than the mean free path of an electron (~40 nm)[4,25], particularly as it is the longitudinal resonance that is of the greatest interest. There are also size-dependent effects on the dielectric constants of VO_2 [26,27] but these are also neglected here and the thin film data of Verleur[27] were used 'as is'. In all cases the external environment is taken as vacuum.
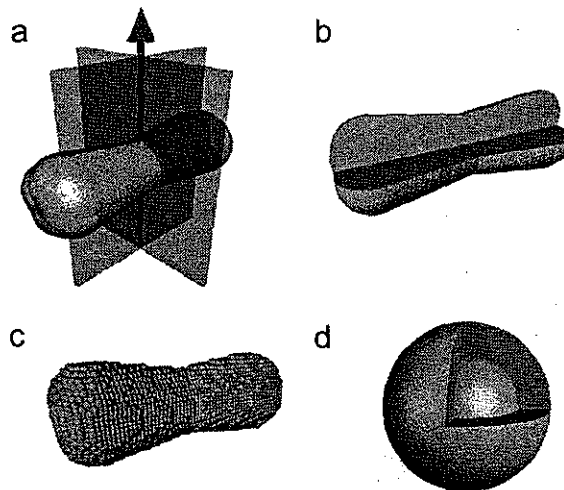

Figure 1. Composite targets investigated in present work consisting of precious-metal core and a VO_2 coating, (a) external view of nanorod target, showing polarizations (blue) and propagation vector (red) of the light, (b) cut-away view of nanorod target showing Au core and VO_2 shell, (c) nanorod target after rendering into array of dipoles, (d) cut-away view of spherical Au@VO_2 core-shell particle.

The simulated VO$_2$-coated nanorod target used in the present work is shown in Figure 1(a)-(c). It consists of a gold or silver nanorod core, 80 nm in length and with a diameter of 20 nm. Vanadium dioxide is then notionally precipitated onto the rod as shown, to form a coating. The composite object was then rendered into ~20,000 dipoles, each with a volume of ~2 nm^3, for use by the DDSCAT code. Simulations of the optical properties of the Au@VO$_2$ core-shell particles, Figure 1(d), and of the solid VO$_2$ spheres were carried out using BHCOAT.

3. RESULTS

The simulated optical properties of the composite nanorods are shown in Figure 2, alongside vacuum data for the corresponding naked particle. It is evident that coating the precious-metal nanorods with VO$_2$ is predicted to markedly attenuate their plasmon resonance, and red-shift the extinction peak due to the longitudinal resonance. The position of the latter can be moved back and forth by about 50 nm, simply by causing the reversible phase transformation between VO$_2$-M and VO$_2$-R to occur. Although attenuated relative to the case of a vacuum environment, the extinction efficiencies of the VO$_2$-coated rods are still large and of technological interest.
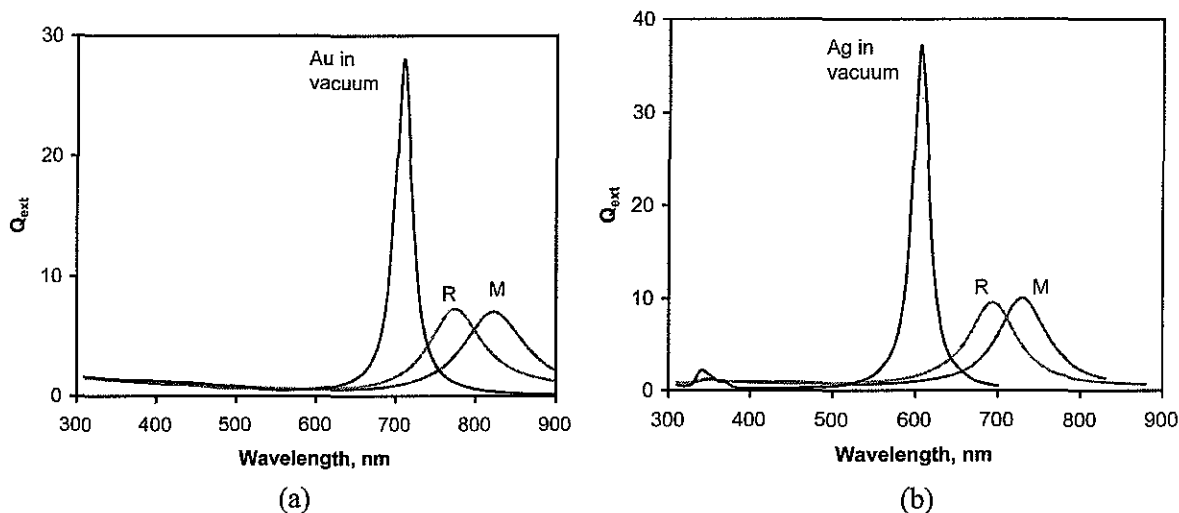

(a)　　　　　　　　　　　　　　　　　(b)

Figure 2. Modulation of the plasmon response of precious metal nanorods of 4:1 aspect ratio that have been coated with VO$_2$, R is prediction for VO$_2$-R, the high-temperature metallic phase, M the prediction for VO$_2$-M, the low-temperature semiconducting phase. (a) Gold nanorod cores. (b) Silver nanorod cores.

A wavelength-dependent figure-of-merit for the change in optical properties, the 'switching ratio', can be defined:

$$\phi_{ext}(\lambda) = \frac{Q_{ext}^{VO_2-M_1}(\lambda)}{Q_{ext}^{VO_2-R}(\lambda)} \tag{1}$$

where λ is the wavelength of light at which the figure-of-merit is evaluated.

In practical terms this modulation can be achieved by varying the temperature of a hypothetical coating containing a dispersion of these rods from about 60 to 75°C and back again[14]. In addition, an interesting, self-regulating thermal response at particular wavelengths has been predicted[13] as the result of the thermochromic variation in absorption efficiencies for the two forms of VO$_2$. This would have the effect of 'locking' the temperature of coating onto about 68°C provided that the intensity of the illumination fell within a particular range . However, in the present work, the point of greater importance is that there is a wavelength (750 nm for the gold nanorods) at which the particles transmit roughly 2½x more light at high temperatures than at low temperatures, and a second wavelength (850 nm) in which this relationship is reversed, with the transmission of light at the lower temperature being 2½x greater than at the higher, Figure 3. The corresponding figures for silver are similar, but the wavelengths of light at which the switching in peaks occur are blue shifted to 670 and 750 nm respectively. Unfortunately, the extinction peaks are not broad or well separated enough to make a meaningful difference for a solar shielding application. However, it is feasible that the effect could be used to modulate a monochromatic beam of appropriate wavelength for some other purpose. It is also

interesting to note that the semiconductor→metal transition can also be very rapidly induced by a laser pulse. In this case, it is not the heat imparted by the laser that causes the transition, rather, the photon-induced change in the electronic structure[15]. This provides additional possibilities for controlling the optical switching[16].
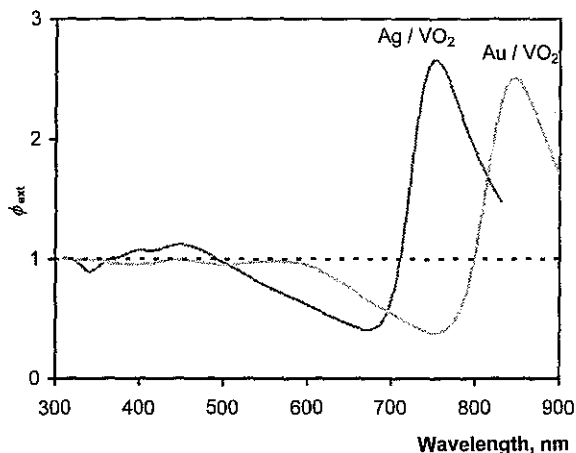

Figure 3. Switching efficiencies of Ag and Au nanorods that have been over-coated with VO_2. The rods have a 4:1 aspect ratio and are 80 nm long. Note that the position at which maximum switching occurs can be readily controlled by changing the aspect ratio.
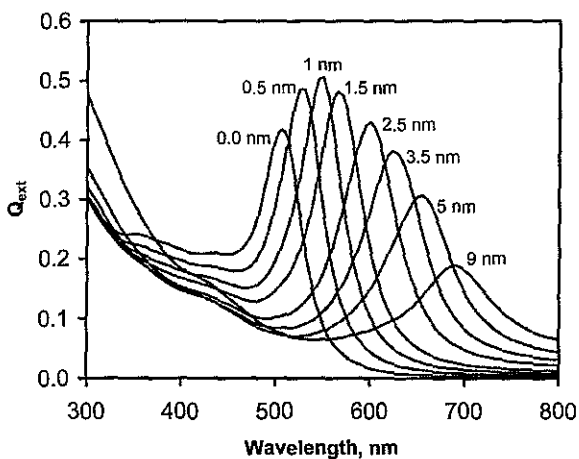

Figure 4. Simulated optical extinction spectra for a series of Au@VO_2 core-shell particles, with a 13 nm diameter Au core, and the indicated thickness of VO_2-M shell.

No attempt has been made here to optimize the thickness of the VO_2 coating on the nanorods. There are three reasons for this. First, the DDA calculations were computationally intensive, and hence slow, secondly a target with sufficiently fine resolution to contain a thin shell would necessarily need to contain a very large number of dipoles (exacerbating the first factor), and thirdly because, in any case, electron scattering effects in a thin shell would be expected to broaden and attenuate the extinction peaks considerably. On the other hand, some qualitative insight into the probable effect of reducing the thickness of the VO_2 layer can be gained by a consideration of the special case of spherical core-shell particles (Figure 1(d)) for which an analytical solution to the optical properties is available. In Figure 4 we show the effect of varying the thickness of a shell of VO_2-M placed on a Au nanosphere of 13 nm diameter. For reasons of clarity the corresponding peaks for the VO_2-R phase are not shown but are in each case blue-shifted and slightly attenuated relative to those for VO_2-M. Switching ratios of nearly 2.5x are possible in the red part of the visible spectrum for a gold core of 13 nm diameter. To fully optimize the effect it is also necessary to systematically vary the core diameter as well as shell thickness. If this is done then ϕ_{ext} up to 2.56 seem feasible for Au@VO_2 core-shell spheres [13]. Even higher

switching ratios, of in excess of 12, have been predicted for the inverse geometry of VO$_2$@Au core-shell spheres. These are attained in the near-infrared[13].

However, there is a second interesting plasmon mode to consider in this system, that of the VO$_2$-R itself. The dielectric properties of this phase provide a plasmon resonance in the technologically important near-infrared, and the gold core in this case is somewhat irrelevant. In Figure 5 we show the switchable optical extinction predicted for a VO$_2$ sphere of 100 nm diameter. In this case there is a plasmon resonance for the sphere in the metallic form but none when it is in the semiconducting form. Rather than being tunable, here it is a case of being able to turn a plasmon resonance on or off. While the plasmon resonance of the VO$_2$-R sphere peaks at 1030 nm, the maximum extent of switching available is at 1771 nm, at which the extinction of the particle in the VO$_2$-R form is 7.3x that of itself in the VO$_2$-M form.
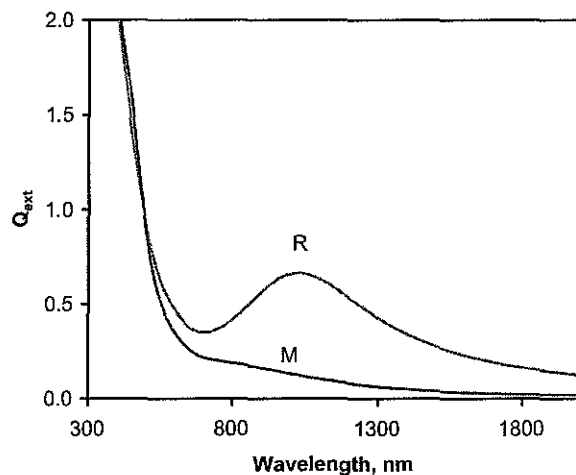

Figure 5. Switchable optical extinction characteristics predicted for a VO$_2$ sphere of 100 nm diameter. (M and R as for Figure 2)

Finally, the plasmon resonance of a VO$_2$ shell on an Au core becomes evident in its own right when the VO$_2$ is present at a sufficiently large thickness. In this case an interesting mixed system results, with a *tunable* plasmon response available from the Au core and a *switchable* one from the VO$_2$ shell, Figure 6.
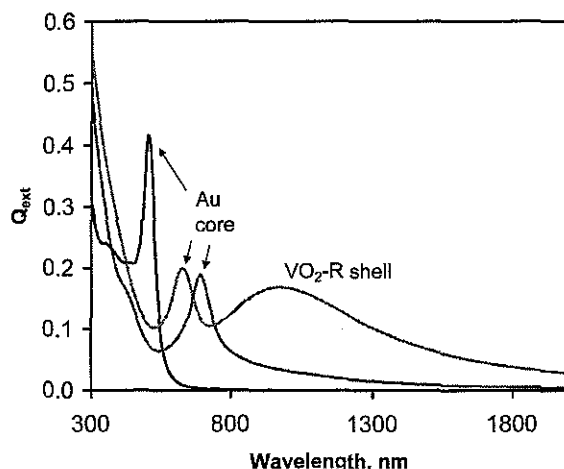

Figure 6. A simulation of the complex, thermochromic plasmonic response available from a 13 nm diameter Au core that has been over-coated with a 9 nm thick VO$_2$ shell. There is a tunable plasmon resonance mode due to the core ('core' on the figure) and a switchable resonance due to the shell ('VO$_2$-R shell' on the Figure).

4. CONCLUSIONS

The combination of a plasmonic nanostructure with a material with controllable dielectric response offers interesting new functionalities. We have coined the term 'active plasmonic control' to describe the phenomena in these new systems. A plasmon resonance in these systems can be either 'tuned', that is shifted in respect of the wavelength of light at which it occurs, or even switched on or off. Switching ratios of at least $2\frac{1}{2}$x are possible with systems based on coinage metal nanorods or nanospheres that have been over-coated with VO_2. In these instances control of the structure of the dielectric phase can be used to 'tune' the wavelength at which a plasmon resonance occurs. However, in the case of VO_2 nanospheres the plasmon resonance can actually be switched on or off by control of its structure. A hybrid response, showing both tunablity and switching is expected in some of these composite particles.

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