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Vanadium dioxide nanopowders with tunable emissivity for adaptive infrared camouflage in both thermal atmospheric windows

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ABSTRACT

Vanadium dioxide, which has been demonstrated as negative differential thermal emissivity materials for emissivity engineering application, is regarded as the most important and promising material for adaptive infrared camouflage. This study describes the synthesis and characterization of high purity, uniform VO_2 nanopowders by a single-step hydrothermal method and their thermal polymorphism. A dramatic phase transition of the monoclinic VO_2 nanopowders to a tetragonal phase upon heating and the accompanying change in the IR emissivity are demonstrated. Importantly, we demonstrate the tunability of the infrared radiation intensity of VO_2 nanopowders in both mid- and far-IR thermal atmospheric windows, for the first time. The structural transition is analyzed by variable temperature XRD and temperature-dependent Raman spectroscopy. Furthermore, an unexpected structural change in the same region of the sample was observed in a transmission electron microscope, which provides a direct mechanistic understanding of the infrared emissivity variation. Our study makes a significant contribution to the state-of-the-art in thermal camouflaging, because this study demonstrates that the VO_2 nanopowders can be extremely promising camouflage materials in the area of adaptive infrared camouflage technology both in the far-infrared and mid-infrared regions and the material is suitable for substrates with large surface areas and/or complex morphologies.

1. Introduction

Adaptive camouflage is a type of technology capable of producing a “chameleon” effect to adapt to the surroundings [1–4]. The most convincing examples of active camouflage in animals are the octopus and chameleons, which can blend into their surroundings by changing skin color [5,6]. Similar to this visual coloration, camouflage in the infrared region is a critically important technique used for cloaking in thermal imaging, which increased attention in numerous military applications [7–9]. The functions of the infrared camouflage materials are mainly obtained through adjustments in its temperature or thermal emissivity to match the environment conditions [10]. Directly adjusting its temperature to that of the target is a feasible but not necessarily an ideal approach, as excessive heat may still be emitted from some areas of the target. Emissivity engineering provides an alternative, practical path for infrared camouflage [11,12]. However, materials suitable for active modulation of emissivity need to be developed.

Vanadium dioxide (VO_2), which undergoes an insulator to metal transition at around 68 °C, has been demonstrated to be an infrared modulating material in emissivity engineering applications [13–16]. Below its phase transition temperature, it has a $P_{21/c}$ monoclinic structure (M phase) with insulating properties, whereas above the phase transition temperature, it transforms to a $P_{42/mnm}$ tetragonal rutile structure (R phase) with metallic properties [17,18]. This reversible phase transition is accompanied by a dramatic change in the infrared optical properties, from a low-temperature transparent state to a high-temperature infrared reflective one, which can result in a change in emissivity. Therefore, VO_2 is considered to be the most important and promising material for adaptive thermal camouflage. Current literature on tuning an object's thermal emissivity using VO_2 has largely focused on the considerable changes in the infrared optical properties of VO_2 films [19–21]. Compared to thin films, VO_2 nanopowders are better suited for substrates with large surface areas and/or complex morphologies owing to both technological and cost issues [22]. In particular, nanopowders can remarkably lessen the stress during phase changes and hence have broader application. In addition, thermal atmospheric windows are conventionally defined by the wavelength limits, 3–5 μm and 8–14 μm, known as the mid wave IR (MWIR) and long wave IR (LWIR) windows, respectively [23]. Currently, the study of the infrared optical properties of VO_2 is mainly focused on the far-infrared regions [11,14,24]. However, the mid-infrared region properties of VO_2 are rarely reported. Thus, application of VO_2 in adaptive

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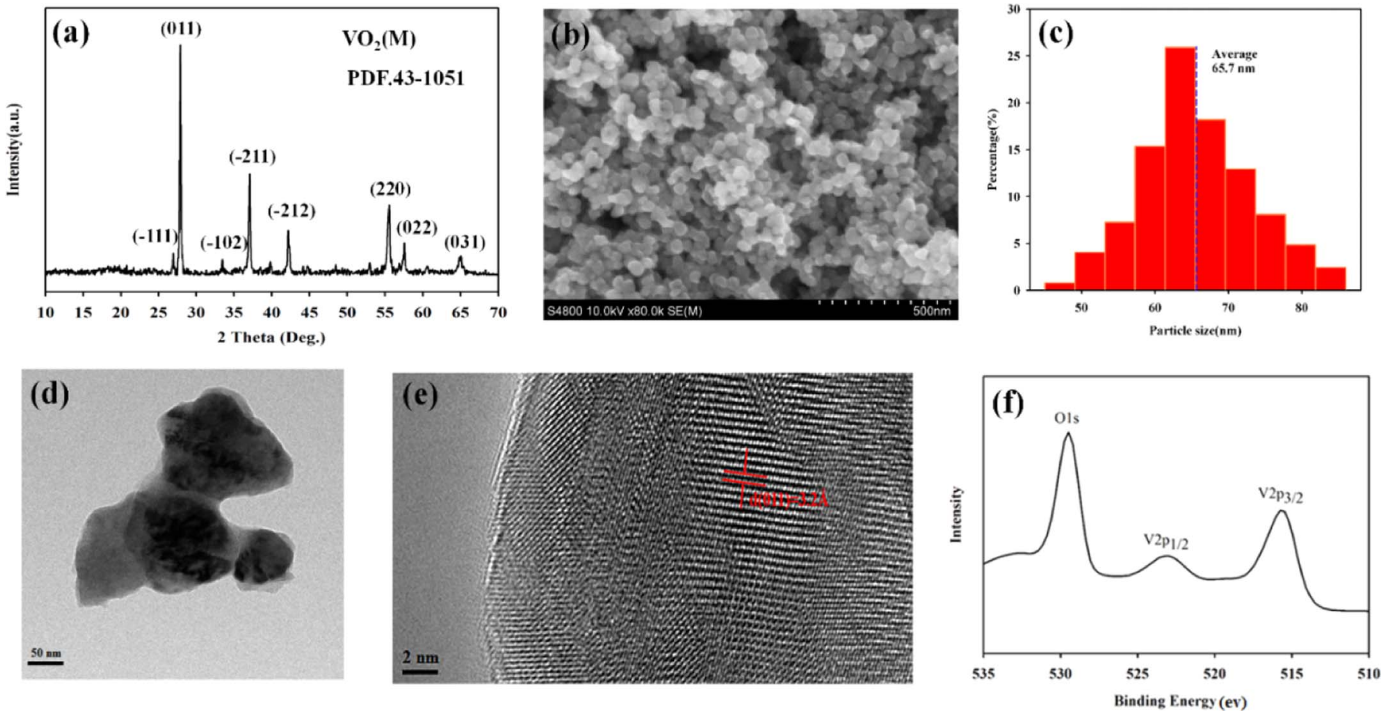

Fig. 1. (a) XRD patterns, (b) SEM images, (c) histogram showing particle size distribution analysis, (d) TEM image, (e) HRTEM, and (f) core level spectrum of V_{2p} of VO_2 samples prepared by a single-step hydrothermal method.

infrared camouflage has been restricted. Consequently, study of the infrared optical properties of VO_2 nanopowders can be considered as an emerging field, and VO_2 nanopowders recognized as promising materials, especially in the wake of recent interest in adaptive thermal camouflage.

Driven by these considerations, uniform VO_2 nanopowders are synthesized by a single-step hydrothermal method. The infrared emissivity variation of the VO_2 nanopowders in both thermal atmospheric windows is then demonstrated. Surprisingly, structural changes in the material could be observed from the same region in a transmission electron microscope, aiding a direct mechanistic understanding of the infrared emissivity variation. This opens new opportunities in adaptive infrared camouflage technology.

2. Experimental section

All reagents were purchased from Aladdin Chemistry Co. Ltd., and were used without further purification. Vanadium pentoxide (V_2O_5, analytically pure) and diamide hydrochloride ($N_2H_4{\cdot}HCl$, analytically pure) were employed as starting materials to prepare a VO^{2+} solution. Concentrated HCl (12 mL, 38%) and a solution containing 2.1 g of $N_2H_4{\cdot}HCl$ were added into an aqueous suspension (50 mL) containing 7.28 g of V_2O_5 with magnetic stirring. After mixing for 30 min, the resulting precursor was transferred into a 100 mL stainless steel autoclave, then being sealed and maintained at 280 °C for 32 h. After the autoclave cooling to room temperature, a dark blue precipitate was obtained. The product was washed with deionized water and ethanol for several times, then centrifuged and dried in vacuum at 60 °C for 12 h.

Nanopowder pellets were all prepared using the same operating conditions by tablet press. A certain mass of VO_2 nanopowders were weighed and fed manually into the die of a single-punch tablet press to produce tablets with about 1 mm thickness using flat-faced punches (13 mm in diameter for emissivity measurement).

The crystalline structure was characterized by XRD through a Rigaku TTR-III equipment with Cu Kα radiation (λ = 0.15418 nm) using a voltage and current of 40 kV and 40 mA, respectively. The microscopic morphology was obtained using a field-emission scanning electron microscope (FESEM, HITACHI S-4800) at an acceleration voltage of 10 kV. The microstructure of the samples were further analyzed using a transmission electron microscope (TEM, JEOL2010) with a LaB_6 source operating at an acceleration voltage of 200 kV. Selected area electron diffraction experiments were carried out in vacuum in a JEOL 2100 transmission electron microscope working at 200 kV. The phase transition behaviors of the resulting products were measured by differential scanning calorimetry (DSC1, METTLER TOLEDO) over the temperature range from 0 to 100 °C using a liquid nitrogen cooling unit. The heating and cooling rates were set at 10 °C/min. Temperature-dependent XRD data were obtined using a diffractometer (Rigaku TTR-III) equipped with a with a Cu Kα radiation (λ = 0.15418 nm). Under steady N_2 flow, the sample was heated (from 20 °C to 100 °C) and cooled (from 100 °C to 20 °C) inside a Rigaku Reactor-X chamber fitted with a Beryllium window. Raman spectra at various temperatures were recorded using a Horiba JY HR Evolution Spectroscopy System. The excitation wavelength is 532 nm, with laser power kept at 1 mW to ensure that thermal heating due to the laser focusing does not trigger the phase transition. External sample temperature was controlled via a programmable heating-cooling stage. The surface roughness of VO_2 nanopowder pellets was measured using Talysurf PGI 1240 profilometer. The profilometer is mounted on an epoxy granite based anti-vibration mount, which provides a firm support for the column and work piece. For measuring roughness, Ra (the arithmetic mean of the departures of the roughness profile from the mean line), and Rq (root mean square (RMS) of average roughness), are considered.

Normal emissivity spectra were measured using a Bruker Vertex 70 Fourier transform infrared spectrometer equipped with a deuterated L-alanine doped triglycine sulfate (DLaTGS) detector and the emission adapter A540. The schematic of experimental setup is shown in Fig. S1 in the Supporting information. The emission adapter allows measuring normal thermal emission spectra of solid samples from 40 °C to 100 °C. A conventional two-temperature calibration procedure was conducted using a polished plate covered with a black organic film (emissivity ε = 0.95) as a blackbody reference. After the calibration, the thermal emission spectra of all samples were acquired at different temperatures