Electronic Supplementary Information

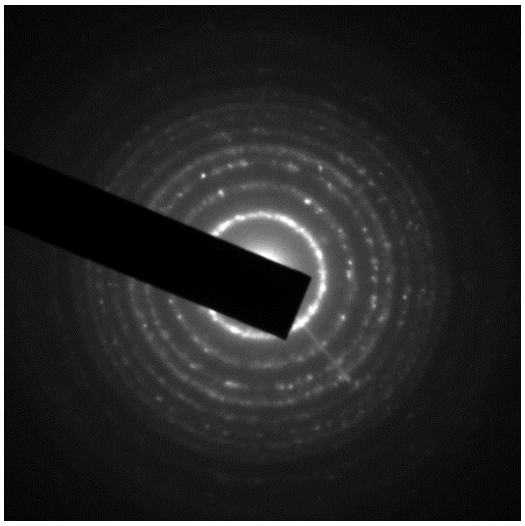

Fig. S1 Selected-area electron diffraction (SAED) pattern of the stable mesoporous black TiO_2 hollow spheres.

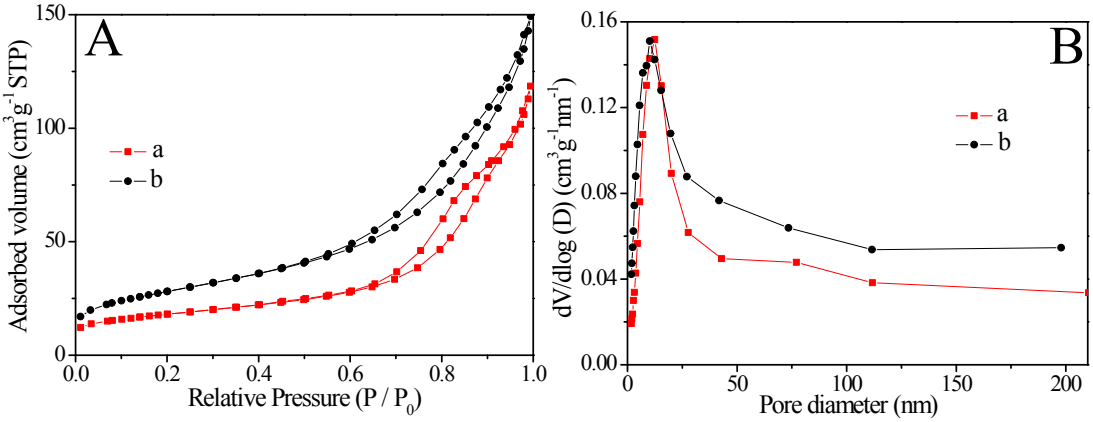

Fig. S2 N_2 adsorption-desorption isotherms (A) and the corresponding Barrett−Joyner−Halenda (BJH) pore size distribution plots (B) of the stable mesoporous black TiO_2 hollow spheres (a) and stable mesoporous TiO_2 hollow spheres (b).

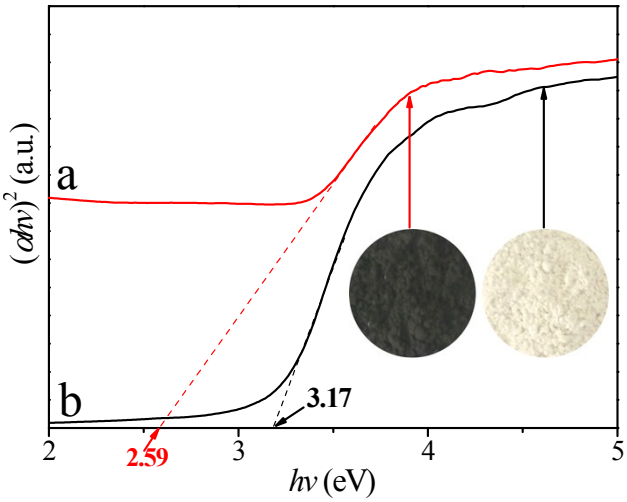

Fig. S3 The optical bandgaps of the stable mesoporous black TiO_2 hollow spheres (a) and stable mesoporous TiO_2 hollow spheres (b). The insets are the photos of (a) and (b).

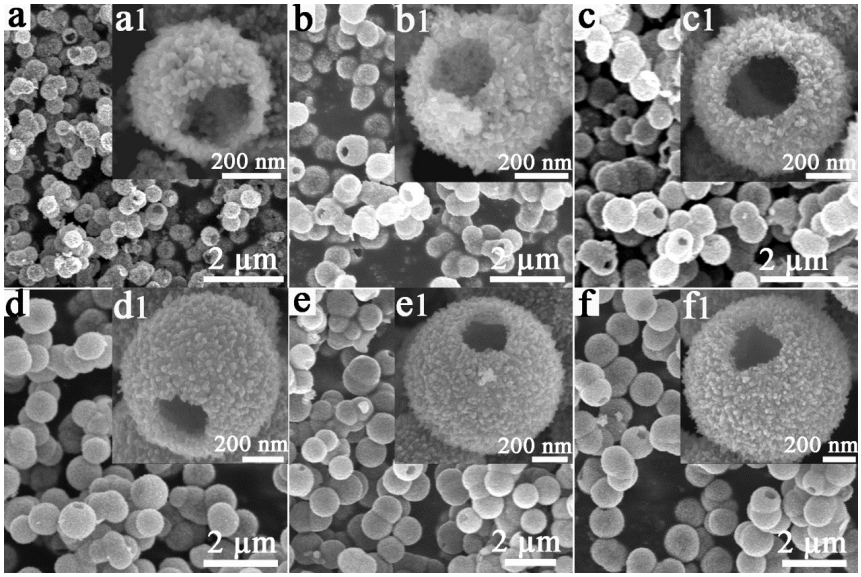

Fig. S4 The diameters evolution of the stable mesoporous black TiO_2 hollow spheres with different amounts of Ti precursors (TBOT). (a~500 nm: 0.06 g; b~600 nm: 0.08 g; c~700 nm: 0.10 g; d~800 nm: 0.12 g; e~900 nm: 0.14 g; f~1000 nm: 0.16 g)

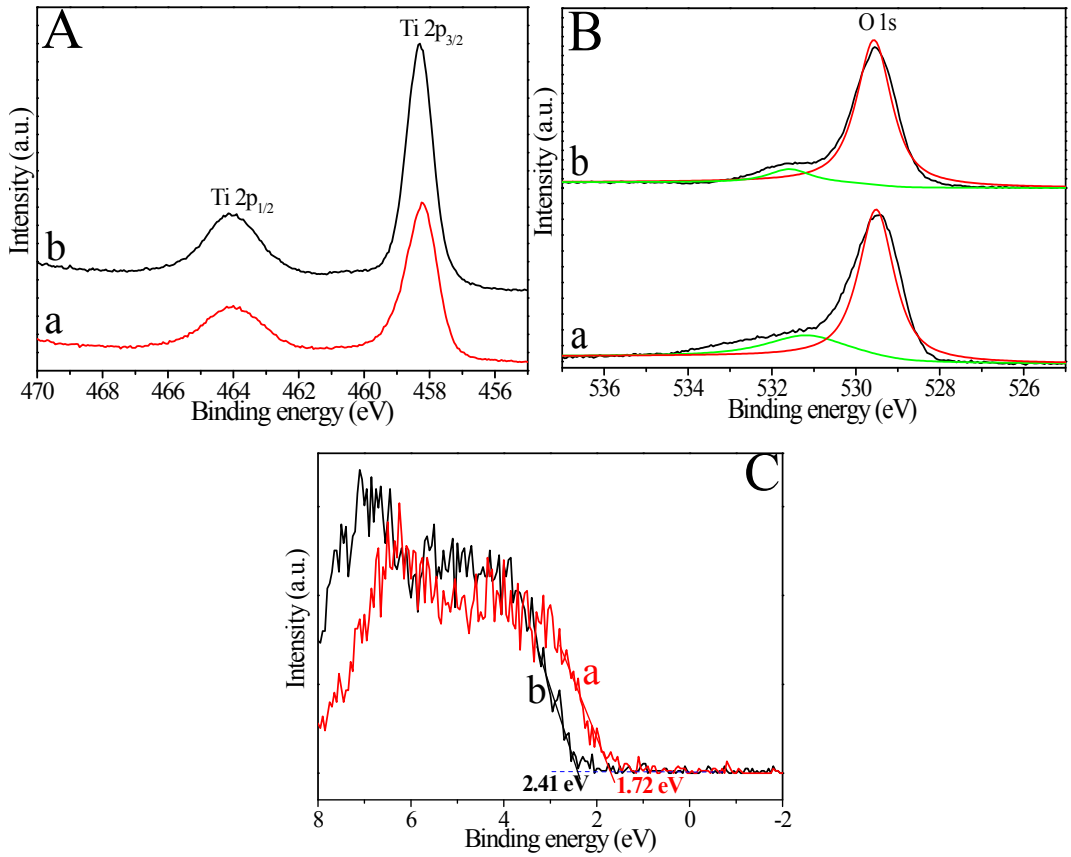

Fig. S5 The Ti 2p (A), O 1s (B) and valence band X-ray photoelectron spectra (C) of the stable mesoporous black TiO_2 hollow spheres (a) and stable mesoporous TiO_2 hollow spheres (b).

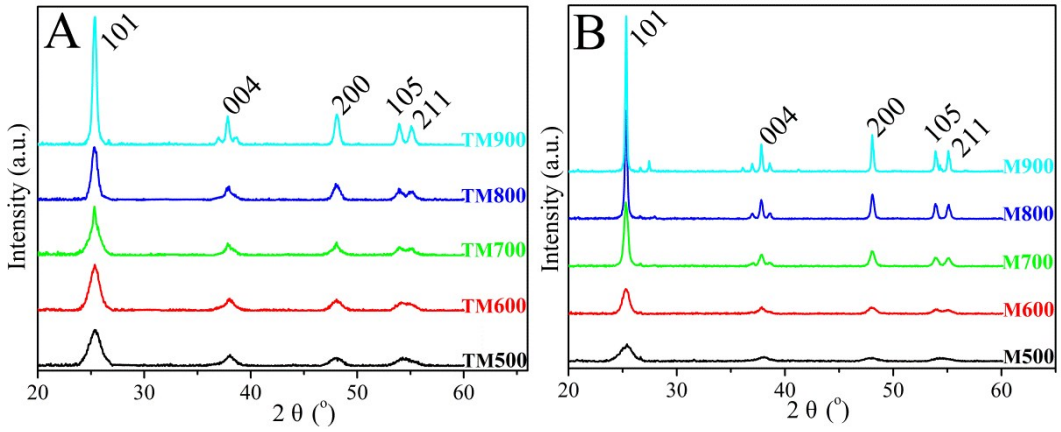

Fig. S6 XRD patterns of mesoporous TiO_2 hollow spheres with (A) and without ethylenediamine encircling treatment (B) after being calcined at different temperatures (500, 600, 700, 800 and 900 °C).

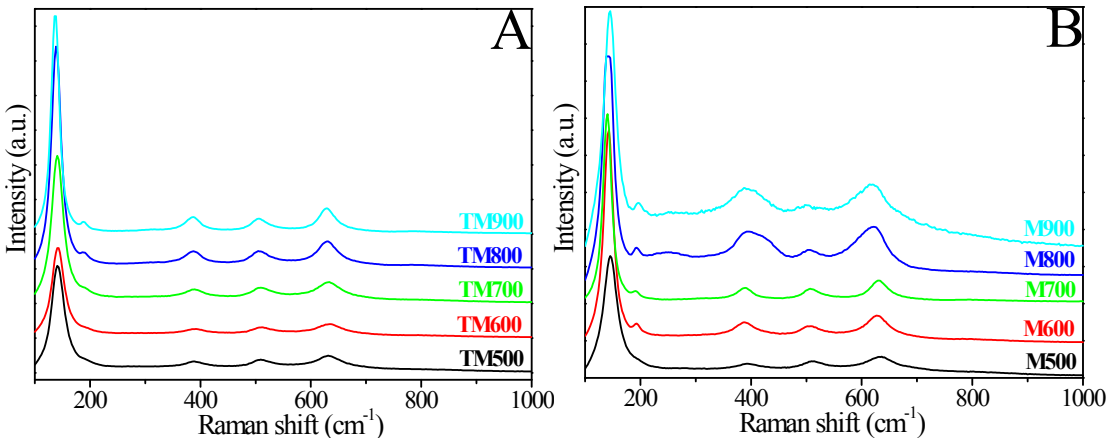

Fig. S7 Raman spectra of the mesoporous TiO_2 hollow spheres with (A) and without ethylenediamine encircling treatment (B) after being calcined at different temperatures (500, 600, 700, 800 and 900 °C).

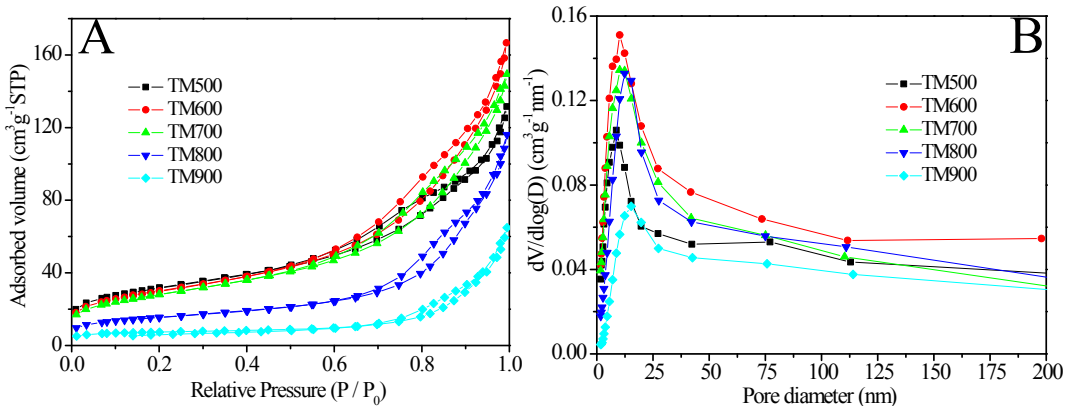

Fig. S8 N_2 adsorption-desorption isotherms (A) and the corresponding Barrett−Joyner−Halenda (BJH) pore size distribution plots (B) of the mesoporous TiO_2 hollow spheres after ethylenediamine encircling treatment and being calcined at different temperatures (500, 600, 700, 800 and 900 °C).

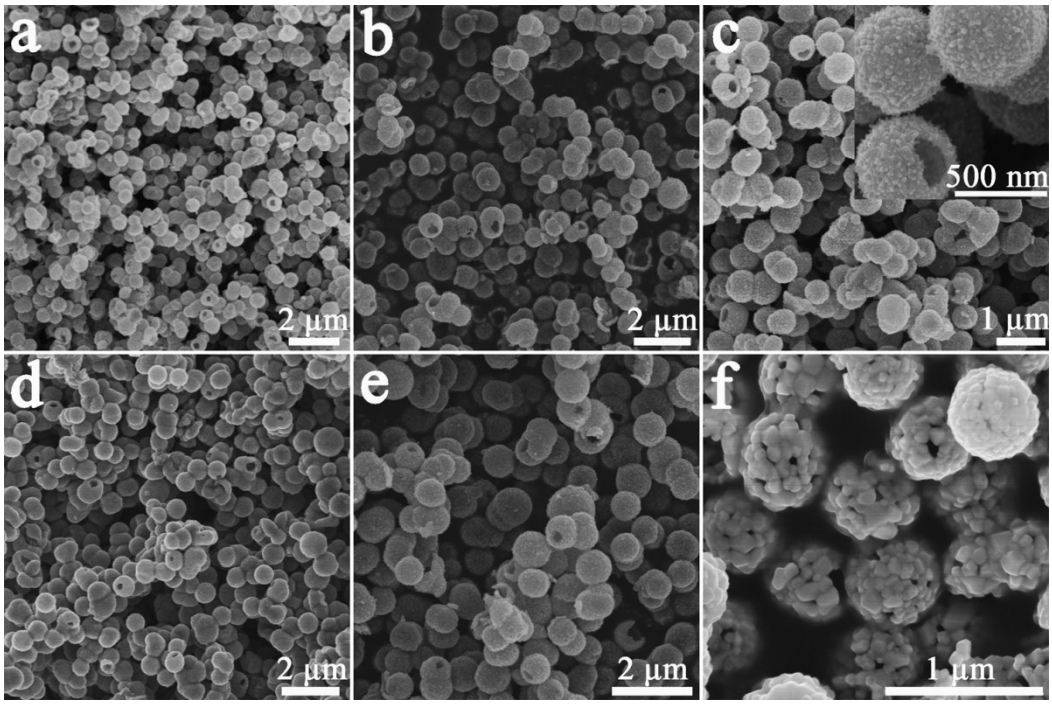

Fig. S9 SEM images of the mesoporous TiO_2 hollow spheres with (a, b, c) and without ethylenediamine encircling treatment (d, e, f) after being calcined at the temperature of 500 °C (a, d), 700 °C (b, e), 900 °C (c, f).

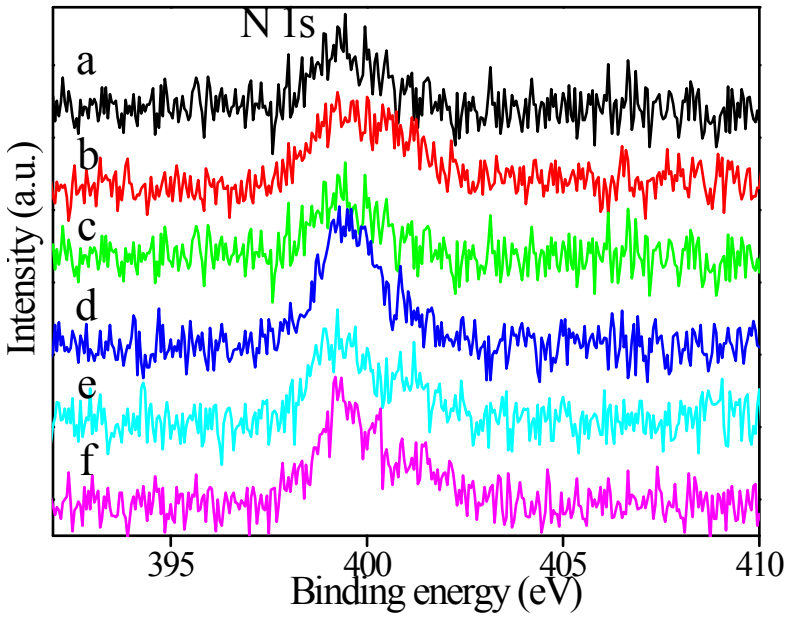

Fig. S10 The N 1s X-ray photoelectron spectra of the stable mesoporous TiO_2 hollow spheres with different pretreatment after being calcined at 600 °C, trimethylamine (a), *n*-butylamine (b), isopropylamine (c), ammonium hydroxide (d), hexamethylenetetramine (e), ethylenediamine (f).

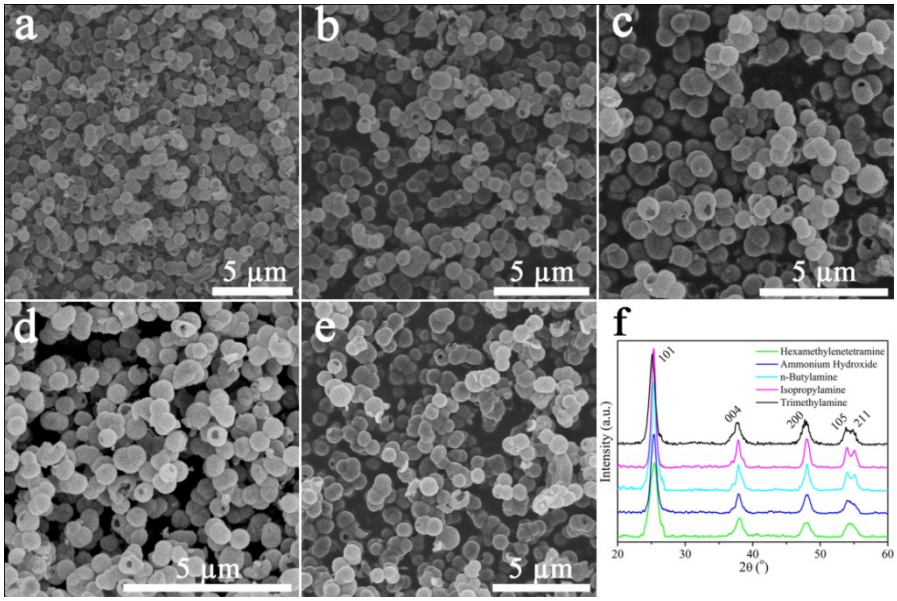

Fig. S11 SEM images (a-e) and XRD patterns (f) of the stable mesoporous black TiO_2 hollow spheres with different pretreatment after being calcined at 600 °C in air and hydrogen gas annealingat 600 °C. Trimethylamine (a), Isopropylamine (b), *n*-Butylamine (c), Hexamethylenetetramine (d), Ammonium Hydroxide (e).

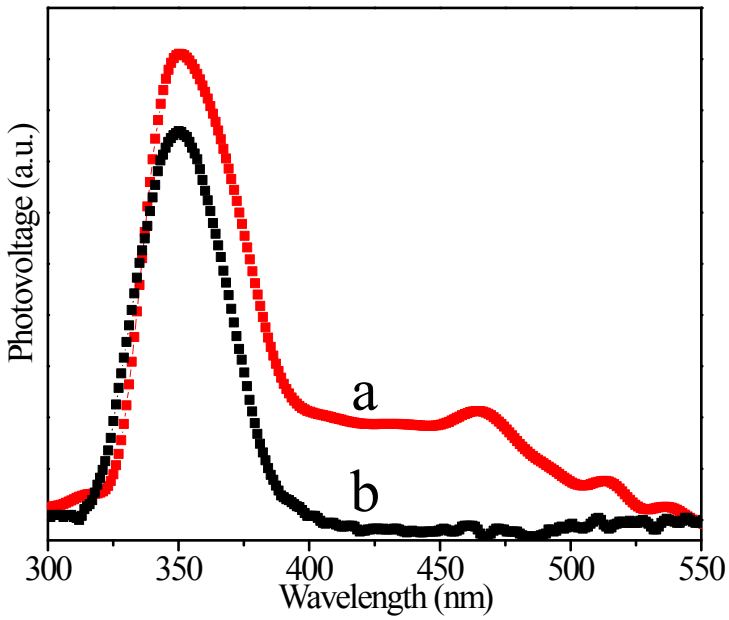

Fig. S12 Surface photovoltage spectroscopy (SPS) of the stable mesoporous black TiO_2 hollow spheres (a) and stable mesoporous TiO_2 hollow spheres (b).

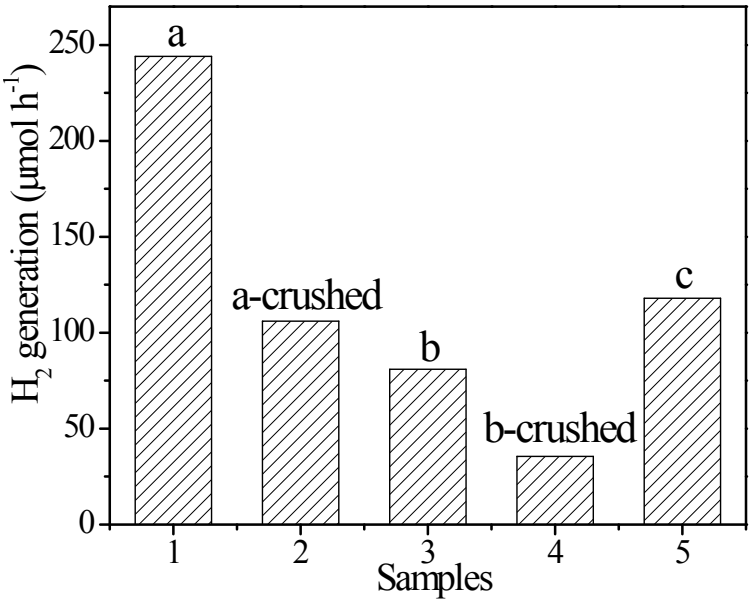

Fig. S13 Photocatalytic hydrogen evolution of the stable mesoporous black TiO_2 hollow spheres (a), stable mesoporous TiO_2 hollow spheres (b) and black TiO_2 nanoparticles (c) under AM 1.5.

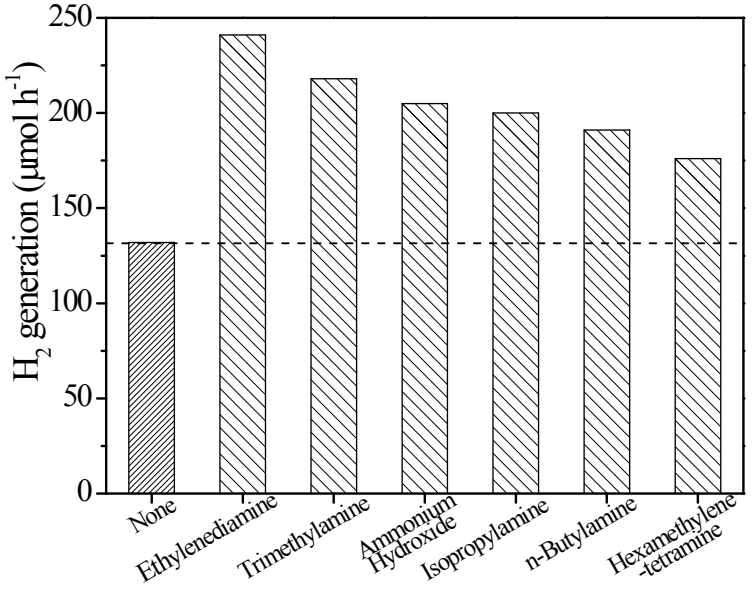

Fig. S14 Photocatalytic hydrogen evolution of the mesoporous black TiO_2 hollow spheres without and with different pre-treatment after being calcined at 600 °C and hydrogen gas annealingat 600 °C (under AM 1.5).

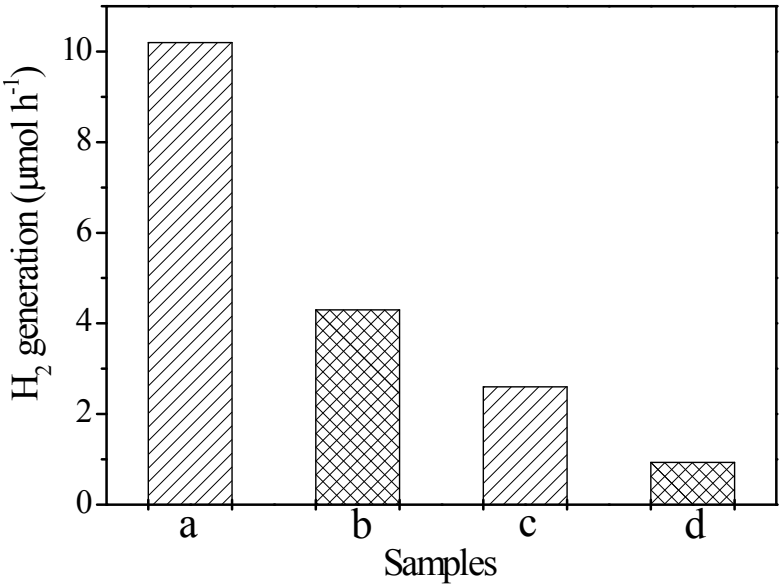

Fig. S15 The H_2 generation rate of the stable mesoporous black TiO_2 hollow spheres (a, c), and stable mesoporous TiO_2 hollow spheres (b, d) under AM 1.5 without Pt as a co-catalyst and in pure water system, respectively.

Table S1 The textual properties of the mesoporous TiO_2 hollow spheres with and without ethylenediamine (EN) encircling treatment after being calcined at different temperatures.

Calcination	BET surface area (m^2 g^{-1})		Pore size (nm)	
temperature	EN treated	Untreated	EN treated	Untreated
500 °C	113.6	108.4	7.91	9.33
600 °C	106.4	40.5	10.65	12.65
700 °C	100.8	31.5	11.06	13.11
800 °C	55.3	23.7	12.23	14.76
900 °C	25.8	4.3	14.97	-

Table S2 The textual properties of the mesoporous TiO_2 hollow spheres with and without different pretreatment after being calcined at 600 °C.

Pretreatment	Crystal phase/ Particle size (nm)	BET surface area (m^2 g^{-1})	Pore size (nm)	Pore volume (cm^3 g^{-1})
None	Anatase / 21.2	40	11.9	0.12
Ethylenediamine	Anatase / 10.6	106	10.6	0.23
Trimethylamine	Anatase / 10.8	101	9.3	0.23
Isopropylamine	Anatase / 11.9	95	9.9	0.23
n-Butylamine	Anatase / 13.2	80	9.5	0.21
Hexamethylenetetramine	Anatase / 12.1	93	9.8	0.23
Ammonium Hydroxide	Anatase / 12.6	86	9.3	0.21

Table S3 Photocatalytic hydrogen evolution of the stable mesoporous black TiO_2 hollow spheres with different diameters under AM 1.5.

Diameter (nm)	500	600	700	800	900	1000
H_2 evolution (μmol h^{-1} 0.1 g^{-1})	178	227	241	208	182	160

Table S4 Photocatalytic hydrogen evolution of the stable mesoporous black TiO_2 hollow spheres with different wall thicknesses under AM 1.5.

Wall thickness (nm)	35	55	75	95	115
H_2 evolution (μmol h^{-1} 0.1 g^{-1})	185	230	241	203	169