Supplementary information

for

Unveiling the crystallographic origin of mechanochemically induced monoclinic to triclinic phase transformation in WO_3

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S.1. Milling induced structural changes and the crystallite size determination

The XRD patterns have been drawn together to realize the significant intensity differences attributed to the crystallite size differences between the γ-WO_3 and δ-WO_3. A substantial reduction in the intensity after HEBM can be observed, as shown in **figure S1**.

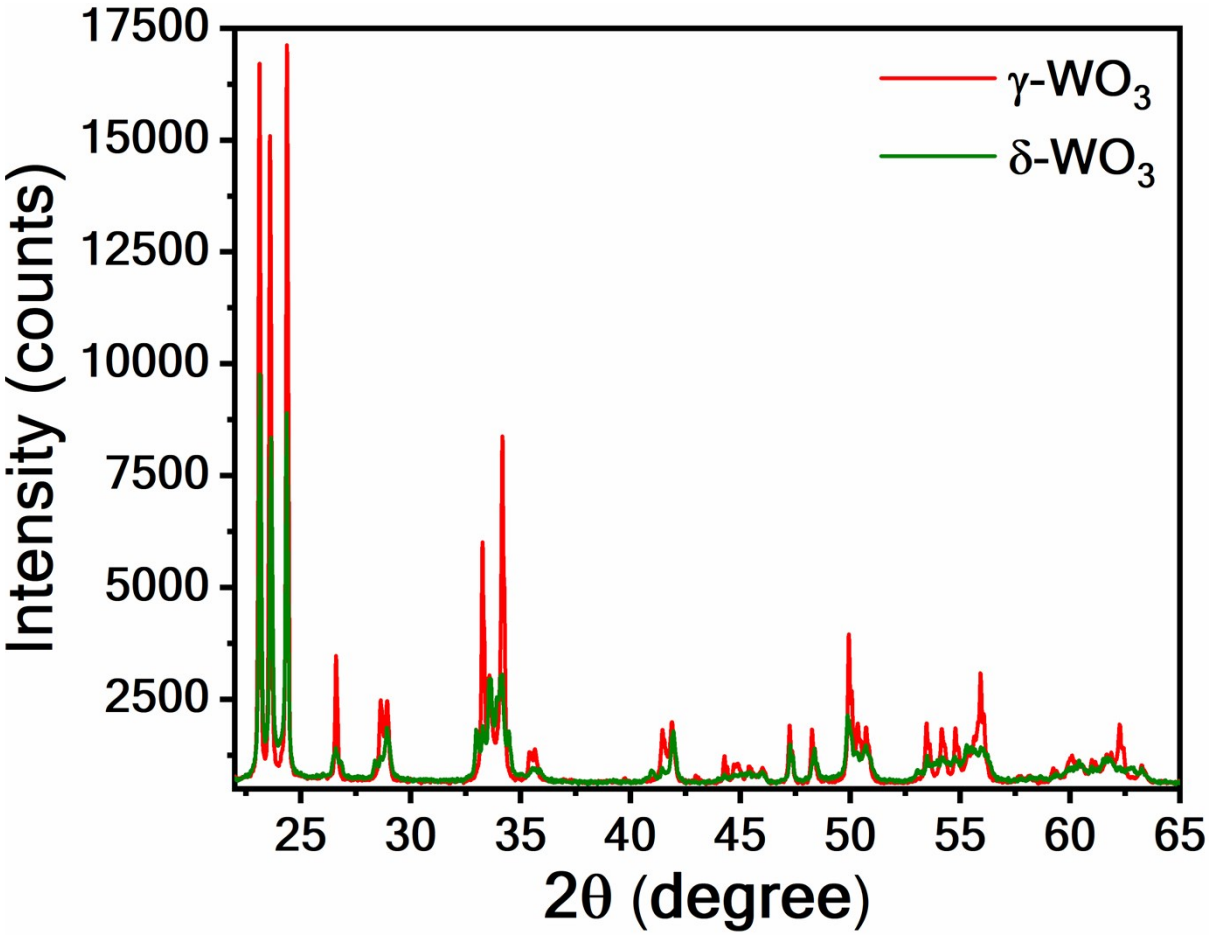

Figure S1. XRD patterns of the γ-WO_3 and δ-WO_3 showing the intensity differences.

An obvious difference in intensities can be observed from the scale enlarged XRD patterns given in **figure S2**. Accordingly, the broadening of peaks is also evidenced (**figure S2b, S2c, S2e, and S2f**). However, the broadening is significant at the higher angle peaks (**figure S2e and S2f**). Thus, we firmly believe that the mentioned differences could be attributed to such a refinement in the crystallite sizes.

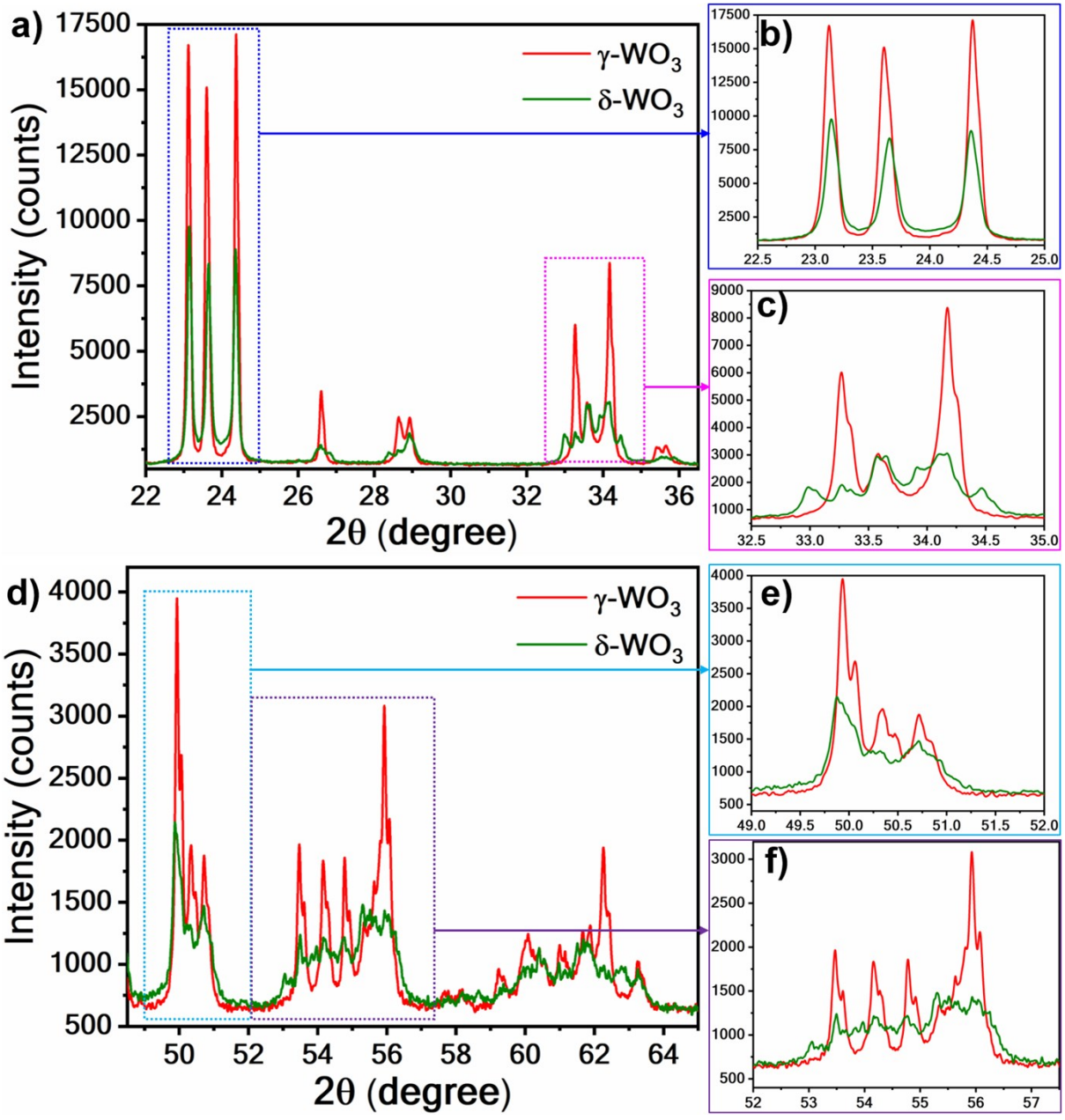

Figure S2. a) The XRD profiles of the γ-WO_3 and δ-WO_3 in the 2θ range of 22 – 36.5°. The highlighted regions in the boxes are shown with enlarged scales in the b) and c). d) Shows the

XRD patterns in the range of 48.5 – 65°, and their enlarged scales are shown in figure e) and f).

Considering the complexities of estimating the crystallite size by XRD data,[3,4] we have approached the electron microscopy techniques to measure the crystallite sizes directly. We have obtained the statistics from the different TEM micrographs to get a more reliable value. The unshown TEM micrographs in the manuscript are provided in **figure S3**. The calculated crystallite size distribution is shown in **figure S3d** with the average crystallite size of 11±6 nm.

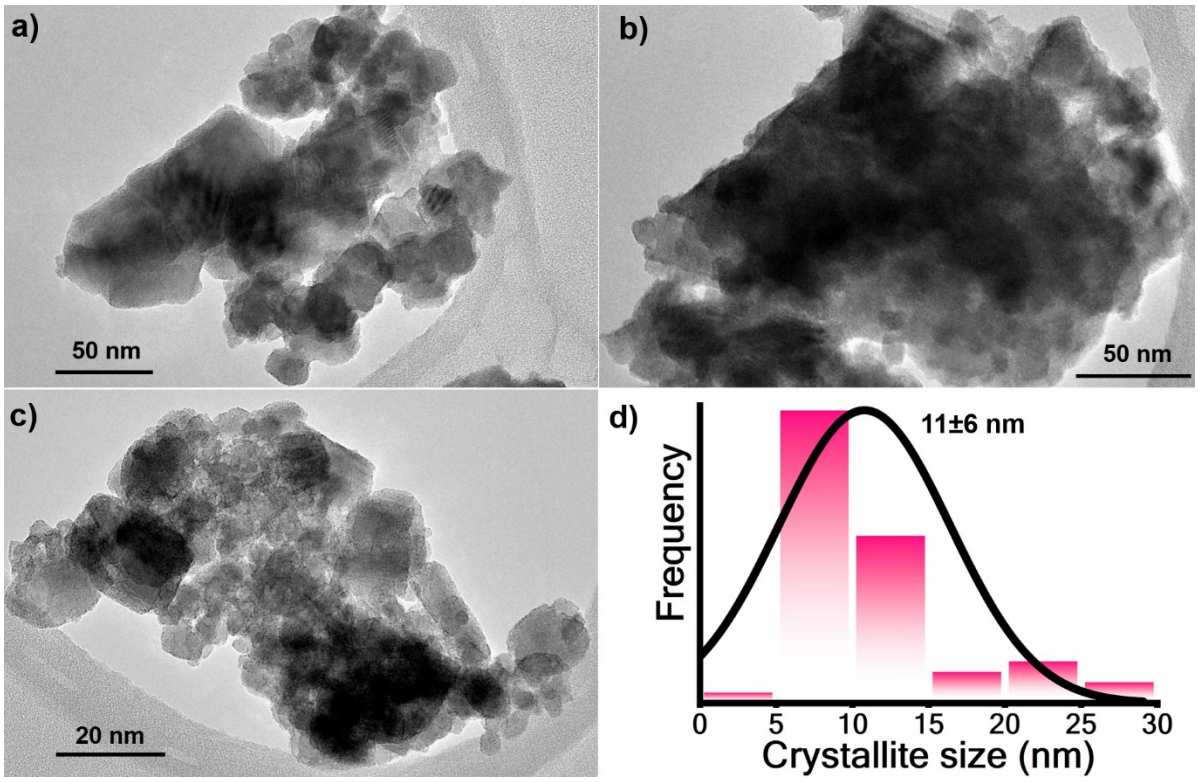

Figure S3. a), b), and c) TEM micrographs, and d) the crystallite size distribution of the δ-WO_3.

S.2. Rietveld refinement

The Rietveld refinement was performed using the FullProf software suite.[1] The pseudo-Voigt function was chosen for the peak fitting. A linear interpolation of a set of data points was adopted for the background method. The parameter refinement was done by following the strategic sequence suggested by Young.[2] The set of parameters refined in the current work were as follows: instrument, background, scale factor, lattice parameters, full width half maximum (FWHM) parameters, and shape parameters.

WO_3-UM: γ-WO_3
Space Group: P $2_1/n$

a = 7.30201Å α = 90.0000°

b = 7.53564Å β = 90.8066°

c = 7.69194Å γ = 90.0000°

V = 423.209 $Å^3$

WO_3-M: δ-WO_3

Space group: $P\bar{1}$

a = 7.30787Å α = 89.02081°

b = 7.52517Å β = 90.86459°

c = 7.68581Å γ = 90.75253°

V = 422.521 $Å^3$

S.3. X-ray photoelectron spectroscopy (XPS)

The area under the peaks of W4f spectra was extracted after peak fitting using XPS peak fit4.1 software. The details are tabulated below.

Table S2. The XPS peak positions and the peak areas of W4f core level spectra of δ-WO_3.

Details	**W^{6+} ($W4f_{5/2}$) eV.**	**W^{6+} ($W4f_{7/2}$) eV.**	**W^{5+} ($W4f_{5/2}$) eV.**	**W^{5+} ($W4f_{7/2}$) eV.**
Peak position	38.29	36.16	37.2	35
Peak area	277017	362568	16966	37008

The ratio of W^{5+}/ W^{6+}= 0.84

The percentage of W^{5+} = 7.8%

The percentage of W^{6+}= 92.2%

Two W^{5+} ions combinedly create one oxygen vacancy. The calculated oxygen vacancies are 1.3%

Let's consider the system composed of 100 W atoms. In principle, with no vacancies, the system should be composed of 100 * 3 = 300 oxygen atoms.

As per the current scenario,

there are 92 W^{6+} ions which coordinate with 92 * 3 = 276 oxygen atoms.

The 8 W^{5+} ions gives (8) * 2.5 = 20 oxygen atoms.

Thus, total oxygen atoms calculated are 276+20 = 296

The missing number of oxygen atoms compared to the perfect system is 300-296 = 4

The percentage of oxygen vacancies = (4/300) * 100 = 1.33%

References

1 J. Rodriguez-Carvajal, *Abstr. Satell. Meet. Powder Diffr. XV Congr. IUCr*, 1990, 127.

2 R. A. Young, *The Rietveld Method*, Oxford University Press, New York, 1993.

3 V. Mote, Y. Purushotham and B. Dole, *J. Theor. Appl. Phys.*, 2012, **6**, 6.

4 C. Kunka, B. L. Boyce, S. M. Foiles and R. Dingreville, *Nanoscale*, 2019, **11**, 22456–22466.