

## Solution-Processed VO<sub>2</sub>@Ag Nanoparticles for Modifying the Color of VO<sub>2</sub> Smart Films

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**Abstract.** Recently, researchers focus on how to prepare practical VO<sub>2</sub> films with varied colors. Herein, we developed a facile solution process to modify the spectrum of VO<sub>2</sub> so that the color of VO<sub>2</sub> film could be tuned. The VO<sub>2</sub> nanoparticles were functionalized by the 3-aminopropyltrimethoxysilane (APTMS), and the reaction condition of APTMS functionalization was investigated. The VO<sub>2</sub>@Ag was obtained by a two-step method. The UV-vis spectrum of VO<sub>2</sub>@Ag exhibited an absorption band at 451 nm, which meant the visible spectrum of VO<sub>2</sub> could be modified by the Ag coating. Therefore, the VO<sub>2</sub>@Ag films can display a corresponding complementary color. This technique will play an important role in practical application of VO<sub>2</sub> smart films.

### Introduction

Vanadium dioxide (VO<sub>2</sub>) has been demonstrated to be a promising candidate material for the thermochromic smart films due to their reversible phase transition [1]. It can be transformed from monoclinic type VO<sub>2</sub> (M) (space group: P2<sub>1</sub>/c) to tetragonal rutile type VO<sub>2</sub> (R) (space group: P4<sub>2</sub>/mnm) at a critical temperature (68 °C for bulk VO<sub>2</sub>), which results in an abrupt change in optical properties from transparent to translucent at the infrared spectral region. However, the VO<sub>2</sub>-based smart films have not been popular because of the high phase transition temperature, low visible transmittance, poor solar energy modulation ability, and undesirable color. The color of intrinsic VO<sub>2</sub> film is not pleasant because it is brown. In a real application, we can find that the color of windows most used in the modern building is the blue color or other similar, which is more likely accepted by people. In this work, we focus on the color modulation of the VO<sub>2</sub>-based films.

Surface plasmon resonance (SPR) is a signature optical property of noble metal nanoparticles such as Au, Ag and Cu. The wavelength at absorption maximum ( $\lambda_{SPR}$ ) and the absorption intensity are sensitive to many factors, including not only the properties of the metal particle but also the surrounding dielectric environment. Xu *et al.* utilized radio frequency magnetron sputtering to deposit Ag [2] or Au [3] nanoparticles on the VO<sub>2</sub> films surface. Binion *et al.* prepared VO<sub>2</sub>/Au composite films with different color via chemical vapor deposition (CVD) [4, 5]. The absorption band of the VO<sub>2</sub> film had been changed with the sizes of metal nanoparticles varied. Thus, the film with different colors. However, whether magnetron sputtering or CVD needs harsh conditions, which is not conducive to practical production of large-scale and cost-effective smart films.

So far until now, there is few report involved in synthesis VO<sub>2</sub>@metal nanoparticles via solution process. In this work, we proposed a solution processing method to modify the spectrum of the VO<sub>2</sub>,

by coating VO<sub>2</sub> with Ag nanoparticles. The VO<sub>2</sub>@Ag exhibited an absorption peak at 451 nm. It demonstrated that this method could modify the spectrum of the VO<sub>2</sub> and tune the color of the VO<sub>2</sub> films. This technique will play a role in practical application of vanadium dioxide smart windows.

## Experiment

0.2M NH<sub>4</sub>HCO<sub>3</sub> aqueous solution was dropped into 0.1M VOSO<sub>4</sub> aqueous solution. The greywhite precipitation was recovered by filtration and washed with copious amounts of water. For attaining VO<sub>2</sub> (M), the greywhite precursor was redispersed in water and then transferred to a 100-mL autoclave. The autoclave was maintained at 280 °C for 24h and then cooled to room temperature naturally. Dark blue black precipitates were obtained and washed with deionized water and ethanol several times, and dried at 60°C for 8h. 0.166g VO<sub>2</sub> (M) above mentioned was dispersed in 200mL absolute ethanol by ultrasonic for 30 min.

Then, excess of 3-aminopropyltrimethoxysilane (APTMS) was added to VO<sub>2</sub> nanoparticles aqueous solution under vigorously stirred and the mixture was allowed to react for 12h at the room temperature. The solution was gently refluxed for 1 additional hour in 80°C to enhance covalent bonding between the APTMS and the VO<sub>2</sub> nanoparticles. The APTMS-functionalized VO<sub>2</sub> nanoparticles were washed by ethanol at least 5 times to remove the unattached APTMS.

The ultrafine Ag nanoparticles as Ag seeds was produced by reduction of silver nitrate. Tannin acid was used as reductant. 0.01g functionalized VO<sub>2</sub> was added into 100 ml deionized water and dispersed by ultrasonic for 30 min. After adjusting the pH, the solution was transferred into a flask contained Ag seeds, then stirred for 1 h, and allowed standing for another 2 h. The resulting was washed by water for several times until there was no free Ag nanoparticle.

Finally, the VO<sub>2</sub>@Ag seeds particles were dispersed in AgNO<sub>3</sub> aqueous solution, then the sodium borohydride as reductant was added into for growth of Ag seed and preparation of VO<sub>2</sub>@Ag nanoparticles.

## Results

### Reaction Condition of the Functionalization with APTMS.

The functionalization was carried out by mixing the solution of nanoparticles with a certain amount of APTMS (sufficient to provide five monolayer coatings of the silica nanoparticles). The area on the nanoparticles surface covered by each APTMS molecule was assumed to be nominally 0.6 nm<sup>2</sup>[6]. Fourier transform infrared (FT-IR) spectra was used to detect the organic functional groups. Fig. 1 (black line) shows FT-IR spectra of intrinsic APTMS. The stretch mode of –NH<sub>2</sub> and N-H groups of APTMS are observed at approximately 3356 cm<sup>-1</sup> and 3284 cm<sup>-1</sup>, respectively. And the bands at 1595 cm<sup>-1</sup> and 1471 cm<sup>-1</sup> are due to the symmetric and asymmetric deformation mode of the hydrogen bonded amine group, respectively. However, there is no any band in the spectrum (Fig.1 blue line) of Sample I (Table 1) near 3356 cm<sup>-1</sup> or 3284 cm<sup>-1</sup>. It indicates that the functionalization was failed.

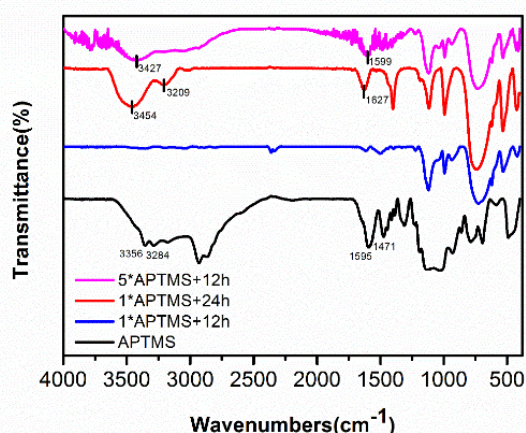


Fig. 1 FT-IR spectra of VO<sub>2</sub> nanoparticles functionalized by APTMS with different concentration and time.

There may be two reasons for the failure of functionalization. First, the concentration of APTMS was too low. In the initial case, the addition amount of APTMS was the theoretical value above mentioned. In fact, considering the hydrolysis of APTMS and the surface activity of VO<sub>2</sub>, these factors make the amount of APTMS less than the amount actually required. Second, the reaction time is inadequate. It may need more energy or more time to bond. Thus, the reaction condition had been investigated. (Table 1)

Table 1. The reaction condition of APTMS functionalization.

Sample	Amount of APTMS	Stirring time	Refluxed time	Functionalization
I	1 aliquot	12 h	1 h	×
II	5 aliquot	12 h	1 h	√
III	1 aliquot	24 h	1 h	√

The pink line and red line in Fig. 1 are the FT-IR spectra of the results of increasing amount (Sample II) and extending time (Sample III), respectively. There are obviously difference from Sample I. The bands at 3427 cm<sup>-1</sup>, 1599 cm<sup>-1</sup> (pink line) and 3454 cm<sup>-1</sup>, 1627 cm<sup>-1</sup> (red line) prove that the APTMS was bonding on the VO<sub>2</sub> surface. The band of -NH<sub>2</sub> have shifted to higher wavenumbers from 3356 cm<sup>-1</sup> to 3454 cm<sup>-1</sup> (red line) and 3427 cm<sup>-1</sup> (pink line). This shift is probably result from the existence of the V-O bond. These results indicated that both the increasing the amount of APTMS and extending the reaction time could functionalized VO<sub>2</sub> with APTMS successfully.

### The UV-vis spectra of VO<sub>2</sub>@Ag seeds and VO<sub>2</sub>@Ag.

UV-vis spectra is an efficient and precise method of characterization of noble metal nanoparticles because of the SPR. Based on Mie theory, the SPR frequency ( $\lambda_{SPR}$ ) is associated with the size, shape, dielectric constant of metal nanoparticle, and the dielectric constant of material around metal particles[7]. In order to prove the Ag seeds had already deposited on the VO<sub>2</sub> surface, the UV-vis spectra of functionalized VO<sub>2</sub>, silver colloids and VO<sub>2</sub>@Ag seeds at different temperature was measured, respectively (Fig.2). It can be found that there is no absorption peak in the curve of VO<sub>2</sub>, whether low or high temperature. And the  $\lambda_{SPR}$  of Ag seeds ( $\lambda_{SPR}=407$  nm) at low temperature is consistent with it at high temperature. Because the test process was completed within 5 minutes, the coagulation

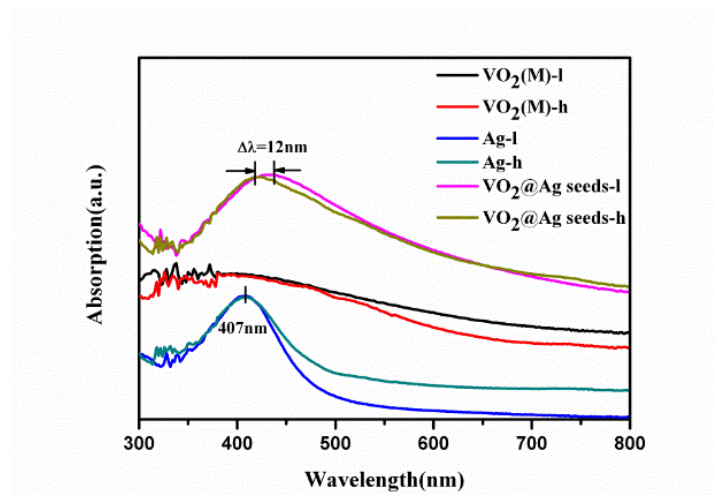


Fig. 2 Absorption spectra of Ag, VO<sub>2</sub>, VO<sub>2</sub>@Ag seeds particles at low and high temperature.

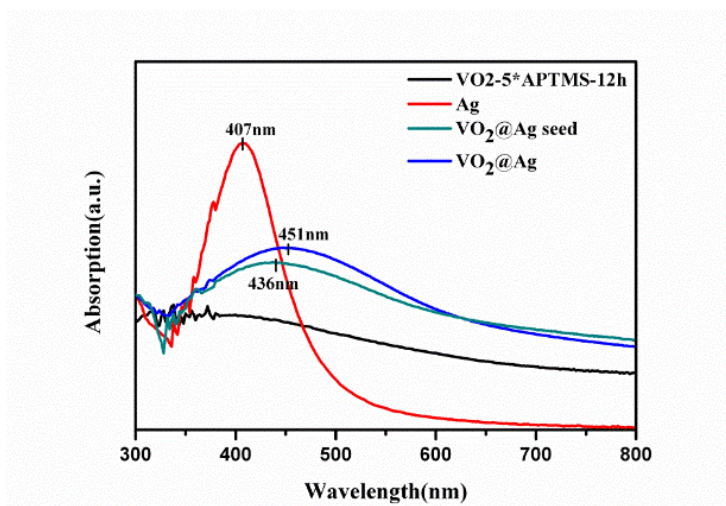


Fig. 3 Absorption spectra of Ag, VO<sub>2</sub>, VO<sub>2</sub>@Ag seeds, and VO<sub>2</sub>@Ag particles.

cause by heating could be ignored. However, the  $\lambda_{\text{SPR}}$  of VO<sub>2</sub>@Ag seeds at low temperature is 436 nm, and 424 nm at high temperature. Because the Fermi level of VO<sub>2</sub> is lower than the Fermi level of Ag, the free electrons on the Ag nanoparticle surfaces will remove to the VO<sub>2</sub> surfaces [8]. That results in decrease of electron density on the Ag nanoparticle surfaces. According the Mie theory, the  $\lambda_{\text{SPR}}$  is inversely proportional to the square root of electron density. Therefore, the  $\lambda_{\text{SPR}}$  shifted from 407 nm to 436 nm when the Ag particles attached the VO<sub>2</sub>. Additionally, the dielectric of VO<sub>2</sub> (M) (low-temperature phase) is lower than VO<sub>2</sub>(R) (high-temperature phase). On the basis of Mie theory mentioned above, the  $\lambda_{\text{SPR}}$  has a blue shift ( $\Delta\lambda_{\text{SPR}}=12$  nm) due to the change of the dielectric constant of VO<sub>2</sub>. All the phenomena can be ascribed to that Ag nanoparticles deposited on the VO<sub>2</sub> surfaces.

After the growth of Ag nanoparticles on VO<sub>2</sub> surface, the  $\lambda_{\text{SPR}}$  was shifted from 436 nm to 451 nm due to the size of Ag particles increase (Fig. 3). It implied that the  $\lambda_{\text{SPR}}$  of the VO<sub>2</sub>@Ag could be easily controlled by the size of Ag particles, which was according to the concentration of AgNO<sub>3</sub>. Therefore, the VO<sub>2</sub>-based smart films with varied colors could be prepared by our method.

## Conclusion

In this work, we developed a facile method to tailor the undesired color of VO<sub>2</sub>-based smart film. VO<sub>2</sub>@Ag core-shell nanoparticles were synthesized via solution process. The UV-vis spectrum of VO<sub>2</sub>@Ag shows that there is an absorption band at 451 nm, which means the visible spectrum of

VO<sub>2</sub> could be modified by the Ag coating. Therefore, the VO<sub>2</sub>@Ag films may display a corresponding complementary color. This work paves the way to the scale-up and fast production of VO<sub>2</sub>-based smart film with varied colors.

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