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# **Supporting Information**

### Layered MoS<sub>2</sub> Coupled MOFs-Derived Dual-Phase TiO<sub>2</sub> for Enhanced Photoelectrochemical Performance

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#### **Supporting Text**

# The effect of Sn<sup>4+</sup> cation exchanging on the structure and morphology of MIL-125(Ti) and MOFs-derived TiO<sub>2</sub>

As shown in Fig. S1 (a), the X-ray diffraction (XRD) patterns of Sn<sup>4+</sup> exchanged and pure MIL-125(Ti) match well with the simulated pattern, demonstrating the good crystallinity of the obtained MOFs. It can be observed in Fig. S1 (b) that the magnified diffraction peaks slightly shift to small angle position, which suggests the interlayer spacing of the framework expands with the cation concentration of Sn<sup>4+</sup> increasing. Considering the radium of  $Sn^{4+}$  (0.70 Å) is slightly larger than that of Ti<sup>4+</sup> (0.60 Å),<sup>1</sup> the expansion of framework is attributed to the lattice points substitution of Ti<sup>4+</sup> by Sn<sup>4+</sup>. In Fig. S2, the FE-SEM images of as-prepared Sn<sup>4+</sup> exchanged MIL-125(Ti) are shown. With the Sn concentration increasing, the morphologies of the production are varied from irregular cubes to uniformed cylinders, and finally change into uniformed cubes. To synthesize dual-phase TiO<sub>2</sub> (denoted as DT) derived from Sn<sup>4+</sup> exchanged MOFs, MOFs powder is annealed in air. As shown in Fig. S1 (c), the XRD patterns of pure MOFs-derived TiO<sub>2</sub> (denoted as 0DT) matches well with the standard anatase TiO<sub>2</sub> (PDF#:21-1272). However, the XRD patterns of DT matches well with not only the anatase phase but also the rutile phase (PDF#: 21-1276). The appearance of DT results from the substitution of Sn<sup>4+</sup> into in the lattice of anatase TiO<sub>2</sub> which leads to a phase transition of anatase  $TiO_2$ , according to the work reported earlier.<sup>2</sup> The magnified XRD patterns of anatase  $TiO_2$  (101) peaks are depicted in Fig. S1 (d). It is shown that the diffraction peak position of DT shifts to a lower angle in comparison with pure  $TiO_2$ , suggesting the crystal lattice distance augments with the concentration of  $Sn^{4+}$  increasing. The calculated lattice constant is shown in **Table S1**. As stated before, due to the radium of Sn<sup>4+</sup> is larger than that of Ti<sup>4+</sup>, the lattice expansion is attributed to the lattice point of Ti<sup>4+</sup> exchanged by Sn<sup>4+</sup>.

 Table S1. Lattice constant of 0DT and DT samples

Samples	2θ (degree)	d <sub>(hkl)</sub> value (Å)	X <sub>rutile</sub> (wt%)
0% DT	25.397	3.5042	0
2.5% DT	25.232	3.5252	35
5% DT	25.243	3.5266	43

To study structure changes of the MOFs and its derivation after  $Sn^{4+}$  exchanged  $Ti^{4+}$ , we further tested the nitrogen absorption-desorption isotherms. As shown in Fig. S3, for both the pure MOFs and  $Sn^{4+}$  exchanged MOFs, the micropore-rich structures do not change obviously while the pore sizes have varied significantly. For pure MOFs, the average pore size is around 0.43 nm, but the average pore sizes vary to 0.45 nm and 0.47 nm for 2.5% and 5.0% Sn exchanged MOFs, respectively. After the MOFs precursor is annealed in air and derived into TiO<sub>2</sub>, it can be seen the micropore disappears and the typical isotherms for mesoporous structure are shown. Similarly, the pore sizes of the productions also vary with the component changing. For pure MOFs derived TiO<sub>2</sub>, the average pore size is around 5 nm. And the average pore sizes of 2.5% and 5.0% Sn exchanged MOFs, the pore size of MOFs precursor and MOFs derived TiO<sub>2</sub> can be efficiently changed. Considering the reason why the pore size of MOFs-derived TiO<sub>2</sub> will change with the variation of the Sn<sup>4+</sup> concentration, it should be attribute to more pore will be produced by the lattice mismatch accumulation leaded by the Sn<sup>4+</sup> exchanging Ti<sup>4+</sup> processes. The structural parameters of as synthesized 0DT and 2.5DT, 5DT are listed as follows (**Table S2**).

Table 52. Structural Parameters of as synthesized 0D1 and D1 samples				
Samples	BET surface area (m²g-¹)	pore diameter (nm)	total pore volume (cm³g⁻¹)	
0DT	89.95	4.91	0.19	
2.5DT	95.85	8.52	0.21	
5DT	100.97	11.32	0.30	

Table S2. Structural Parameters of as synthesized 0DT and DT samples

It has been reported that the DT with about 30 wt % rutile phase shows the best photocatalytic activity.<sup>3, 4</sup> According to Wang's work,<sup>5</sup> to analysis the phase fraction of rutile phase ( $X_{rutile}$ ) of the dual-phase TiO<sub>2</sub>,  $X_{rutile}$  can be calculated by following equations:

$$X_{rutile} = (1 + K(\frac{I_A}{I_R}))^{-1}$$
(1)

$$X_{anatase} = 1 - X_{rutile} \tag{2}$$

where  $I_A$  is the diffraction intensity of anatase (101) plane and  $I_R$  is that of rutile (110) plane. The experimental constant *K* was determined via an XRD analysis of powders of known proportions of pure anatase and pure rutile, and is equal to 0.79. The calculated rutile phase content is listed in Table S1. For DT, 2.5% DT sample has the closest rutile proportion of 30 wt% (35 wt%) and, with the content of Sn<sup>4+</sup> increasing, the rutile proportion further

increasing to 43 wt%. From this point, it can be concluded that *via* tailoring the component of  $Sn^{4+}$  exchanged MOF, content adjustable dual-phase TiO<sub>2</sub> can be conveniently synthesized. The following experiments in the main text are based on 2.5%  $Sn^{4+}$  exchanged MOFs-derived dual-phase TiO<sub>2</sub>, which is directly denoted as DT.



Fig. S1 (a, c) Wide-angle XRD patterns and (b, d) magnified XRD patterns of as synthesized  $Sn^{4+}$  exchanged MIL-125(Ti) (the mole ratio of  $Sn^{4+}$  equals to 0, 2.5 and 5.0 mol%) and corresponding MOFs-derived dual-phase TiO<sub>2</sub>.



Fig. S2 FE-SEM images of as-prepared  $Sn^{4+}$  exchanged MIL-125(Ti) (the mole ratio of  $Sn^{4+}$  equals to 0, 2.5 and 5.0 mol%).



Fig. S3 (a-b) The  $N_2$  adsorption–desorption curves and (c-d) pore size distribution plots for as-prepared pure MOFs and Sn<sup>4+</sup> exchanged MOFs and the corresponding MOFs-derived TiO<sub>2</sub>.



Fig. S4 FE-SEM images of as-prepared (a) 0.25 MDT and (b) 1MDT samples.



Fig. S5 EDS elemental mapping images of  $0.5MoS_2/dual$ -phase TiO<sub>2</sub>.



Fig. S6 Magnified TEM images of the MoS<sub>2</sub> nanosheet.



Fig. S7 (a) TEM image and (b) magnified TEM images of as synthesized dual-phase TiO<sub>2</sub>.



Fig. S8 (a) The  $N_2$  adsorption–desorption curves and (b) pore size distribution plots for as-prepared 0DT, DT, MoS<sub>2</sub> and *x*MDT samples.



Fig. S9 The incident light multi-scattering process illustration of the few-layered MoS<sub>2</sub>/dual-phase TiO<sub>2</sub> structure.



Fig. S10 Photoluminescence spectra of as synthesized few-layered MoS<sub>2</sub> and *x*MDT heterostructures.



Fig. S11 Picosecond-resolved fluorescence transients of 0DT, DT and xMDT samples (excitation at 405 nm).



Fig. S12 Sketch map of the photo-induced charge separation and transfer processes between dual-phase  $TiO_2$  and few-layered  $MoS_2$ .



Fig. S13 Long cyclic curves of DSSCs based on 0DT, DT and 0.5MDT heterostructured photoanode.



Fig. S14 LSV curves under AM 1.5G at 100 mW/cm<sup>2</sup> illumination for the *x*MDT heterostructured samples.



Fig. S15 Photocurrent stability measurement for  $0.5MoS_2/dual$ -phase TiO<sub>2</sub> sample at 1.2 V versus RHE under 100 mW/cm<sup>2</sup> illumination.

Sample	$T_1(ns)$	$T_2(ns)$	$B_1$	B <sub>2</sub>	τ(ns)
0DT	0.3	4.17	67.29	32.71	3.67109
DT	0.39	4.61	64.97	35.03	4.03766
0.25MDT	1.93	8.87	69.47	30.53	6.57179
0.5MDT	0.72	8.14	41.87	58.13	7.69558
1MDT	0.42	4.57	47.6	52.4	4.25023

Table S3. Dynamics of Picosecond-Resolved Fluorescence Transients of 0DT, DT and xMDT samples

Table S4. Band structure position of anatase, rutile  $TiO_2$  and  $MoS_2$  (eV vs. NHE)

	Conduction Band	Valence Band
Anatase TiO <sub>2</sub>	-0.29	2.91
Rutile TiO <sub>2</sub>	-0.48	2.52
$MoS_2$	-0.60	1.30

## References

- 1. L. Ran, D. Zhao, X. Gao and L. Yin, CrystEngComm, 2015, 17, 4225-4237.
- 2. J. Li and H. C. Zeng, J. Am. Chem. Soc., 2007, 129, 15839-15847.
- 3. L. Zhao, M. Han and J. Lian, Thin Solid Films, 2008, 516, 3394-3398.
- 4. R. Bacsa and J. Kiwi, Appl. Catal. B: Environ., 1998, 16, 19-29.
- 5. S. Wang, J. Lian, W. Zheng and Q. Jiang, Appl. Surf. Sci., 2012, 263, 260-265.