

## Supporting Information

# Controllable synthesis of porous TiO<sub>2</sub> with hierarchical nanostructure for efficient photocatalytic hydrogen evolution

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Table S1. Photocatalytic H<sub>2</sub> evolution

Material	Cocatalyst	Light source <sup>a</sup>	Reaction solution <sup>b</sup>	H <sub>2</sub> Activity (μmol g <sup>-1</sup> h <sup>-1</sup> )	Reference (year)
TiO <sub>2</sub>	Pt	UV-Vis (H) 150 W	TEOA	3667	1 (2012)
TiO <sub>2</sub>	Au	UV-Vis (Hg) 300 W	Methanol	2785	2 (2005)
TiO <sub>2</sub>	Rh	Hg 500 W	water vapor	449	3 (1985)
TiO <sub>2</sub>	CuO	UV-Vis (Hg) 400 W	Methanol	18 500	4 (2009)
TiO <sub>2</sub>	Cu(OH) <sub>2</sub>	UV-Vis (Hg) 400 W	Methanol	14 940	5 (2013)
TiO <sub>2</sub>	Ni(OH) <sub>2</sub>	365 nm (LED) 3 W	Methanol	3056	6 (2011)
TiO <sub>2</sub>	C <sub>60</sub> -CNT	UV-Vis (Xe) 300 W	TEOA	6510	7 (2013)
TiO <sub>2</sub>	MoS <sub>2</sub> -RGO	UV-Vis (Xe) 350 W	Ethanol	2066	8 (2012)
TiO <sub>2</sub>	NiO	UV-Vis (Hg) 300 W	Methanol	813	9 (2005)

<sup>a</sup> H: halogen lamp, Xe: xenon lamp, Hg: mercury lamp.

<sup>b</sup> TEOA: triethanolamine.

**Table S2. Compositions of the solutions for hydrothermal reaction of porous TiO<sub>2</sub> hierarchical microspheres synthesized under different conditions**

Sample	TTIP (g)	Volume ratio of HCl:EG	CTAB (g)	H <sub>2</sub> O (mL)	Average diameters of the constituent units (nm)
TiO <sub>2</sub> -15	0.6	7:5	0.5	2.5	15
TiO <sub>2</sub> -10	0.6	7:21	0.5	2.5	10
TiO <sub>2</sub> -5	0.6	7:35	0.5	2.5	5

**Table S3. Surface analysis data**

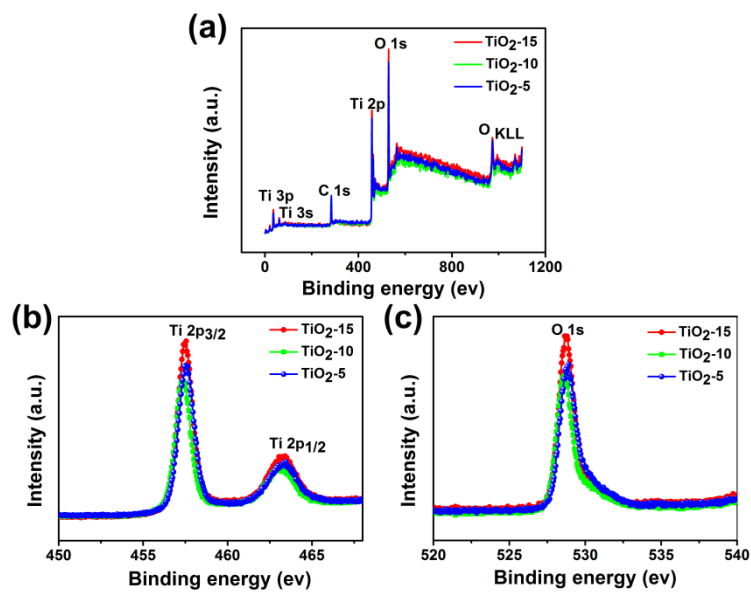
Sample	Specific surface area (m <sup>2</sup> g <sup>-1</sup> ) <sup>a</sup>	Average pore size (nm) <sup>b</sup>	Pore volume(cm <sup>3</sup> g <sup>-1</sup> )
TiO <sub>2</sub> -15	72.317	5.0	0.087
TiO <sub>2</sub> -10	111.147	4.9	0.122
TiO <sub>2</sub> -5	216.607	3.8	0.241

<sup>a</sup> Specific surface area was calculated from the linear part of BET plot.

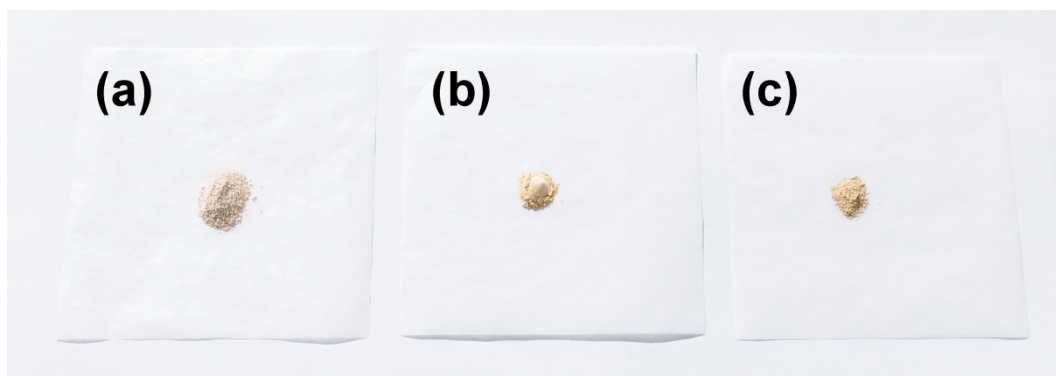
<sup>b</sup> Average pore diameter was estimated.

**Table S4. Photocatalytic activities of the samples**

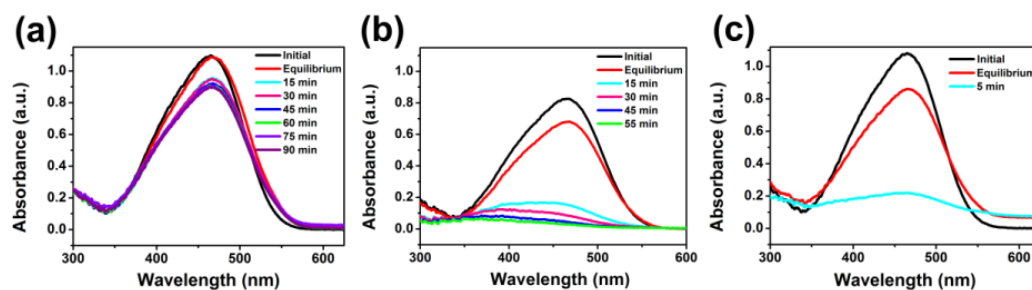
Samples	H <sub>2</sub> activity (mmol g <sup>-1</sup> h <sup>-1</sup> )	QE (%)
P25	18.94	14.59
TiO <sub>2</sub> -15	12.38	9.59
TiO <sub>2</sub> -10	14.33	11.05
TiO <sub>2</sub> -5	23.74	18.34



**Figure S1.** XPS spectra of TiO<sub>2</sub>-15, TiO<sub>2</sub>-10 and TiO<sub>2</sub>-5; (a) showing the three characteristic peaks of Ti, O and C of them, (b) and (c) showing the two characteristic peaks of Ti and O.

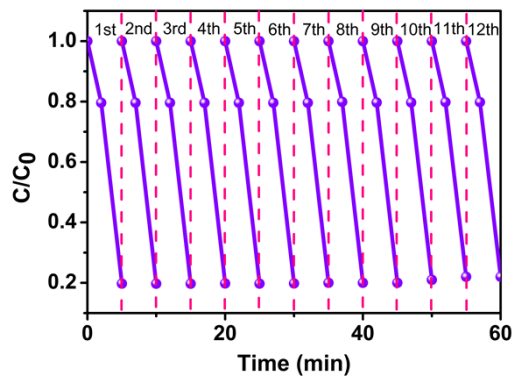


**Figure S2.** The photograph of all the products: (a) TiO<sub>2</sub>-15, (b) TiO<sub>2</sub>-10; (c) TiO<sub>2</sub>-5.

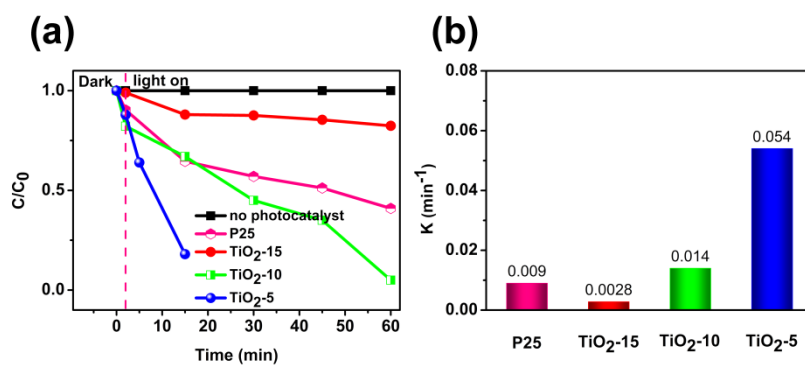


**Figure S3.** Photocatalytic degradation of MO under UV-visible light for 0.08 g, (a) TiO<sub>2</sub>-15, (b) TiO<sub>2</sub>-10, (c) TiO<sub>2</sub>-5 as photocatalyst. After 90 min 18.5% of the MO has been degraded for TiO<sub>2</sub>-15, after 15 min 80% of the

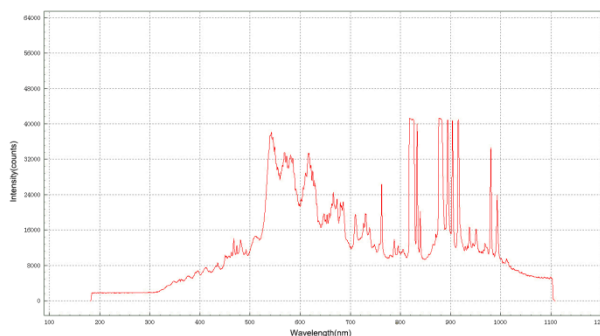
MO has been degraded for TiO<sub>2</sub>-10, but only after 5 min 80% of the MO has been degraded for TiO<sub>2</sub>-5.



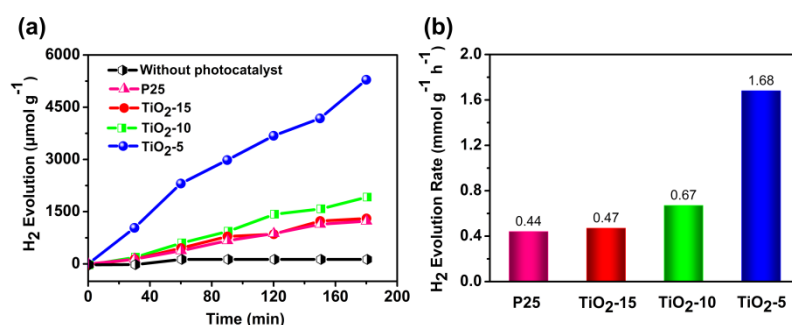
**Figure S4.** Cycling runs in photocatalytic degradation of MO in the presence of TiO<sub>2</sub>-5 under UV-visible light.



**Figure S5.** (a) and (b) Photocatalytic degradation of phenol under UV-visible light of P25, TiO<sub>2</sub>-15, TiO<sub>2</sub>-10 and TiO<sub>2</sub>-5 for 0.08 g, respectively: (a) C/C<sub>0</sub> of them and without photocatalyst; (b) First-order rate constant k (min<sup>-1</sup>) of them.



**Figure S6.** The UV-Vis spectra of 300 W Xenon lamp.



**Figure S7.** Photocatalytic generation of H<sub>2</sub> under UV-visible light irradiation for them: (a) Time evolution of photocatalytic generation of H<sub>2</sub> without Pt for the samples and without catalyst; (b) Comparison of H<sub>2</sub> evolution activities of them.

## References

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