Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for A Synergy Effect of Sodium on the Phase Transition of Tungsten-doped Vanadium Dioxide

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EXPERIMENTAL METHODS

Materials Synthesis.

V_2O_5 (3.00 g) and dopants were mixed by grinding and put into a ceramic crucible. The mixture was heated to 800 °C in a retort furnace for about 30 min. Then the mixed molten liquid was quickly poured into demonized water to form doped V_2O_5 sol by stirring in high speed. The sol was dried at 80 °C over night. Then an amorphous dried gel was obtained. The dried gel was collected annealing at 500 °C for 2h. Reduction of the doped V_2O_5 precursor to doped VO_2 was carried out according to our previously reported procedure. Doped V_2O_5 particles were heated under mixed gas flow of ammonia (NH_3, 15 ml/min) and nitrogen (N_2, 150 ml/min) at 500 °C for 1 h, and further annealed in N_2 at 700 °C for 5h. At last, blue black powder products were synthesized. The condition of high temperature annealing is in N_2 at 1100 °C for 2h. Doped VO_2 samples were prepared with different extents of dopants requiring: 0.5 at% Na_2WO_4 doping sample with 0.049g of Na_2WO_4 powders, 1.0 at% Na_2WO_4 doping sample with 0.097g of Na_2WO_4, 1.5 at% Na_2WO_4 doping sample with 0.156g of Na_2WO_4, 2.0 at% Na_2WO_4 doping sample with 0.194g of Na_2WO_4 powders, 1.0 at% WO_3 doping sample with 0.077g of WO_3 and 2.0 at% NaOH doping sample with 0.026g of NaOH.

Materials Characterization

Crystalline phase identification was characterized by powder X-ray diffraction (XRD) on a Rigaku D/max 2400 X-ray equipped with graphite monochromatized Cu Kα radiation (λ = 1.5406 Å)with samples mounted using a grooved glass sample holder. A scan rate of 0.02° s^{-1} was applied to record the pattern in the 2θ range from

5° to 80°. The phase transitions in the as-prepared VO_2 powders was studied via Differential scanning calorimetry (DSC, Netzsch, Germany) under a flowing gaseous ultra pure nitrogen atmosphere over a temperature range from -20 to 100 °C at a heating rate of 10 K/min. Valences of the elements were studied by X-ray photoelectron spectroscopy (XPS, VG ESCALAB MK II). The morphologies and surface chemical elements of the final products were examined by scanning electron microscopy SEM, JSM- 5610LV and Hitachi SU-70 operated at 20 kV equipped with an energy dispersive X-ray analysis detector. The Raman spectra were taken with a double monochromator with a spectral resolution of $<2cm^{-1}$ and were excited by 0.3~1 μW of the 532nm line laser. Raman spectra were acquired using a Thermo Fisher Scientific DRX microscope.

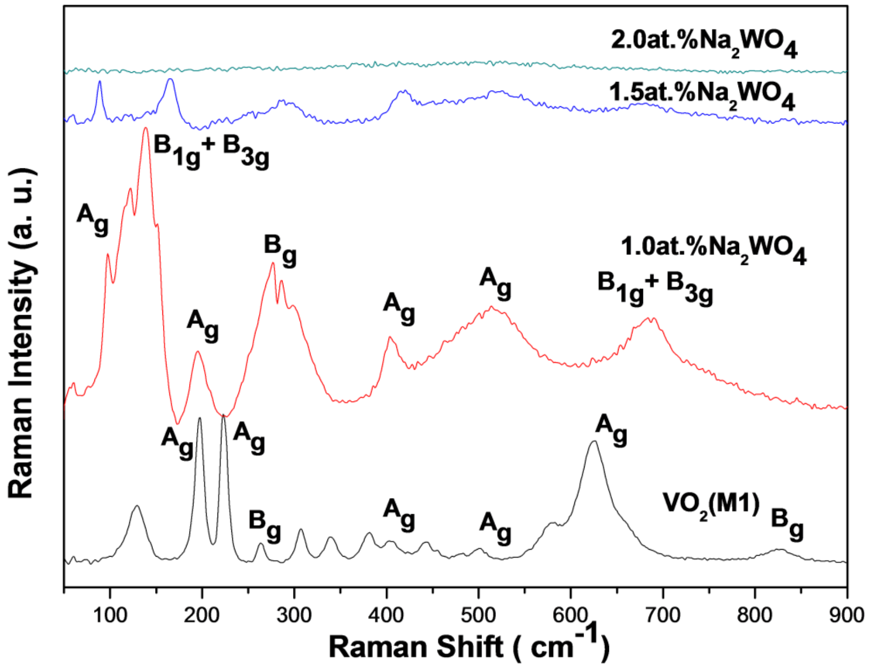

Figure **S1**. Room-temperature Raman spectra acquired for VO_2 samples with increasing using. The mode assignments noted in Figure S1 are based on previously reported polarized Raman studies and group theory predictions. The M1 phase is discernible up to 1.0 at. % Na_2WO_4 using and the rutile phase surmised from the absence of Raman bands in the sample with 2.0 at.% Na_2WO_4 using. Characteristic modes of the V_2O_5 are observed in the samples of 2.0at.% and 1.5 at. % Na_2WO_4 using, it may be due to surface oxidation of the particles in the atmospheric and further oxidation because of local heating of the laser. [1-3]

[1] Luisa Whittaker, Tai-Lung Wu, Adam Stabile, Sambandamurthy, and Sarbajit Banerjee, Single-Nanowire Raman Microprobe Studies of Doping-, Temperature-, and Voltage-Induced Metal_Insulator Transitions of $W_xV_{1-x}O_2$ Nanowires, ACS Nano, 2011, 5, 8861–8867

[2] Peter Schilbe, Raman scattering in VO_2, Physica B 2002, 316–317, 600–602

[3] Bo Zhou and Deyan He Raman spectrum of vanadium pentoxide from density-functional perturbation theory *J. Raman Spectrosc.* 2008, 39, 1475–1481

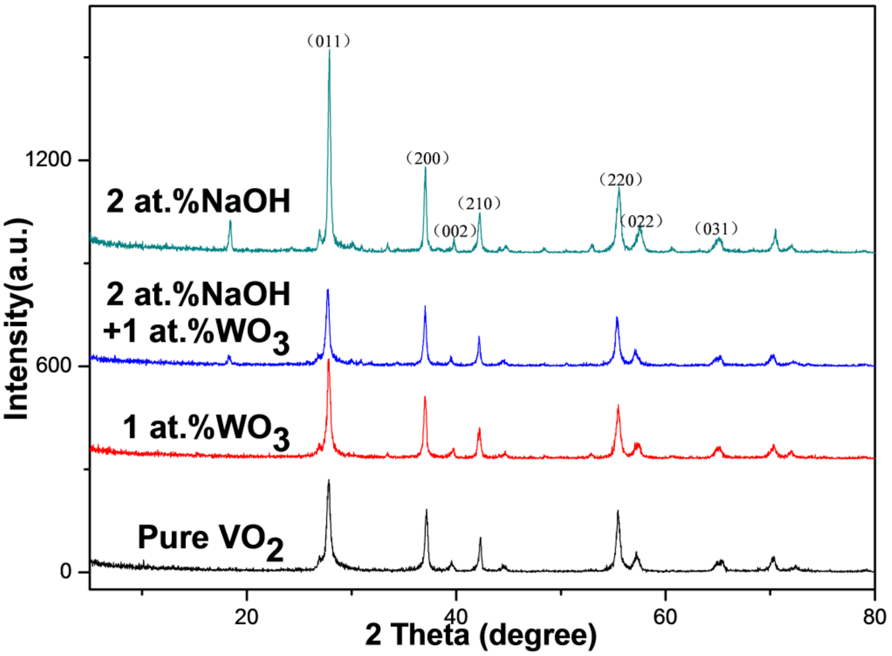

Figure S2. X-ray diffraction pattern for pure VO_2 and doped VO_2 samples with different dopants. The indexed diffraction patterns are expected for monoclinic VO_2 (M1) from JCPDS Card no. 043-1051.

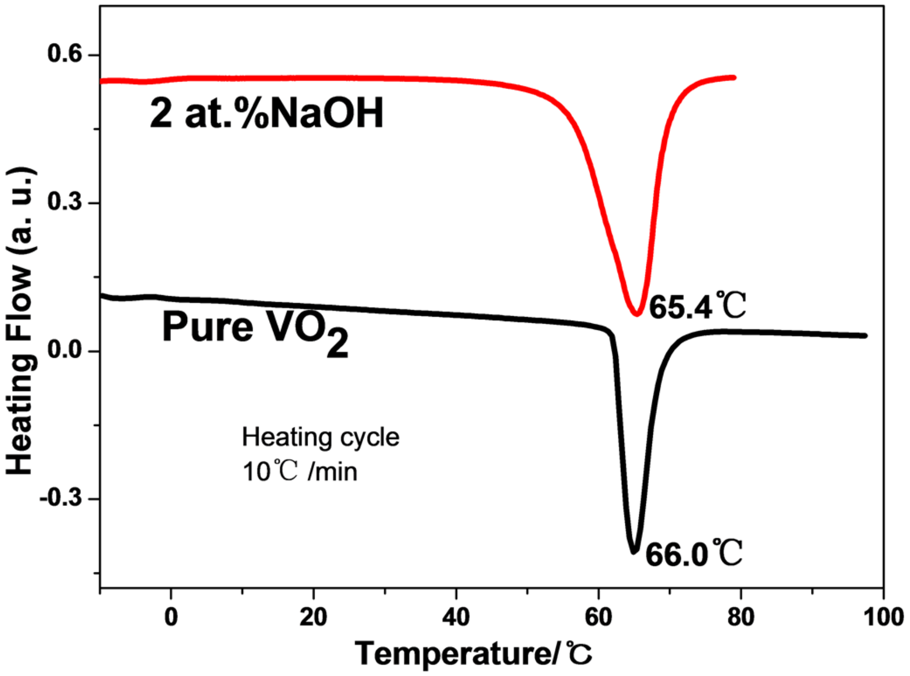

Figure S3. DSC for pure VO_2 and doped VO_2 samples with different dopants. The vertical lines indicate the peak positions expected for monoclinic VO_2 (M1) from JCPDS Card no. 043-1051.

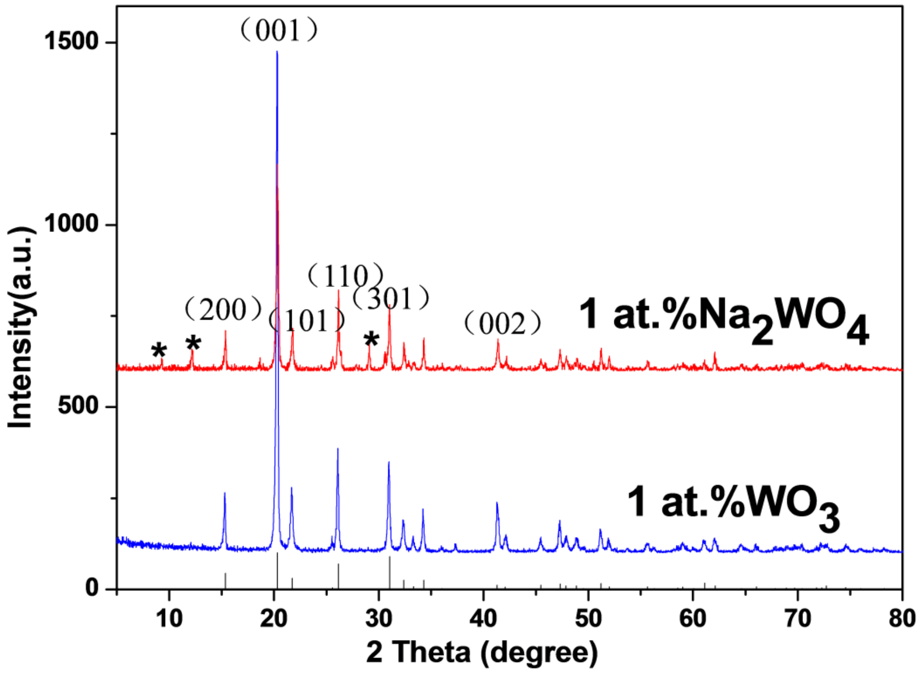

Figure S4 XRD pattern for V_2O_5 precursors adding with 1at.% content Na_2WO_4 and WO_3。 The vertical lines indicate the peak positions expected for orthorhombic V_2O_5 from JCPDS Card no. 065-0131, while the additional peaks (indicated by asterisks) correspond to Monoclinic Card no. $Na_{0.33}V_2O_5$ JCPDS-48-0382

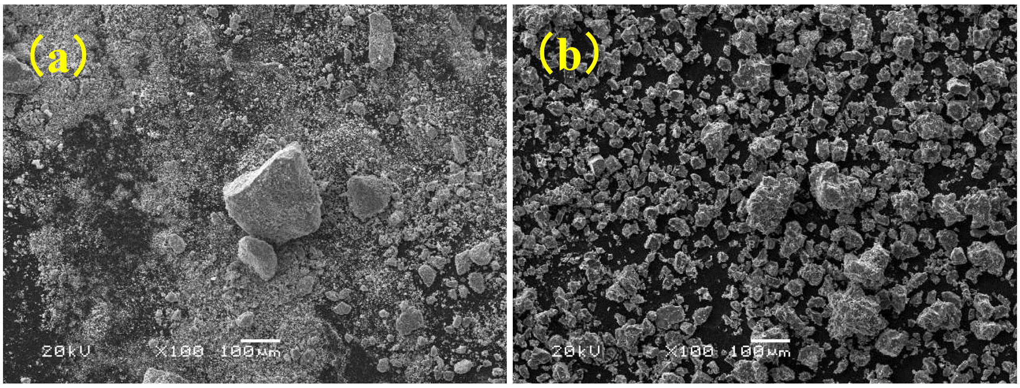

Figure S5 Low magnification SEM images of 1.0at.% Na_2WO_4 doped VO_2 samples (a) have been annealed in N_2 at 700 °C for 5h and (b) further annealed in N_2 at 1100 °C for 2h.

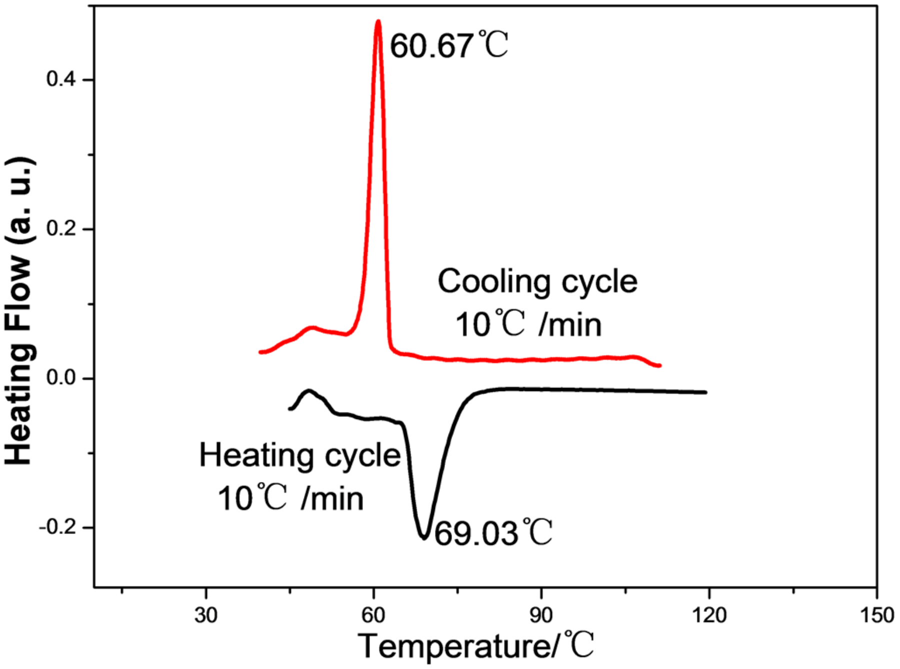

Figure S6 DSC curve of Pure VO_2 have been annealed in N_2 at 700 °C for 5h and further annealed in N_2 at 1100 °C for 2h.

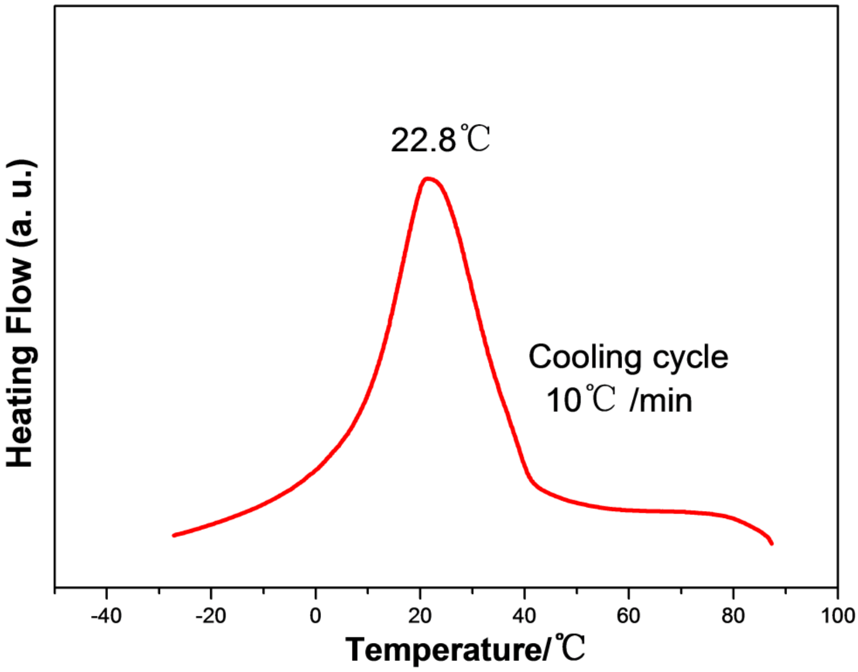

Figure S7 DSC curve of doped VO_2 sample with 1.0 at. % Na_2WO_4 have been annealed in N_2 at 700 °C for 5h.