A plasmonic non-stoichiometric WO_{3-x} homojunction with stabilizing surface plasmonic resonance for selective photochromic modulation

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Experimental Section.

Synthesis of crystalline-amorphous WO_{3-x} nanoparticles: The WO_{3-x} nanopowder was also prepared by a simple hydrothermal method with ammonium tungstate and oxalic acid. Ammonium tungstate was added into the mixture of 50ml distilled water with different content saturated oxalic acid, and then added dropwise hydrochloric acid into PH=1 and then transfer the mixture into the Teflon-line stainless steel autoclave for hydrothermal treatment at 120℃, 48h. After reaction, the white precipitates cooled naturally to room temperature, following which the products were filtered and washed several times with deionized water, and then dried in ambient air at 50 °C for 4 h.

Table s1. Samples and experimental conditions

Reaction factor	sample	pH	OA/ml	Ammonium tungstate
Oxalic Acid (OA)	S1	1	0	15.6g
	S2	1	5	15.6g
	S3	1	10	15.6g
	S4	1	15	15.6g
	S5	1	20	15.6g

WO_{3-x} homojunction based polymer film preparation.

To prepare WO_{3-x} based photochromic film, the as-synthesized particles were firstly dispersed in water to form a homogeneous suspension by sonication (different concentration). Then an appropriate amount of commercially resin (Bayer) was added under continuous stirring, with curing agent (Bayer) and dispersing agents (PVA), respectively. A well dispersed suspension can be obtained after further stirring for at least 120 min. Afterwards, the suspension was blade-coated on clean glass or PET substrates and dried in furnace at ~ 100 ^{o}C for 30 min for completing polymer solidification.

Characterization Techniques. The crystal phase of the as-prepared powders were determined by x-ray diffraction (XRD) with Cu-Kα radiation (1.541 Å, 40 mA, 40 kV) at a scanning rate of 5° /min over a 2θ range from 10° to 90° . The microscopic powder morphology was obtained by using a field-emission scanning electron microscope (FE-SEM, HITACHIS-3400, Japan) at an acceleration voltage of 15 kV. The powder composition and microstructure were investigated by TEM (JEOL2010) with an energy dispersive spectrometer (EDS) attachment (HITACHIH-800, Japan). Selected-area electron diffraction (SAED) was also used to characterize the powder.

The optical properties were characterized by applying UV–visible spectrometry (HITACHI U-3010) over 350–2600 nm. The scanning speed was 600 nm/min. “Virgin” samples refer to samples before irradiation, whereas “colored” samples refer to samples in the colored state (i.e., after 300 W UV irradiation for ~5 min by a xenon lamp).

The photoluminescence spectrum was tested by the fluorescent spectrometer Lumina (Thermo Fisher Scientific) and the valence state and elemental composition of the MT powder were analyzed by x-ray photoelectron spectrometry (XPS, XPSESCAlab250, Thermo Fisher Scientific) with irradiation at the Al Kα line. The pass energy and step size were 20.0 eV and 0.05 eV, respectively. All XPS spectra were calibrated by using the C 1s peak at 284.8 eV.

The electronegativity is tested by the Rhodamine B (RhB) and Methylene blue (MB) solution with the concentration of 10mg/L mixed with 50mg S1 and stirred.

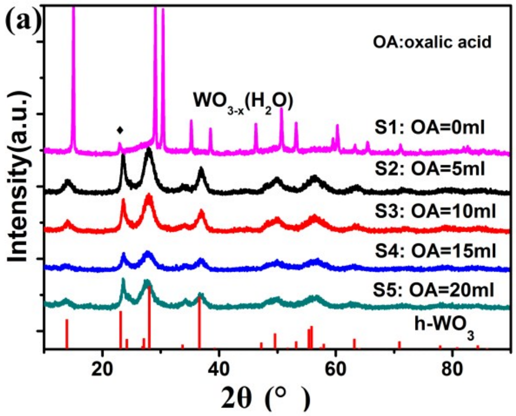

Figure s1 a) XRD pattern of the as prepared WO_{3-x} homojunction nanocrystals

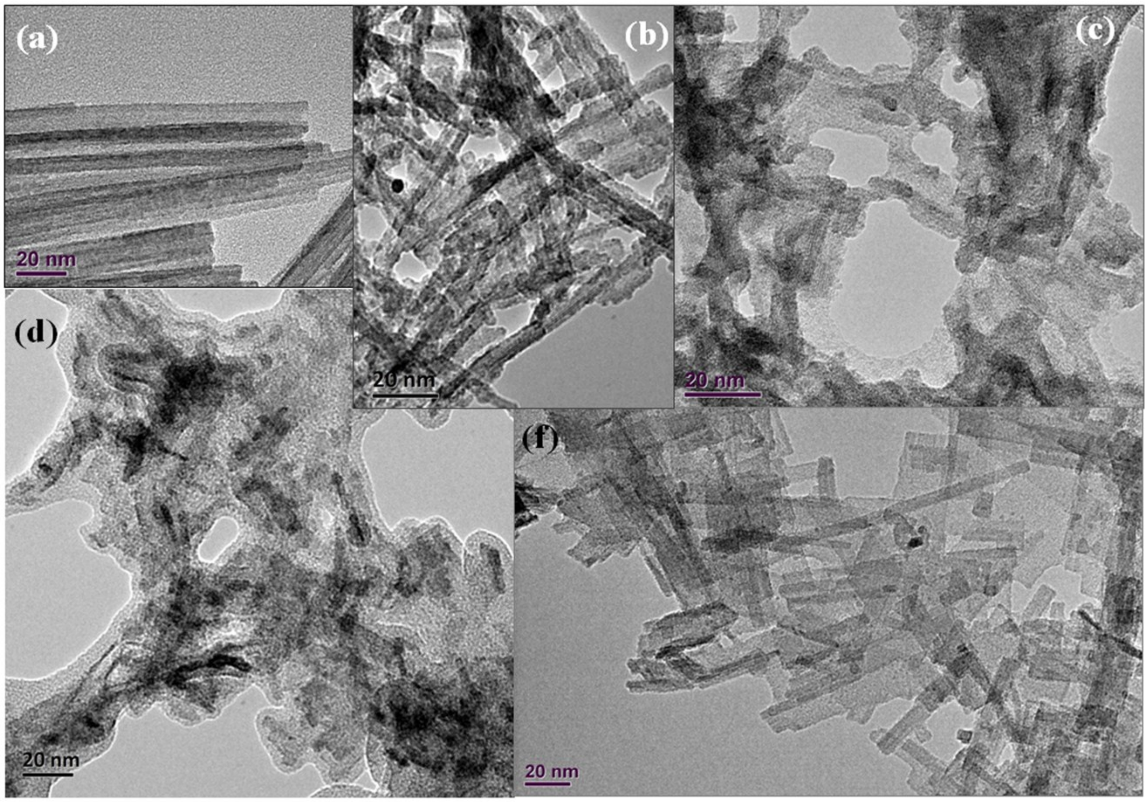

Figure s2 a) is the TEM image of S1 nanorod without homojunction, and b)、c)、d)、f) TEM image of S2、S3、 S4 and S5 with amorphous-crystalline homojunction.

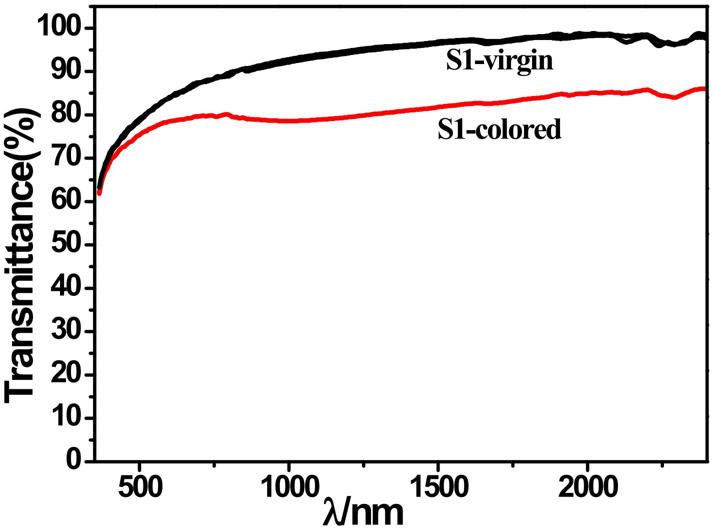

Figure s3 Transmittance of s1 before and after illumination

S1 without the homojunction shows poor solar modulation efficiency.

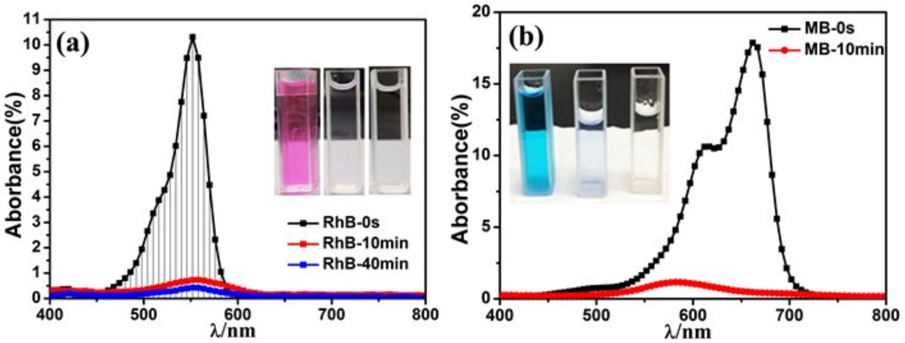

Figure s4 High electronegativity and large absorption surface area.

S3 absorb 90%of MB and RHB only after 10 min stirred and 100% of them after 40min, demonstrating the surface of S3 is negative due to the positive surface of MB and RhB**.** The strong negativity of S3 implied it contains rich oxygen vacancies in the surface.

According to the equation

$\alpha h v = B(hv - Eg)^2$

The value of Eg is calculated according to the absorption and transmittance spectra of samples.

The Mie theory is

$$E(\lambda) = \frac{24\pi^2 N a^3 \varepsilon_m^{3/2}}{\lambda \ln(10)}\left[\frac{\varepsilon_i}{(\varepsilon_r + \chi\varepsilon_m)^2 2 + \varepsilon_i^2}\right]$$

E(λ)= Extinction spectrum= absorption + scattering, a is related to the size(the diameter of sphere), χ is the shape factor (2 for sphere, >2 for spheroid)related to the morphology[1]. According to the Mie theory, the size increase, the absorption peak shift to long wavelength range.

For nanorod, according to Gans theory, the size is expressed by aspect ratio R=A/B (A is the length, B is the diameter). The nanorod has two extinction Modes: Transverse

Mode in visible region and Longitudinal Mode in Near-infrared region. When the aspect ratio decreases, the longitudinal Mode shifts to short wavelength range.

References:

[1] K. Manthiram, A. P. Alivisatos, *J. Am. Chem. Soc.* **2012,** *134*, 3995-3998.