Electronic Supplementary Material

Highly Depressed Temperature-induced Metal-insulator Transition in Synthetic Monodisperse 10-nm V_2O_3 Pseudocubes Enclosed by {012} Facets

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S1. Experimental details for irregular V_2O_3 particles with sizes ranging from 10 nm to 2 µm

Preparation of 10-nm irregular rhombohedral V_2O_3 nanoparticles: 66 mg $VO(acac)_2$ was added into a solution of 4 mL benzyl alcohol and 4 mL oleylamine. After vigorous stirring for 30 min, the mixture was transferred into a 10 mL Teflon-lined autoclave, sealed and heated at 220 °C for 48 h. After cooling to room temperature naturally, the final product was collected by centrifuging the mixture, washed with cyclohexane and absolute ethanol for many times, and then dried in vacuum overnight for further characterization.

Preparation of 20-nm irregular rhombohedral V_2O_3 nanoparticles: 66 mg $VO(acac)_2$ was added into a solution of 7 mL benzyl alcohol and 1 mL oleylamine. After vigorous stirring for 30 min, the mixture was transferred into a 10 mL Teflon-lined autoclave, sealed and heated at 220 °C for 48 h. After cooling to room temperature naturally, the final product was collected by centrifuging the mixture, washed with cyclohexane and absolute ethanol for many times, and then dried in vacuum overnight for further characterization.

Preparation of 40-nm irregular rhombohedral V_2O_3 nanoparticles: 0.3 mL $VO(OC_3H_7)_3$ was added into a solution of 4 mL benzyl alcohol and 4 mL oleylamine. After vigorous stirring for 30 min, the mixture was transferred into a 10 mL Teflon-lined autoclave, sealed and heated at 220 °C for 48 h. After cooling to room temperature naturally, the final product was collected by centrifuging the mixture, washed with cyclohexane and absolute ethanol for many times, and then dried in vacuum overnight for further characterization.

Preparation of 170-nm irregular rhombohedral V_2O_3 nanoparticles: 0.1 mL $VO(OC_3H_7)_3$ was added into a solution of 4 mL isopropanol and 4 mL oleic acid. After vigorous stirring for 30 min, the mixture was transferred into a 10 mL Teflon-lined autoclave, sealed and heated at 220 °C for 48 h. After cooling to room temperature naturally, the final product was collected by centrifuging the mixture, washed with cyclohexane and absolute ethanol for many times, and then dried in vacuum overnight for further characterization.

Preparation of 2-μm irregular rhombohedral V_2O_3 particles: 1.5 g V_2O_5 and 0.96 g 1,6-diaminohexane were added into 35 ml distilled water. After vigorous stirring for 30 min, the mixture was transferred into a 40 mL Teflon-lined autoclave, sealed and heated at 250 °C for 48 h. After cooling to room temperature naturally, the final product was collected by centrifuging the mixture, washed with distilled water and absolute ethanol for several times, and then dried in vacuum overnight for further characterization.[1]

In order to precisely illustrate the particle size deviation for these synthesized V_2O_3 samples, the standard deviations (σ) were calculated for each sample to evaluate how widely spread the values in the data were, on the basis of the follwing formula:

$$\sigma = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(x_i - \bar{x})^2}$$

Where x_i is the particle diameter directly measured from the corresponding TEM images, $\bar{x}$ is the average particle diameter of all the measured particle diameters, and N is the particle number. The size deviations for the 10 nm V_2O_3 pseudocubes and the irregular V_2O_3 particles with size of 10 nm, 20 nm, 40 nm, 170 nm and 2 μm were 1.2, 3.3, 5.3, 10, 11 and 20, respectively.

S2. Structural analysis for rhombohedral and monoclinic V_2O_3

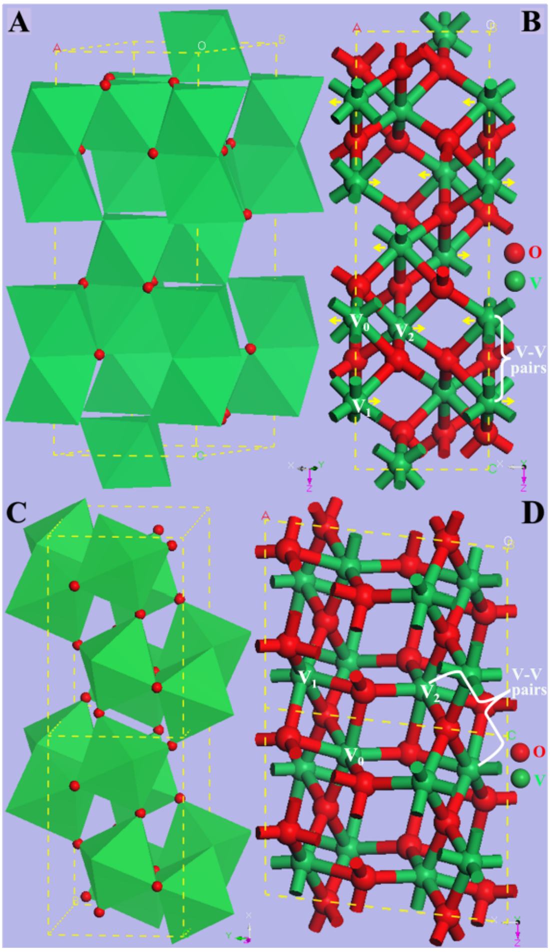


Figure S1. (A, B) Crystal structure for rhombohedral V_2O_3; the arrows in (B) indicate the translation direction of the V-V pairs at the metal-insulator transition. (C, D) Crystal structure for monoclinic V_2O_3; the brackets in (B, D) show the V-V pairs. The crystal structures of rhombohedral and monoclinic V_2O_3 are simulated according to the crystallographic data of ICSD 201107 and ICSD 6286 given by the Inorganic Crystal Structure Database.

As clearly shown in Figures S1A and B, rhombohedral V_2O_3 consists of V-V pairs through face-sharing O octahedrons along the Z axis. Such V-V pairs form chains through edge-sharing O octahedrons in the X-Z plane, which are further interconnected to form a three-dimensional framework (Figure 1B) [2, 3]. Notably, the rhombohedral structure of V_2O_3 could be distorted to form monoclinic phase during cooling, which results in an expansion of the distance between V-V pairs. Specifically, in the phase transition from rhombohedral to monoclinic V_2O_3 (Figures S1B and D), the V_0-V_1 distance across the face-sharing O octahedral increases from 2.669 Å to 2.744 Å. Meanwhile, the V_0-V_2 distance across the edge-sharing O octahedral increases from 2.868 Å to 2.984 Å, which is larger than the critical value of 2.94 Å calculated by Goodenough, thus breaking its 3-dimensional V-V framework into 2-dimensional V-V network (Figure 1B and D) [2-5]. In this case, the V3d electrons that originally itinerate along the V-V chains in the rhombohedral V_2O_3 structure (Figure 1B) will be localized at individual V ions in monoclinic V_2O_3 (Figure 1D), switching the V_2O_3 material from metal to insulator state.

S3. Characterizations for the monodisperse 10-nm V_2O_3 pseudocubes with {012} facets exposed on surface

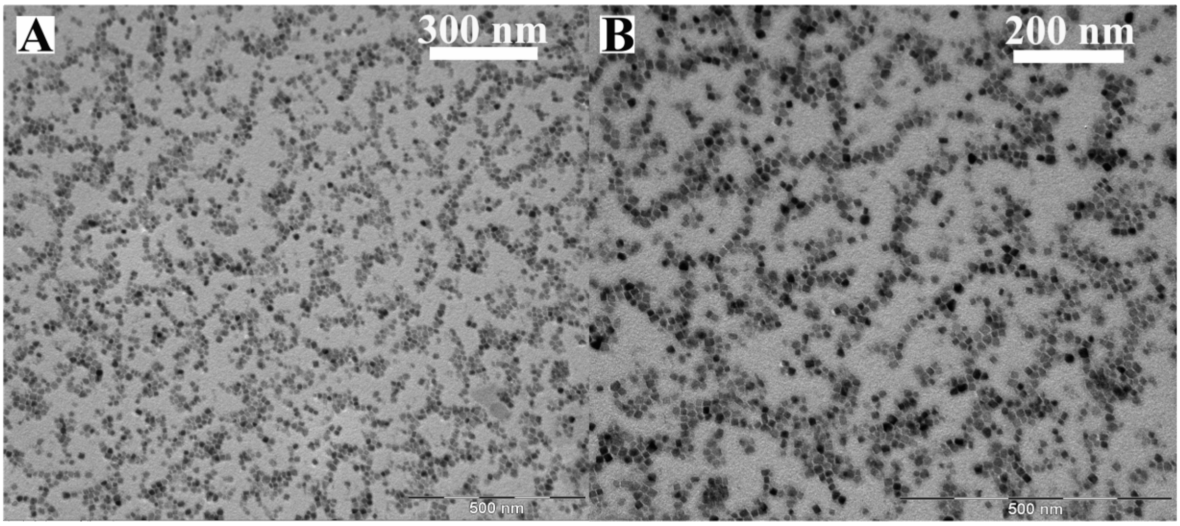


Figure S2. (A, B) TEM images of monodisperse 10-nm rhombohedral V_2O_3 pseudocubes.

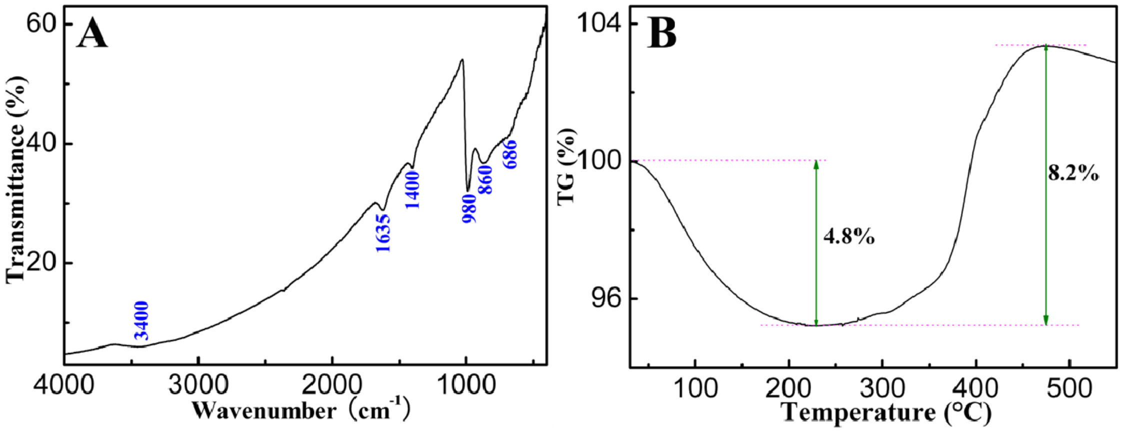


Figure S3. (A) FT-IR spectrum of the 10-nm rhombohedral V_2O_3 pseudocubes; (B) the typical TGA curve of rhombohedral V_2O_3 pseudocubes measured between 20 °C and 550 °C with a heating rate of 10 °C min^{-1} in N_2.

The N-H mode of 1635 cm^{-1} in FT-IR spectrum indicates that the 10-nm rhombohedral V_2O_3 pseudocubes are capped with oleylamine.[6] The broad band at 3400 cm^{-1} could be assigned to the adsorbed water. The 1400 cm^{-1} and 686 cm^{-1} belong to the C-H bending vibration. The band at 980 cm^{-1} belongs to the stretching vibration of V=O in rhombohedral V_2O_3, while the peak at 860 cm^{-1} could be assigned to its C-C vibration frequency.[7-9]

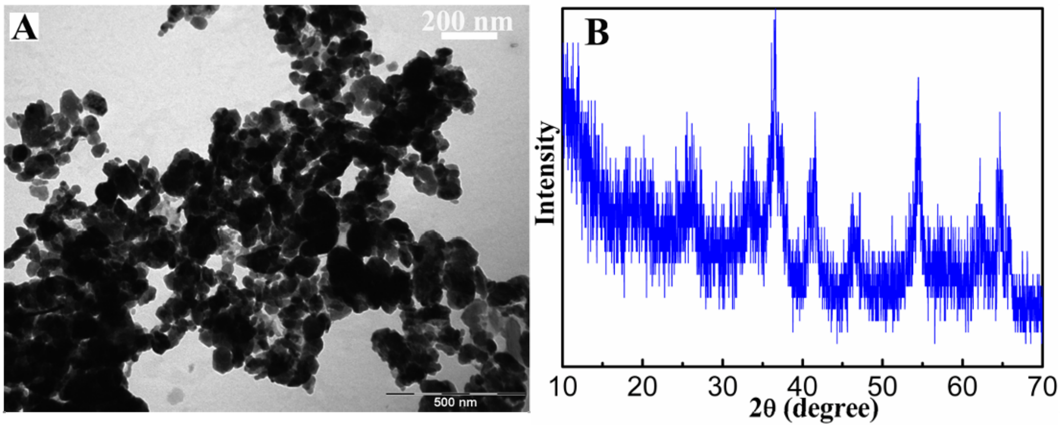
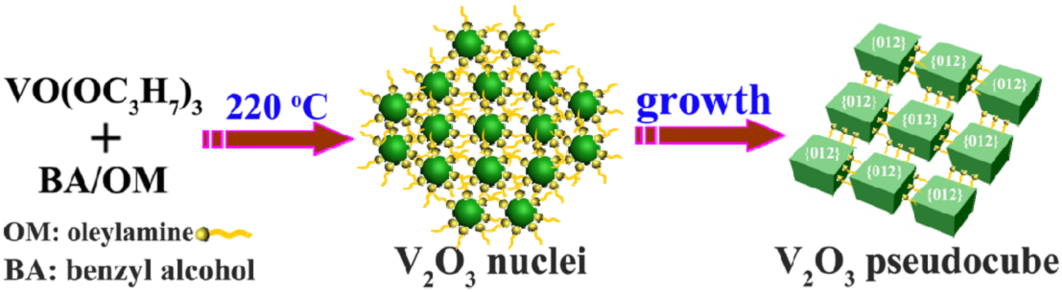


Figure S4. (A) TEM image of rhombohedral V_2O_3 obtained in the sole solvent of benzyl alcohol and (B) the XRD pattern obtained in the sole solvent of oleylamine.



Scheme S1. Schematic illustration for the formation of monodisperse 10-nm rhombohedral V_2O_3 pseudocubes with {012} facets exposed on surface.

S4. Characterizations for irregular V_2O_3 particles with average sizes of 10 nm, 20 nm, 40 nm, 170 nm and 2 μm

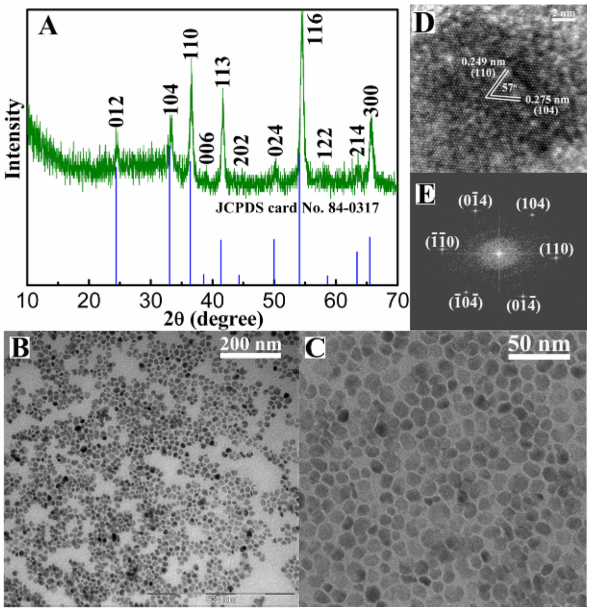


Figure S6. (A) XRD pattern and (B, C) TEM images of 10-nm irregular rhombohedral V_2O_3 nanoparticles obtained at 220 °C for 48 h; (D) HRTEM image and (E) the corresponding fast Fourier transform image of a single rhombohedral V_2O_3 nanoparticle. The panel A also shows the corresponding standard pattern of JCPDS card No. 84-0317.

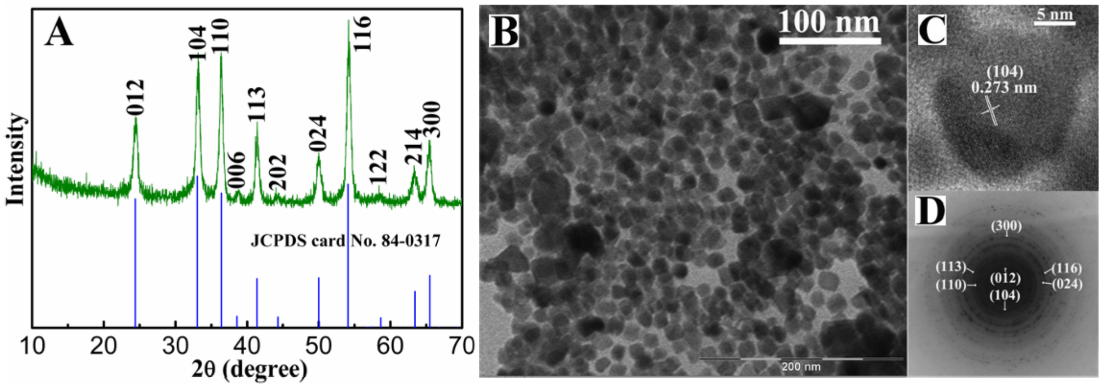


Figure S7. (A) XRD pattern, (B) TEM image, (C) HRTEM image and (D) selected-area electron diffeaction pattern of 20-nm irregular rhombohedral V_2O_3 nanoparticles obtained at 220 °C for 48 h. The panel A also shows the corresponding standard pattern of JCPDS card No. 84-0317.

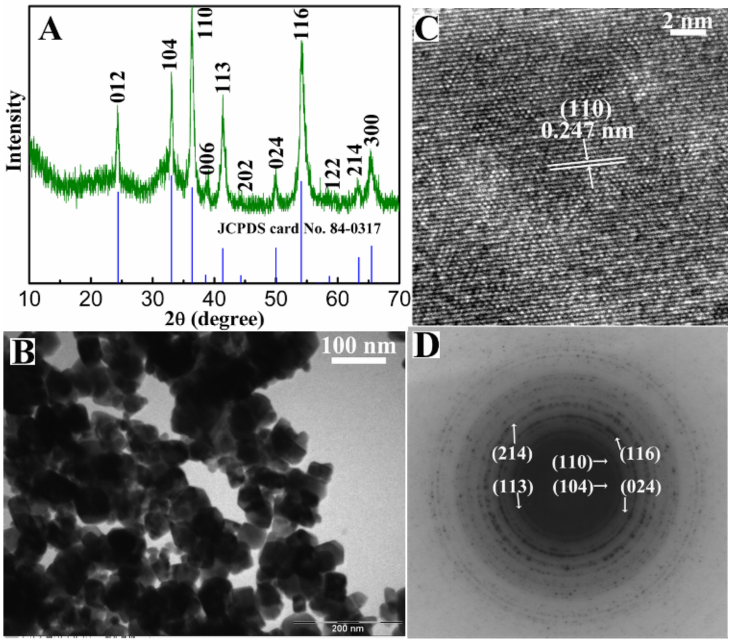


Figure S8. (A) XRD pattern, (B) TEM image, (C) HRTEM image and (D) selected-area electron diffraction pattern of 40-nm irregular rhombohedral V_2O_3 nanoparticles obtained at 220 °C for 48 h. The panel A also shows the corresponding standard pattern of JCPDS card No. 84-0317.

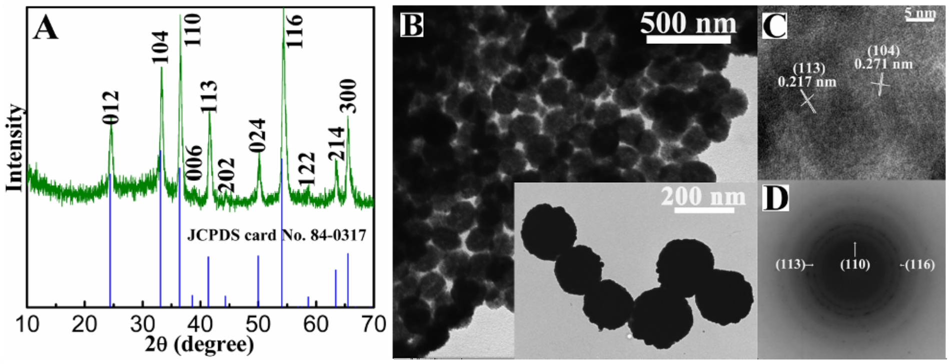


Figure S9. (A) XRD pattern, (B) TEM images, (C) HRTEM image and (D) selected-area electron diffeaction pattern of 170-nm irregular rhombohedral V_2O_3 nanoparticles obtained at 220 °C for 48 h. The panel A also shows the corresponding standard pattern of JCPDS card No. 84-0317.

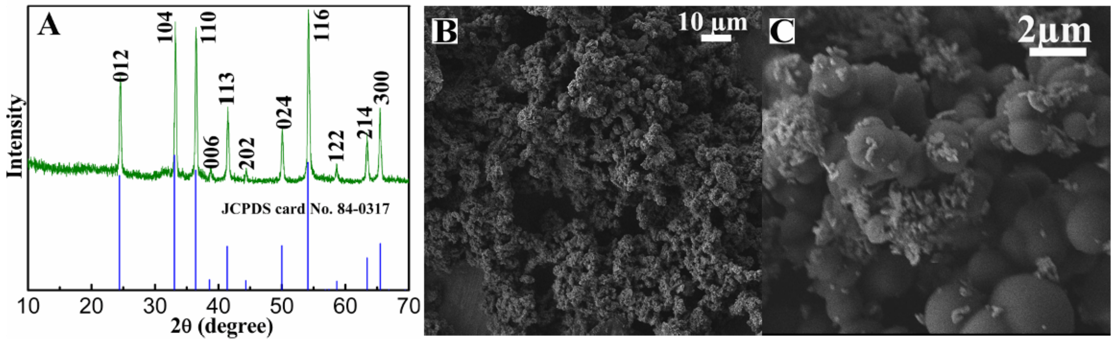


Figure S10. (A) XRD pattern, (B, C) SEM images of 2-µm irregular rhombohedral V_2O_3 particles obtained at 250 °C for 48 h. The panel A also shows the corresponding standard pattern of JCPDS card No. 84-0317.

References

[1] Sediri, F.; Hgarbi, N. *Mater. Sci. Eng., B* **2005**, *123*, 136-138.

[2] H. Katzke, R. Schlögl, Acta Cryst. 2003, B59, 456-462.

[3] Taylor, J. W.; Smith, T. J.; Andersen, K. H.; Capellmann, H.; Kremer, R. K.; Simon, A.; Schärpf, O.; Neumann, K. U.; Ziebeck, K. R. A. *Eur. Phys. J. B* **1999**, *12*, 199-207.

[4] Dernier, P. D.; Marezio, M. *Phys. Rev. B*, **1970**, *2*, 3771-3776.

[5] Goodenough, J. B. *Annu. Rev. Mater. Sci.* **1971**, *1*, 101-138.

[6] Xu, X. G.; Wang, X. *Inorg. Chem.* **2009**, *48*, 3890.

[7] Caravati, M.; Grunwaldt, J. D.; Baiker, A. *Phys. Chem. Chem. Phys.* **2005**, *7*, 278.

[8] Boscencu, R.; Ilie, M.; Socoteanu, R.; Oliveira, A.; Constantin, S. C.; Neagu, M.; Manda, G.; Ferreira, L. F. V. *Molecules* **2010**, *15*, 3731.

[9] Botto, I. L.; Vassallo, M. B.; Baran, E. J.; Minelli, G. M. *Chem. Phys.* **1997**, *50*, 267.