

Experimental Sections

Materials: The chemicals and materials used in the experiment were all of analytic or chromatographic purity and used straight without further purification.

Synthesis of VO₂(D) nanostars: In a typical synthesis, 0.4 mmol of vanadiumoxy (IV) acetylacetonate (C₁₀H₁₄O₅V) and 3 mmol of oxalic acid (C₂H₂O₄) dissolved in a mixed solution of 30 mL of distilled water and 30 mL of tert-Butanol, and stirred for 30 minutes at room temperature. And then, the mixture solution into a 100 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 12 hours. A black product was isolated by centrifugation, washed with distilled water and absolute ethanol for 3 times and dried at 50 °C in vacuum.

Synthesis of VO₂(D) nanospheres: In a typical synthesis, 1 mmol of vanadium(IV)oxy acetylacetonate (C₁₀H₁₄O₅V) and 6 mmol of oxalic acid (C₂H₂O₄) dissolved in a mixed solution of 20 mL of distilled water and 20 mL of tert-Butanol, and stirred for 30 minutes at room temperature. And then, the mixture solution into a 100 mL Teflon-lined stainless steel autoclave and heated at 210 °C for 12 hours. A black product was isolated by centrifugation, washed with distilled water and absolute ethanol for 3 times and dried at 50 °C in vacuum.

Synthesis of Vo-rich VO₂(D) nanospheres: In a typical synthesis, 200 mg of black VO₂(D) nanospheres powder was added to 20 mL of distilled water and stirred for 5 minutes. Then 1 mmol Potassium borohydride (KBH₄) was slowly added into the solution, and stirred for 2 hour at 60 °C. A navy blue product was isolated by centrifugation, washed with distilled water and absolute ethanol for 3 times and dried at 50 °C in vacuum.

Raman Tests. To study the SERS performance of the as-synthesized VO₂ samples, a confocal-micro Raman spectrometer (Renishaw-inVia) was used as the measuring instrument. In all SERS tests, if no special statement, the adopted excitation wavelength is always 532 nm, the laser power is 0.5 mW, and the magnification of the objective is × 50 L. A series of standard solutions, such as Rh6G with concentrations of 10⁻⁵-10⁻⁹ M were adopted as the standard probe molecules. To improve the signal

reproducibility and uniformity, 60 mg of the VO₂ samples were dipped into 40 mL of the probe molecule aqueous solution maintained for 30 min for maximum adsorption. Then, 2 mL of the obtained suspension was uniformly coated on a glass slide by spin coating, and dried for 10 minutes under infrared irradiation in air. In all SERS detections, the laser beam is perpendicular to the top of the sample to be tested with a resultant beam spot diameter of 5 μm.

Enhanced Factor Calculation: To calculate the EF of the VO₂ (D) nanostructures, the ratio of SERS to normal Raman spectra (NRS) of RH6G was determined by using the following calculating formula:

$$EF = (I_{SERS}/N_{SERS}) / (I_{NRS}/N_{NRS})$$

where I_{SERS} and I_{NRS} refer to the peak intensities of the SERS and NRS, respectively. N_{SERS} and N_{NRS} refer to the number of R6G molecules in the SERS substrate and normal Raman sample, respectively. In the SERS measurements, two Raman scattering peaks, R_1 at 612 cm⁻¹ was selected for the calculations of the EF. For comparison, the peak intensities of the bulk R6G directly placed on bare glass slide were detected as NRS data. The intensity was obtained by making average 20 laser spots measurements. Substituting these values of above variable into the equation, the optimum EFs could be concluded to be about 3.8×10^5 (nanospheres) and 6.1×10^4 .

Characterization: XRD patterns of the products were characterized by a Bruker D8 Focus X-ray diffractometer equipped with CuK α radiation ($\lambda = 1.54178 \text{ \AA}$). Scanning electron microscopy (SEM) images and energy dispersive spectrometer (EDS) were obtained on a Hitachi S-4800. The transmission electron microscopy (TEM) images were performed with a Tecnai G F30 operated at 300 kV. Ultraviolet–vis absorption spectra were recorded by a Shimadzu UV-3600 with integrating sphere. X-ray Photoelectron Spectroscopy (XPS) were performed in a Theta probe (Thermo Fisher) using monochromated Al K α X-rays at $h\nu \frac{1}{4} 1486.6 \text{ eV}$. Peak positions were internally referenced to the C1s peak at 284.6 eV. The specific surface area was measured in a Micro Tristar II 3020.

Figures

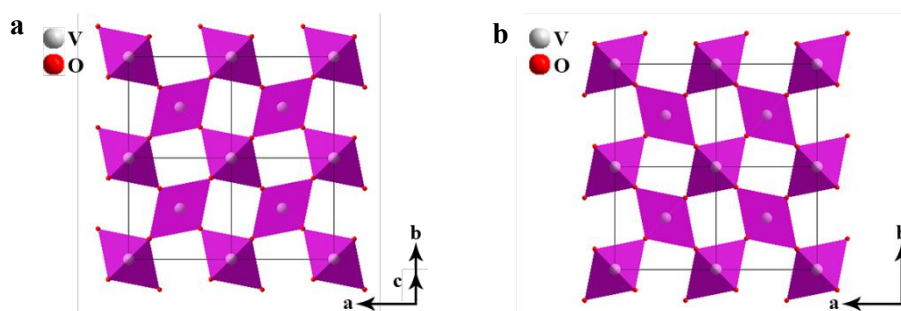


Figure S1. (a) The projection of the $\text{VO}_2(\text{D})$ structure along (100), and (b) the projection of the rutile-type $\text{VO}_2(\text{R})$ structure along (001).

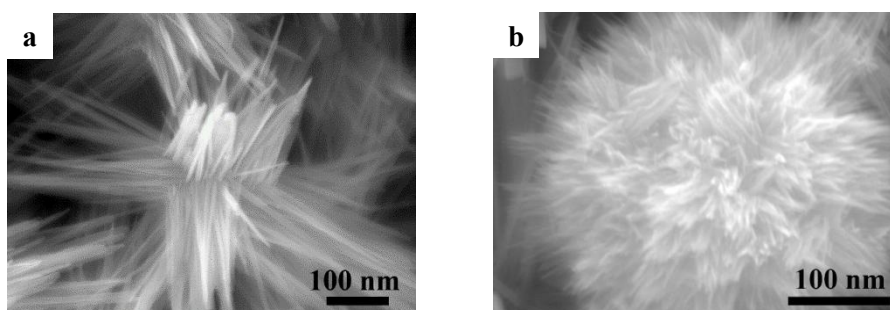


Figure S2. (a) SEM image of the as-synthesized VO_2 nanostars, and (b) SEM image of the as-synthesized VO_2 nanospheres, which indicates that the surfaces of nanostars and nanospheres are very rough, showing a large number of sharp protrusions.

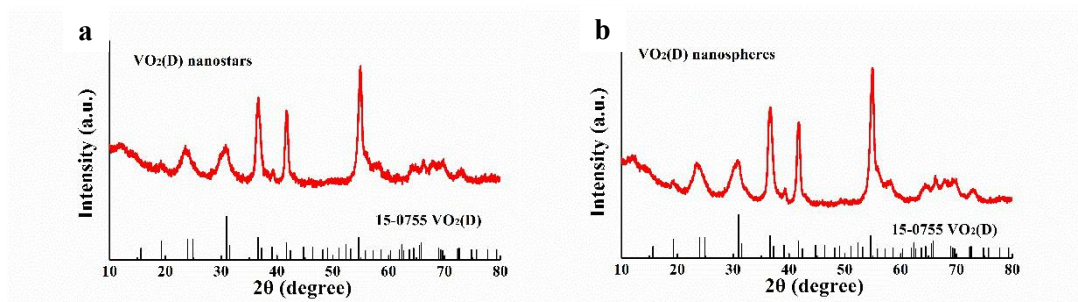


Figure S3. (a) XRD pattern of the as-synthesized VO₂ nanostars, and (b) XRD pattern of the as-synthesized VO₂ nanospheres.

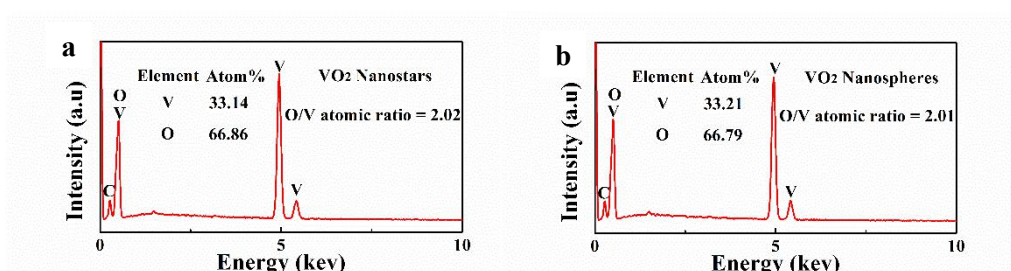


Figure S4. (a) EDS spectrum of the as-synthesized VO₂ nanostars, and (b) EDS spectrum of the as-synthesized VO₂ nanospheres.

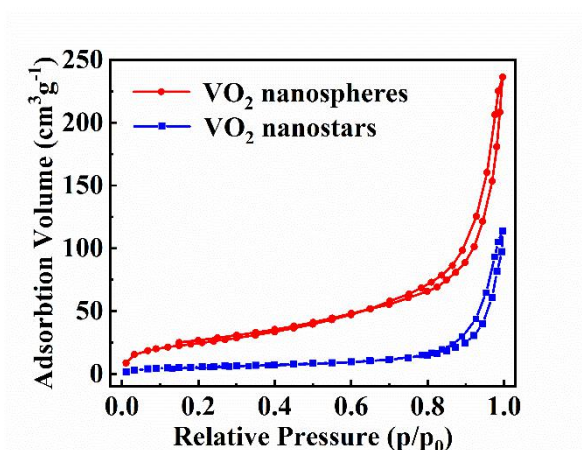


Figure S5. N₂ adsorption-desorption isotherms of VO₂ (D) nanospheres (red line) and VO₂ nanostars (blue line). The BET surface area is 62.9 m²g⁻¹ and 26.6 m²g⁻¹, respectively.

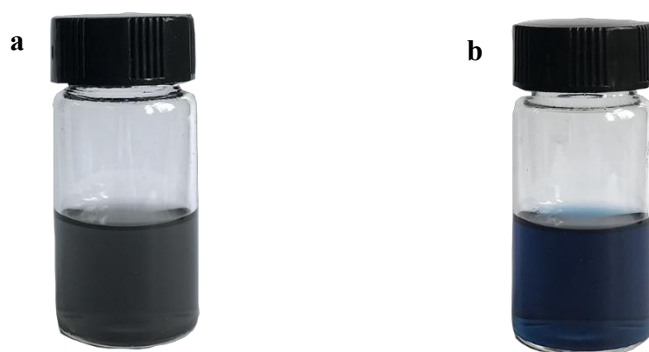


Figure S6. (a) The photograph of the VO₂ sample. (b) The photograph of the reduced VO₂ samples.

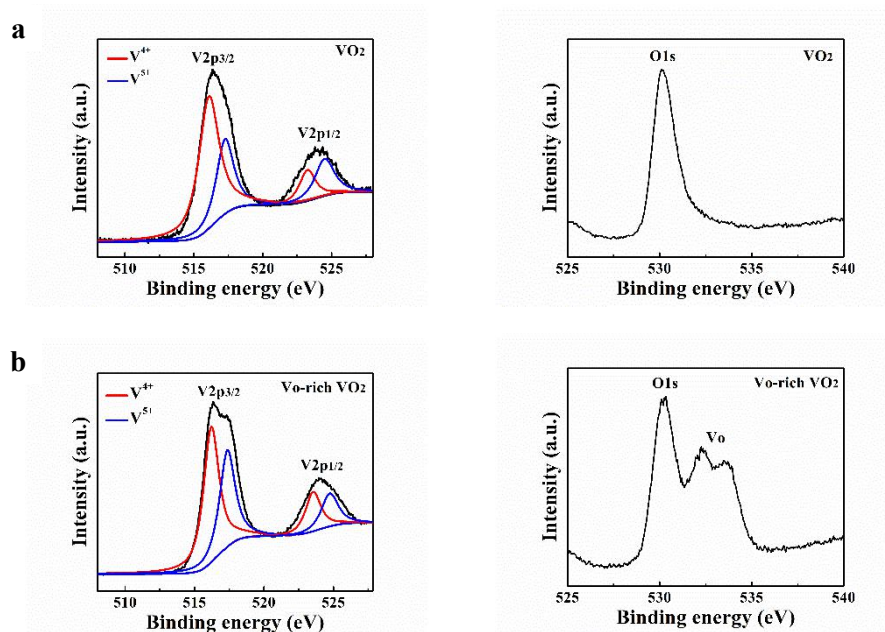


Figure S7. (a) XPS spectrum of the VO₂ sample. (b) XPS spectrum of the V_o-rich VO₂ sample.

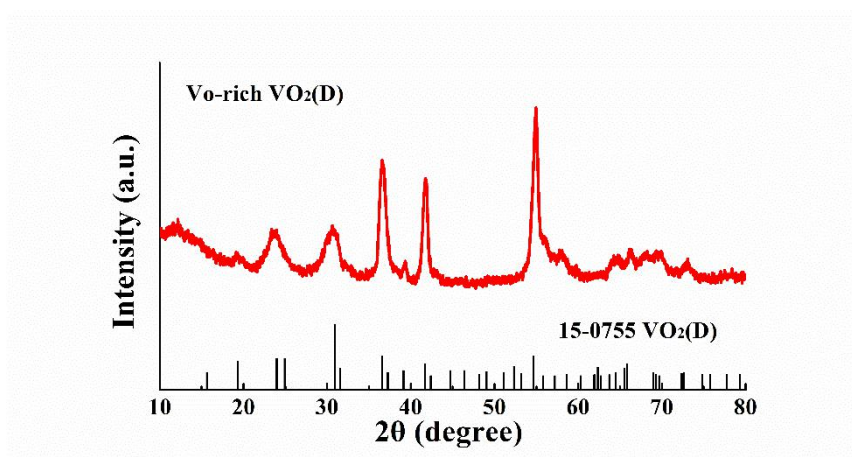


Figure S8. After adding reductants, the Vo-rich VO₂ still showed almost unchanged XRD patterns.

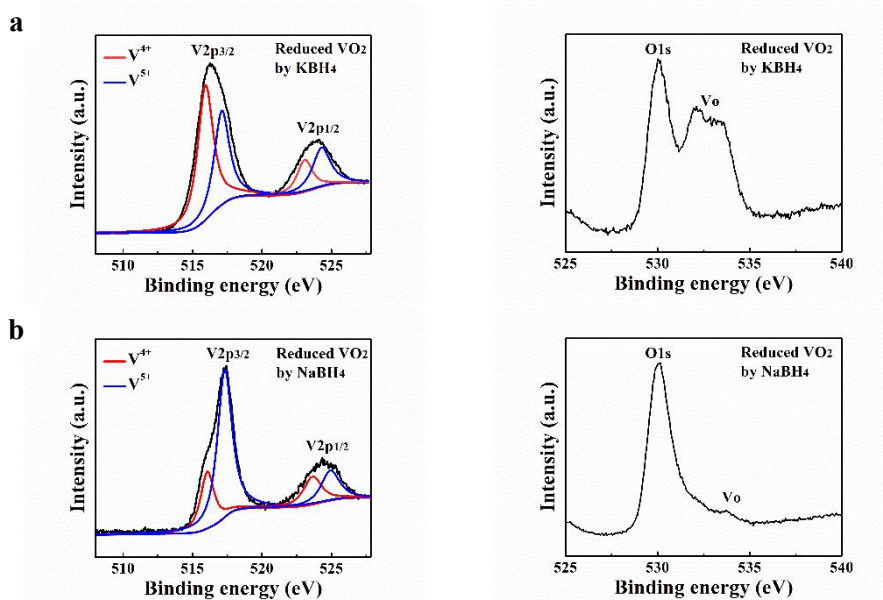


Figure S9. (a) XPS spectrum of the reduced VO₂ sample by KBH₄ after 3 months. (b) XPS spectrum of the reduced VO₂ sample by NaBH₄ after 3 months.

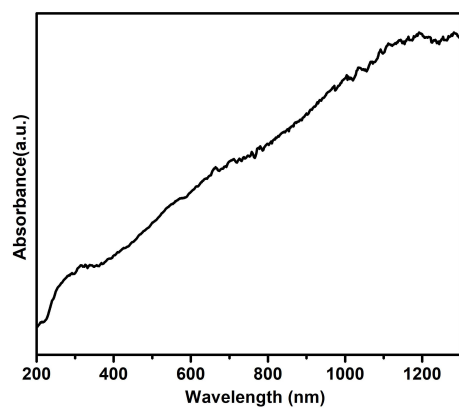


Figure S10. UV-Vis-NIR absorption of the VO₂ (D) nanospheres reduced by KBH₄.

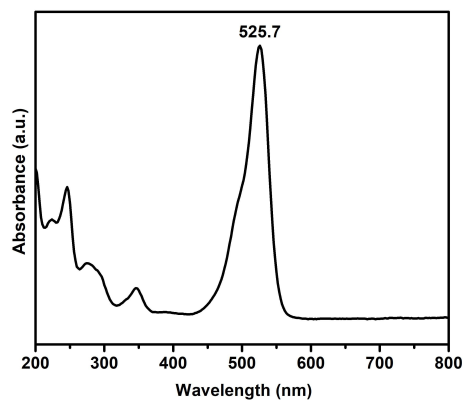


Figure S11. UV-Vis absorption of R6G molecule.

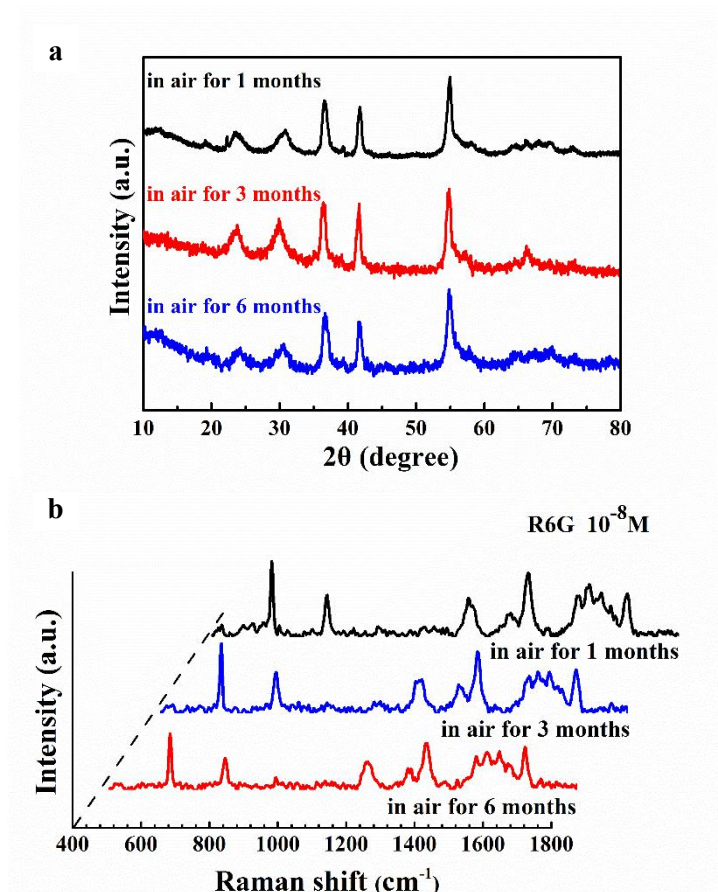


Figure S12. This new SERS substrate has good stability, even if it is stored in air for three months or even six months, these Vo-rich VO₂ still exhibit almost invariable XRD pattern (a) and SERS activity (b).

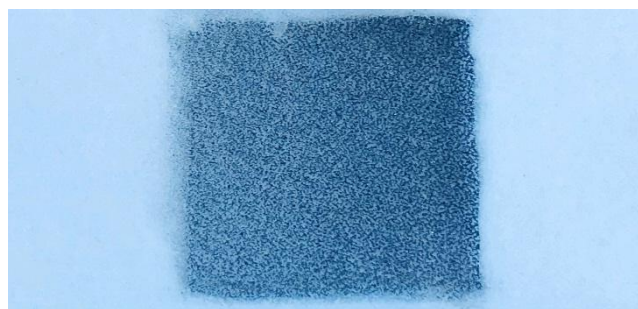


Figure S13. Uniform SERS substrate composed of the V_o-rich VO₂.

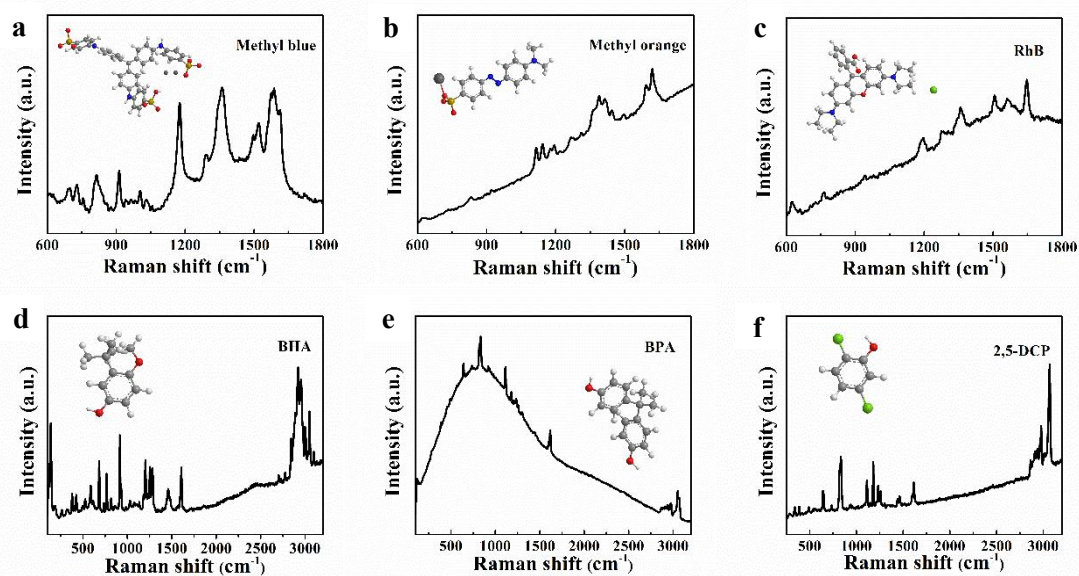


Figure S14. SERS spectra of some typical azo dyes and dangerous compounds obtained on the V_o-rich VO₂. (a) methyl blue. (b) methyl orange. (c) RhB. (d) BHA. (e) BPA. (f) 2,5-DCP.

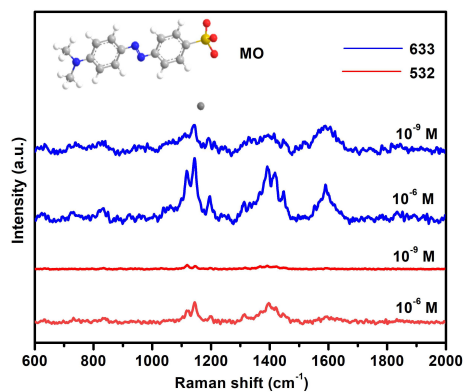


Figure S15. The SERS spectra of MO probe molecules on the V_o-rich VO₂ (D) substrate with different excitation wavelength.



Figure S16. (a)When the sample is heated in air at 300 °C and 400 °C for 5 h, with the decrease of V_o , the sample finally becomes V_2O_5 .

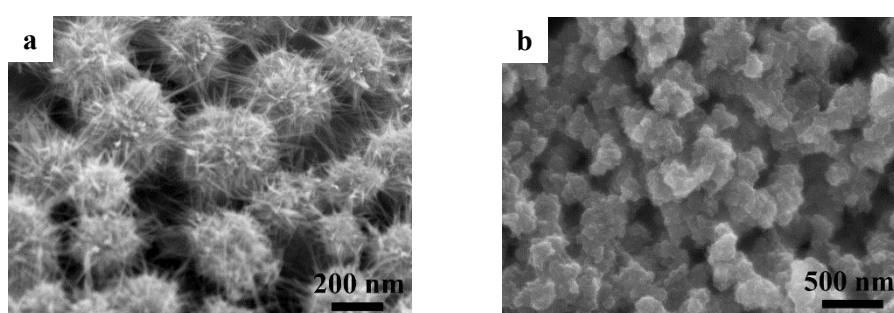


Figure S17. (a)SEM image of VO_2 reduced by 1mmol KBH_4 . (b) SEM image of VO_2 reduced by 10mmol KBH_4 , which indicates that excessive KBH_4 will destroy the morphology of the sample.

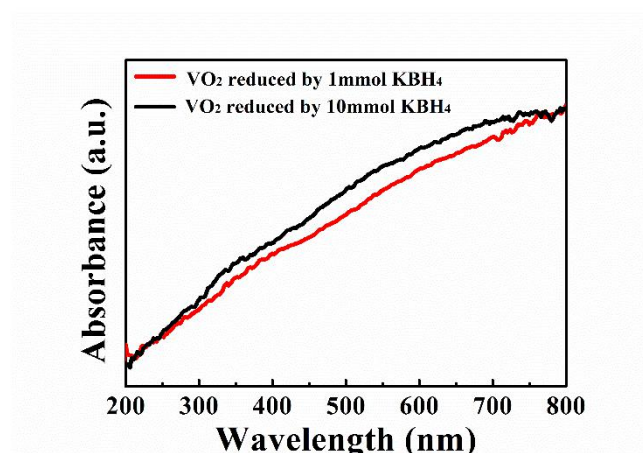


Figure S18. Ultraviolet-Visible Absorption Spectra of VO₂ reduced by 1mmol KBH₄ and 10mmol KBH₄.

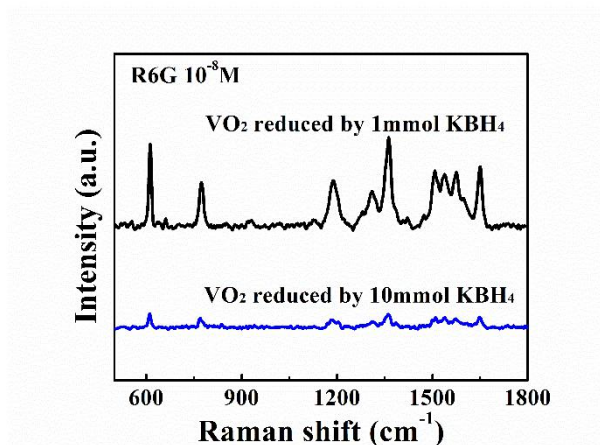


Figure S19. Adding too much reductant makes the SERS performance of the sample lower.