Supporting information

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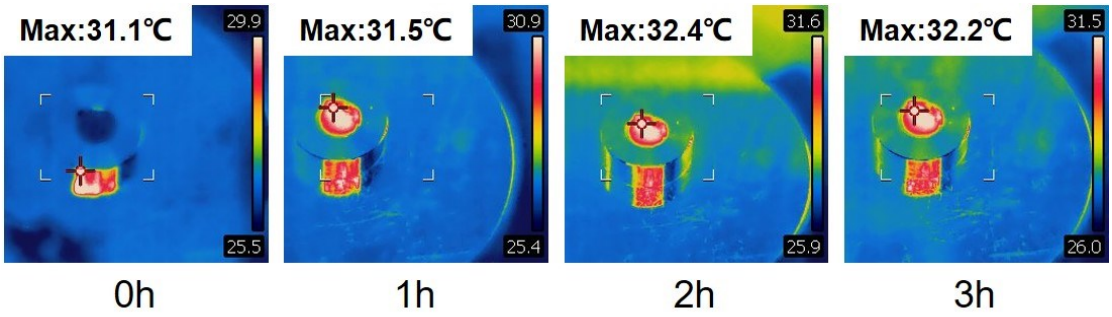

Figure S1: Photothermal images of TW0 under irradiation of 300-800 nm light with an intensity of 100 mW/cm^2 .

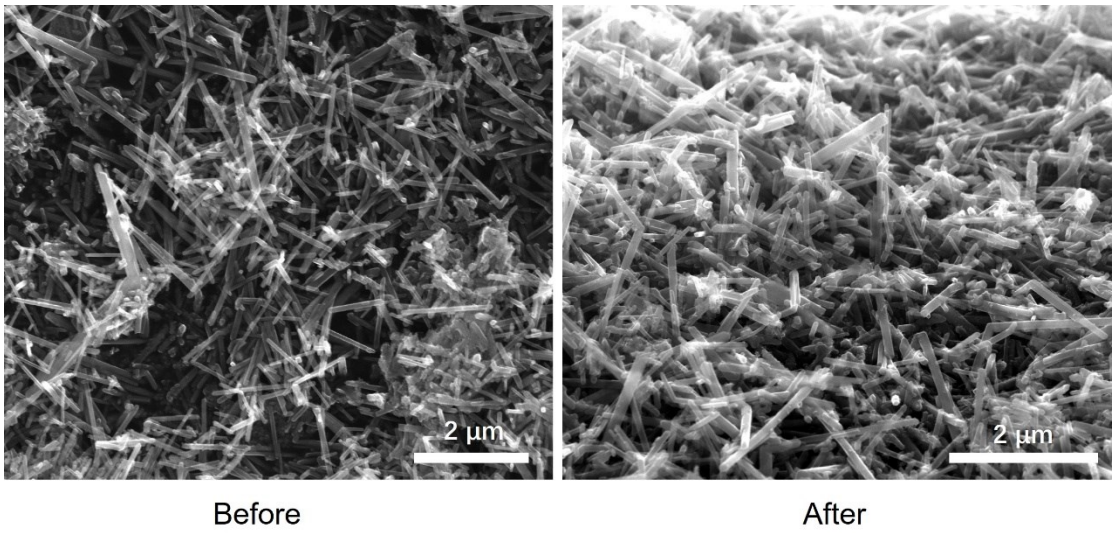

Figure S2: SEM images of TW4 before and after photothermocatalytic CO_2 reduction.

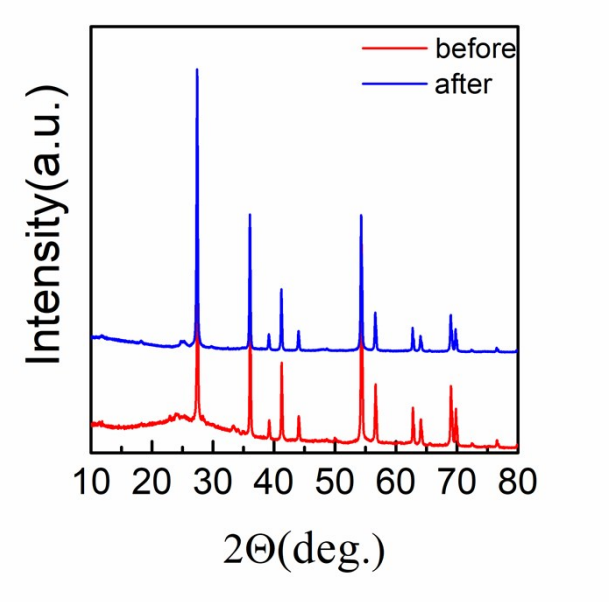

Figure S3: XRD patterns of TW4 before and after photothermocatalytic CO_2 reduction.

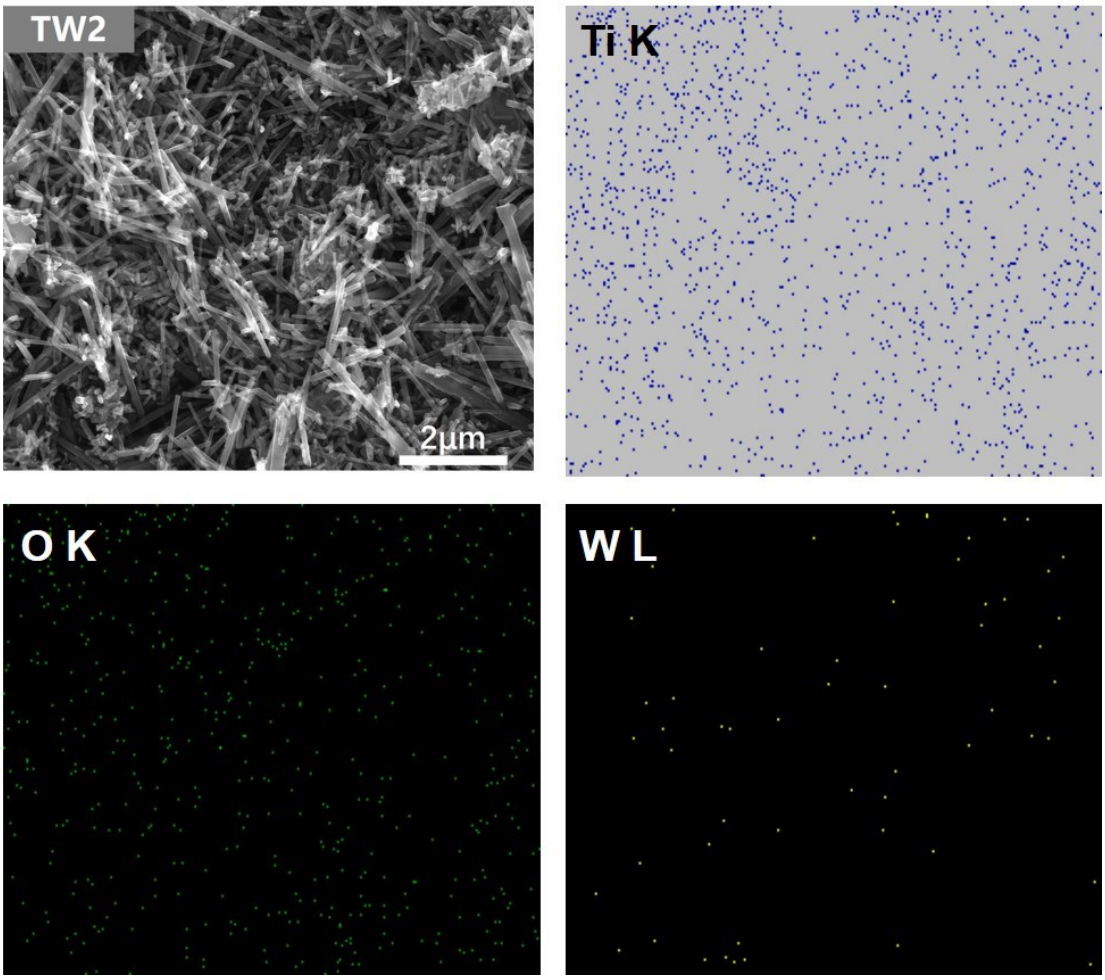

Figure S4: SEM image and element distribution of Ti, O, and W atoms over sample TW2.

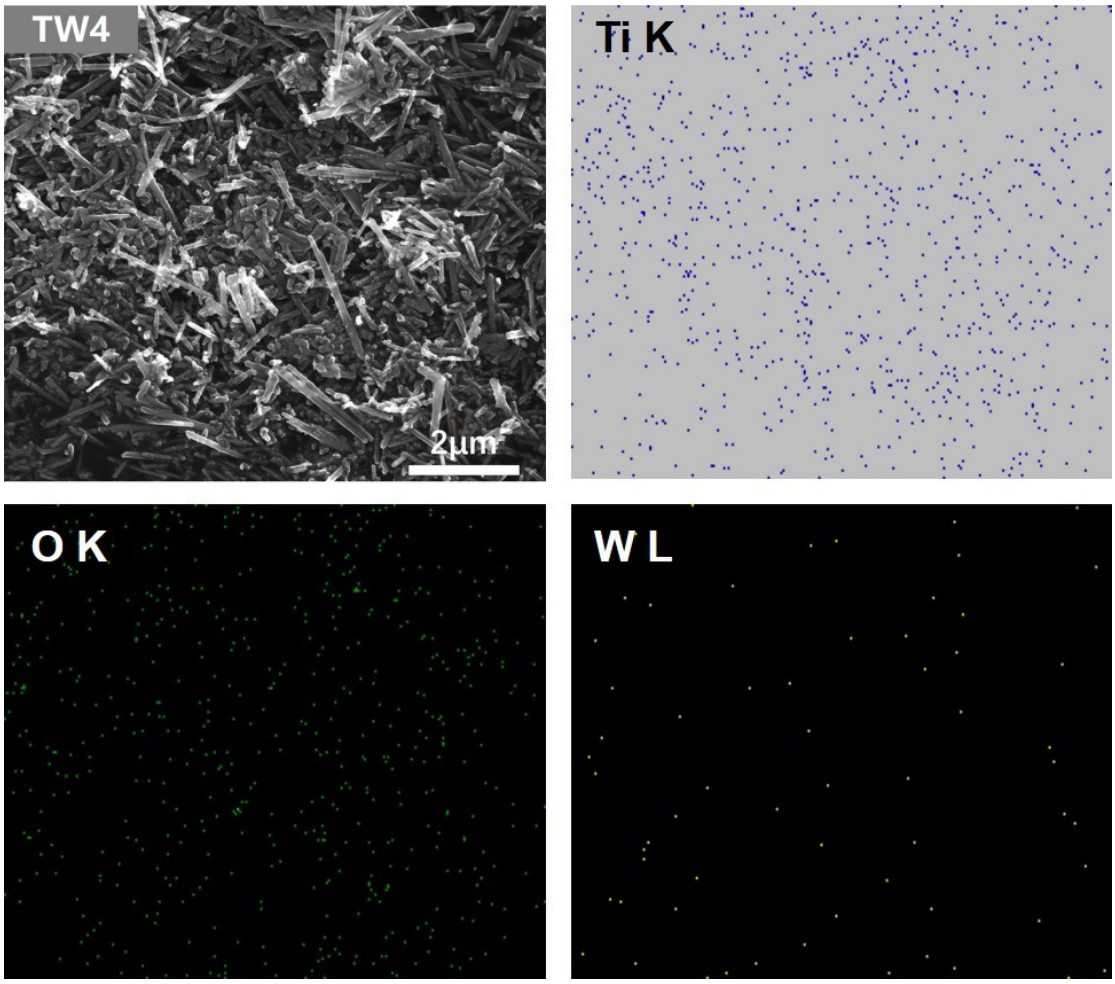

Figure S5: SEM image and element distribution of Ti, O, and W atoms over sample TW4.

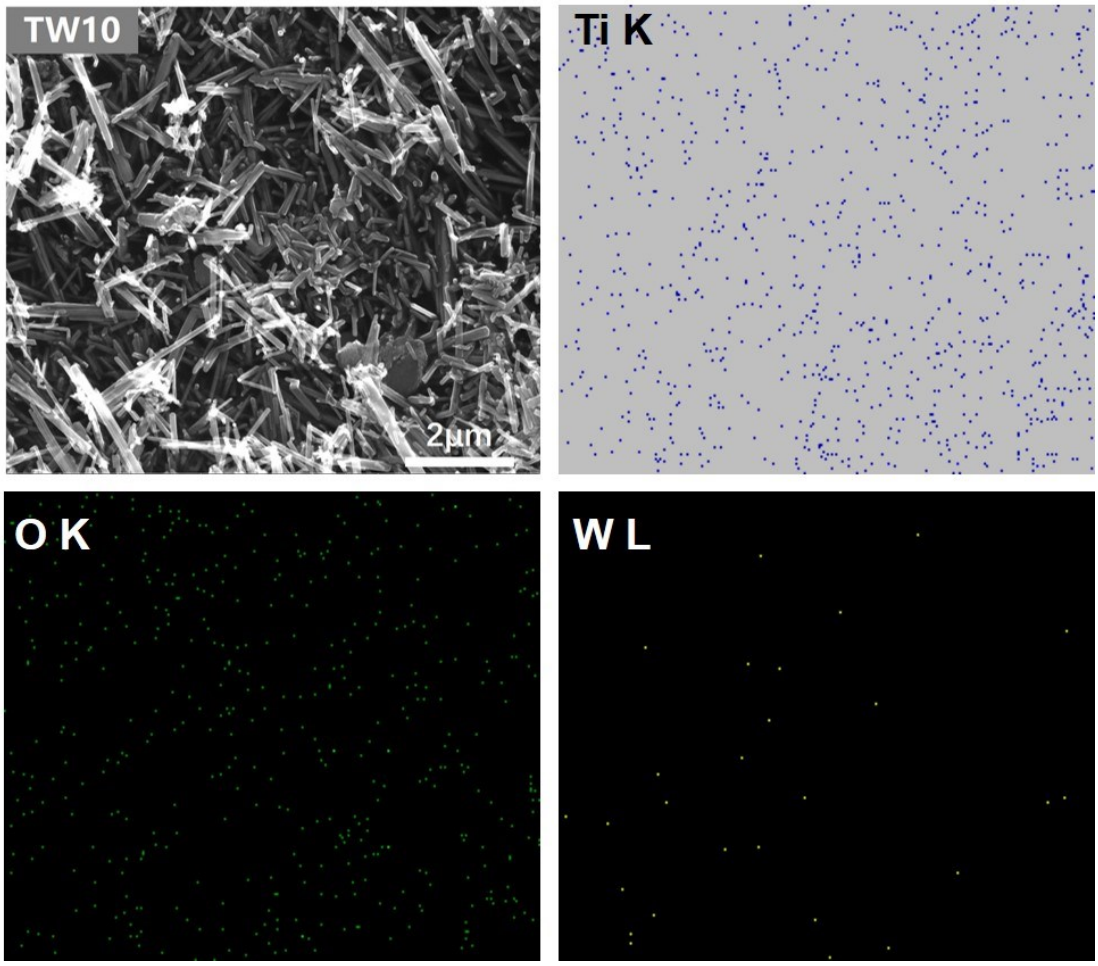

Figure S6: SEM image and element distribution of Ti, O, and W atoms over sample TW10.

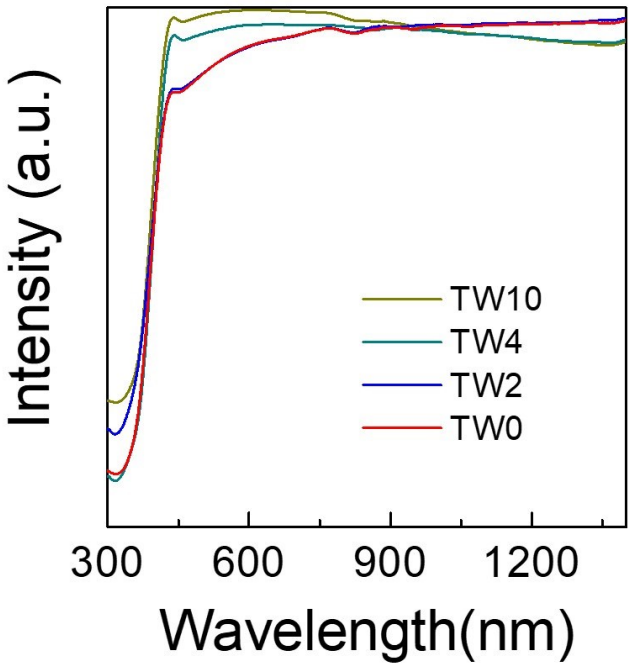

Figure S7: UV-Vis spectra of TW0, TW2, TW4, and TW10. For sample TW4 and TW10, there is a wide absorption in near-infrared region, which indicates that shallow energy levels appear under TiO_2 conduction band.

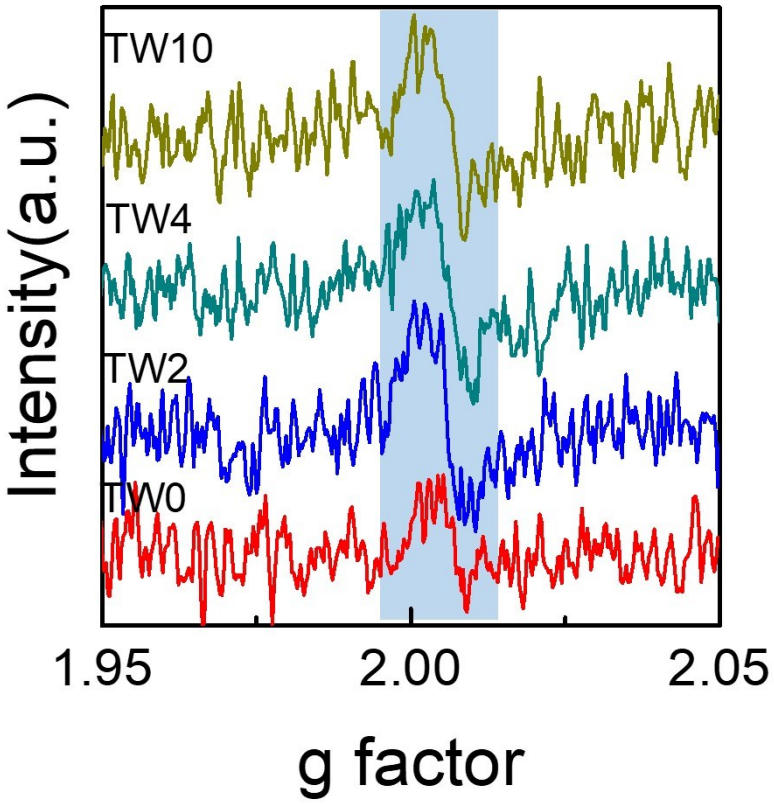

Figure S8: ESR spectra of different samples at 110 K with UV irradiation.

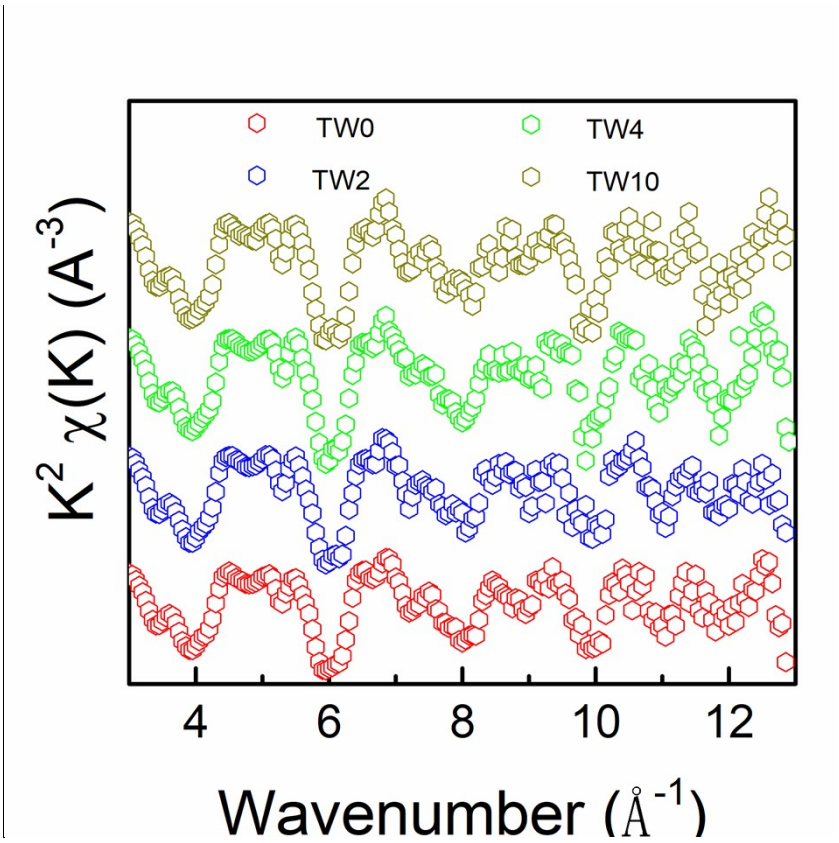

Figure S9: Ti K-edge EXAFS spectra of different samples.

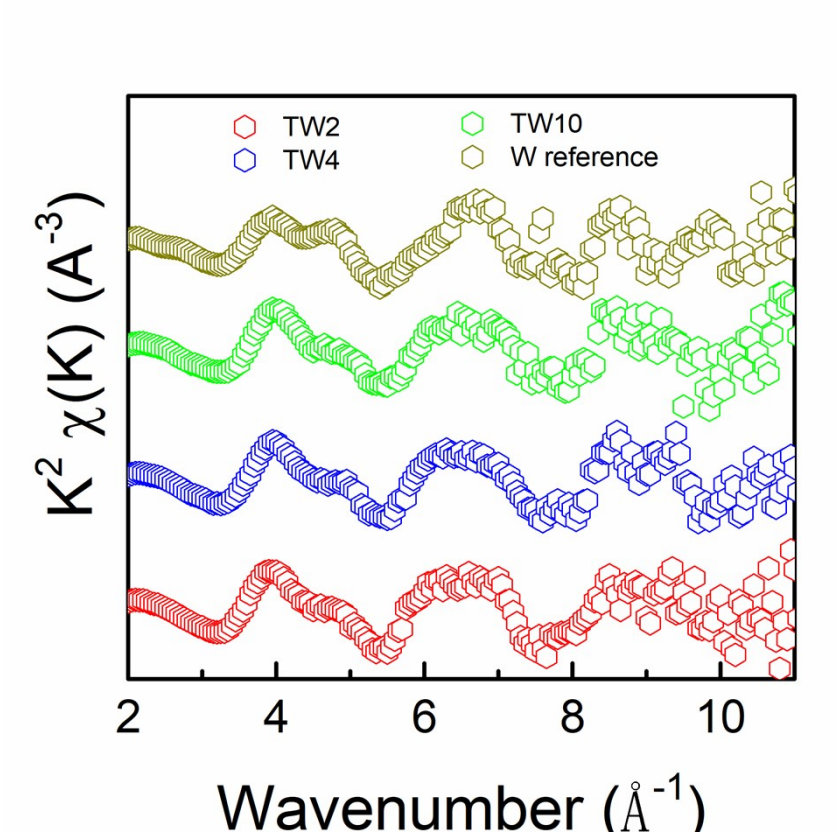

Figure S10: W L_{III}-edge EXAFS spectra of different samples.

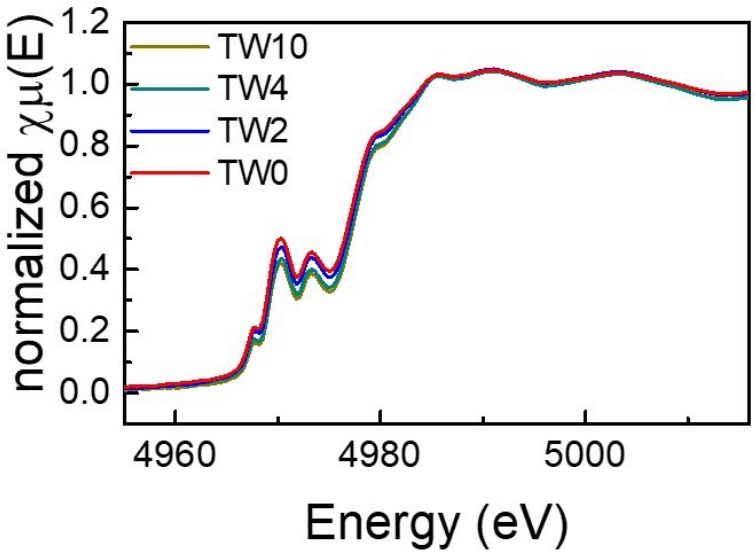

Figure S11: Ti K-edge XANES spectra of different samples.

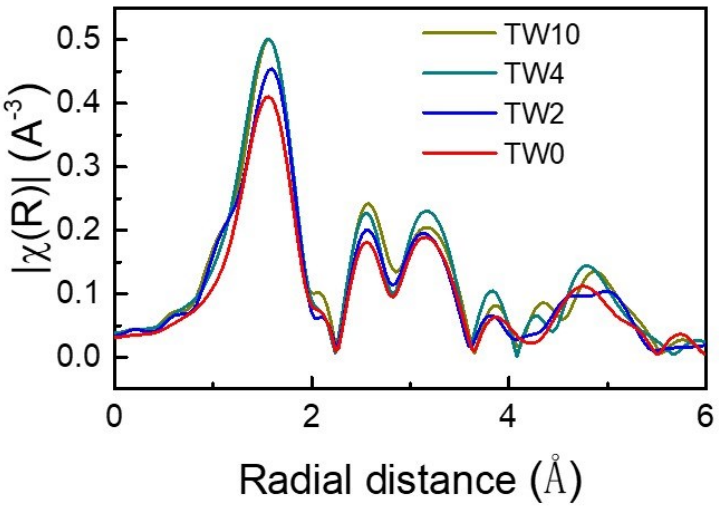

Figure S12: Ti K-edge FT spectra of different samples.

Table S1 W-O bond distances of W reference

W_1-O	W_2-O	W_3-O	W_4-O	W_5-O	W_6-O
1.92012	1.88164	2.03681	2.18778	2.23066	2.26398
2.01686	1.84144	2.15896	1.89132	2.34611	1.94090
1.72191	1.70987	1.75051	2.24440	1.94391	2.19829
2.30365	2.29690	2.18786	1.95492	1.86406	1.95695
1.80985	1.93387	1.88231	1.77405	1.72376	1.75852
1.86420	1.95530	1.79305	1.74242	1.75391	1.74152

The value unit of bond distance is Å.

Table S2 Coordination number of W reference

	R	Number of bonds	Average bond distance	Coordination Number
*Group I	< 2.1 Å	26	1.852 Å	4.33
*Group II	>2.1 Å	10	2.242 Å	1.67

*All bonds were divided into two groups according to whether the bond length was greater than 2.1 Å.