

Supporting Information (SI)

Monoclinic WO₃ Nanorods-Rutile TiO₂ Nanoparticles Core-shell Interface for Efficient DSSCs

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SI (I): Experimental Details

Synthesis of WO₃ Nanorods

In a typical synthesis, 1 g of ammonium paratungstate {(NH₄)₁₀(W₁₂O₄₂)·5H₂O} was dissolved in 95 ml de-ionized (D. I) water. 1-10 ml of concentrated HCl was added (0.125-1.25 M) in drops to above aqueous solution and stirred. The stirring time was dependent on the amount of HCl added. The solution initially turns to transparent light yellow and then yellow with formation of gelatinous precipitate. 2 ml of H₂O₂ was added and stirred strongly for 1 h to dissolve tungstic acid. This results in the formation of stable and transparent solution that is stable up to 2 days. As-prepared solution was transferred to Teflon-lined autoclave to fill 80% of its total capacity. FTO substrate, previously cleaned sequentially by D.I Water, acetone and isopropanol, was placed tilted against the wall of the Teflon-liner with the conducting side facing downwards. The

hydrothermal synthesis was conducted at 120~200 °C for 1~14 h. After synthesis, the autoclave was cooled down to room temperature naturally. The FTO substrate was taken out and rinsed with de-ionized water and annealed at 500 °C for 1 h.

Synthesis of TiO₂ Nanoparticles

The chemicals used for synthesis of TiO₂ were titanium trichloride, hydrogen peroxide and thiourea. In detail, first take 2 ml of titanium (III) chloride, about 10 wt% solution in 20– 30 wt% hydrochloric acid, was added drop-wise to a well stirred hydrogen peroxide (H₂O₂) and distil water solution. The pH was adjusted ~2 using an addition of 7% liquid ammonium hydroxide with constant stirring. To this, 0.1 M thiourea was added slowly while stirring. A transparent solution with a reddish-yellow color was obtained after vigorous stirring for 30 min at room temperature. The resulting solution was then refluxed for 1 h in a controlled temperature oil bath preheated at 50 °C. The WO₃ NRs substrate was transferred into a jar containing the resulting solution, and then the jar was sealed to avoid thermal evaporation of solution and put into an oven maintained at 70 °C for about 2 h. Finally, the films were washed with de-ionized water several times to remove any residue and then air dried. Heat the film at 350 °C for 1h at 5 deg/min constant heating rate. After annealing, the substrate was immersed into dye solution for 24 h to adsorption of dye molecule.

Measurements

Crystalline phases of the as-prepared powders were investigated by an X-ray diffraction (XRD) method (XRD-6000 X-ray diffractometer (Shimadzu) with a Cu-K α radiation source and a fixed power source (40 kV and 40 mA). The morphologies of the as-prepared WO₃ NRs and WO₃ NRs-TiO₂ NPs were analyzed using a field emission scanning electron microscope (FE-SEM S-4100), and high-resolution transmission electron microscope (HR-TEM, Tecnai G20). UV-Vis absorption spectra were recorded using a Varian Cary 5000 spectrophotometer instrument. Sun 2000 solar simulator (ABET Technologies, USA) calibrated to AM 1.5 irradiance conditions was used as light source. The incident photon-to-current conversion efficiency (IPCE) measurements were carried out using a Thermo Oriel xenon arc lamp (Thermo Oriel 66902) combined with a Thermo Oriel Cornerstone 7400 1/8 m monochromator (Thermo Oriel 7400). An electrochemical interface (Iviumstat) was employed to record the solar cell performance. X-ray photoelectron spectroscopy (XPS) measurements were performed with (PHI 5000 Versa Probe, Japan) using a monochromatic Mg source (Mg K α 1253.6 eV, 200 W) and a standard peak of C1s (284.6 eV). Moreover, the Brunauer–Emmett–Teller (BET) surface area and pore volume were measured by the nitrogen gas adsorption–desorption method at 77 K using on a (Belsorp II, BET, Japan Inc.).

Fig. S1

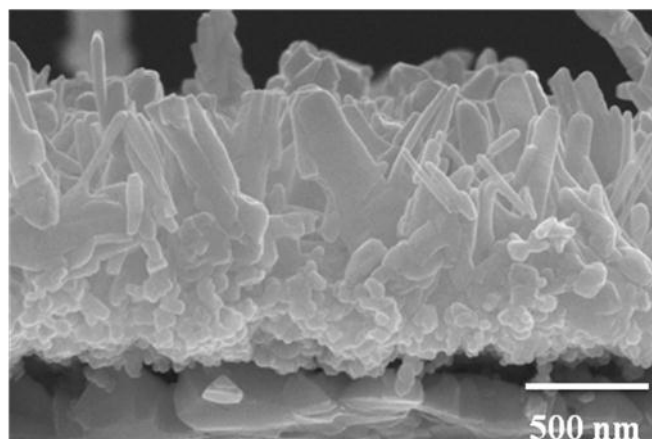


Fig. S1: Close cross-sectional view of WO₃ NRs.

SI (II): X-ray diffraction (XRD) studies

The XRD spectra were obtained for WO₃ NRs and WO₃ NRs-TiO₂ NPs electrodes at room temperature. The crystalline and nearly amorphous phases of WO₃ NRs and WO₃ NRs-TiO₂ NPs electrodes were confirmed. The sharp peaks were noticed for WO₃ NRs electrode which practically remained unchanged after TiO₂ NPs over loading it. The XRD pattern of WO₃ NRs can be indexed monoclinic phase with unit cell parameter $a=0.7297\text{nm}$, $b=0.7539\text{nm}$, $c=0.7688\text{nm}$ and $\beta=90.91^\circ$ compared to the JCPDS (43-1035) database¹ in Fig.S2. From the XRD spectrum of WO₃ NRs-TiO₂ NPs it was difficult to confirm exact phase of TiO₂ NPs. There were no peaks belong to any phase of TiO₂ NPs.

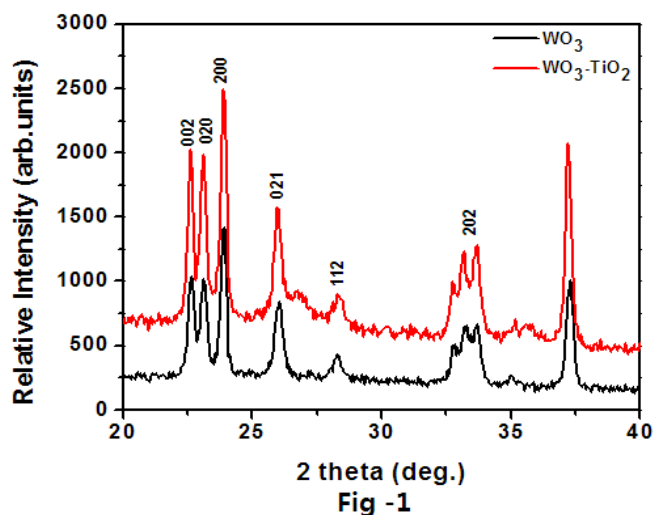


Fig. S2: X-ray diffraction pattern of WO_3 NRs and $\text{WO}_3\text{NRs-TiO}_2$ NPs

SI (III): BET surface area and pore size

Nitrogen adsorption–desorption isotherms were measured to determine the specific surface area and pore size volume of the WO_3 NRs [Fig. S3 (a, b)]. The isotherm displays a typical type IV curve with a hysteresis loop at relative pressure (P/P_0) between 0.0 and 1.0, suggesting the presence of mesoporosity in the products.²⁻⁴

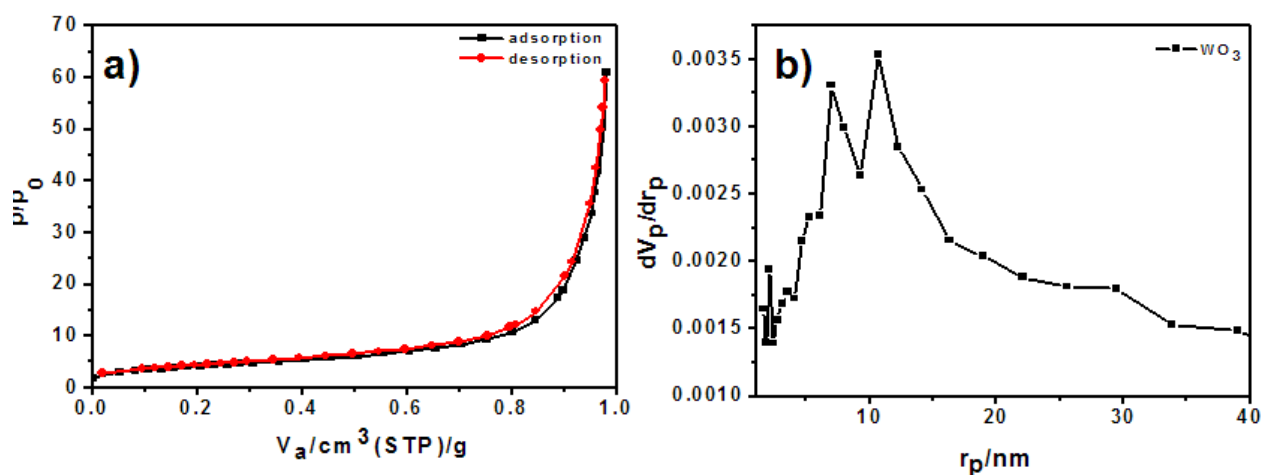


Fig.S3 (a, b): a) Nitrogen adsorption–desorption isotherm, and b) Pore size distribution of WO_3 NRs powder.

SI (IV): The X-ray photoelectron spectroscopy (XPS) study

The XPS spectra of the $\text{WO}_3\text{NRs-TiO}_2$ NPs are shown in (Fig.S4 (a-c)). These indicate that the $\text{WO}_3\text{NRs-TiO}_2$ NPs core-shell structure has been formed.^{5,6}

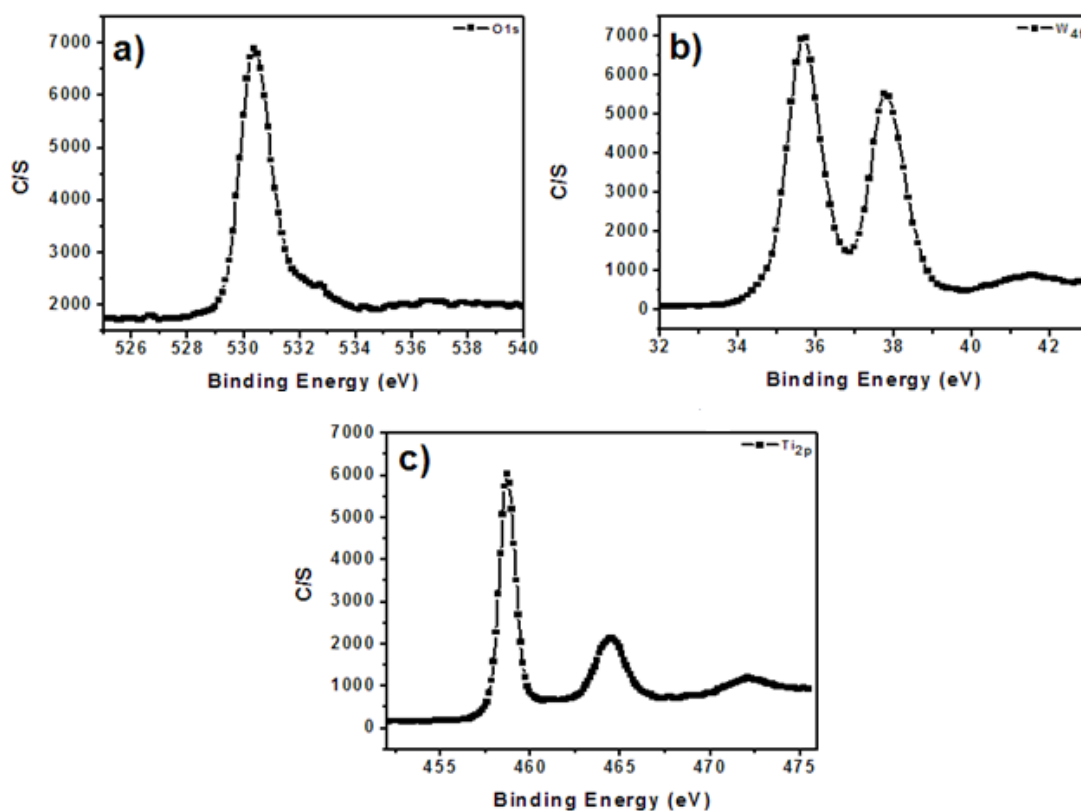


Fig.S4 (a-c): XPS spectra of; a) O1s, b) W4f, and c) Ti2p.

Table S1: Photovoltaic parameters obtained from *J-V* curves for Monoclinic WO₃ NRs- Rutile TiO₂ NPs measured under 1 Sun illumination.

Electrodes	<i>J</i>_{sc} (mA/cm⁻²)	<i>V</i>_{oc} (V)	FF (%)	Efficiency (%)
WO₃ NRs	0.14	0.19	20.7	0.006
WO₃ NRs-dye	0.90	0.35	38.0	0.12
WO₃-TiO₂-dye	5.60	0.44	49.0	1.21

Table S2: Electronic parameter was used for fitting Nyquist plots, of WO₃ NRs, WO₃ NRs –dye and WO₃-TiO₂-dye electrodes.

Electrodes	R_s (Ω.cm²)	R₁ (Ω.cm²)	R₂ (Ω.cm²)
WO₃ NRs	9.21	3.40	4561.44
WO₃ NRs-dye	16.61	3.68	2794.76
WO₃-TiO₂-dye	10.07	3.21	2120.68

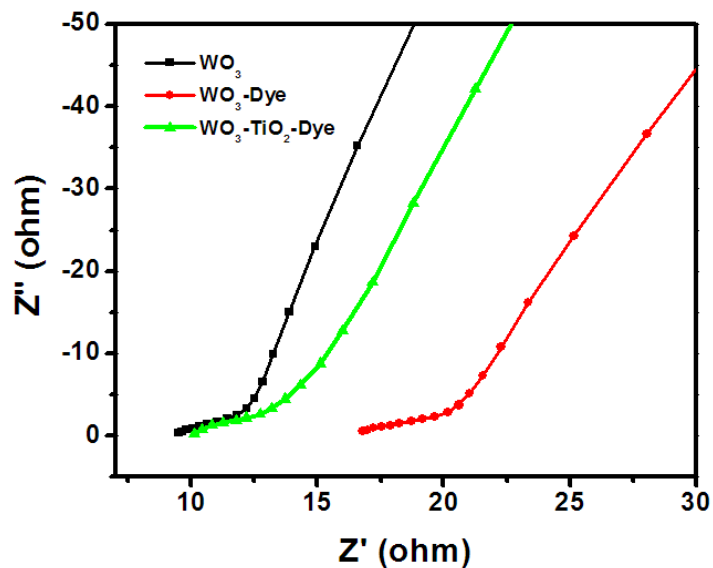


Fig. S5. High frequency region of the Nyquist plots.

References

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