Supplemental Information

Efficient Bias-Free Degradation of Sulfamethazine by TiO_2 Nanoneedle Arrays Photoanode and Co_3O_4 Photocathode System under LED-Light Irradiation

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1. Experimental Section

1.1 Chemicals and materials.

The Ti mesh was purchased from Anping Anheng metal mesh manufacture Co., Ltd. Cobalt nitrate ($Co(NO_3)_2·6H_2O$, ≥ 99.99%), ethylenediaminetetraacetic acid disodium (Na_2EDTA, 99.0%), acetylacetone (99 %) and ammonium fluoride (NH_4F, 98%) were purchased from Macklin Biochemical Co., Ltd. Titanium (IV) isopropoxide (≥ 98%) was bought from Acros Organics (China) Co., LTD. sulfamethazine (SMT, 98%) and 5,5-dimethyl-1-pyrroline N-oxide (DMPO, 97%) were bought from Shanghai Aladdin Chemistry Co., Ltd., China. Isopropanol (IPA, ≥ 99.7%), ammonium oxalate (AO, ≥ 99.8%), sodium chloride (NaCl), sodium sulfate (Na_2SO_4), sodium carbonate (Na_2CO_3), trisodium phosphate (Na_3PO_4) were provided by Damao Chemical reagent factory, China.

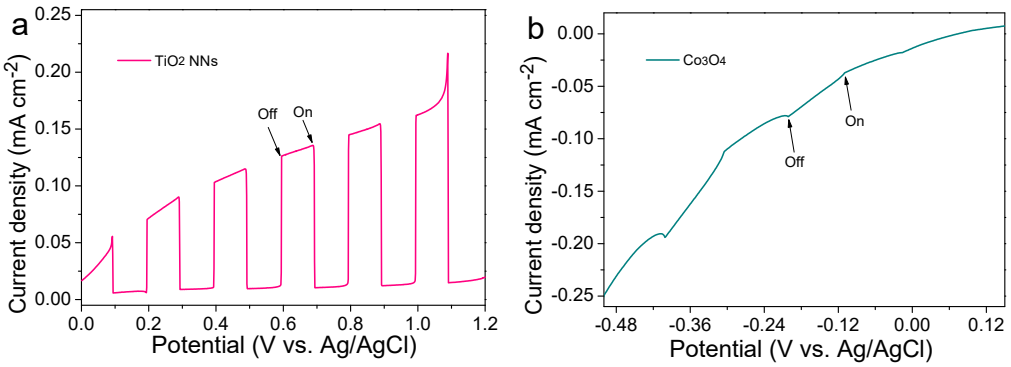


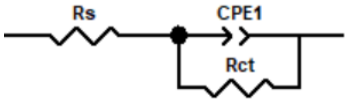
Figure S1. Linear sweep voltammetry (LSV) curves of the as-prepared TiO_2 NNs photoanode (a) and Co_3O_4 photocathode (b).

As depicted in the **Figure S1a**, the obvious and reproducible photocurrent indicated the high-efficiency and stability of TiO_2 NNs photoanode. Although the Co_3O_4 photocathode has strong light response ability, the photocurrent is small due to the low separation and transfer rate of photogenerated carriers (**Figure S1b**). Therefore, the Co_3O_4 photocathode has two functions in bias-free TiO_2 NNs-Co_3O_4 PEC system. On the one hand, it is to increase the photovoltage to the level that could make this system operate without external bias. On the other hand, it is to improve the utilization rate of solar energy and further reduce external energy input.

Table S1. The quality parameters of the actual environmental matrices.

Parameters	pH	Conductivity ($\mu S\ cm^{-1}$)	COD ($mg\ L^{-1}$)	TOC ($mg\ L^{-1}$)	Cl^- ($mg\ L^{-1}$)	SO_4^{2-} ($mg\ L^{-1}$)
Pharmaceutical wastewater	7.2	1986	93	33.1	334.8	302.5
Mariculture wastewater	8.0	32000	24	-	9000	4500

Table S2. Equivalent circuits fitting of EIS data for TiO_2 NNs-Co_3O_4, TiO_2 NNs-Pt and Pt-Co_3O_4 system with or without LED lamp illumination

PEC system	Condition	Rct (Ω)	Equivalent Circuits
TiO_2 NNs-Co_3O_4	Light	16.4	
	Dark	21.78	
TiO_2 NNs-Pt	Light	22.22	
	Dark	34.45	
Pt-Co_3O_4	Light	115.5	
	Dark	407.8	