

Electronic Supplementary Material (ESI) for Energy & Environmental Science

Defect-rich Decorated TiO₂ Nanowires for Super-efficient Photoelectrochemical Water Splitting Driven by Visible Light

Supporting information

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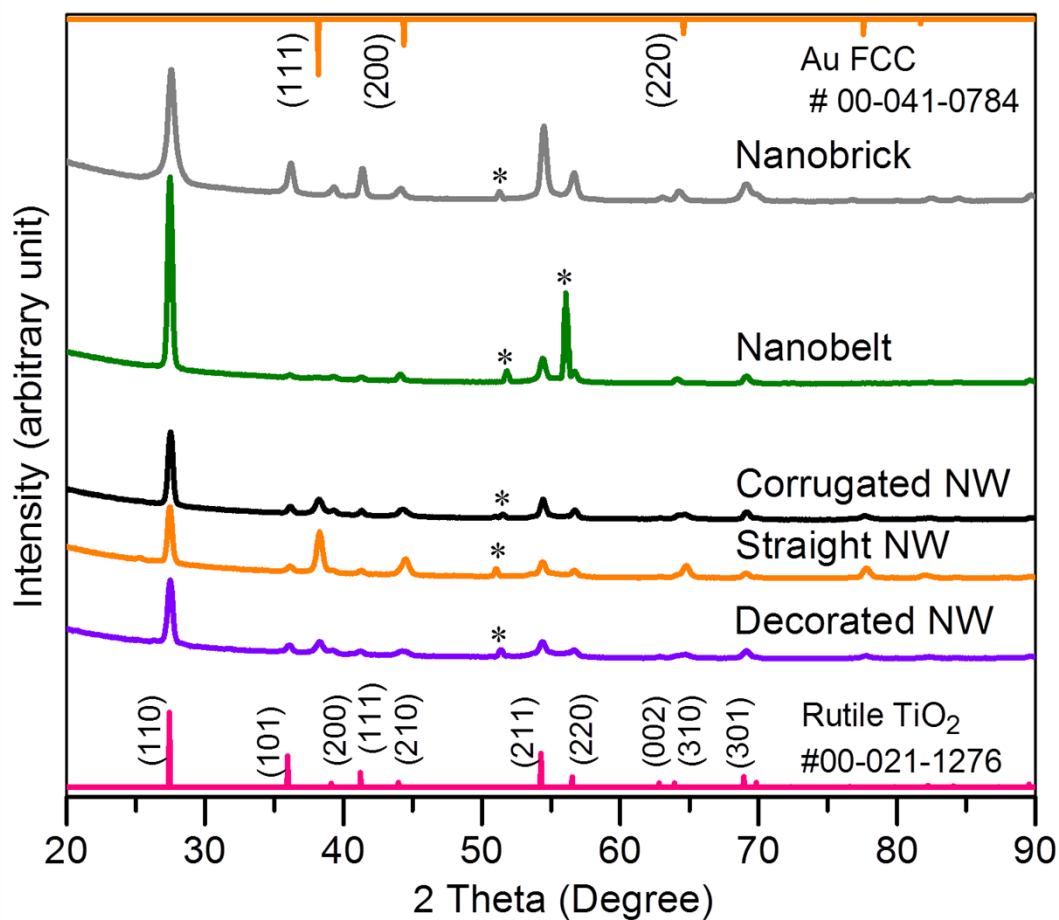


Fig. S1 Glancing-incidence XRD patterns of different rutile TiO₂ nanostructures obtained at an incidence angle of 0.4°. The PDF2 reference patterns of the FCC phase of Au (#00-041-0784) and of rutile TiO₂ (#00-021-1276) are shown as top and bottom bar graphs, respectively. The features marked by asterisks (*) correspond to the modified Si substrate.

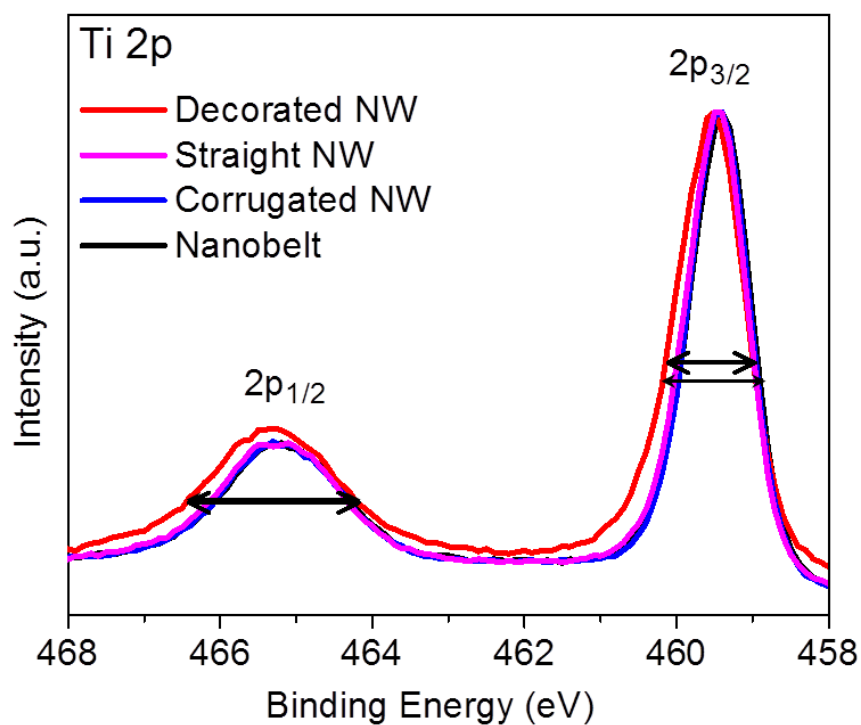


Fig. S2 XPS spectra of the Ti 2p region, relatively normalized at the Ti 2p_{3/2} peak maxima, for TiO₂ nanobelts, corrugated nanowires (NWs), straight NWs, and decorated NWs. The arrows indicate the full widths at half maxima of 2p_{3/2} and 2p_{1/2} peaks of the decorated NWs.

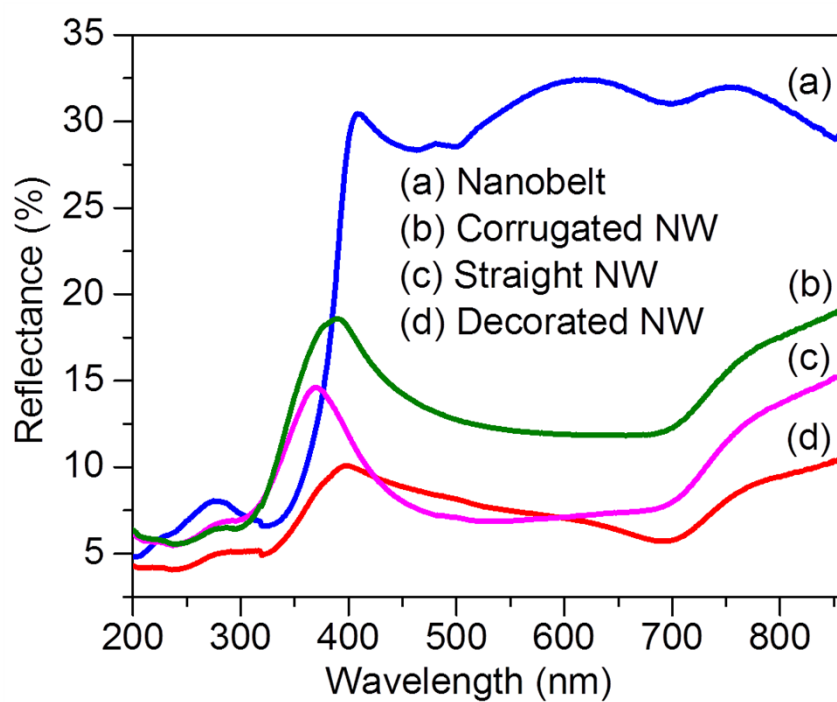


Fig. S3 UV-Vis reflectance spectra of TiO₂ nanobelts, corrugated nanowires (NWs), straight NWs, and decorated NWs.

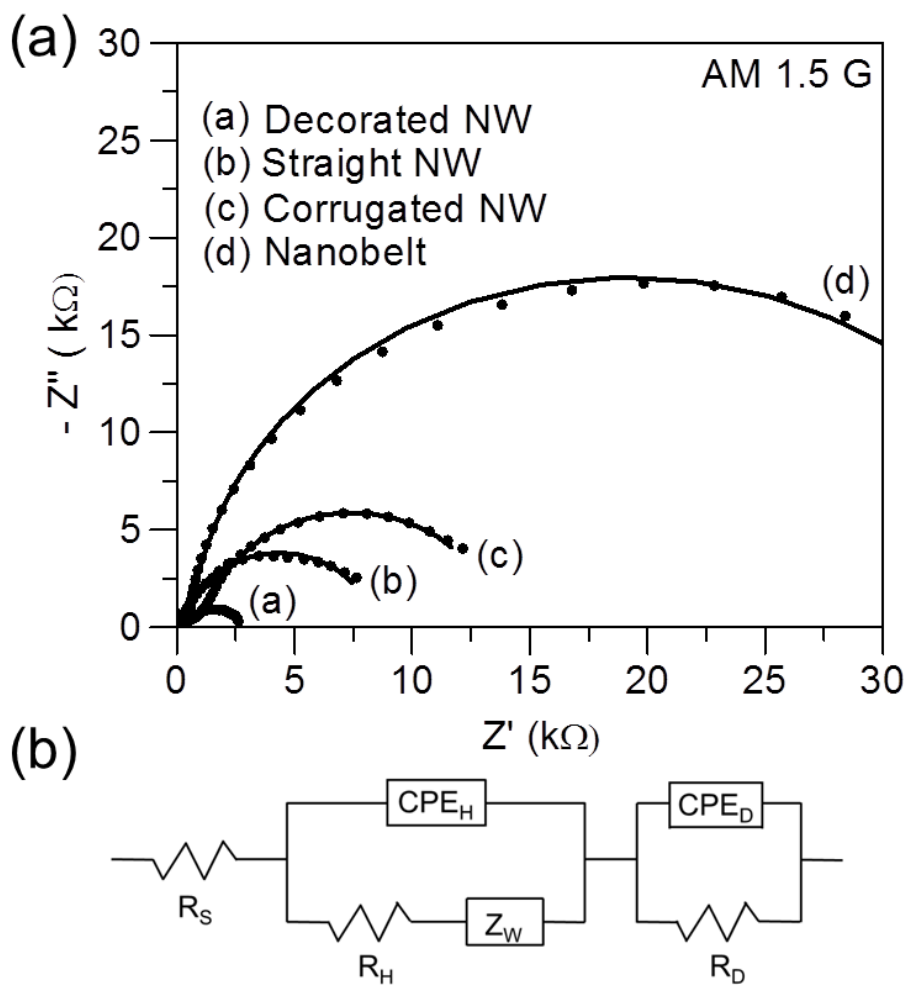


Fig. S4 Nyquist plots of predominant TiO_2 nanostructured films (a) under illumination of simulated sunlight (100 mW/cm^2). The experimental data (symbols) are collected in a frequency range between 0.01 Hz and 100 Hz with an ac voltage amplitude of 10 mV and a dc bias of -0.5 V , and they are fitted with (b) an equivalent circuit model (solid lines).

Table S1 Parameters extracted from fitted results of electrochemical impedance spectra for TiO₂ nanostructured films under simulated sunlight.

	AM 1.5 G		
	R _S (Ω)	R _H (kΩ) CPE _H (μF)	R _D (kΩ) CPE _D (μF)
Nanobelt	254	20 110	33 2.7
Corrugated Nanowire	35.0	2.1 130	8.0 56
Straight Nanowire	32.8	1.6 221	6.9 92
Decorated Nanowire	20.5	1.4 264	1.3 210

Gas quantification:

The SRS-UGA system can be used to analyze a gas sample at atmospheric pressure via a specially designed 6 feet long capillary tube (175 μm ID). The measurement is done with the three-electrode electrochemical cell in a sealed quartz beaker, with the capillary inserted to sample the gases generated by the reaction. As shown in the below plot, we monitor the partial pressures of H_2 , O_2 , N_2 , H_2O and CO_2 with light off and light on during the water-splitting reaction. Evidently, only H_2 and O_2 pressures are found to increase as the reaction commences (with light on) while those of all the other gases remain flat and unchanged. The pressure change for H_2 ($\Delta P = 18 \times 10^{-8}$ Torr) is found to be almost twice (1.8 times) that of O_2 ($\Delta P = 10 \times 10^{-8}$ Torr), which further confirms stoichiometric splitting of water. It should be noted that the amount of time for the evolved gases to reach saturation will depend on the amount of catalysts on the sample and the efficiency of gas production (both of which will affect the amounts of H_2 and O_2 produced by the water-splitting reaction), as well as the volume of space above the liquid solution in the beaker. Evidently, it only takes about 20 minutes for the produced gases to displace the air in the volume above the solution.

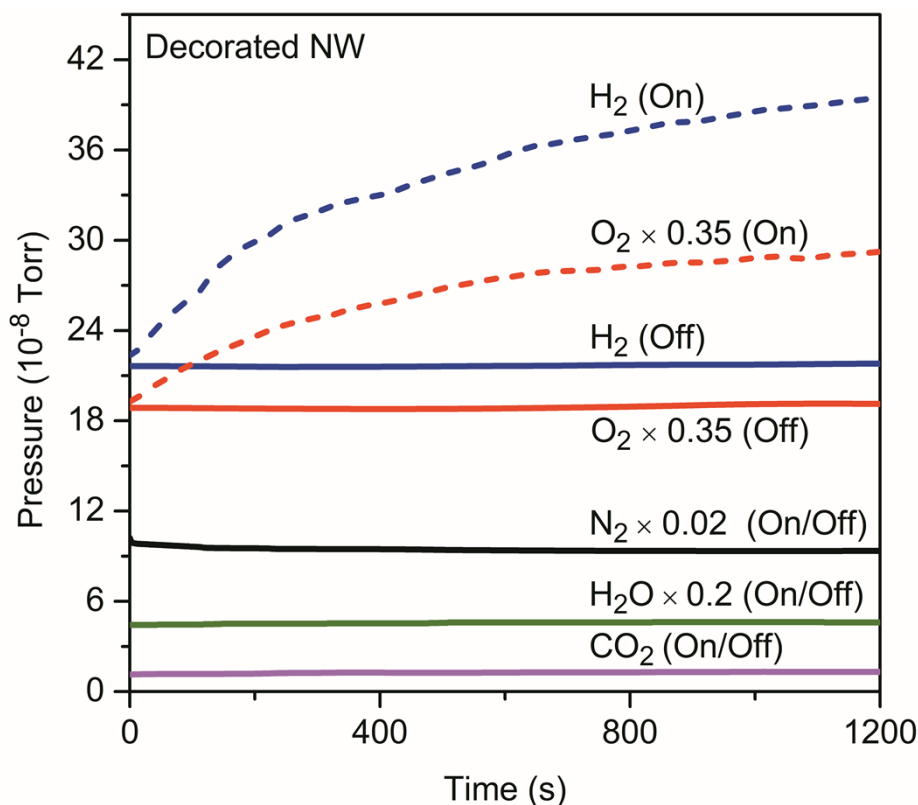


Fig. S5 Quantification of gas evolution for photoelectrochemical water splitting reaction with decorated TiO_2 nanowires as the photoanode with light on and light off.

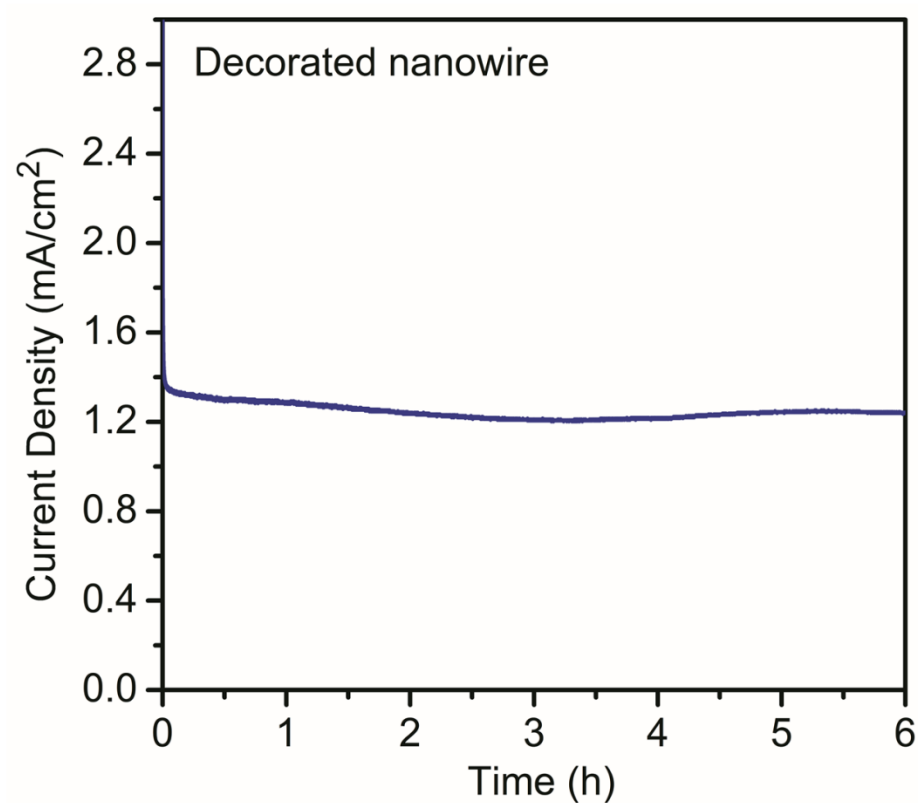


Fig. S6 Photocurrent density of decorated TiO₂ nanowire at -0.2 V versus Ag/AgCl in 1 M KOH solution under simulated sunlight.