Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Fast Tuning of Covalent Triazine Frameworks for Photocatalytic Hydrogen Evolution

Sophie Kuecken,[a] Amitava Acharjya,[a] Linjie Zhi,[b] Michael Schwarze,[c] Reinhard Schomäcker,[d] and Arne Thomas[a]

[a] *Technische Universität Berlin,Fakultät II, Institut für Chemie: Funktionsmaterialien,Sekretariat BA2, Hardenbergstraße 40, 10623 Berlin, Germany.*

[b] *National Center for Nanoscience and Technology of China, No. 11, Beiyitiao Zhongguancun, 100190 Beijing, P. R. China*

[c] *Technische Universität Berlin, Fakultät III, Institut für Prozess- und Verfahrenstechnik, Sekretariat TK 0-1, Straße des 17. Juni 135, 10623 Berlin, Germany*

[d] *Technische Universität Berlin, Fakultät II, Institut für Chemie, Sekretariat TC 8, Straße des 17. Juni 124, 10623 Berlin, Germany*

S1. Experimental section and methods

Chemicals. Trifluoromethane sulfonic acid (>98%) was purchased from TCI and used as received. 1,4-Dicyanobenzene (Aldrich, 98%) and zinc chloride (Aldrich, Redi-Dry, anhydrous, 98%) were stored in a glove and used as received. Triethanolamine and 8 wt% H_2PtCl_6 solution were purchased from Sigma-Aldrich and were used without further purification.

General. Thermogravimetric analyses (TGA) were carried out on a TGA 1 instrument from Mettler Toledo at 10 K min^{-1} under N_2 or O_2 atmosphere. IR spectra were collected on a Varian 640IR spectrometer equipped with an ATR cell. Powder X-Ray diffractograms were performed in reflection mode on a Bruker D8 Advanced instrument with Cu-K_α radiation ($\lambda = 0.154$ nm). Elemental analyses were obtained from a Thermo Flash EA 1112 Organic Elemental Analyzer. Solid-state NMR (cross-polarization magic-angle spinning (CP/MAS)) spectra were carried out on a Bruker Avance 400 MHz spectrometer operating at 100.6 MHz for ^{13}C. Nitrogen sorption measurements were performed at 77 K using a Quadrasorb from Quantachrome. The samples were degassed at 150 °C for 12 h before analysis. A Nabertherm N7/H argon oven was used to heat the samples under inert atmosphere to the desired temperature.

Synthesis of the acid catalyzed triazine network (pre-CTF). In an inert argon atmosphere, 30 ml of $CHCl_3$ and trifluoromethanesulfonic acid (19.96 g, 133.0 mmol, 4 eq) were added into a dry 2-neck round bottom flask. After cooling the mixture to 0 °C in an ice bath, 1,4-dicyanobenzene (4.260 g, 33.25 mmol) dissolved in 200 ml $CHCl_3$ was added slowly over 30 min under stirring. The reaction mixture was stirred for 2 h at 0 °C before heating it up to 40 °C and further stirring for 48 h. The reaction mixture turned from colorless to yellow and a solid precipitate was formed. After cooling to RT, 660 ml of deionized water containing 34 ml of ammonia solution (25%) was added and the mixture was stirred for 2 h. The precipitate was isolated by vacuum filtration and washed successively with deionized water, ethanol, acetone and chloroform. The product was dried under vacuum for 12 h at 120 °C. Pre-CTF (2.681 g, 63% yield) was obtained as a yellow solid. FT-IR (ATR, cm^{-1}): 2232, 1500, 810. Anal. calcd for $C_8H_4N_2$: C, 74.99; N, 21.86; H, 3.15. Found: C, 66.32; N, 19.10; H, 3.69.

Synthesis of CTF-1-X min materials in open crucibles. Pre-CTF (2.100 g, corresponding to 16.39 mmol reacted DCB units, 1 eq) was thoroughly mixed with $ZnCl_2$ (1.787 g, 13.11 mmol, 0.8 eq) in an inert argon atmosphere. This large batch of starting reaction mixture was evenly separated into 6 parts which were each transferred to a porcelain crucible with lid and stored in a closed storage box to maintain the inert argon atmosphere. After preheating the argon oven for 30 min under a regulated argon flow of 2.5 l/min to 400 °C, the crucibles were quickly placed into the argon oven and heated at 400 °C for times between 2.5 min and 30 min. After the respective times, the crucibles were immediately removed from the hot oven and allowed to quickly cool down under argon atmosphere. The crude products were grounded and stirred in deionized water (150 ml) for 12h at 60 °C, filtered and washed thoroughly with water to remove the majority of the salt. The mixtures were further stirred in 0.1 M HCl (150 ml) for 12 h at 60 °C to remove the residual $ZnCl_2$, filtered and subsequently washed with water and THF. The product was dried under vacuum for 12 h at 150 °C. CTF-1_X min materials were obtained as solids from dark yellow to dark brown in yields decreasing with reaction time from 80% to 62% (see table S1). For example, CTF-1_10 min was obtained as a dark brown solid with 77% yield. FTIR (ATR, cm^{-1}): 2227, 1504, 1346, 804. Anal. Calcd for $C_8H_4N_2$: C, 74.99; N, 21.86; H, 3.15. Found: C, 72.83; N, 20.61; H, 3.25. See table S1 for yields and table S2 for elemental analysis of all CTF-1_X min materials.

Table S1: Yields of CTF-1 materials in dependence of reaction time

sample	reaction time	yield
CTF-1_2.5 min	2.5 min	80%
CTF-1_5 min	5 min	78%
CTF-1_10 min	10 min	77%
CTF-1_15 min	15 min	73%
CTF-1_20 min	20 min	68%
CTF-1_30 min	30 min	62%

Photocatalytic Hydrogen evolution experiments.

Photocatalytic hydrogen evolution experiments were performed in a 38 mL teflon reactor fitted with quartz glass window and temperature controller maintaining the temperature at 30±1˚C.[1] The reactor was filled with 25 mg of catalyst, 34 mL water (0.05M phosphate buffer) + Acetonitrile mixture (1:1) and 4 mL TEOA degassed and then irradiated with a 300 W Xe lamp (L.O.T.-Quantum design) with a cut off filter of 420 nm. Pressure vs time profile was recorded and at the end of the reaction which was then converted to volume vs time, the obtained gas from the head space was injected into GC to determine the volume %. The irradiation area of the light was 12.5 cm^2. The amount of evolved H_2 in μmol was calculated from the volume.

Determination of apparent quantum efficiency.

Hydrogen evolution experiments for quantum efficiency were carried out in a 60 mL reactor (same configuration as above) with 450±10 nm light. The intensity of the light was to 190 mW measured by Laser point plus+ power meter equipped with a power sensor y CEL-NP 2000 spectroradiometer and averaged. The apparent quantum efficiency (AQE) has been calculated by following the equation:

$$AQE = \frac{2 \times number\ of\ hydrogen\ molecules}{number\ of\ incident\ photons} \times 100$$

S2. Elemental analysis

Table S2: Elemental analysis of pre-CTF and CTF-1_X min

sample	C [wt%]	N[wt%]	C/N[a]	H[wt%]
CTF-1$_{\text{(theor.)}}$	**75.00**	**21.86**	**4.00**	**3.15**
pre-CTF	66.32	19.10	4.05	3.69
CTF-1_2.5 min	70.21	20.14	4.07	3.38
CTF-1_5 min	71.47	20.26	4.12	3.28
CTF-1_10 min	72.83	20.61	4.12	3.25
CTF-1_15 min	73.25	20.93	4.08	3.12
CTF-1_20 min	73.93	21.34	4.04	3.13
CTF-1_30 min	74.11	21.51	4.02	3.09

S3. X-ray diffraction analysis

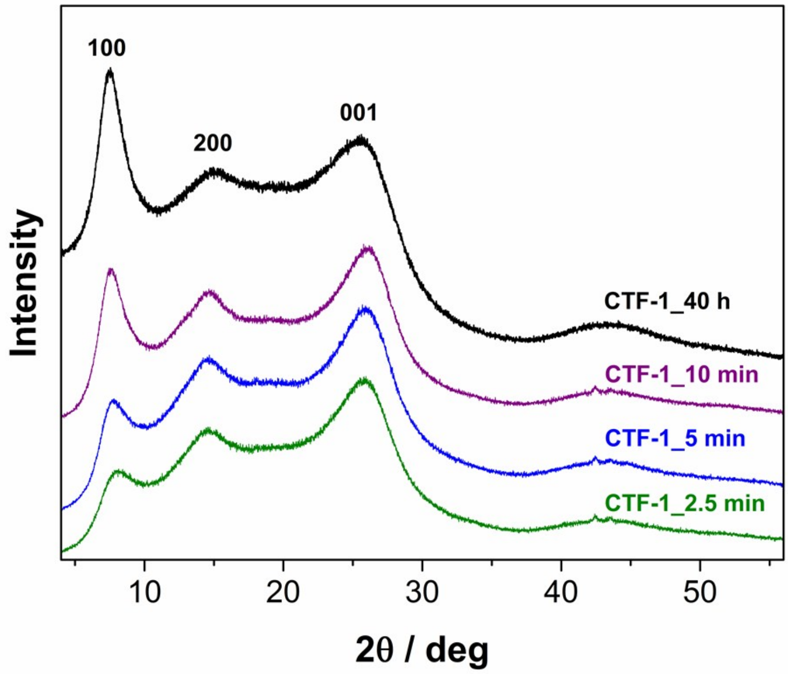

Figure S 1: Powder XRD patterns of CTF-1_40 h prepared by the two-step method and CTF-1_X min materials with X = 2.5 – 10 min

S.4. NMR spectroscopy

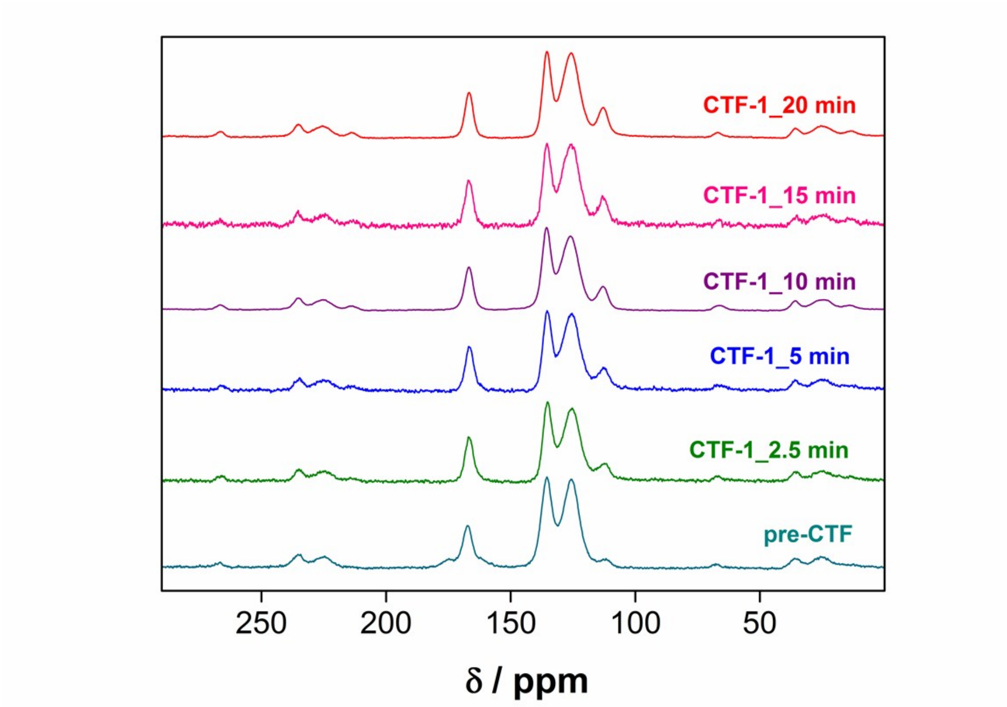

Figure S 2: Solid state ^{13}C-MAS-NMR spectra of pre-CTF and CTF-1_X min samples with X = 2.5 – 20 min

S.5. Infrared spectroscopy

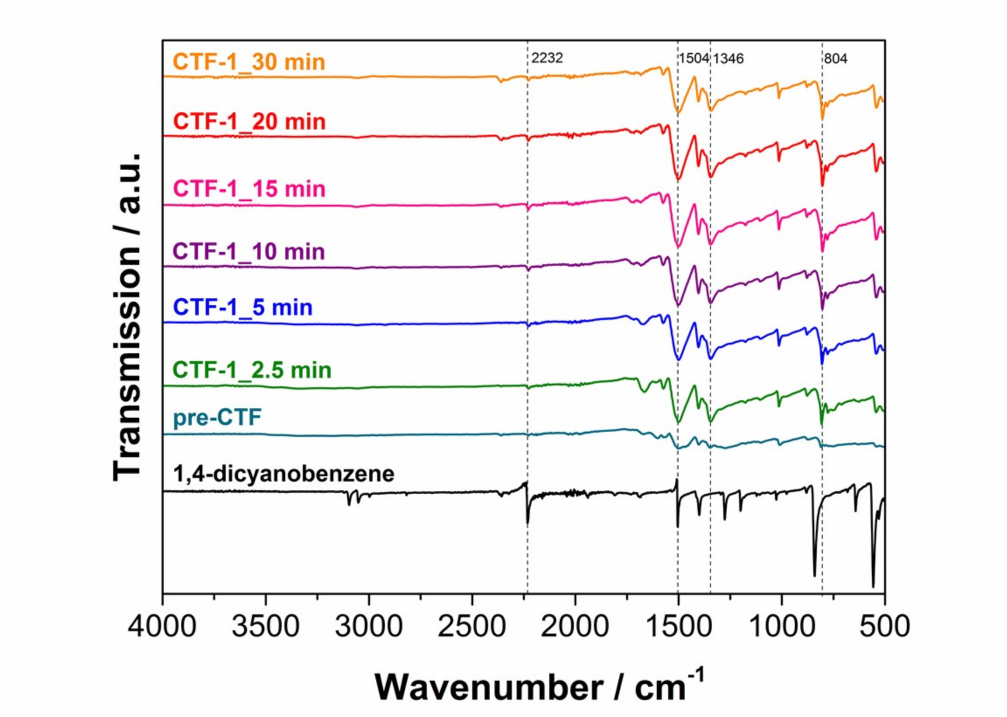

Figure S 3: Infrared spectra of 1,4-dicyanobenzene, pre-CTF and CTF-1_X min samples with X = 2.5 – 30 min

S6. UV/Vis spectroscopy

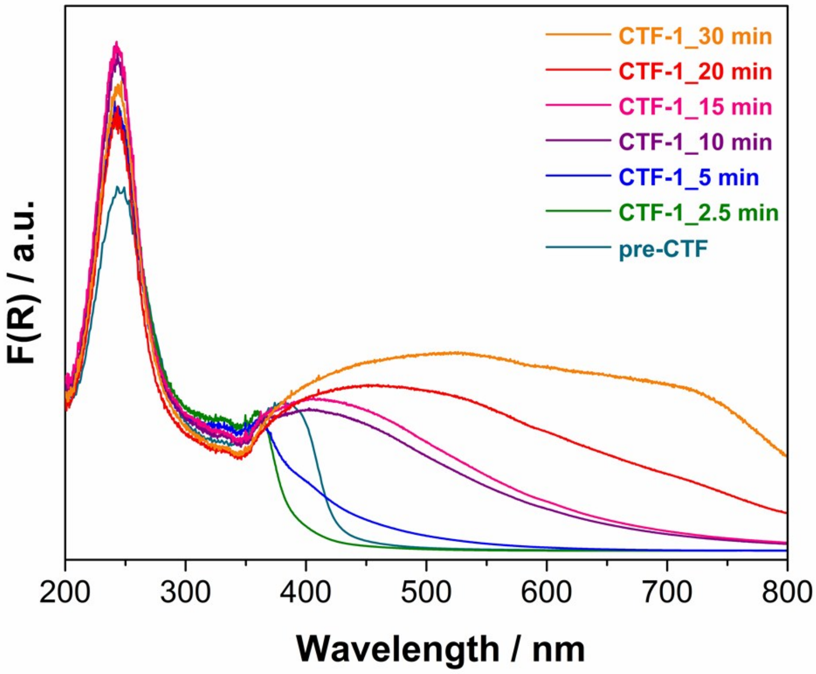

Figure S 4: UV/Vis spectra of pre-CTF and CTF-1_X min samples with X = 2.5 – 30 min.

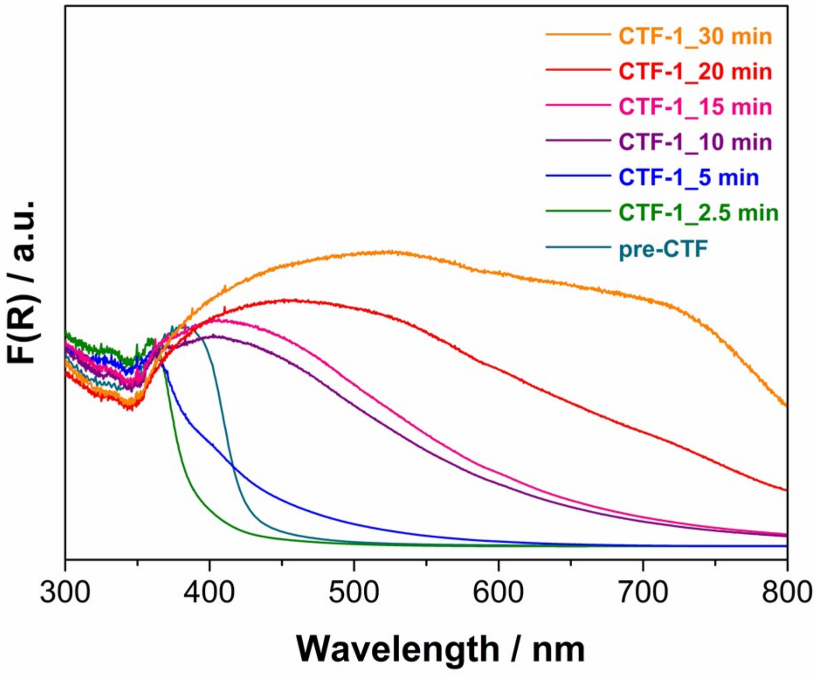

Figure S 5: Zoom of UV/Vis spectra of pre-CTF and CTF-1_X min samples with X = 2.5 – 30 min

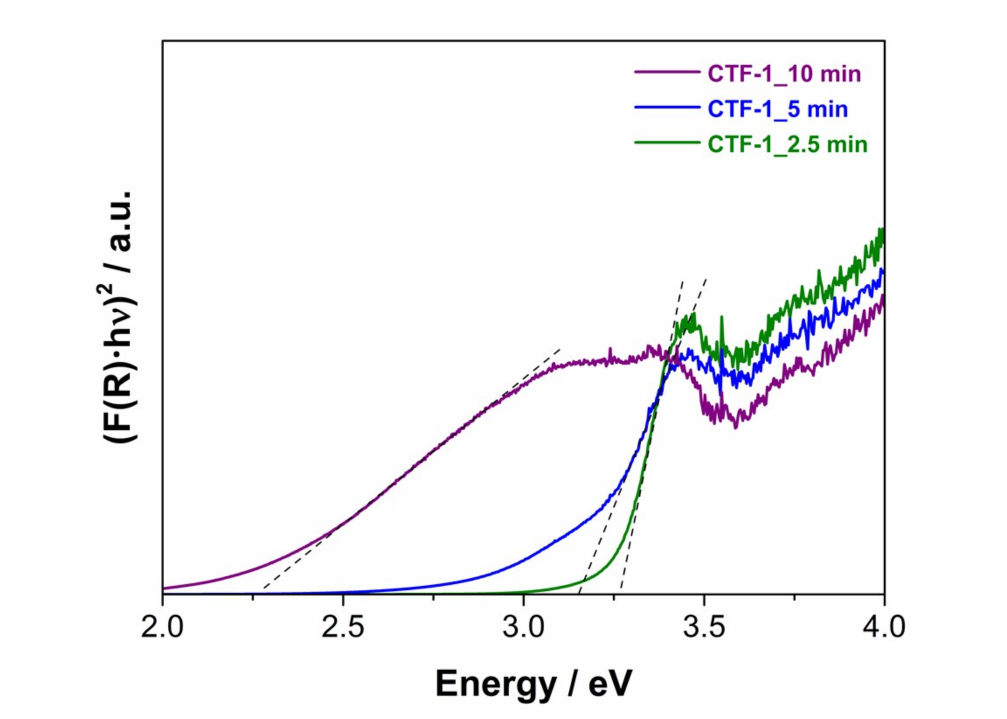

Figure S 6: Tauc Plots of CTF-1_X min samples with X = 2.5 – 10 min.

S7. Hydrogen evolution measurements

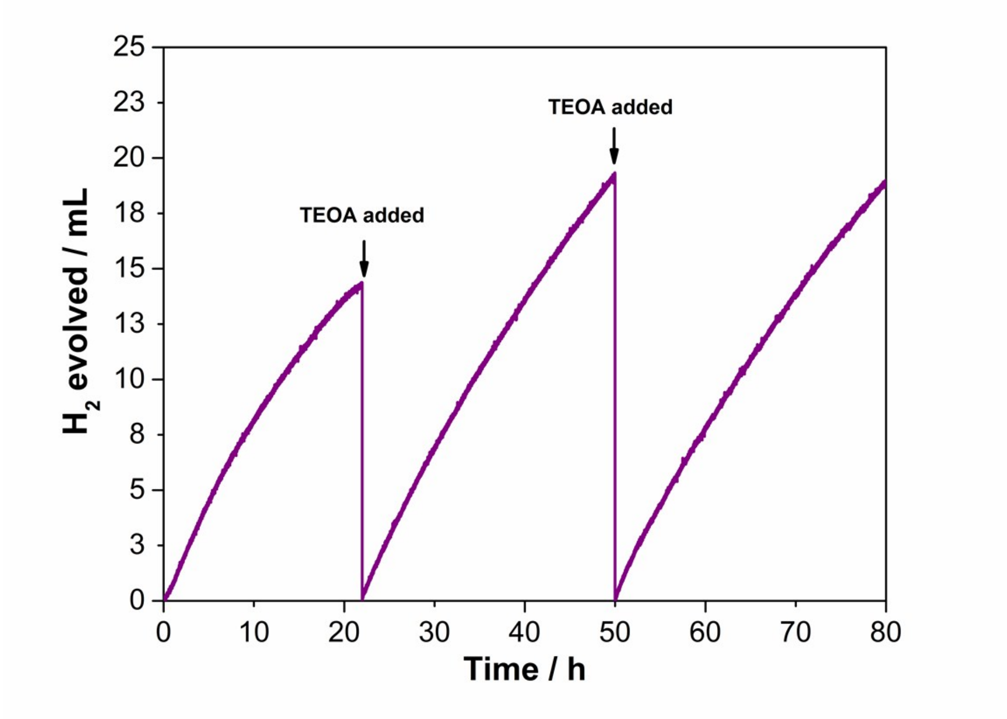

Figure S 7: Long term photocatalytic hydrogen evolution of CTF-1_10 min under visible light irradiation (λ≥ 420 nm) using a 300 W Xenon lamp.

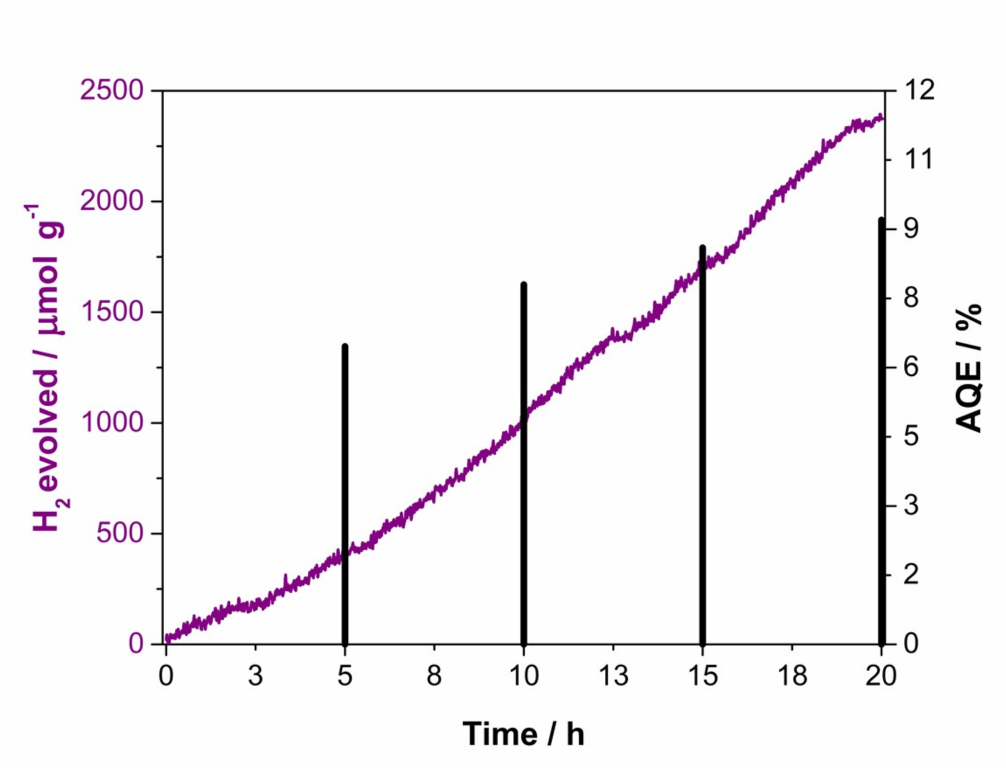

Figure S 8: Photocatalytic hydrogen evolution of CTF-1_10 min under 450 nm visible light irradiation and corresponding apparent quantum efficiencies using a 300 W Xenon lamp equipped with 450±10 nm bandpass filter.

S8. TEM images

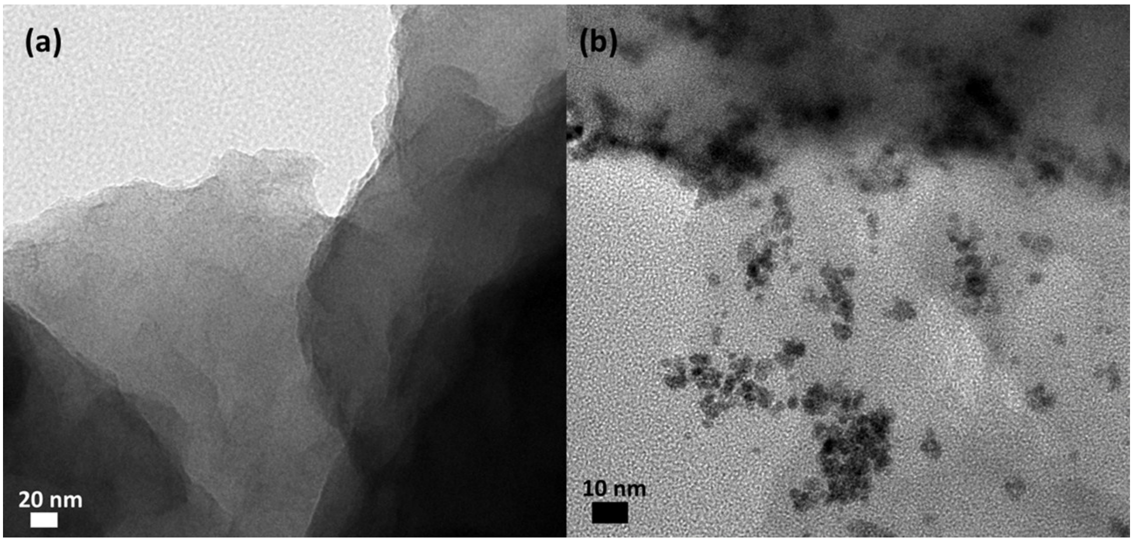

Figure S 9: TEM images of the photocatalyst (a) before and (b) after photocatalytic reaction.

References

1 M. Schwarze, D. Stellmach, M. Schröder, K. Kailasam, R. Reske, A. Thomas and R. Schomäcker, *Phys. Chem. Chem. Phys.*, 2013, **15**, 3466.