

Supporting Information

Subphthalocyanine-sensitized TiO₂ photocatalyst for Photoelectrochemical and Photocatalytic Hydrogen Evolution

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1. Synthesis and Characterization

All chemicals were purchased from Aldrich and used without further purification. Column chromatography was carried out on silica gel Merck-60 (230–400 mesh, 60 Å), and TLC was carried out on aluminum sheets percolated with silica gel 60 F254 (E. Merck). The IR spectra were performed with Perkin-Elmer, FT-IR/MIR-FIR (ATR, Attenuated total reflectance) spectrophotometer. Mass spectrometry analysis was performed on an autoflex III MALDI TOF/TOF MS system (Bruker Daltonics, Bremen, Germany). 4-iodophthalonitrile (4) [1] 4-ethynylbenzoic acid [2] and 4,5-bis(4-tert-butylphenylthio) phthalonitrile [3] were prepared according to procedures previously reported in the literature.

- *4'-tert-butylphenol* [2-iodo-9, 10, 16, 17-tetra (4'-tert-butylphenylthio)-subphthalocyaninato] boron (III) (SubPc 4):

A mixture of 4-iodophthalonitrile (56 mg, 0.22 mmol) and 4,5-bis(4-tert-butylphenylthio) phthalonitrile (250 mg, 0.55 mmol) in a 1M solution of BCl₃ in p-xylene (0.77 ml, 0.77 mmol), was stirred 140 °C for 3 h under argon atmosphere. After cooling to room temperature, the solvent was evaporated to dryness. Dry toluene (4ml) and 4-tertbutylphenol (578 mg, 3.85 mmol) were added to the crude mixture and stirring was continued at 110 °C for 3 h. The solvent was removed by *vacuum* distillation and the solid was washed with a

mixture of methanol/water (4:1). The compound was purified by column chromatography on silica gel (Hexane/EtOAc 6:1) as eluent to give SubPc 4 (110 mg, 0.83 mmol) in 38 % yield.

^1H NMR (400 MHz, CDCl_3): δ (ppm)= 9.04 (s, 1H), 8.51 (d, $J=2$, 2H), 8.41-8.38 (m, 3H), 8.12– 8.10 (m, 1H), 7.52 - 7.50 (d, $J=8$, 8H), 7.44 (s, 8H), 6.71 (d, $J=8$, 2H), 5.20 (d, $J=8$, 2H), 1.43 (d, $J=4$, 9H), 1.38 (s, 18 H), 1.05 (s, 9 H).

IR (ATR): ν , cm^{-1} = 2956, 2902, 2855, 2306, 1988, 1735, 1597, 1512, 1456, 1396, 1259, 1176, 1058, 1011, 896, 880, 815, 758, 706, 542.

UV-vis (CHCl_3): λ_{max} , nm (log ϵ): 358 (4.47), 541 (4.59), 593 (5.09).

MALDI (ditranol): m/z: 1326.316 (M^+).

- *4'-tert-butylphenol* [(2-(4''ethynylbenzoic acid)-9,10,16,17-tetra(4'-tert-butylphenylthio)-subphthalocyaninato)] boron (III) (SubPc 2):

To a freshly distilled and deaerated THF/ Et_3N (4:1) mixture, SubPc 4 ((100 mg, 0.75 mmol), CuI (0.5 mg, 0.002 mmol) and $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ (5 mg, 0.007 mmol), 4-ethynylbenzoic acid (27 mg, 0.187 mmol) was added. The mixture was stirred at room temperature under argon atmosphere for 4h. The solution was then washed with brine, dried over Mg_2SO_4 , filtered and evaporated in *vacuo*. The crude solid was purified by column chromatography on silica gel ($\text{CH}_2\text{Cl}_2/\text{MeOH}$, 10:1) to give SubPc 2 (67 mg, 0.05 mmol) as a purple solid in 67% yield.

^1H NMR (400 MHz, CDCl_3): δ (ppm)= 8.89 (s, 1H), 8.66 (d, $J=8$, 1H), 8.50 (d, $J=4$, 2H), 8.42 (s, 2H), 8.15 (br s, 2 H), 7.96 (d, $J=8$, 1H), 7.70 (d, $J=8$, 2H), 7.51 (s, 8H), 7.43 (s, 8H), 6.72 (d, $J=8$, 2H), 5.23 (d, $J=8$, 2H), 1.42 (s, 18H), 1.38 (s, 18 H), 1.05 (s, 9 H).

IR (ATR): ν , cm^{-1} = 3075, 2957, 2920, 2851, 2126, 2002, 1909, 1722, 1601, 1557, 1512, 1488, 1459, 1400, 1363, 1259, 1175, 1059, 1012, 952, 893, 856, 827, 750, 708, 549.

UV-vis (CHCl_3): λ_{max} , nm (log ϵ): 373 (4.47), 540 (4.36), 599 (4.88).

MALDI: m/z: 1345.424 (M^+).

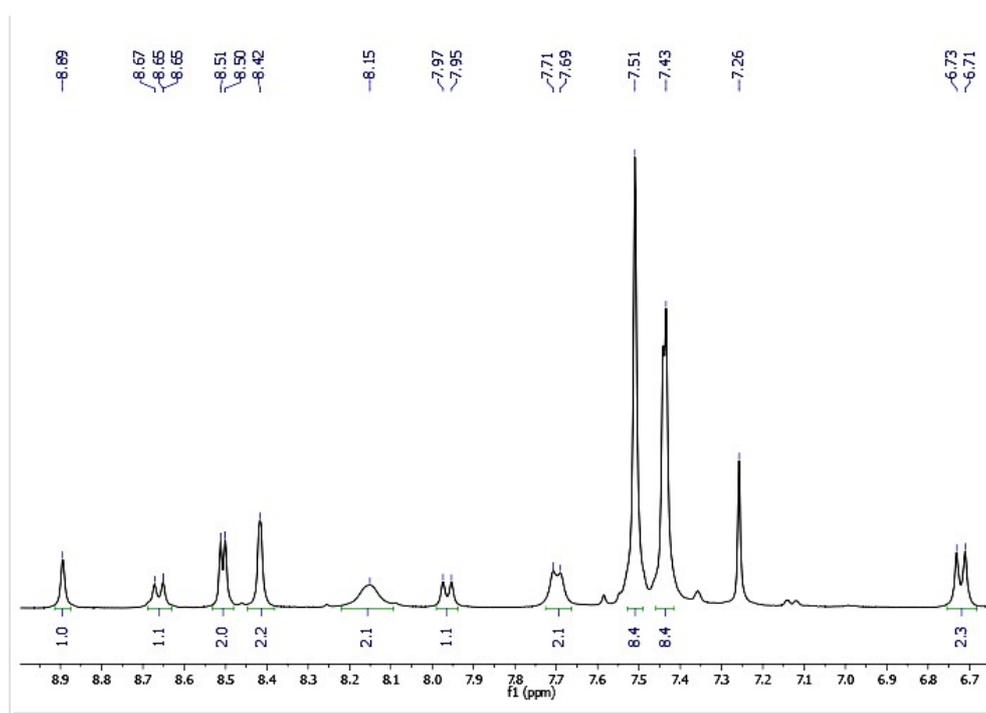


Figure S1. ¹H-NMR spectrum of SubPc 2 (CDCl₃).

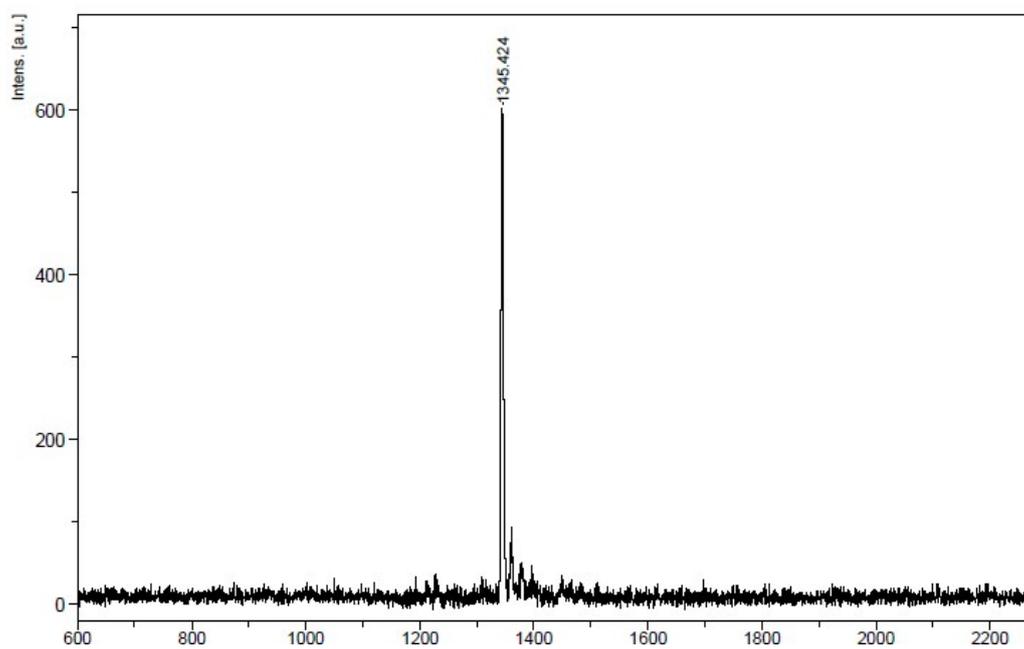


Figure S2. MALDI-TOF MS spectrum of SubPc 2.

2. Optical and electrochemical characterization of SubPcs sensitized TiO₂

UV-vis spectra were recorded with an Analytic JENA S 600 UV-vis spectrophotometer. The electrochemical measurement of SubPc sensitizer series (SubPc 1, SubPc 2 and SubPc 3) was carried out by using an IviumStat electrochemical analyzer at room temperature. Tetrabutylammonium hexafluorophosphate (0.1M) as supporting electrolyte, a Pt wire as a counter electrode, glassy carbon as a working electrode, Ag/AgNO₃ as a reference electrode and ferrocene/ferrocenium (Fc/Fc⁺) as an internal standard were used. All measurements were carried out in DMF solution with a scan rate of 100 mVs⁻¹.

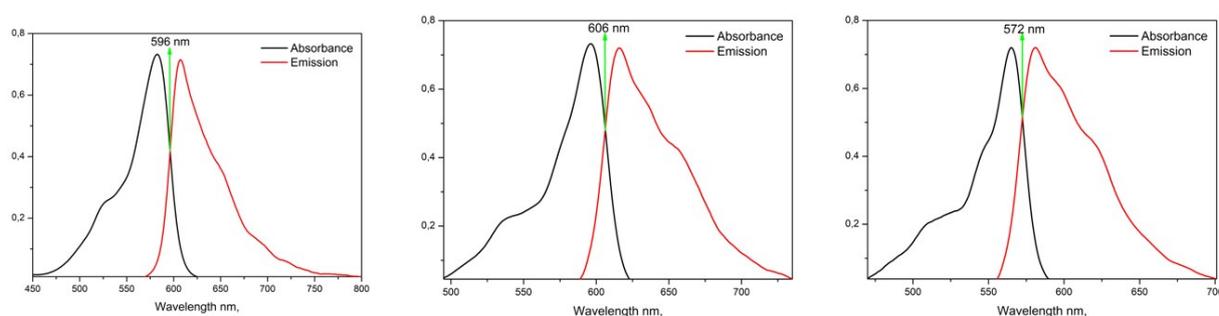


Figure S3. Normalized absorption and fluorescence spectra of SubPcs 1–3 in THF.

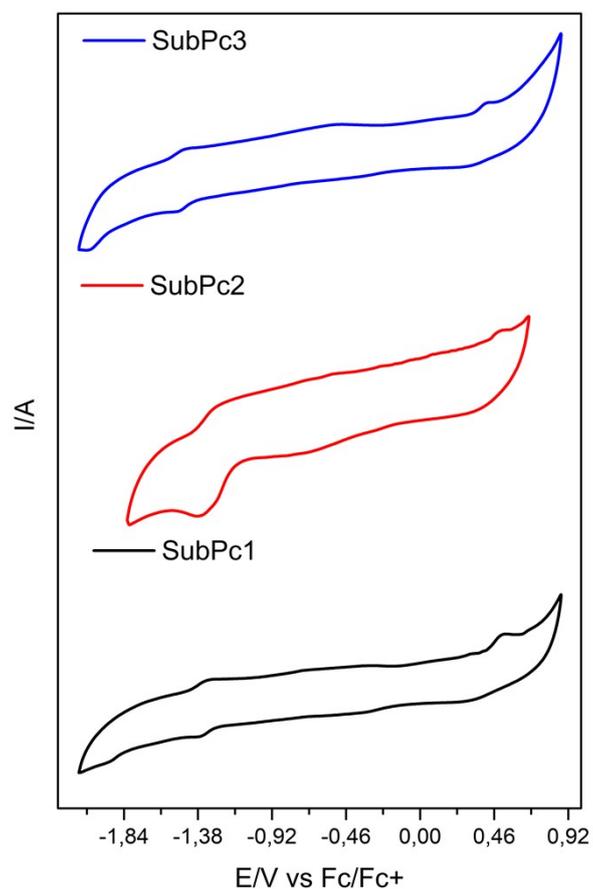


Figure S4. CV voltammograms of SubPc 1-3 with Ferrocene

Preparation of SubPc/TiO₂ samples

100 mg TiO₂ (Degussa P25) was mixed with 10 ml of SubPc solution (1.10⁻⁵ M in THF) under stirring for overnight at dark, afterwards the product was filtered washed with THF and dried overnight under vacuum. For photoelectrochemical studies, the commercially available TiO₂ electrodes (Dyesol MS001630) were sintered at 500 °C for 30 min before they were dipped into the dye solution. Afterwards, TiO₂ electrodes were immersed into the Pc solutions (1. 10⁻⁵ M in DMSO), and kept at room temperature for overnight.

Photoelectrochemical and Photocatalytic Hydrogen Evolution

Linear sweep voltammetry (LSV) and chronoamperometry (CA) methods (CH Instruments 760D potentiostat) were used to determine the photoelectrochemical properties of all SubPcs under anaerobic condition. Photoelectrochemical HER studies were carried out by CH Instruments 760D potentiostat in a standard three-electrode-cell, which includes SubPc sensitized TiO₂ electrodes, platinum plate, Ag/AgCl as the working, counter and the reference electrode, respectively, in the sacrificial electron donor/supporting electrolyte solution (TEOA/Na₂SO₄) under visible light illumination. The potential of Ag/AgCl reference electrode determined according to standard electrode potential (+0.211 V vs. NHE).

In the photocatalytic hydrogen evolution experiments, SubPc **1**, **2** and **3** sensitized TiO₂ and aqueous triethanolamine (TEOA) as the photocatalyst and sacrificial electron donor, respectively. TEOA solution (5%) was bubbled with nitrogen gas to remove oxygen before the photocatalytic HER. SubPc sensitized TiO₂ powder catalysts were taken in quartz glass photocatalytic reaction bottle (135 ml) at room temperature conditions (25 ± 2 °C) thereafter, these materials were transferred into glovebox atmosphere. In the anaerobic glove box condition, TEOA (20 mL, pH 7) was added on to the catalyst (10 mg SubPc **1**/TiO₂, SubPc **2**/TiO₂ and SubPc **3**/TiO₂) and reaction cell was sealed under nitrogen atmosphere. The solution was taken out of the glovebox for ultrasonic treatment to achieve a homogeneous mixing. To begin photocatalytic, HER, this system placed the view of the solar simulator and was vigorously stirred magnetically for the homogeneity of the experiment. Thus, photocatalytic HER was performed under the visible light source (Solar Light – XPS 300™ with cut-off filter $\lambda \geq 420$ nm). The evolved hydrogen gas was hourly taken from the headspace of photocatalyst-solution suspension by a syringe and analyzed by using gas chromatography (Shimadzu GC2010Plus).

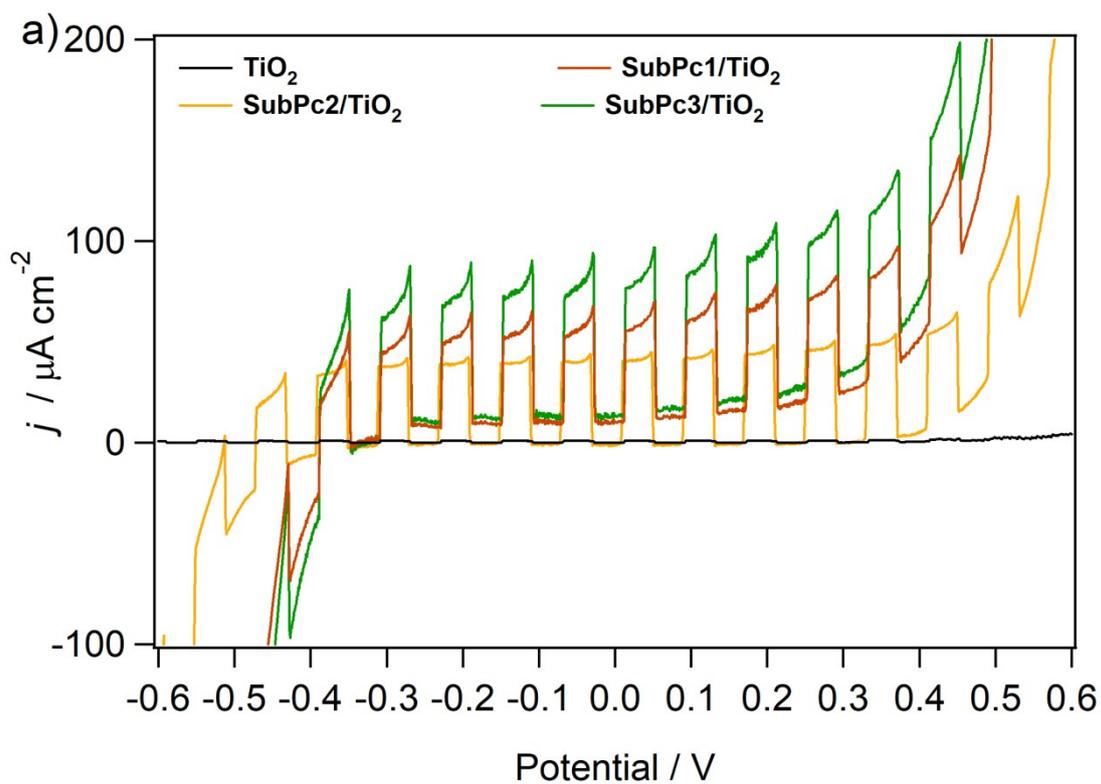


Figure S5. Photoelectrochemical responses of SubPcs sensitized TiO_2 electrodes by using LSV in wide potential window under light/dark cycles.

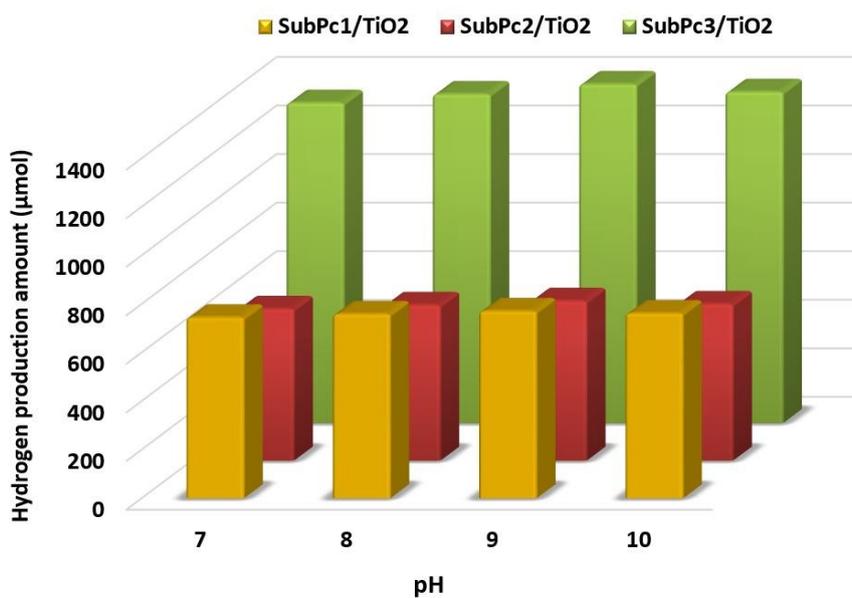


Figure S6. pH dependency of photocatalytic hydrogen evolution by using SubPcs/ TiO_2

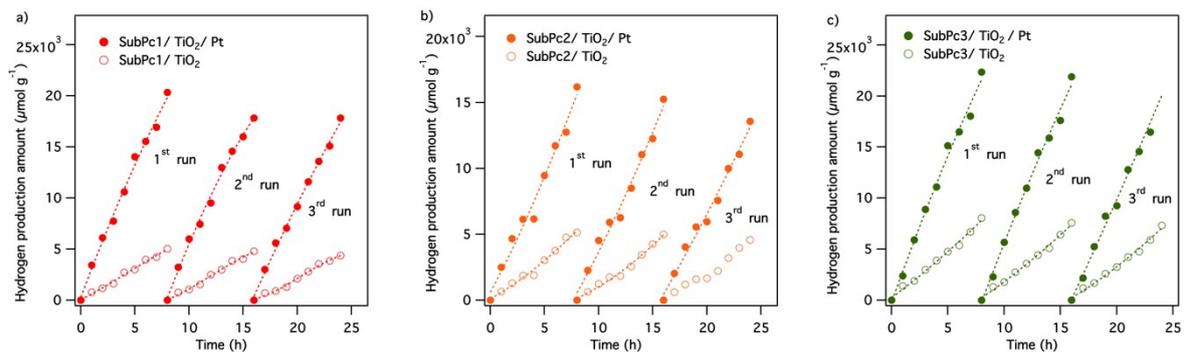


Figure S7. Recycle tests for the photocatalytic hydrogen generation in the presence of SubPcs/TiO₂ photocatalysts.

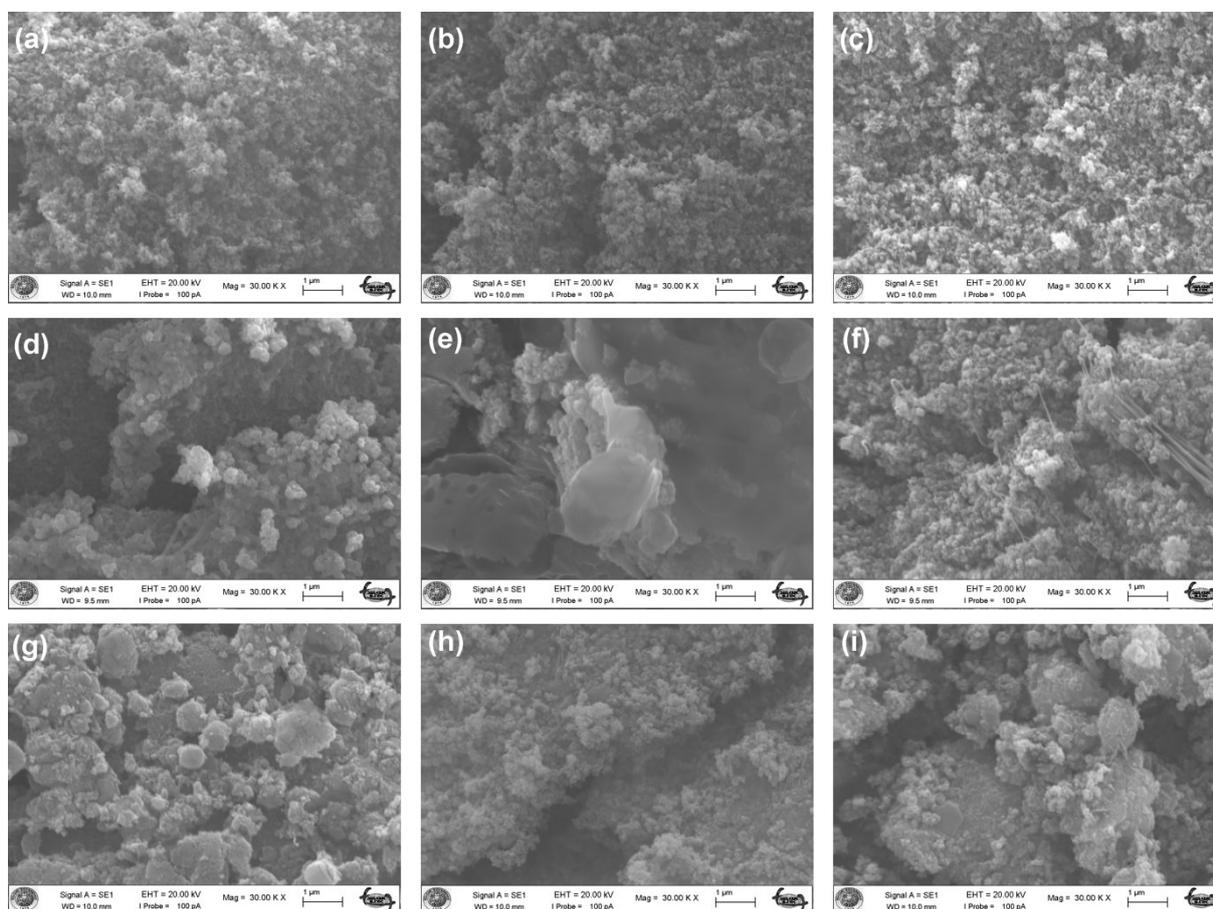


Figure S8. SEM images of SubPcs/TiO₂ before (a,b,c) and after photocatalytic reactions (in the absence of co-catalyst; d, e, f and in the presence of co-catalyst; g, h, i). (SubPc1/TiO₂: a-d-g; SubPc2/TiO₂: b-e-h; SubPc3/TiO₂: c-f-i).

References

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- 2 M. Ince, A. Medina, J.H. Yum, A. Yella, C.G. Claessens, M.V. Martínez-Díaz, M. Grätzel, M.K. Nazeeruddin, T. Torres, *Chem. Eur. J.* 2014, **20**, 2016 – 2021.
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