Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting information

Architecting smart "umbrella" Bi_2S_3/rGO-modified TiO_2 nanorods array structure in nanoscales for efficient photoelectrocatalysis under visible light

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1. Structure analysis with FESEM and TEM

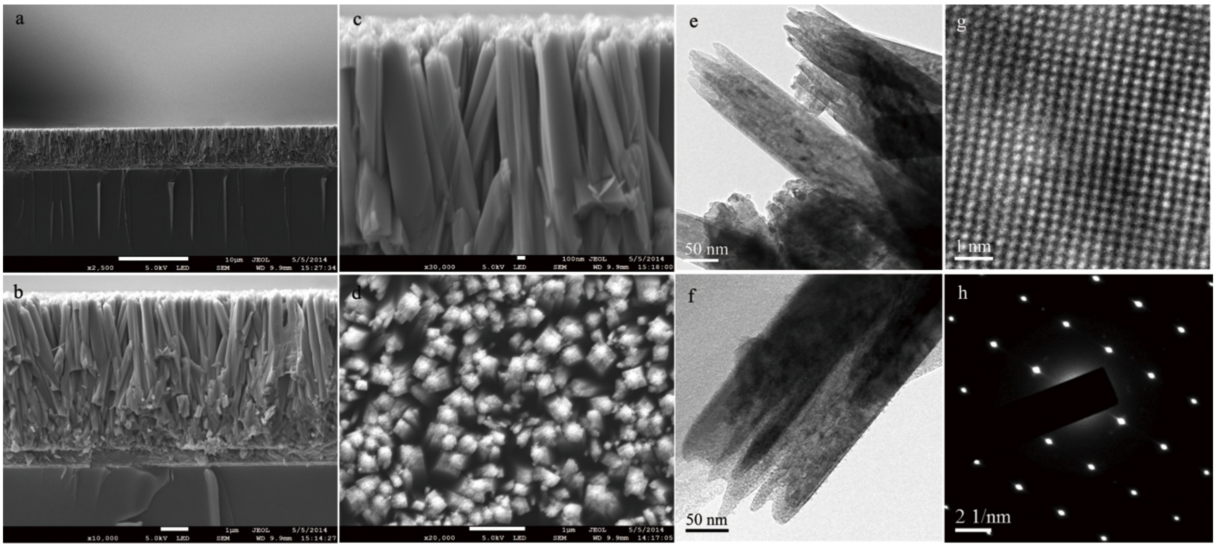

Figure S1. TiO_2 nanorod arrays (NRs) on FTO substrates.

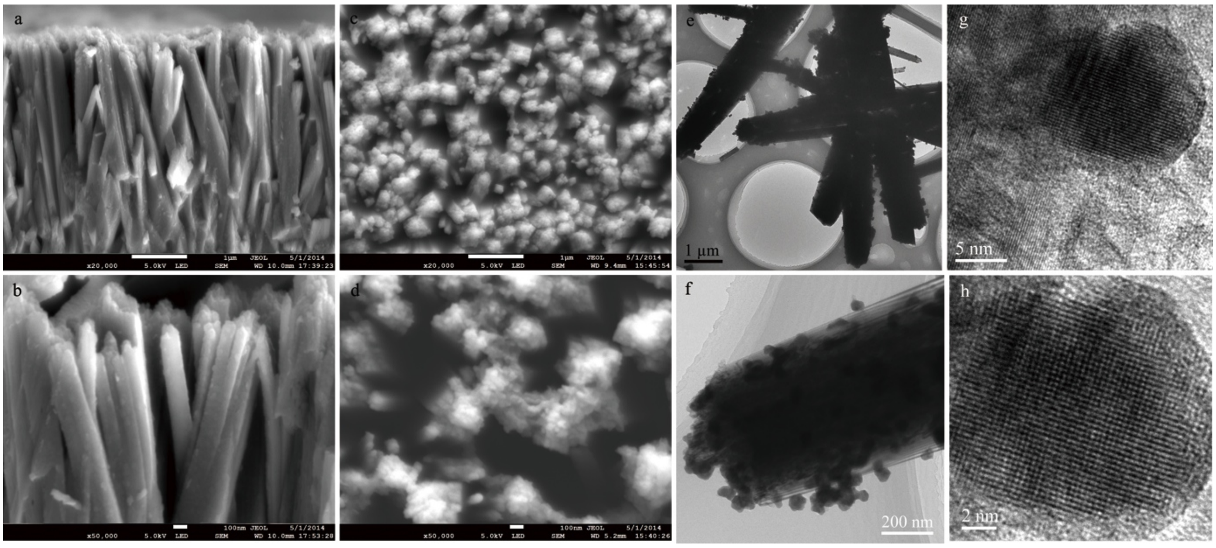

Figure S2. Bi_2S_3 nanoparticles decorated TiO_2 NRs on FTO substrates.

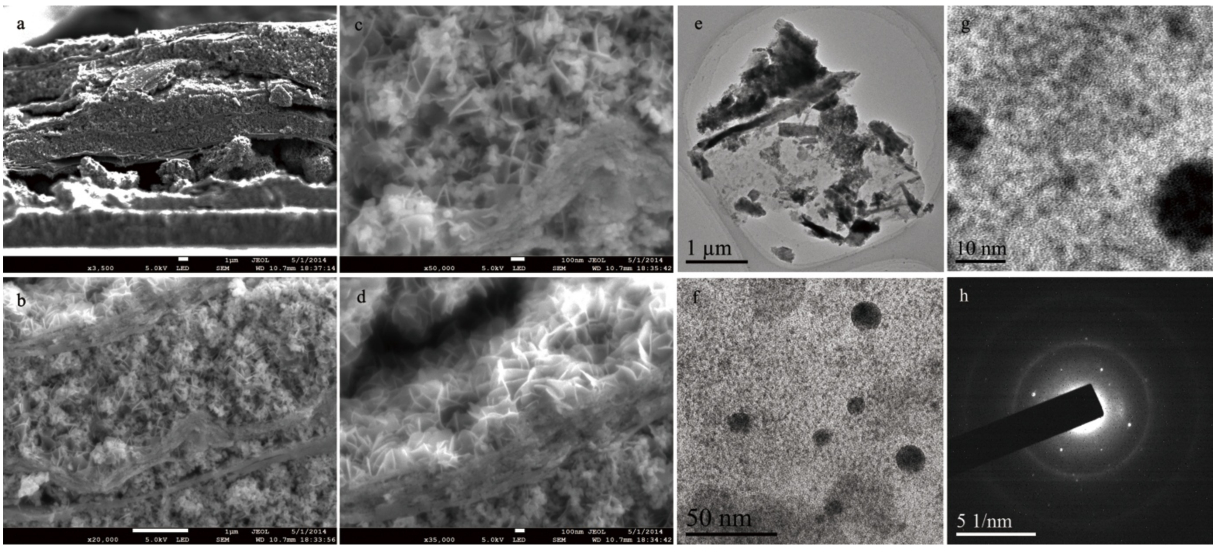

Figure S3. Bi_2S_3/rGO multilayer modified TiO_2 NRs.

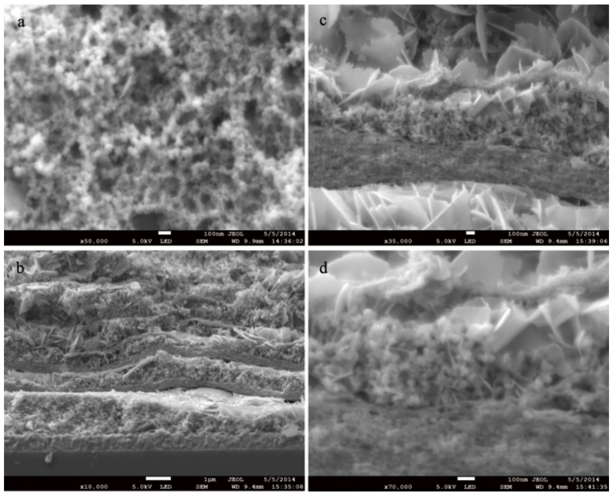

Figure S4. Bi_2S_3/rGO multilayer on TiO_2 nanoparticles thin film.

2. Crystal structure and composition analysis with XRD and EDS

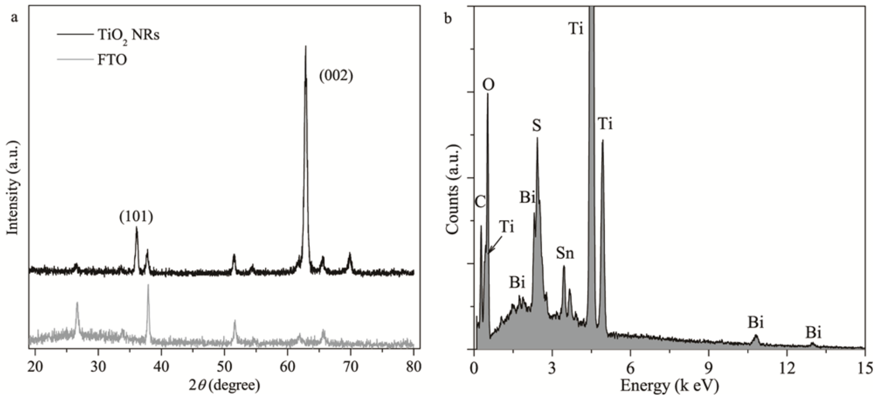

Figure S5. a. XRD pattern of TiO_2 NRs on FTO substrates. b. Typical EDS pattern of $(Bi_2S_3/rGO)_5/TiO_2$ NRs electrodes.

3. Effect of rGO modification on TiO_2 NRs on the photoelectrochemical performance

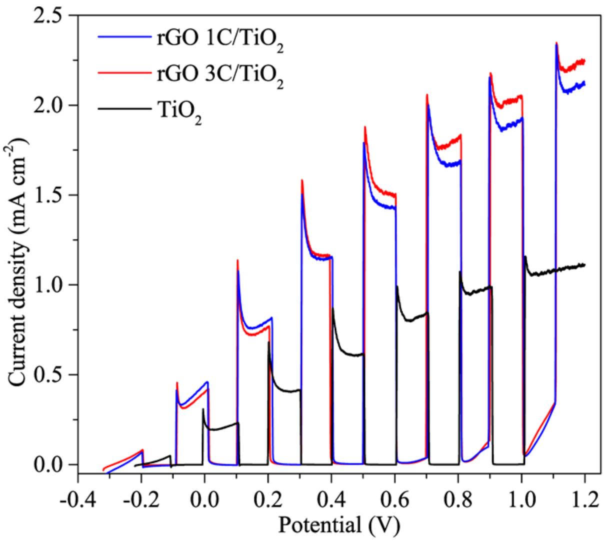

Figure S6. LSV plots of different amounts of rGO modified TiO_2 NRs in two-electrode system under full-solar-spectrum irradiation (>100 mW cm^{-2}). (C is a short of spin coating cycle.)

4. Effect of Bi_2S_3 modification on TiO_2 NRs on the photoelectrochemical performance

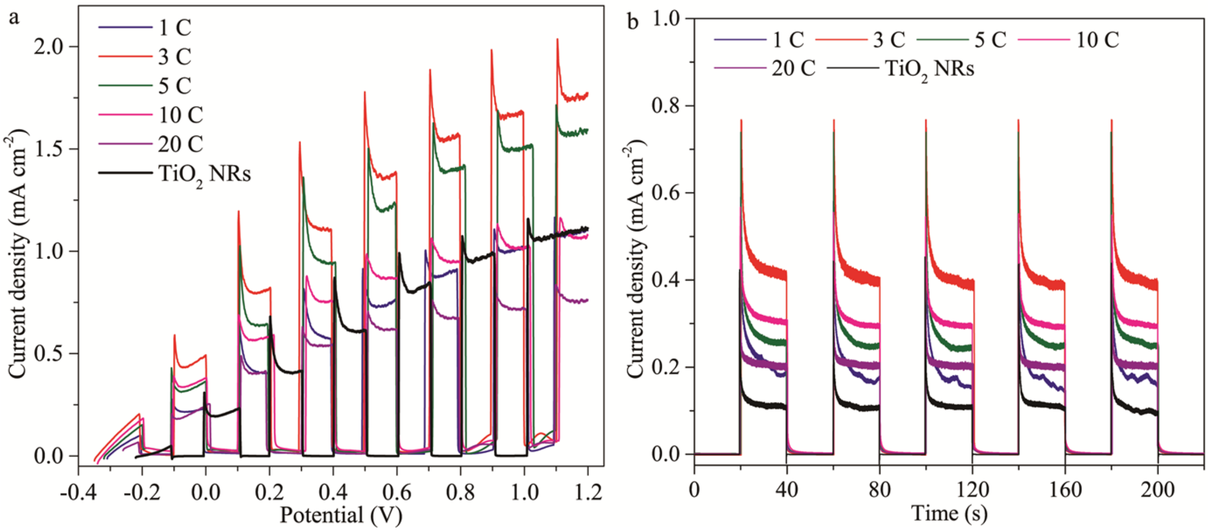

Figure S7. Photoelectrochemical performances of different amount of Bi_2S_3 nanoparticles modified TiO_2 NRs in two-electrode system under full-solar-spectrum irradiation (>100 mW cm^{-2}). (C is a short of SILAR cycle. Figure S7b: measured at bias of 0.0 V.)

5. Layer effect of Bi_2S_3/rGO on the photoelectrochemical performance

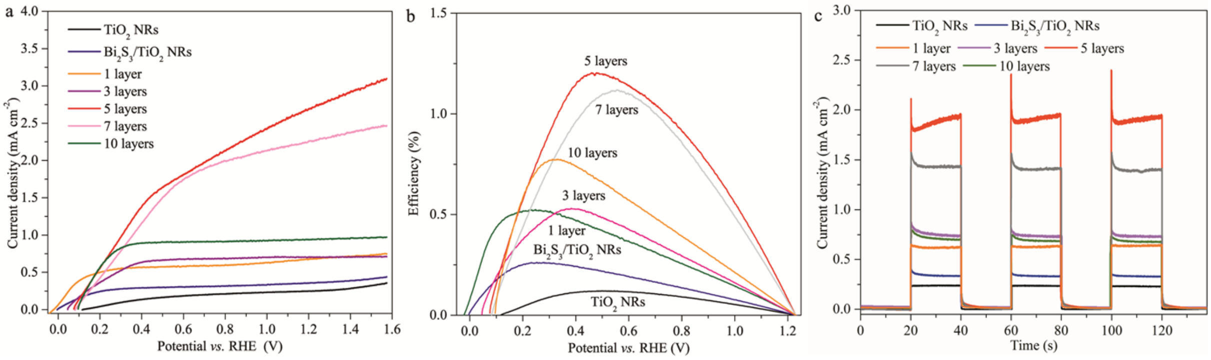

Figure S8. Photoelectrochemical performances of different layers of Bi_2S_3/rGO modified TiO_2 NRs in three-electrode system under visible light. (Reference electrode: SCE, Counter electrode: Pt, Figure S8(c): measured at bias of 0.0 V vs. SCE.)

6. Calculated electronic parameters from EIS spectra.

Table S1. Calculated electronic parameters from Nyquist plots.

Electrode	R_s [a] / Ω	CPE_{Dp} [a] (×10^{-6})	n_{Dp} [a]	R_{Dp} [a] / Ω	CPE_H (×10^{-6}) [a]	n_H [a]	R_H [a] / Ω
TiO_2 NRs	33.09 (2.1193)	6.58 (0.5312)	0.7894 (0.0080)	145.000 (7.5030)	107.27 (0.3818)	0.71462 (0.0077)	2924 (97.7870)
Bi_2S_3/TiO_2 NRs	26.53 (0.0761)	22.52 (0.6710)	0.7912 (0.0028)	9.973 (0.1089)	238.63 (0.8045)	0.85303 (0.0008)	794.1 (3.1518)
$(Bi_2S_3/rGO)_5/$ TiO_2 NPs	20.14 (0.2965)	29.81 (1.3043)	0.9060 (0.0052)	65.260 (4.1467)	208.88 (7.9597)	0.62823 (0.0052)	1316.0 (37.1350)
$(Bi_2S_3/rGO)_5/$ TiO_2 NRs	34.61 (0.1470)	50.42 (3.7993)	0.7990 (0.0093)	6.261 (0.2189)	507.02 (8.0235)	0.79572 (0.0042)	434.6 (5.2670)

[a] Standard error from the fit of the EIS spectra.

7. Performance of related nanostructure electrodes in the literatures

Table S2. Summary of PEC performance and test conditions in the literatures.

Reference	**Structure**	**Photocurrent (Bias)**	**Efficiency (%)**	**Illuminated light & intensity**	**Cell**	**Electrolyte**
1	TiO_2 nanotube array	0.9 mA/cm^2 (1.23 V vs. RHE)	0.49	AM 1.5G, 100 mW/cm^2	3-electrode cell	1 M KOH
2	TiO_2 nanorod array	18 uA/cm^2 (1.0 V vs. Ag/AgCl)	0.10	AM 1.5G, 100 mW/cm^2	3-electrode cell	0.5 M $NaClO_4$
3	Branched TiO_2 nanorod	0.83 mA/cm^2 (0.8 V vs. RHE)	0.49	AM 1.5G, 88 mW/cm^2	3-electrode cell	1 M KOH
4	GO/TiO_2 nanotube array	~0.05 mA/cm^2 (0.45 V vs. Ag/AgCl)	0.049	Visible light, 100 mW/cm^2	3-electrode cell	0.5 M Na_2SO_4
5	rGO/TiO_2 nanotube array	10.3 uA/cm^2 (1.0 V vs. SCE)	-	Visible light, 2.7 mW/cm^2	3-electrode cell	0.1 M Na_2SO_4
6	Bi_2S_3 nanoparticle	1.0 mA/cm^2 (0.23 V vs. Ag/AgCl)	-	AM 1.5G, 100 mW/cm^2	3-electrode cell	1.0 M Na_2SO_3
6	Bi_2S_3 nanotube	1.9 mA/cm^2 (0.23 V vs. Ag/AgCl)	-	AM 1.5G, 100 mW/cm^2	3-electrode cell	1.0 M Na_2SO_3
7	Bi_2S_3/CdS/TiO_2 nanotube array	2.16 mA/cm^2 (0.0 V vs. Ag/AgCl)	-	AM 1.5G, 100 mW/cm^2	3-electrode cell	0.25 M Na_2S and 0.35 M Na_2SO_3
8	Bi_2S_3/TiO_2 nanotube array	4.54 mA/cm^2 (0.0 V vs. SCE)	1.86	AM 1.5G, 100 mW/cm^2	3-electrode cell	0.5 M Na_2S
9	Bi_2S_3/TiO_2 nanocrystal	~0.42 mA/cm^2 (0.0 V vs. Ag/AgCl)	-	AM 1.5G, 100 mW/cm^2	3-electrode cell	1.0 M Na_2S
10	CdS/TiO_2 nanorod array	5.8 mA/cm^2 (0.0 V vs. Ag/AgCl)	-	AM 1.5G, 100 mW/cm^2	3-electrode cell	0.25 M Na_2S and 0.35 M Na_2SO_3
11	**α**-Fe_2O_3 Nanorod/Graphene/$BiV_{1-x}Mo_xO_4$	~1.97 mA/cm^2 (1.0 V vs. Ag/AgCl)	~0.53	AM 1.5G, 100 mW/cm^2	3-electrode cell	0.01 M Na_2SO_4
11	**α**-Fe_2O_3 Nanorod/Graphene/$BiV_{1-x}Mo_xO_4$	0.39 mA/cm^2 (0.9 V vs. Ag/AgCl)	~0.17	Visible light, 64 mW/cm^2	3-electrode cell	0.01 M Na_2SO_4
12	rGO/CdTe/TiO_2 nanotube array	~1.09 mA/cm^2 (0.0 V vs. SCE)	-	Xe lamp, 100 mW/cm^2	3-electrode cell	0.5 M Na_2SO_4
13	CdS/rGO/TiO_2 nanocomposit	~80 uA/cm^2 (0.0 V vs. Ag/AgCl)	-	Visible light, 300 W Xe lamp	3-electrode cell	0.5 M Na_2SO_4
14	CdS/Graphene/TiO_2 nanotube array	~0.8 mA/cm^2 (0.0 V vs. Ag/AgCl)	-	Xe lamp, 265 mW/cm^2	3-electrode cell	0.05 M Na_2S
This work	Bi_2S_3/rGO/TiO_2 nanotube array	2.0 mA/cm^2 (0.0 V vs. SCE)	1.2%	Visible light, 100 mW/cm^2	3-electrode cell	0.25 M Na_2S and 0.35 M Na_2SO_3

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