

Electronic Supplementary Information

Synthesis of Monodispersed VO₂@Au Core-semishell Submicroparticles and Their Switchable Optical Properties

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Experimental section

Materials

Vanadium isopropoxide (VO(OiPr)₃, 97%), pyridine (Py, 99%), Au(99.99%), acetone(99%) were obtained from Sigma-Aldrich. All chemicals were used as received without further purification.

Synthesis of V₂O₅·xPy·yH₂O microspheres

The V₂O₅·xPy·yH₂O spheres were prepared by hydrolysis of vanadium isopropoxide VO(OiPr)₃ in acetone/pyridine/water solution. Acetone (24 mL), pyridine (13 mL) and various amounts of distilled water (50 μL for final VO₂ particles with average size 600 nm, 55 μL for 500 nm, 70 μL for 400 nm and 100 μL for 360 nm, respectively) were mixed in a 100 mL flask under vigorous stirring. And then VO(OiPr)₃ (0.3 mL) was quickly injected into the mixture at room temperature and the solution was kept under vigorous stirring for about several minutes. The reaction time was inversely proportional to the amount of water.

The color of the reaction solution changed from clear yellow to cloudy orange. After centrifugation, the resulting precipitation was washed once with acetone and then dried in vacuum overnight.

Thermal treatment

The powders of complex were further dried in a crucible in air at 150°C for one hour to remove most of the Py and water, heated at 300°C for one hour at a rate of 1°C/min to form crystalline

V₂O₅, and reduced to V₂O₃ by annealing in a tube furnace at 500°C for 2 hours at a heating rate of 5°C/min under hydrogen flow (purity 99%, flow rate 0.15 SCFH). The V₂O₃ particles were then exposed to air after cooling them down to room temperature. Finally the powders were converted to VO₂ at 400°C for 2 hours under N₂ atmosphere (purity 99.995%).

Surface reaction

The V₂O₅·xPy·yH₂O submicrospheres were spin-coated on the silicon or glass substrate at a rate of 2000 rpm for 30 seconds. After that all the thermal treatment mentioned before could be transferred to substrate to proceed. Au (99.99%) was evaporated by KYKY deposition apparatus at the voltage of 110V for several minutes to form a firm gold layer depositing on the particles.

FDTD Simulation

We model the VO₂@Au core-semishell submicroparticles with overlapping VO₂ spheres and gold spheres with radiuses are 250 nm, confined in a hollow air cylinder with an inner diameter of 250 nm. We consider the excitation light as a normal incident plane wave at the wavelength of 365 nm, where the wavevector *k* is perpendicular to the plasmonic surface.

Characterization

The morphologies and structural details of our products were examined by field-emission scanning electron microscopy (FESEM, Ultra 55, Zeiss, Germany). X-ray diffraction was carried out to verify the crystal structures on an X-ray diffractometer (XRD, Ultima III, Rigaku, Japan) using K α radiation (40 kV, 40 mA). The scattering spectrum is measured by Olympus BX51 optical microscopy with LDLS laser driven light source (170-2100nm white light), Princeton spectrograph and INSTEC TS102G heating and cooling stage.

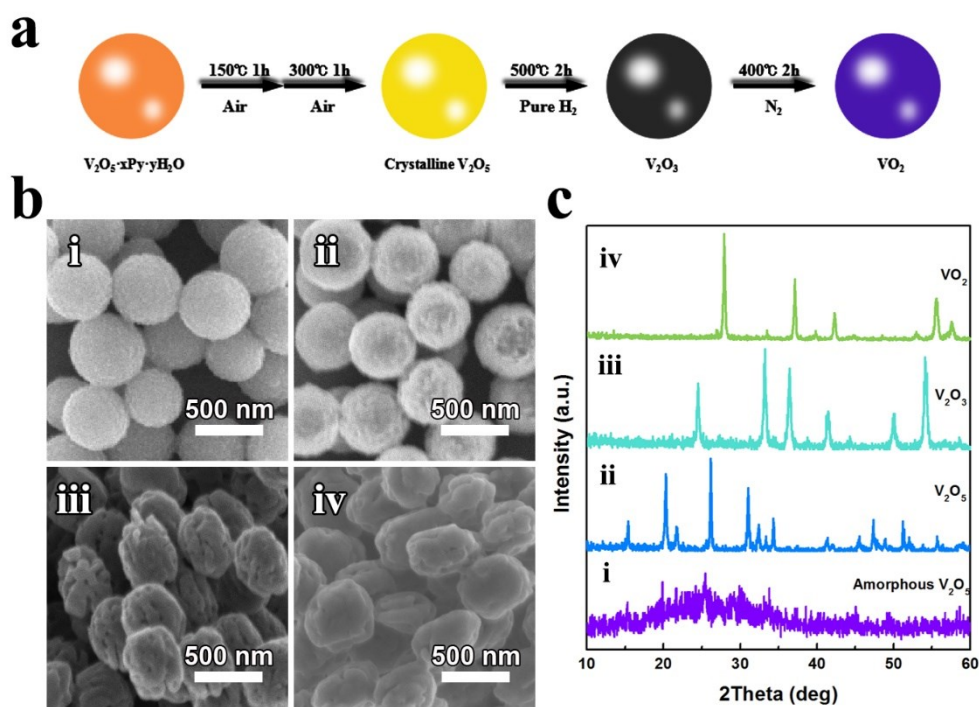


Fig. S1 a) Synthetic scheme for the vanadium oxide particles. b) SEM images of (i) amorphous $V_2O_5 \cdot xPy \cdot yH_2O$, (ii) crystalline V_2O_5 , (iii) V_2O_3 and (iv) VO_2 (M) submicrostructures. All scale bars are 500 nm. c) The corresponding XRD patterns.

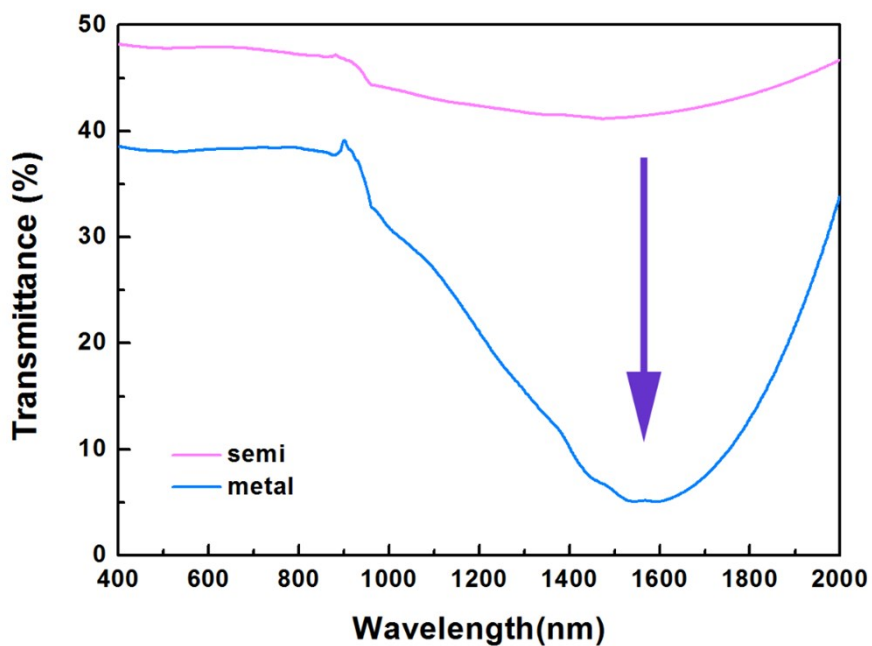


Fig. S2 Transmittance spectrum of the fine VO_2 submicroparticles on a quartz substrate

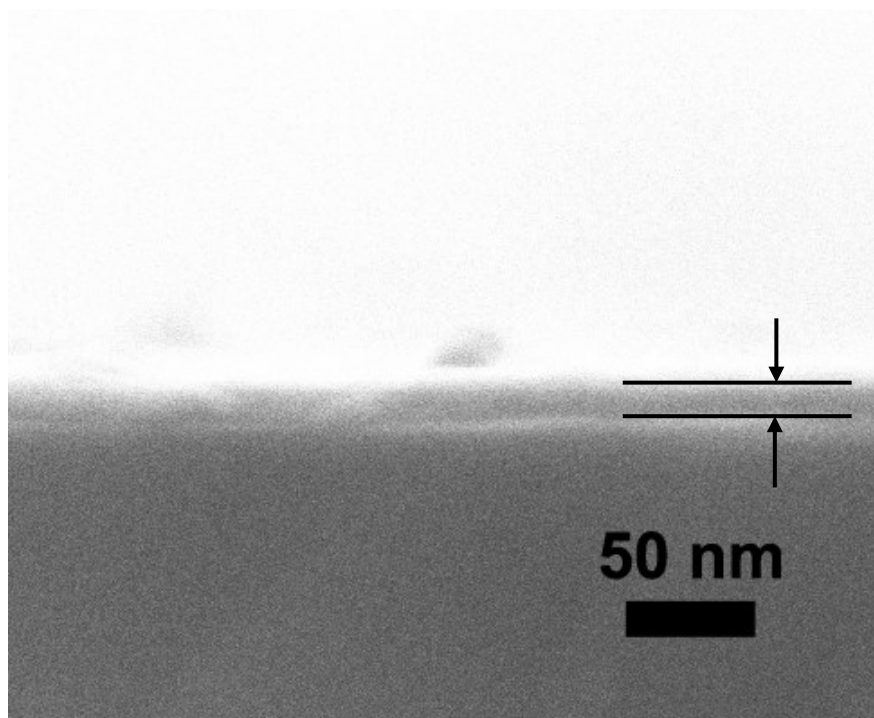


Fig. S3 Side view of the SEM images of a 15 nm-thick Au film deposited by vacuum evaporation. The scale bar is 50 nm.

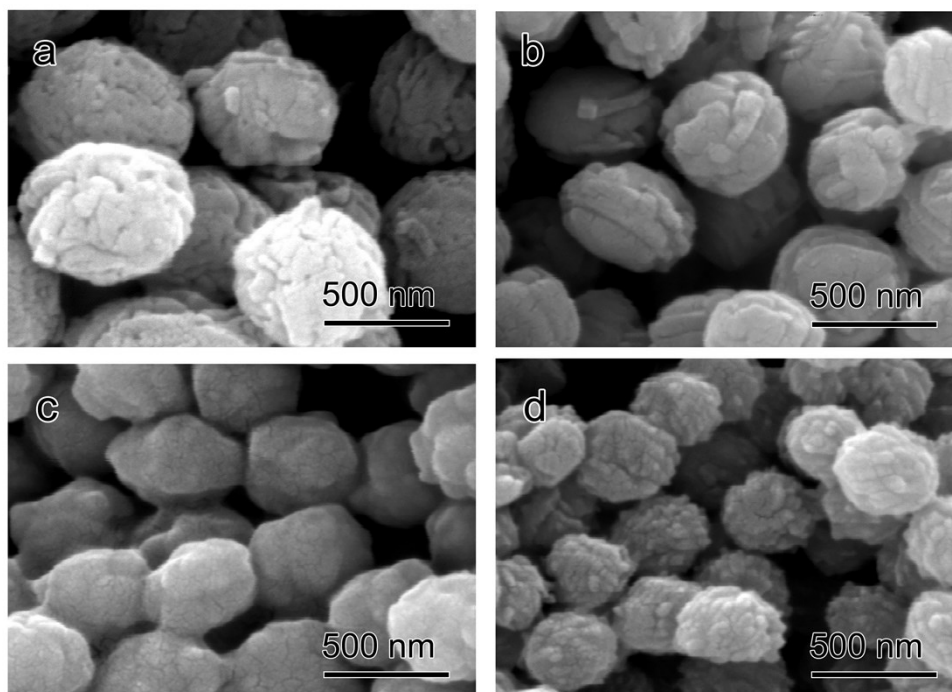


Fig. S4 The SEM images of VO₂ submicroparticles with different sizes.