Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2020

Electronic Supplementary Information

2D Nonlayered Ferromagnetic VO_2(M) Nanosheets Induced by the Strain Engineering of CO_2

Li Zhang,[‡a] Yannan Zhou,[‡a] Xiaoli Zheng,[a] Jingyun Jiang,[a] Qun Xu*[ab]

[a] Department of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, P.R. China.

[b] Henan Institute of advanced technology, Zhengzhou University, Zhengzhou 450001, P.R. China.

‡ These authors contributed equally to this work

* Address correspondence to qunxu@zzu.edu.cn

Experimental Section

Materials. V_2O_5 (99%) powder and N-Methyl pyrrolidone (NMP, 99.5%) were provided by Shanghai Macklin Biochemical Co., Ltd and directly used without further purification. Hydrazine hydrate (99%), H_2SO_4 (A.R.), and NaOH (A.R.) were purchased from Beijing Chemical Works. CO_2 with a purity of 99.99% was purchased from the Zhengzhou Shuangyang Gas Co., Ltd. Deionized water was prepared with double-distilled water.

Preparation of samples.

(1) Preparation of bulk VO_2 (M). Bulk VO_2 (M) was prepared according to the previous report[1]. Typically, 0.99 g V_2O_5 was dispersed in deionized water to form a yellow suspension. Then, 60.72 mL of 0.5 M H_2SO_4 was added to the above suspension at 60 °C. Subsequently, 0.55 mL of hydrazine hydrate was added, the color of solution first turns to greyish-green, and following blue (VO^{2+} solution), which indicates the reduction of V^{5+} to V^{4+}. Then, a pink precipitate can be formed by adjusting the pH of VO^{2+} solution to 4 using NaOH solution. The precipitate was further centrifuged and washed using water for several times and then collected without drying, which are further dispersed in 22 mL of water. Hydrothermal reaction was carried out in a Teflon-lined autoclave with a capacity of 50 mL containing the suspension of the precipitate at 230 °C for 48 h. The final black product (VO_2(B)) was collected and dried in a vacuum oven at 50 °C for 6 h. The as-obtained VO_2(B) was heated to 700 °C for 2h in the flow of high purity of argon. During the calcination, the VO_2(B) converted to rutile VO_2(R) through an irreversible structural phase transition (SPT) and then a reversible SPT into monoclinic VO_2(M) when cooled to room temperature.

(2) 2D defective VO_2(M) nanosheets treated by supercritical CO_2. 10 mg of bulk VO_2(M) products were dispersed in 10 mL of NMP/water (V / V = 9 : 1) solution through ultrasonication under inert atmosphere for 6 h. The obtained dispersion was directly transferred into the supercritical CO_2 apparatus composed mainly of a stainless-steel autoclave with a heating jacket and a temperature controller. The autoclave was heated to 80 °C, and then CO_2 was charged into the reactor to 16 MPa and maintained for 6 h under continually stirring. After the CO_2 was slowly released, the supernatant was collected by centrifugation at 9000 rpm for 10 min, the obtained specimens were denoted as 2D defective VO_2(M) nanosheets (NSs).

Characterization.

Powder XRD patterns of the samples were collected at room temperature on a Bruker D8 Advance diffractometer using a germanium monochromatic (CuKa radiation, 40 kV and 40 mA). Transmission electron

microscope (TEM) images were recorded on a FEI Tecnai G2 F20 at an acceleration voltage of 200 kV using a carbon-coated copper grid. The thickness of the exfoliated nanosheets was measured by AFM (NanoMan VS). SEM images were recorded using a Quanta 250 FEG FEI at 20 kV in gentle-beam mode without any metal coating. X-ray photoelectron spectroscopy was performed using Thermo Scientific K-Alpha system. Raman measurements were performed using BWS435-532SY with laser wavelength of 532 nm. The magnetic measurement was carried out with a Physical Property Measurement System (quantum design, PPMS-9).

Results and Discussion

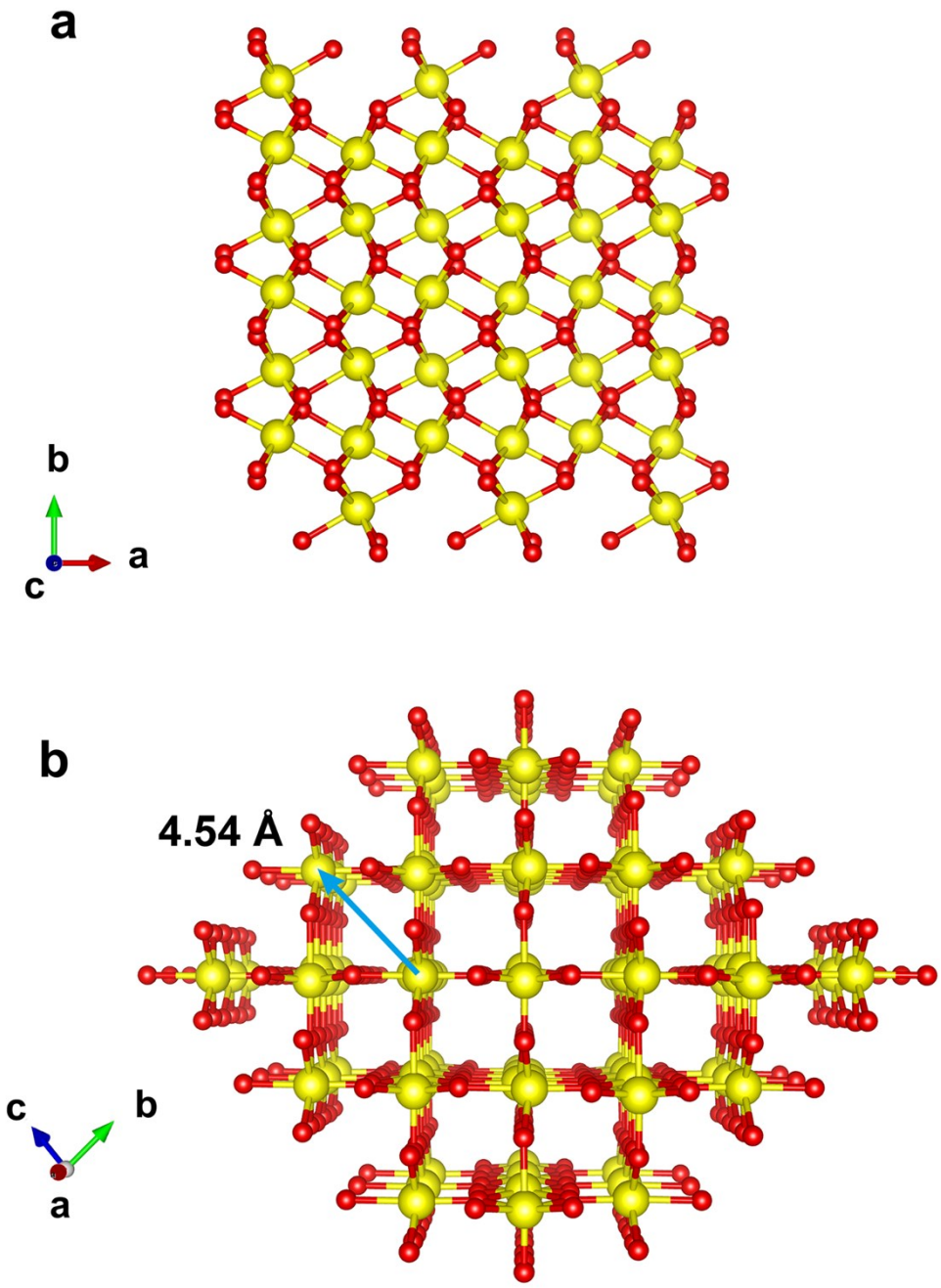

Fig. S1 The crystal structures of VO_2(M). (a) V-V dimers along the *c*-axis. (b) VO_2(M) features a tunnel-like structure with a size of 4.54 Å along [100] direction.

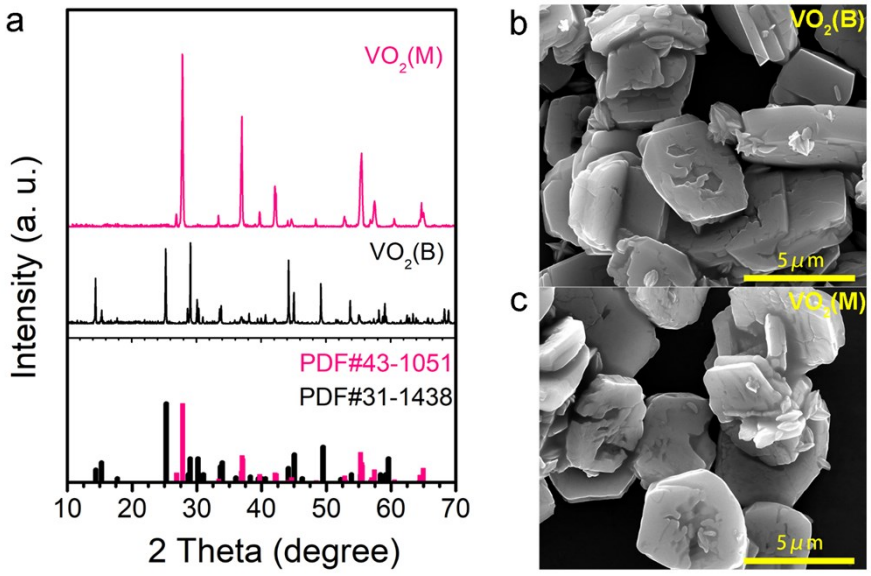

Fig. S2 (a) XRD patterns and the corresponding SEM images (b, c) for the synthetic precursor VO_2(B) and VO_2(M), respectively.

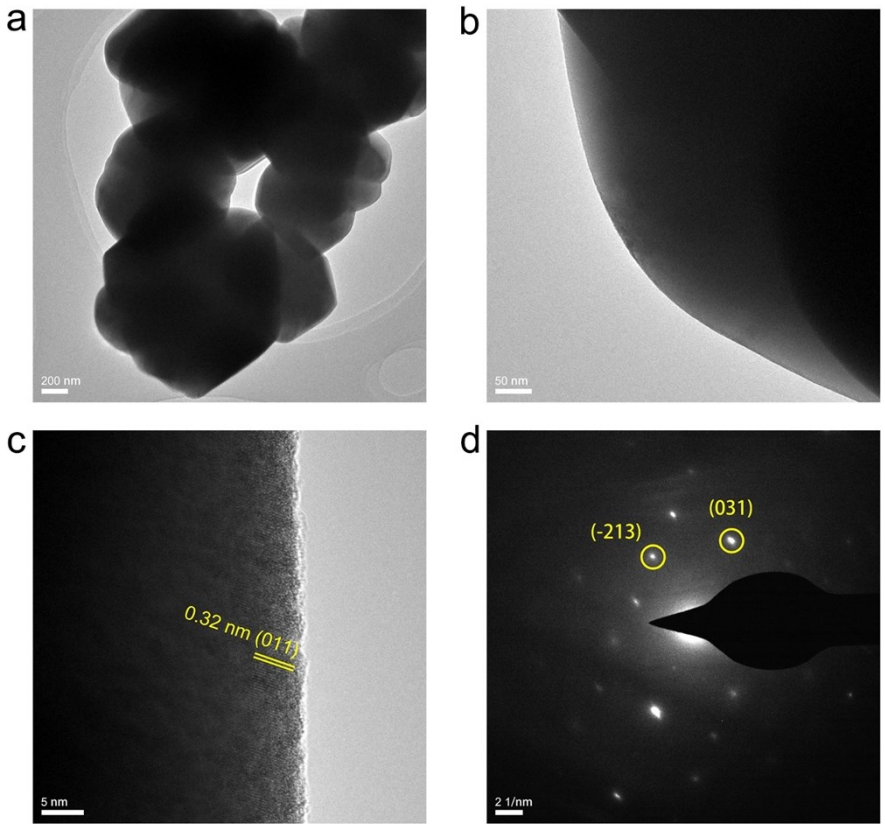

Fig. S3 Microscopic characterization of VO_2(M) after ultrasonication treatment. (a, b) TEM images, (c) HRTEM image, (d) the corresponding SAED pattern.

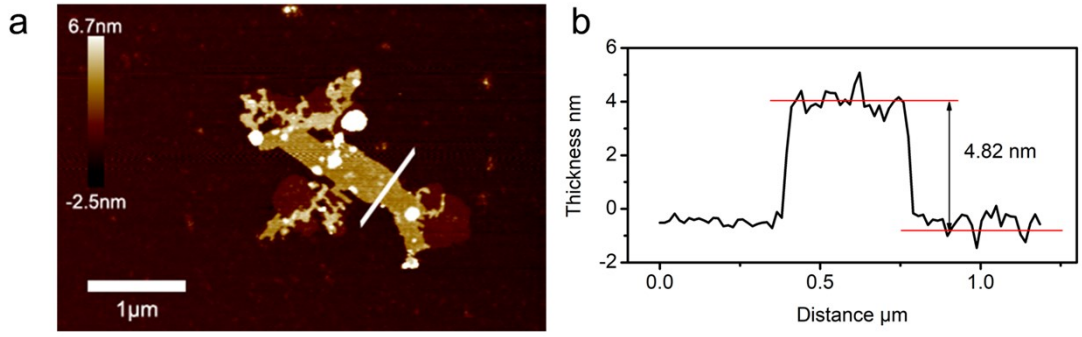

Fig. S4 AFM image (a) and corresponding height profile (b) of 2D defective VO_2(M) NSs.

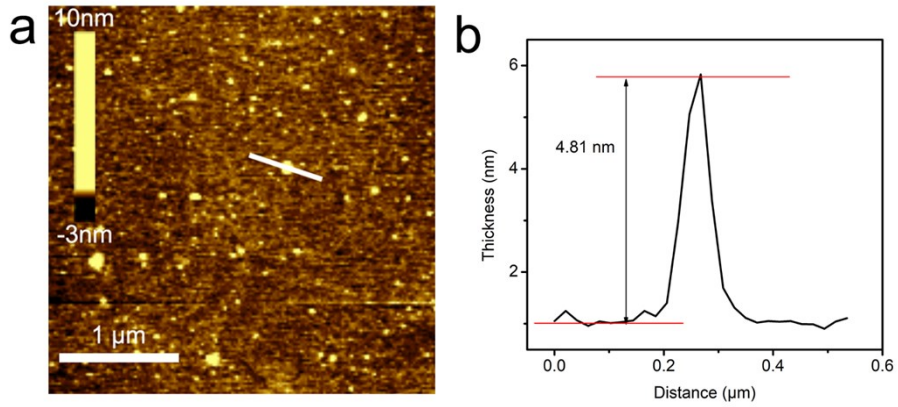

Fig. S5 (a) AFM images and (b) the corresponding height profiles of the obtained VO_2(M) Nanosheets at 80 °C and 16 MPa for 4 h.

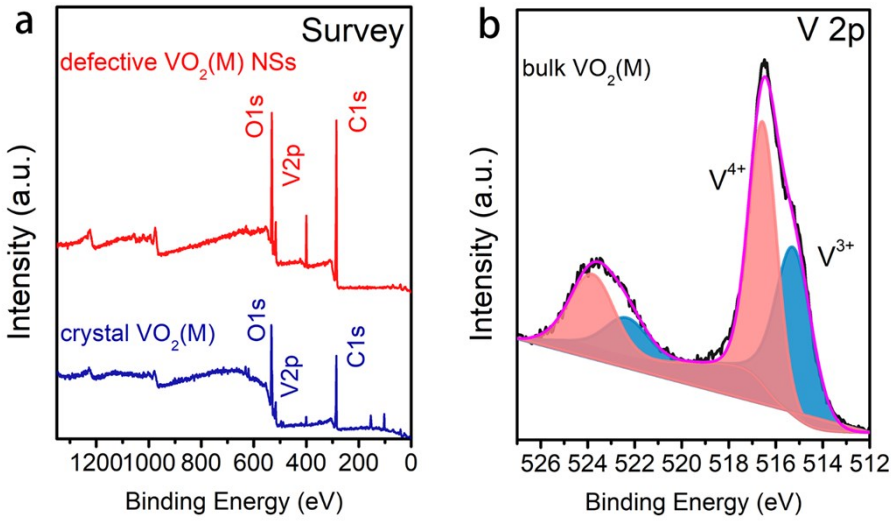

Fig. S6 XPS characterization of 3D crystal and 2D defective VO_2(M) NSs. (a) Survey spectra. (b) V 2p high-resolution of 3D pristine VO_2(M) bulk materials.

Table S1. Ferromagnetic behavior comparison of 2D VO_2(M) nanosheets with the state-of-the-art V-based material.

Ref.	Sample (300 K)	H_c (Oe)	M_s (emu g^{-1})
This work	2D VO_2(M) nanosheets	17	0.0295
Angew. Chem. Int. Ed., 2013, 52, 10477-10481	VSe_2 ultrathin nanosheets	43	0.0080
Adv. Mater., 2017, 29, 1700715	2D VS_2nanosheets	~100	~0.0200
Mater. Lett., 2014, 124, 282-285.	VS_2 ultrathin nanosheets (10 K)	494	0.0750

Reference

1 J. Son, J. Wei, D. Cobden, G. Cao and Y. Xia, *Chem. Mater.*, 2010, **22**, 3043-3050.