

**Toward rational photocatalyst design: A new formation strategy of  
co-catalyst/semiconductor heterostructure via *in situ* exsolution**

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## Experimental Procedure

### Material Fabrication

The fabrication procedure of  $\text{WS}_2\text{-SrTiO}_3$  was detailed shown in schematic 1. Specifically, the pristine W doped  $\text{SrTiO}_3$  was prepared by a modified hydrothermal process. Typically, certain amount of  $\text{Sr}(\text{NO}_3)_2$  was dissolved in 30 ml ethylene glycol at 80 °C. After cooling to room temperature, stoichiometric amount of tetrabutyl titanate (TBT) was added dropwise to get solution A (the molar ratio of Sr:Ti.=1). Meanwhile,  $\text{Na}_2\text{WO}_4$  was dissolved in 5M NaOH solution to get clean solution B. (the molar ratio of W:Ti.=0.05/0.95). After adding B to A, the mixture was stirred for another 30 min and then transferred into autoclave at 200 °C for 24h. The obtained product was washed by deionized water and alcohol for three times, respectively. Finally, the dried sample was calcined at 500 °C for 6 h in Ar, denoted as  $\text{SrTiWO}_3$ .  $\text{SrTiWO}_3$  was exposed to 5% $\text{H}_2\text{-N}_2$  at 800 °C for 10 h and further *in-situ* treated in  $\text{CS}_2$  flow at 350 °C for 2 h, using Ar as a carrier gas with the flow rate at 10 ml min<sup>-1</sup>. The resulting materials were washed thoroughly using acetone and subsequently dried at 60 °C in oven, denoted as  $\text{WS}_2\text{-SrTiO}_3$ . As a reference, commercial  $\text{WS}_2$  was physically mixed with  $\text{SrTiO}_3$  sample prepared by hydrothermal method to generate sample:  $\text{WS}_2 + \text{SrTiO}_3$ . The preparation approach of  $\text{MoS}_2\text{-SrTiO}_3$  is similar to that of  $\text{WS}_2\text{-SrTiO}_3$ , in which Ammonium molybdate tetrahydrate is used as Mo source.

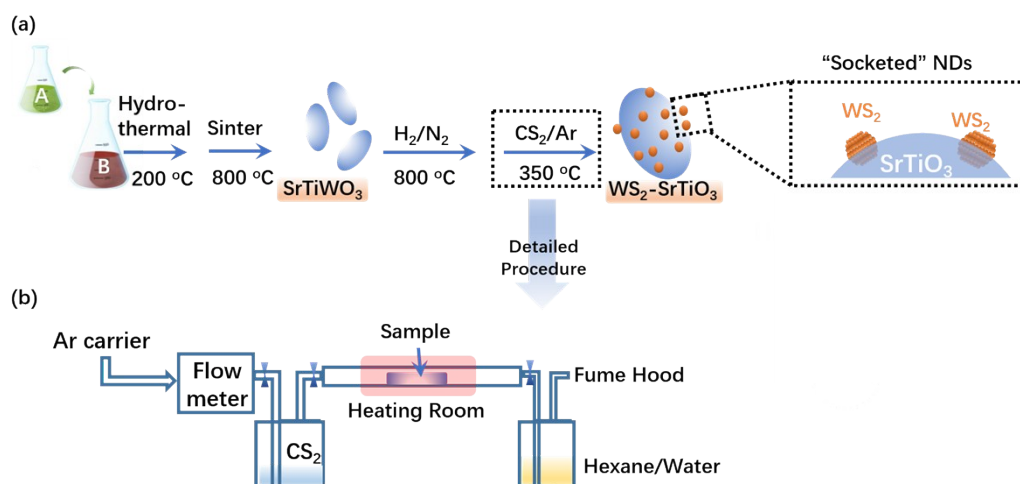
### Characterizations

Powder X-ray diffraction (XRD) patterns of the samples were obtained from a Panalytical X'pert PRO diffractometer (Philips, Netherlands). The samples were scanned from 20 to 80° 2 $\theta$  at 5 ° min<sup>-1</sup>. Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm) generated at 40 kV and 30 mA was used as the X-ray source. X'Pert Highscore Plus 3.0 software was utilized to analyze results. X-ray photoelectron spectroscopy (XPS) analysis was conducted on Omicron Sphera II hemispherical electron energy analyzer (U.K.) with Al K $\alpha$  irradiation at the pressure of  $5.0 \times 10^{-9}$  mbar. The spectra were corrected by C1s labeled peak at 286.4 eV. The BET surface areas of the samples were determined from the  $\text{N}_2$  adsorption and desorption isotherms using an automated Micromeritics Tristar 3000 equipment (Norcross, GA, U.S.A.). The samples were multipoint BET equation on an automated Micromeritics Tristar 3000 apparatus (Norcross, GA, U.S.A.). The micromorphology of the materials was illustrated by a JEOL 6301F Scanning Electron Microscopy (SEM). The TEM characterization was performed in the H-9500 environmental transmission electron microscope (ETEM) with accelerating voltage of 300 kV. UV-vis diffuse reflectance spectra were collected using a Varian Cary 5000 UV-Vis-NIR spectrometer equipped with an integrating sphere, and  $\text{BaSO}_4$  was as a reference standard. Before Mott-Schottky test, all samples were pre-electrophoretic deposited on conducting Fluorine doped Tin Oxide (FTO) substrate. Specifically, the FTO electrode is immersed in the 25 ml acetone solution with 10 mg iodine and suitable amount of catalyst powder. Pt electrode was

used as counter electrode with the distance of 10 cm from FTO side. A standard calomel electrode (SCE) is used as reference electrode. The deposition was accomplished at 10 V bias for 5 min. The as-prepared electrode were dried and sinter at 300 °C for 30 min to form good adhesion.

The Photocatalytic hydrogen evolution tests were conducted in 50 ml quartz reactor. The 300 W xenon arc lamp was used as light source and UV-cutoff filter (JB420) was used to generate visible light. In a typical reaction, 0.1 g catalyst was dispersed in 35 ml aqueous solution containing 10 vol% methanol as sacrificial agent. The system was vacuumed and purged with 99.99% N<sub>2</sub> for at least 30 min prior to irradiation. The evolved gases are detected by using an online gas chromatograph (GC-2014C, Shimadzu) equipped with a thermal conductivity detector (TCD).

Photo-electrochemical (PEC) measurements were performed on a standard three-electrode cell and a CHI-660E electrochemical instrument with as-prepared photocatalyst as working electrode, a platinum wire as counter electrode and a standard calomel electrode (SCE) as reference electrode, respectively. A 300W Xe lamp through a cut-off filter (>420) as the light source. Na<sub>2</sub>SO<sub>4</sub> aqueous solution (0.1 M) was used as the electrolyte. The working electrodes were prepared as follows: 1 mg of as-prepared photocatalyst was dispersed in mixture of 1 mL isopropanol and 150 µL Nafion solution (5 wt%) to produce a slurry. Then 100 µL suspension was coated onto a 1 cm\*1.25 cm indium tin oxide (ITO) glass plate at room temperature and then drying in a vacuum oven for 12 h at 40 °C.



Scheme S1. The schematic of *in situ* growth of  $\text{WS}_2$  nanodots on  $\text{SrTiO}_3$  semiconductor

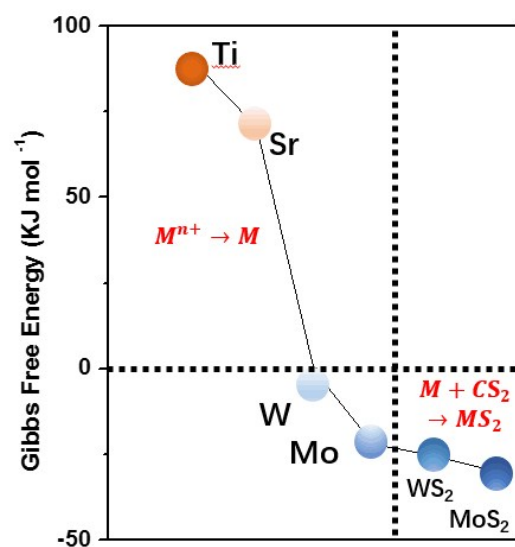
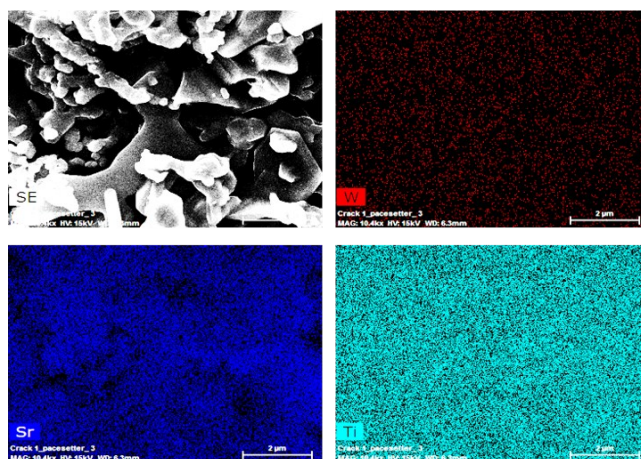


Figure S1. Theoretical value of Gibbs free energy for different reactions ( $\text{H}_2 + \text{M}^{n+} \rightarrow \text{M}$  at 800 °C and  $\text{M} + \text{CS}_2 \rightarrow \text{MS}_2$  at 350 °C, respectively). The results Calculated by HSC 6.0 software. The W and Mo elements are only ones show negative Gibbs free energy upon reduction. Also, the sulfuration reactions are thermodynamically favorable.

Table S-1 Unit cell parameters, color and energy gaps of each samples

	a (Å)	V(Å <sup>3</sup> )	Color	Bandgap (eV)
SrTiO <sub>3</sub>	3.904	59.50	white	3.05
SrTiWO <sub>3</sub>	3.891	58.92	Light yellow	2.95
WS <sub>2</sub> -SrTiO <sub>3</sub>	3.898	59.24	black	2.45

(a)  $\text{SrTiWO}_3$



(b)  $\text{WS}_2 + \text{SrTiO}_3$

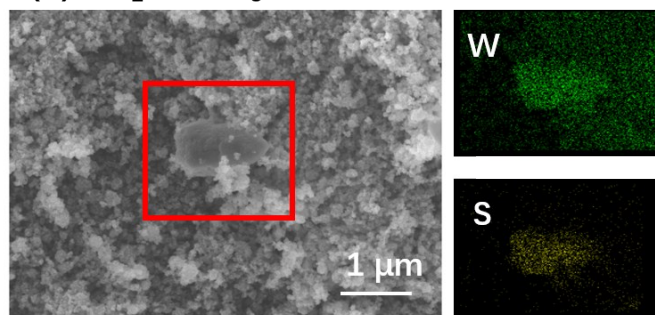


Figure S2 SEM images and corresponding EDX element mappings of (a)  $\text{SrTiWO}_3$  and (b)  $\text{WS}_2 + \text{SrTiO}_3$

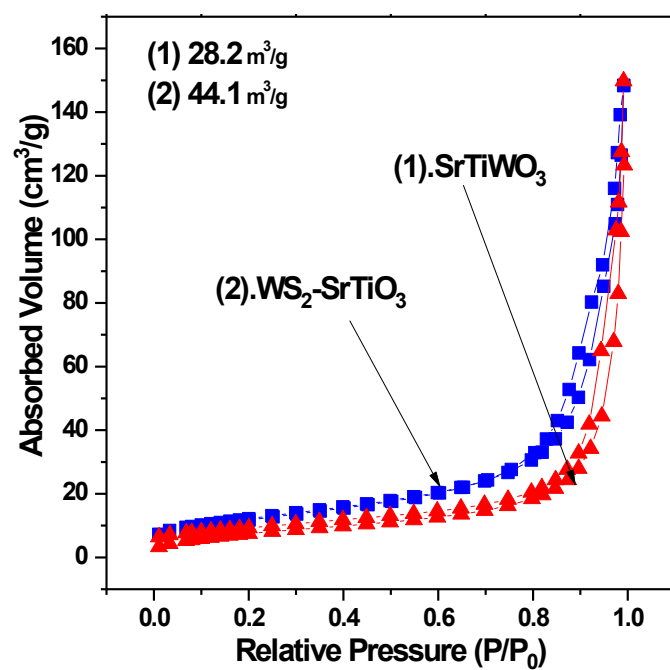


Figure S3 Nitrogen adsorption/desorption isotherm of various materials and their corresponding BET surface area values were summarized



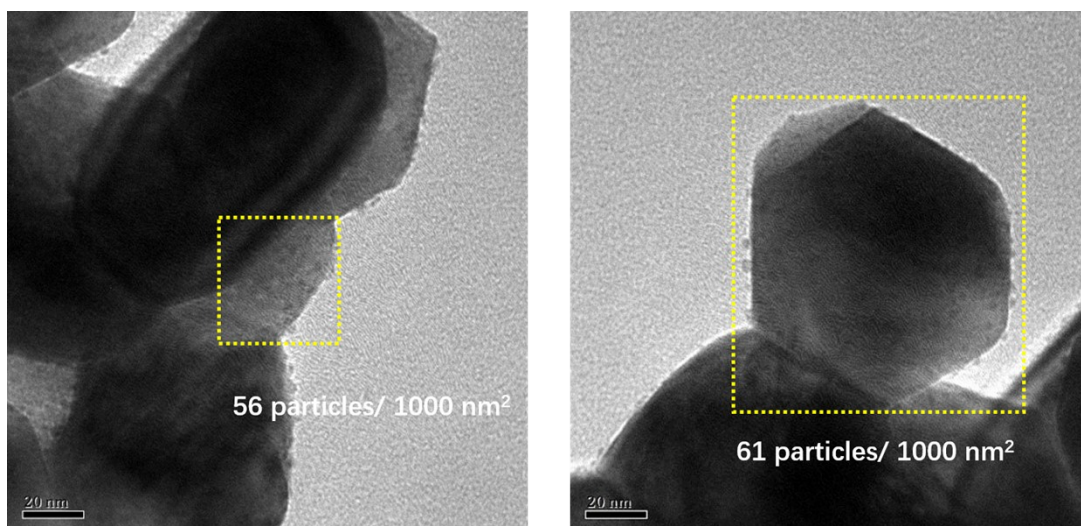


Figure S4 TEM images of  $\text{WS}_2$ - $\text{SrTiO}_3$  sample. The calculated number density of  $\text{WS}_2$  nanodots in selected area was also shown.

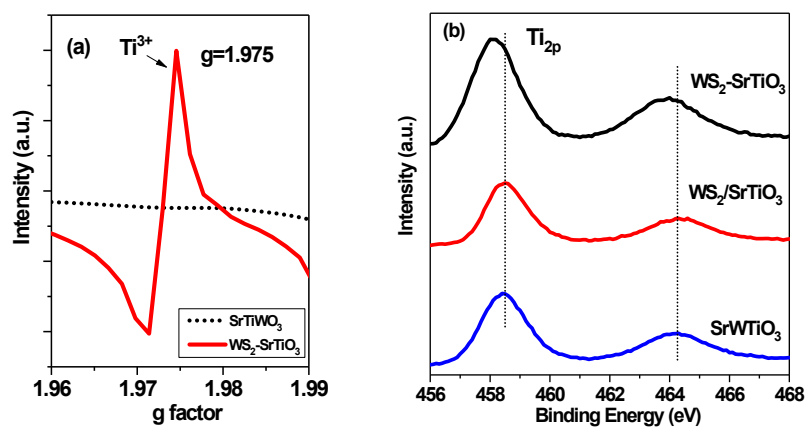


Figure S5 (a) EPR (at 77 K) of pristine  $\text{SrTiWO}_3$  and  $\text{WS}_2\text{-SrTiO}_3$  (b) XPS plot of  $\text{Ti}_{2p}$  of different samples.

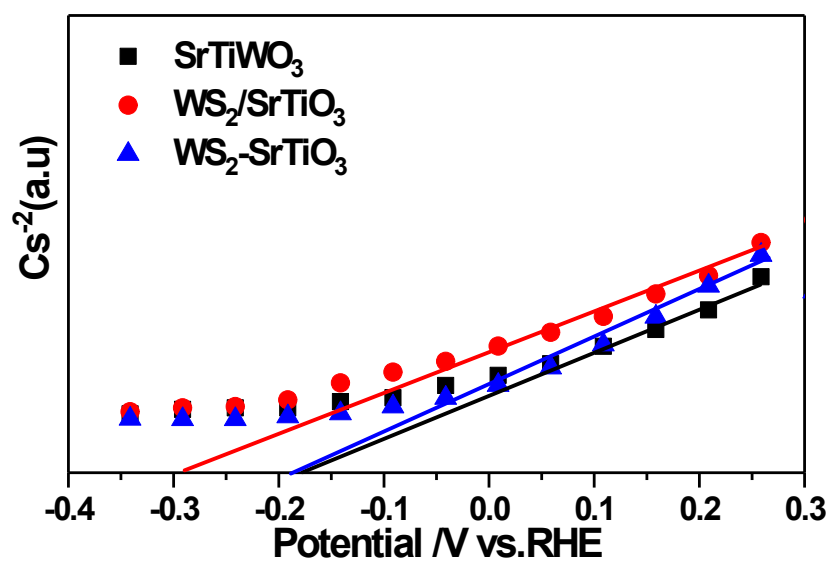


Figure S6 The Mott-Schottky curves of different samples.

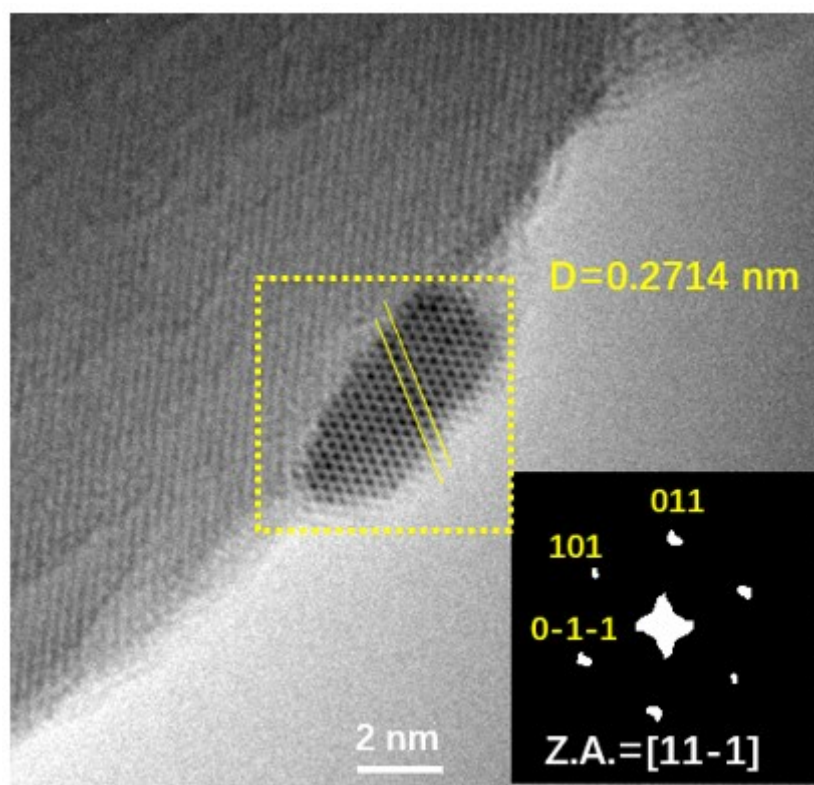


Figure S7 HR-TEM image of MoS<sub>2</sub> nanodots grown on SrTiO<sub>3</sub> and Corresponding FFT pattern.