

## Supporting Information

# Development of bi-compound heterogeneous cocatalyst modified p-Si photocathode for boosting the photoelectrochemical water splitting performance

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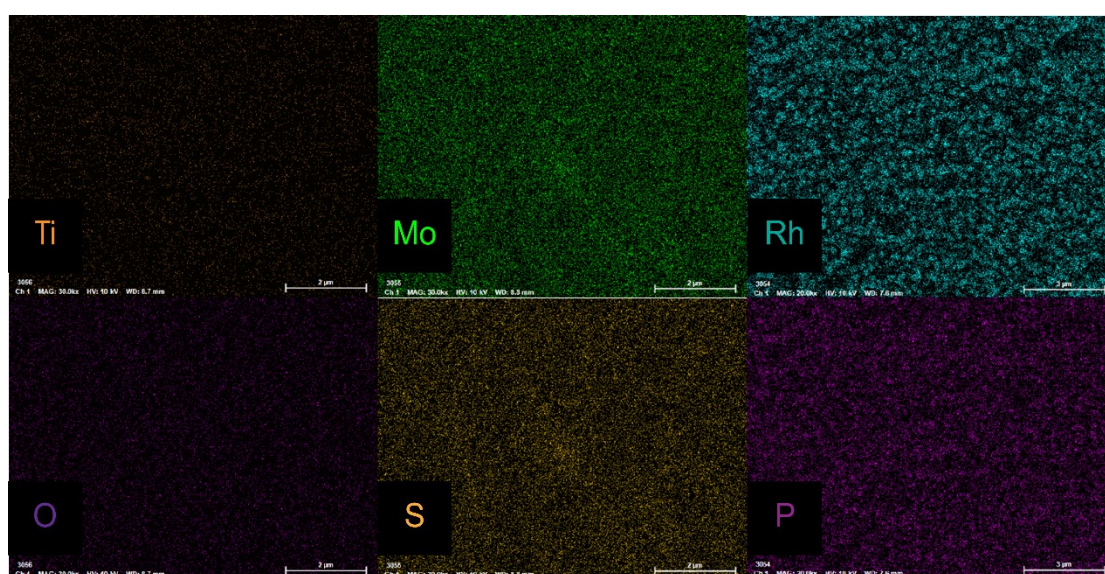


Figure S1. EDS mapping images of p-Si-TiO<sub>2</sub>-MoS<sub>2</sub>/Rh-P.

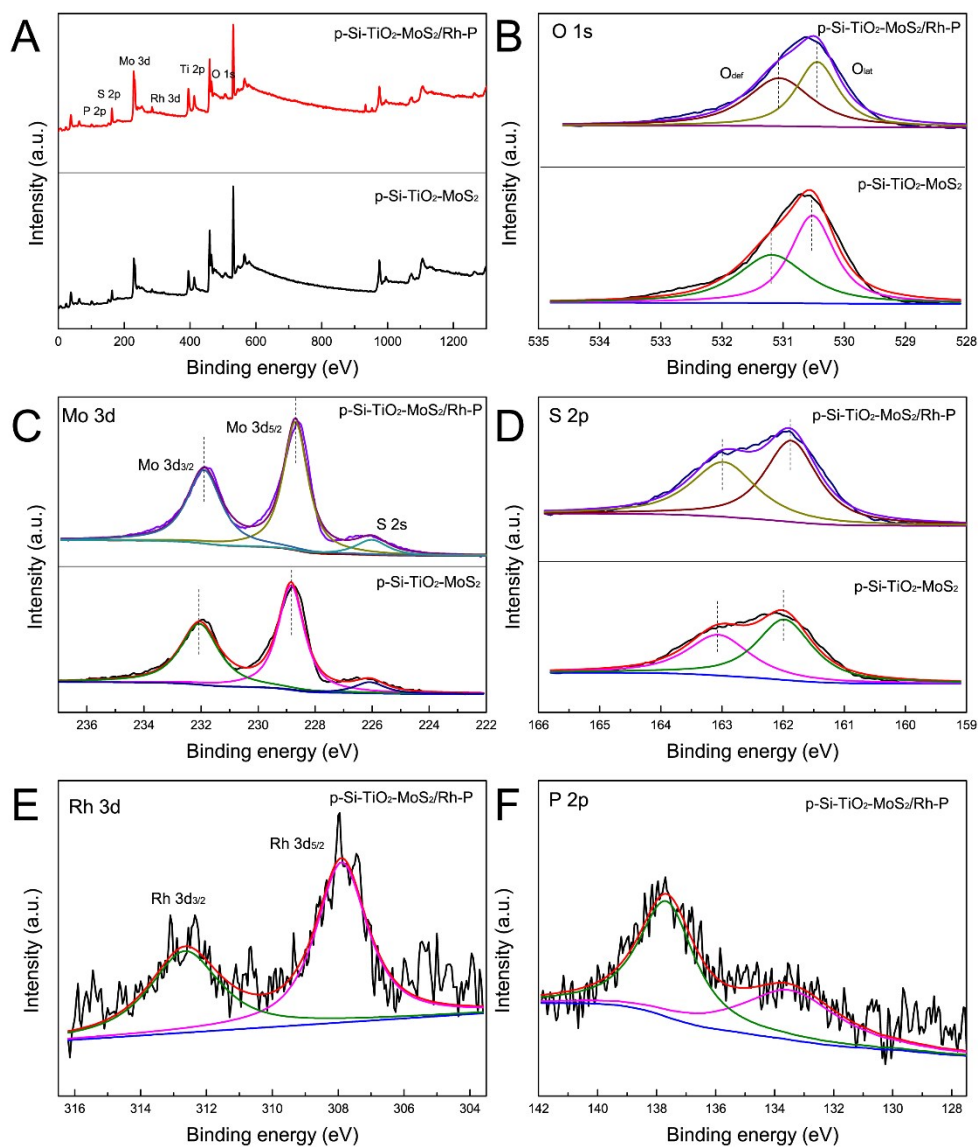


Figure S2. The total XPS survey spectra (A) and high resolution O 1s (B), Mo 3d (C), S 2p (D) XPS spectra of  $p\text{-Si-TiO}_2\text{-MoS}_2$  and  $p\text{-Si-TiO}_2\text{-MoS}_2/\text{Rh-P}$ , high resolution Rh 3d (E) and P 2p (F) XPS spectra of  $p\text{-Si-TiO}_2\text{-MoS}_2/\text{Rh-P}$ .

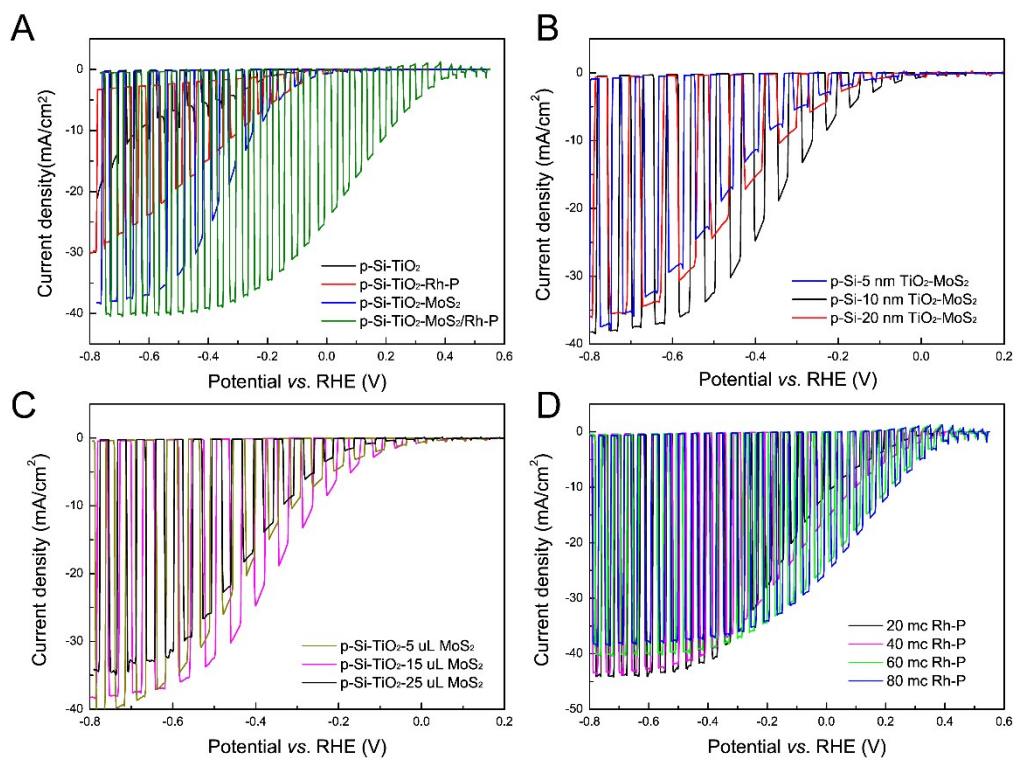


Figure S3. (A) Current density-potential curves of the series photocathodes. Current density-potential curves of p-Si-TiO<sub>2</sub>-MoS<sub>2</sub> with different deposition conditions of (B) TiO<sub>2</sub>, (C) MoS<sub>2</sub> and (D) Rh-P.

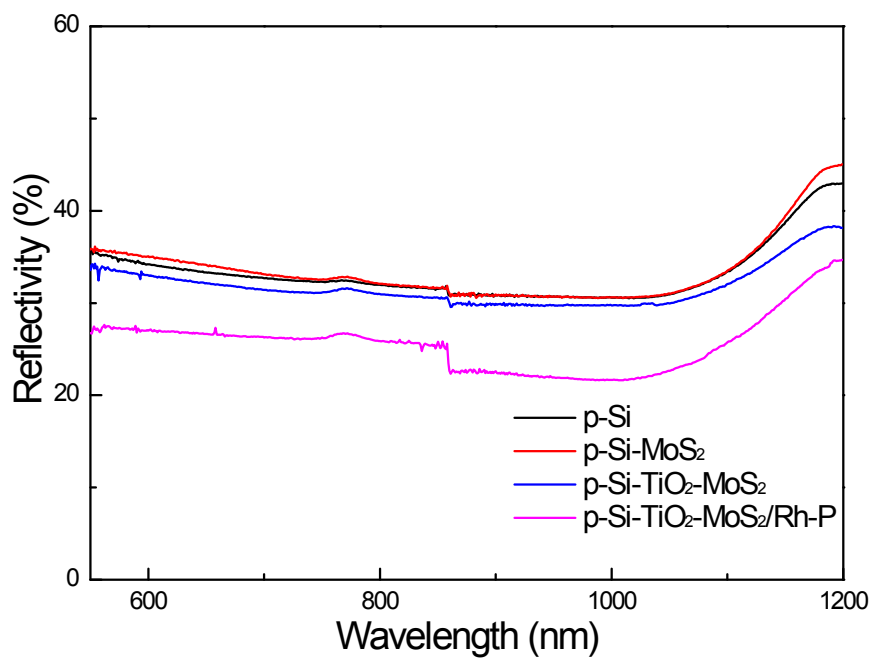


Figure S4. Surface reflectivity of the series photocathodes.

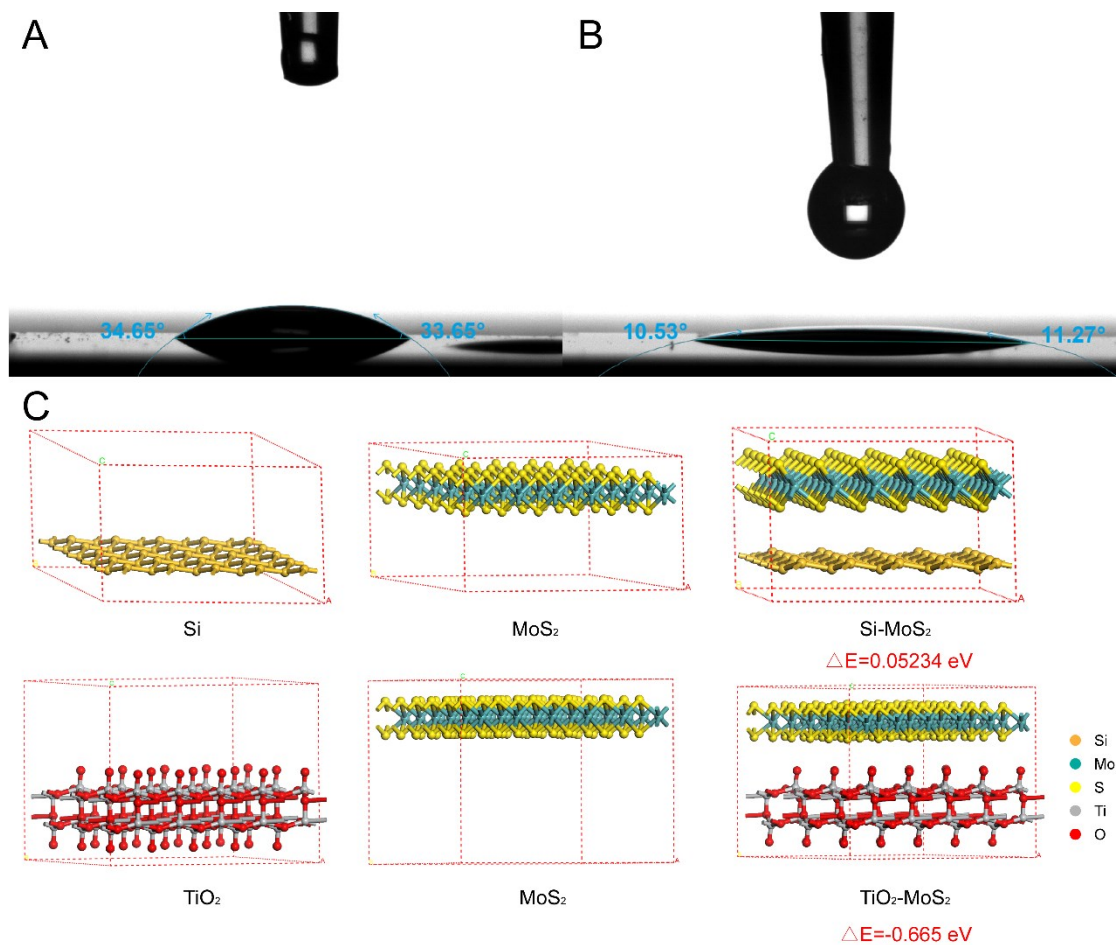


Figure S5. Contact angle test results of (A) p-Si and (B) p-Si-TiO<sub>2</sub>, (C) the optimization model for Si, MoS<sub>2</sub>, Si-MoS<sub>2</sub>, TiO<sub>2</sub> and TiO<sub>2</sub>-MoS<sub>2</sub>.

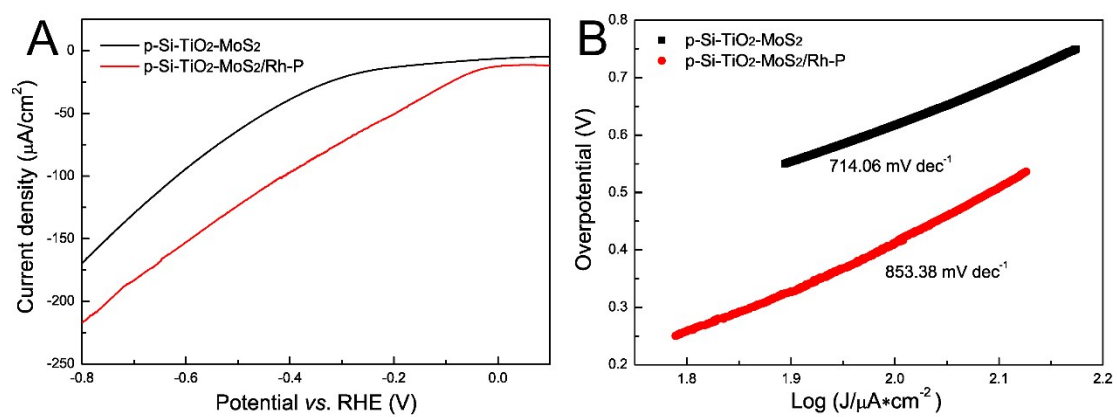


Figure S6. (A) LSV curves of p-Si-TiO<sub>2</sub>-MoS<sub>2</sub> and p-Si-TiO<sub>2</sub>-MoS<sub>2</sub>/Rh-P for HER. (B) The corresponding Tafel plots.

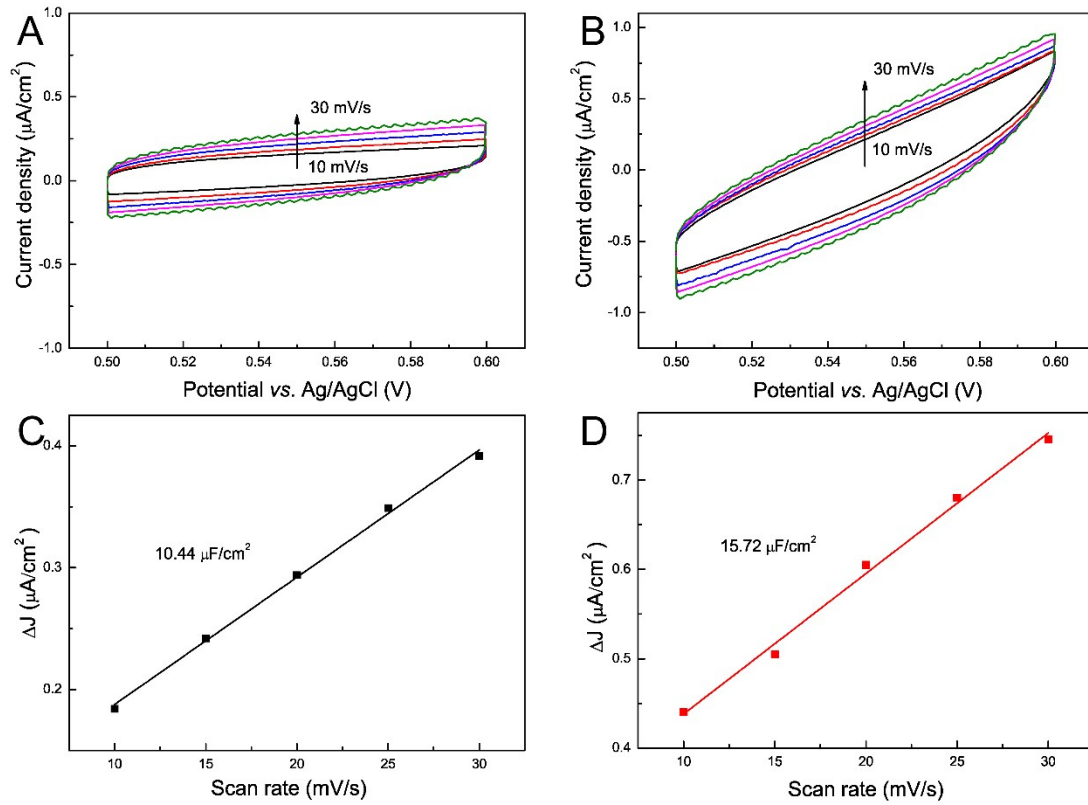


Figure S7. Cyclic voltammograms of (A) p-Si-TiO<sub>2</sub>-MoS<sub>2</sub> and (B) p-Si-TiO<sub>2</sub>-MoS<sub>2</sub>/Rh-P against different scan rates. The corresponding charging current density differences of (C) p-Si-TiO<sub>2</sub>-MoS<sub>2</sub> and (D) p-Si-TiO<sub>2</sub>-MoS<sub>2</sub>/Rh-P.

Table S1. Parameters fitted from the PEIS curves of the series photocathodes.

Sample	$R_s$ ( $\Omega$ cm <sup>-2</sup> )	$R_t$ ( $\Omega$ cm <sup>-2</sup> )	$R_i$ ( $\Omega$ cm <sup>-2</sup> )
p-Si	3.99	12.58 k	\
p-Si-MoS <sub>2</sub>	17.08	753.46	\
p-Si-TiO <sub>2</sub> -MoS <sub>2</sub>	6.66	22.74	49.94
p-Si-TiO <sub>2</sub> -MoS <sub>2</sub> /Rh-P	6.14	4.90	6.37