ویژگی‌های نوری نانوکره اکسید وانادیم دارای تغییر فاز

نوشین ولی‌زاده شهمیرزادی و توکل پاکیزه

دانشکده مهندسی برق دانشگاه خواجه نصیرالدین طوسی

چکیده –. در این مقاله ویژگی‌های نوری نانو کره همگن وغیر مغناطیسی اکسید وانادیم که در هوا قرار دارد مطالعه می‌شود و اثر ابعاد بر روی این مشخصه‌ها نیز بررسی می‌گردد. VO_2 در دمای اتاق عایق می‌باشد و در دمایی بالاتر از دمای بحرانی (۳۴۱*K*) به فلز تبدیل می‌شود. در فاز فلزی، رزونانس پلاسمون سطحی محلی (*LSPR*) در نانوکره‌های VO_2 شکل می‌گیرد که با افزایش دما، شیفت قرمز کمی می‌یابد و در حالت عایق این رزونانس ناپدید می‌گردد. میدان الکتریکی در این رزونانس به شکل دوقطبی می‌باشد. افزایش ابعاد در فاز عایق، منجر به ایجاد مقدار بیشینه‌ای در طیف نوری می‌گردد که محل این رزونانس در طول‌موج نور مرئی می‌باشد. نانوکره‌های VO_2 در فاز فلزی در مقایسه با نانوکره نقره طیف وسیع‌تری دارند، بعلاه میدان الکتریکی نانو کره نقره در *LSPR*، شدیدتر از VO_2 می‌باشد. با این وجود، *LSPR* موجود در VO_2 قادر است با حرارت سوییچ شود که موجب شده است این ماده در کاربردهای نوری جایگاه ویژه‌ای داشته باشد.

کلید واژه- تغییر فاز، وانادیم دی‌اکسید، ویژگی‌های نوری، دمای بحرانی، رزونانس پلاسمون سطحی محلی

Optical Properties of VO_2 Nanosphere with Phase Transition

N. Valizade Shahmirzadi and T. Pakizeh

Faculty of Electrical Engineering, K.N. Toosi University of Technology, Tehran 163171419, Iran.

Abstract- *In this paper the optical properties of the homogeneous nonmagnetic vanadium dioxide (VO_2) nanosphere embedded in the air and also size effect on these characteristics are studied. VO_2 is an insulator at room temperature and becomes metal above a critical temperature (T_c=341K). In the metallic phase, a localized surface plasmon resonance (LSPR) forms in VO_2 nanosphere, which red shifts slightly by increasing dimension, its associated electric field is in form of dipole, and disappears in insulator phase. The increment in the dimension of nanosphere in insulator case, results in the appearance of a peak in the visible wavelength that its origin is combined modes. VO_2 nanosphere in metallic case has much broader optical spectra in comparison to silver (Ag) nanosphere, as well as, the electric field of Ag nanosphere in LSPR is more intense than its counterpart in VO_2. Nevertheless the LSPR of VO_2 can be switched thermally, making this material peculiar in optical applications.*

Keywords: *Phase Transition, Vanadium Dioxide, Optical Properties, Critical Temperature, Surface Plasmon Resonance,*

Optical Properties of VO_2 Nanosphere with Phase Transition

Nooshin Valizade Shahmirzadi
n.valizade@email.kntu.ac.ir

Tavakol Pakizeh
t.pakizeh@kntu.ac.ir

1 Introduction

Phase transition is an abrupt change in some physical and structural properties of the materials. Insulator-metal-transition (IMT) which is accompanied by extreme variations in electrical conducting is a class of phase transition. IMT occurs in a wide range of metal oxide materials such as titanium trioxide, manganese oxide, vanadium dioxide (VO_2) and etc. [1-2]. Among these IMT materials, VO_2 that its properties were observed by Morin [2] has an outstanding importance. VO_2 thin film is a monoclinic insulator at room temperature (RT). By approaching to a critical temperature (T_c = 341 K), VO_2 undergoes IMT and converts to a rutile metallic structure which results in dramatic variations in its optical and electrical properties [2]. In the metallic phase, the real part of VO_2 dielectric constant becomes negative as the wavelength increases, which can lead to plasmon resonance. Due to unique properties of VO_2, this material has emerged new applications in optics and nanooptics [3-4]. Despite of the fact that localized surface plasmon resonance (LSPR) of noble metallic nanostructures is independent of temperature, VO_2 can tune LSPR of these structures thermally in temperature dependent optical devices [5]. Moreover, an array of silver nanorods which lies on a thin film of VO_2, can rotate the polarization axis of incident visible light [4]. According to suitability of VO_2 in many optical applications, the understanding of VO_2 properties in different phases seems to be necessary. In this paper, optical characteristics of VO_2 nanosphere and the temperature effect on these characteristics are investigated. The obtained results demonstrate that individual VO_2 nanosphere experiences LSPR at about 1000 nm and can switch LSPR thermally.

2 Theories and Models

Optical properties of VO_2 nanosphere are studied by exploiting various methods such as dipole approximation (DA), modified long wavelength approximation (MLWA) and Mie theory. In order to investigate temperature effect on these characteristics, the optical constants of VO_2 at room temperature and above the T_c are used in calculations. Since there is no unique function that can thoroughly describe the temperature dependent dielectric constant of VO_2, the experimental data are utilized for this purpose extracted from [6]. It is assumed that the surrounding medium of the nanosphere is air.

2.1 Dipole Approximation

Optical responses of a VO_2 nanosphere with optical constant $\varepsilon = \varepsilon_1 + i\varepsilon_2$, immersed in a medium with permittivity of ε_m are simply computed by dipole approximation. Notice that the dimension of nanosphere must be much smaller than wavelength (>1% wavelength). The real (ε_1) and imaginary parts (ε_2) of VO_2 dielectric constants above and below the T_c are shown in Fig.1. By applying this method, the absorption, scattering and extinction cross sections are expressed respectively as follow:

$$C_{\text{abs}} = k\,\mathrm{Im}\{\alpha\}, C_{\text{sca}} = \frac{k^4}{6\pi}|\alpha|^2, C_{\text{ext}} = C_{\text{abs}} + C_{\text{sca}} \quad (1)$$

where k is the wave number and α is polarizability coefficient of nanosphere obtained by ($\alpha = 4\pi a^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}$) [7]. The parameter a is the radius of nanosphere. The dimensionless optical efficiencies are computed as follow:

$$Q_i = \frac{C_i}{A} \quad i \in \{\text{abs}, \text{sca}, \text{ext}\} \tag{2}$$

in which A is geometrical cross section illuminated by incident light. This parameter corresponds to πa^2. The polarizability experiences a resonant enhancement when the ($|\varepsilon+2\varepsilon_m|$) is minimized, which for the small or slowly varying ε_2, simplifies to $\varepsilon = -2\varepsilon_m$ (Fröhlich condition) [8]. This enhancement is observed in metallic phase of VO_2 nanosphere (355 K). In this case, the real part of dielectric constant becomes negative as can be seen in Fig. 1.

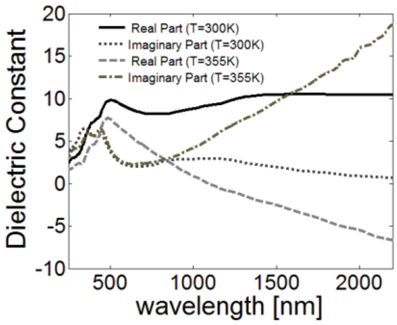

Figure 1: Experimental dielectric constant of VO_2, below and above the T_c, extracted from [6]

2.2 Modified Long Wavelength Approximation

As the radius of nanospheres increases, DA loses its accuracy and is not applicable. However, by using modified polarizability ($\tilde{\alpha}$), DA can be utilized for the nanospheres in which dimensions are less than 10% of wavelength. By calculating $\tilde{\alpha}$, the optical cross sections and efficiencies can be obtained by prior equations. The modified polarizability is expressed as $\dfrac{\alpha}{1-\frac{2}{3}ik^3\alpha-\frac{1}{a}k^2\alpha}$ [9].

2.3 Mie Theory

Mie theory is a powerful method in computing optical properties of nanospheres. In this procedure, electromagnetic fields are described by spherical harmonics in spherical coordinate. By satisfying the boundary conditions and calculating the scattering coefficients $\{a_n, b_n\}$, optical cross sections are achieved as follow:

$$C_{\text{ext}} = \frac{2\pi}{k^2}\sum_{n=1}^{\infty}(2n+1)\,\text{Re}\left[a_n + b_n\right]$$
$$C_{\text{sca}} = \frac{2\pi}{k^2}\sum_{n=1}^{\infty}(2n+1)\left(|a_n|^2 + |b_n|^2\right) \tag{7}$$

where n is the order of the Riccati-Bessel functions. In order to obtain optical efficiencies, equation (2) is used [7].

3 Results and Discussion

The optical efficiencies and electric field distribution of a 20 nm nanosphere in metallic phase are presented in Fig.2 (a,b) and compared with the same dimension Ag nanosphere.

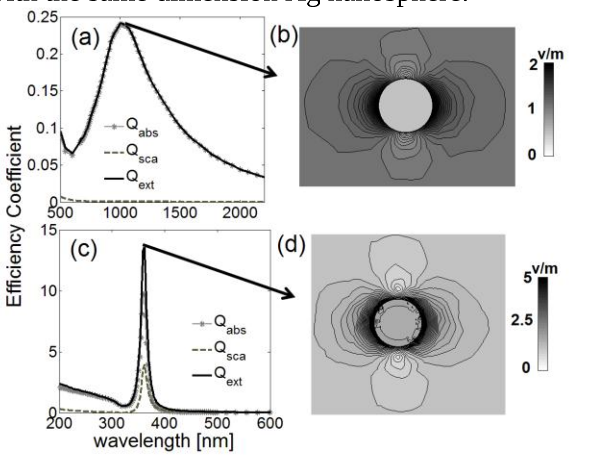

Figure 2: (a) and (b) Efficiency coefficients and electric field distribution of 20 nm VO_2 nanosphere at T=355K, (c) and (d) Efficiency coefficients and electric field distribution of 20 nm Ag nanosphere

There is a resonance around 1000 nm in spectra of VO_2 in metallic phase. Due to the electric field distribution, the origin of this resonance is an electric dipole. The extinction efficiency of a 20 nm Ag nanosphere is shown in the Fig. 2(c). The enhancement in LSPR of Ag is much higher than VO_2 in metallic phase. However, there is a little change in the LSPR of Ag nanoparticle when the particles are heated from RT up to 500 °C [10]. According to Fig. 1, the real part of VO_2 is close to zero in resonance wavelength that is contrary to plasmon resonance condition. It seems that the imaginary part of VO_2 has an extreme effect on the resonance wavelength; therefore the effect of this parameter on VO_2 resonance is examined.

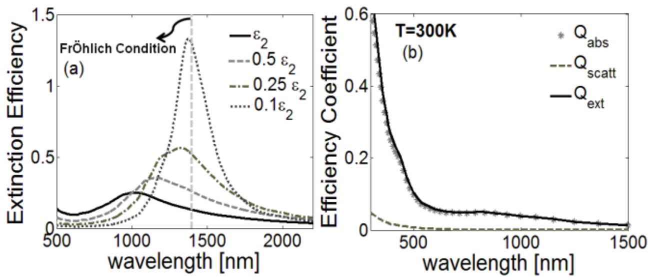

Figure 3: (a) Effects of imaginary part of VO_2 dielectric constant on the spot of LSPR wavelength, (b) Optical properties of 20 nm VO_2 nanosphere at RT.

Fig. 3(a) shows that the extinction spectrum of 20 nm nanosphere approaches to Fröhlich condition as the value of imaginary part for VO_2 is lowered by 0.5, 0.25 and 0.1 factors. It can be concluded that the principle of resonance around 1000 nm is the LSP which is influenced severely by the imaginary part of the dielectric constant. By lowering the temperature, LSPR disappears; therefore this resonance can be switched thermally as can be seen in Fig.3 (a).

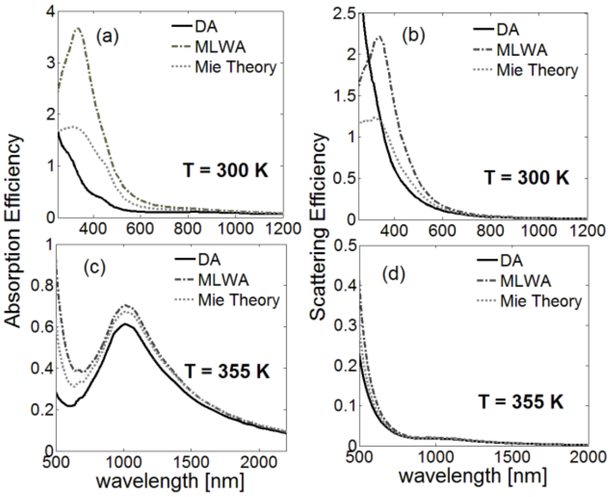

Figure 4: Optical properties of 50 nm VO_2 nanosphere, (a) and (b) at RT, (c) and (d) above T_c.

The size effect on the optical spectra of VO_2 nanospheres for insulator and metallic phases is investigated. For this reason, the absorption and scattering efficiencies of 50 nm and 100 nm are illustrated in Fig. 4, and Fig. 5, respectively.

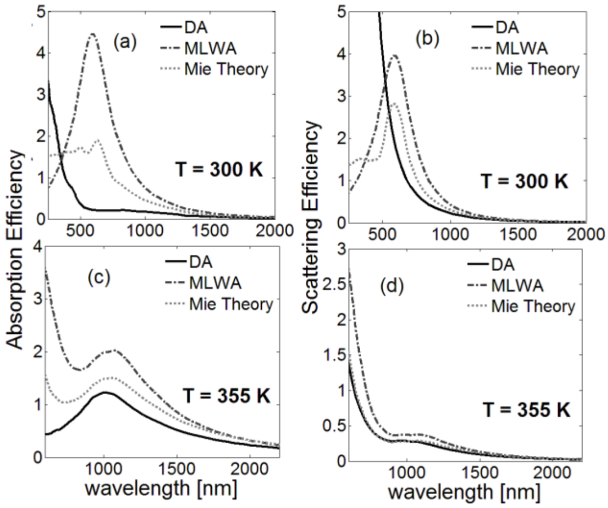

Figure 5: Optical properties of 100 nm VO_2 nanosphere, (a) and (b) at RT, (c) and (d) above T_c.

According to the obtained results, in the insulator phase (T=300K), there is a peak in the optical spectra for 50 nm and 100 nm nanospheres in the visible range. This peak is associated with combined modes. By raising the temperature, VO_2 experiences IMT and becomes metal, conducts to a large absorption and extinction coefficients at the wavelength of 1011 nm for 50 nm nanosphere. The LSPR redshifts and broadens as the radius increases, which occurs in 1064 nm for 100 nm nanosphere. This LSPR is obvious in scattering spectra for $r \geq 100\ nm$. More surprisingly, the absorption efficiency is higher than the scattering in the vicinity of the LSPR peaks in all cases.

4 Conclusion

The optical properties of VO_2 nanosphere in insulator and metallic phases, and also size effect on these characteristics have been investigated. VO_2 nanosphere exhibits LSPR in metallic phase, which disappears in insulator case. Consequently VO_2 can switch its LSPR thermally, which makes this material practical in temperature dependent optical devices. By increasing dimension of VO_2 nanosphere, the LSPR redshifts slowly and also a peak is observed in optical spectra in insulator case which its origin is combined modes.

5 References

[1] F.J. Morin, “Oxides which show a metal to insulator transition at the Neel temperature”, Phys. *Rev. Lett.*, Vol. 3, No. 1, pp. 34-36, 1959.

[2] V. P. Malinenko, L. A. Aleshina, A. L. Pergament, et al, “Switching effects and metal− insulator transition in Manganese Oxide”, *J. Sel. Top. Nano Electron. Comput.*, Vol. 1, No.1, pp: 44-50, 2013.

[3] S.K. Earl, T.D. James, T.J. Davis, et al., “Tunable optical antennas enabled by the phase transition in vanadium dioxide”, *Opt. Express*, Vol. 21, No. 22, pp. 27503-27508.

[4] S.K. Earl, T.D. James, D.E. Gómez, et al., “Switchable polarization rotation of visible light using a plasmonic metasurface”, *APL Photonics*, Vol. 2, No. 1, pp. 016103-1-8.

[5] H. Zhou, X. Cao, M. Jiang, et.al, “Surface plasmon resonance tunability in VO2/Au/VO2 thermochromic structure”, *Laser Photon Rev*., Vol. 8, No. 4, pp. 617-625, 2014.

[6] H.W. Verleur, A.S. Barker Jr, C.N. Berglund, “Optical properties of VO_2 between 0.25 and 5 eV”, *Phys. Rev.*, Vol. 172, No. 3, pp. 788-798, 1968.

[7] C.F. Bohren, D.R. Huffman, “*Absorption and scattering of light by small particles*”, John-Wiley 2008.

[8] S.A. Maier, 2007. “*Plasmonics: fundamentals and applications*”,Springer 2007.

[9] K.L. Kelly, E. Coronado, L.L. Zhao, et al., “The optical properties of metal nanoparticles: the influence of size, shape, and dielectric environment”, *J. Phys. Chem. B*, Vol. 107, No. 3, pp. 668-677, 2003.

[10] R. H. Doremus, “Optical properties of small silver particles*”, J. Chem. Phys.*, Vol. 42, No. 1, pp: 414-417, 1965.