Supporting Information

Highly Efficient Doping Titanium Dioxide with Sulfur using Disulfide-linked Macrocycles for Hydrogen Production under Visible Light

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Contents

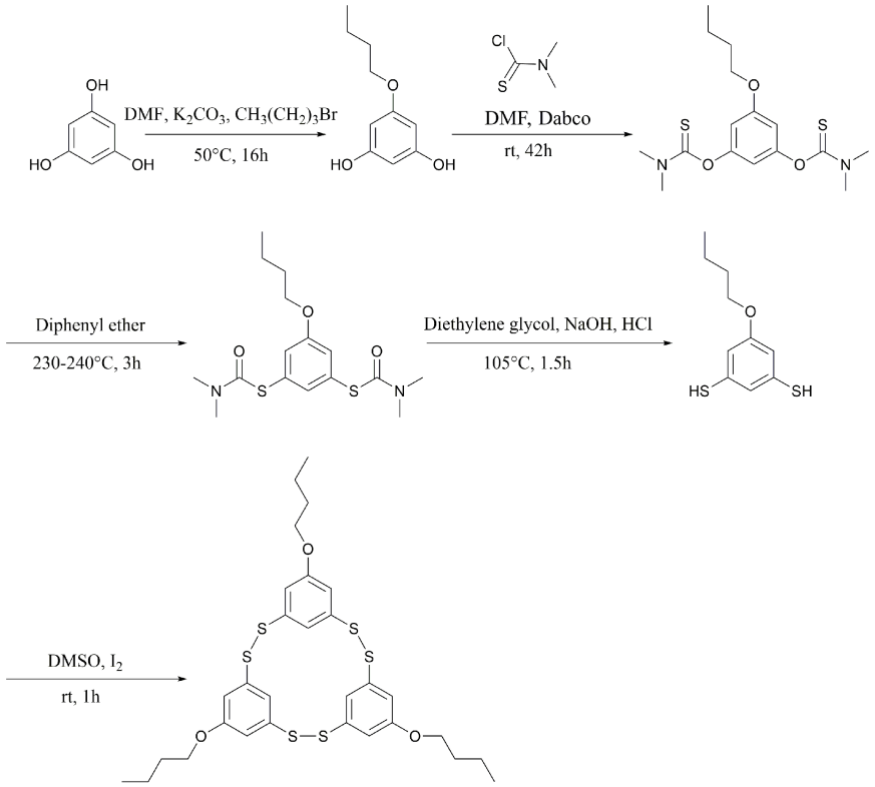

Fig. S1 Synthetic routes to the disulfide macrocycle (DSM).

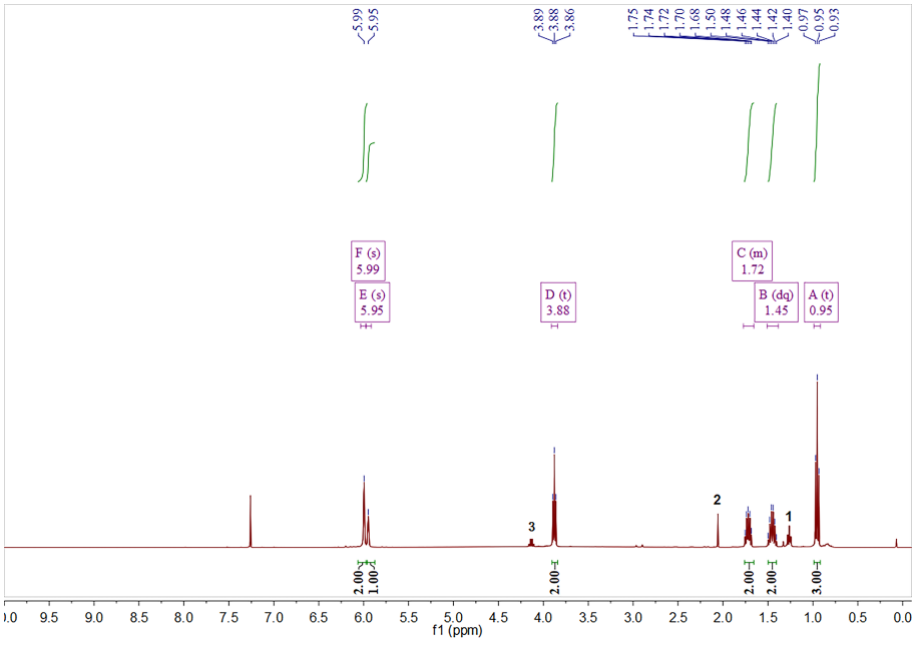

Fig. S2 ^{1}H NMR of 5-butoxybenzene-1,3-diol in $CDCl_3$, in which the peaks 1, 2, 3 are assigned to the residual solvent ethyl acetate.

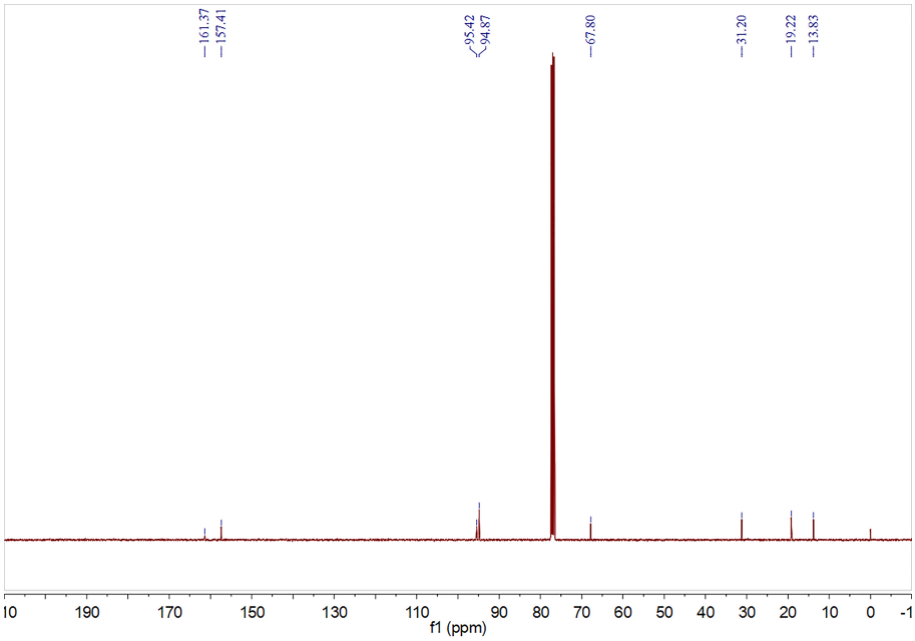

Fig. S3 ^{13}C NMR of 5-butoxybenzene-1,3-diol in $CDCl_3$.

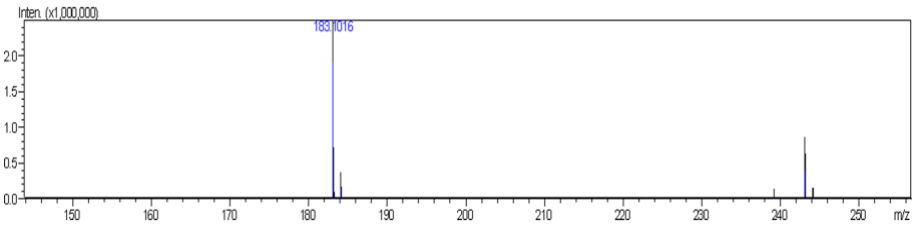

Fig. S4 High resolution mass spectrum of 5-butoxybenzene-1,3-diol.

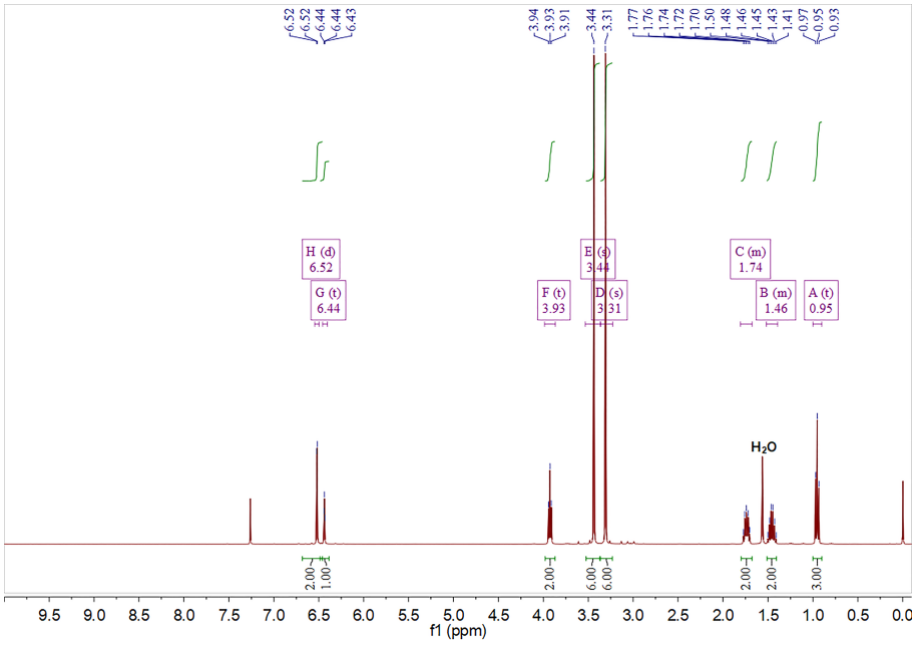

Fig. S5 ^{1}H NMR of O,O'-(5-butoxy-1,3-phenylene) bis (dimethylcarbamothioate) in $CDCl_3$.

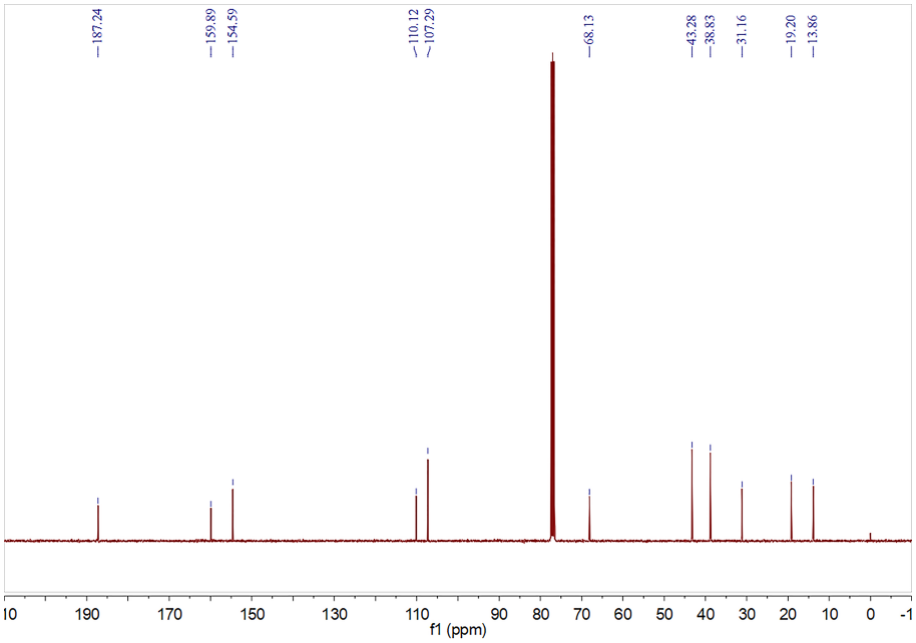

Fig. S6 ^{13}C NMR of O,O'-(5-butoxy-1,3-phenylene) bis (dimethylcarbamothioate) in $CDCl_3$.

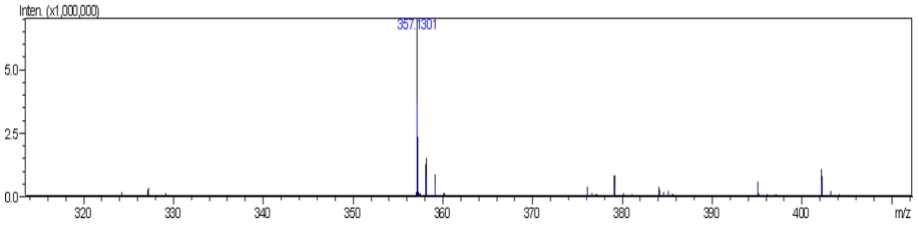

Fig. S7 High resolution mass spectrum of O,O'-(5-butoxy-1,3-phenylene) bis (dimethylcarbamothioate).

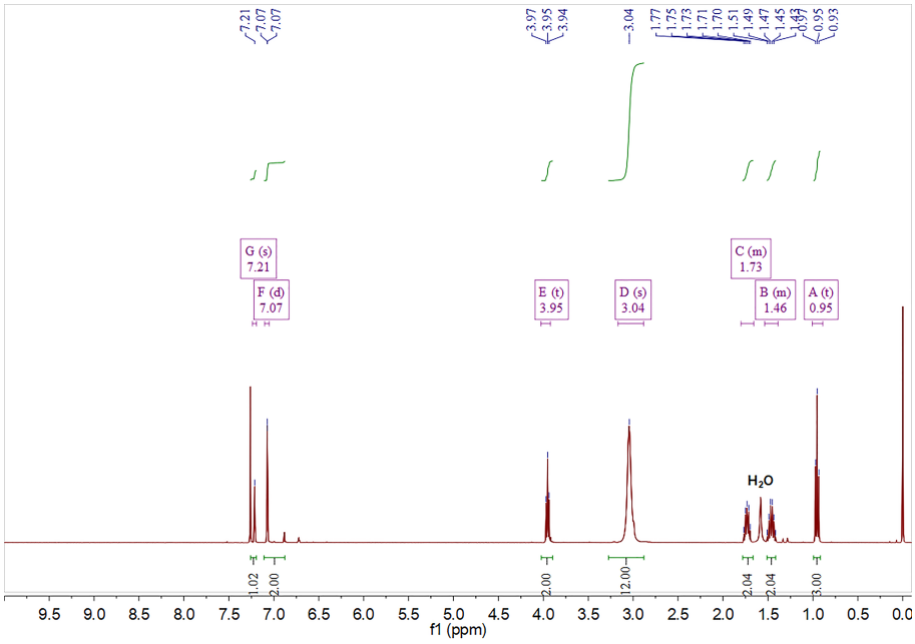

Fig. S8 ^{1}H NMR of S,S'-(5-butoxy-1,3-phenylene) bis(dimethylcarbamothioate) in $CDCl_3$.

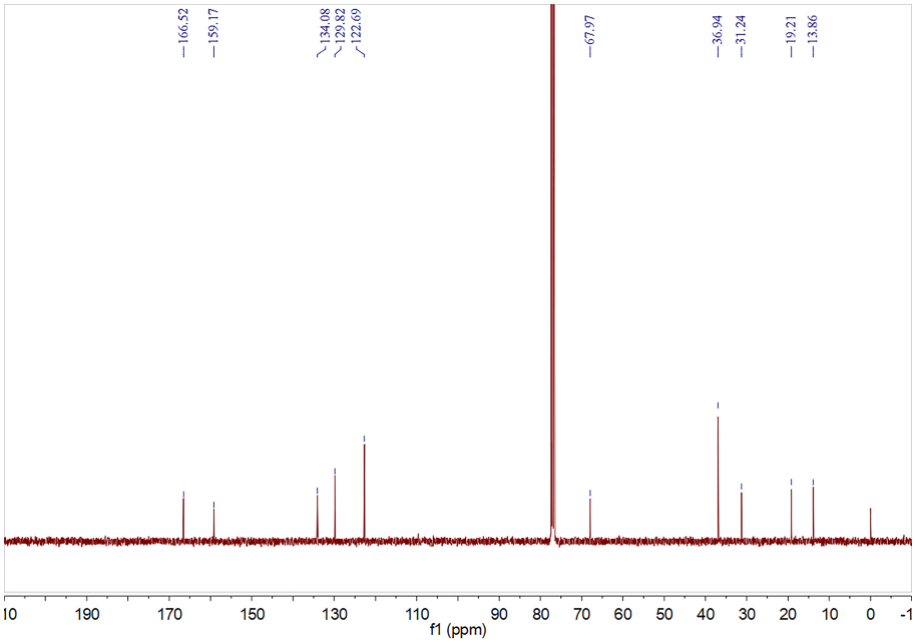

Fig. S9 ^{13}C NMR of S,S'-(5-butoxy-1,3-phenylene) bis(dimethylcarbamothioate) in $CDCl_3$.

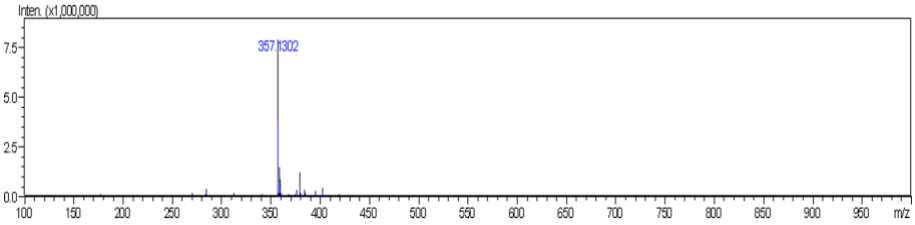

Fig. S10 High resolution mass spectrum of S,S'-(5-butoxy-1,3-phenylene) bis(dimethylcarbamothioate).

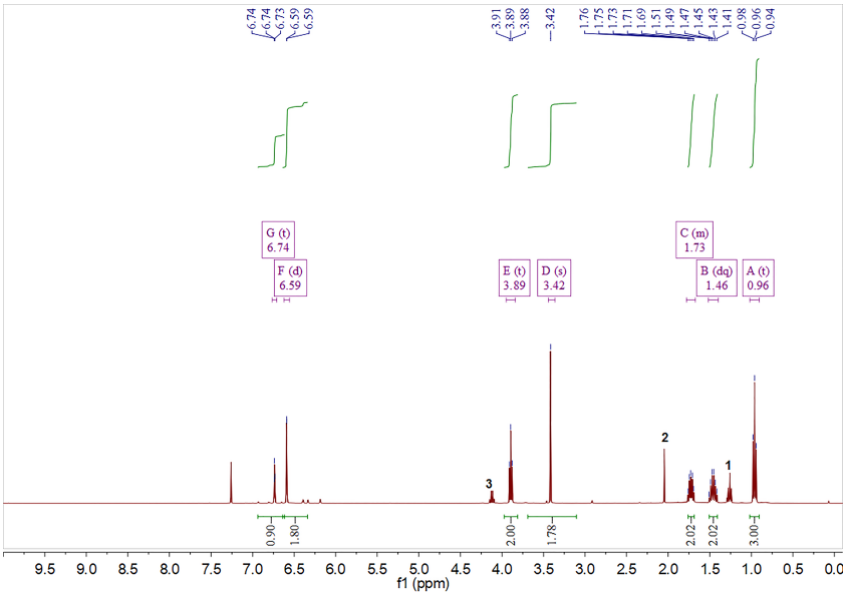

Fig. S11 ^{1}H NMR of 5-butoxybenzene-1,3-dithiol in $CDCl_3$, in which the peaks 1, 2, 3 are assigned to the residual solvent ethyl acetate.

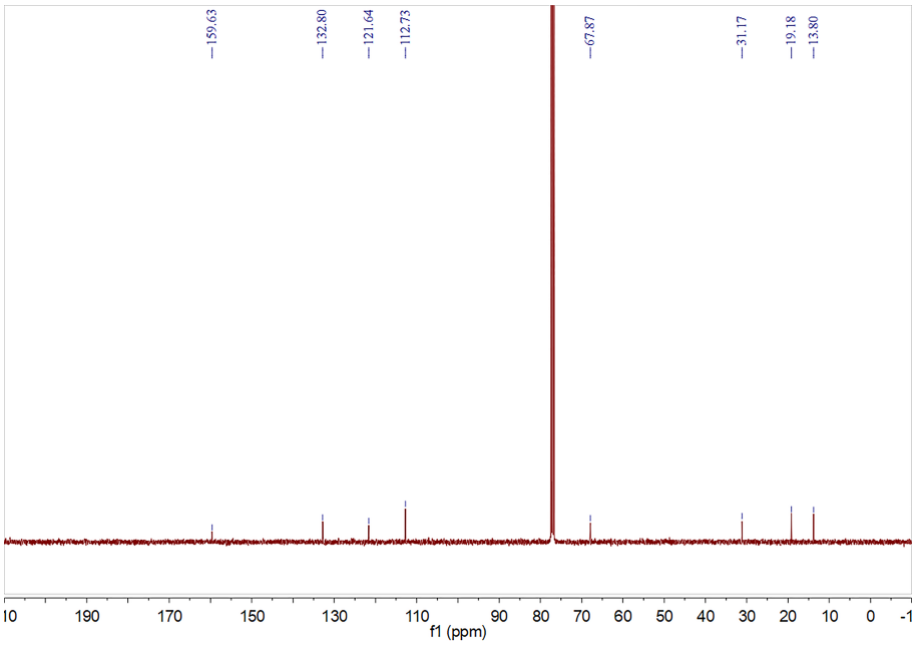

Fig. S12 ^{13}C NMR of 5-butoxybenzene-1,3-dithiol in $CDCl_3$.

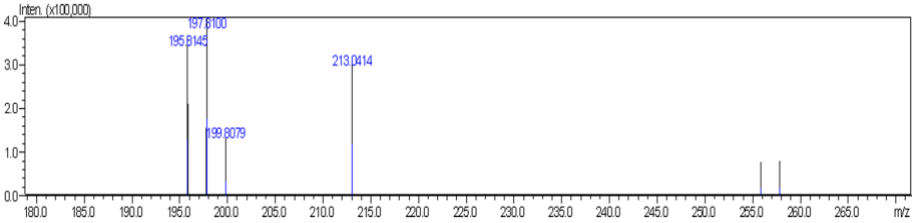

Fig. S13 High resolution mass spectra of 5-butoxybenzene-1,3-dithiol.

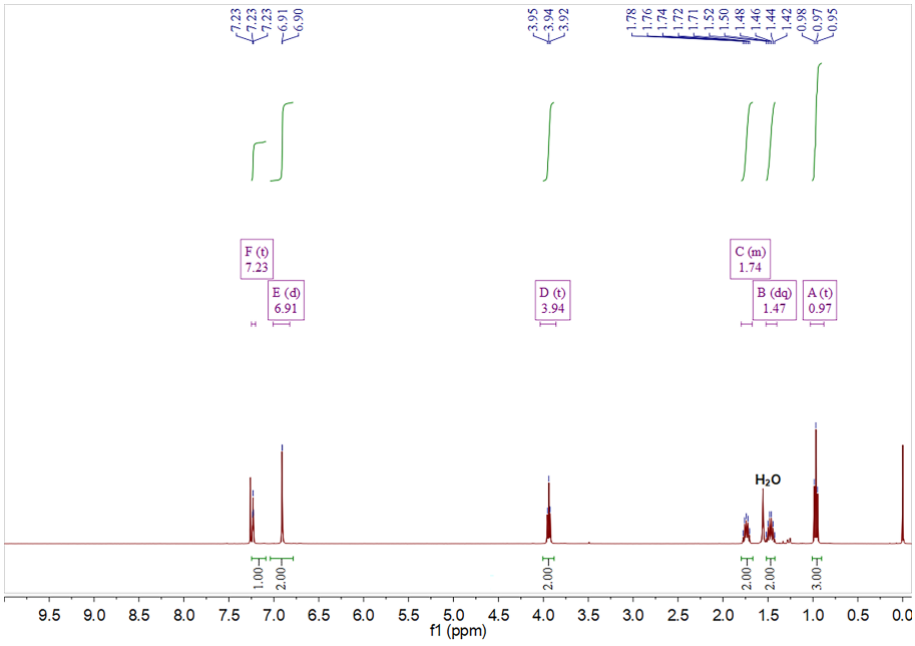

Fig. S14 ^{1}H NMR of the disulfide macrocycle (DSM) in $CDCl_3$.

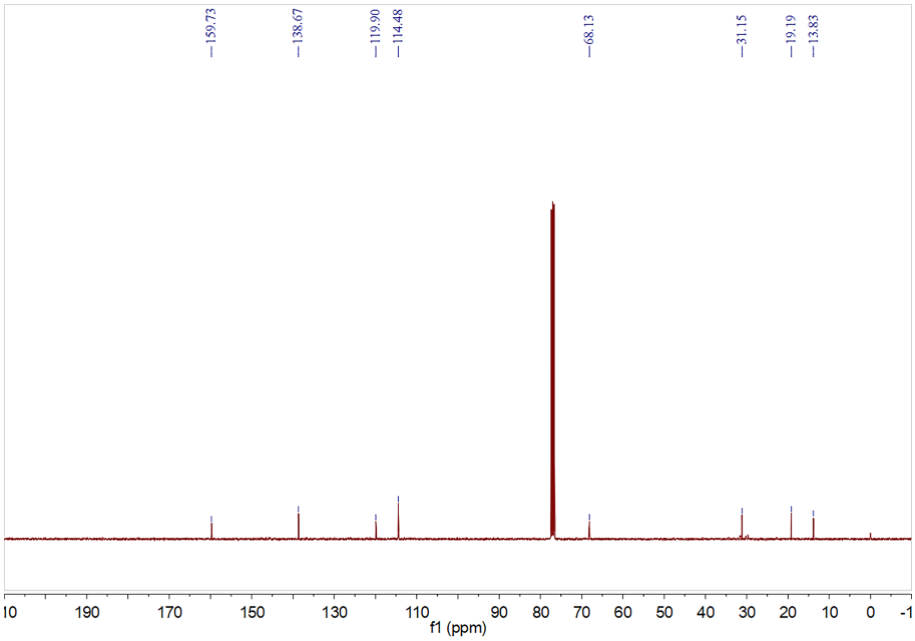

Fig. S15 ^{13}C NMR of the disulfide macrocycle (DSM) in $CDCl_3$.

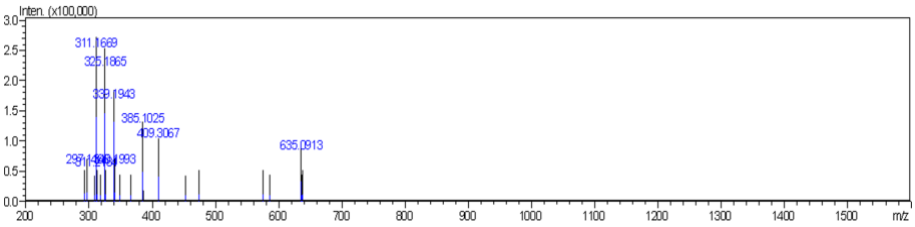

Fig. S16 High resolution mass spectrum of the disulfide macrocycle (DSM).

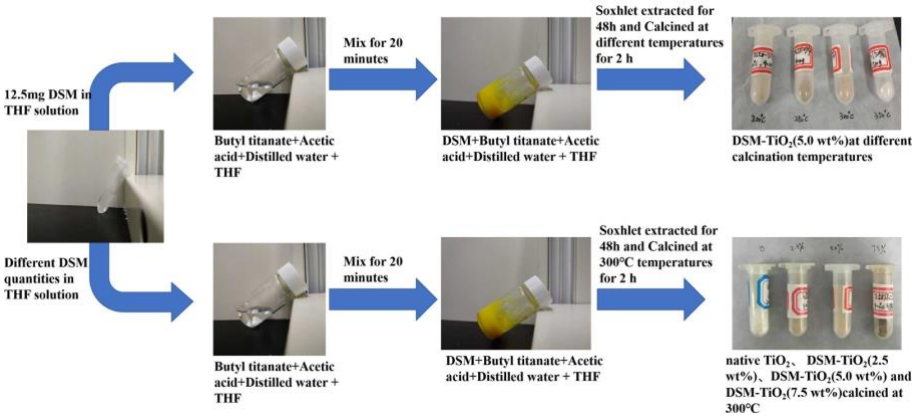

Fig. S17 DSM-TiO_2(5.0 wt%) at different calcination temperatures and DSM-TiO_2 with different DSM content (native TiO_2、DSM-TiO_2(2.5 wt%)、DSM-TiO_2(5.0 wt%)、DSM-TiO_2(7.5 wt%)) at 300℃ were synthesized.

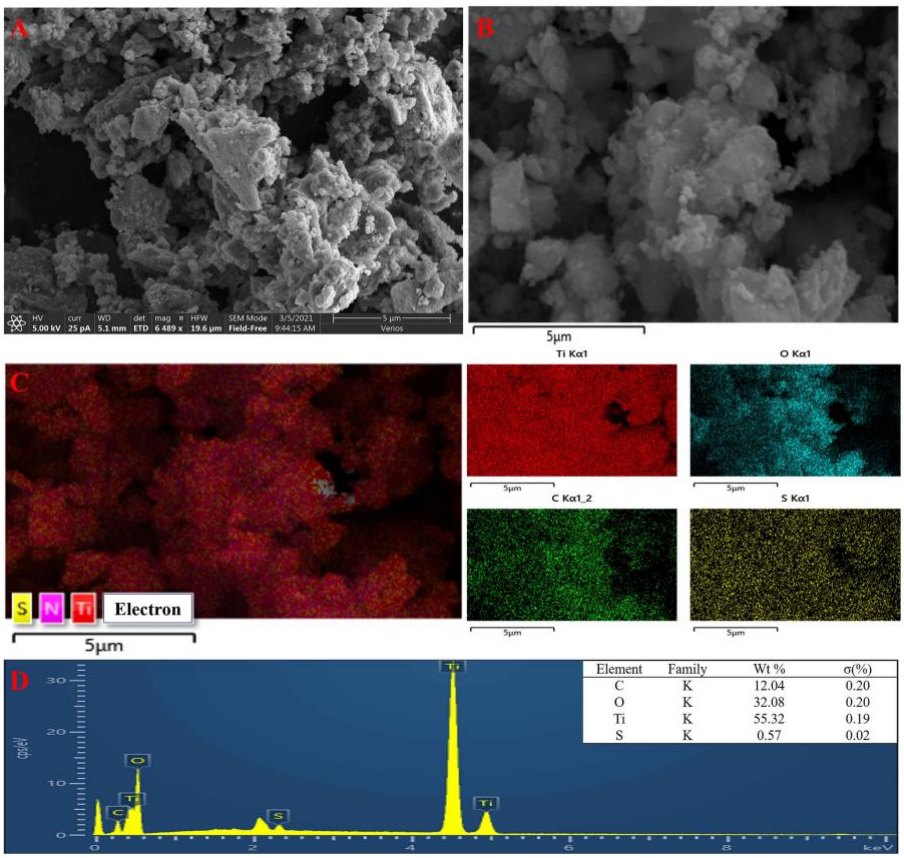

Fig. S18 (A) and (B) SEM, (C) the elemental mapping image, and (D) EDX analysis of DSM-TiO_2(5.0 wt%).

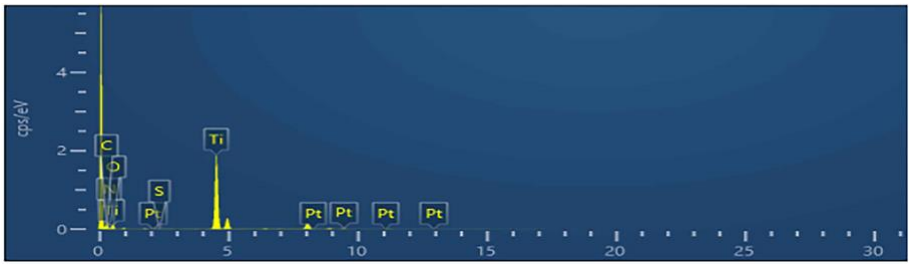

Fig. S19 The EDX analysis of the Pt/DSM-TiO_2(5.0 wt%).

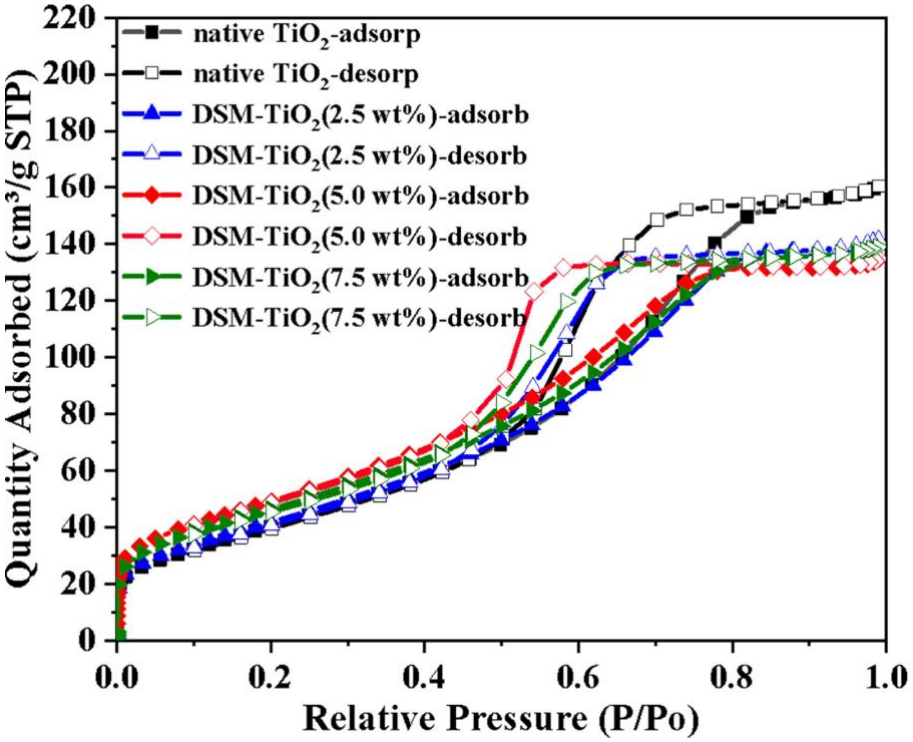

Fig. S20 The physical absorption and desorption measured at 77K of native TiO_2 and DSM-TiO_2(2.5/5.0/7.5 wt%).

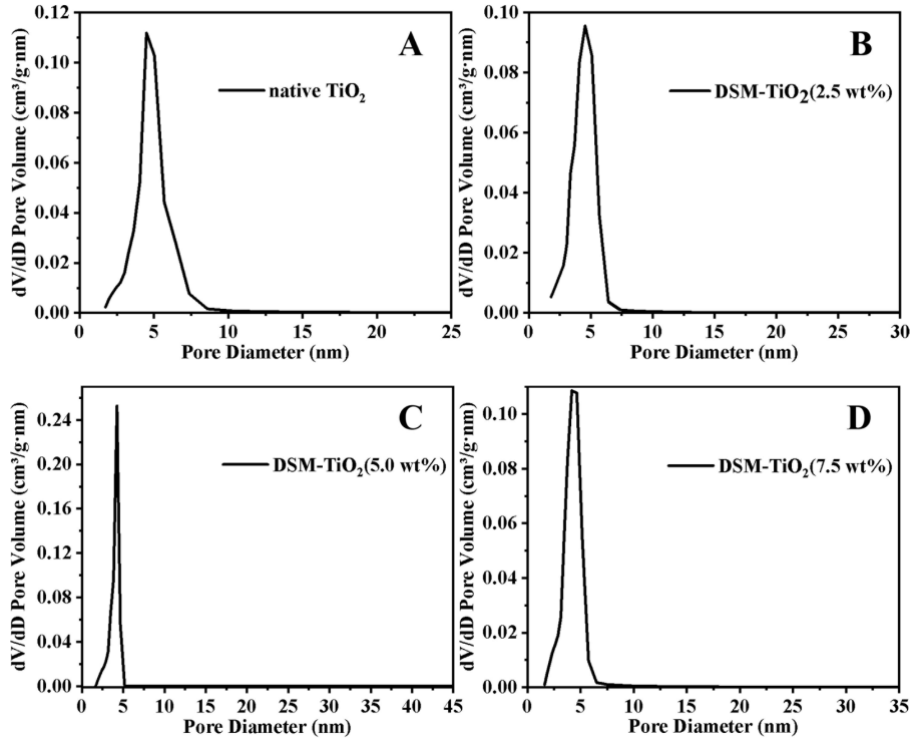

Fig. S21 Pore distribution of native TiO_2 and DSM-TiO_2(2.5/5.0/7.5 wt%).

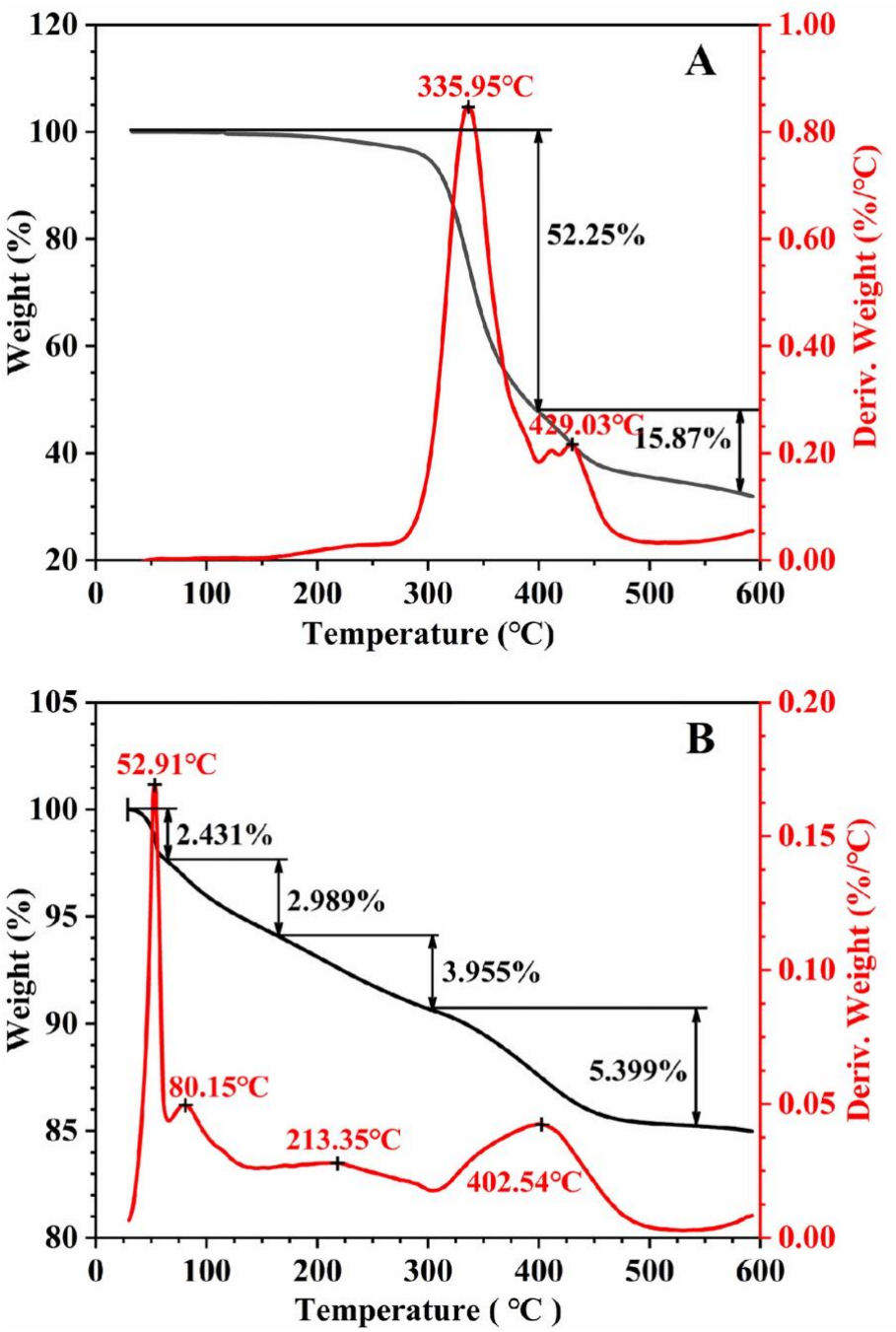

Fig. S22 Thermogravimetric analysis of (A) DSM and (B) DSM-TiO_2(7.5 wt%) materials. The temperature gradient was from room temperature to 600℃ at a heating rate at 10 ℃/min.

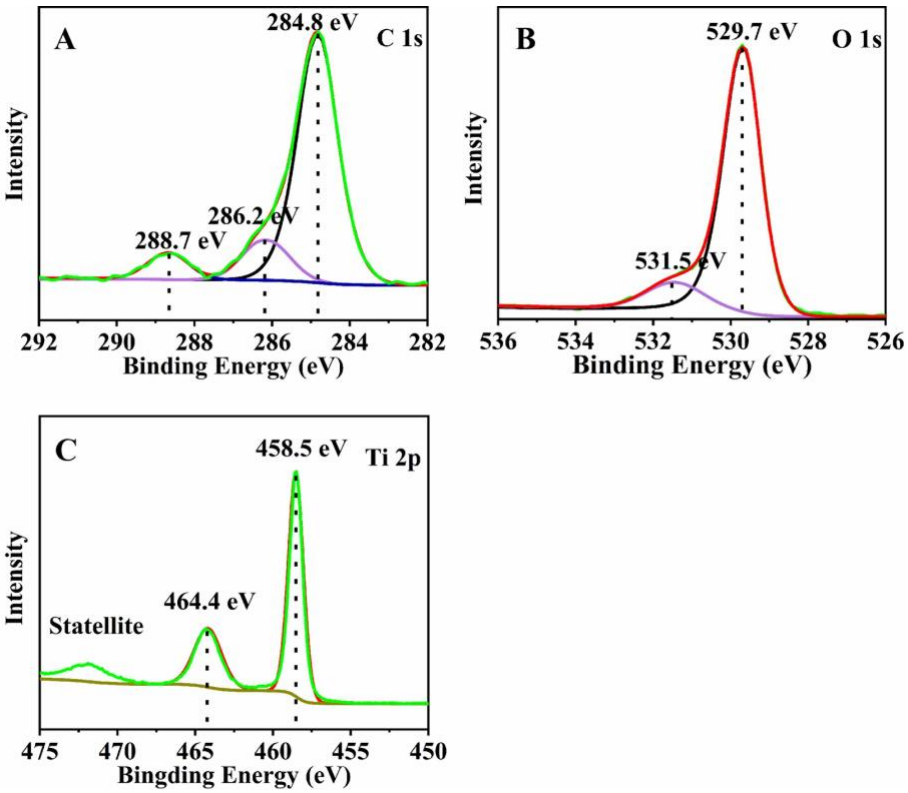

Fig. S23 X-ray photoelectron spectra for Ti and O of native TiO_2. Atomic ratio of Ti : O = 36% : 63% ≈ 1 : 2.

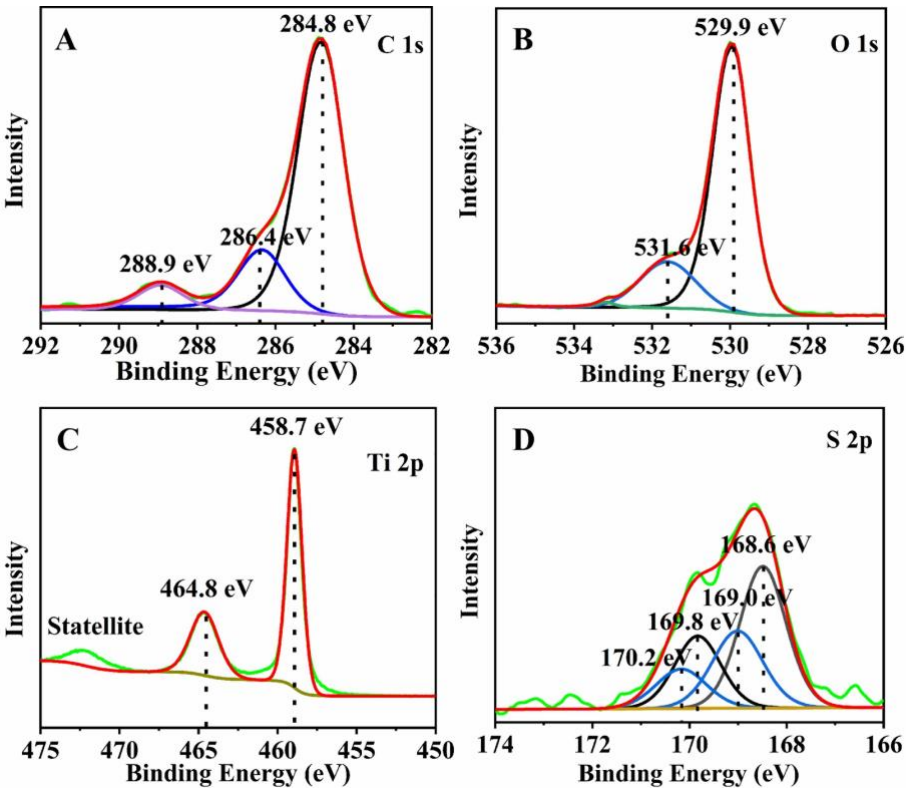

Fig. S24 X-ray photoelectron spectra for Ti, O and S of DSM-TiO_2(5.0 wt%). The weight ratio of Ti : O : S = 50% : 36% : 2.0%; Atomic ratio of Ti : O = 25% : 53% ≈ 1 : 2.

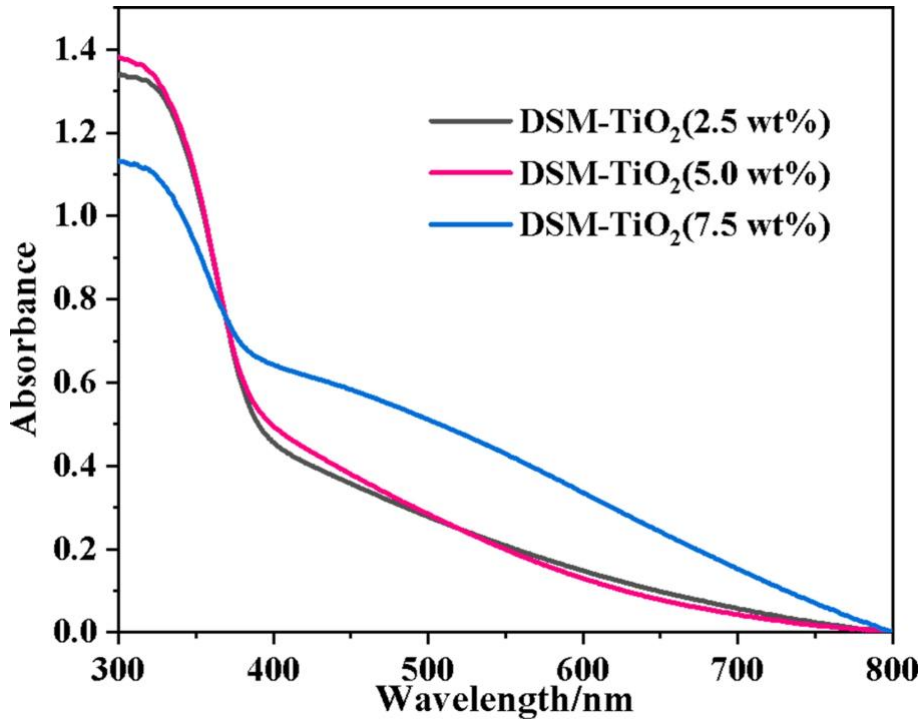

Fig. S25 The solid UV-vis spectrum of DSM-TiO_2(2.5\5.0\7.5 wt%).

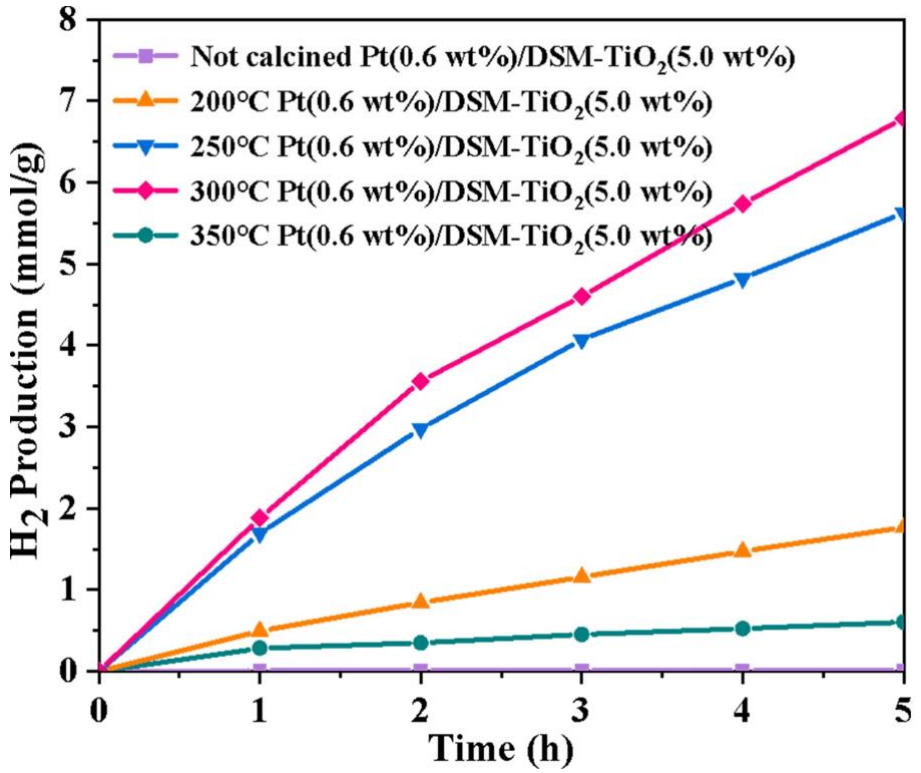

Fig. S26 Hydrogen production performance of DSM-TiO_2(5.0 wt%) calcined at different temperatures.

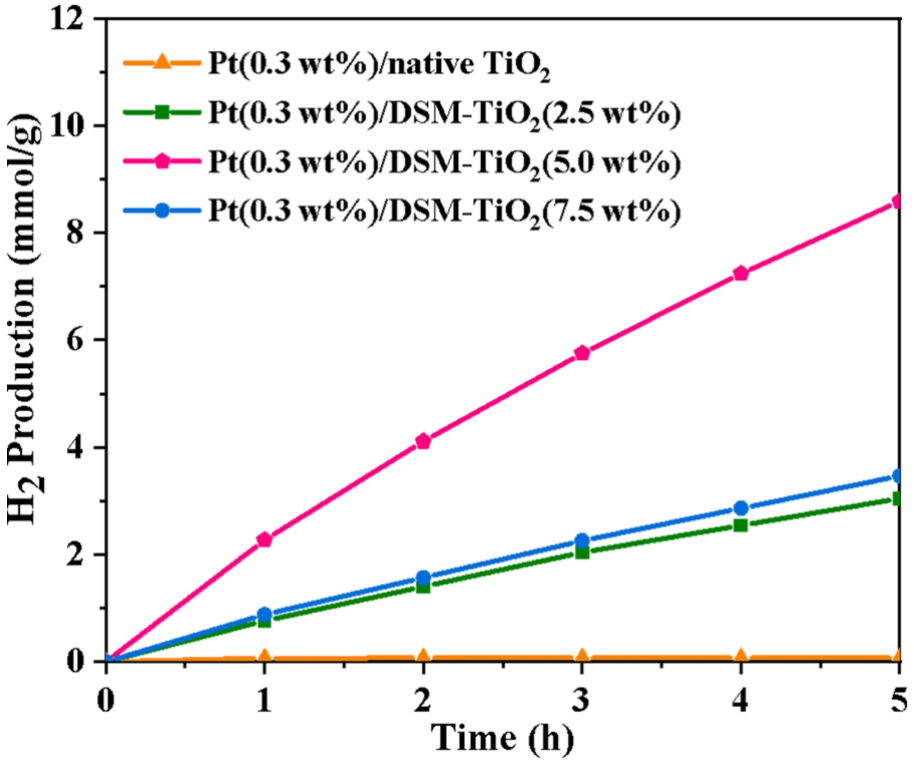

Fig. S27 Hydrogen production performance of DSM-TiO_2 with different dosages of DSM dopant.

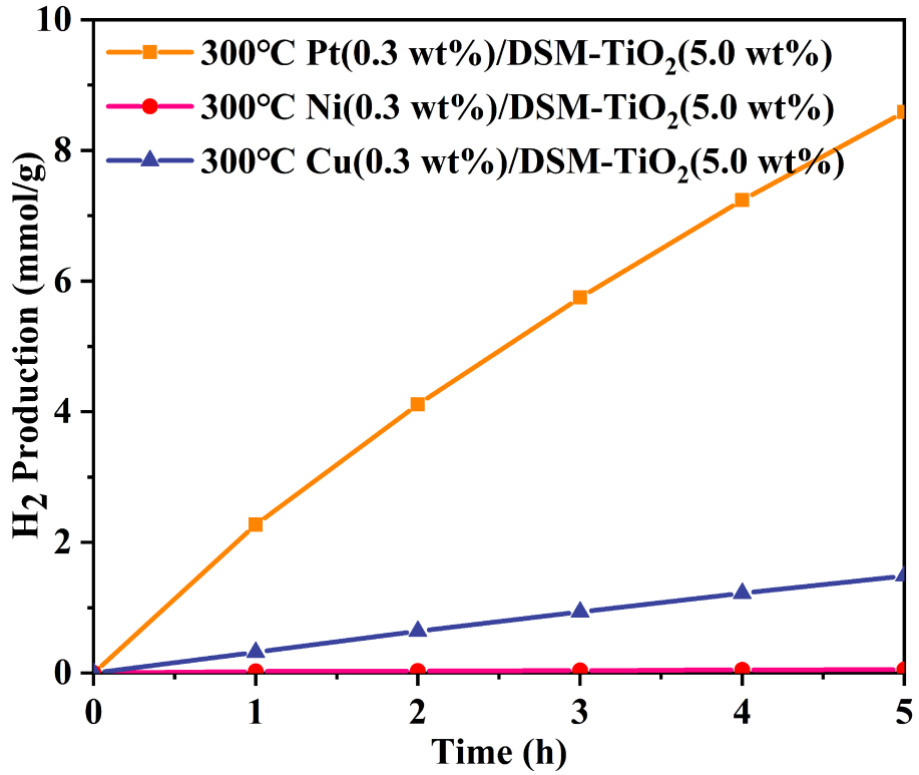

Fig. S28 Hydrogen production performance of DSM-TiO_2 with Pt, Ni and Cu.

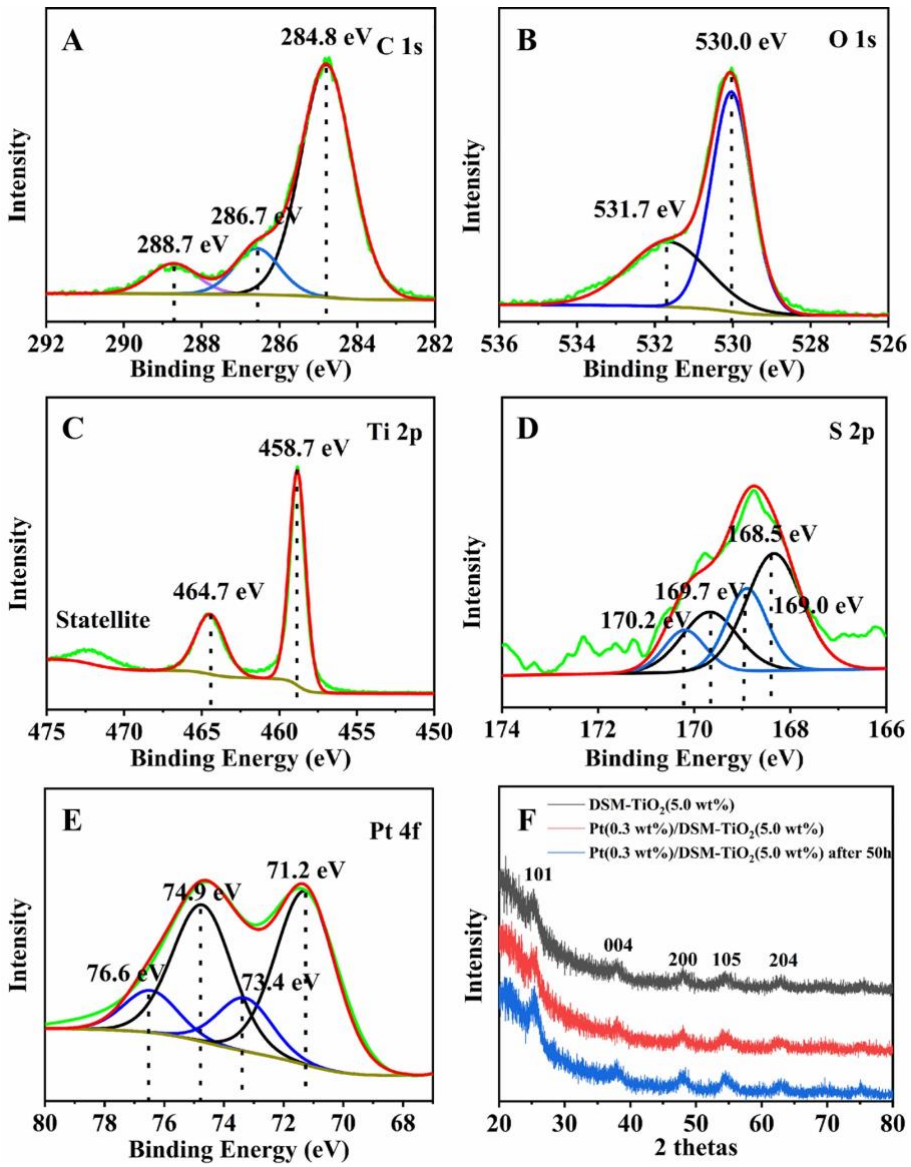

Fig. S29 XPS and XRD analysis of Pt(0.3 wt%)/DSM-TiO_2(5.0 wt%) after the 50 hours' cycle stability experiment.

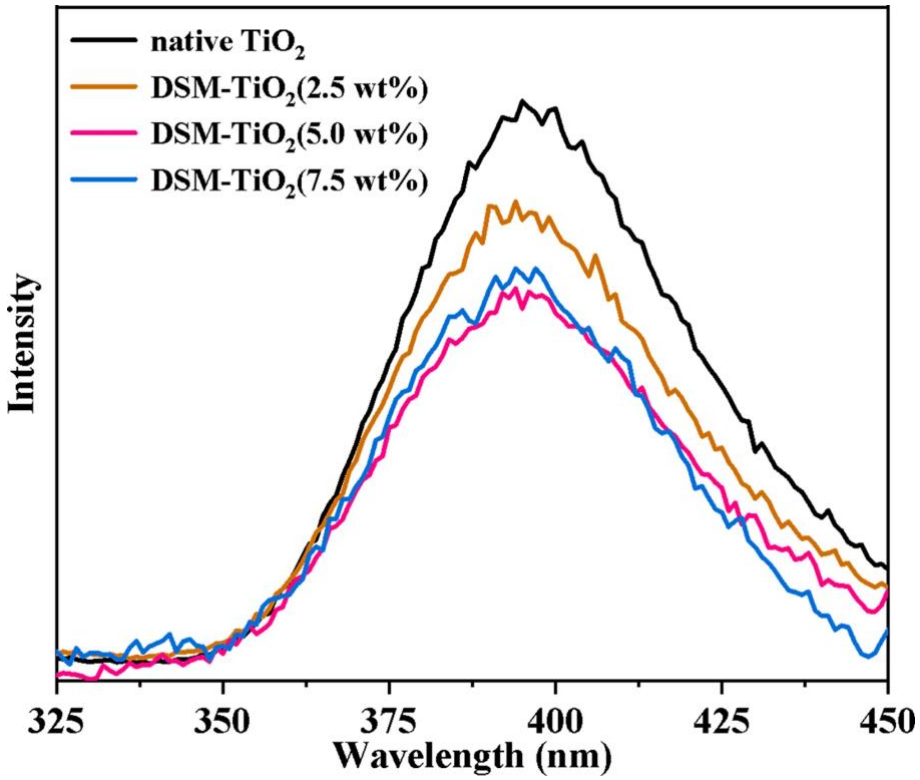

Fig. S30 Solid steady state fluorescence spectrum of native TiO_2 and DSM-TiO_2(2.5/5.0/7.5 wt%).

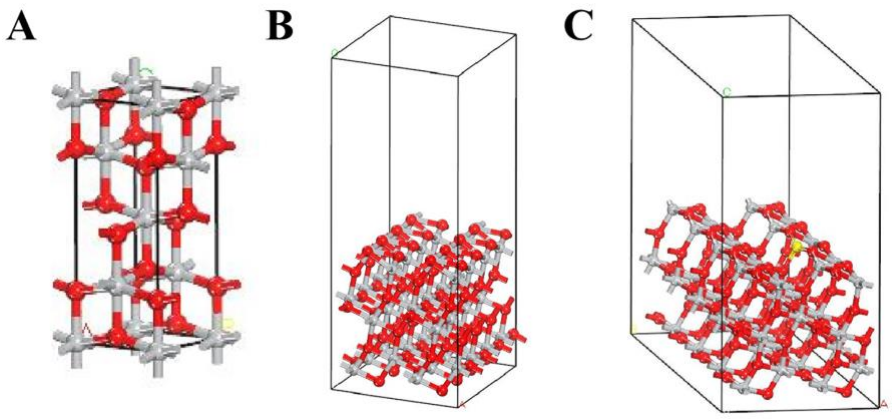

Fig. S31 Density Functional theory (DFT) computes the structural model: (A) Anatase TiO_2 cell, (B) Calculation model of anatase TiO_2, (C) Calculation model of S-TiO_2. Red is oxygen, silver is titanium, and yellow is sulfur.

Table. S1 Pt and S contents in DSM-TiO_2(5.0 wt%) analysed by ICP-AES.

Sample	Pt content（wt%）
Pt(0.3 wt%)/DSM-TiO_2 (5.0 wt%)	0.3
Pt(0.6 wt%)/DSM-TiO_2 (5.0 wt%)	0.5
Pt(1.0 wt%)/DSM-TiO_2 (5.0 wt%)	0.8
Pt(1.5 wt%)/DSM-TiO_2 (5.0 wt%)	1.4
Pt(2.0 wt%)/DSM-TiO_2 (5.0 wt%)	2.0
Sample	S content（wt%）
DSM-TiO_2 (5.0 wt%)	1.5

Table. S2 Specific surface area, pore size and pore volume of native TiO_2 and DSM-TiO_2 materials measured by adsorption isotherm at 77K.

Sample	Surface area (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)
native TiO_2	154.73	4.80	0.252
DSM-TiO_2(2.5 wt%)	159.08	5.40	0.219
DSM-TiO_2(5.0 wt%)	181.07	3.91	0.216
DSM-TiO_2(7.5 wt%)	172.44	4.20	0.221

Table. S3 The apparent quantum yield of 20mg DSM-TiO_2(5.0 wt%) material that was irradiated under 405 nm and 450 nm LED lamps for 1 hour respectively.

Sample	Pt(0.3 wt%)/DSM-TiO_2 (5.0 wt%)	Pt(0.3 wt%)/DSM-TiO_2 (5.0 wt%)
Wavelength(nm)	405	450
AQY	1.15	0.64