

## ویژگی‌های نوری نانوکره اکسید وانادیم دارای تغییر فاز

نوشین ولی‌زاده شه‌میرزادی و توکل پاکیزه

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چکیده - در این مقاله ویژگی‌های نوری نانوکره همگن و غیر 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 ( $341K$ ) 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 طول موج نور مرئی می‌باشد. نانوکره‌های  $VO_2$  در فاز فلزی در مقایسه با نانوکره نقره طیف وسیع‌تری دارند، بعلا‌ه میدان الکتریکی نانوکره 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

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**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<sub>2</sub> Nanosphere with Phase Transition

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## 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<sub>2</sub>) and etc. [1-2]. Among these IMT materials, VO<sub>2</sub> that its properties were observed by Morin [2] has an outstanding importance. VO<sub>2</sub> thin film is a monoclinic insulator at room temperature (RT). By approaching to a critical temperature ( $T_c = 341$  K), VO<sub>2</sub> 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<sub>2</sub> dielectric constant becomes negative as the wavelength increases, which can lead to plasmon resonance. Due to unique properties of VO<sub>2</sub>, 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<sub>2</sub> 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<sub>2</sub>, can rotate the polarization axis of incident visible light [4]. According to suitability of VO<sub>2</sub> in many optical applications, the understanding of VO<sub>2</sub> properties in different phases seems to be necessary. In this paper, optical characteristics of VO<sub>2</sub> nanosphere and the

temperature effect on these characteristics are investigated. The obtained results demonstrate that individual VO<sub>2</sub> nanosphere experiences LSPR at about 1000 nm and can switch LSPR thermally.

## 2 Theories and Models

Optical properties of VO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>, 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<sub>2</sub> nanosphere with optical constant  $\varepsilon = \varepsilon_1 + i\varepsilon_2$ , immersed in a medium with permittivity of  $\varepsilon_m$  are simply computed by dipole approximation. Notice that the dimension of nanosphere must be much smaller than wavelength ( $>1\%$  wavelength). The real ( $\varepsilon_1$ ) and imaginary parts ( $\varepsilon_2$ ) of VO<sub>2</sub> 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:

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

where  $k$  is the wave number and  $\alpha$  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:

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

in which  $A$  is geometrical cross section illuminated by incident light. This parameter corresponds to  $\pi a^2$ . The polarizability experiences a resonant enhancement when the  $(|\varepsilon + 2\varepsilon_m|)$  is minimized, which for the small or slowly varying  $\varepsilon_2$ , simplifies to  $\varepsilon = -2\varepsilon_m$  (Fröhlich condition) [8]. This enhancement is observed in metallic phase of VO<sub>2</sub> nanosphere (355 K). In this case, the real part of dielectric constant becomes negative as can be seen in Fig. 1.

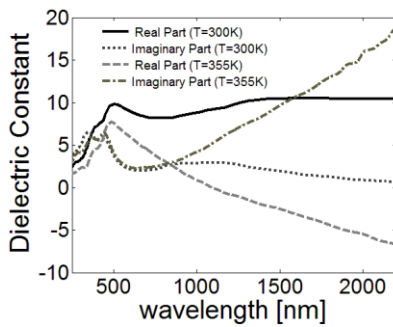


Figure 1: Experimental dielectric constant of VO<sub>2</sub>, below and above the T<sub>c</sub>, extracted from [6]

## 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  $\frac{\alpha}{1 - \frac{2}{3}ik^3\alpha - \frac{1}{a}k^2\alpha}$  [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:

$$C_{\text{ext}} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n+1) \text{Re}[a_n + b_n] \quad (7)$$

$$C_{\text{sca}} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n+1) (|a_n|^2 + |b_n|^2)$$

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.

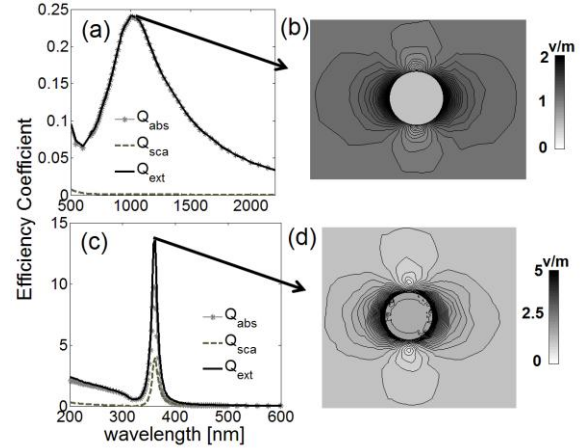


Figure 2: (a) and (b) Efficiency coefficients and electric field distribution of 20 nm VO<sub>2</sub> nanosphere at T=355K, (c) and (d) Efficiency coefficients and electric field distribution of 20 nm Ag nanosphere

There is a resonance around 1000 nm in spectra of VO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> is close to zero in resonance wavelength that is contrary to plasmon resonance condition. It seems that the imaginary part of VO<sub>2</sub> has an extreme effect on the resonance wavelength; therefore the effect of this parameter on VO<sub>2</sub> resonance is examined.

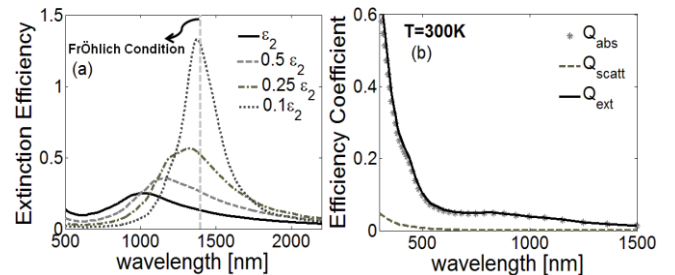


Figure 3: (a) Effects of imaginary part of VO<sub>2</sub> dielectric constant on the spot of LSPR wavelength, (b) Optical properties of 20 nm VO<sub>2</sub> nanosphere at RT.

Fig. 3(a) shows that the extinction spectrum of 20 nm nanosphere approaches to Fröhlich condition as the value of imaginary part for VO<sub>2</sub> 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).

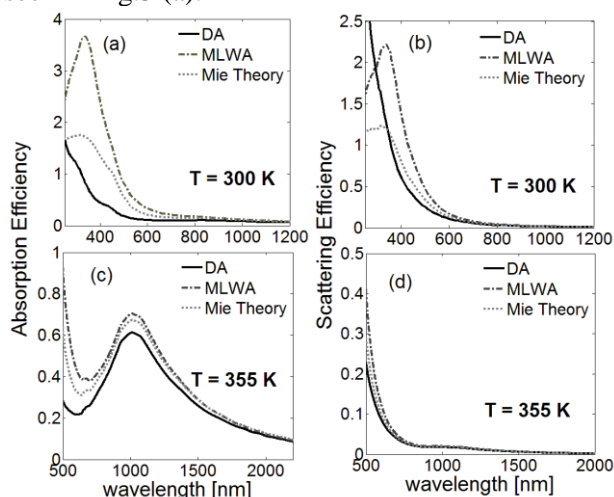


Figure 4: Optical properties of 50 nm VO<sub>2</sub> nanosphere, (a) and (b) at RT, (c) and (d) above T<sub>c</sub>.

The size effect on the optical spectra of VO<sub>2</sub> 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.

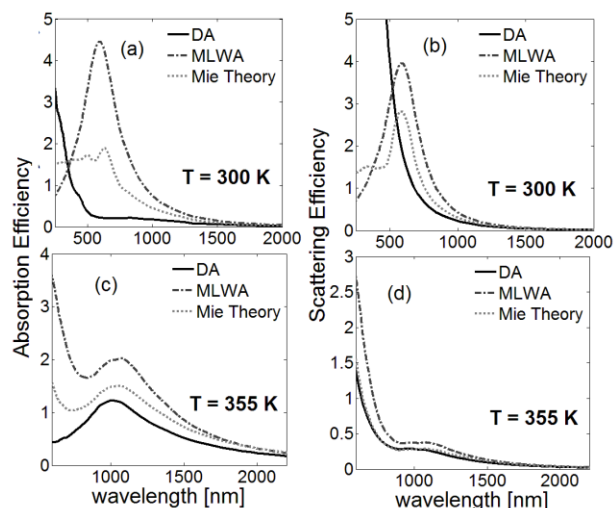


Figure 5: Optical properties of 100 nm VO<sub>2</sub> nanosphere, (a) and (b) at RT, (c) and (d) above T<sub>c</sub>.

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<sub>2</sub> 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<sub>2</sub> nanosphere in insulator and metallic phases, and also size effect on these characteristics have been investigated. VO<sub>2</sub> nanosphere exhibits LSPR in metallic phase, which disappears in insulator case. Consequently VO<sub>2</sub> can switch its LSPR thermally, which makes this material practical in temperature dependent optical devices. By increasing dimension of VO<sub>2</sub> nanosphere, the LSPR redshifts slowly and also a peak is observed in optical spectra in insulator case which its origin is combined modes.

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