Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Titanocene dichloride (Cp_2TiCl_2) as precursor for template-free fabricating hollow TiO_2 nanostructures with enhanced photocatalytic hydrogen production

*Haiqing Wang, Haifeng Lin, Yong Long, Bing Ni, Ting He, Simin Zhang, Huihui Zhu and Xun Wang**

Key Lab of Organic Optoelectronics and Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing 100084, China.

E-mail: wangxun@mail.tsinghua.edu.cn

Table S1 Control experiments for the tunable synthesis of TiO2 nanostructures

Series	Variables		
A	The amount of ammonia (25 wt.%)	Sample	Ammonia /mL.
		A-0.2	0.2
		A-0.5	0.5
		A-1.0	1.0
		A-2.0	2.0
		A-3.0	3.0
		A-5.0	5.0
B	The amount of titanocene dichloride (without ammonia)	Sample	Titanocene dichloride /g
		B-0.05	0.05
		B-0.08	0.08
		B-0.10	0.10
		B-0.12	0.12
		B-0.15	0.15
		B-0.17	0.17
		B-0.20	0.20
C	Ammonia concentration	Sample	Concentration /wt.%
		D-0	0
		D-10	10
		D-25	25
D	The amount of titanocene dichloride (0.5 mL 25 wt.%)	Sample	Titanocene dichloride /g
		C-0.07	0.07
		C-0.10	0.10
		C-0.12	0.12
		C-0.15	0.15
E	Temperature	Sample	T /^{o}C
		E-150	150
		E-180	180
		E-200	200
		E-220	220
F	Reaction time	Sample	t /h
		F-2	2
		F-6	6
		F-8	8
		F-12	12
		F-16	16
		F-24	24
S	Types of solvents	solvent	
		Deionized water	
		Ethanol	
		Acetic acid	
		Glycol	

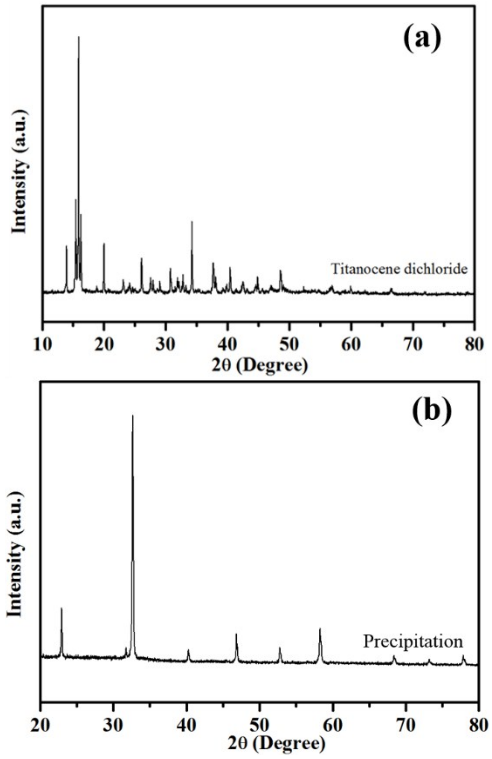


Fig. S1 XRD patterns of titanocene dichloride (a) and the collected precipitation before heat-treatment (b).

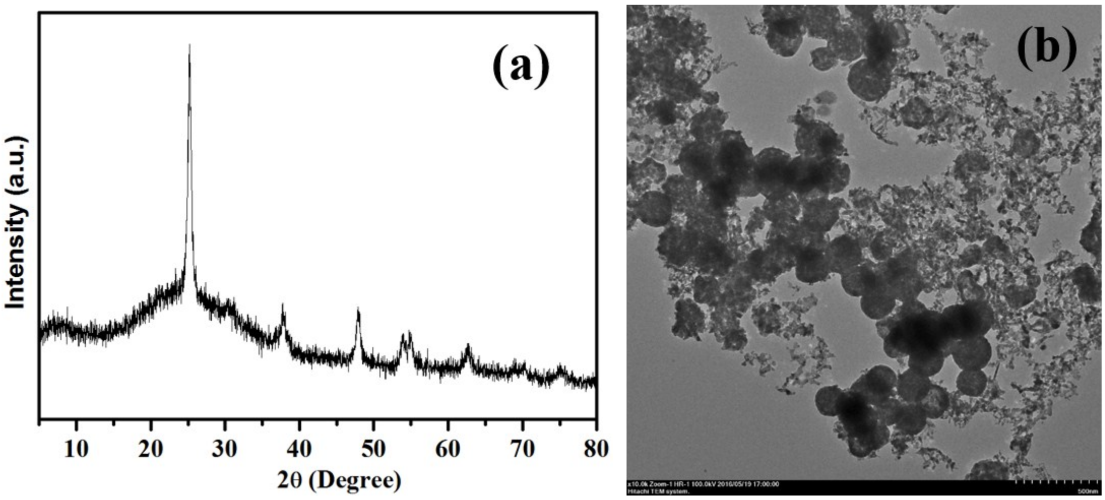


Fig. S2 (a) XRD pattern and (b) TEM image of TiO_2 synthesized with direct calcination.

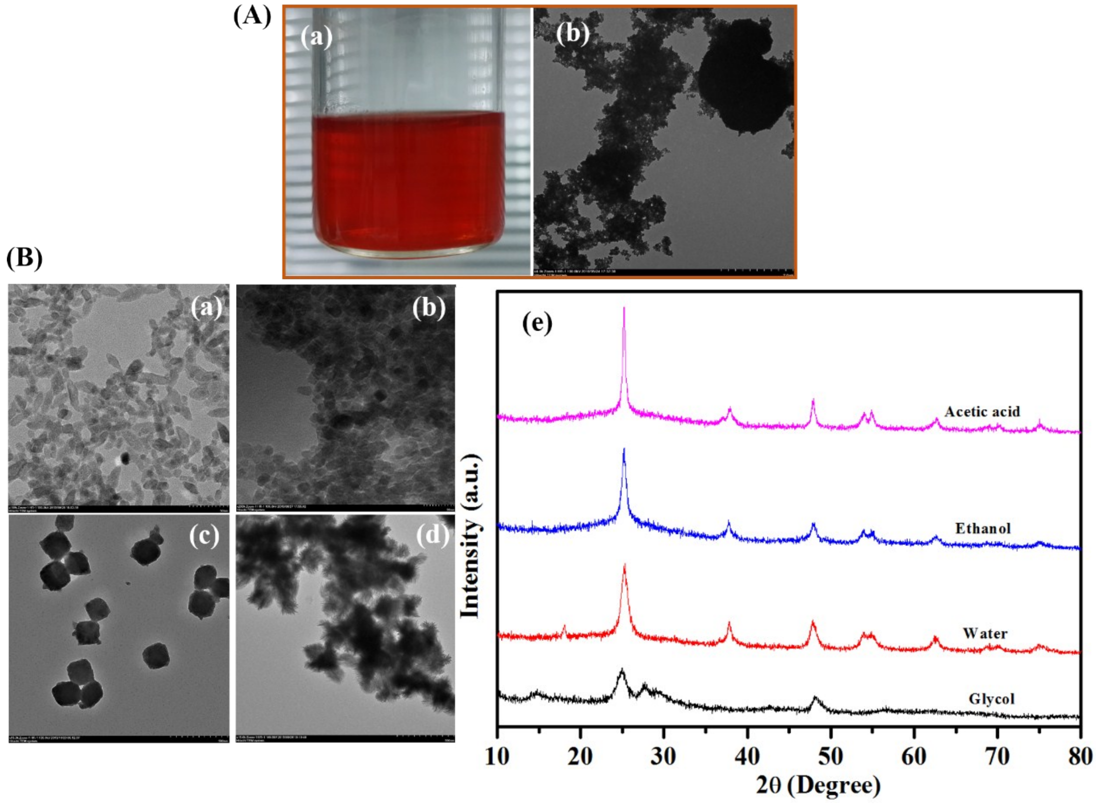
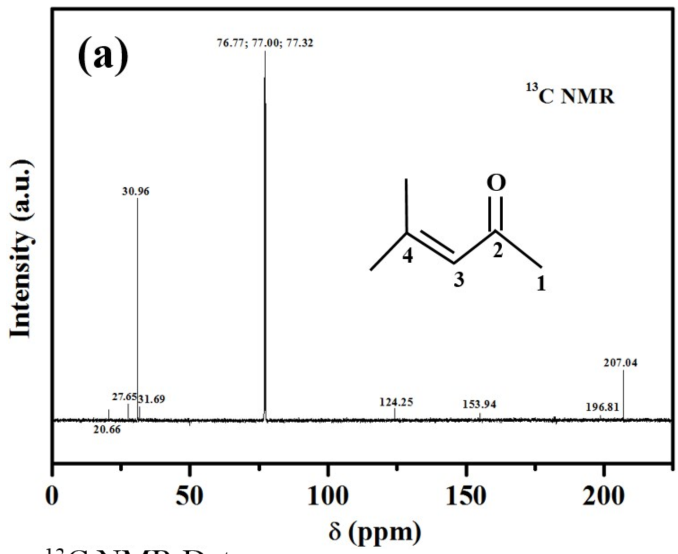


Fig. S3 (A) Digital photo (a) and TEM image (b) of TiO_2 with NaOH as alkali source, and (B) TEM images of TiO_2 anoparticles/nanosheet synthesized with (a) deionized water, (b) ethanol, (c) acetic acid, and (d) glycol as solvent, and (e) their corresponding XRD patterns.



^{13}C NMR Data

Mesitl oxide (4-methyl-3-penten-2-one)

^{13}C NMR δ= 196.8 (C2), 153.9 (C4), 124.2 (C3), 31.6 (C1), 27.6, 20.6 (CH_3)

(b)

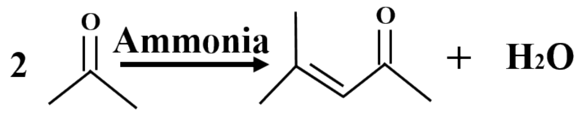


Fig. S4 (a) ^{13}C NMR data of the production solution and (b) chemical reaction of acetone at given conditions.

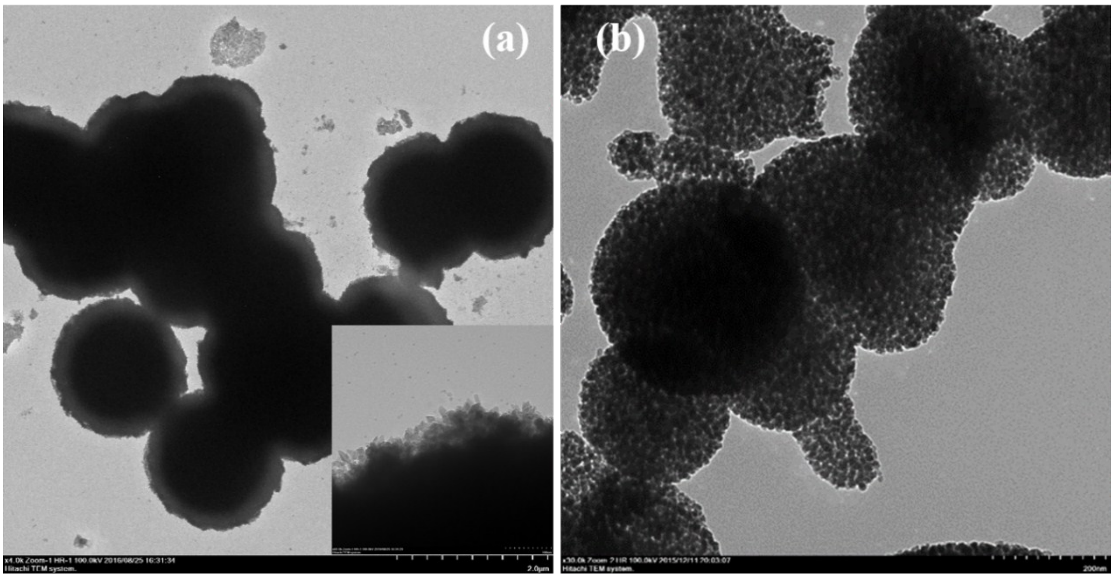


Fig. S5 TEM images of TiO_2 synthesized with $TiCl_4$ (a) and titanate tetrabutyl (b) as titanium source.

The inset of Fig. S5a shows that the edge of microsphere consists of octahedral double cones. Then, the formation of octahedral double cone in this paper should be arisen from the presence of chloride ion (Cl^-).

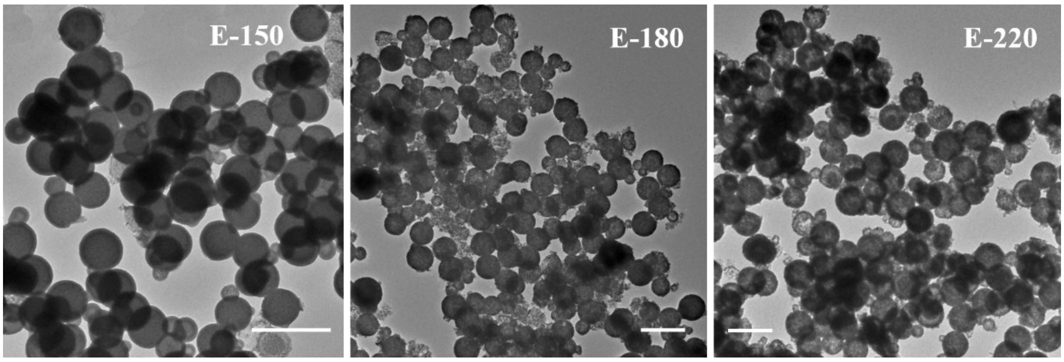


Fig. S6 TEM images of E series HTSs synthesized with different solvothermal temperature (scale bar 500 nm).

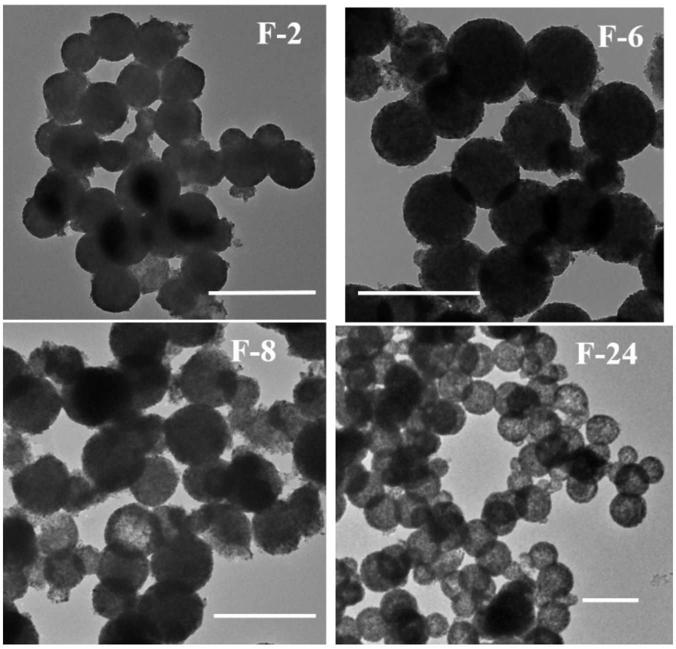


Fig. S7 TEM images of F series HTSs synthesized with different solvothermal time (scale bar 500 nm).

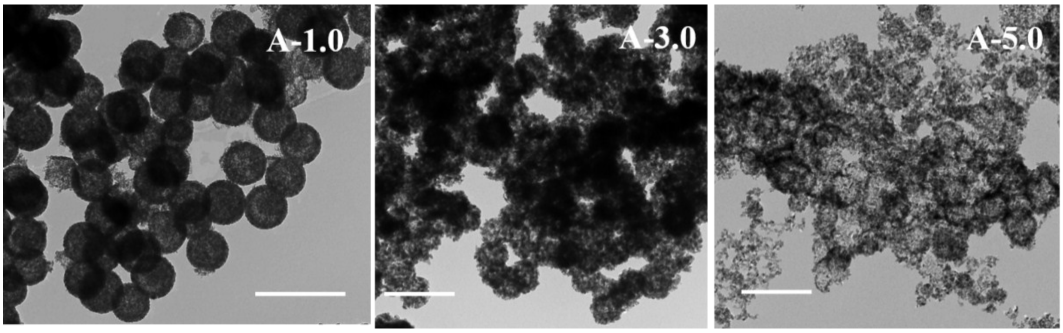


Fig. S8 TEM images of A series HTSs synthesized with varied amount of ammonia (scale bar 500 nm).

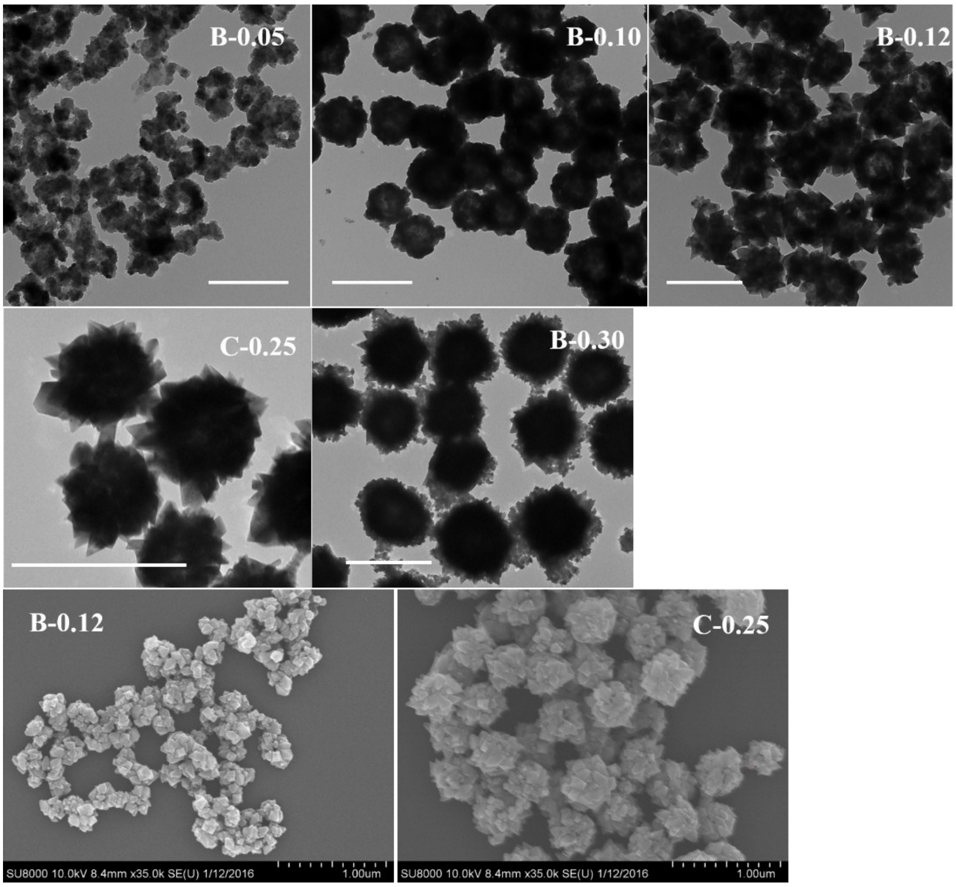


Fig. S9 TEM and SEM images of B series HTSs synthesized with varied amount of titanium precursor (without ammonia, scale bar 500 nm).

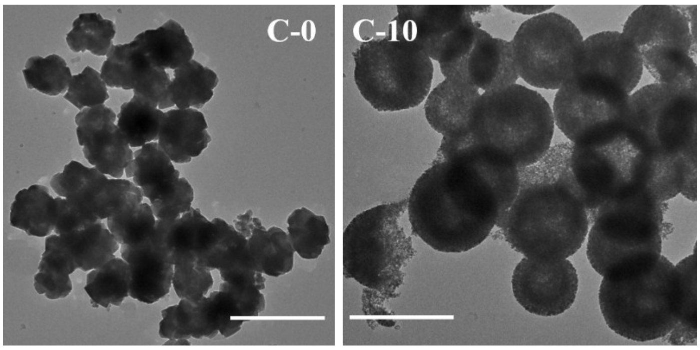


Fig. S10 TEM images of C series HTSs synthesized with varied concentration of ammonia (0.5 mL, scale bar 500 nm).

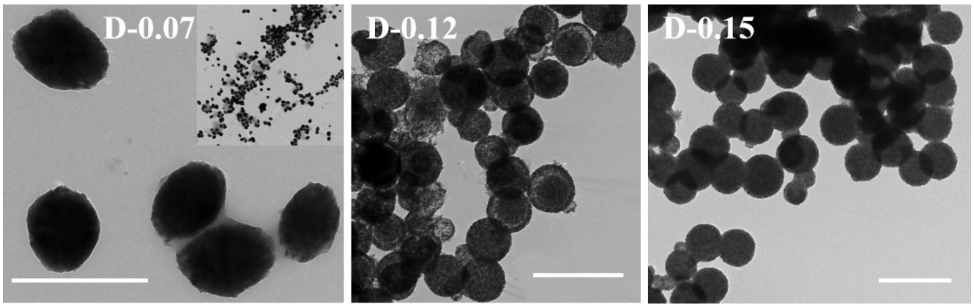


Fig. S11 TEM images of D series HTSs synthesized with varied amount of titanium precursor (0.5 mL concentrated ammonia, scale bar 500 nm).

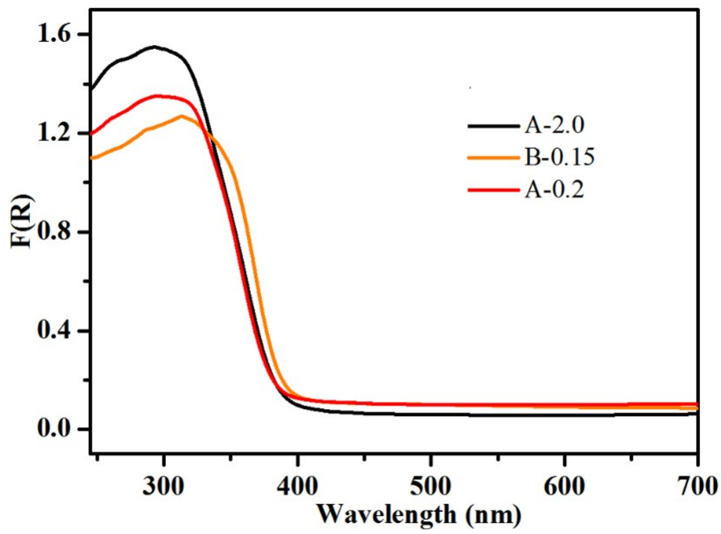


Fig. S12 UV-vis spectra of calcined A-2.0, B-0.15, and A-0.2 samples (450 ^{o}C for 2h).

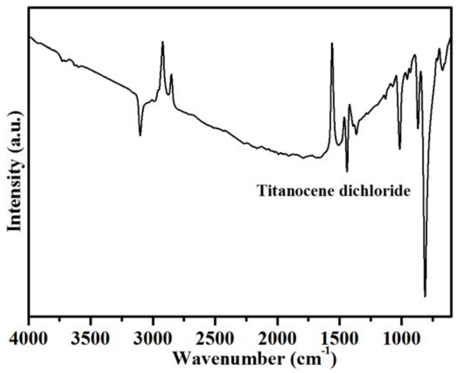


Fig. S13 FTIR spectrum of titanocene dichloride

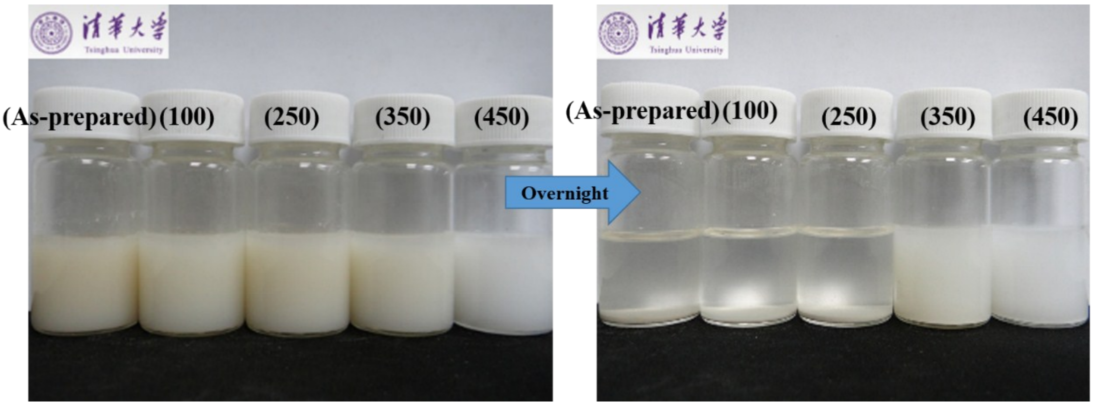


Fig. S14 Digital photos of dispersion in water of THSs calcined with different temperatures (as-prepared, 100, 250, 350, and 450 for 2h).

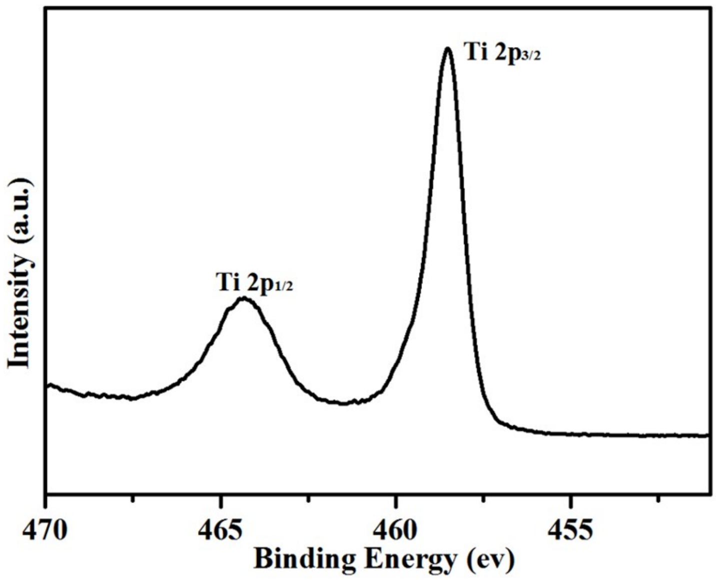


Fig. S15 XPS spectra of Ti 2p of calcined HTSs (450^{o}C, 2h).

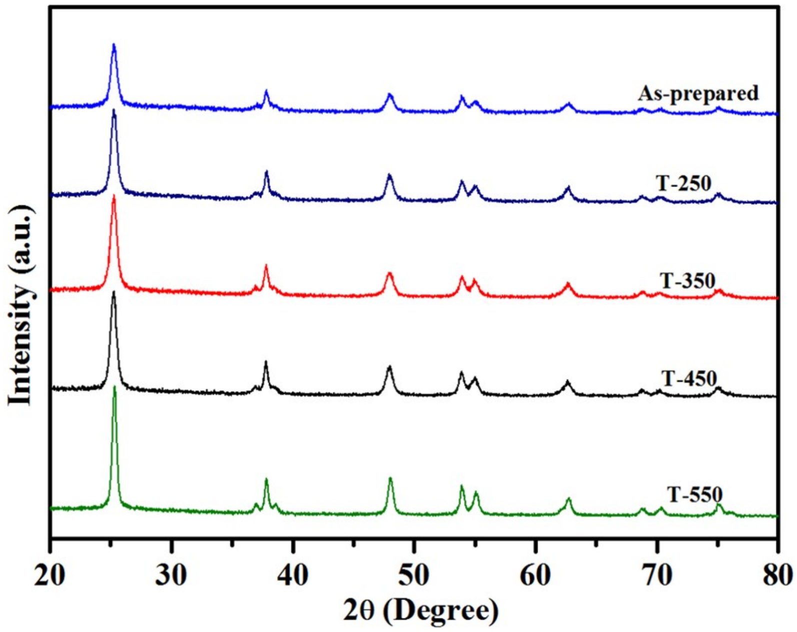


Fig. S16 XRD patterns of HTSs calcined with different temperatures (as-prepared, 250, 350, 450, and 550).