Supplementary Materials

Blue Order/Disorder Janus-Type TiO_2 Nanoparticles for Enhanced Photocatalytic Hydrogen Generation

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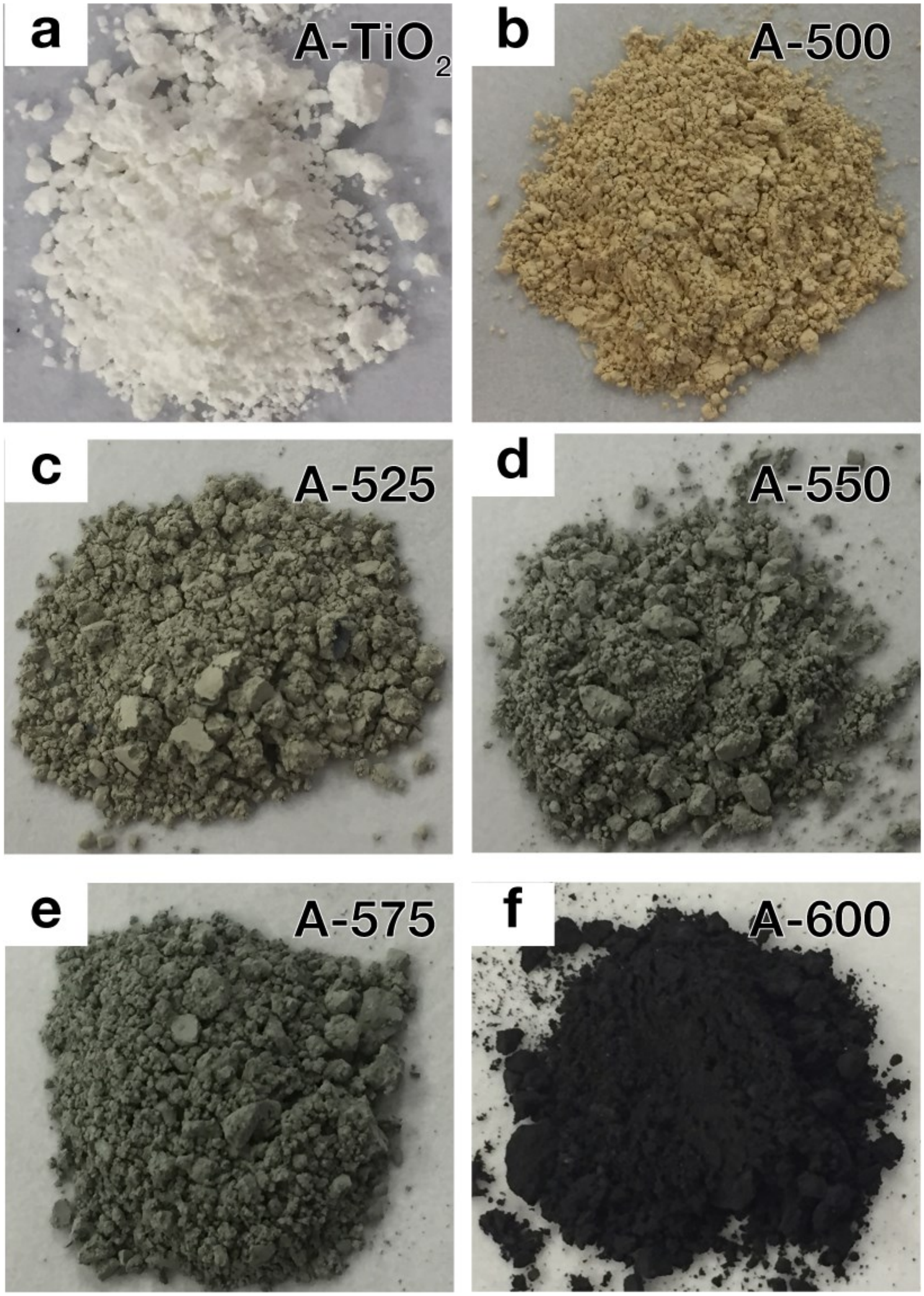

Fig. S1. Digital photos of (a) pristine A-TiO_2 and the A-TiO_2 samples treated by magnesiothermic reduction (MTR) at (b) 500, (c) 525, (d) 550, (e) 575, and (f) 600 °C. The MTR reaction time was 30 min.

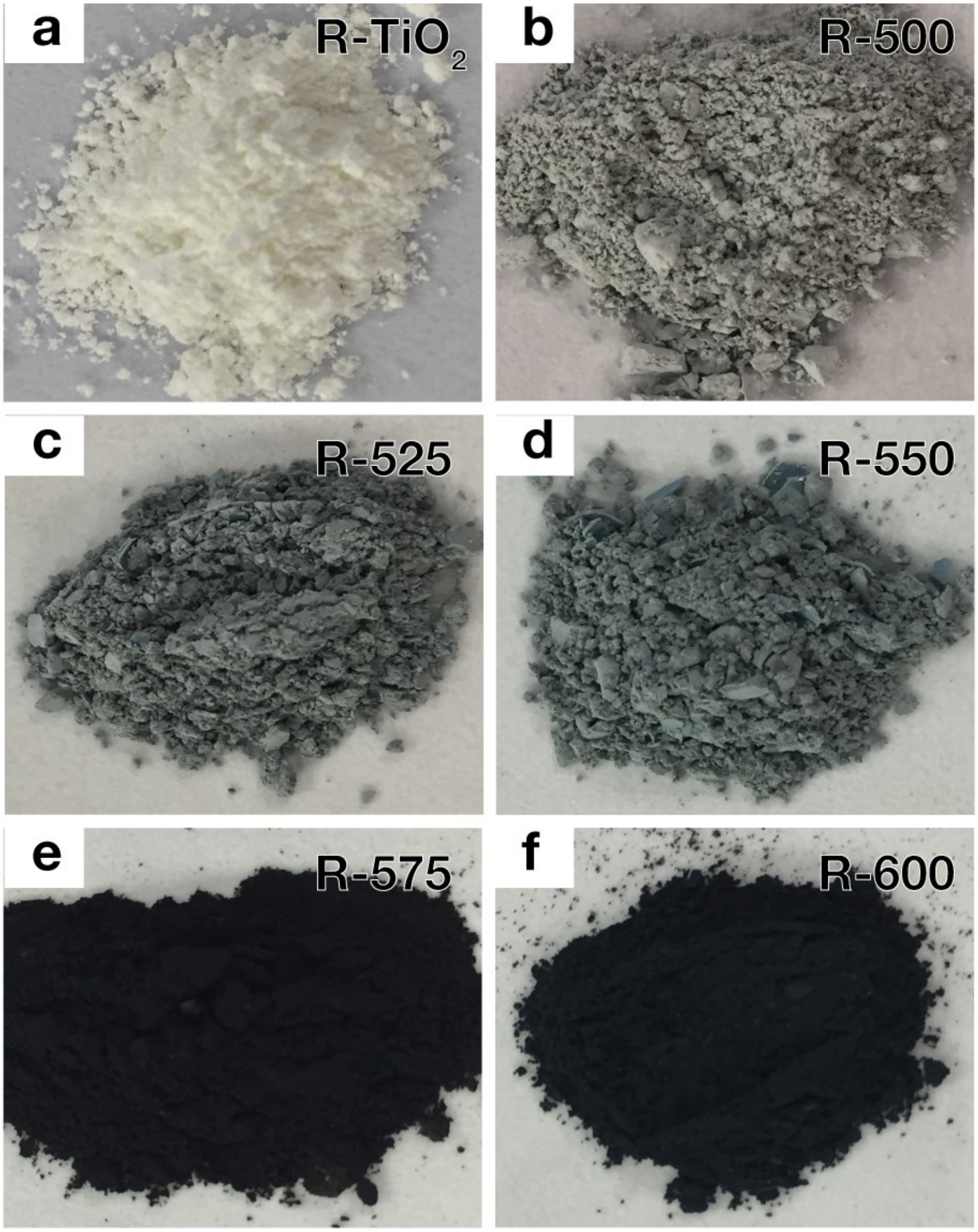

Fig. S2. Photographic images of (a) pristine R-TiO_2 and R-TiO_2 samples treated by magnesiothermic reduction at (b) 500, (c) 525, (d) 550, (e) 575, and (f) 600 °C. The reaction time was 30 min for all samples.

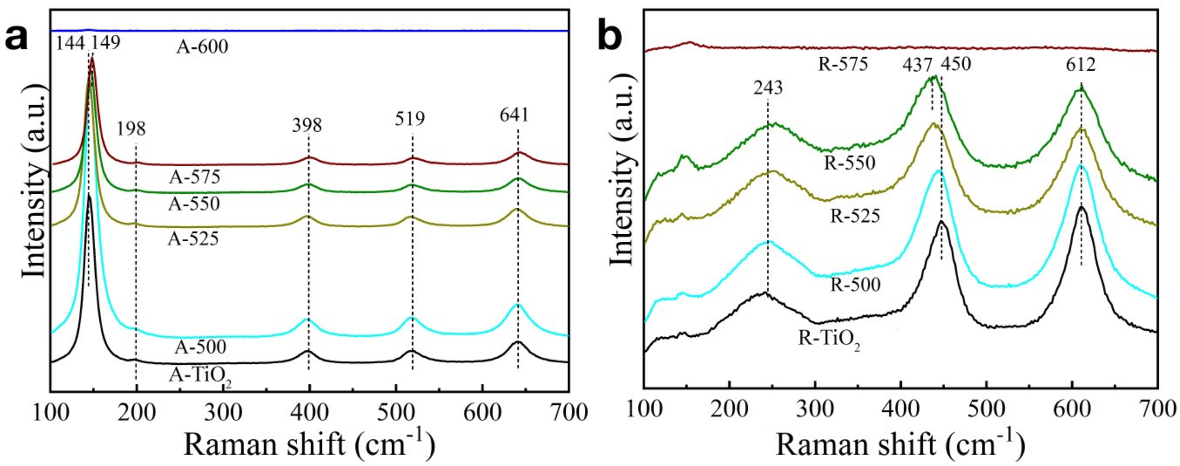

Fig. S3. Raman shifts of (a) untreated anatase TiO_2 and reduced A-TiO_2 samples from 500 °C to 600 °C and (b) untreated rutile TiO_2 and reduced A-TiO_2 samples from 500 °C to 575 °C.

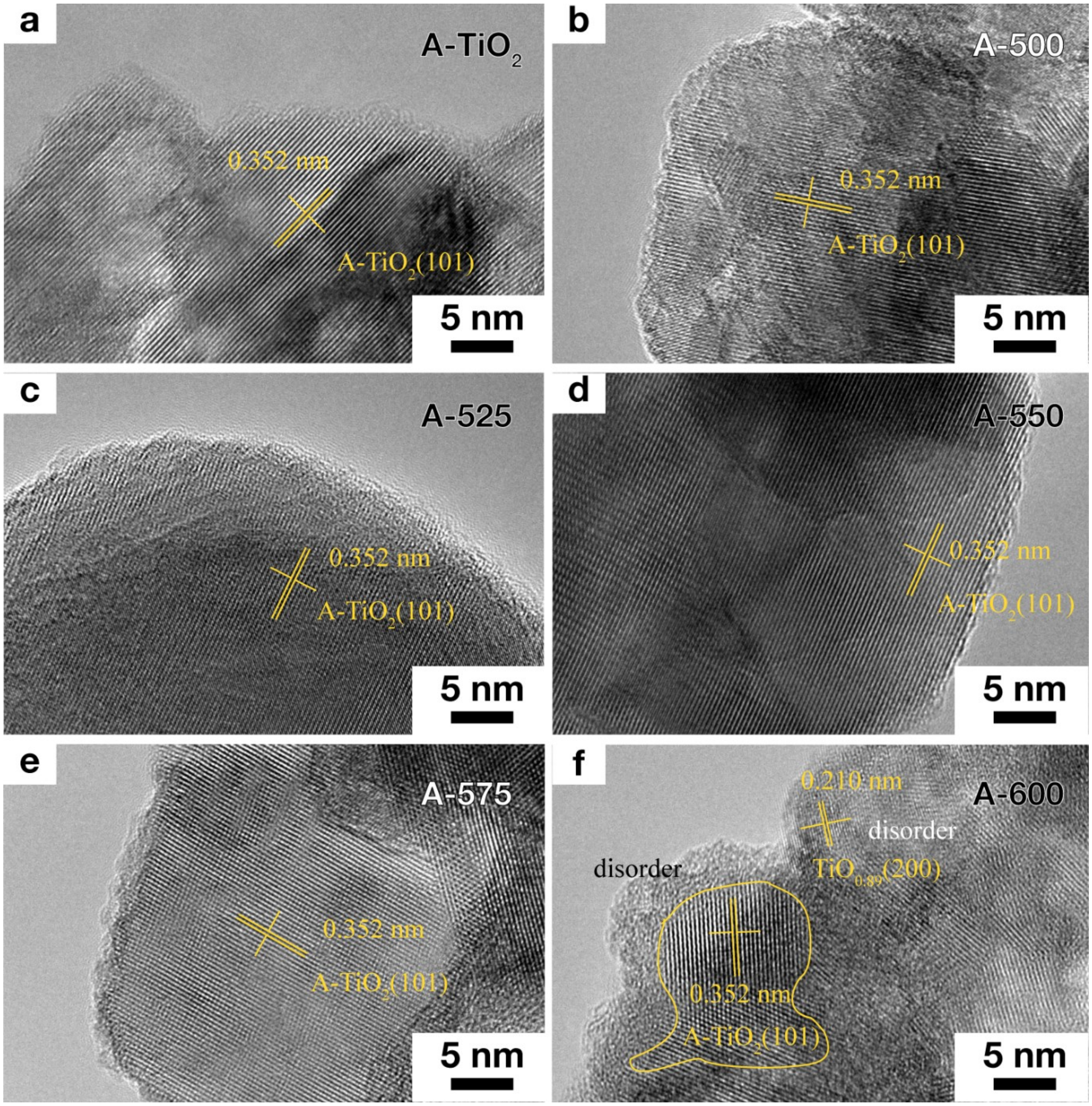

Fig. S4. HR-TEM images of (a) untreated anatase TiO_2 (A-Untreated) and (b-f) A-TiO_2 samples treated by magnesiothermic reduction at 500 to 600 °C for 30 min.

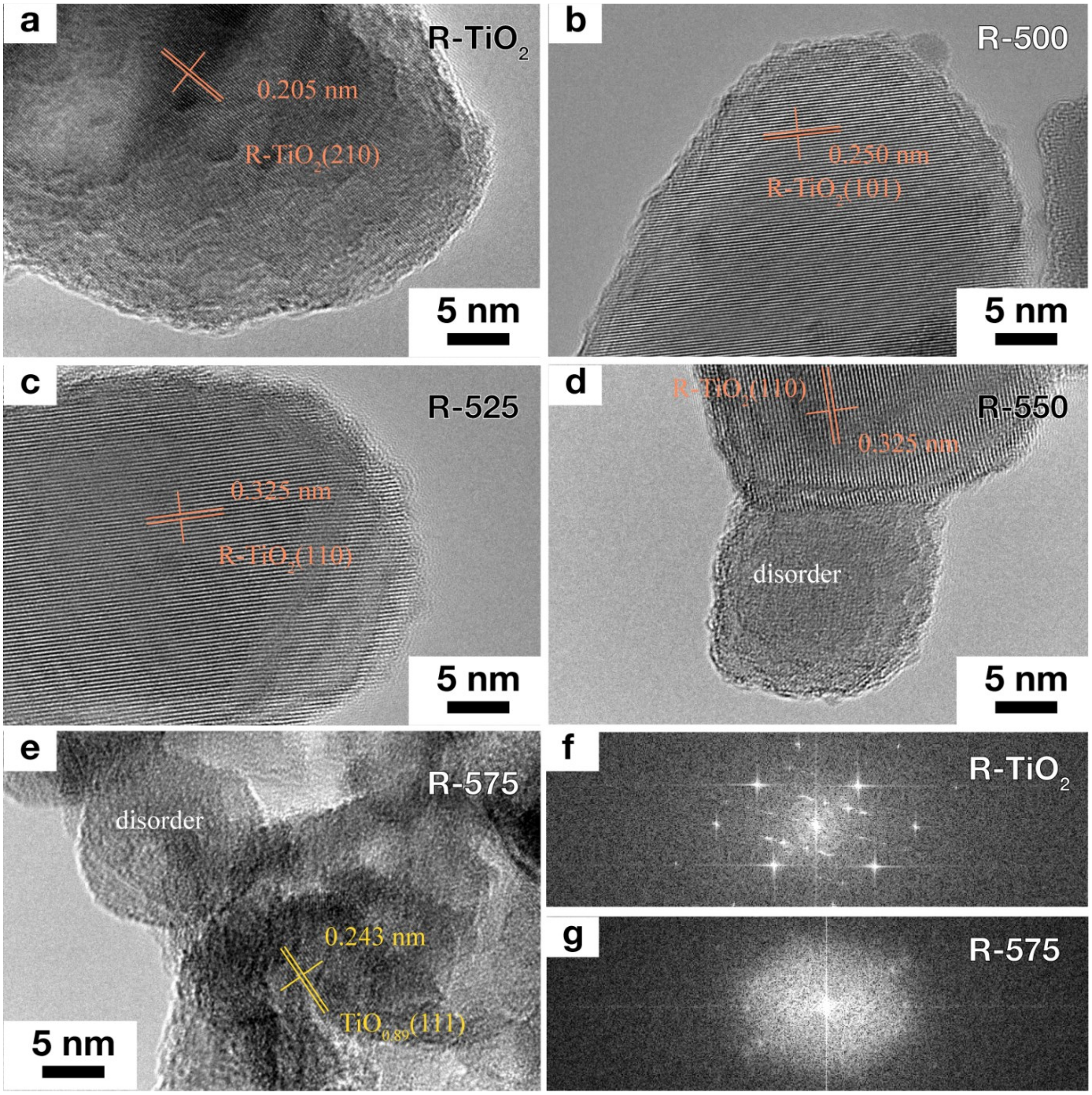

Fig. S5. (a-e) HR-TEM images of untreated rutile TiO_2 (R-Untreated) and R-TiO_2 samples treated by magnesiothermic reduction at 500 to 600 °C for 30 min. (f) and (g) are the fast Fourier transformation (FFT) images for (a) and (e), respectively.

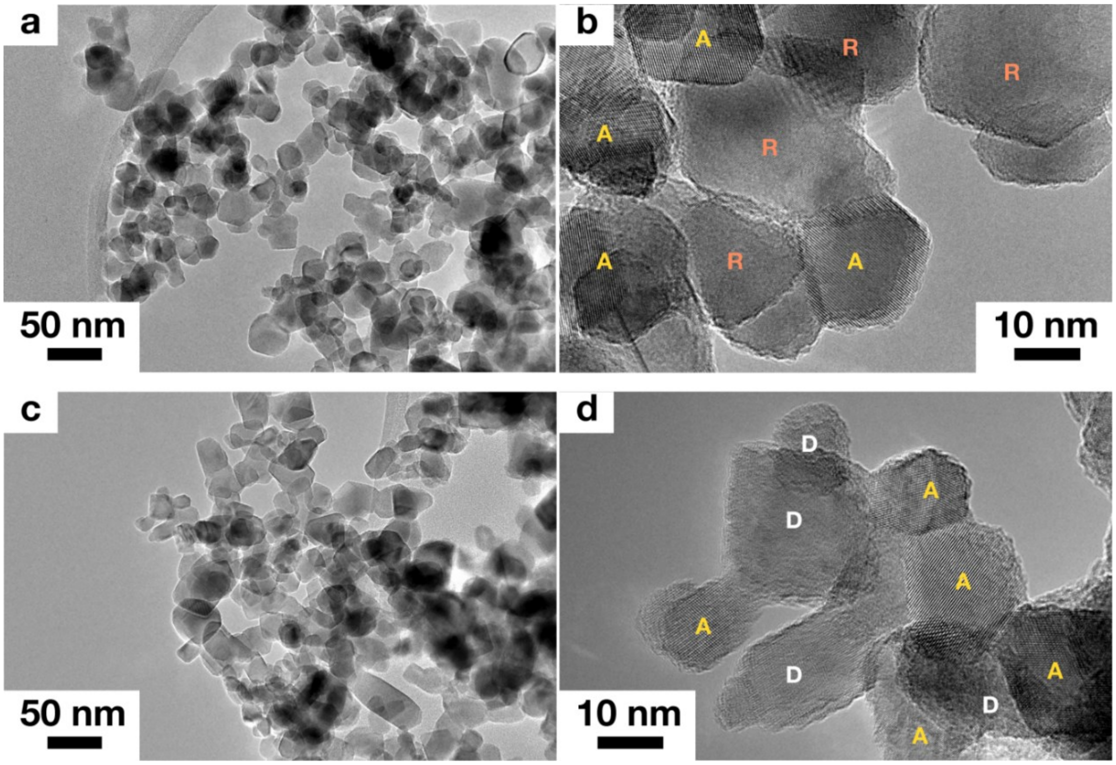

Fig. S6. Low- and high-magnification TEM images of (a-b) P25 and (c-d) B-P25 TiO_2 samples. A: Anatase TiO_2, R: Rutile TiO_2, D: disorder.

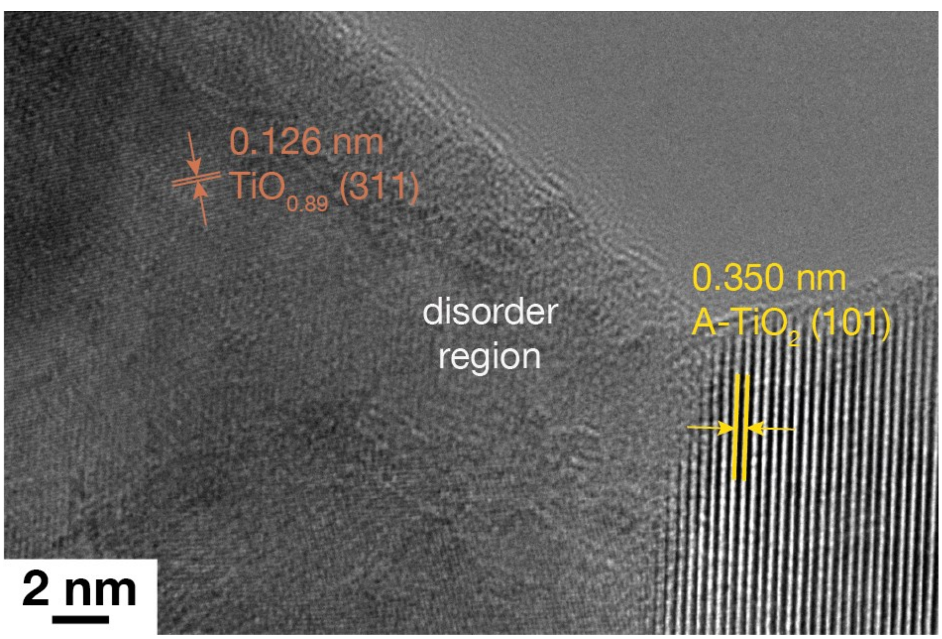

Fig. S7. High-resolution TEM image of B-P25 TiO_2 showing a larger area in the disordered region.

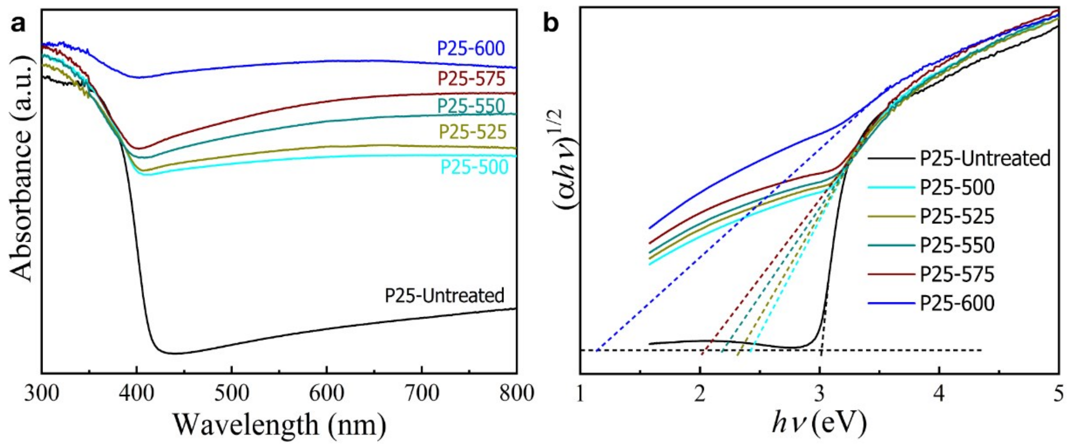

Fig. S8. (a) UV-Vis absorption spectra and (b) the corresponding Tauc plots of untreated P25 and treated P25 by MTR at 500 to 600 °C for 30 min.

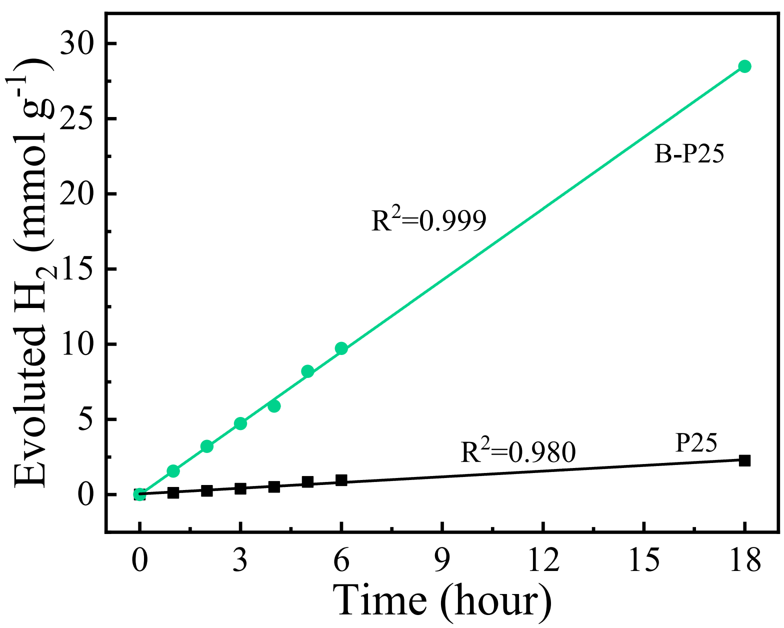

Fig. S9. Hydrogen production during a continuous 18-hour HER photocatalysis over P25 and B-P25.

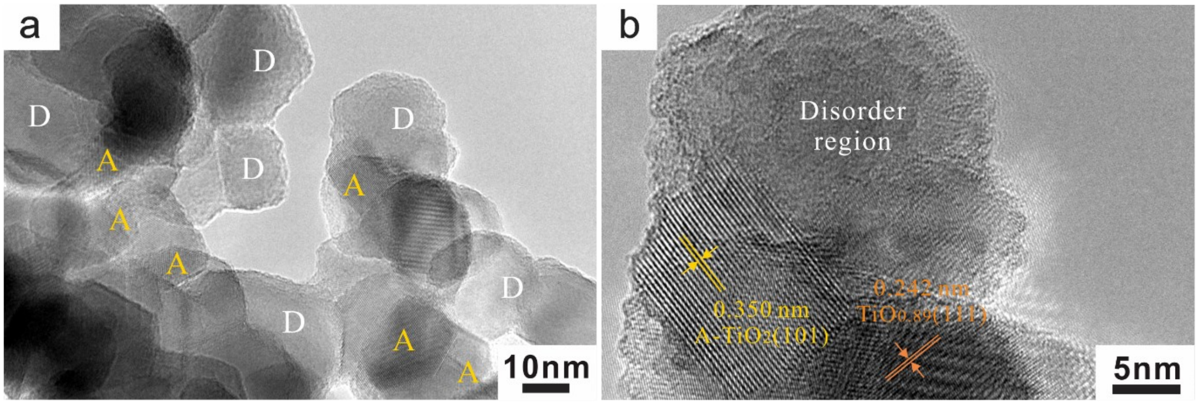

Fig. S10. Low- and high-magnification TEM images of B-P25 TiO_2 after the cyclic photocatalytic reactions.

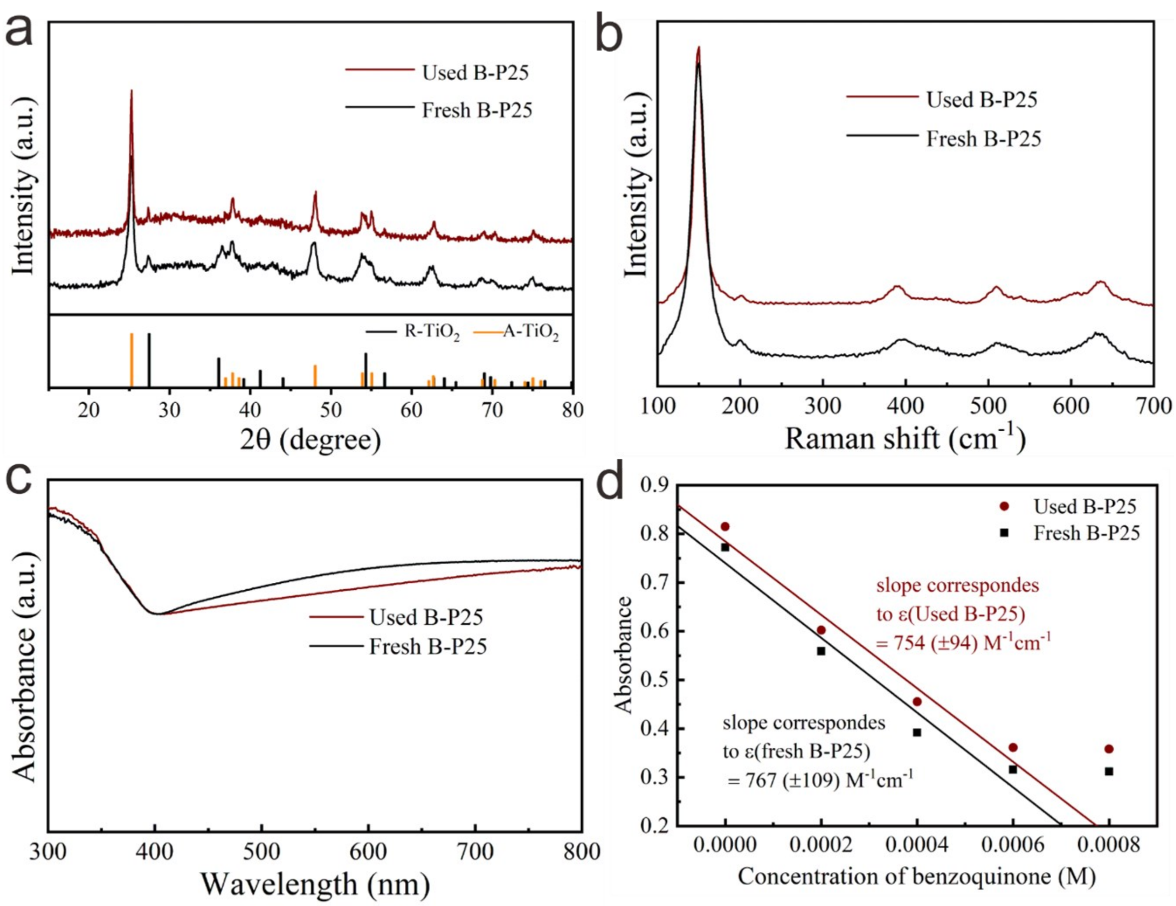

Fig. S11. Comparisons of (a) XRD patterns, (b) UV-Vis absorption spectra, (c) Raman spectra, and (d) extinction coefficients of B-P25 TiO_2 before (fresh) and after (used) the cyclic photocatalytic reactions.

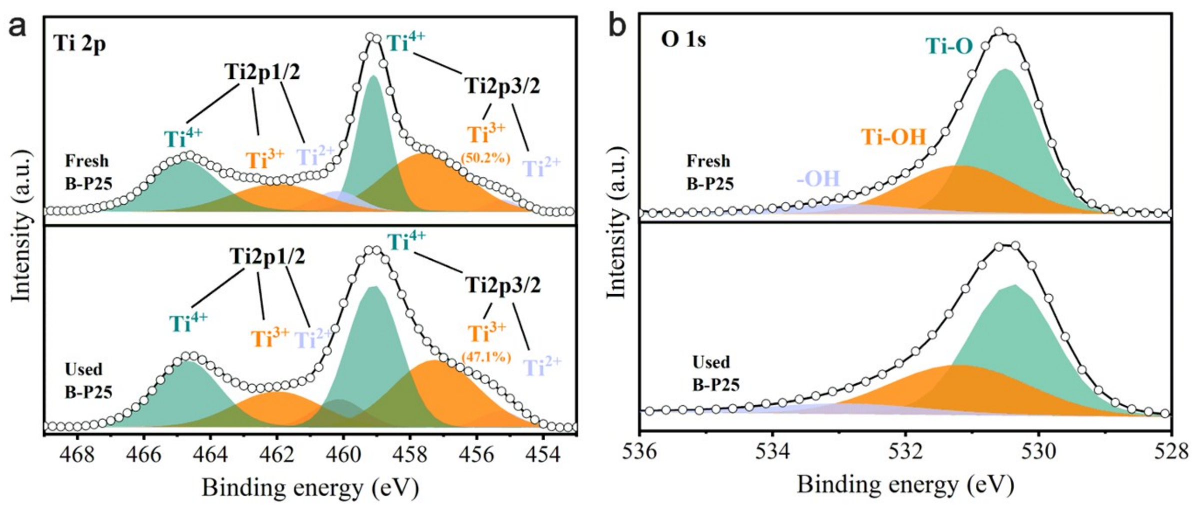

Fig. S12. Comparisons of high-resolution XPS (a) Ti 2p and (b) O 1s spectra of B-P25 TiO_2 before (fresh) and after (used) the cyclic photocatalytic reactions.

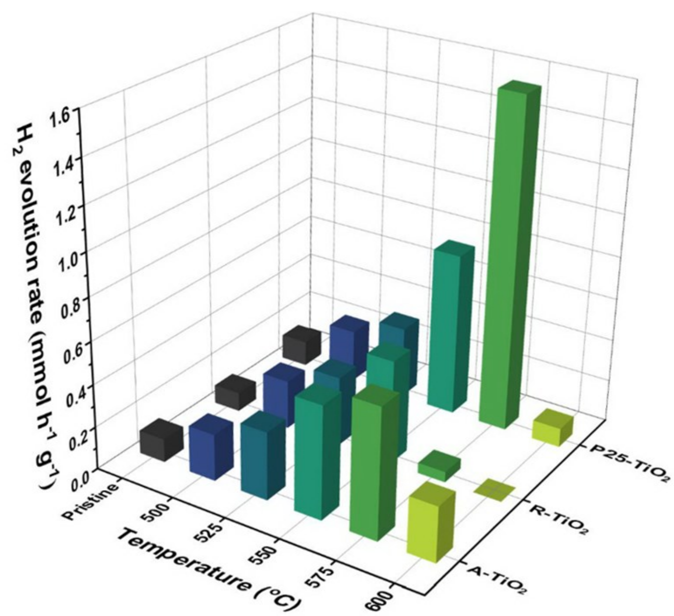

Fig. S13. Comparison of photocatalytic HER rates among A-TiO_2, A-TiO_2, P25-TiO_2, and treated A-TiO_2, A-TiO_2, P25-TiO_2 samples.

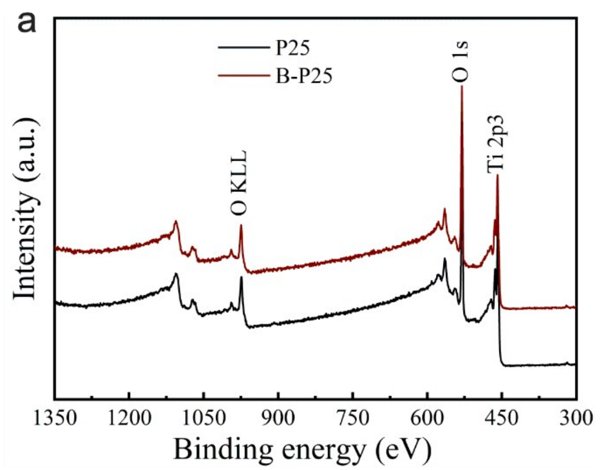

Fig. S14. (a) Full XPS survey and (b) solid-state EPR spectra of P25 and B-P25 recorded at 25 °C.

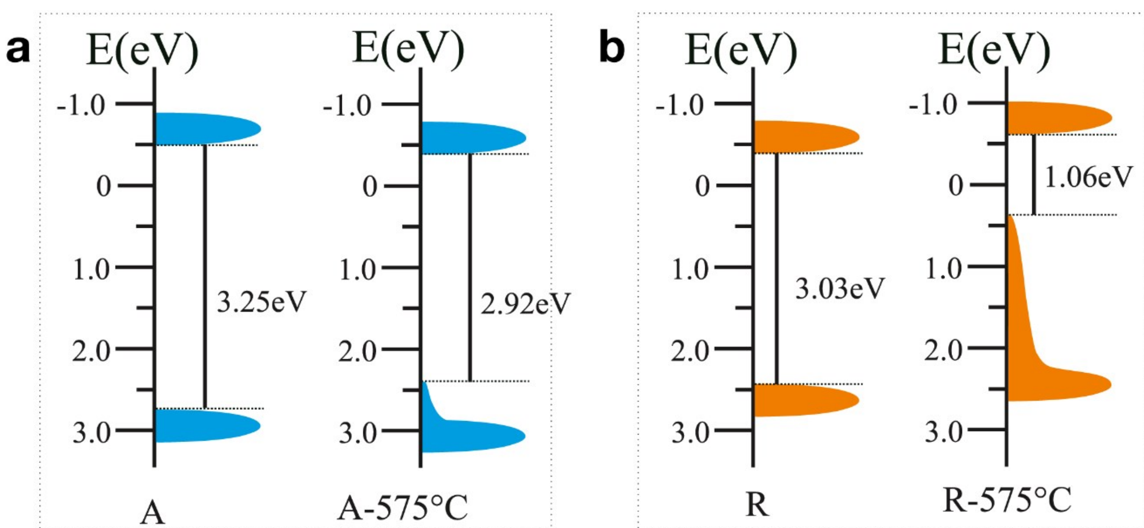

Fig. S15. Schematic illustrations of density of states (DOS) of (a) A-TiO_2 and A-575 and (b) R-TiO_2 and R-575.

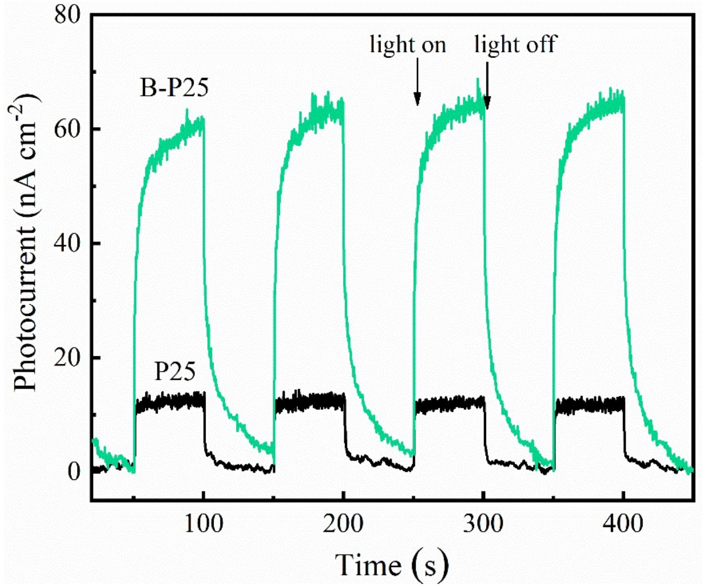

Fig. S16. Photocurrent response of P25 and B-P25 under visible light irradiation.

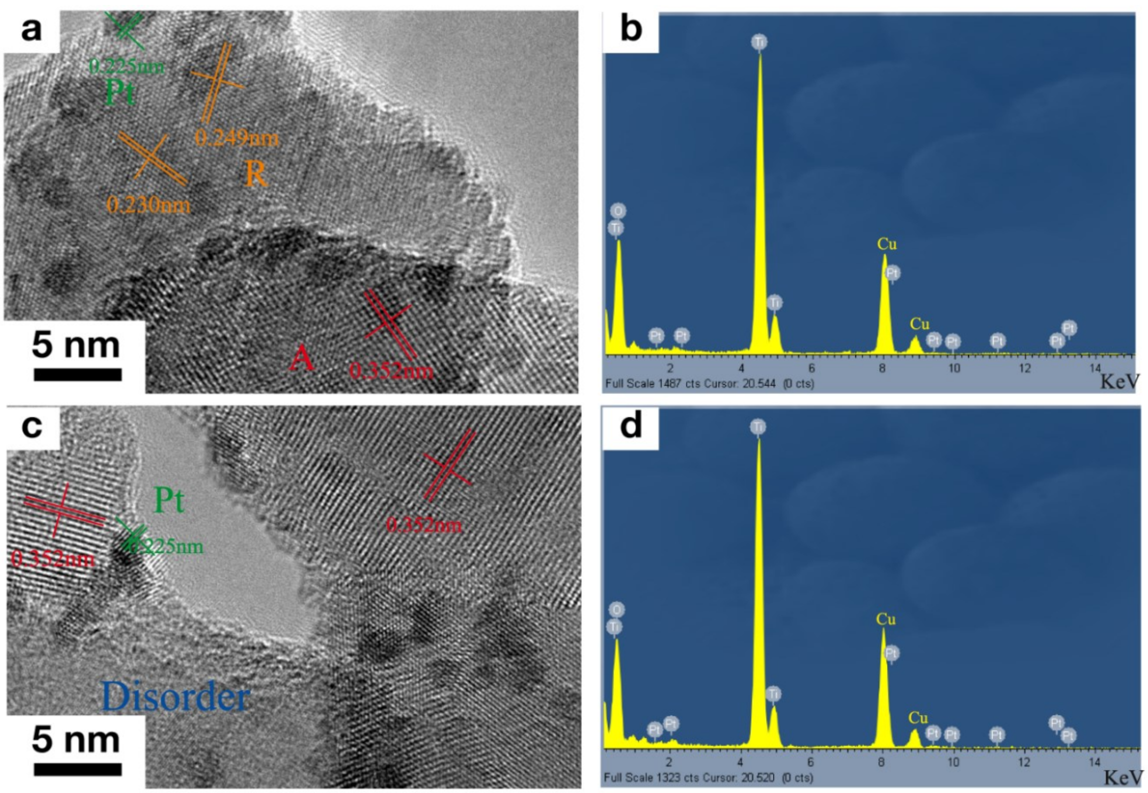

Fig. S17 (a) HR-TEM image and (b) EDX spectrum of P25/Pt. (c) HR-TEM image and (d) EDX spectrum of B-P25/Pt.

Table S1. Comparison of HER rates of recently reported black TiO_2–based photocatalysts.

Photocatalyst	Structure	Cocatalyst	Light source	HER rate (mmol h^{-1} g^{-1})	Ref.
Hydrogenated anatase TiO_2	Core/shell	0.5 wt.% Pt	300 W Xe lamp, Visible light (λ > 420 nm)	0.064	1
Hydrogenated N-doped anatase TiO_2	Core/shell	0.5 wt.% Pt	300 W Xe lamp, AM1.5	1.5	2
$NaBH_4$-reduced rutile TiO_2	Core/shell	0.2 wt.% Pt	300 W Xe lamp	7.34	3
$NaBH_4$-reduced rutile TiO_2	Core/shell	1 wt.% Pt	300 W Xe lamp	0.11	4
			Visible light (λ > 420 nm)	0.02	
$NaBH_4$ reduced P-25	Core/shell	1 wt.% Pt	300 W Xe lamp	6.5	5
			Visible light (λ > 400 nm)	0.18	
Zn reduced Rutile TiO_2	Core/shell	1 wt.% Pt	300 W Xe lamp	6.0	6
			Visible light (λ > 420 nm)	0.08	
Li-EDA treated P25	Heterojunction	No	300 W Xe lamp	3.46	7
		0.5 wt.% Pt	300 W Xe lamp	13.89	
Al reduced N-doped P25	Core/shell	0.5 wt.% Pt	300 W Xe lamp	15.0	8
			Visible light (λ > 400 nm)	0.2	
Mg reduced B–N co-doped TiO_2	Core/shell	1.0 wt.% Pt	300 W Xe lamp	18.8	9
Hydrogenated TiO_2	Core/shell	0.6% Pt	AM 1.5 solar simulator	10.0	10
Hydrogenated F-doped TiO_2	Core/shell	0.6% Pt	AM 1.5 solar simulator	3.76	11
B-P25 NPs	Order/disorder Janus structure	No	150 W Xe lamp, simulated solar light	1.56	**This work**
			Visible light (λ > 400 nm)	0.38	
		1 wt.% Pt	150 W Xe lamp, simulated solar light	11.53	
			Visible light (λ > 400 nm)	3.52	

Reference

1. J. W. Xue, X. D. Zhu, Y. Zhang, W. D. Wang, W. Xie, J. L. Zhou, J. Bao, Y. Luo, X. Gao, Y. Wang, L. Y. Jang, S. Sun and C. Gao, *ChemCatChem*, 2016, **8**, 2010-2014.
2. K. F. Zhang, W. Zhou, L. N. Chi, X. C. Zhang, W. Y. Hu, B. J. Jiang, K. Pan, G. H. Tian and Z. Jiang, *ChemSusChem*, 2016, **9**, 2841-2848.
3. F. Xiao, W. Zhou, B. J. Sun, H. Z. Li, P. Z. Qiao, L. P. Ren, X. J. Zhao and H. G. Fu, *Sci. China-Mater.*, 2018, **61**, 822-830.
4. Z. Zhao, X. Y. Zhang, G. Q. Zhang, Z. Y. Liu, D. Qu, X. Miao, P. Y. Feng and Z. C. Sun, *Nano Research*, 2015, **8**, 4061-4071.
5. H. Tan, Z. Zhao, M. Niu, C. Mao, D. Cao, D. Cheng, P. Feng and Z. Sun, *Nanoscale*, 2014, **6**, 10216-10223.
6. Z. Zhao, H. Q. Tan, H. F. Zhao, Y. Lv, L. J. Zhou, Y. J. Song and Z. C. Sun, *Chem. Commun.*, 2014, **50**, 2755-2757.
7. K. Zhang, L. Wang, J. K. Kim, M. Ma, G. Veerappan, C.-L. Lee, K.-j. Kong, H. Lee and J. H. Park, *Energy Environ. Sci.*, 2016, **9**, 499-503.
8. T. Lin, C. Yang, Z. Wang, H. Yin, X. Lü, F. Huang, J. Lin, X. Xie and M. Jiang, *Energy Environ. Sci.*, 2014, **7**, 967-972.
9. Y. Li, R. Fu, M. Gao and X. Wang, *Int. J. Hydrogen Energy*, 2019, **44**, 28629-28637.
10. X. Chen, L. Liu, Y. Y. Peter and S. S. Mao, *Science*, 2011, **331**, 746-750.
11. Q. Gao, F. Si, S. Zhang, Y. Fang, X. Chen and S. Yang, *Int. J. Hydrogen Energy*, 2019, **44**, 8011-8019.