Supplementary Information for

## Surface precleaning strategy intensifies interface coupling of $Bi_2O_3/TiO_2$ heterostructure for enhanced photoelectrochemical detection properties

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**Figure S1**. SEM images of (a)  $TiO_2$ , (b) *c*- $TiO_2$ , (c)  $Bi_2O_3/c$ - $TiO_2$  for 1 cycle, and (d) EDS spectrum from TEM image of  $Bi_2O_3/c$ - $TiO_2$ .



Figure S2. TEM image of a single TiO<sub>2</sub> nanotube.



Figure S3. Raman spectra (a) and XPS Survey patterns (b) of TiO<sub>2</sub>, *c*-TiO<sub>2</sub>, and Bi<sub>2</sub>O<sub>3</sub>/*c*-TiO<sub>2</sub> NTAs.



**Figure S4.** Photocurrents and current response of  $Bi_2O_3/c$ -TiO<sub>2</sub> NTAs with different cycles: (a) current-time curves, (b) plots of photocurrent and current response *vs.* deposition cycle.



**Figure S5.** High resolution XPS spectrum of Ti 2p and Bi 4f spectrum for the tested  $Bi_2O_3/TiO_2$  and  $Bi_2O_3/c$ -TiO<sub>2</sub> respectively.

Composite	Current	Sensitivity µA/(µM)	Linear	Limit of
	noise		range	Detection *
	μΑ		μΜ	μΜ
TiO <sub>2</sub>	0.812	0.088	985.8	27.68
<i>c</i> -TiO <sub>2</sub>	0.431	0.142	888.1	8.37
Bi <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub>	0.669	0.162	1088.03	12.39
Bi <sub>2</sub> O <sub>3</sub> / <i>c</i> -TiO <sub>2</sub>	0.372	0.214	1185.5	5.21

Table S1. Detection parameters of TiO<sub>2</sub>, *c*-TiO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>, and Bi<sub>2</sub>O<sub>3</sub>/*c*-TiO<sub>2</sub> NTAs.



**Figure S6**. Transformed Kubelka–Munk function versus photon energy curves of TiO<sub>2</sub>, *c*-TiO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>, and Bi<sub>2</sub>O<sub>3</sub>/*c*-TiO<sub>2</sub> NTAs, respectively.

Transformed Kubelka–Munk function versus photon energy curves were applied to investigate the band gap of as-obtained four samples (**Figure S6**). Thereby, on the one hand, compared with TiO<sub>2</sub>, the Eg of c-TiO<sub>2</sub> is reduced with the low temperature hydrogen thermal treatment; on the other hand, the Eg of Bi<sub>2</sub>O<sub>3</sub>/c-TiO<sub>2</sub> is obviously changed when compared with c-TiO<sub>2</sub>, while there is no much difference between the Bi<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> and TiO<sub>2</sub>, which further proves that such an surface precleaning strategy can greatly facilitate the strong coupling in Bi<sub>2</sub>O<sub>3</sub>/c-TiO<sub>2</sub> NTAs.