# Electronic Supplementary Information

## A Thienothiophene and Anthracene Based Functional Hyperbranched Polymer: Synthesis, Photophysical Properties and Photocatalytic Studies

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**Table S1:** Some recent reports on photocatalytic hydrogen evolution (HER) using polymers and metal cocatalyst.

| **Catalyst & amount** | **Co-catalyst (w%)** | **Sacrificial Agent** | **Max. HER rate (µmol $g^{-1}$ $h^{-1}$)** | **irradiation** | **Highlight** | **Year & Reference** |
|---|---|---|---|---|---|---|
| **TT-Ant** (25 mg) | 1% Pt | MeOH | 700 | 150 W medium pressure Hg immersion lamp | Donor-acceptor hypercrosslinked polymer formed from Thienothiophene and anthracene units, which are important moieties for photovoltaics and photon upconversion, respectively. | **This Work** |
| Py-C-BT-COF (10 mg) | 5% Pt | sodium ascorbate | 253 | 300 W Xenon lamp with a UV-cutoff filter λ > 420 nm | regulating the electron delocalization via manipulating heteroatoms resulted in improvement on HER from 0 to 253 µmol $g^{-1}$ $h^{-1}$ | 2024/REF[1] |
| 3CN-COF (10 mg) | 2% Pt | Ascorbic acid | 71 | 300 W Xenon lamp with a UV-cutoff filter λ > 420 nm) | tuning the amount of electron withdrawing groups along the polymeric backbone by adjusting CN content improved HER from 30 to 71 µmol $g^{-1}$ $h^{-1}$ | 2023/REF[2] |
| P2-CN (10 mg) | 3% Pt | triethanolamine | 167 | 300 W Xenon lamp with a UV-cutoff filter (λ > 300 nm) | tuning the amount of electron withdrawing groups along the polymeric backbone by adjusting CN content improved HER from 4 to 167 µmol $g^{-1}$ $h^{-1}$ | 2023/REF[3] |

| | | | | | | |
|---|---|---|---|---|---|---|
| Co-TPFO-COF (5 mg) | 3% Pt | Ascorbic acid | 1015 | A xenon lamp, equipped with a long-pass filter (λ > 420 nm) | integration of independently active donor-acceptor groups for individual hydrogen (1015 μmol $g^{-1}$ $h^{-1}$) and oxygen (2399 μmol $g^{-1}$ $h^{-1}$) production | 2024/REF[4] |
| Py-DNII-COF (1 mg) | 2% Pt | Ascorbic acid | 625 | 350 W Xe light source (1000 Wm−2; λ = 380-780 nm) | forming push-pull-pull systems for an enhanced charge separation | 2024/REF[5] |
| TP-COF (5 mg) | ca. 4% Pt (Described as 8% H2PtCl6) | triethanolamine | 29120 | visible light (λ > 420 nm) | Amount of the catalyst to the HER performances 3 mg: 23.41 mmol $g^{-1}$ $h^{-1}$ 5 mg: 29.12 mmol $g^{-1}$ $h^{-1}$ 10 mg: 23.41 mmol $g^{-1}$ $h^{-1}$ 20 mg: 14.86 mmol $g^{-1}$ $h^{-1}$ | 2023/REF[6] |
| TP-BTDO-2 (10 mg) | 1% Pt | Ascorbic acid | 161280 | 300 W Xe lamp λ > 300 nm | Very high HER performance | 2022/REF[7] |
| ThSo-1 (6 mg) | None | Ascorbic acid | 111790 | 300 W Xe lamp λ > 300 nm | Very high HER performance | 2024/REF[8] |

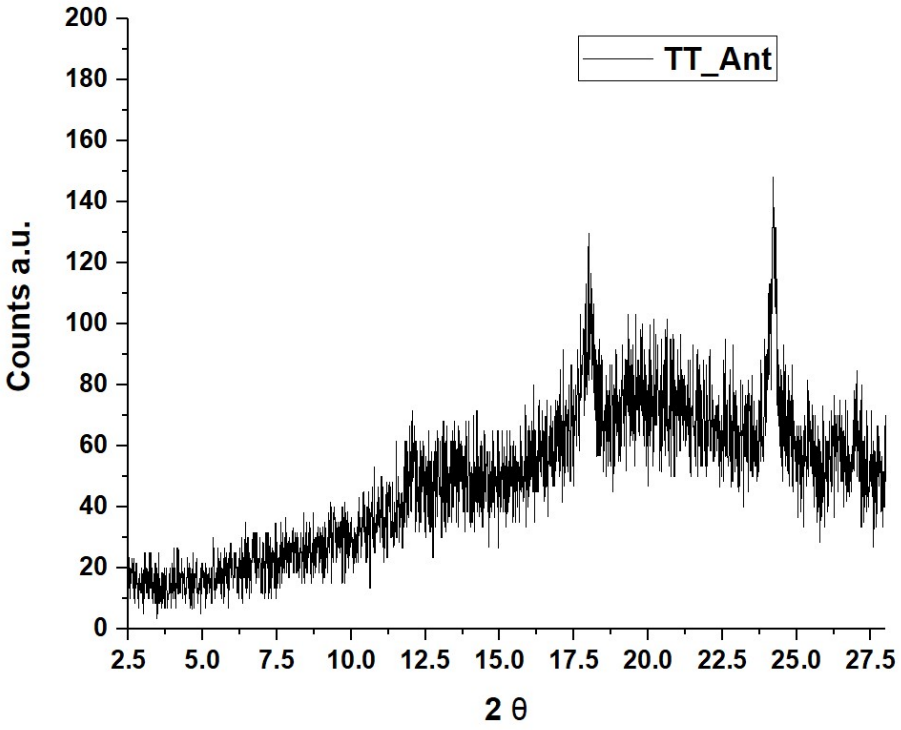


**Fig. S1.** pXRD pattern of **TT-Ant**.

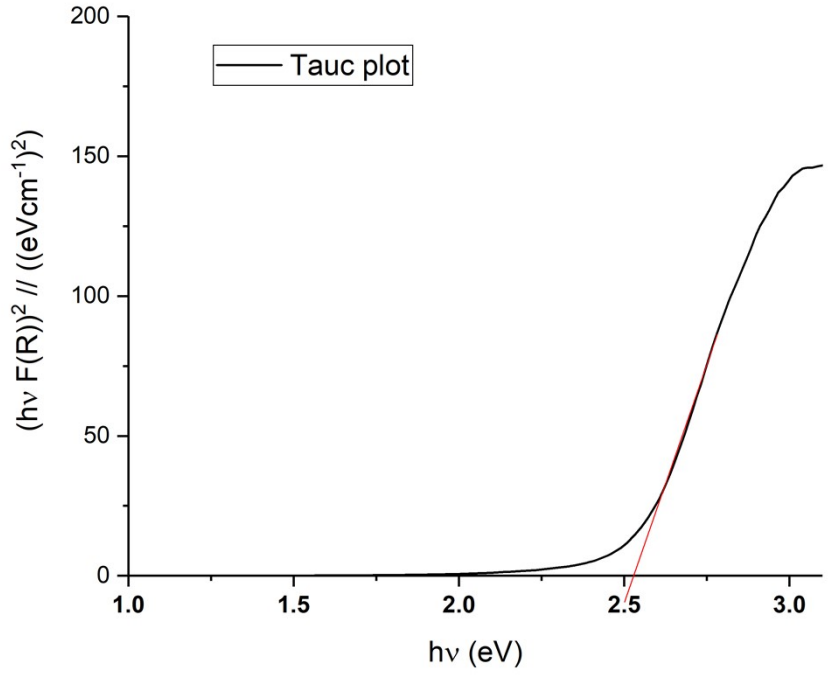


**Fig. S2.** Tauc plot derived from DR.

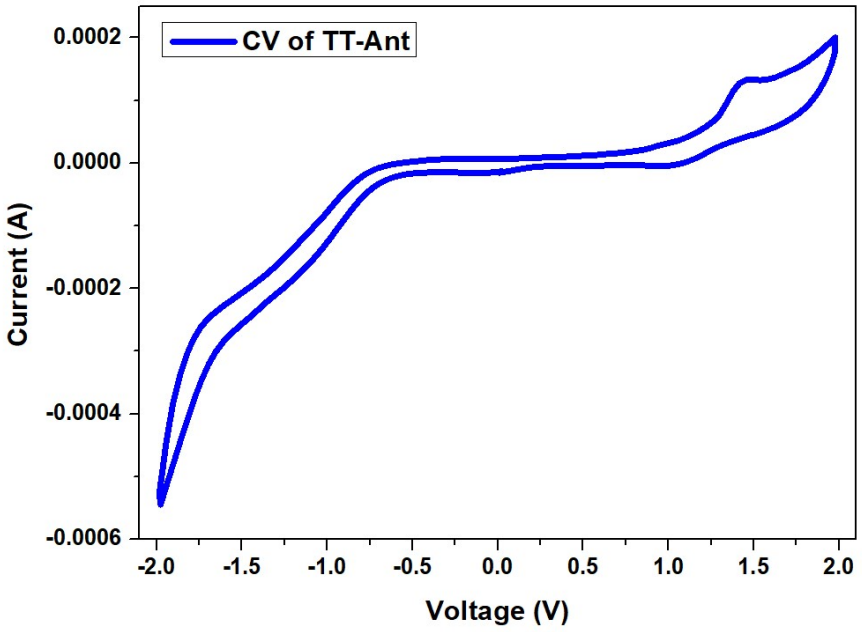


**Fig. S3.** Cyclic voltammogram of **TT-Ant.**

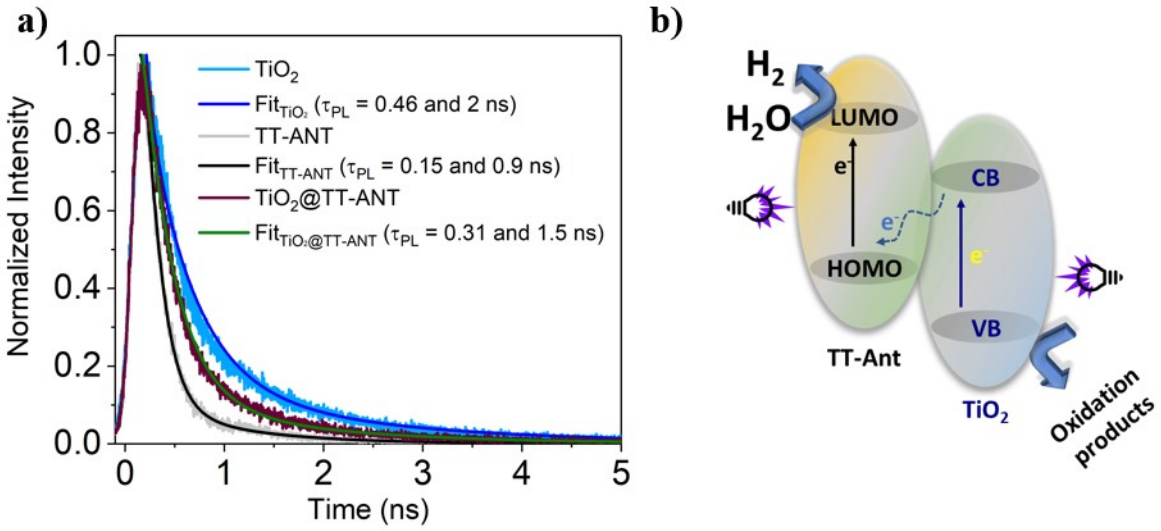


**Fig. S4.** a) Time-resolved photoluminescence (TRPL) studies for $TiO_2$, **TT-Ant**, and their hybrid **$TiO_2$@TT-Ant** were conducted under UV light irradiation (at 372 nm) through a band-pass filter centered at 500 nm. b) illustration of the Z-Scheme mechanism for photocatalytic hydrogen production.

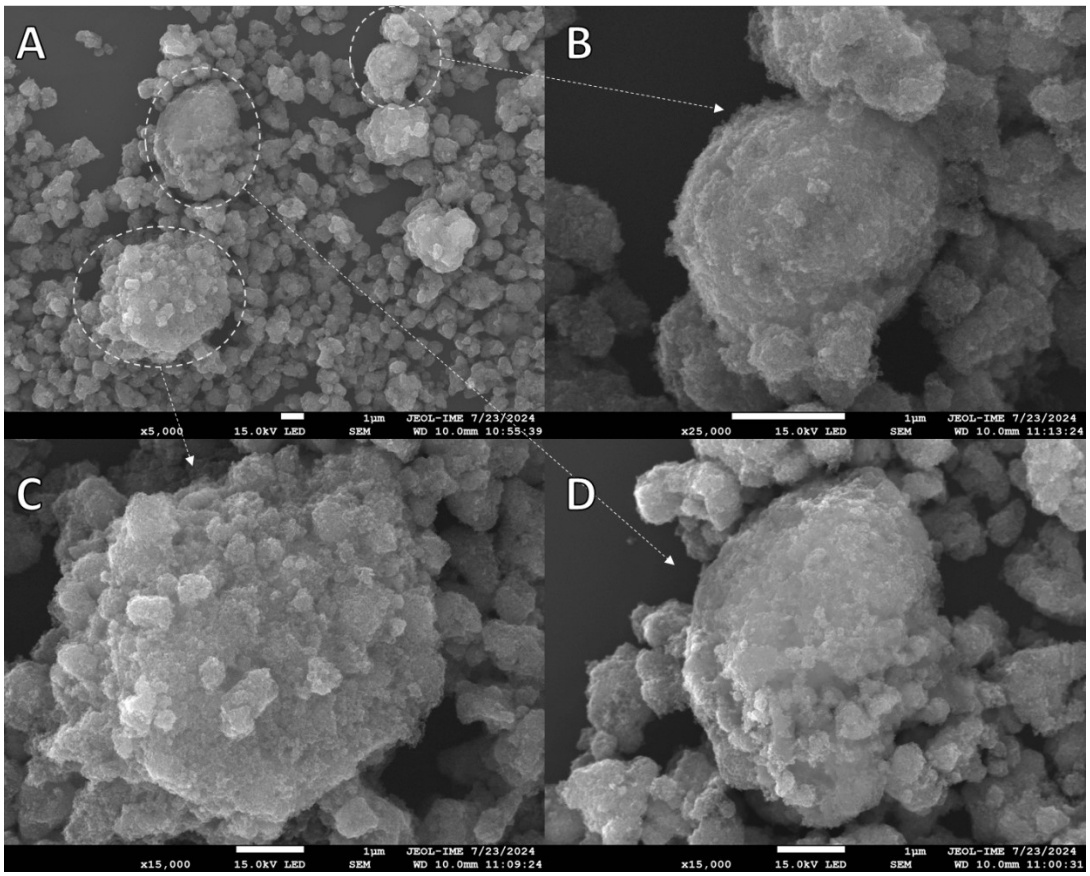


**Fig. S5.** Field emission scanning electron microscopy (FE-SEM) images of **$TiO_2$@TT-Ant** before the HER test; A) scale: 1 µm and magnification: x5000 B) scale: 1 µm magnification: x25000 C) scale: 1 µm magnification: x15000 D) scale: 1 µm magnification: x15000.

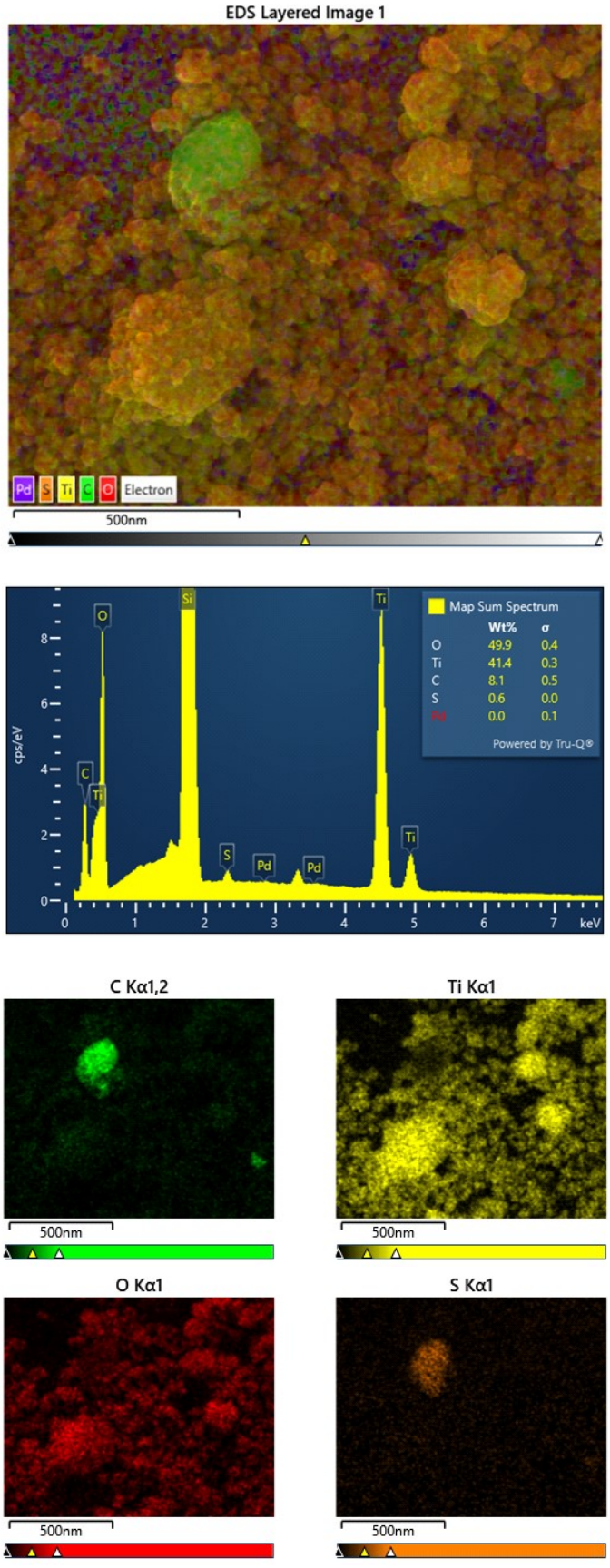


**Fig. S6.** Elemental mapping and EDX spectrum of **$TiO_2$@TT-Ant** before the HER test.

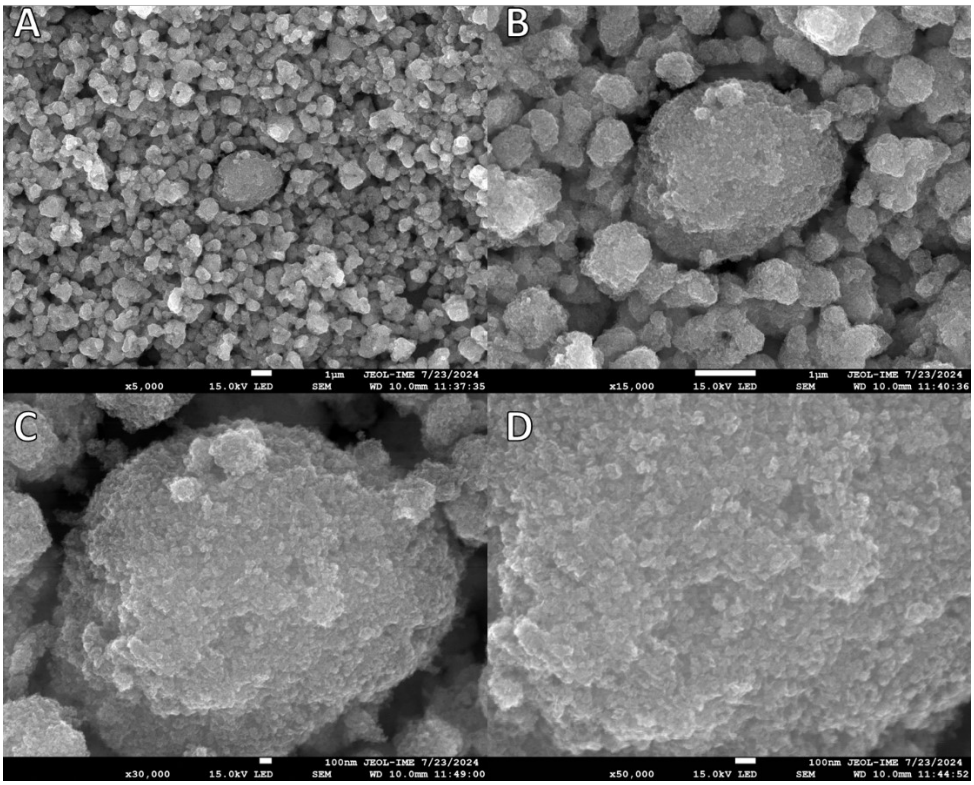


**Fig. S7.** FE-SEM images of **$TiO_2$@TT-Ant** after the HER test; A) scale: 1 µm and magnification: x5000 B) scale: 1 µm magnification: x15000 C) scale: 100 nm magnification: x30000 D) scale: 100 nm magnification: x50000.

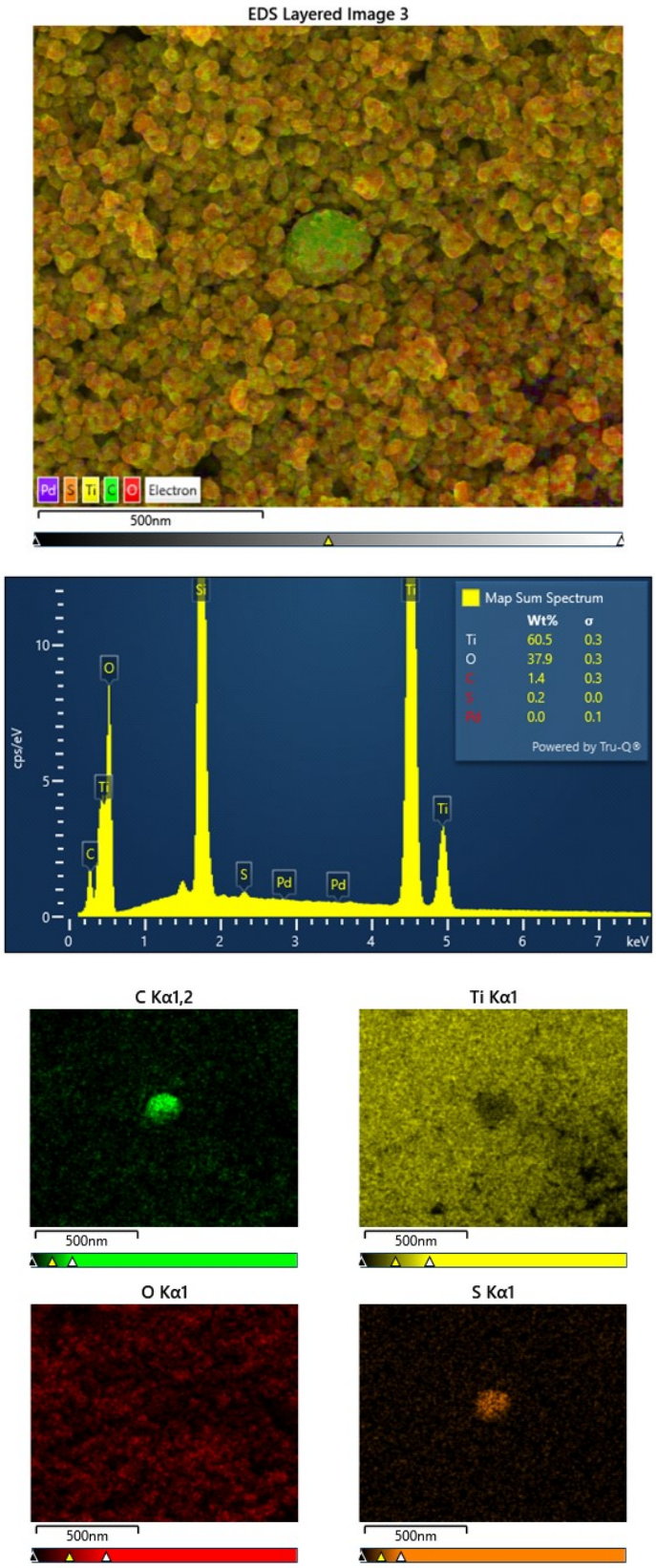


**Fig. S8.** Elemental mapping and EDX spectrum of **$TiO_2$@TT-Ant** after the HER tests.

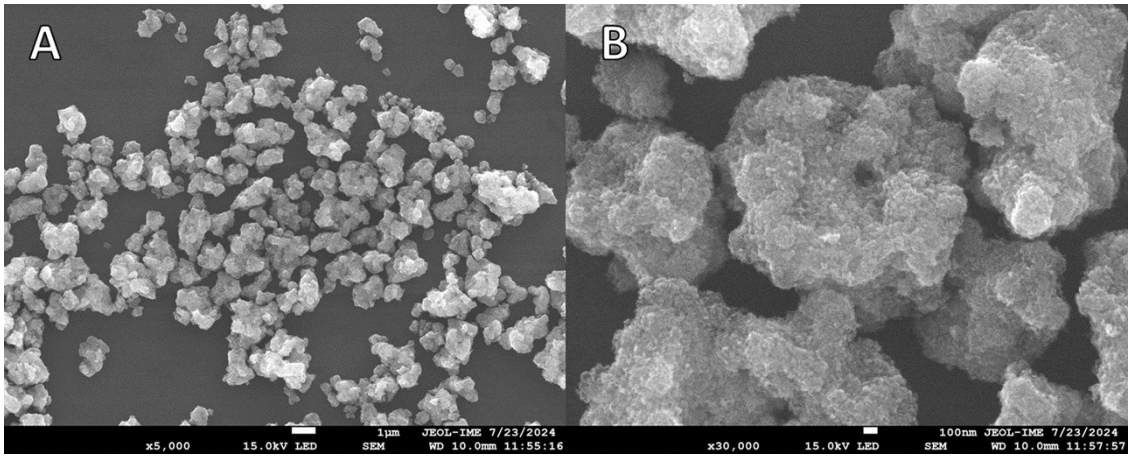


**Fig. S9.** FE-SEM images of $TiO_2$; A) scale: 1 µm and magnification: x5000 B) scale: 100 nm magnification: x30000

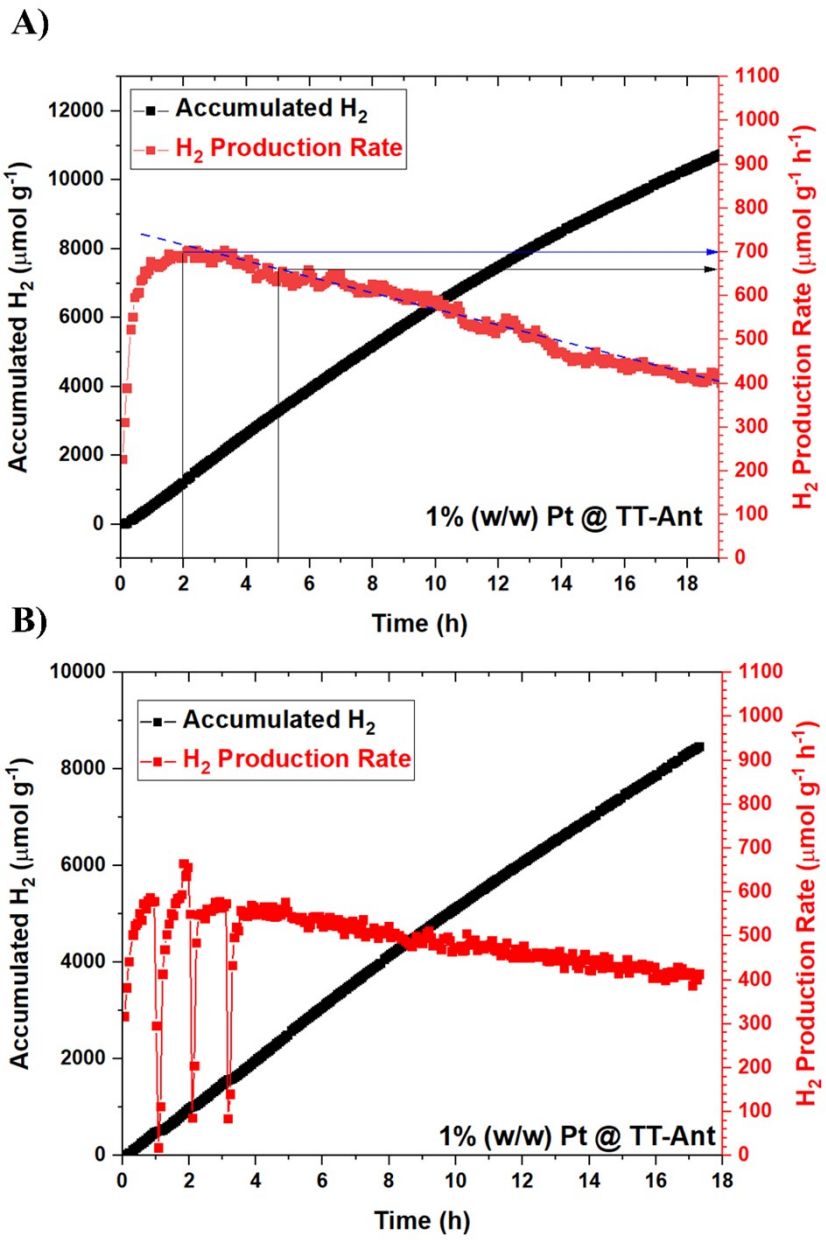


**Fig. S10**. Two independent long-term experiments for **Pt@TT-Ant**; accumulated total $H_2$ on left Y axis (black) and the detected $H_2$ production rate on the individual measurement (ca. 3.8 mins time interval) on left Y axis (red) a) Direct test without any interruption. b) Extension of the "light on-off test" (the rate is relatively less than uninterrupted measurement due to the on-off switching).

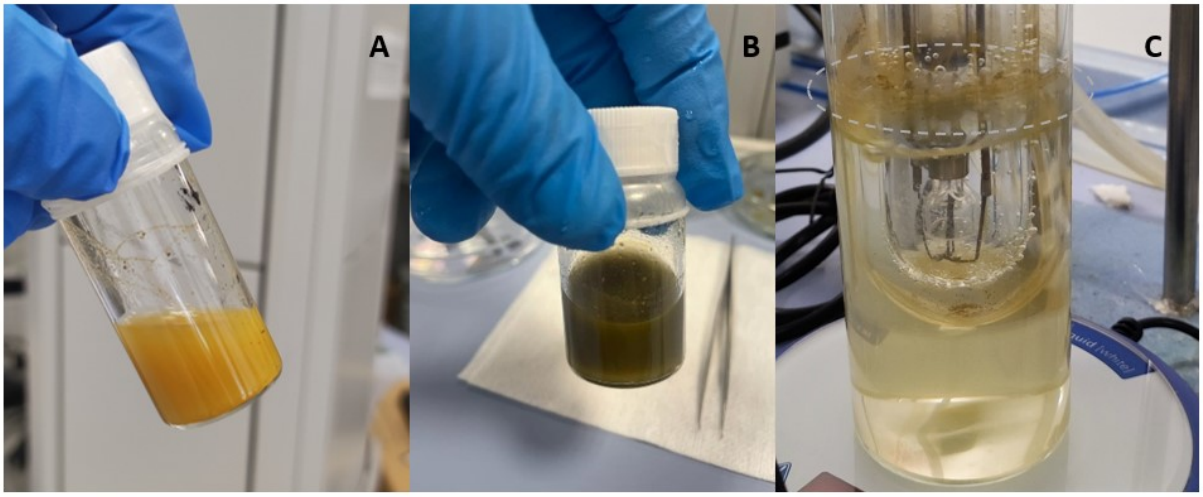


**Fig. S11.** a) 3 mg **TT-Ant** sonicated in 4 mL MeOH and 6 mL water for 15 mins. b) 25 mg **TT-Ant** sonicated in 4 mL MeOH and 6 mL water for 15 mins. c) Reactor after 18 h reaction of **Pt@TT-Ant.**

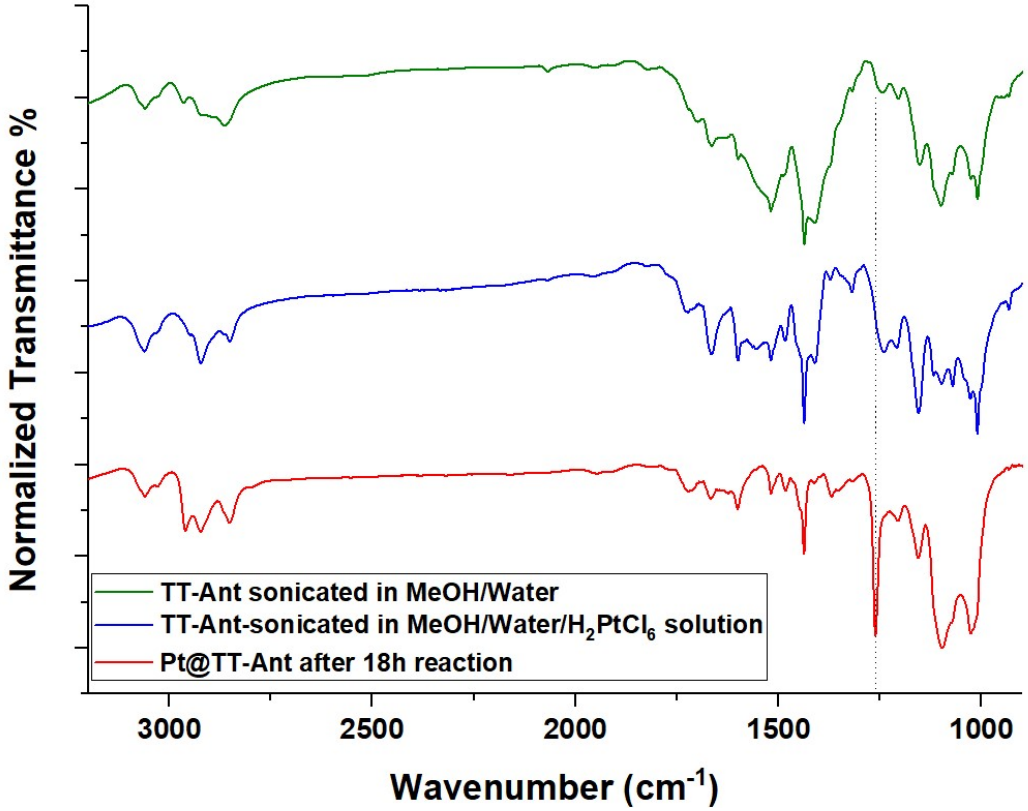


**Fig. S12.** IR spectrums (recorded in KBr pellets) of; **TT-Ant** soncated in 4mL MeOH and 6 mL water mixture for 15 mins (green), **TT-Ant** + $H_2PtCl_6$ solution (ca. 6.5 µL from the stock $H_2PtCl_6$ solution used for the reaction to obtain the same concentration with the reaction) sonicated in 4mL MeOH and 6 mL Water mixture for 15 mins (blue), **Pt@TT-Ant** after 18 h reaction (red).

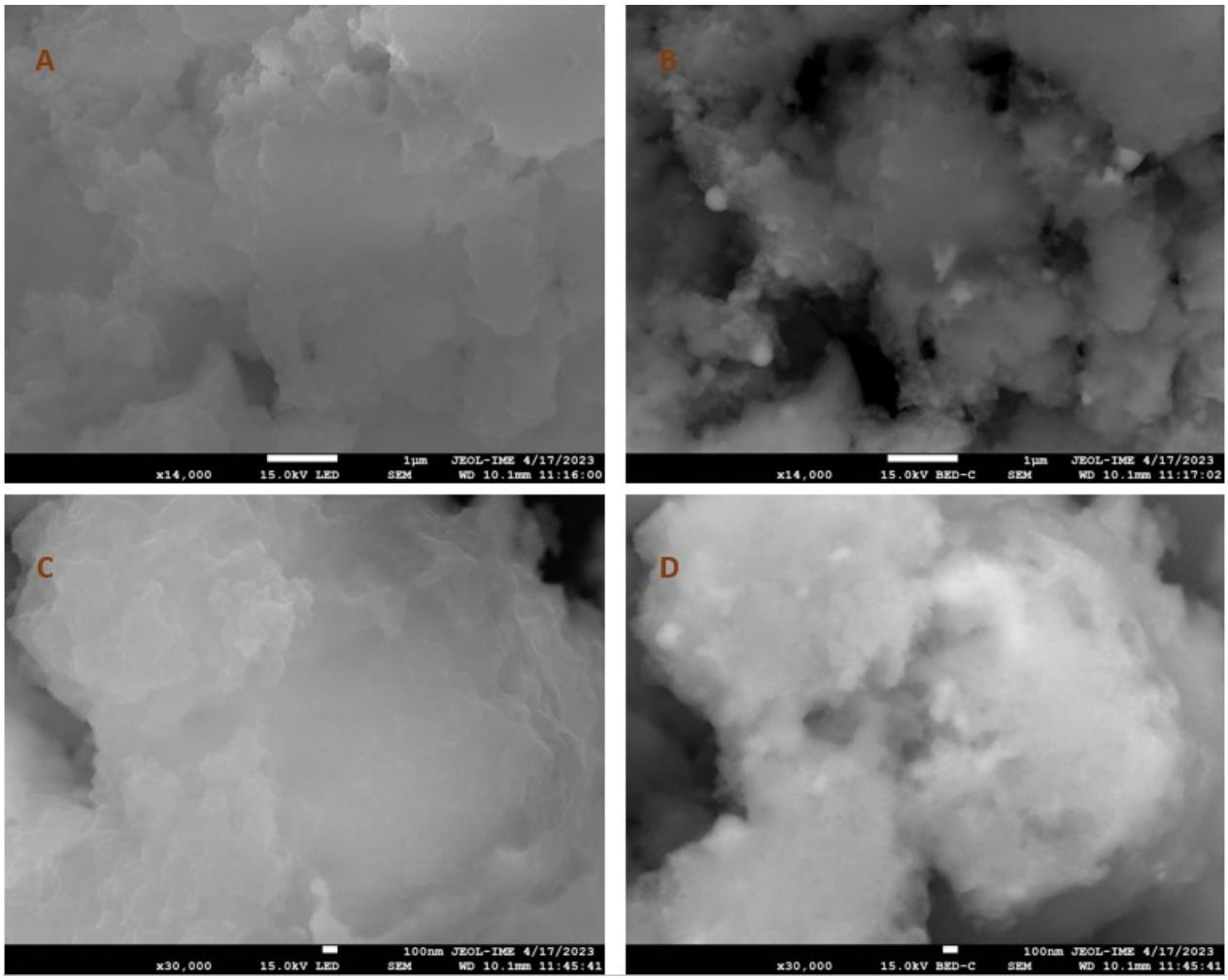


**Fig. S13.** FE-SEM images of **TT-Ant** in different scales and magnifications, a) secondary electron image in 14000x - scale 1 µm, b) corresponding backscattered electron image of Fig S7a in 14000x - scale 1 µm c) secondary electron image in 30000x - scale 100 nm, d) corresponding backscattered electron image of Fig S7c in 30000x - scale 100 nm.

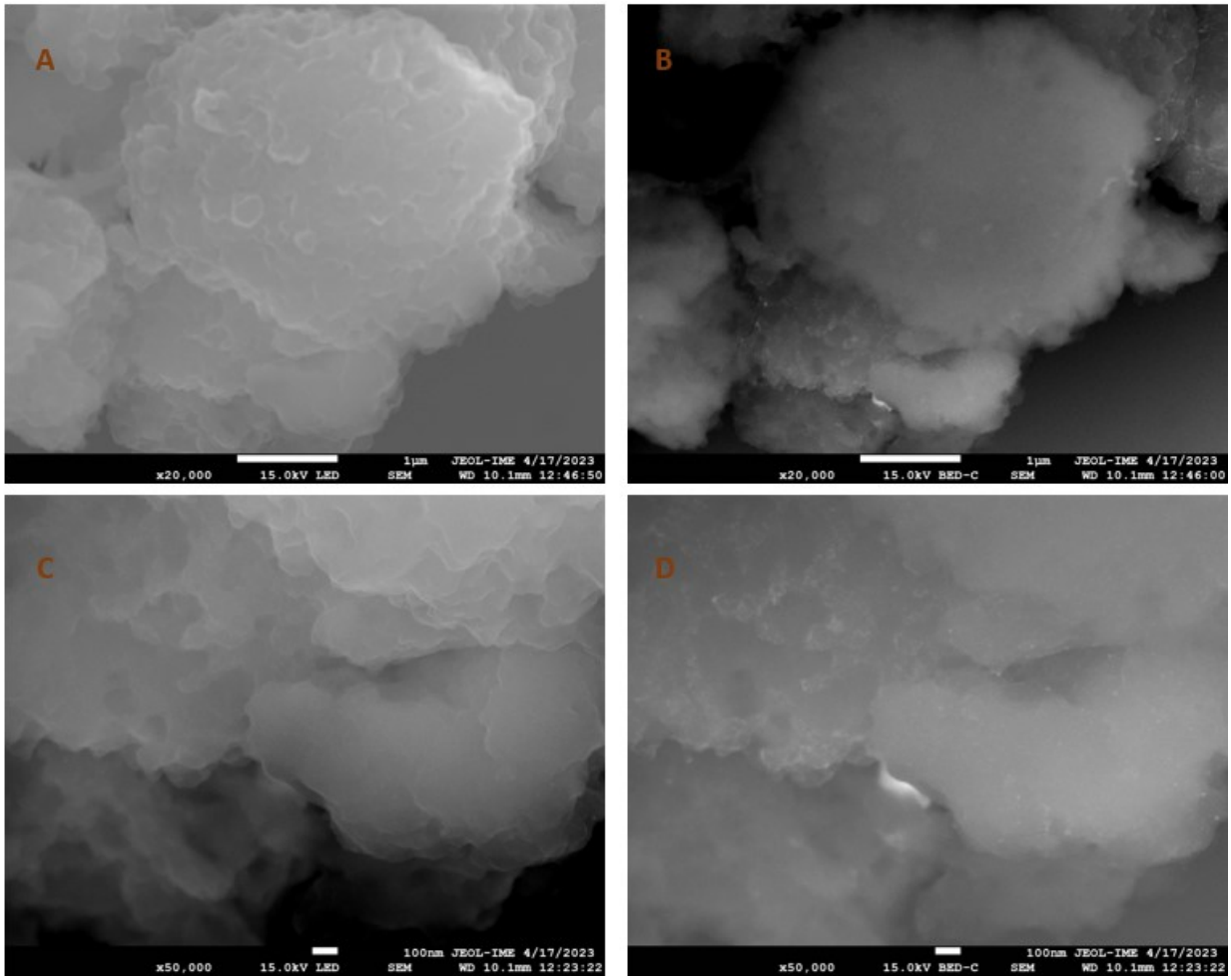


**Fig. S14.** FE-SEM images of **Pt@TT-Ant** in different scales and magnifications a) secondary electron image in 20000x - scale 1 µm. b) corresponding backscattered electron image of Fig S8a in 20000x - scale 1 µm. c) secondary electron image in 50000x - scale 100 nm. d) corresponding backscattered electron image of Fig S8c in 50000x - scale 100 nm.

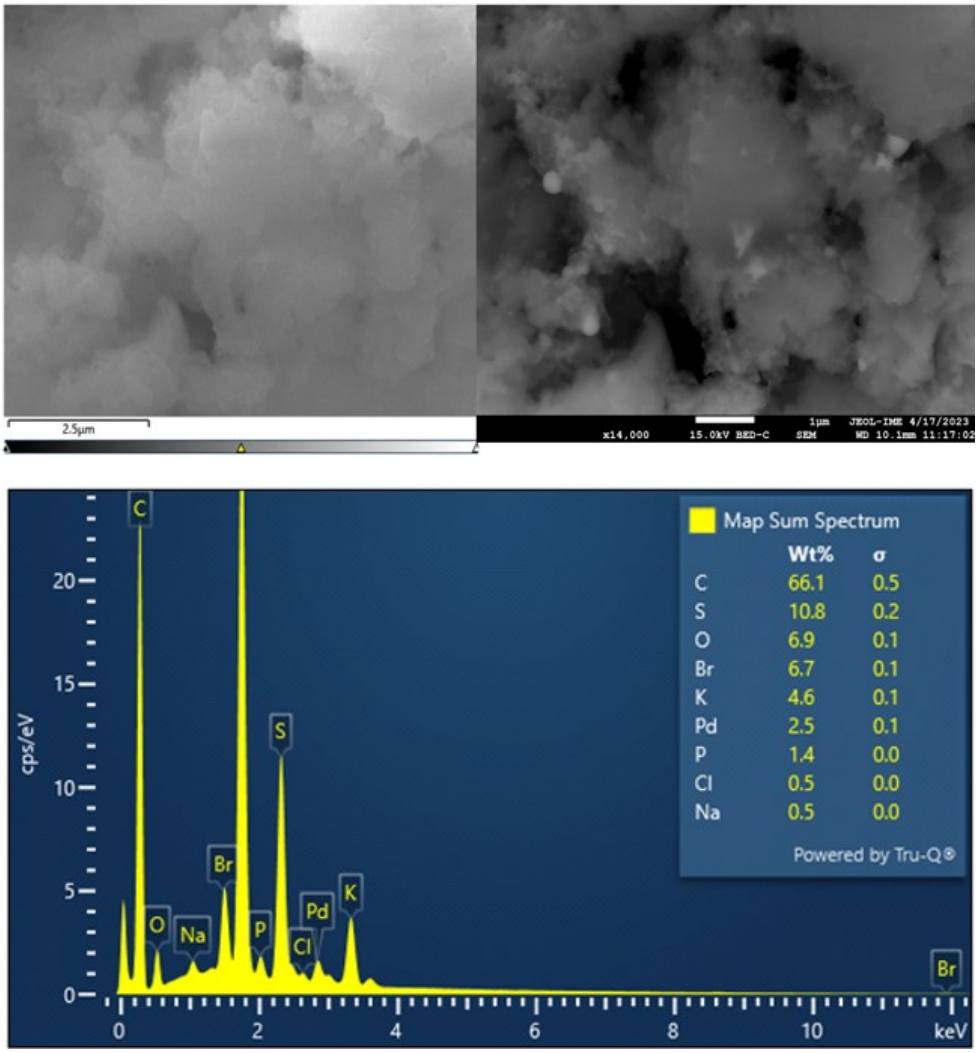


**Fig. S15.** Overall SEM-EDX spectrum of the pictured area of **TT-Ant**.

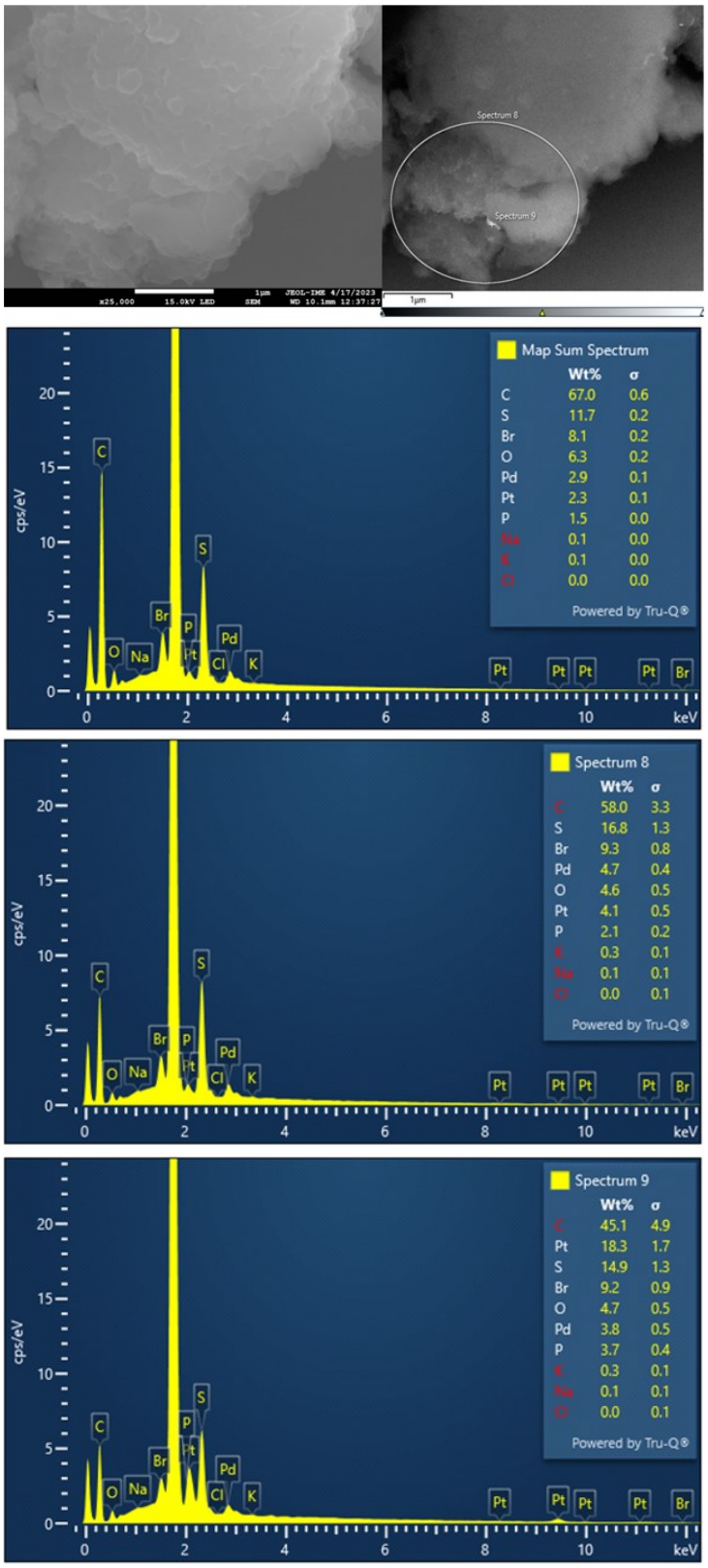


**Fig. S16.** SEM-EDX spectrum of **Pt@TT-Ant** including overall and highlighted areas as Spectrum 8 and Spectrum 9.

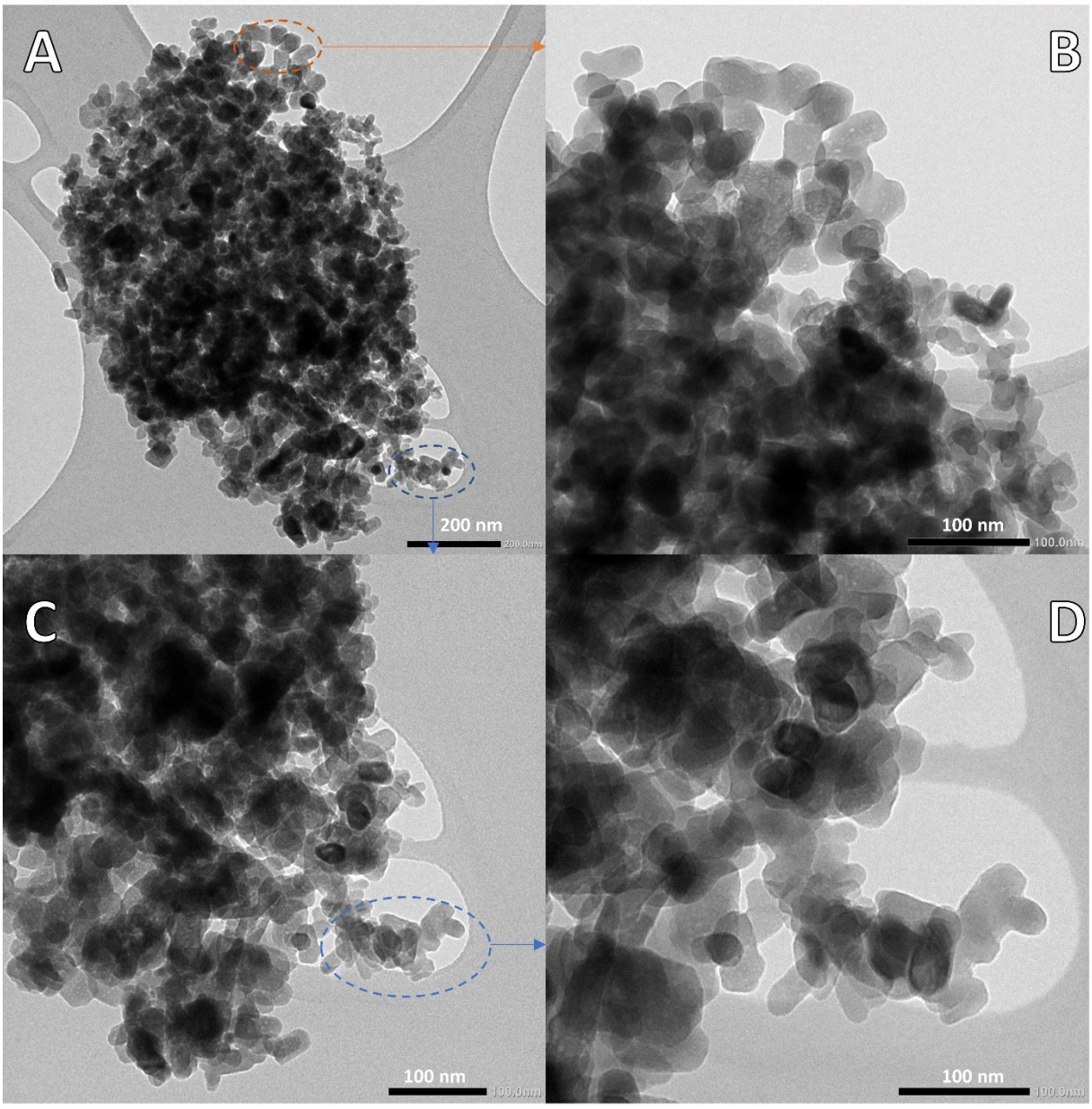


**Fig. S17.** TEM images of **TT-Ant**: A) Overall image with scale 200 nm. B) Magnification of the highlighted area with the orange circle in Fig. S11A (scale 100 nm). C) Magnification of the highlighted area with the blue circle in Fig. S11A (scale 100 nm). D) Magnification of the highlighted area with the blue circle in Fig. S11C (scale 100 nm).

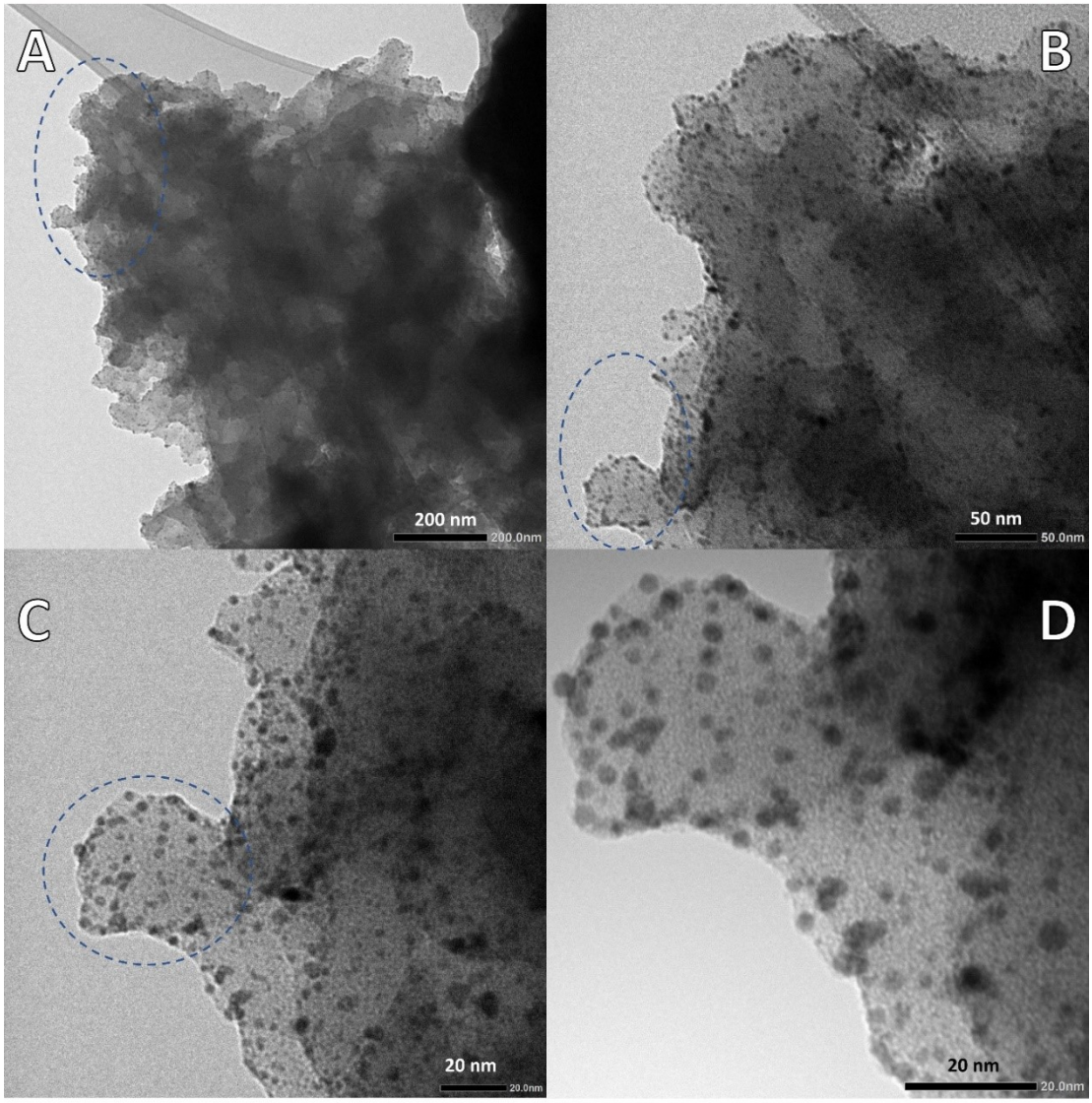


**Fig. S18.** TEM images of **Pt@TT-Ant**: A) Overall image with scale 200 nm. B) Magnification of the highlighted area with the blue circle in Fig. S12A (scale 50 nm). C) Magnification of the highlighted area with the blue circle in Fig. S12B (scale 20 nm). D) Magnification of the highlighted area with the blue circle in Fig. S12C (scale 20 nm).

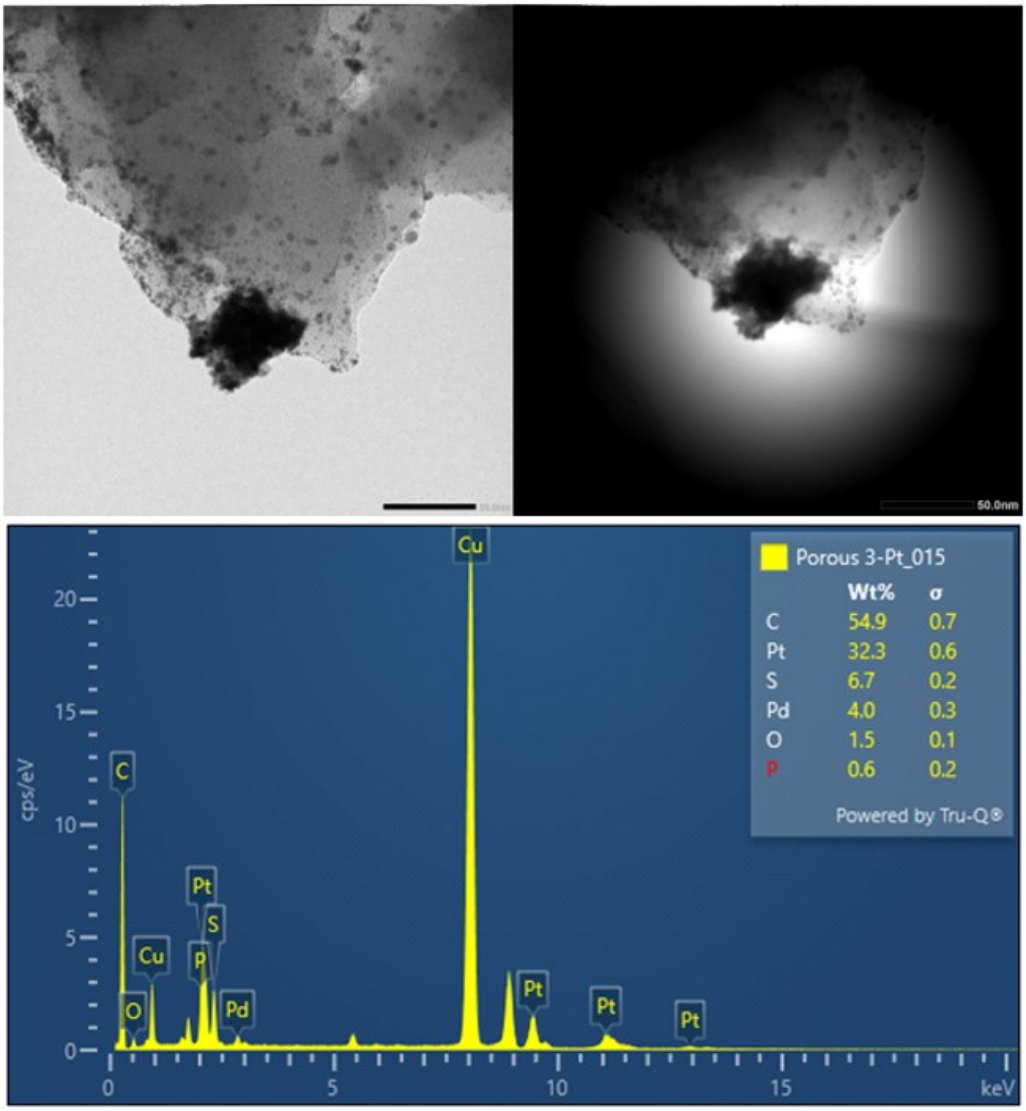


**Fig. S19.** TEM-EDX spectrum of **Pt@TT-Ant** of the highlighted area (scales of the images are 50 nm).

## References


1. X. Ren, M.-Y. Wen, X. Hou, J. Sun, F. Bai, Y. Li, Covalent organic framework isomers with divergent photocatalytic properties. *Chem. Commun.* 2024, **60**, 4423-4426.
2. N. Qin, A. Mao, L. Li, C. Lin, L. Zhai, J. Liu, J. Zou, C.-X. Cui, L. Mi, Rational Design of Vinylene-Linked Covalent Organic Frameworks for Modulating Photocatalytic $H_2$ Evolution. *ChemSusChem* 2023, **16**, e202300872.
3. X. Chi, Q. Chen, Z.-A. Lan, X. Zhang, X. Chen, X. Wang, Structure–Property Relationship of Cyano-Functionalized Conjugated Polymers for Photocatalytic Hydrogen Production. *Chem.-A Eur. J.* 2023, **29,** e202202734.

4. Z. Xiao, H. Wu, L. Jiao, X. Zhang, Y. Wang, A dual-functional metalloporphyrin-fluorenone covalent organic framework for solar hydrogen and oxygen production *J. Mater. Chem. A* 2024, **12,** 7515-7521.
5. I. Mekhemer, M. Elsenety, A. Elewa, K. D. G. Huynh, M. Mohamed Samy, M. G. Mohamed, D. M. Dorrah, D. C. K. Hoang, A. F. Musa, S.-W. Kuo, H.-H. Chou, Push–pull–pull interactions of 2D imide–imine-based covalent organic framework to promote charge separation in photocatalytic hydrogen production. *J. Mater. Chem. A* 2024, **12,** 10790-10798.
6. H. Liu, D. Wang, Z. Yu, Y. Chen, X. Li, R. Zhang, X. Chen, L. Wu, N. Ding, Y. Wang, Y. Zhao, Fully conjugated two-dimensional $sp^2$-carbon covalent organic frameworks for efficient photocatalytic hydrogen generation. *Sci. China Mater.* 2023, **66,** 2283-2289.
7. C. Han, S. Xiang, S. Jin, L.-W. Luo, C. Zhang, C. Yan, J.-X. Jiang, Linear multiple-thiophene-containing conjugated polymer photocatalysts with narrow band gaps for achieving ultrahigh photocatalytic hydrogen evolution activity under visible light. *J. Mater. Chem. A* 2022, **10,** 5255–5261.
8. Z. Li, F. Zhao, Y. Chu, F. Meng, Y. Dong, H. Zhang, J. Zhao, Y. Du, S. Wang, Fused-Thiophene and Sulfone-Based Donor-Acceptor Conjugated Polymers for Enhanced Hydrogen Production. *ACS Sustain. Chem. Eng.* 2024, **12**, 1072–1083.