Electronic Supporting Information (ESI)

Ytterbium-nitrogen co-doped ordered mesoporous TiO_2: The innovative hetero-phase photocatalyst for harnessing solar energy in green hydrogen production[†]

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[†]*Dedicated to Professor Dr. Dionisios G. Vlachos on the occasion of his 60th birthday*

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Table S1. Electrochemical data (EIS and MS) of various titania samples.

Photocatalyst	†R_{ct} (Ω)	‡C_{dl} (μF)	§V_{fb} (V *vs* RHE)	¶N_D (cm^{-3})	$$V_{fb}^{maj}$ (V *vs* RHE)	£N_D^{maj} (cm^{-3})
Yb/N-TMF-127(350)	738	99.7	– 0.469	1.32×10^{14}	– 0.765	2.36×10^{14}
N-TMF-127(350)	746	22.9	– 0.440	1.81×10^{14}	– 0.759	2.15×10^{14}
P-25	813	12.4	– 0.461	1.58×10^{15}	– 0.626	2.76×10^{15}

†Charge transfer resistance; ‡Double layer capacitance ($-1/2\pi f Z_{max}$); §Minor flat-band potential; ¶ Minor carrier density (donor density); $Major flat- band potential; £Major carrier density (donor density).

Table S2. Equivalent circuit fitted data for various titania samples.

Photocatalyst	R_1 † (Ω)	CPE_1 ‡ (μF)	n ($0 < n < 1$)	R_2 § (Ω)	CPE_2 ‡ (μF)	n ($0 < n < 1$)	R_3 § (Ω)	W¶ ($S.s^{1/2}$)	χ^2 $
Yb/N-TMF-127(350)	0.9	31.7	0.9	320	45.6	1	362	0.02	0.000166
N-TMF-127(350)	0.8	15.9	0.9	764	0.20	1	1	0.87	0.000648
P-25	0.5	0.16	0.9	475	0.20	0.9	342	2.20E+10#	0.000237

† R_1 - Solution resistance; ‡ Constant phase element; § R_2 and R_3 - Charge transfer resistance; ¶ W-Warburg diffusion; # This is fitted data value, the high slope value of Nyquist tail which can be seen at low frequency.

Table S3. Recent advances in developing low-cost photocatalysts for solar hydrogen generation.

Photocatalyst	Cocatalyst	Sacrificial agent	Light source	Hydrogen evolution ($mmol\ g^{-1}\ h^{-1}$)	Ref.
Yb/N-TMF-127(350)	NIL	Methanol-water	Solar Simulator (150 W)	1.3	This work
Yb/N-TMF-108(350)	NIL	Methanol-water	Solar Simulator (150 W)	1.2	This work
N-TMF-127(350)	NIL	Methanol-water	Solar Simulator (150 W)	1.0	This work
N-TMF-108(350)	NIL	Methanol-water	Solar Simulator (150 W)	0.9	This work
TiO2 (P-25)	NIL	Methanol-water	150 W Solar Simulator	0.4	This work
TiO_2	WSe_{2+x}	Ethanol-water	3W-LED (365 nm)	3.8	1
TiO_2	MoS_2	Methanol-water	3W-LED (365 nm)	2.4	2
TiO_2	MoS_{2+x}	Methanol-water	3W-LED (365 nm)	1.8	3
TiO_2	MoC	Methanol-water	3W-LED (365 nm)	0.5	4
TiO_2	Fe-Ni	Ethanol-water	Lamp (> 400 nm)	0.4	5
TiO_2	NiS	Methanol	350 W Xe lamp	0.7	6
TiO_2	Ni	Triethanolamine-water	UV-Visible lamp	1.2	7
TiO_2	Au@$ReSe_{2+x}$	Triethanolamine-water	3W-LED (365 nm)	6.0	8
TiO_2	NiS_x	Methanol-water	Xe lamp (300 W)	1.0	9
h-TiO_2	CoO	Methanol-water	Xe lamp (300W)	2.6	10
TiO_2	Cu_xP	Methanol-water	3W-LED 365 nm	1.9	11
10Yb10Bi_2S_3/TiO_2	Na_2S	Methanol-water	1000 W Xenon Lamp	0.1	12
Yb-doped TiO_2	Pt	Methanol-water	300 W Ultra Vitalux Lamp	8.4	13
La-doped TiO_2	Pt	Methanol-water	300 W Ultra Vitalux Lamp	7.8	13
Gd-doped TiO_2	Pt	Methanol-water	300 W Ultra Vitalux Lamp	13.2	13

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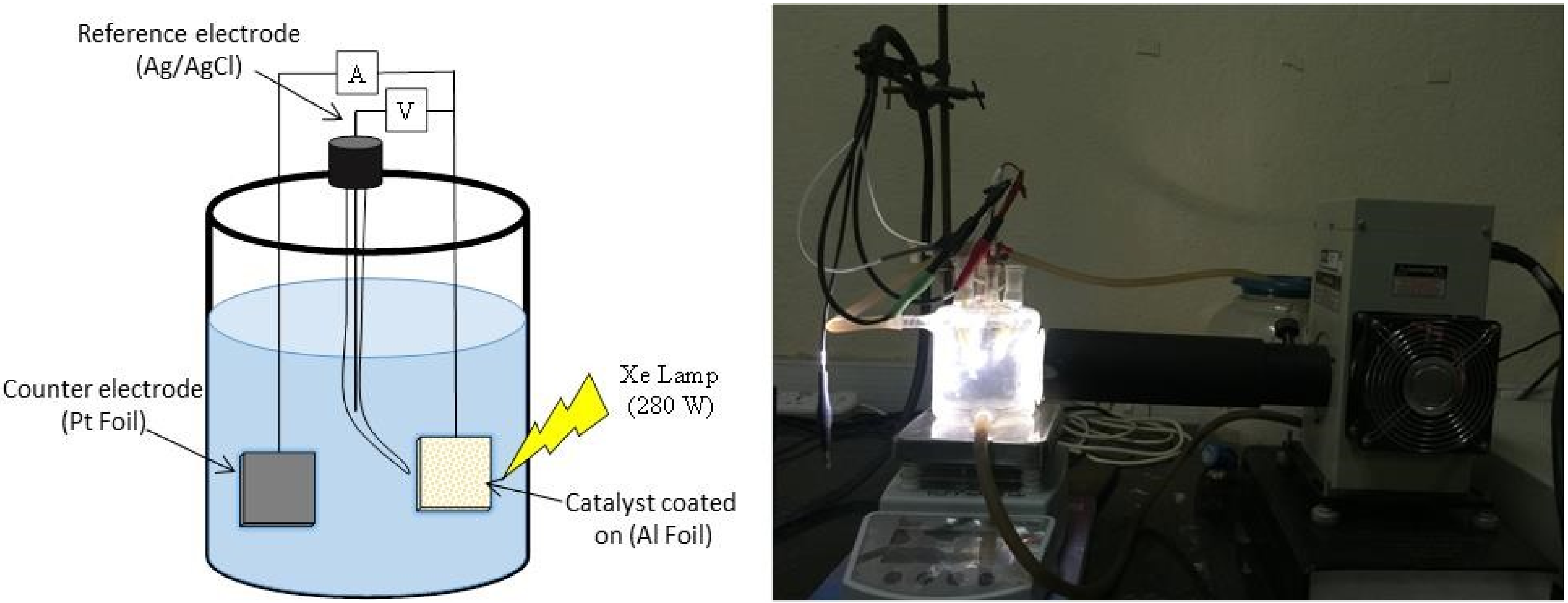

Figure S1. Photo-electrochemical reactor set-up: (a) Schematic; (b) Experimental system.

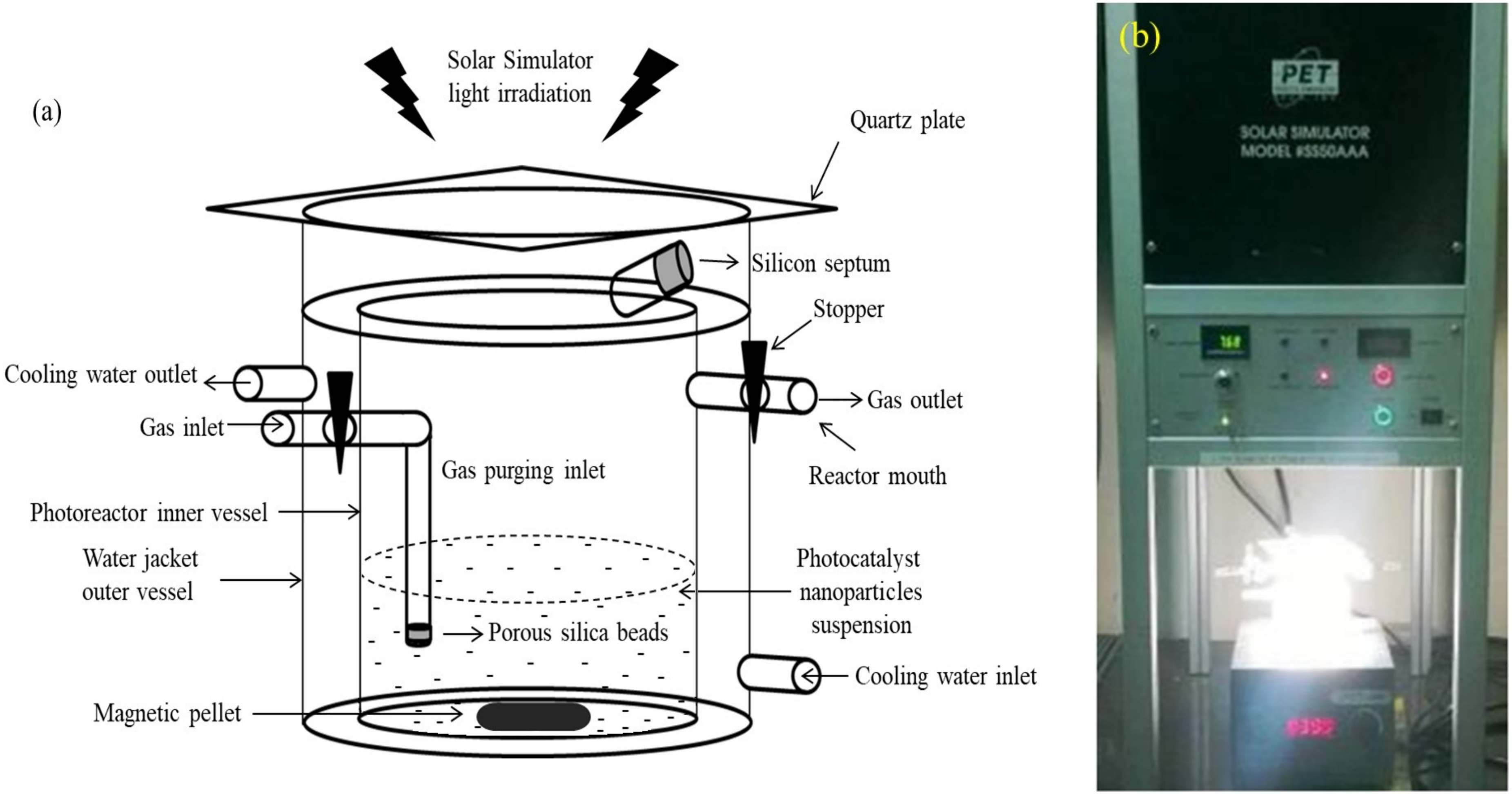

Figure S2. (a) A schematic photocatalytic reactor set-up. (b) Photocatalytic reactor system in a solar simulator.

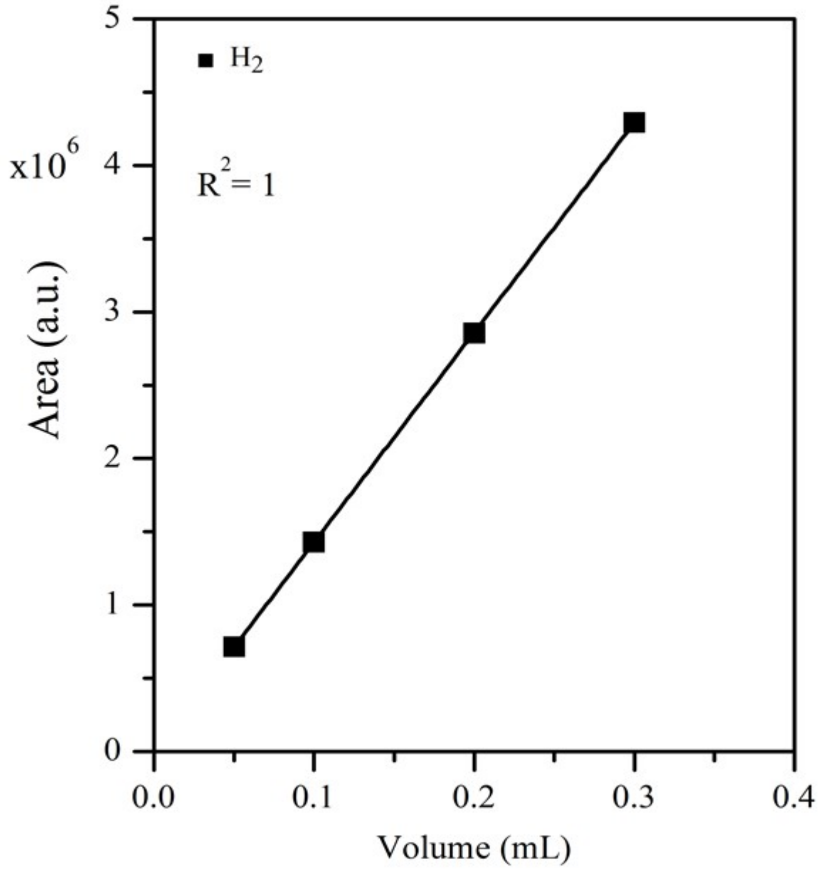

Figure S3. Calibration plot of hydrogen for quantitative analysis.

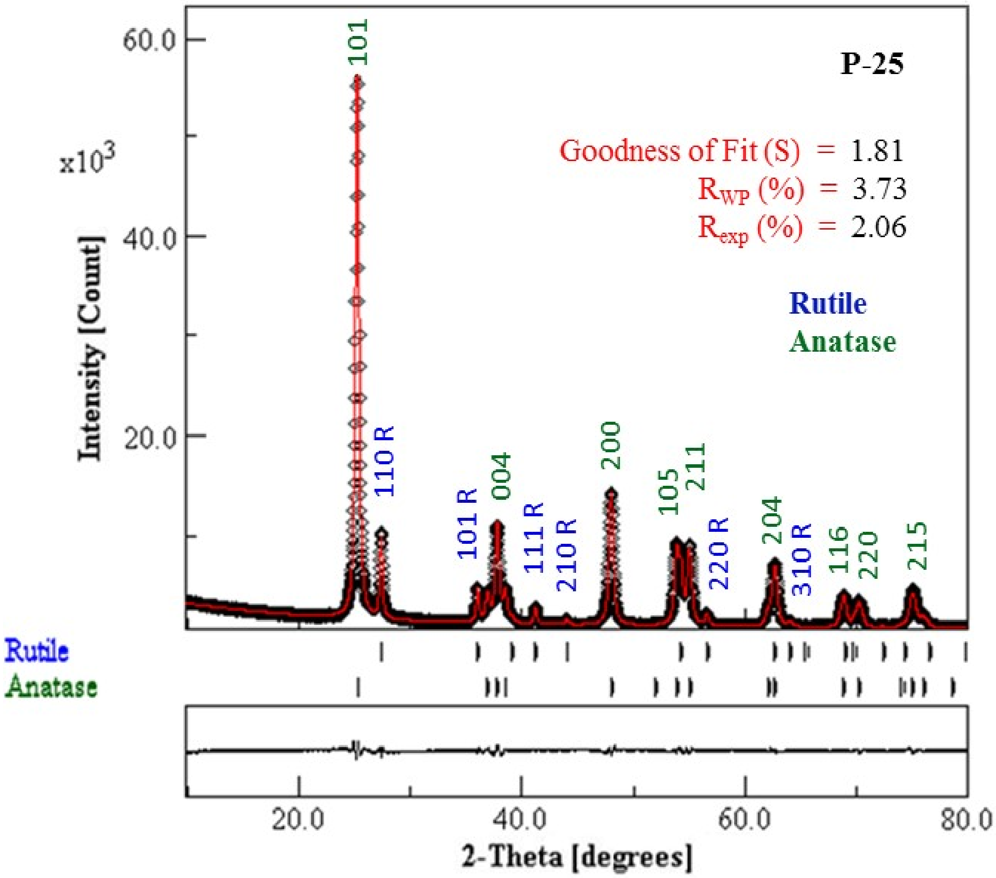

Figure S4. The Rietveld refined powder XRD pattern of P-25.

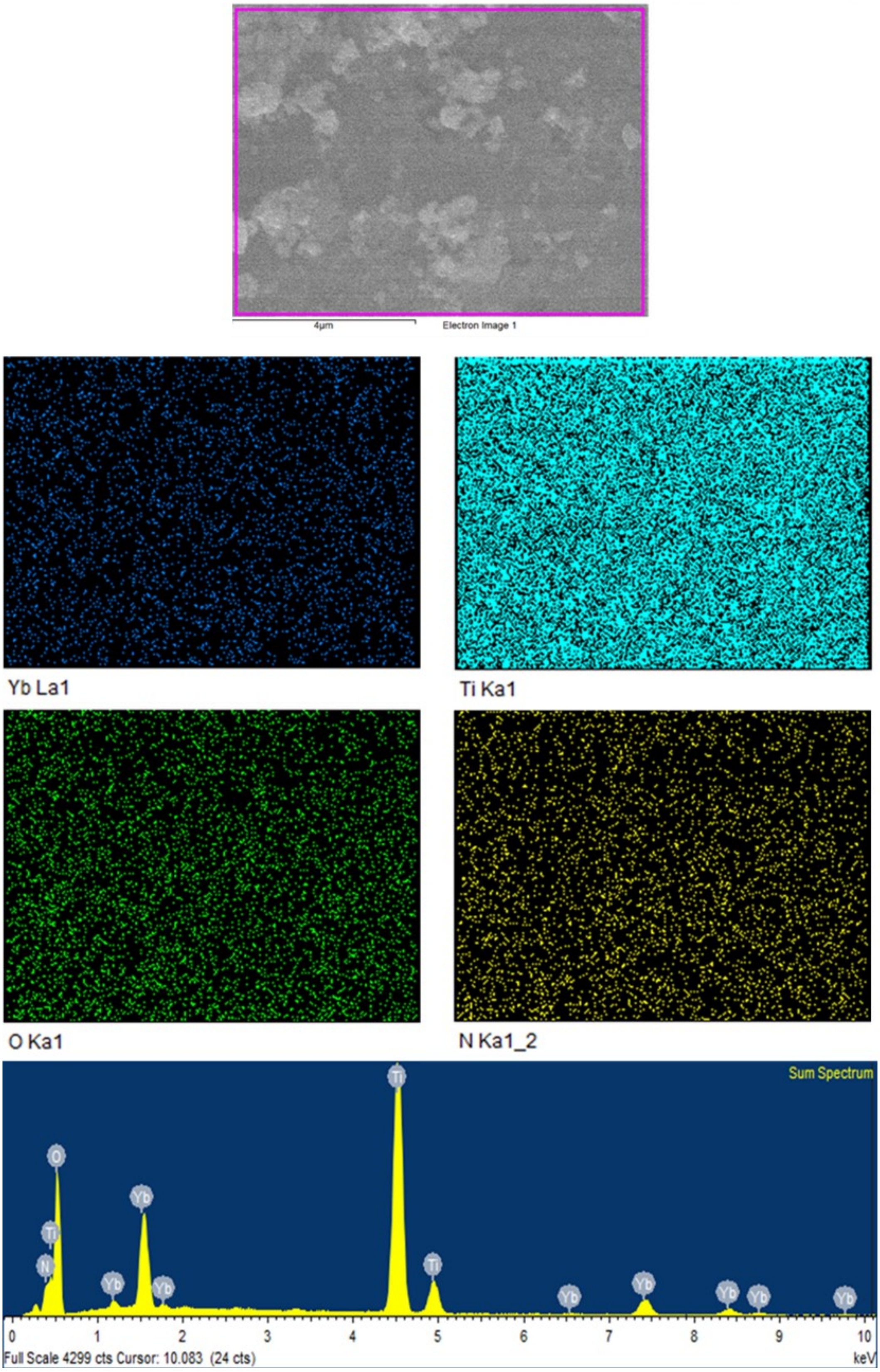

Figure S5. SEM image; EDX mapping and EDS spectra of Yb/N-TMF-127(350).

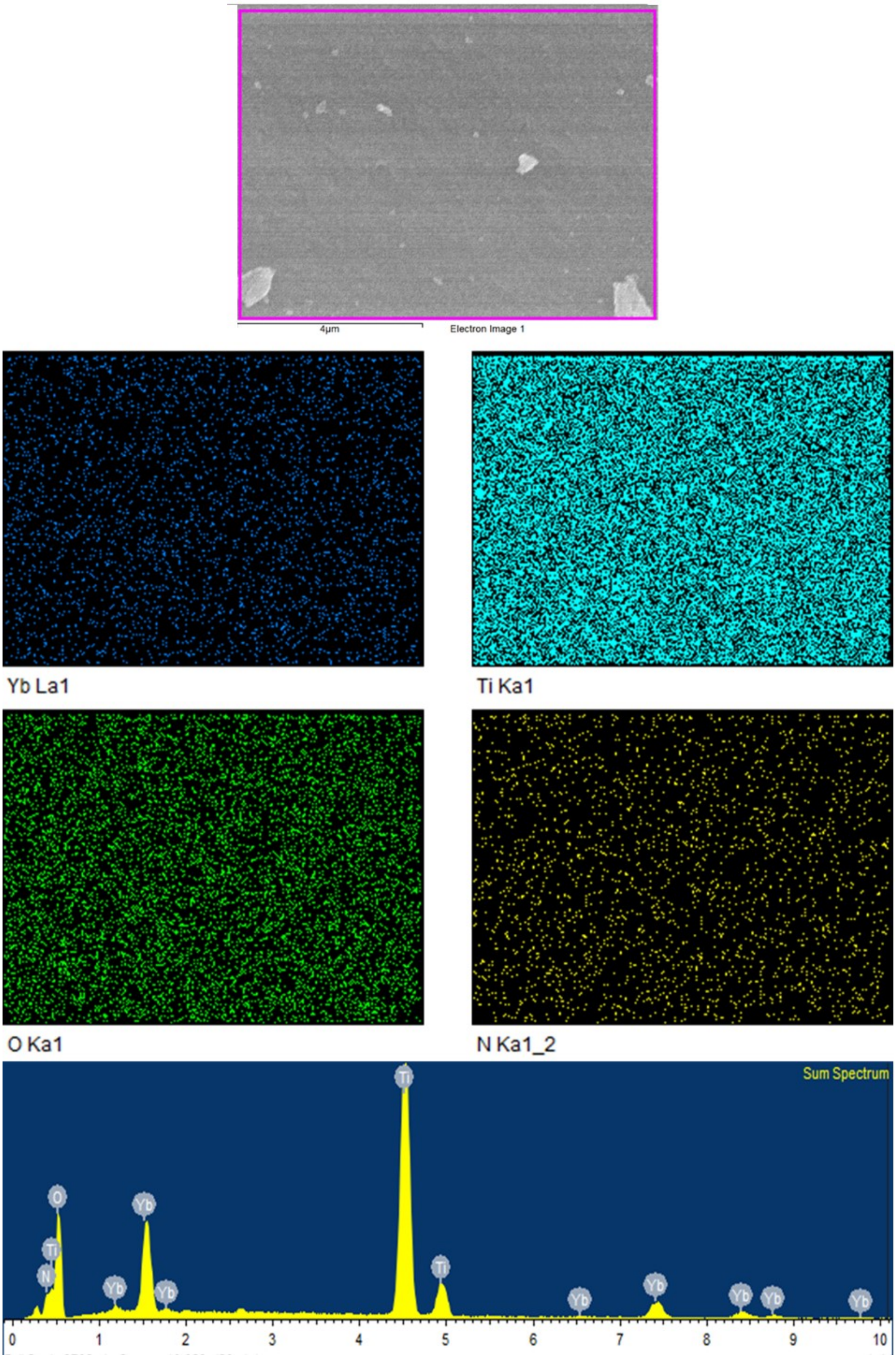

Figure S6. SEM image; EDX mapping and EDS spectra of Yb/N-TMF-108 (350).

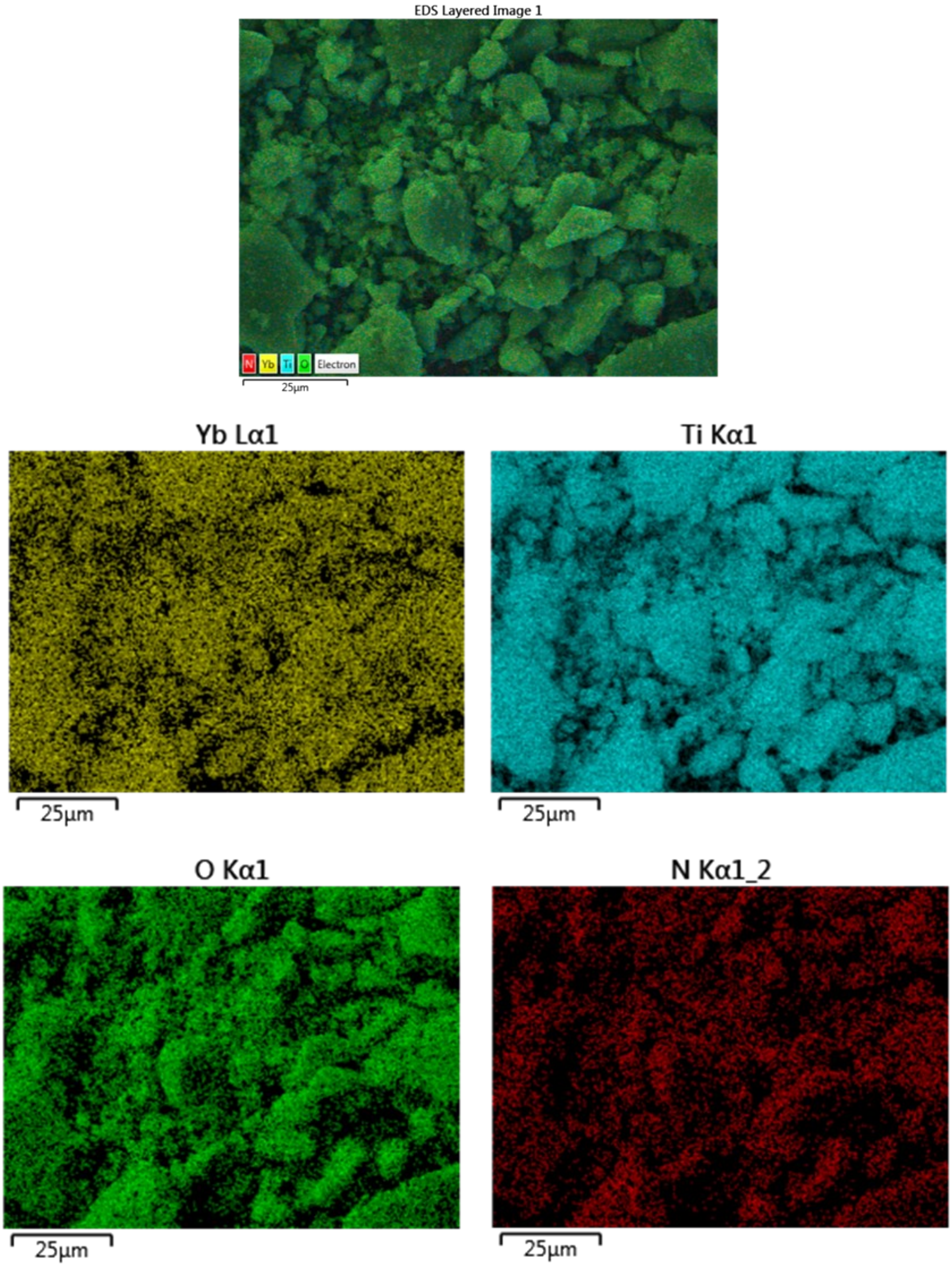

Figure S7. SEM image; EDX mapping and EDS spectra of Yb/N-TMF-127 (550).

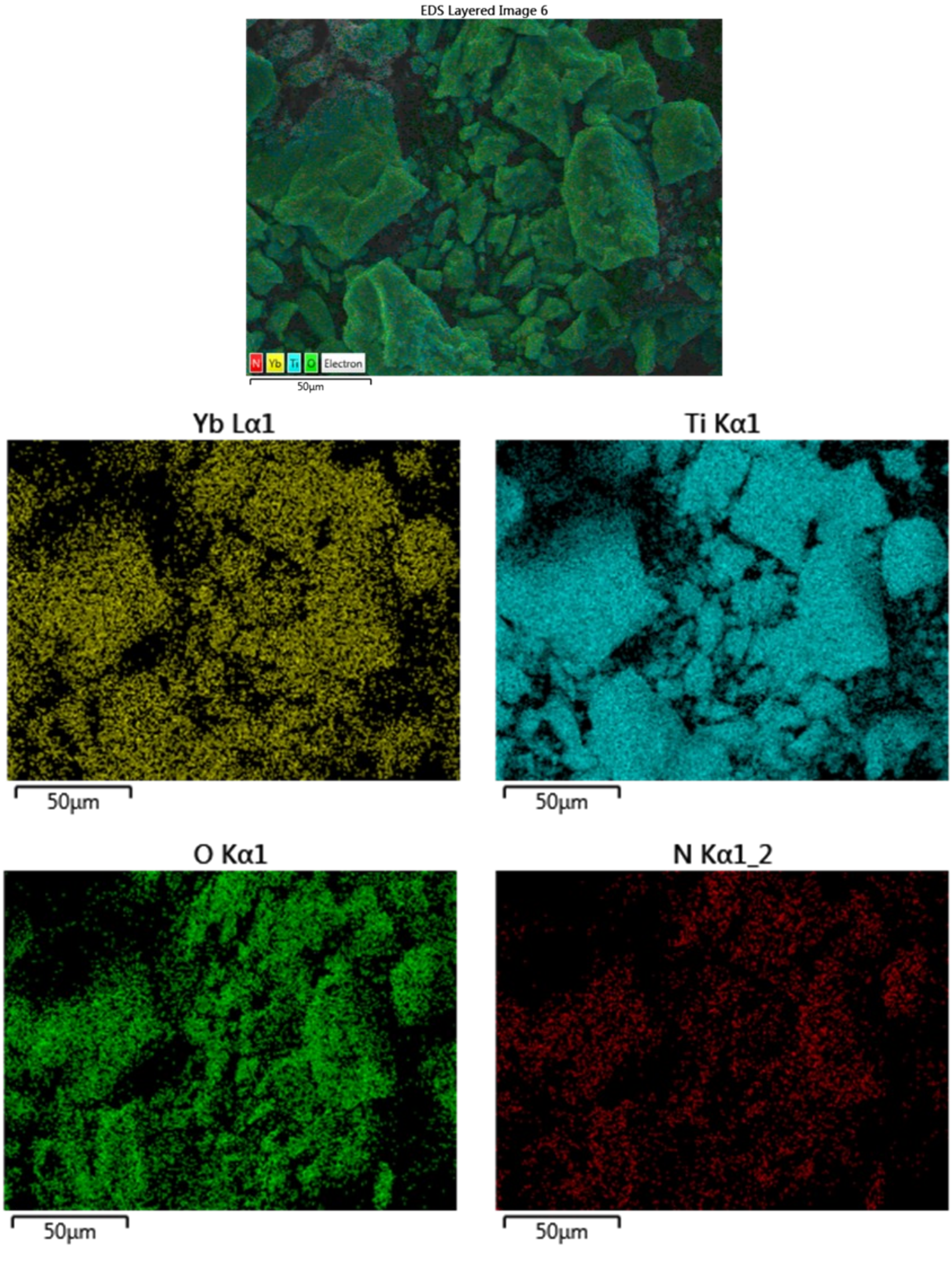

Figure S8. SEM image; EDX mapping and EDS spectra of Yb/N-TMF-108 (650).

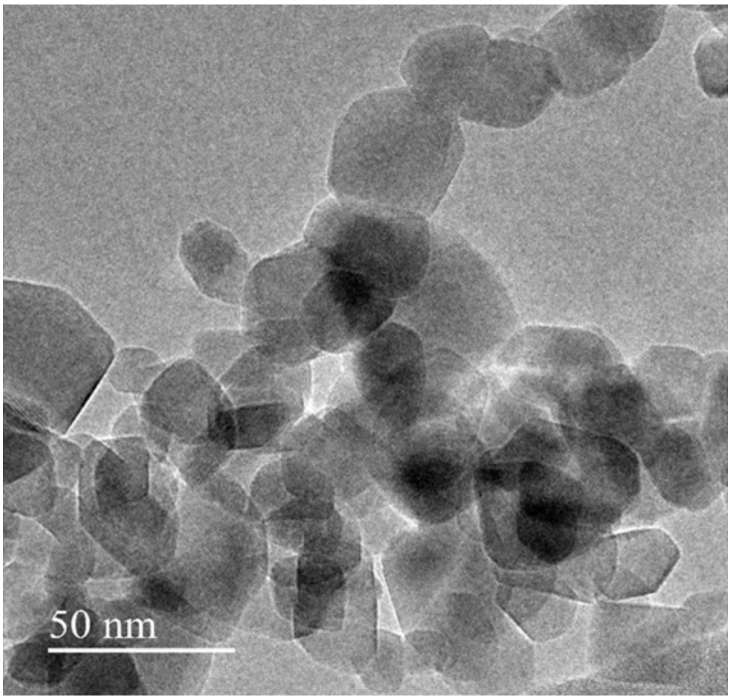

Figure S9. TEM image of TiO_2 (P-25) catalyst.

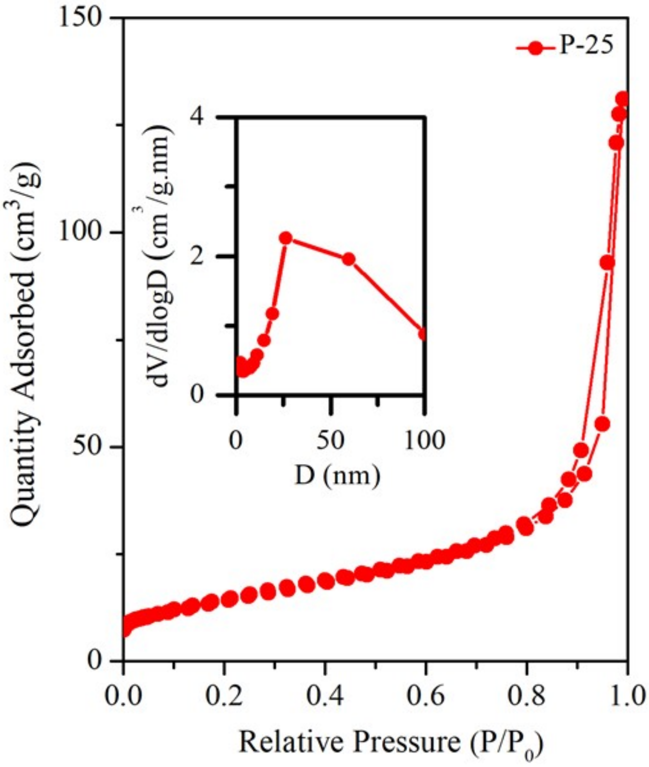

Figure S10. Nitrogen sorption isotherm of P-25

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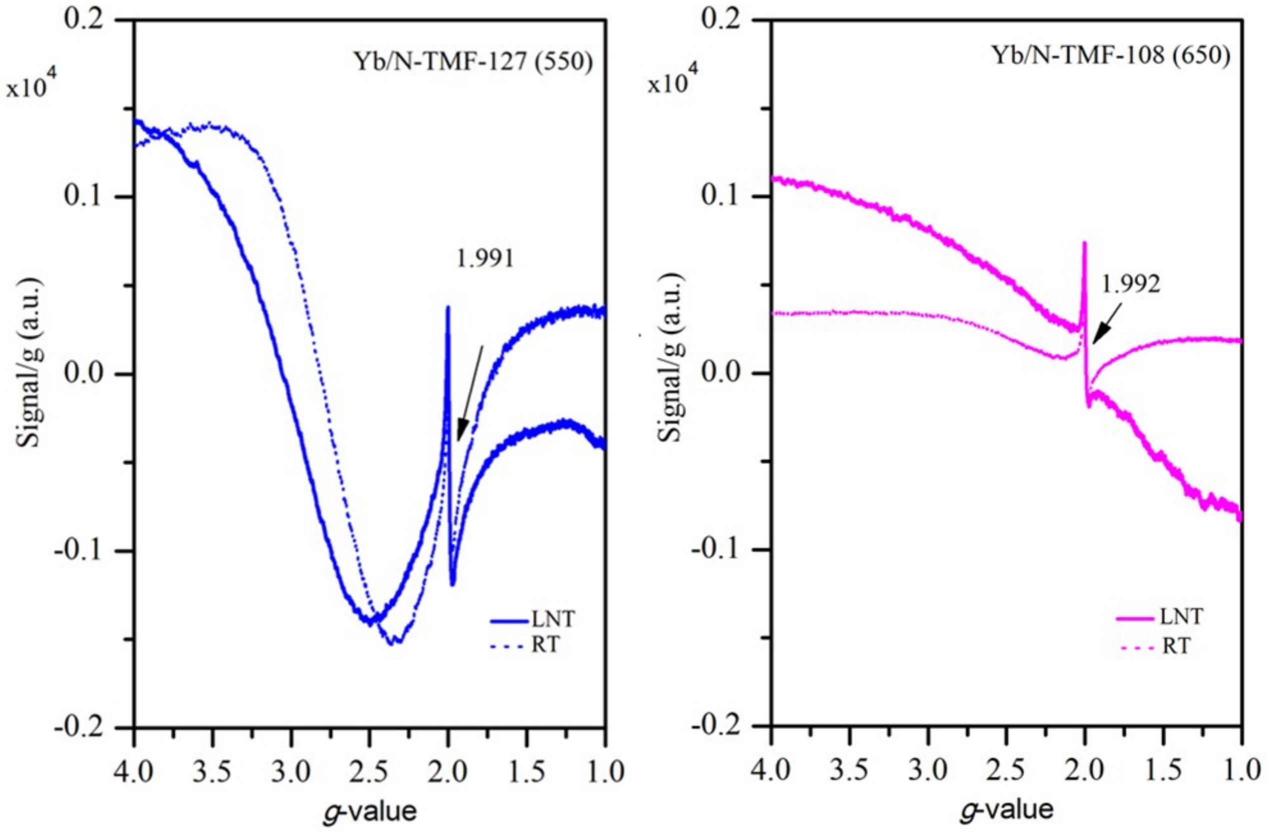

Figure S11. EPR spectra of Yb/N-OMT.

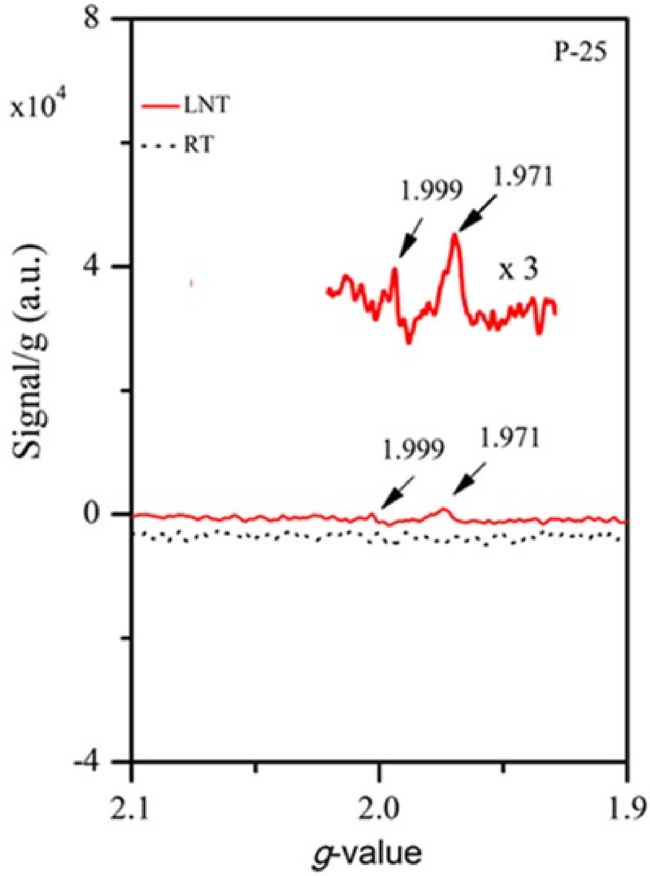

Figure S12. EPR spectra of P-25.