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Supporting Information

Planar transition metal oxides SERS chips: a general strategy

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Supplementary results

Section S1: The UPS spectra of TMOs after annealing

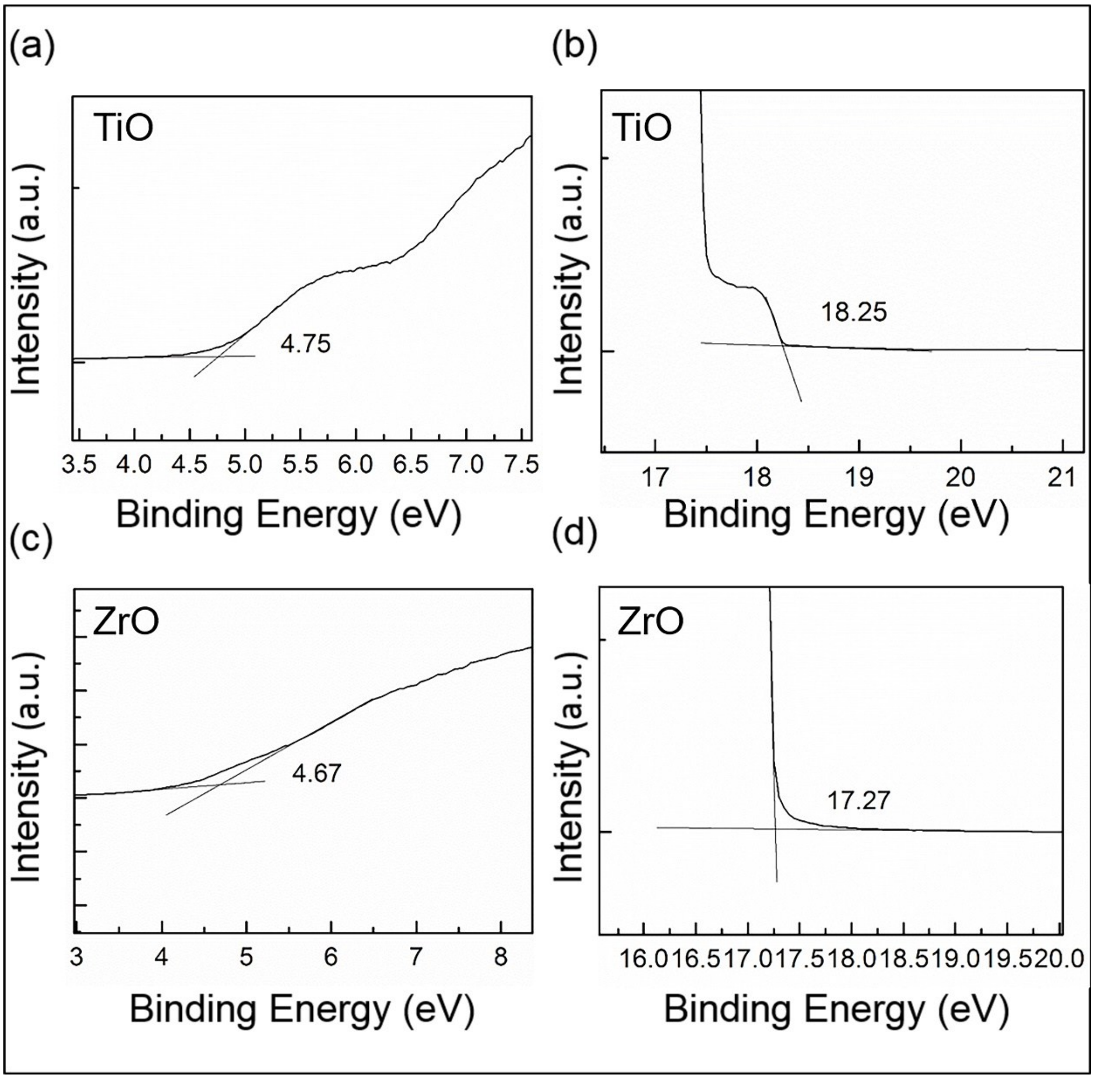

Fig. S1 The UPS spectra of (a and b) TiO and (c and d) ZrO after annealing. The work function of TiO is 2.97 eV (21.22 – 18.25). The VB level of TiO is situated at 7.72 eV (2.97 + 4.75).[1] The work function of ZrO is 3.95 eV (21.22 – 17.27). The VB level of ZrO is situated at 8.62 eV (3.95 + 4.67).

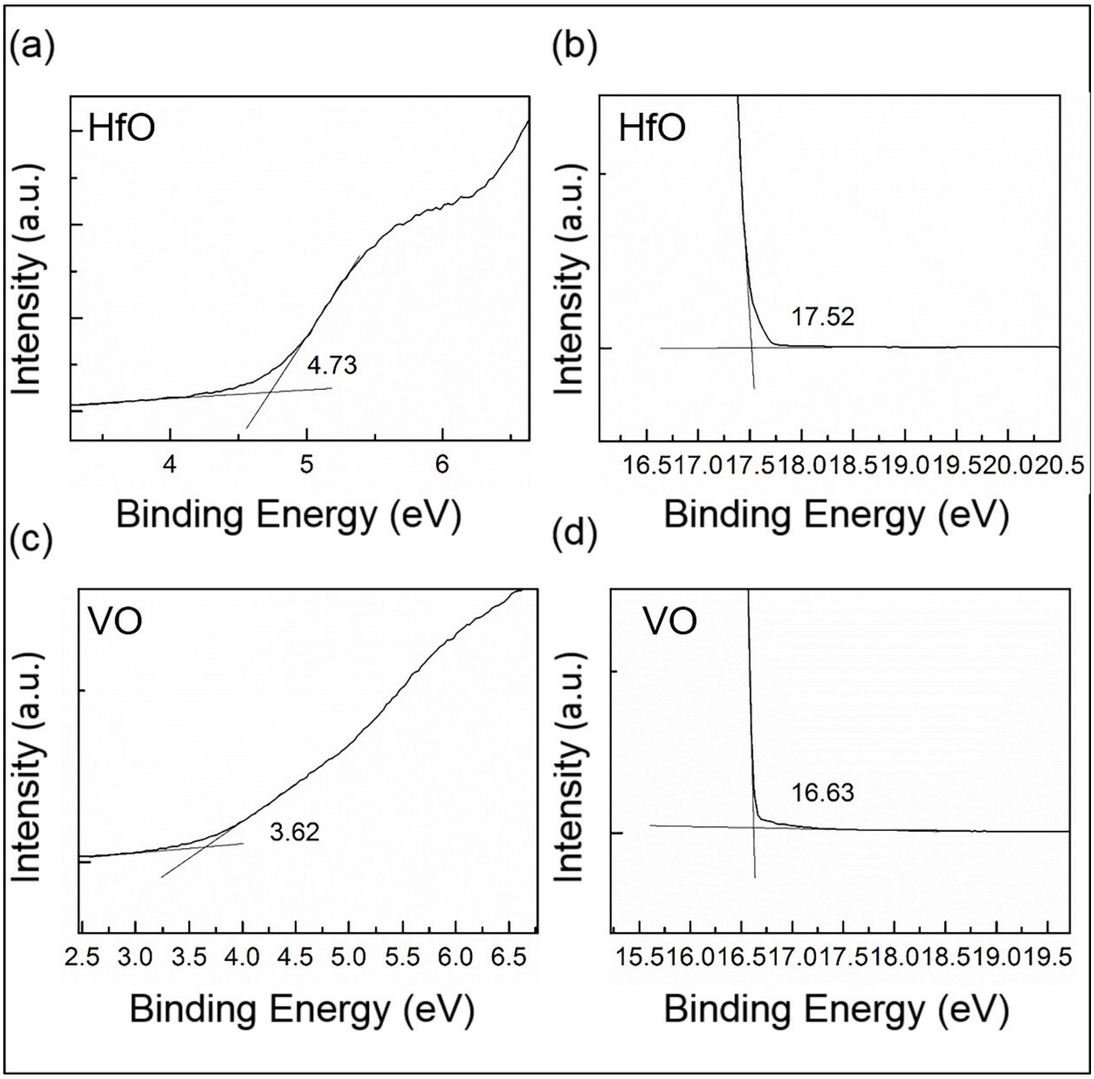

Fig. S2 The UPS spectra of (a and b) HfO and (c and d) VO after annealing. The work function of HfO is 3.70 eV (21.22 – 17.52). The VB level of HfO is situated at 8.43 eV (3.70 + 4.73). The work function of VO is 4.59 eV (21.22 – 16.63). The VB level of VO is situated at 8.21 eV (4.59 + 3.62).

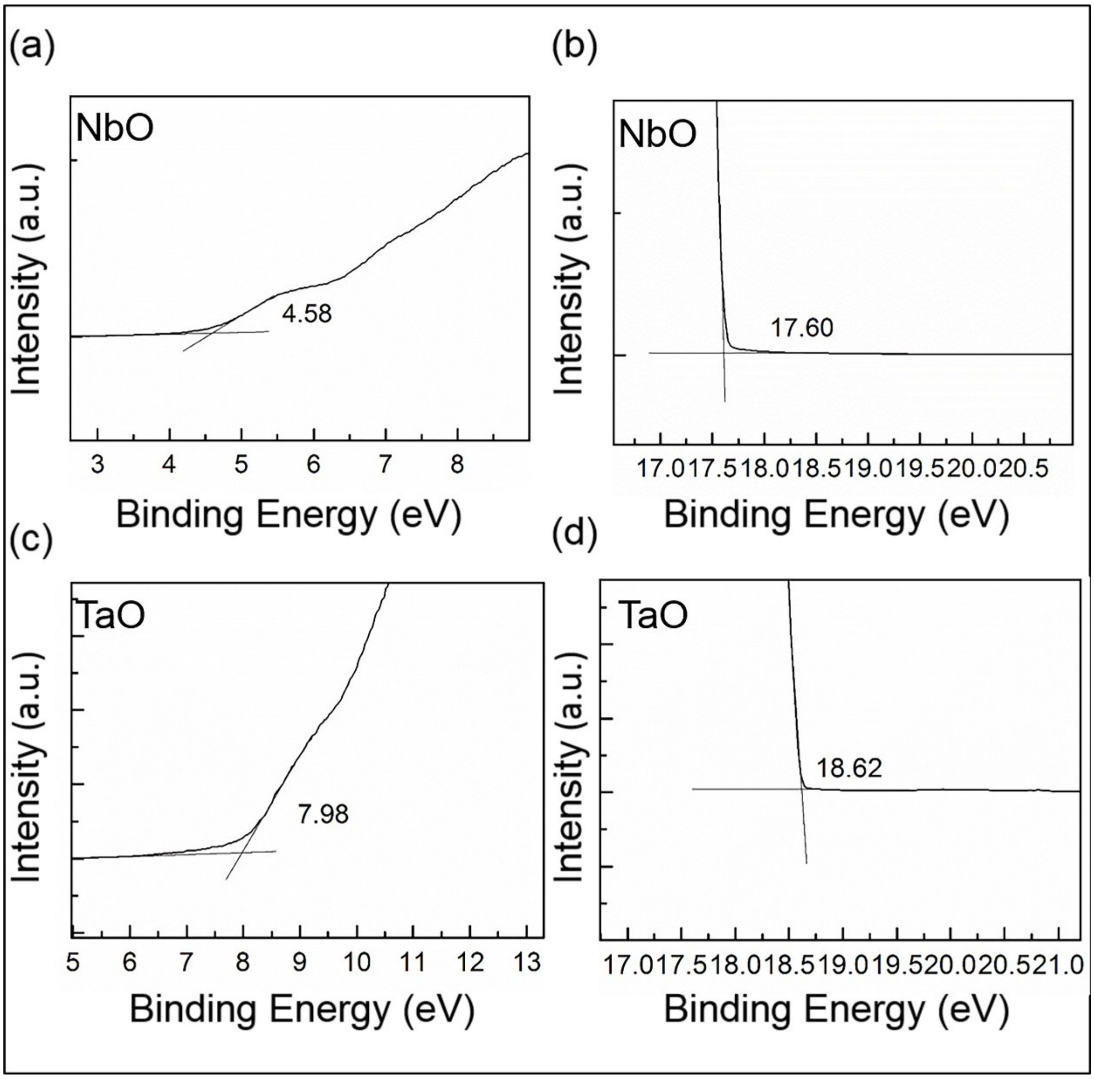

Fig. S3 The UPS spectra of (a and b) NbO and (c and d) TaO after annealing. The work function of NbO is 3.62 eV (21.22 – 17.60). The VB level of NbO is situated at 8.20 eV (3.62 + 4.58). The work function of TaO is 2.60 eV (21.22 – 18.62). The VB level of TaO is situated at 10.58 eV (2.60 + 7.98).

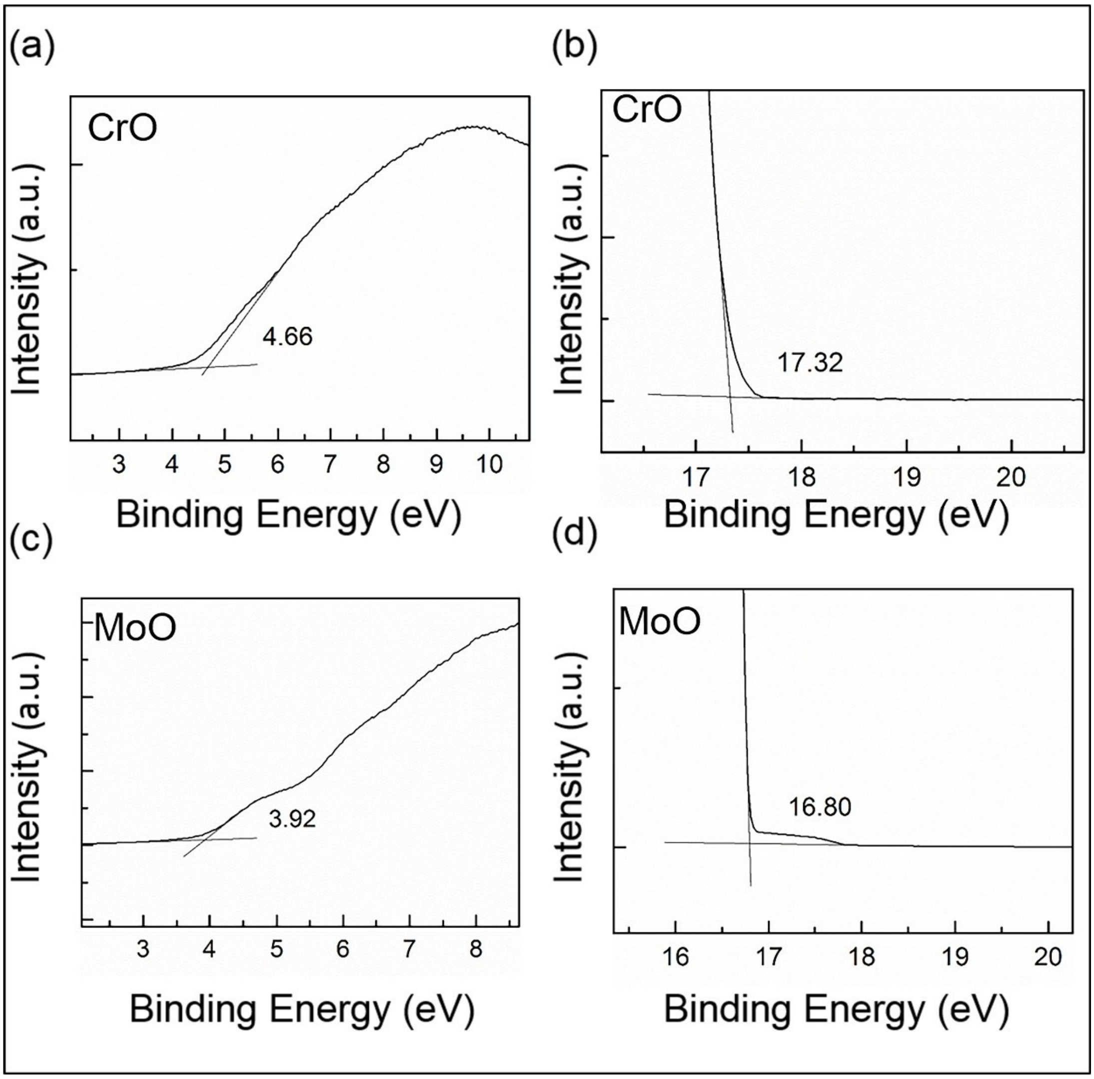

Fig. S4 The UPS spectra of (a and b) CrO and (c and d) MoO after annealing. The work function of CrO is 3.90 eV (21.22 – 17.32). The VB level of CrO is situated at 8.56 eV (3.90 + 4.66). The work function of MoO is 4.42 eV (21.22 – 16.80). The VB level of MoO is situated at 8.34 eV (4.42 + 3.92).

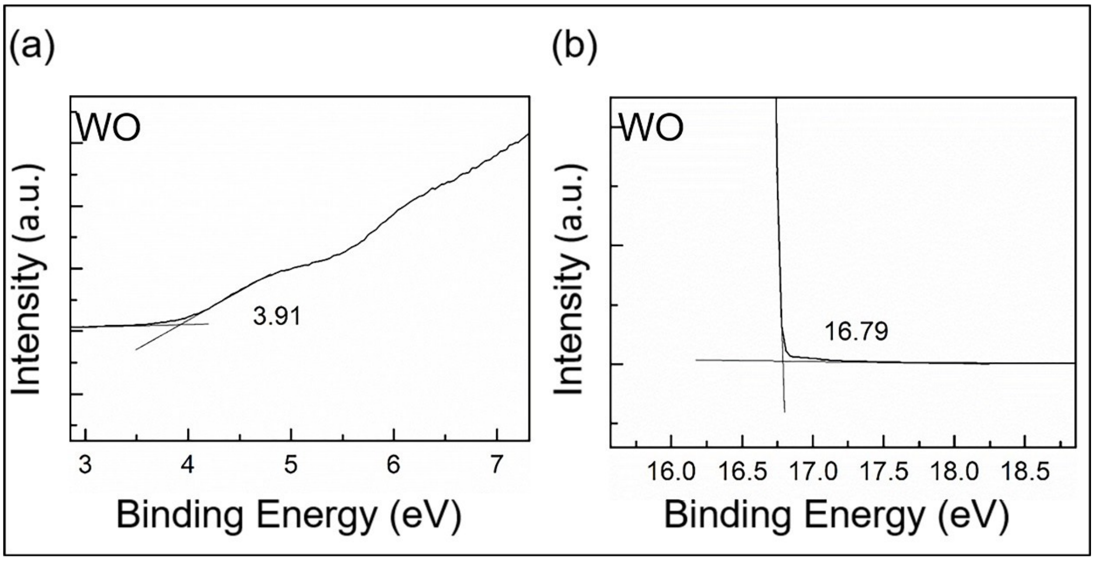

Fig. S5 The UPS spectra of (a and b) WO after annealing. The work function of WO is 4.43 eV (21.22 – 16.79). The VB level of WO is situated at 8.34 eV (4.43 + 3.91).

Section S2: The optical energy band gap of TMOs after annealing

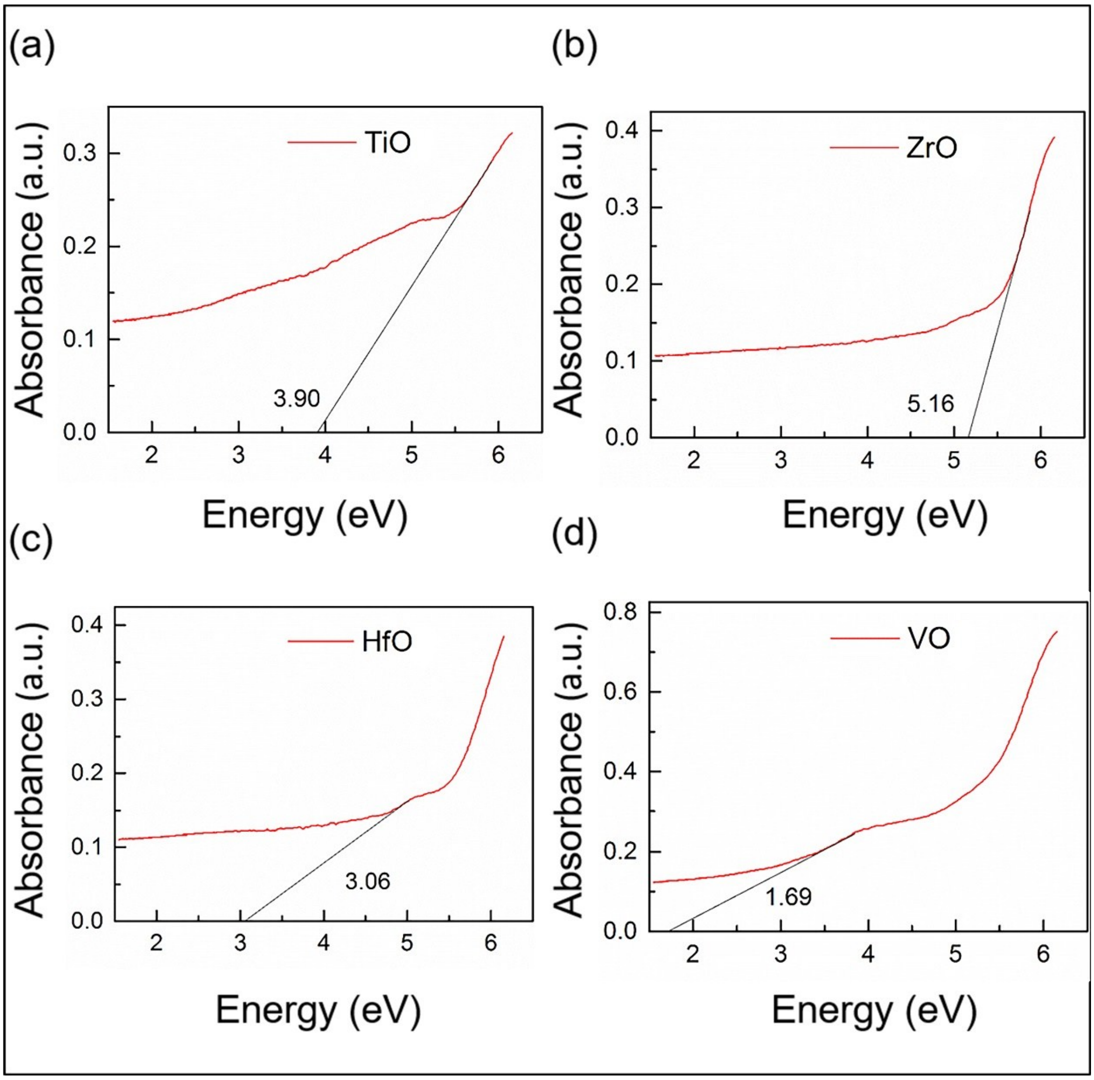

Fig. S6 $(\alpha\hbar w)^{1/2}$ as a function of photon energy ($\hbar w$) for (a) TiO, (b) ZrO, (c) HfO and (d) VO. The optical energy band gap (E_g) are 3.90 eV (TiO), 5.16 eV (ZrO), 3.06 eV (HfO) and 1.69 eV (VO), respectively.[2] The CB level of TiO is situated at 3.82 eV (7.72 – 3.90). The CB level of ZrO is situated at 3.46 eV (8.62 – 5.16). The CB level of HfO is situated at 5.37 eV (8.43 – 3.06). The CB level of VO is situated at 6.52 eV (8.21 – 1.69).

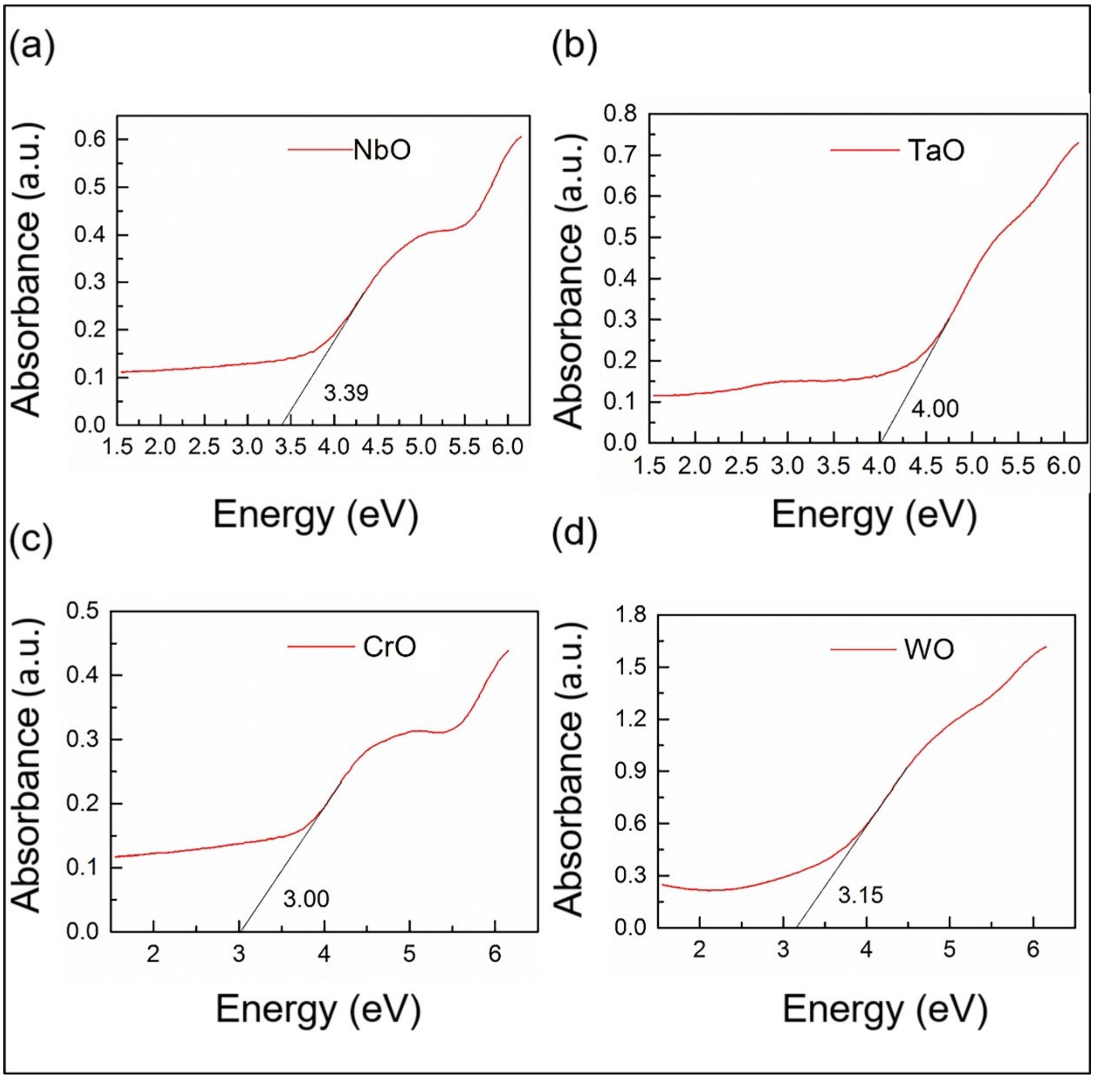

Fig. S7 $(\alpha\hbar w)^{1/2}$ as a function of photon energy ($\hbar w$) for (a) NbO, (b) TaO, (c) CrO and (d) WO. E_g are 3.39 eV (NbO), 4.00 eV (TaO), 3.00 eV (CrO) and 3.15 eV (WO), respectively. The CB level of NbO is situated at 4.81 eV (8.20 – 3.39). The CB level of TaO is situated at 6.58 eV (10.58 – 4.00). The CB level of CrO is situated at 5.56 eV (8.56 – 3.00). The CB level of WO is situated at 5.19 eV (8.34 – 3.15).

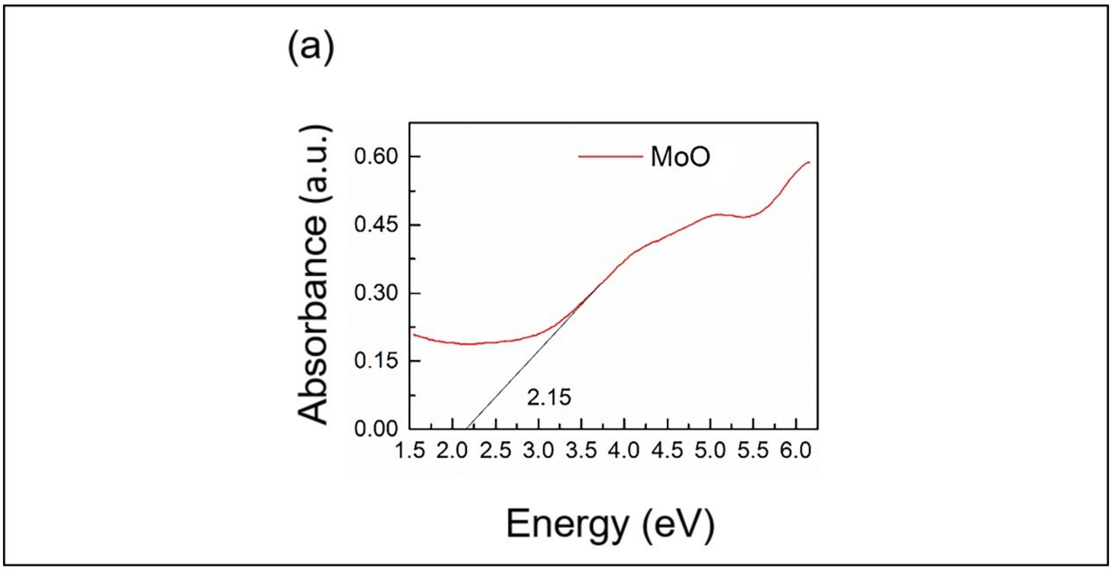

Fig. S8 $(\alpha\hbar w)^{1/2}$ as a function of photon energy (ħw) for MoO. E_g is 2.15 eV. The CB level is situated at 6.19 eV (8.34 – 2.15).

Section S3: The thickness and roughness of TMOs

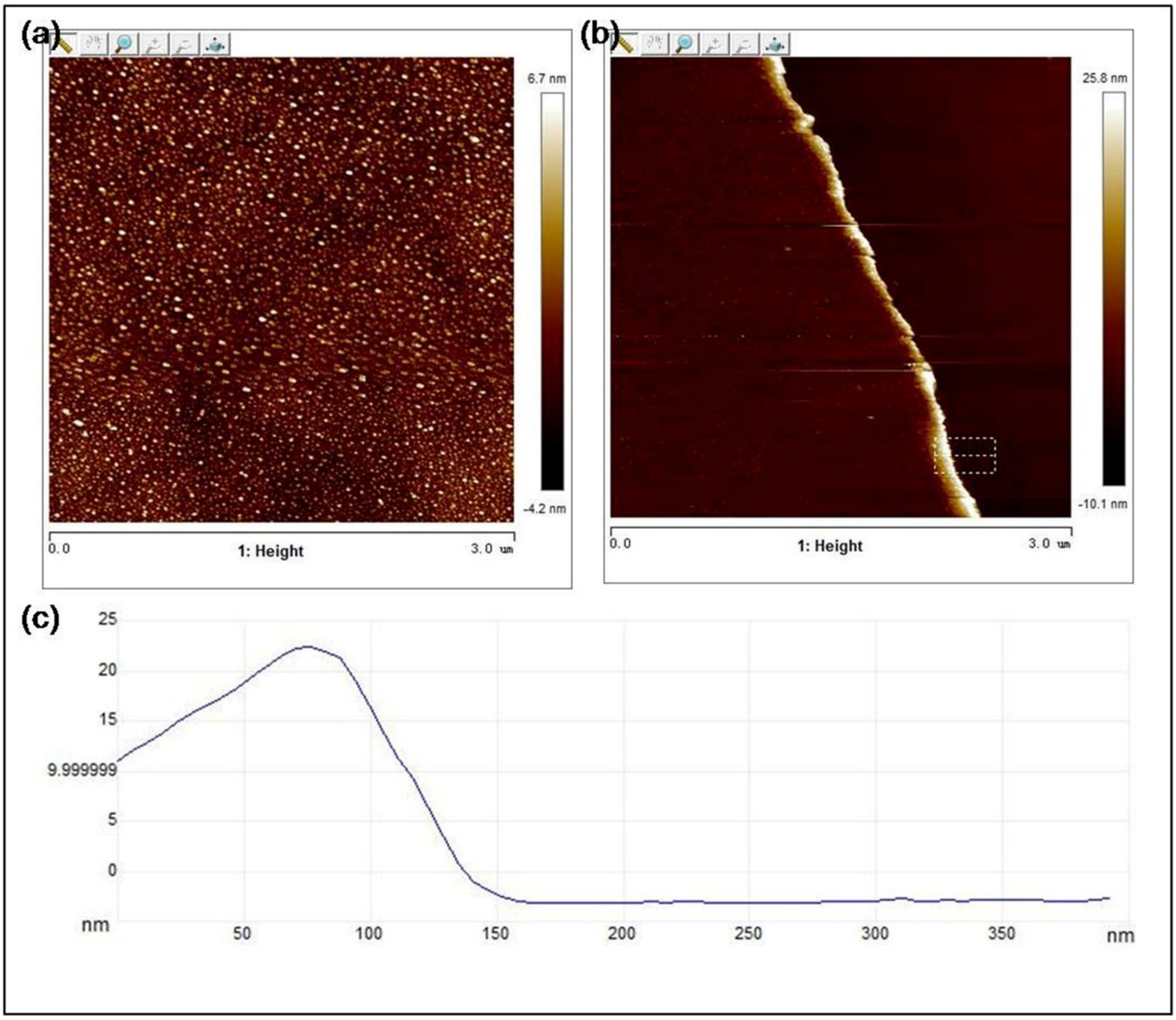

Fig. S9 The roughness (a) and thickness (b) of TiO. The Ra value of roughness is 1.130 nm. (c) The value of thickness is below 25 nm.

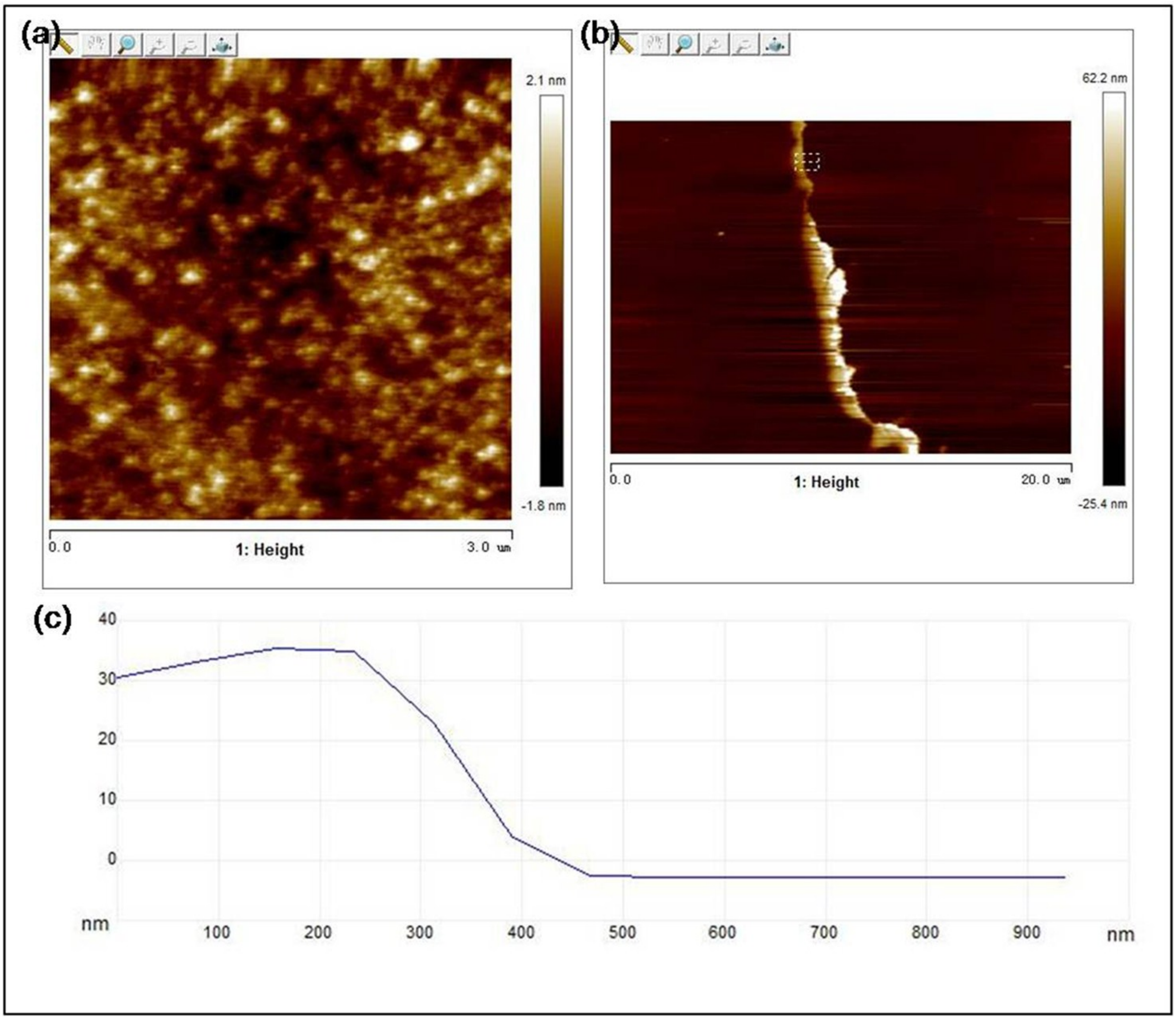

Fig. S10 The roughness (a) and thickness (b) of ZrO. The Ra value of roughness is 0.360 nm. (c) The value of thickness is below 40 nm.

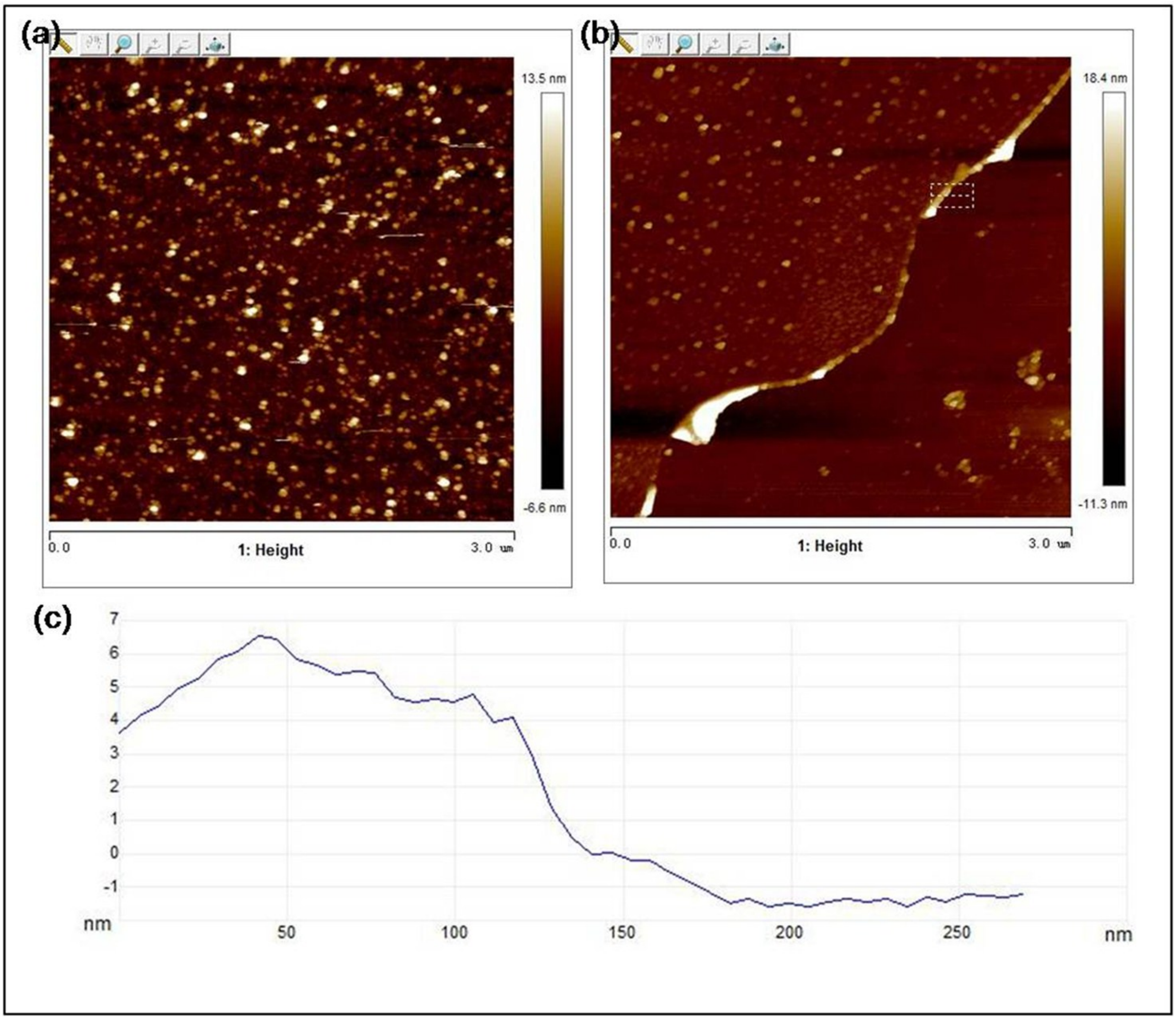

Fig. S11 The roughness (a) and thickness (b) of HfO. The Ra value of roughness is 1.840 nm. (c) The value of thickness is below 9 nm.

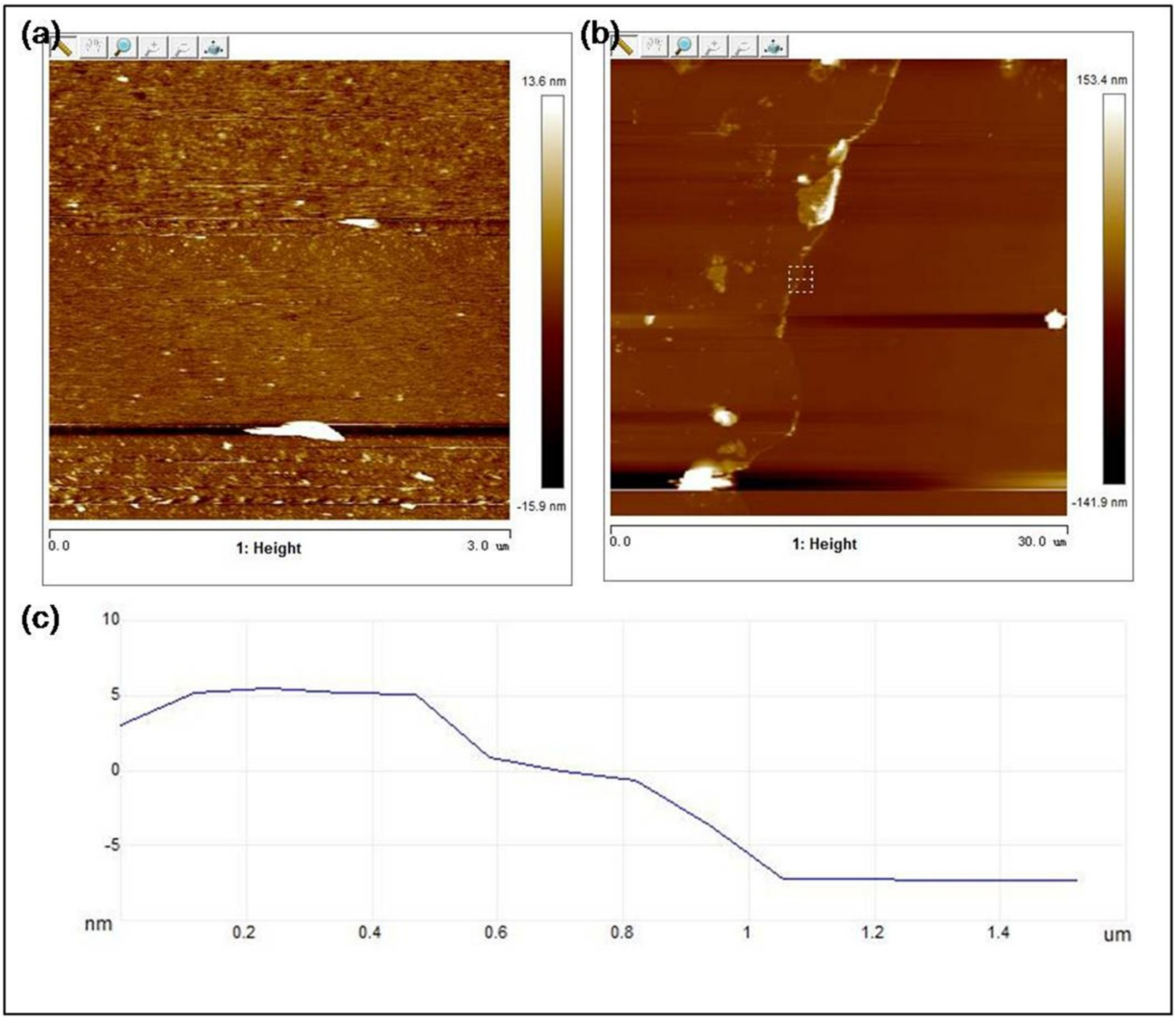

Fig. S12 The roughness (a) and thickness (b) of VO. The Ra value of roughness is 1.730 nm. (c) The value of thickness is below 13 nm.

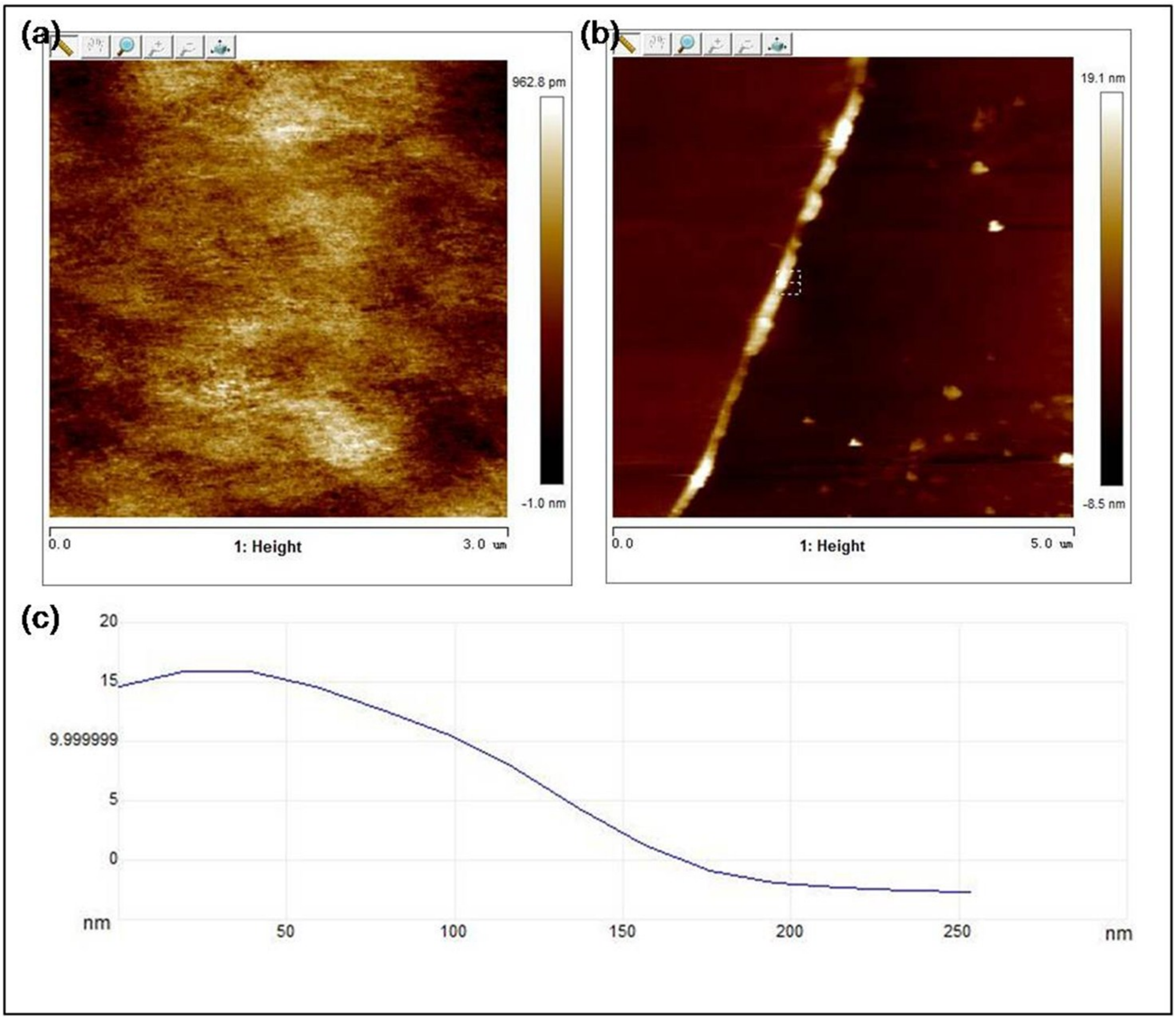

Fig. S13 The roughness (a) and thickness (b) of NbO. The Ra value of roughness is 0.134 nm. (c) The value of thickness is below 20 nm.

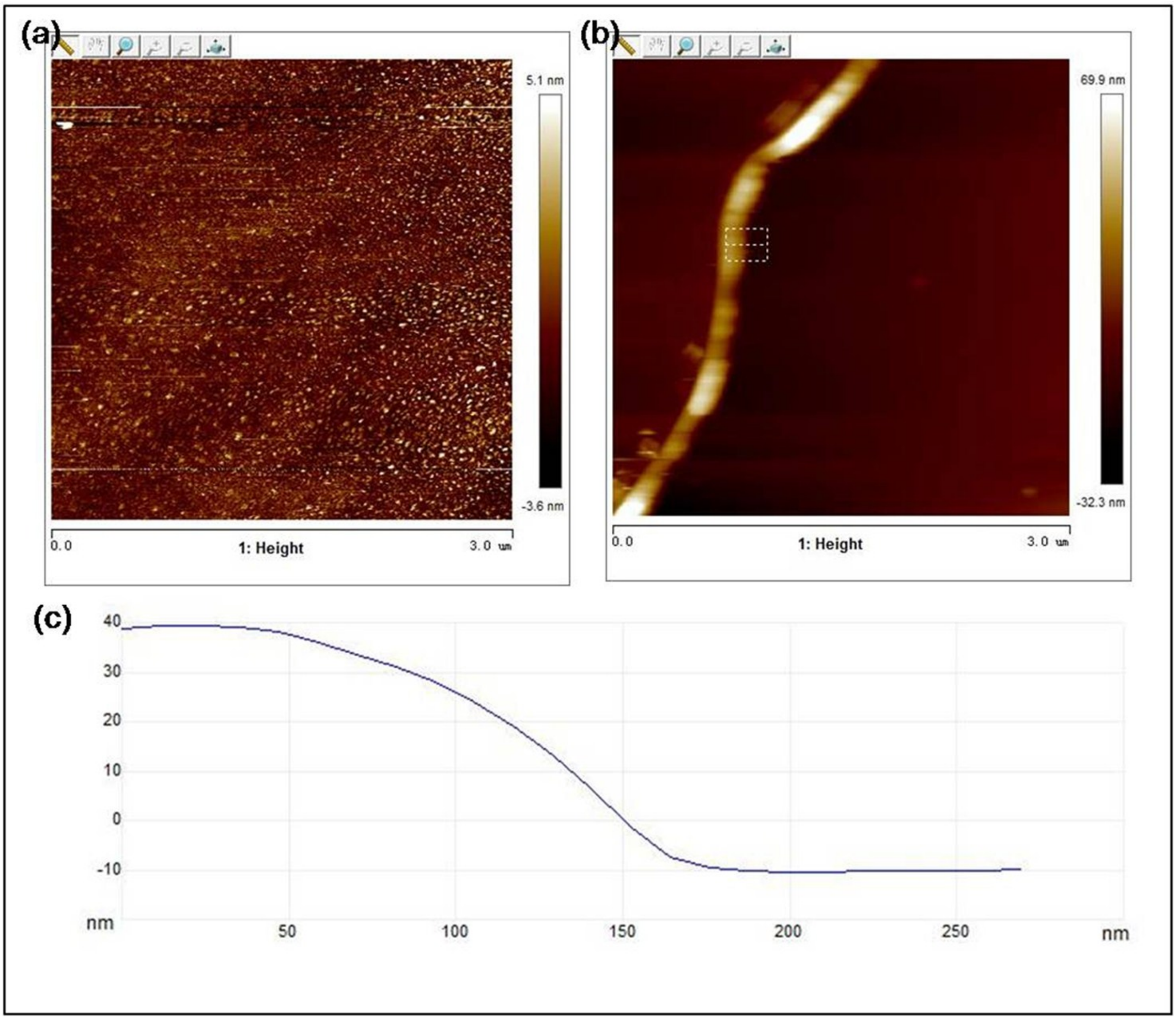

Fig. S14 The roughness (a) and thickness (b) of TaO. The Ra value of roughness is 0.786 nm. (c) The value of thickness is below 50 nm.

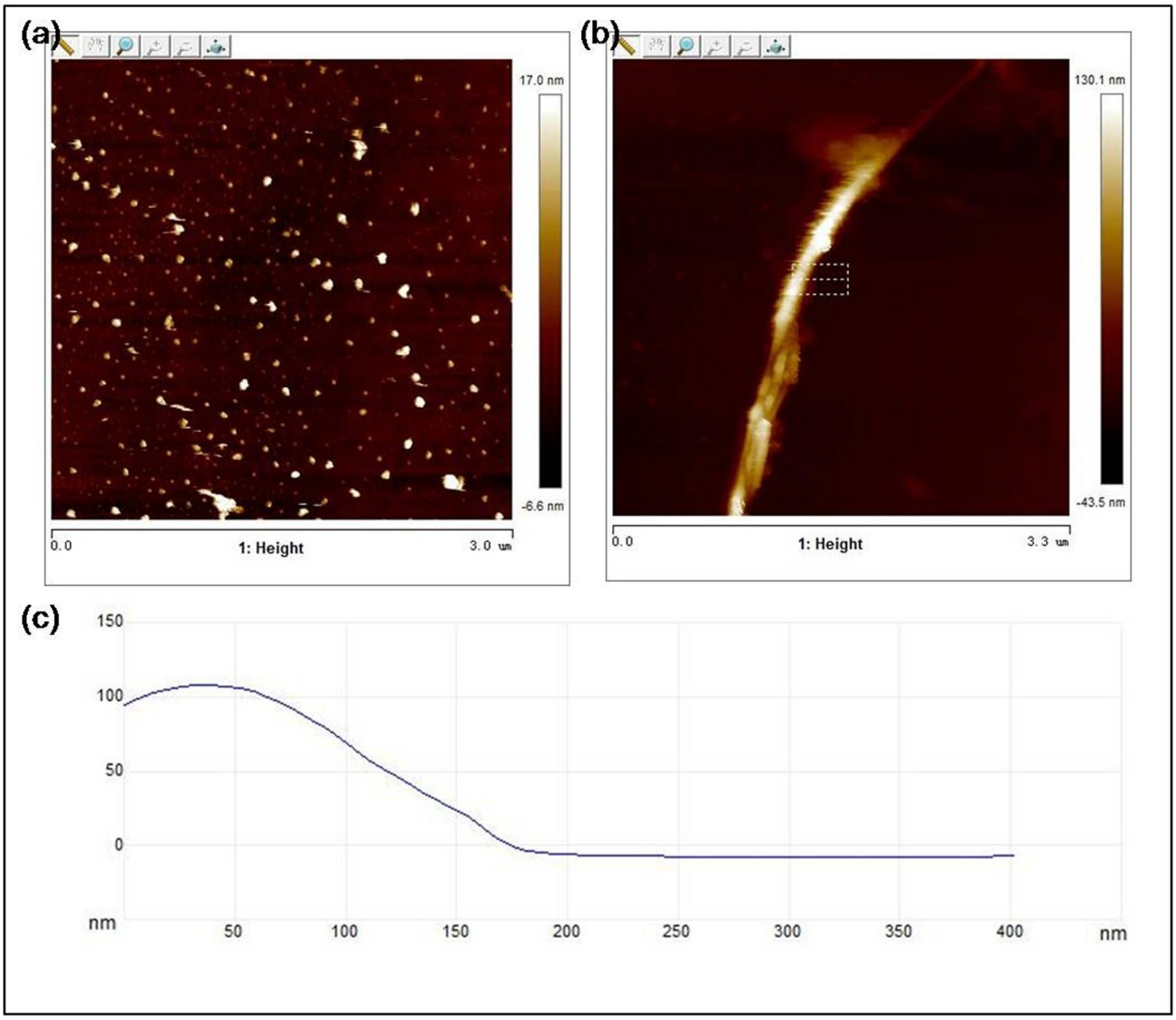

Fig. S15 The roughness (a) and thickness (b) of CrO. The Ra value of roughness is 1.250 nm. (c) The value of thickness is below 110 nm.

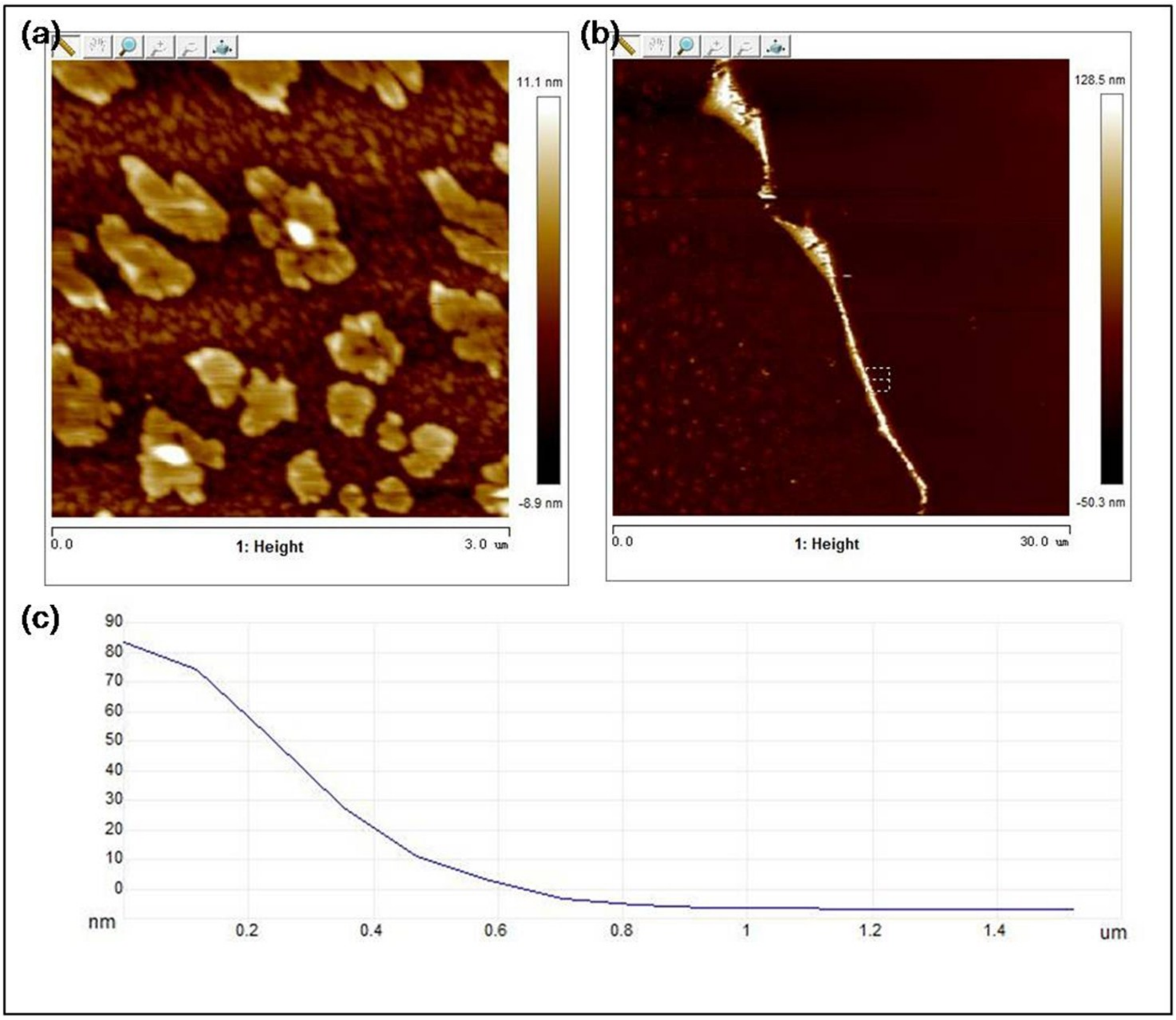

Fig. S16 The roughness (a) and thickness (b) of MoO. The Ra value of roughness is 2.510 nm. (c) The value of thickness is below 90 nm.

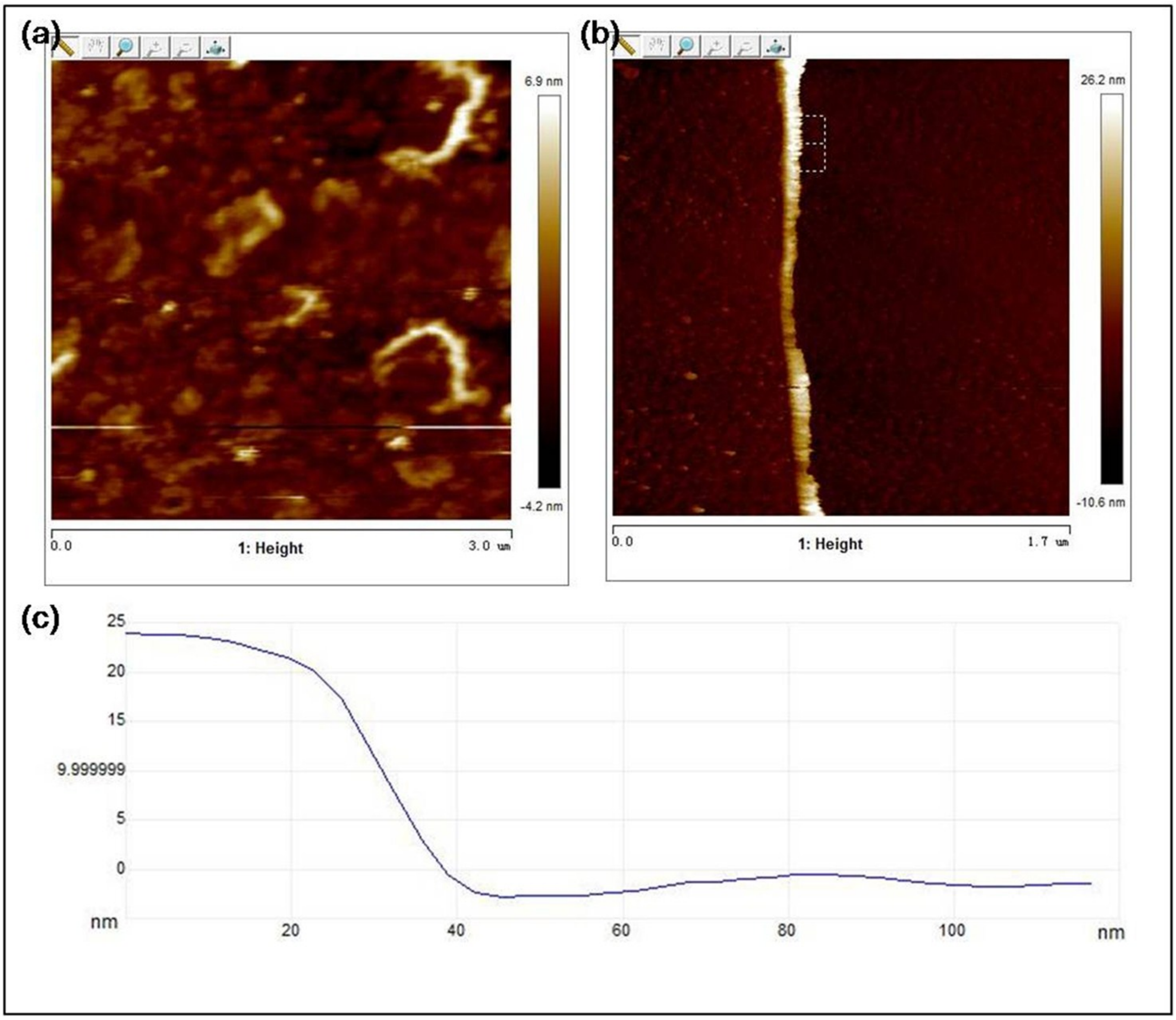

Fig. S17 The roughness (a) and thickness (b) of WO. The Ra value of roughness is 0.826 nm. (c) The value of thickness is below 30 nm.

Section S4: UV-vis absorption spectra of TMOs before and after annealing

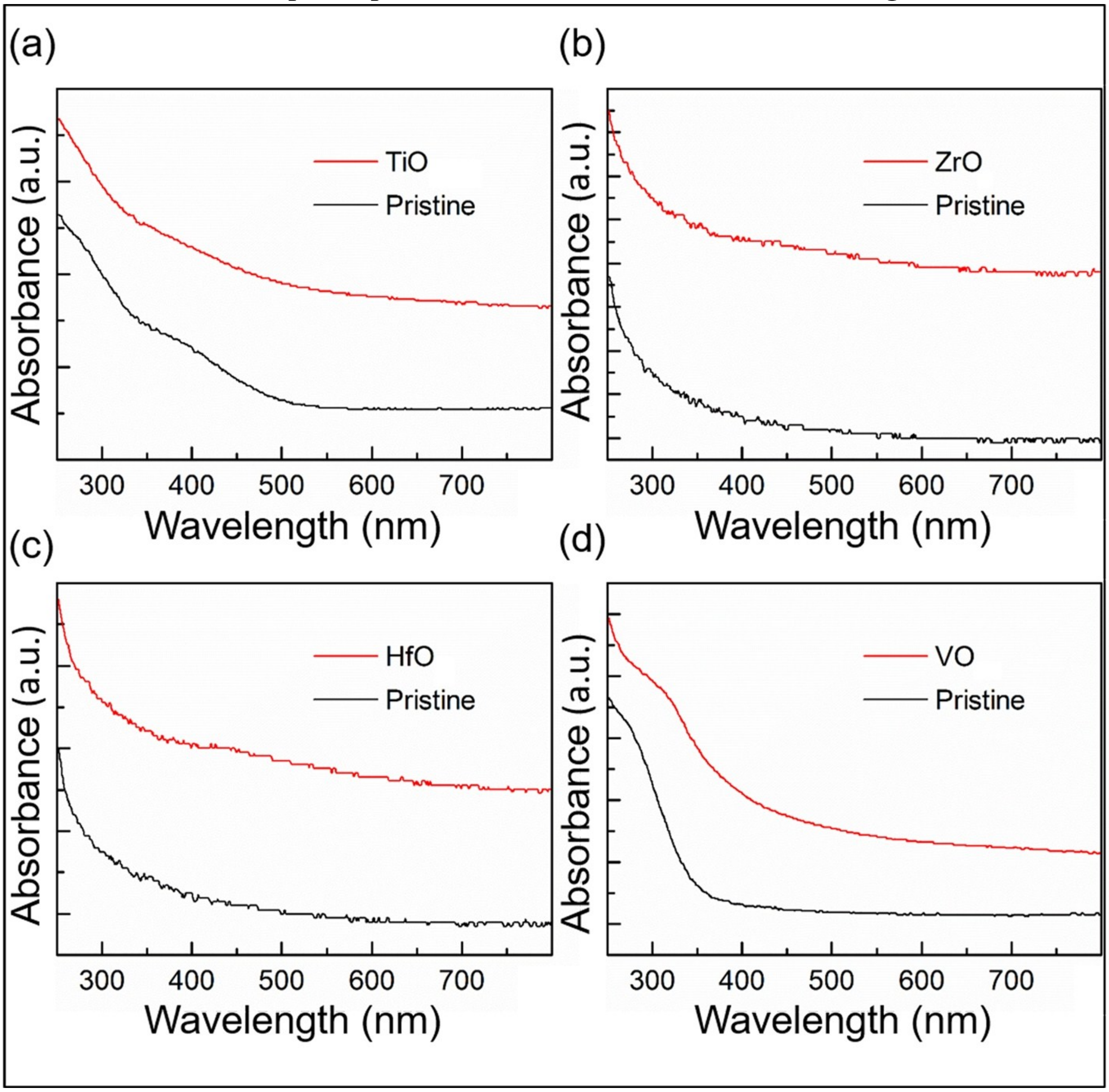

Fig. S18 UV-vis absorption spectra of (a) TiO, (b) ZrO, (c) HfO, (d) VO before and after H_2 annealing treatment.

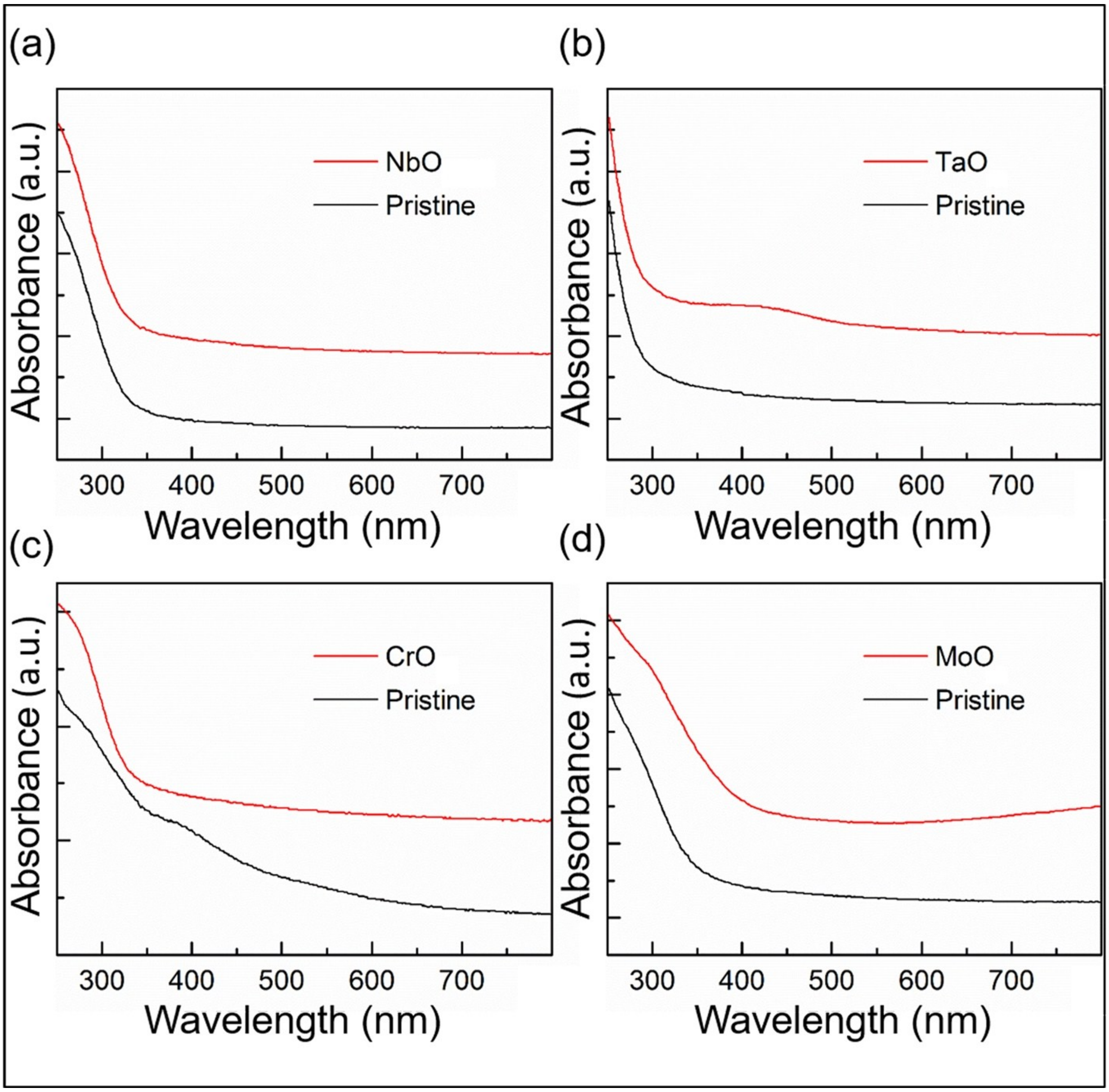

Fig. S19 UV-vis absorption spectra of (a) NbO, (b) TaO, (c) CrO, (d) MoO before and after H_2 annealing treatment.

Section S5: SERS of TMOs and a SiO_2 dielectric layer coated on them

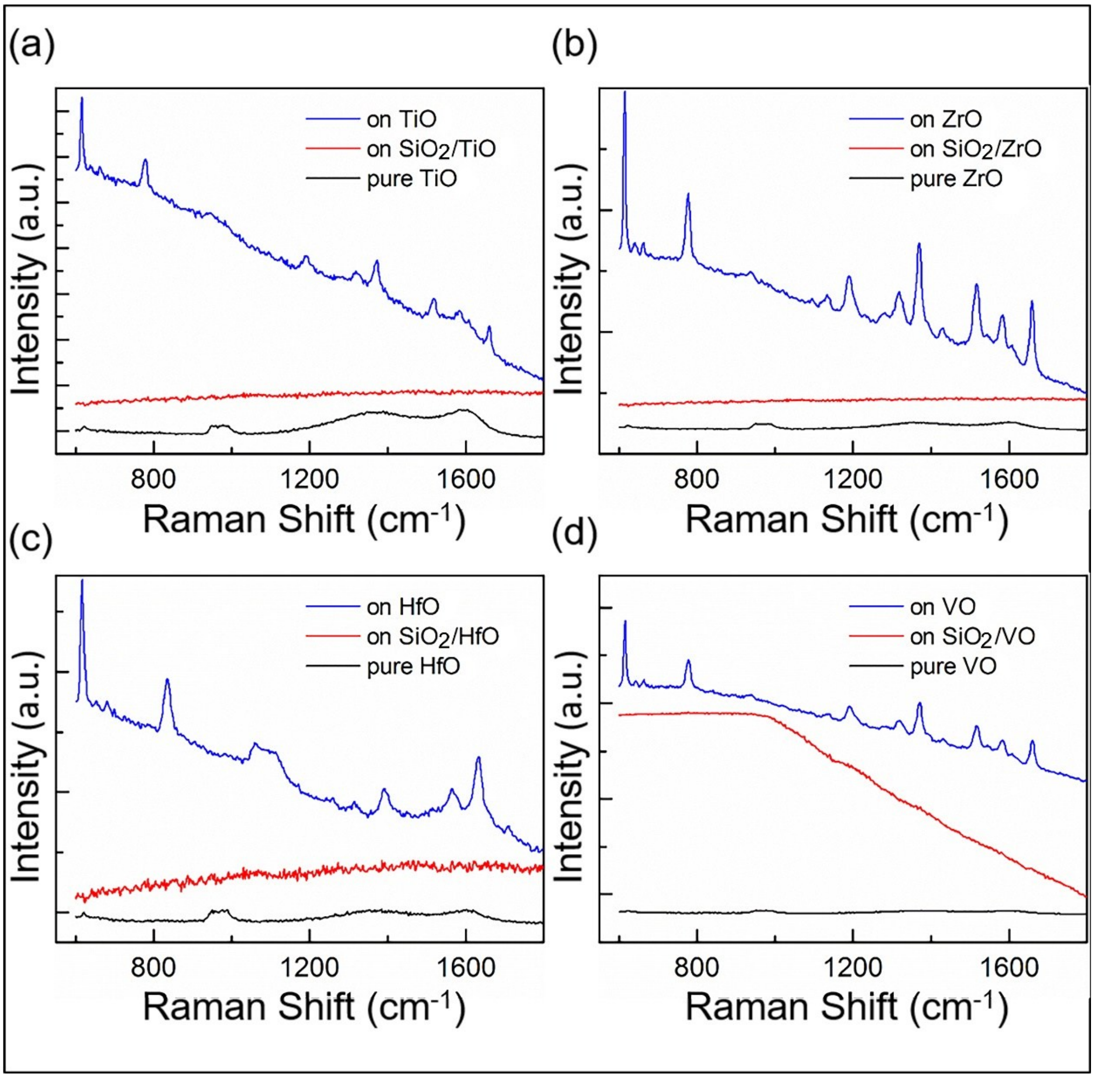

Fig. S20 The Raman spectra of R6g at a concentration of 10^{-5} M absorbed on (a) TiO, (b) ZrO, (c) HfO, (d) VO and a SiO_2 dielectric layer coated on them after H_2annealing treatment.

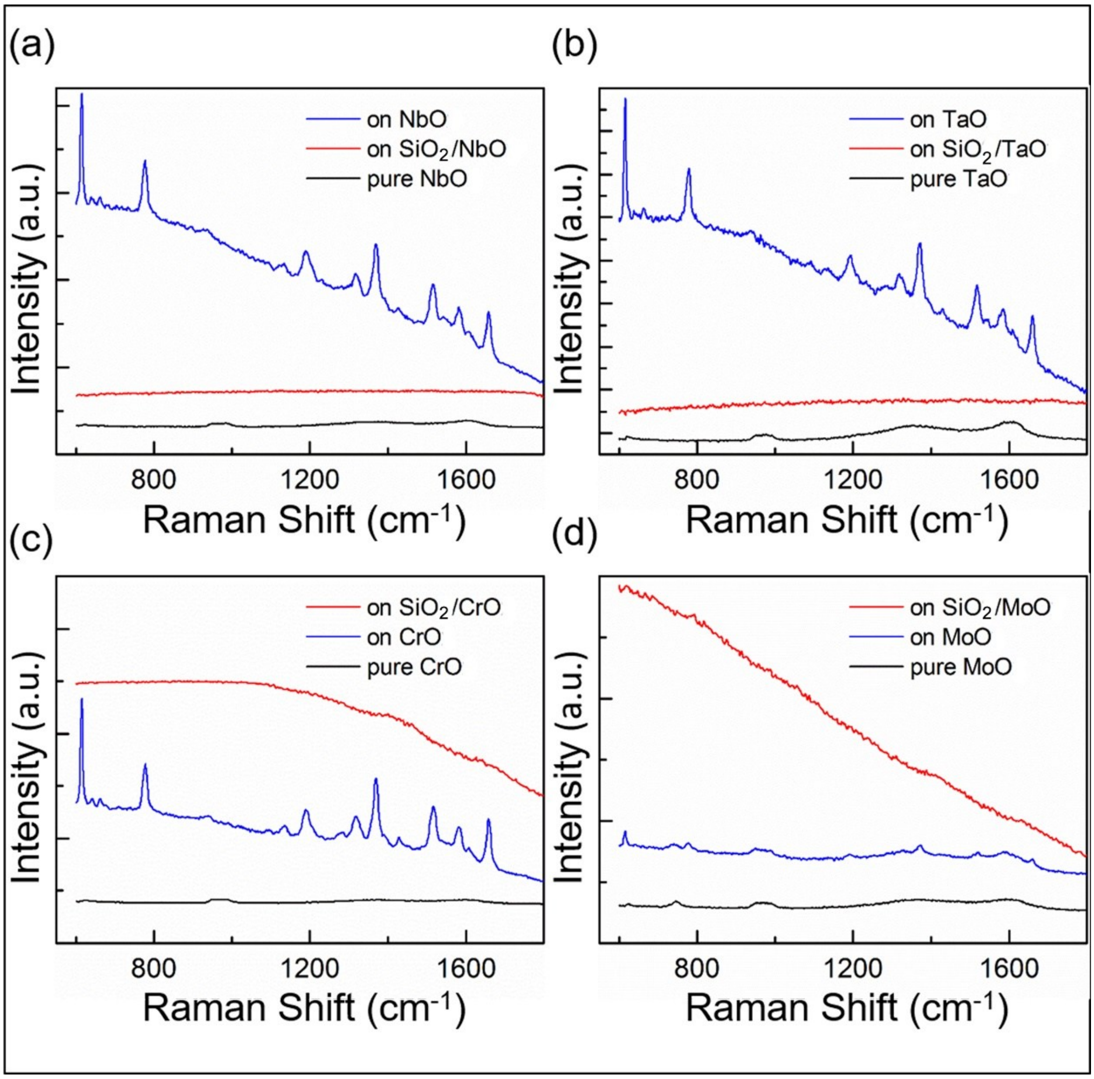

Fig. S21 The Raman spectra of R6g at a concentration of 10^{-5} M absorbed on (a) NbO, (b) TaO, (c) CrO, (d) MoO and a SiO_2 dielectric layer coated on them after H_2 annealing treatment.

Section S6: XPS spectra of TMOs before and after annealing

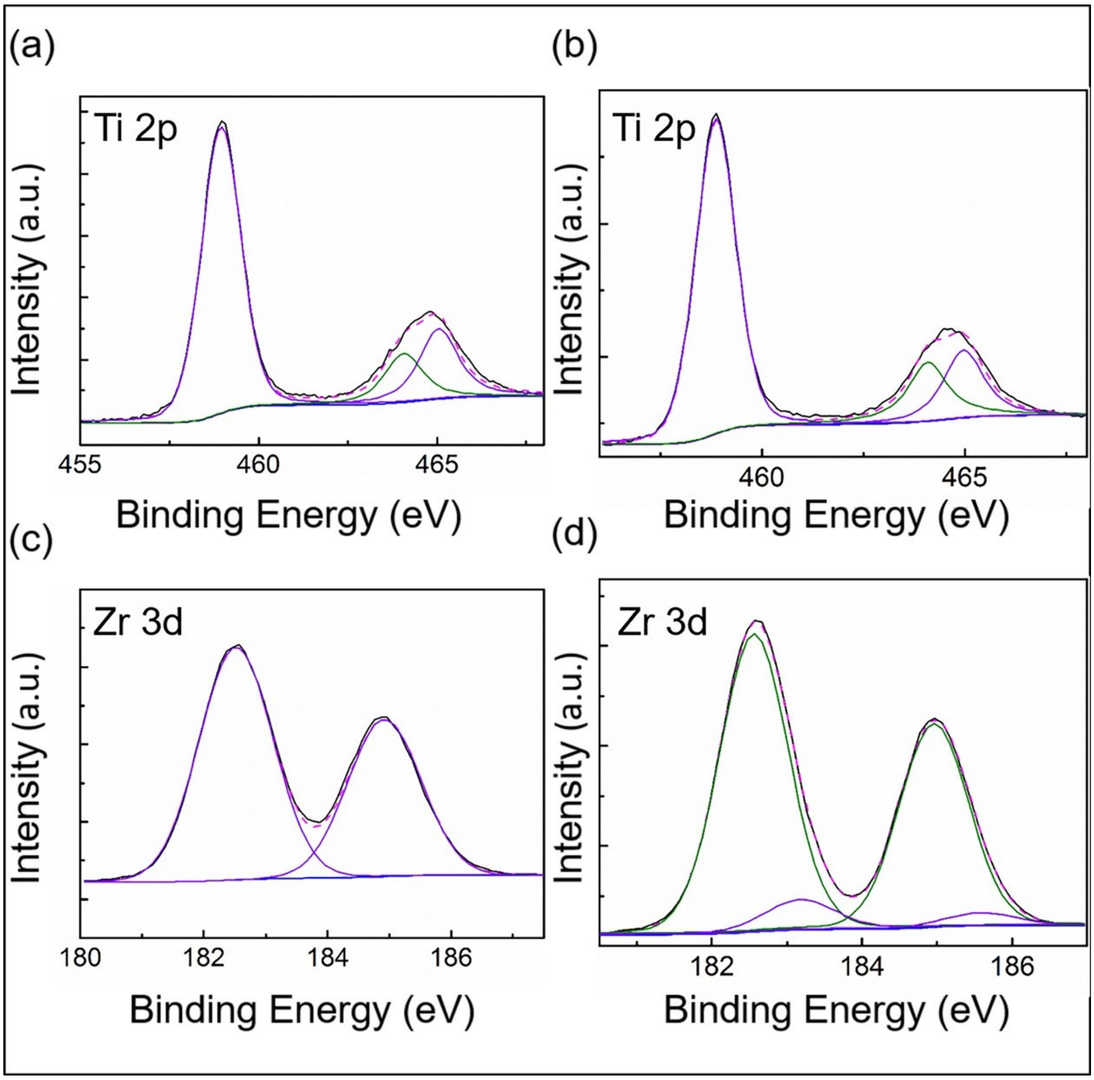

Fig. S22 XPS spectra of (a and b) Ti 2p core levels for TiO and (c and d) Zr 3d core levels for ZrO before and after annealing, respectively.

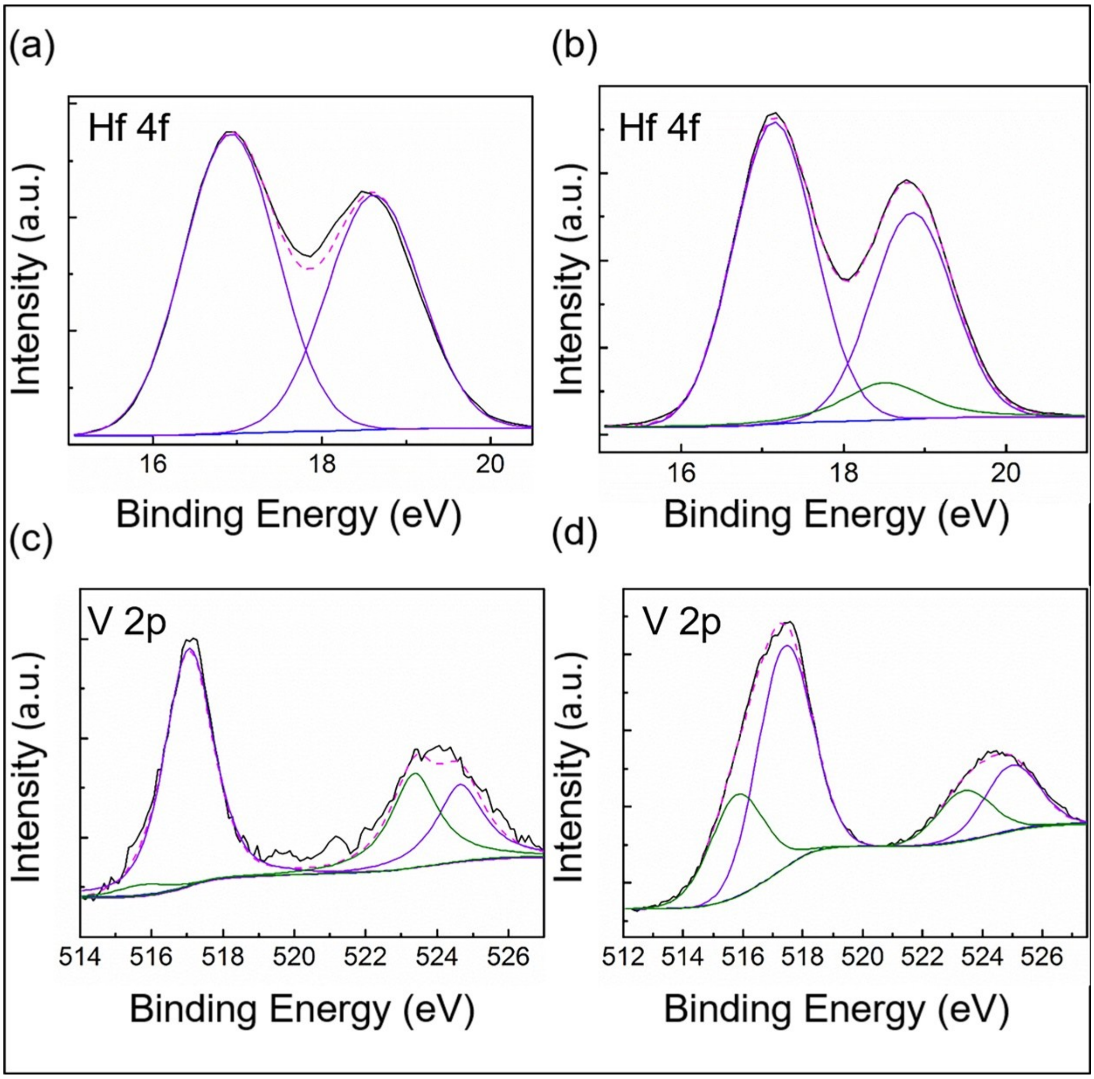

Fig. S23 XPS spectra of (a and b) Hf 4f core levels for HfO and (c and d) V 2p core levels for VO before and after annealing, respectively.

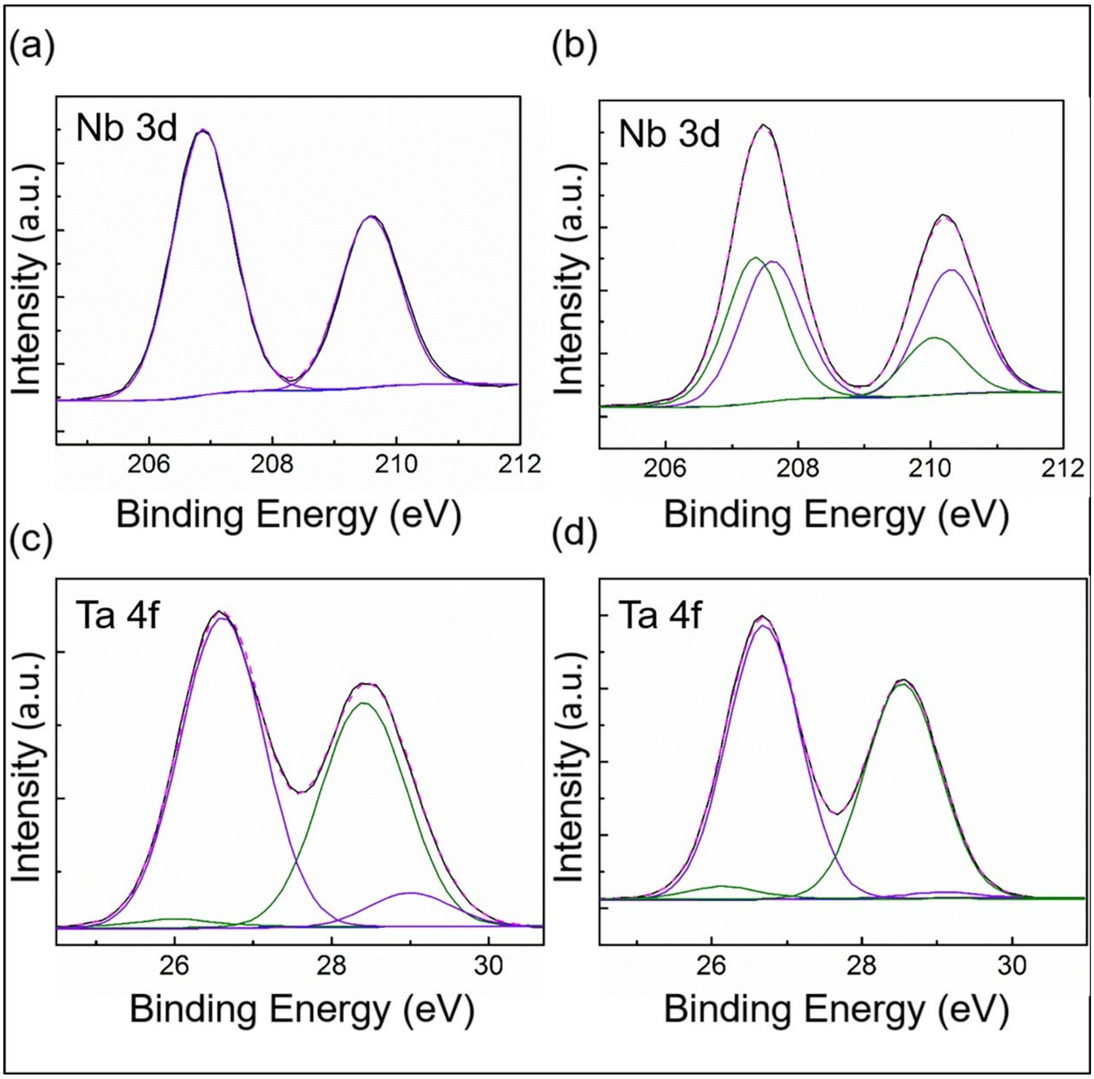

Fig. S24 XPS spectra of (a and b) Nb 3d core levels for NbO and (c and d) Ta 4f core levels for TaO before and after annealing, respectively.

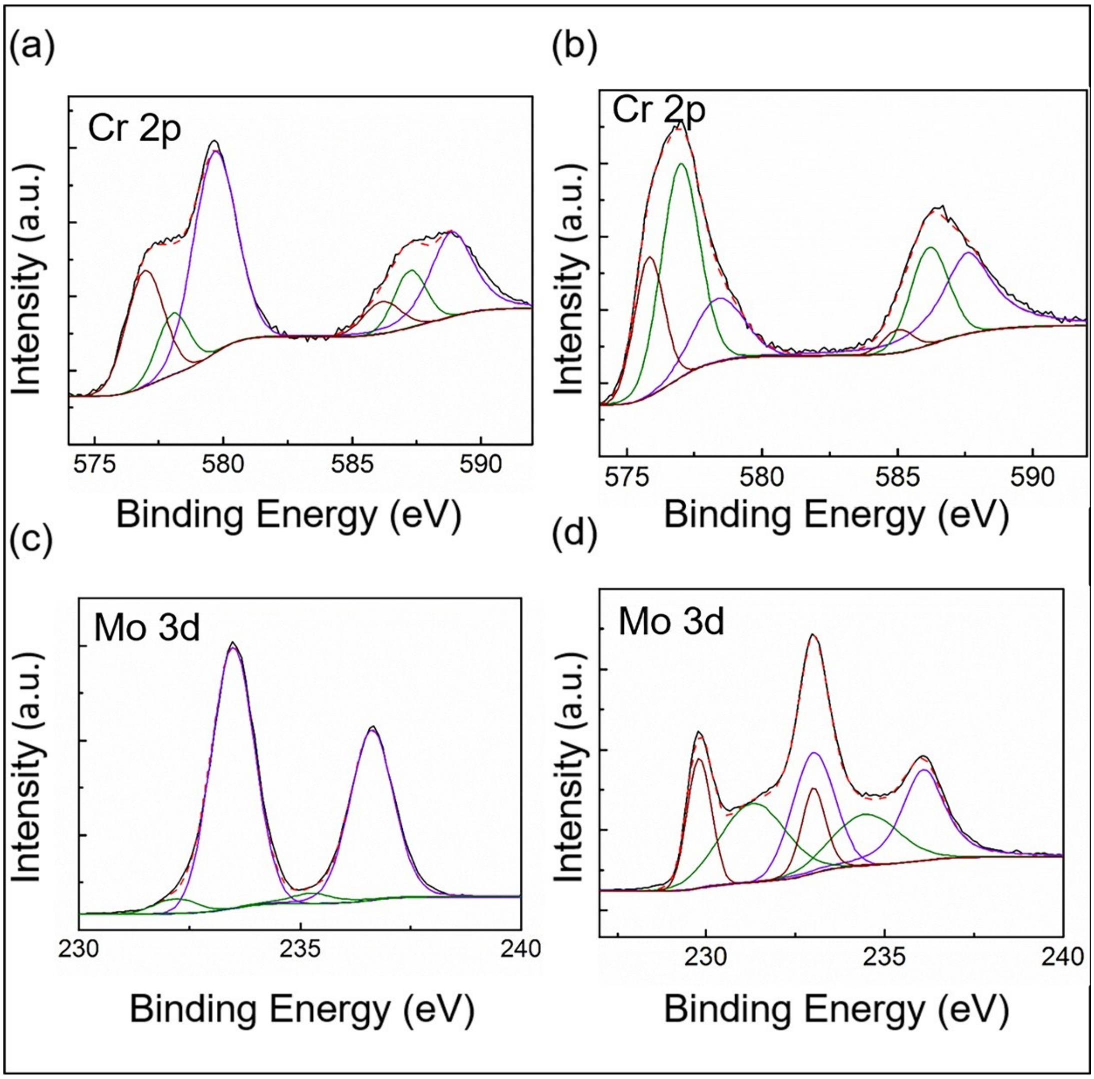

Fig. S25 XPS spectra of (a and b) Cr 2p core levels for CrO and(c and d) Mo 3d core levels for MoO before and after annealing, respectively.

Section S7: The PDOS of TMOs before and after annealing

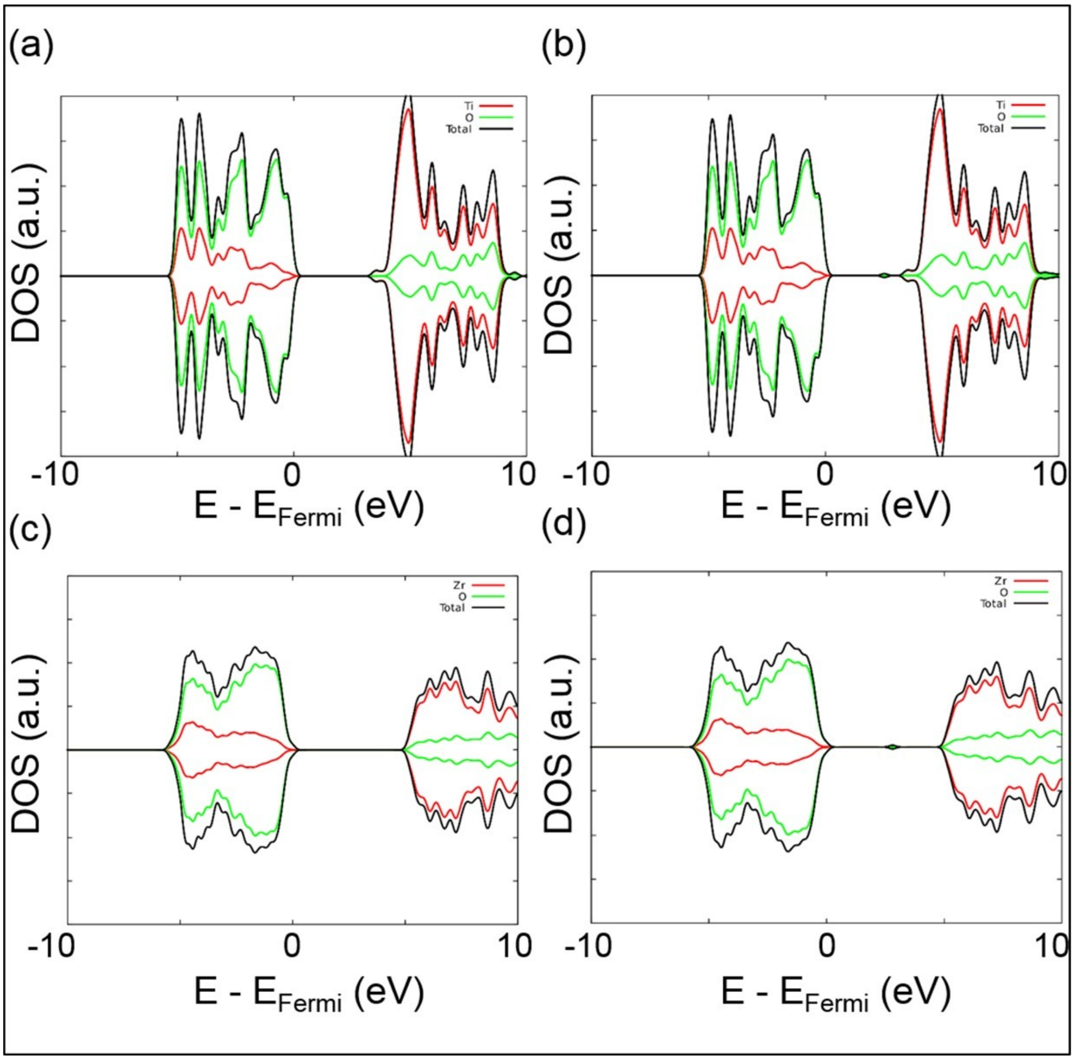

Fig. S26 The PDOS of (a and b) TiO and (c and d) ZrO before and after annealing, respectively.

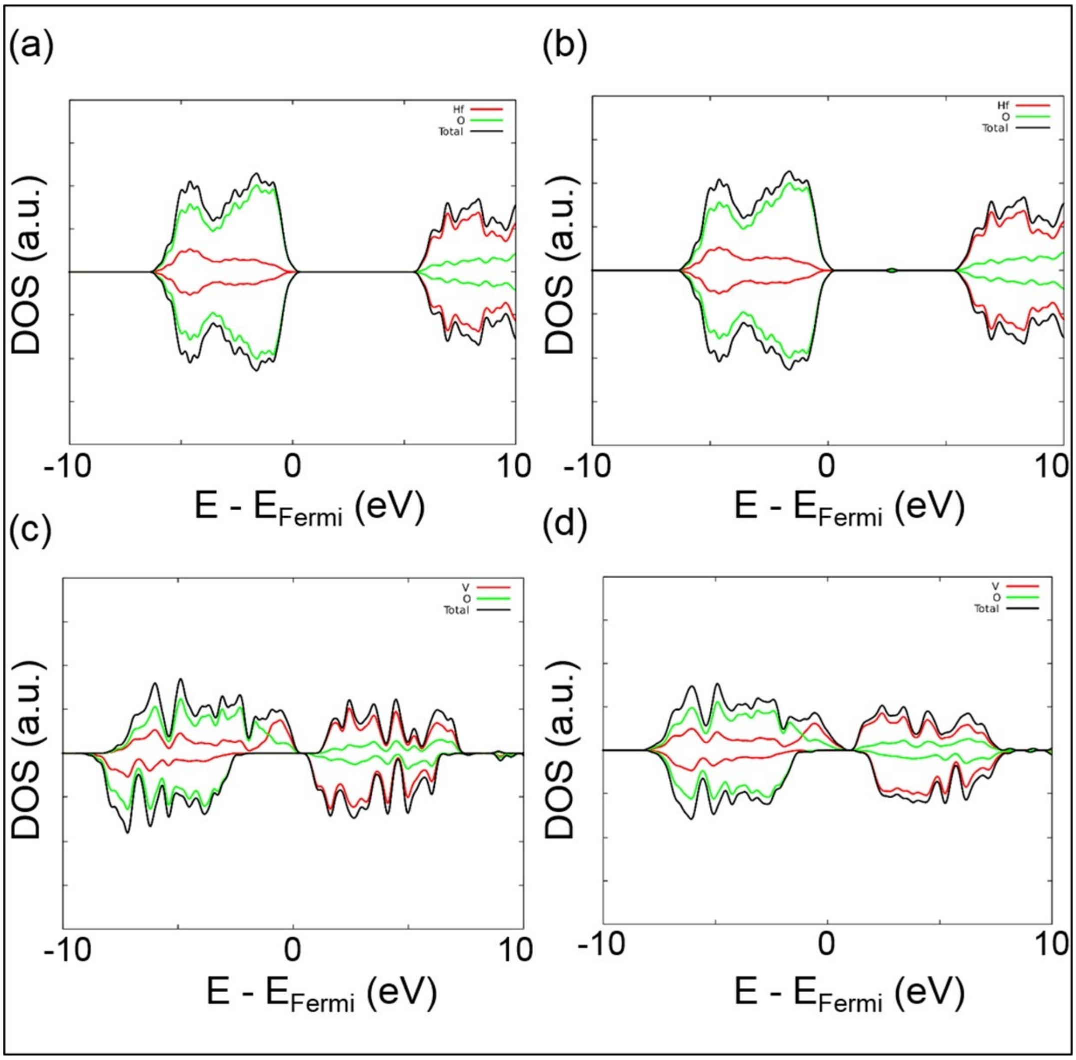

Fig. S27 The PDOS of (a and b) HfO and (c and d) VO before and after annealing, respectively.

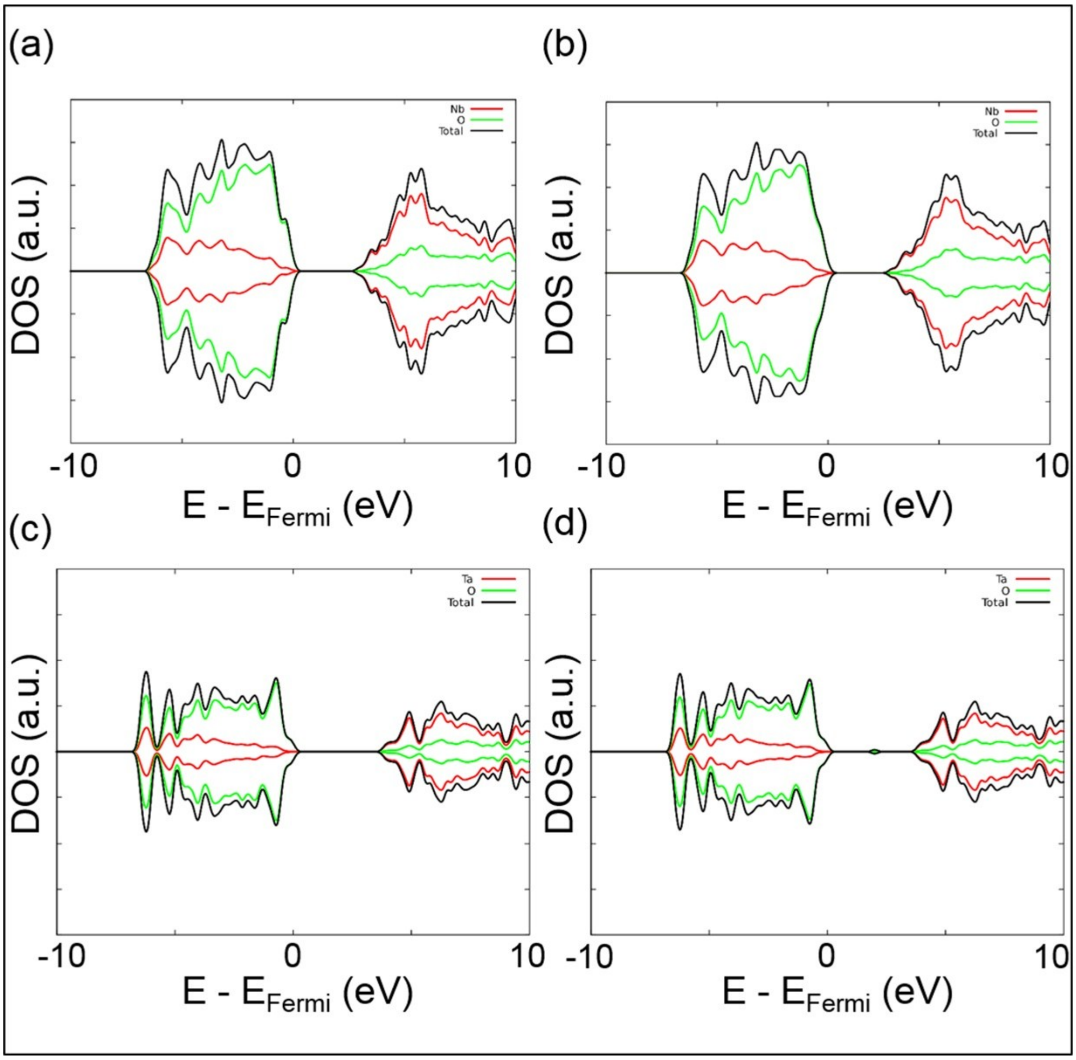

Fig. S28 The PDOS of (a and b) NbO and (c and d) TaO before and after annealing, respectively.

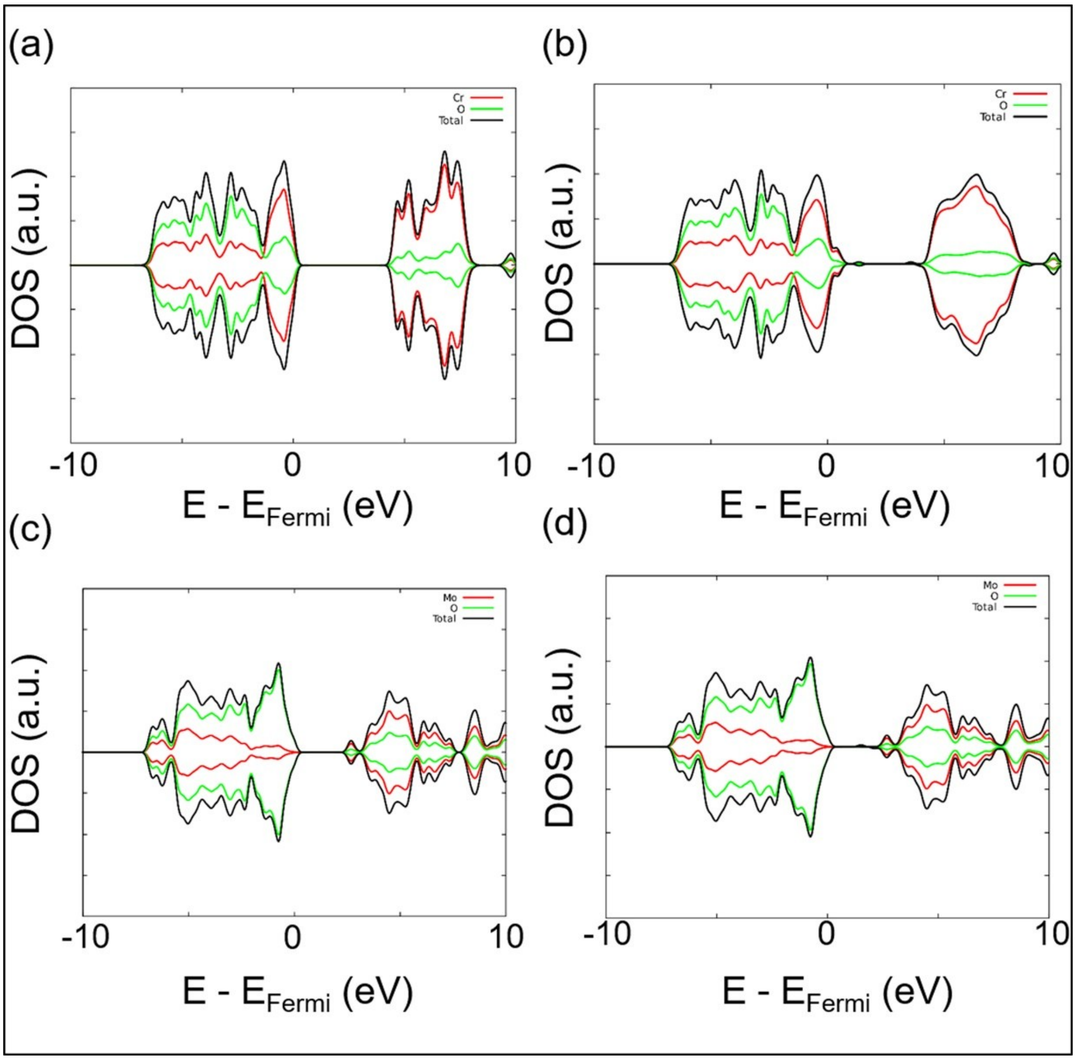

Fig. S29 The PDOS of (a and b) CrO and (c and d) MoO before and after annealing, respectively.

Section S8: Raman spectra of TMOs before and after annealing

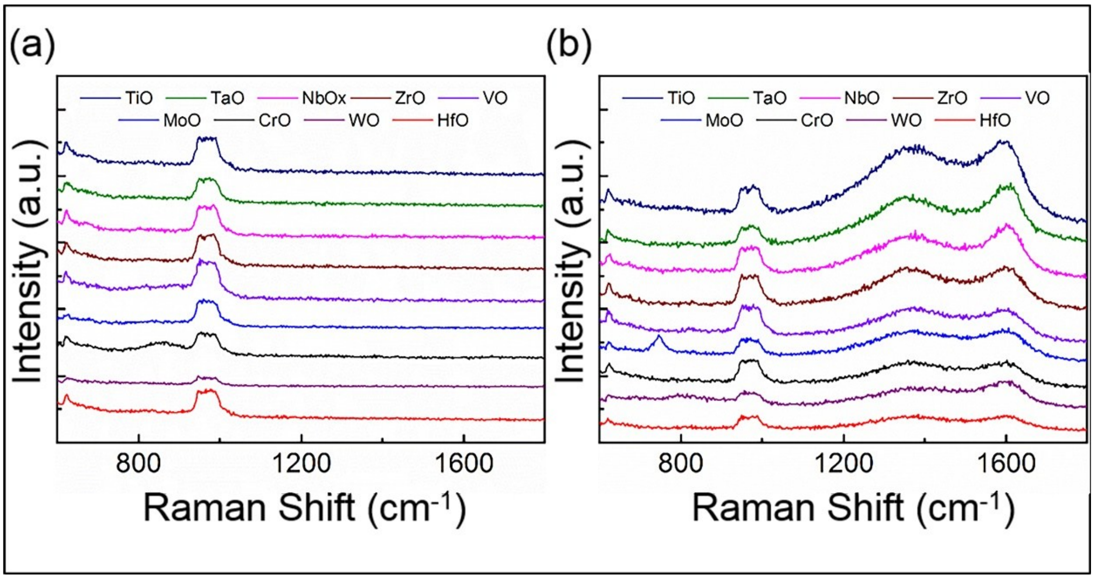

Fig. S30 Raman spectra of TMOs(a) before and (b) after H_2 annealing treatment.

Table S1: Price comparison of different targets

Targets (50 mm-diameter and 3 mm-thickness)	Price (yuan/per plate)
Au	40, 950
Ag	600
Ti	200
Zr	300
Hf	1, 600
V	900
Nb	400
Ta	1, 000
Cr	400
Mo	300
W	400

Table S2. The atomic percentage of TMOs before and after annealing by the XPS spectra.

TMOs	Valence state	Atomic percentage (%)	
		Before annealing	After annealing
TiO	Ti^{4+}	86.41	83.32
	Ti^{3+}	13.59	16.68
ZrO	Zr^{4+}	100.00	8.02
	Zr^{3+}	0.00	91.98
HfO	Hf^{4+}	100.00	91.28
	Hf^{3+}	0.00	8.72
VO	V^{5+}	72.89	64.09
	V^{4+}	27.11	35.91
NbO	Nb^{5+}	100.00	56.16
	Nb^{4+}	0.00	43.84
TaO	Ta^{5+}	58.48	54.23
	Ta^{4+}	41.52	45.77
CrO	Cr^{6+}	58.74	35.46
	Cr^{5+}	16.67	46.04
	Cr^{4+}	24.59	18.50
WO	W^{6+}	100.00	92.00
	W^{5+}	0.00	8.00
MoO	Mo^{6+}	93.75	41.65
	Mo^{5+}	6.25	36.19
	Mo^{4+}	0.00	22.16

Table S3. Energy levels of TMOs after annealing.

TMOs	CB (eV)	VB (eV)	V_0min (eV)	V_0max (eV)
TiO	-3.82	-7.72	-4.85	-4.53
ZrO	-3.46	-8.62	-5.72	-5.40
HfO	-5.37	-8.43	-6.91	-6.59
VO	-6.52	-8.21	-7.76	-7.44
NbO	-4.81	-8.20	-5.14	-4.82
TaO	-6.58	-10.58	-8.29	-7.97
CrO	-5.56	-8.56	-7.28	-6.96
WO	-5.19	-8.34	-5.81	-5.49
MoO	-6.19	-8.34	-6.53	-6.21

References

1 X. Wang, Y. Wang, H. Sui, X. Zhang, H. Su, W. Cheng, X. X. Han and B. Zhao, *J. Phys. Chem. C*, 2016, **120**, 13078–13086.

2 J. H. Seo and T. Nguyen, *J. Am. Chem. Soc.*, 2008, 2–5.