Electronic Supplementary Material (ESI) for ChemComm.
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Supplementary Information for

Coupling Ti-doped and oxygen vacancies in tungsten oxide for photochromic applications with high performance

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Materials and characterization

Materials: Titanium tetrachloride ($TiCl_4$, 99.0%), ammonium metatungstate ($(NH_4)_6H_2W_{12}O_{40}.xH_2O$, 99.5%) and polyvinylpyrrolidone (PVP, 580000) were purchased from Aladdin Chemical Reagent Co., Ltd; Ethylene glycol ($(CH_2OH)_2$,99.0%) was obtained from Tianjin Kemio Chemical Reagent Co., Ltd. All reagents applied as obtained with out further purification. Deionized water (>18 M Ω) was self-made in the laboratory.

X-ray diffraction (XRD) : XRD was performed by a Bruker D8 X-ray diffractometer with Cu Kα radiation (λ=1.5418 Å) in the 2θ range of 5−90°.

Scanning electron microscopy (SEM): SEM analysis was investigated by a FEI Quanta 250 FEG field-emission scanning electron microscope.

X-ray photoelectron spectroscopy (XPS): XPS was carried out by a NEXSA X-ray photoelectron spectrometer equipped with a monochromatic Al-Kα X-ray source (1486.6 eV),

Transmission Electron Microscope (TEM): TEM measurements were performed by Hitachi-7700 and FEI Tecnai G2 F20 microscope.

Electron spin resonance (EPR): EPR spectrum was obtained with a Bruker E500 spectrometer. UV–vis-NIR diffuse reflectance spectra was measured by HITACHI U-4100 UV-vis-NIR spectrophotometer.

Experimental Procedures

a. $H_{28}N_6O_{41}W_{12}$ (5 g) was dissolved in ethylene glycol (30 mL) with magnetic stirring, variable quantities of $TiCl_4$ was added into the above solution. After stirring for 30 minutes, the final pale yellow solution was then heated in a Teflon autoclave at 180 °C for 5 h. When the Teflon autoclave was cooled to room temperature, the collected precipitates were washed by the distilled water for three times, and dried in vacuum at 70 °C for 24 h, the TWOs were obtained finally.

b. Firstly, TWOs (0.05 g) and PVP (1.45g) were mixed into the solution of ethylene glycol and deionized water (ethylene glycol: 3 mL, deionized water: 10 mL), under stirring until PVP was completely dissolved, then ultrasonic for 10 min to form a suspension. Finally, 500 μL suspension solution was applied on the glass sheet (0.5 ×5 cm^2), and the glass was dried at 70℃ for 2 h to fabricate photochromic film.

c. 500 μL suspension solution was soaked a fiber paper and was dried for 30 min in a vacuum oven at 70°C, and the process was repeated for three times to obtain rewritable paper with photochromic property.

d. Suspension solution of TWOs/PVP (8 mL) were applied on the glass sheet(10.5×10.5 cm^2), and the glasses were dried at 70℃ to fabricate photochromic films, respectively. Further, the photochromic glass is installed on the model house(23×20×13 cm^3), and the model house with photochromic glass is irradiated for ninety minutes under visible light(380-800 nm, 400 W) .

For TWO-1, the transmittance of photochromic glass is high, the optical modulation range is small in the same condition, the internal temperature is the highest. The transmittance of photochromic glass TWO-2 and TWO-3 have a little gap, but the optical modulation range of TWO-2 is higher than TWO-3. In consequence, the internal temperature of TWO-3 rises even faster. The internal temperature of model house with TWO-5 and TWO-4 photochromic glass is lower than the other three. It is due to the dark color of TWO-5 and TWO-4 result in the

transmittance of photochromic films are low, which blocks out most of the heat.

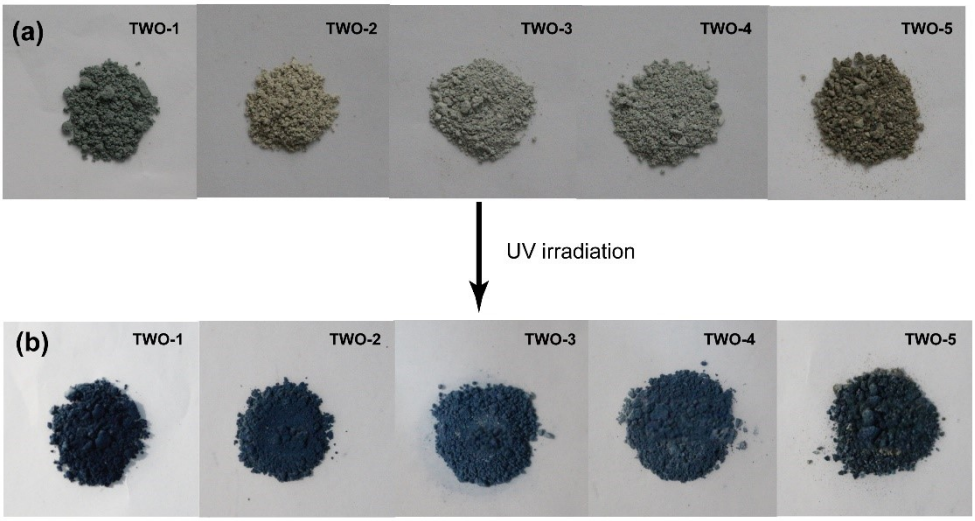

Fig. S1 Digital photographs of TWOs before (a) and after UV irradiation 5 min (b)

In the entire solvothermal procedure, when titanium tetrachloride is added into ethylene glycol, the related chemical reactions occurred as follows.

$HOCH_2CH_2OH \longrightarrow CH_3CHO + H_2O$ equation (1)

$TiCl_4 + H_2O \longrightarrow H_6TiO_6 + HCl$ equation (2)

The five TWOs showed blue, pale yellow, white, grayish white and brown colors, respectively (Fig. S1), revealing an effective influence of Ti doping on the color of a TWO sample.

According the above equations, the color of TWO-1 is blue due to the reducibility of ethylene glycol and HCl, and the low doping amount is owing to the small dosage of titanium tetrachloride. Because of the high doping amount, the color of TWO-2 and TWO-3 become lighter, and the doping amount is dominant the color of TWO-2 and TWO-3, but the photochromic property of TWO-3 is poor than TWO-2 and the morphology of TWO-3 is a little aggregate. Further increase the dosage of titanium tetrachloride, HCl is dominant the color of TWO-4 and TWO-5, and WO2 is found in TWO-5 from XRD spectrum. Commonly, WO2 is reddish brown in colour.

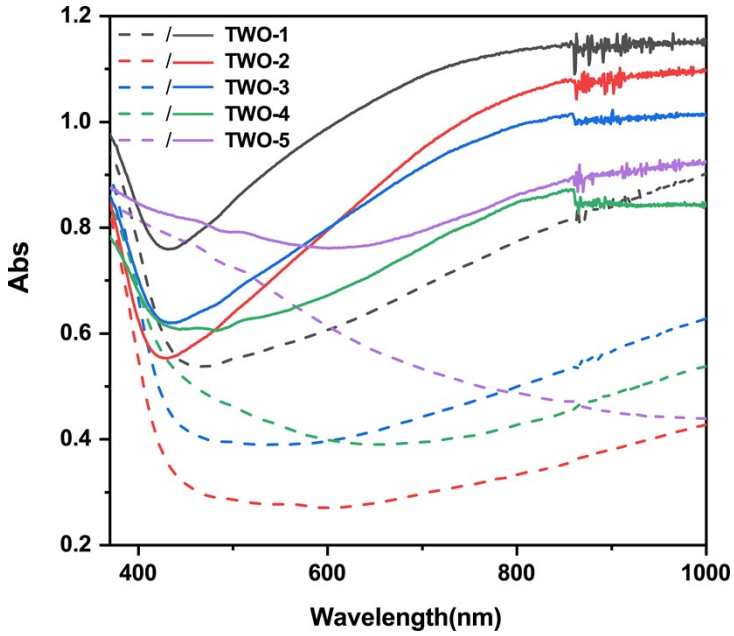

Fig.S2 UV–Vis absorption spectroscopy of TWOs before (dashed lines) and after UV irradiation 5 min (solid lines)

Table S1 the wavelength range and intensity that can induce photochromism

Wavelength (nm)	power density (W/m^2)	Power (W)
365	10.32	30
372	10.36	33
429	10.34	69
470	10.38	50

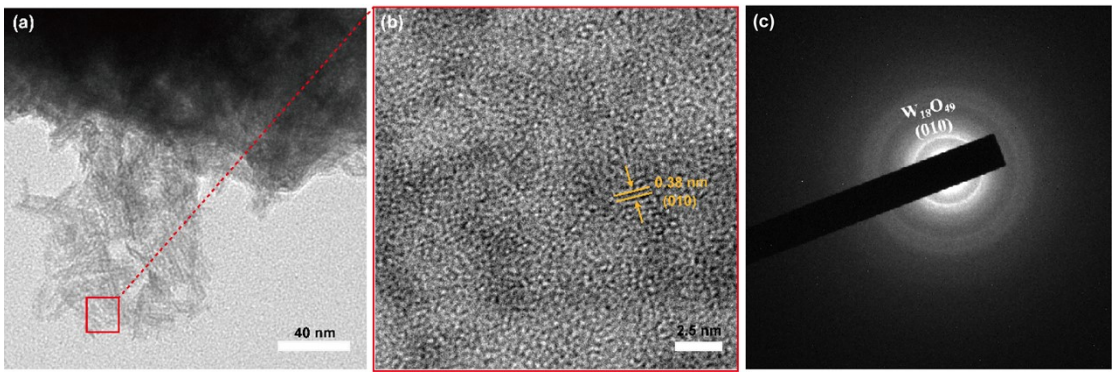

Fig.S3 transmission electron microscopy (TEM) image (a), high-resolution TEM (HRTEM) image (b) and selected area electron diffraction (SAED) (c) of TWO-2

As shown in Fig. S3, an interplanar spacing of 0.38 nm, corresponding to the (010) plane of monoclinic $W_{18}O_{49}$, was observed, consistent with the XRD results.

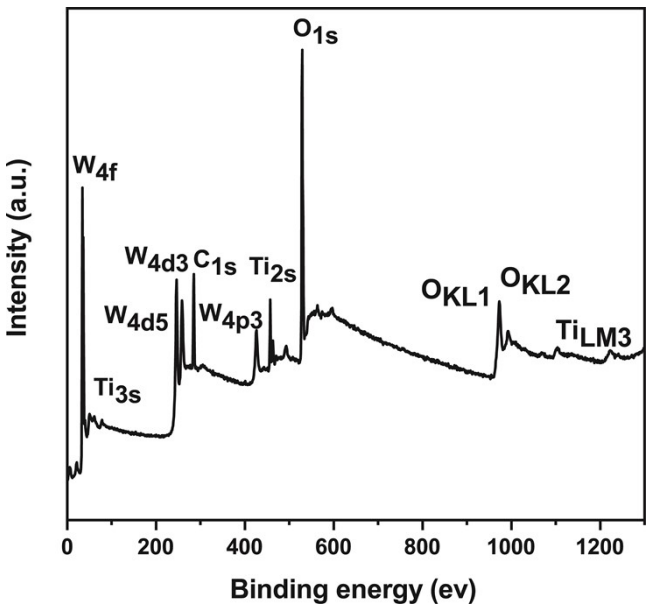

Fig.S4 Full XPS spectrum of TWO-2

Next, the chemical composition and electronic state of TWO-2 were analyzed using XPS. As shown in Fig. S4, only peaks corresponding to W, Ti, O and C were observed. The C 1s peak originated from adventitious carbon on the surface of TWO-2, with the carbon used as a reference to calibrate the XPS spectra.

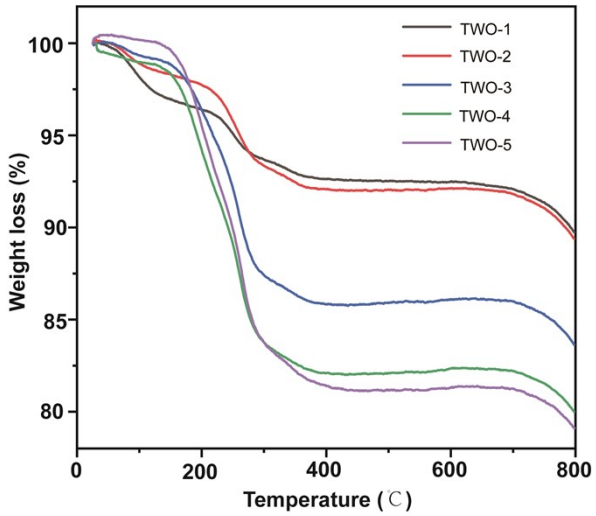

Fig. S5 Thermogravimetric analysis of TWOs

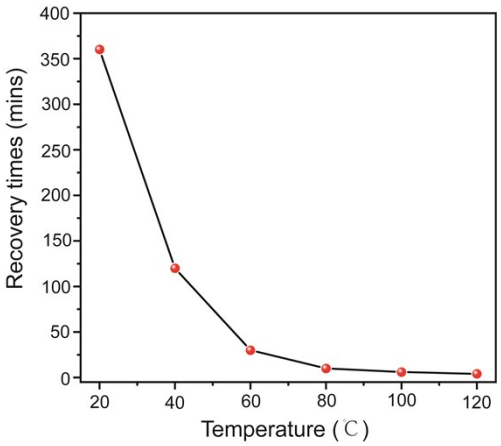

Fig. S6 Recovery times of TWO-2 at different temperature under 365 nm UV-light for 5 min

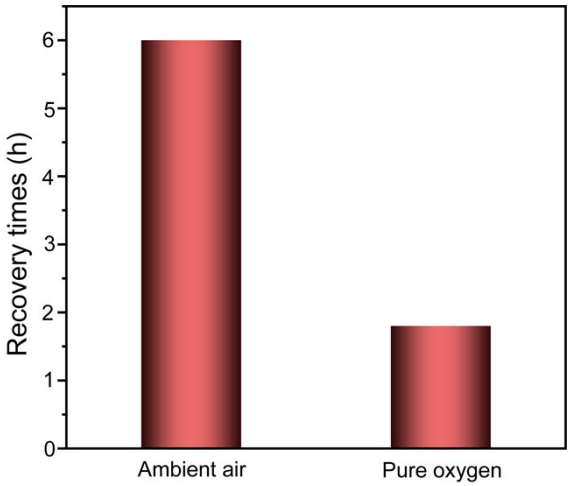

Fig. S7 Recovery times of TWO-2 at ambient air and pure oxygen under 365 nm UV-light for 5 min

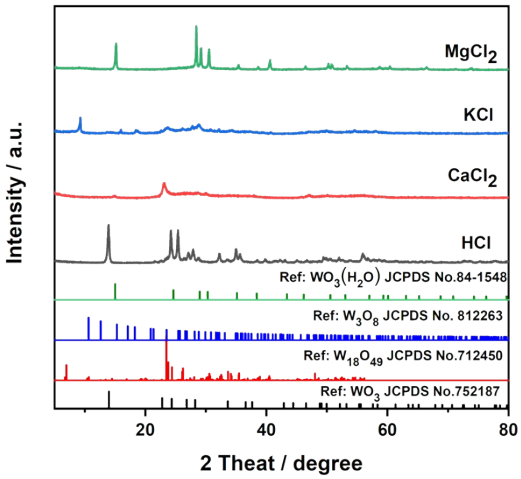

Fig. S8 XRD spectrum of materials with different chloride ions

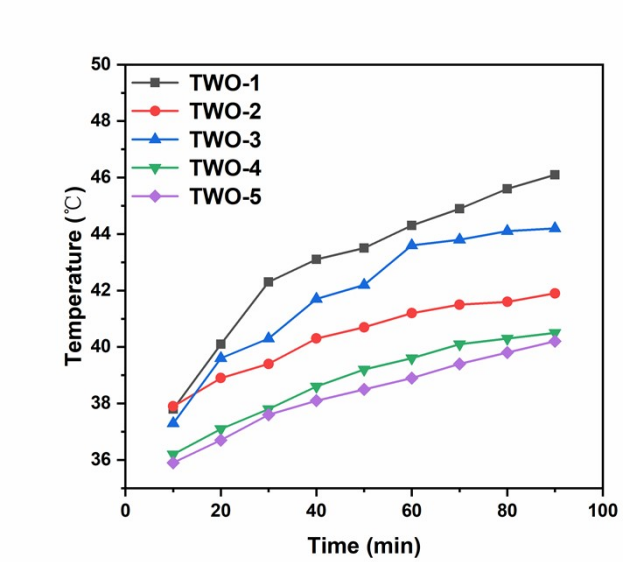

Fig.S9. The temperature changes of TMOs on the model house under visible light (380-800 nm, 400 W).

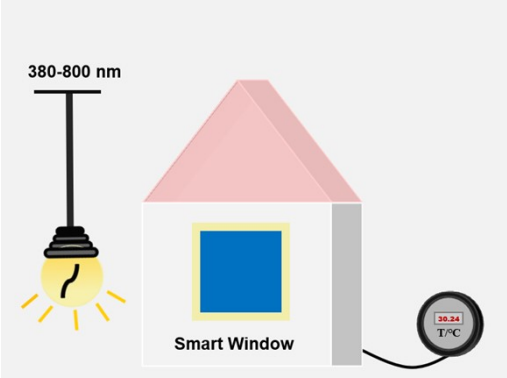

Fig.S10. Schematic diagram of test procedure for the model house with photochromic glass