

VO₂/ZnS core-shell nanoparticle for the adaptive infrared camouflage application with modified color and enhanced oxidation resistance

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ABSTRACT

VO₂ has attracted extensive attention as an adaptive camouflage material due to its structural change during the metal-insulator transition (MIT) at 68 °C, which can fast respond to ambient temperature and actively modulate infrared emissivity. However, the thermal instability and undesirable color have restricted its applications in multi-spectral camouflage. In this study, the VO₂/ZnS core-shell nanoparticles were synthesized via a homogeneous precipitation method. The VO₂ nanoparticle core exhibited a remarkable infrared emissivity modulation ability in the mid-wavelength and long-wavelength thermal atmospheric windows. The ZnS shell, as an infrared transparent material, not only modified the color of VO₂ nanoparticle from unpleasant blue-black to gray-green that adapts to visible camouflage in the woodland background, but also significantly enhanced the oxidation resistance. This is the first report of such a single nanoparticle structure with both variable infrared emissivity and desirable color that offer significant potential for multi-spectral camouflage application.

1. Introduction

Vanadium dioxide (VO₂) has drawn significant attention for its metal-insulator transition, which can respond to environmental temperatures to modulate infrared irradiation from a transparent state at low-temperature to a reflective state at high-temperature [1–3]. Accompanied by the phase transition, the infrared emissivity of VO₂ changes significantly. The variable emissivity of VO₂ that can sense and adapt to temperature variations of the object coated by the pellets, coatings or thin films, provides a feasible approach for adaptive infrared camouflage through regulating the thermal power to always maintain the minimum radiation energy difference between the object and background. Therefore, VO₂ is considered to be the most important and promising material for adaptive infrared camouflage [4–6].

However, the unpleasant color of VO₂ restricts its application to the camouflage due to the existence of incompatible with the visible light band [7,8]. It is difficult to apply to multi-spectral camouflage. Besides, VO₂ is gradually oxidized into toxic V₂O₅ in higher temperature [9,10], which leads to a considerable deterioration of its infrared optical properties. Therefore, it is urgently required to modify the color and enhance stability against oxidation without affecting its infrared optical performance. The core-shell structure can enhance oxidation resistance and modify the color of powders [11–15]. Some pioneering works using VO₂ as a core and SiO₂ [16–19], TiO₂ [12] as a shell for the formation of core-shell composites have been reported. Gao [16] et al. prepared

VO₂@SiO₂ core-shell nanoparticles which improved anti-oxidation and optical properties. Li [12] et al. prepared VO₂@TiO₂ core-shell nanorods which modified the intrinsic color of VO₂ from yellow to light blue and enhanced the chemical stability of VO₂. These shells have high visible or near infrared transmittance, but low long-wave infrared transmittance owing to the existence of strong phononpolariton resonances of SiO₂ at 9.7 μm and broad absorption peaks of TiO₂ in the infrared region [20,21]. Zinc sulfide (ZnS) crystal is usually used in multi-band visible and infrared systems because of its wide transmission wavelength region [22,23]. Although ZnS exhibits advantages over SiO₂ and TiO₂, because of its infrared transparency, there are no reports on the production of high performance VO₂/ZnS core-shell nanoparticle for the adaptive camouflage application with modified color and enhanced oxidation resistance.

In this study, we report the synthesis of novel VO₂/ZnS core-shell nanoparticles with thioglycolic acid as ligand via a homogeneous precipitation method. The VO₂/ZnS core-shell nanoparticles exhibit excellent performances: infrared emissivity modulation ability from VO₂ core for infrared camouflage, modified color from ZnS shell for visible camouflage and enhanced the stability of VO₂. This is the first report of such a single nanoparticle structure with both variable infrared emissivity and desirable color that offer significant potential for multi-spectral camouflage application.

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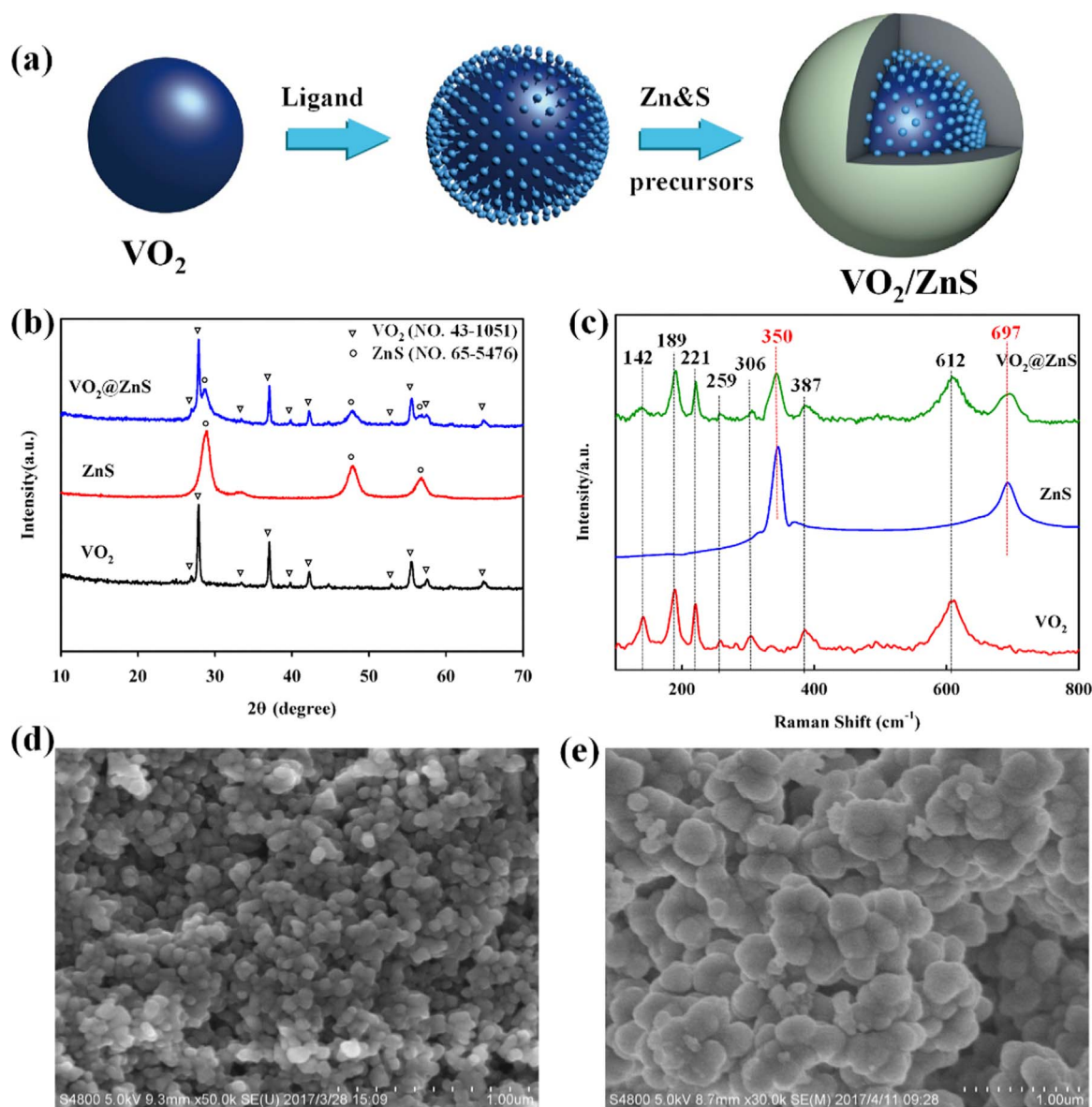


Fig. 1. (a) Schematic illustration of the route to synthesize VO_2/ZnS core-shell nanoparticles, (b) XRD patterns and (c) Raman spectra of VO_2 , ZnS and VO_2/ZnS core-shell nanoparticles, SEM images of (d) VO_2 and (e) VO_2/ZnS core-shell nanoparticles.

2. Experimental section

2.1. Preparation of VO_2 nanoparticles

All reagents were purchased from Aladdin chemical reagent corporation and used without further purification. VO_2 nanoparticles were prepared by the one-step hydrothermal method using a vanadium source of ammonium metavanadate (NH_4VO_3) and a reducing agent of diamide hydrochloride ($\text{N}_2\text{H}_4\cdot\text{HCl}$). In a typical synthesis, 1.17 g NH_4VO_3 and 0.70 g $\text{N}_2\text{H}_4\cdot\text{HCl}$ were dispersed in 70 mL deionized water. The mixture was stirred for 45 min and then transferred to a 100 mL Teflon-lined stainless-steel autoclave. The hydrothermal reaction was carried out at 280 °C for 18 h and then air-cooled to room temperature. The final products were collected via centrifugation, washed with deionized water and ethanol three times and dried in a vacuum drying oven at 80 °C for 10 h.

2.2. Preparation of VO_2/ZnS core-shell nanoparticles

To prepare the VO_2/ZnS core/shell nanoparticles, the as-

synthesized VO_2 nanoparticles were ultrasonically dispersed in 100 mL of deionized water to obtain a well-dispersed suspension. Then, 2 mL of thioglycolic acid was added into the suspension under vigorous stirring, and the mixture was incubated at 60 °C for 2 h. The mixture was concentrated by centrifugation at 8000 rpm for 10 min. After the supernatant was removed, the isolated nanoparticles were dispersed in an aqueous PVP solution. The mixture solution of PVP and nanoparticles were vortexed for 10 min, followed by the addition of 2.20 g zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$). Finally, 0.75 g thioacetamide (CH_3CSNH_2) was added. The reaction mixture was incubated at 90 °C for 2 h. The final products were collected via centrifugation, washed with deionized water and ethanol three times and dried in a vacuum drying oven at 80 °C for 10 h.

2.3. Characterization

X-ray diffraction (XRD) analyses were conducted on a Bruker D8 advance diffractometer equipped with monochromatic $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406$ nm) using a voltage and current of 40 kV and 40 mA, respectively. The composition of the nanoparticles was measured via a

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