Synergistic Promotion of Photoelectrochemical Water Splitting Efficiency of TiO_2 Nanorod Arrays by Doping and Surface Modification

Zhao Liang[1], Ding Chen[1], Shang Xu[1], Zhi Fang[2], Lin Wang[2], Weiyou Yang[2] and Huilin Hou[2*]*

[a] State Key Laboratory of Advanced Design and Manufacturing for Vehicle Body, College of Mechanical and Vehicle Engineering, Hunan University, Changsha City,410082, P.R. China

[b] Institute of Materials, Ningbo University of Technology, Ningbo City, 315211, P.R. China

[*] Corresponding authors. E-mails: chending@hnu.edu.cn (D. Chen) and houhuilin86@163.com (H. Hou)

Tel: +86-574-87080966, Fax: +86-574-87081221.

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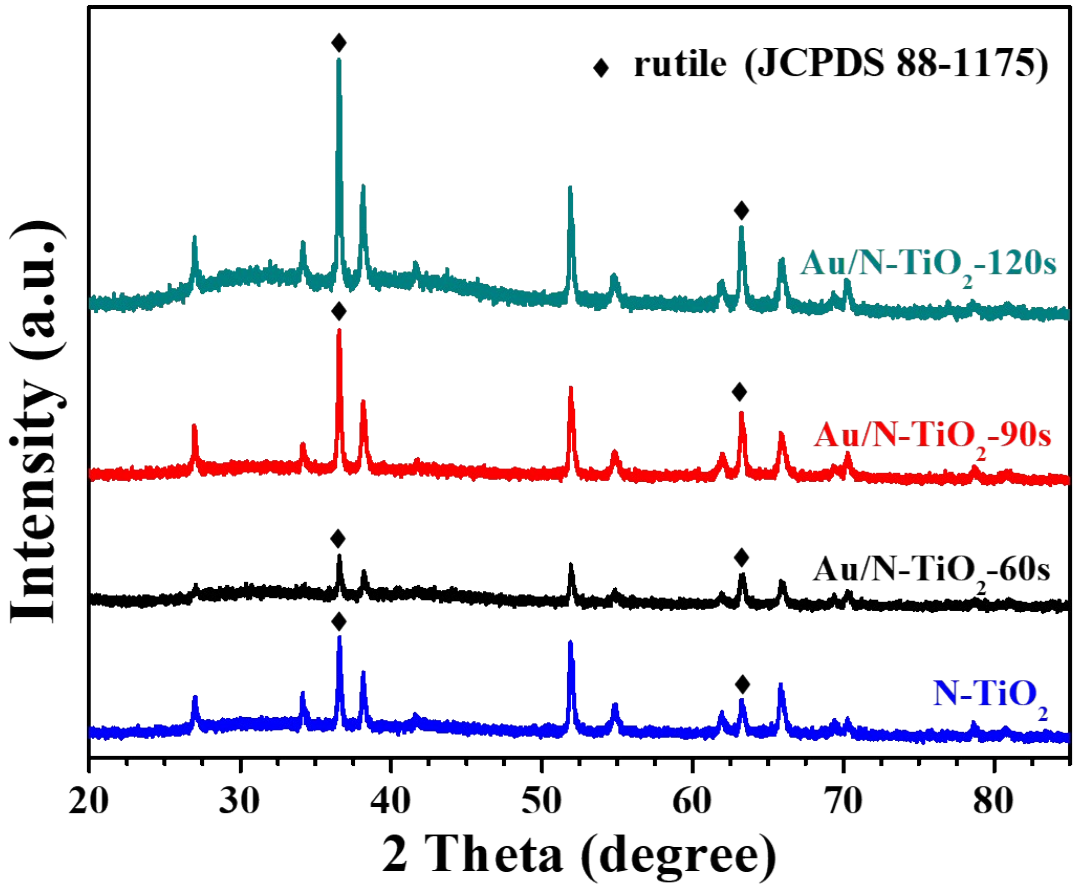

Fig. S1 XRD patterns of N-TiO_2 nanorods and Au/N-TiO_2 nanorods by magnetron sputtering of Au with different time (60 s, 90 s, 120 s).

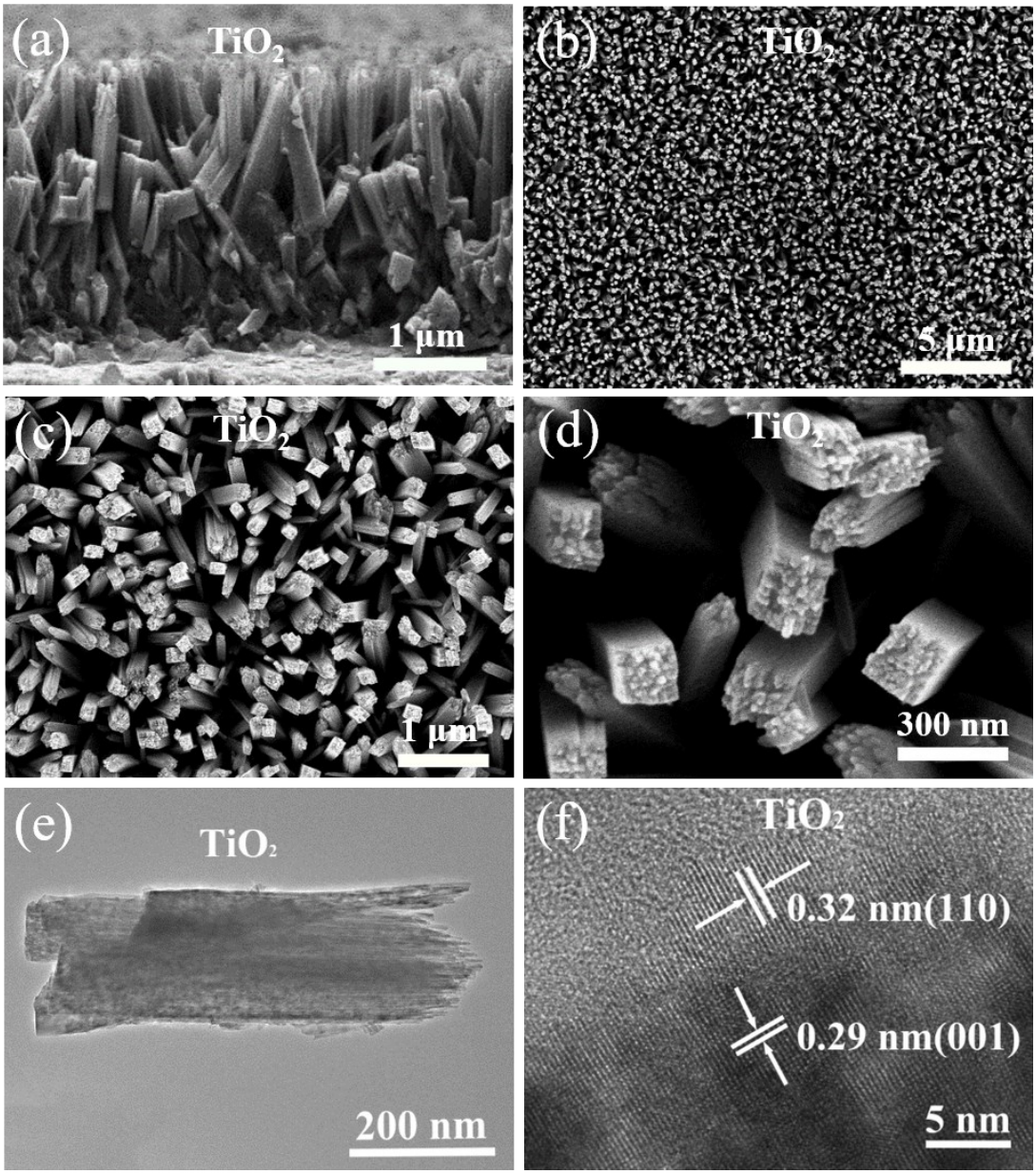

Fig. S2 (a) The cross-sectional SEM images of the pristine TiO_2. (b~d) SEM images of the pristine TiO_2 under different magnification (e~f) Representative TEM and HRTEM images of the pristine TiO_2.

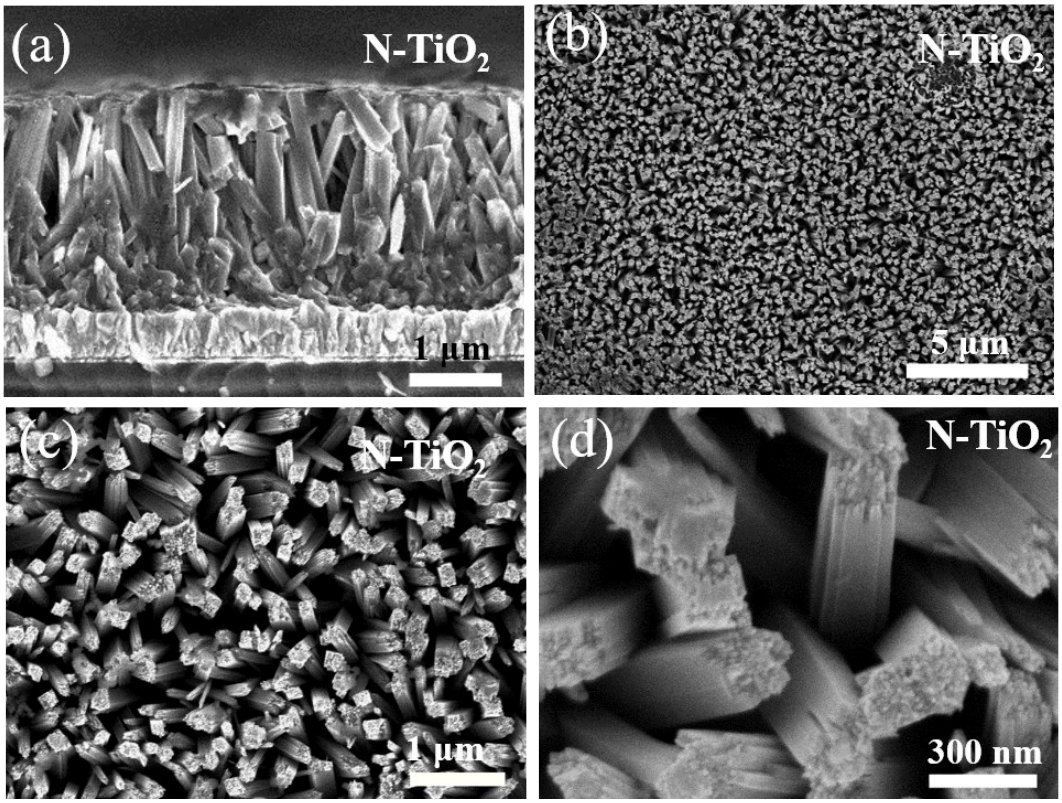

Fig. S3 (a) The cross-sectional SEM images N-TiO_2. (b~d) SEM images of N-TiO_2 under different magnification.

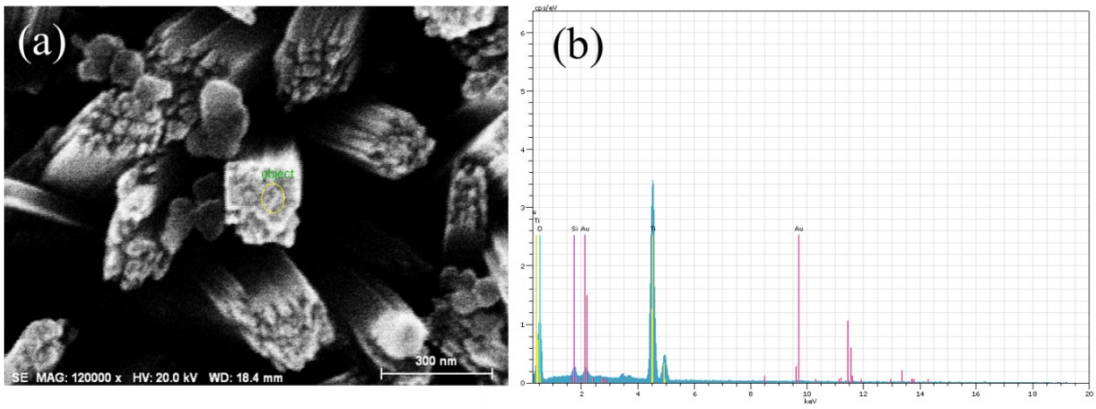

Fig. S4 Morphological and elemental characterizations of as-prepared Au/N-TiO_2 nanoarrays. Typical SEM image (a) and EDX spectrum of Au/N-TiO_2 (b).

Table S1. Chemical compositions of Au/N-TiO_2 nanoarrays

Element	Weight %	Atom %
O	53.7	77.9
Ti	43.61	21.14
Au	1.78	0.21
Si	0.91	0.75
N	0	0

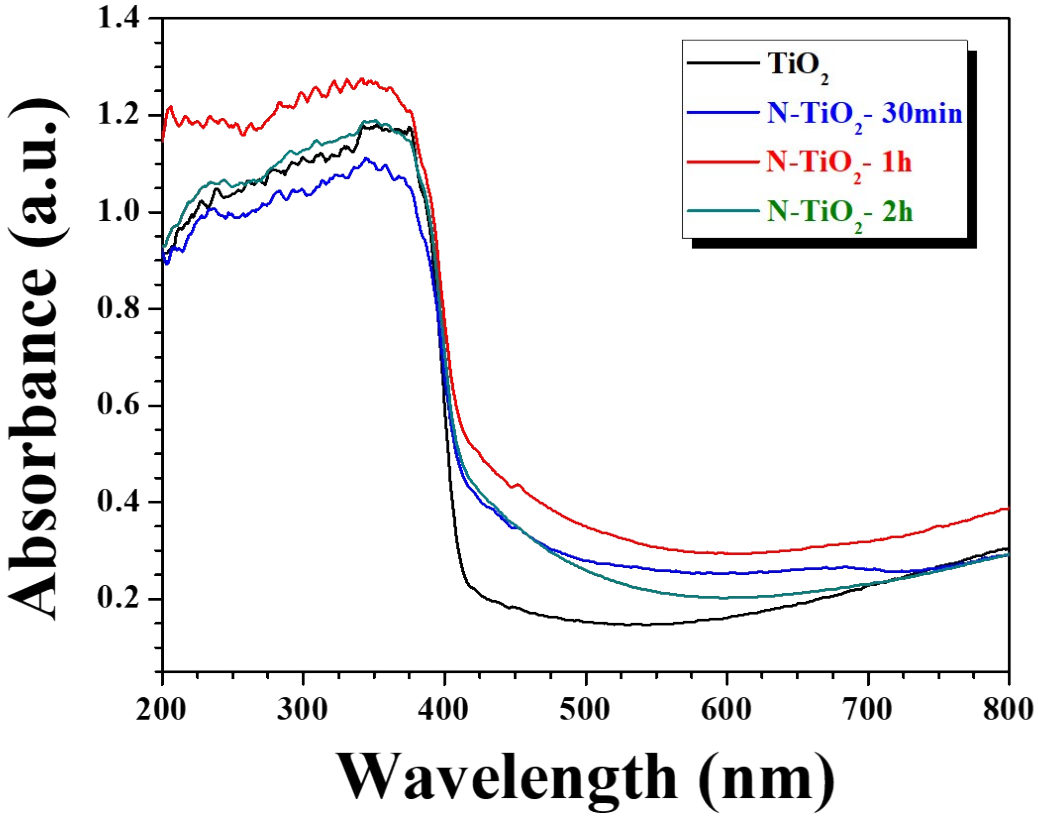

Fig. S5 The UV-Vis spectra of pristine TiO_2 nanorods and N-TiO_2 nanorods calcined in ammonia with different time (30 min, 1 hour and 2 hours).

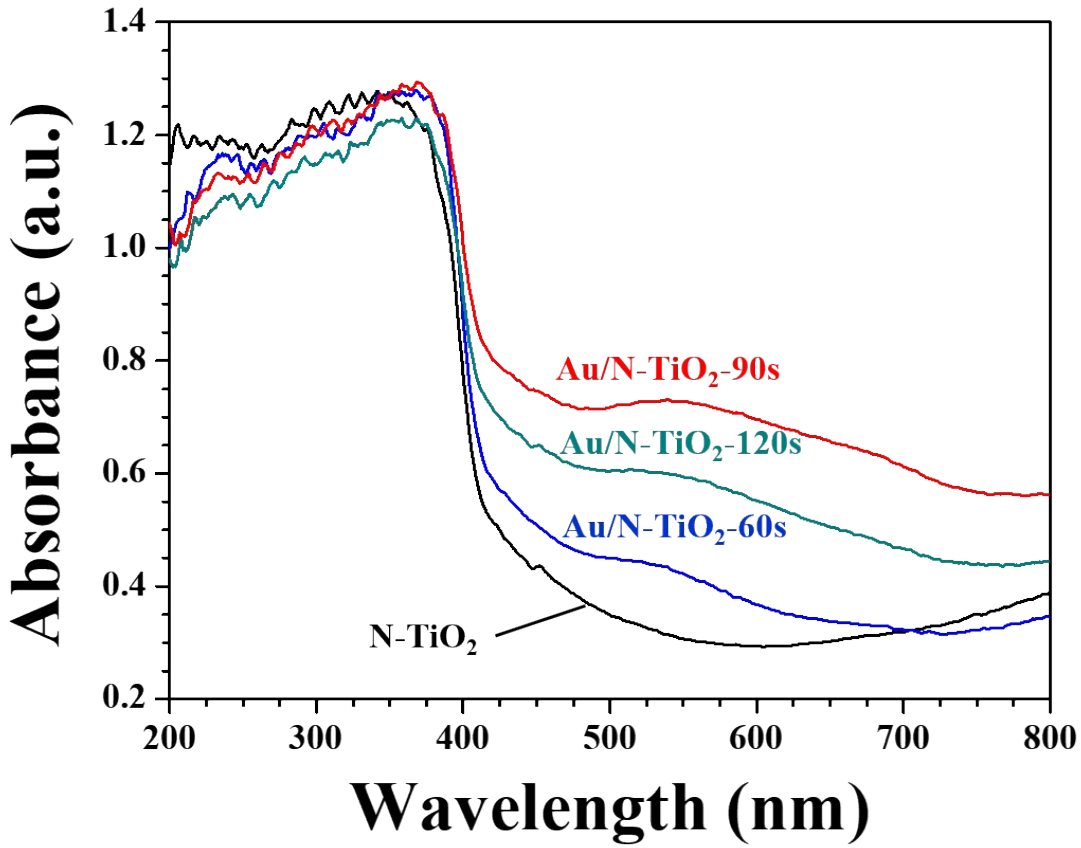

Fig. S6 The UV-Vis spectra of N-TiO_2 nanorods and N-TiO_2 nanorods modified with Au nanoparticle by magnetron sputtering with different time (60 s, 90 s, 120 s).

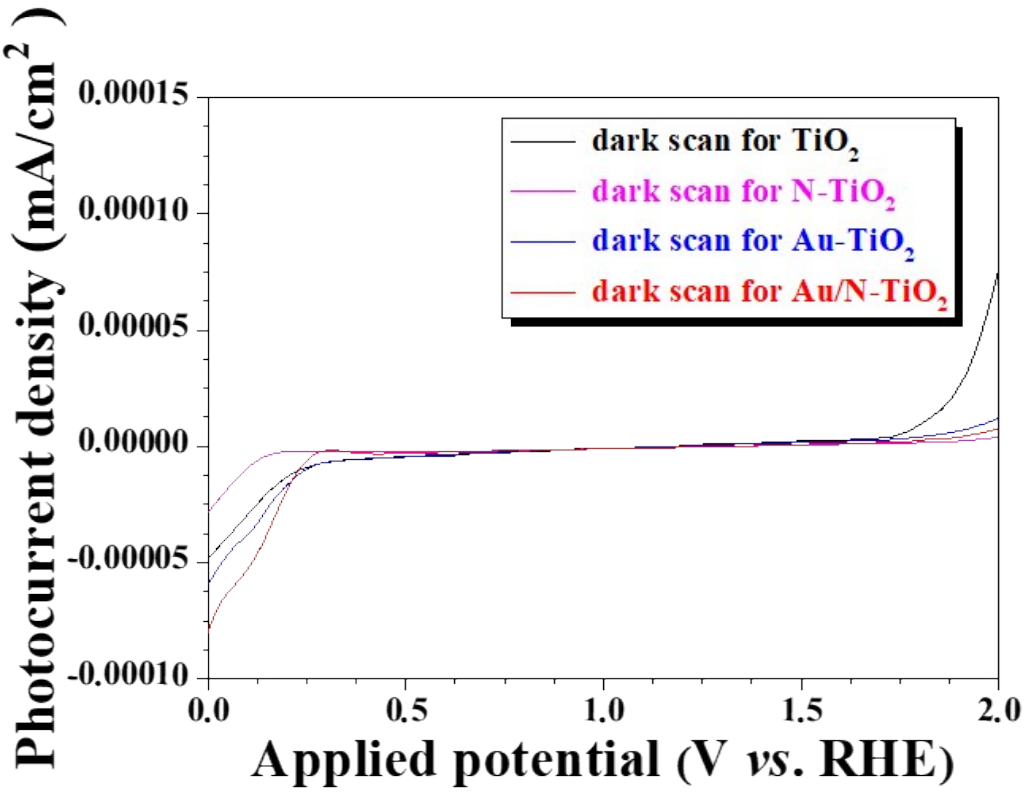

Fig. S7 The dark scans of pristine TiO_2, N-TiO_2, Au-TiO_2 and Au-N-TiO_2 photoanodes.

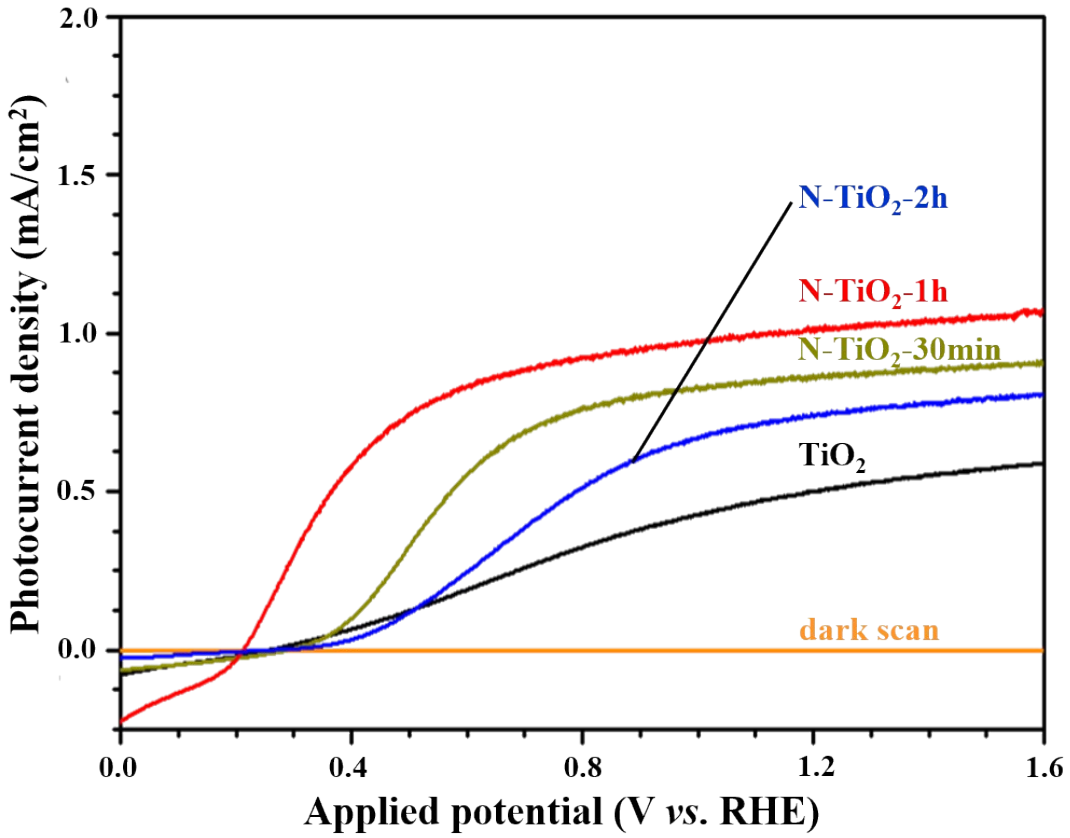

Fig. S8 The linear sweep voltammetry curves of pristine TiO_2 and TiO_2 nanorarrays treated by ammonification with different times of 30 minutes, 1 hour and 2 hours under simulated sunlight.

Table S2. Representive summary of the recent reports on TiO_2-based photoanodes for PEC (Since 2009)

Synthesis approach	Electrolyte	Photocurrent density (at 1.23V *vs.* RHE)	Reference
Hydrogen plasma-treated 1D/3D TiO_2 nanorod arrays	0.5 M H_2SO_4	0.369 mA/cm^2	1
TiO_2 nanowire arrays via cotreatment with H_2 and NH_3	1 M KOH	0.454 mA/cm^2	2
Fe-doped TiO_2 nanorod arrays	1M NaOH	~0.7 mA/cm^2	3
Si-doped TiO_2 nanorod arrays heated in air and in vacuum	0.1M NaOH	0.83 mA/cm^2	4
TiO_2 nanorod array annealed in argon	1M NaOH	0.978 mA/cm^2	5
Au nanoparticles decorated TiO_2 nanorod arrays	0.5 M Na_2SO_4	~1 mA/cm^2	6
1.8 μm long TiO_2 nanowires arrays coated by ALD TiO_2	1M NaOH	~1.08 mA/cm^2	7
Flower-like branched TiO_2 nanorod arrays	1.0 M KOH	~1.1 mA/cm^2	8
TiO_2 Nanorod @ Nanobowl arrays	1M NaOH	1.24 mA/cm^2	9
C doped TiO_2 nanowire arrays	1M NaOH	1.3 mA/cm^2	10
IrO_2−hemin−TiO_2 nanowire arrays	phosphate buffer saline	1.4 mA/cm^2	11
TiO_2-$SrTiO_3$ core-shell nanowire arrays	1 M NaOH	1.43 mA/cm^2	12
Post-annealed N-TiO_2 nanowire arrays	1M NaOH	~1.5 mA/cm^2	13
Etching and W doping of TiO_2 nanowire arrays	1 M KOH	1.53 mA/cm^2	14
TiO_2@g-C_3N_4@CoPi nanorod arrays	0.1 M Na_2SO_4	1.6 mA/cm^2	15
MoS_2 nanosheets coated on TiO_2 nanorod arrays	0.35 M Na_2S and 0.25 M Na_2SO_3	1.7 mA/cm^2	16
TiO_2 nanorod array modified by Au NPs and graphene quantum dots	1M NaOH	1.75 mA/cm^2	17
1T-Phase MoS_2 nanosheets on TiO_2 nanorod arrays	0.5 M Na_2SO_4	~1.8 mA/cm^2	18
CoO_x nanoparticles modified TiO_2 nanowire arrays	0.1 M KOH	2.09 mA/cm^2	19
Hydrogen-treated TiO_2 nanowire array	1 M NaOH	2.5 mA/cm^2	20
Au nanoparticles modified branched TiO_2 nanorod arrays	0.5 M Na_2SO_4	2.5 mA/cm^2	21

TiO_2 nanowire/ gold or silver film	1 M NaOH	2.6 mA/cm^2	22
Hydrogenated TiO_2/ZnO heterojunction nanorod arrays	•0.5 M Na_2SO_4	2.7 mA/cm^2	23
Au/N-TiO_2 nanowire arrays	1 M KOH	2.8 mA/cm^2	This study

Table S3. Fitted results of the EIS curves in Fig. 5c.

Sample	TiO_2	N-TiO_2	Au-TiO_2	Au/N-TiO_2
R_S (Ω)	49.6	24.5	20.46	13.52
R_{trap} (Ω)	1530.2	1078	1267	309.8
R_{ct} (Ω)	3546	2413	1112	919.6

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