

Supporting Information

Facile Synthesis of New, Highly Efficient SnO₂/Carbon Nitride Composite Photocatalysts for Hydrogen Evolution Reaction

Christian Fettkenhauer,^a Guylhaine Clavel,^a Kamalakannan Kailasam,^b Markus Antonietti,^a
and Dariya Dontsova^{*,a}

[a] Max Planck Institute of Colloids and Interfaces

Department of Colloid Chemistry

Research Campus Golm

Am Mühlenberg 1

144476 Potsdam/Golm, Germany

[b] Technische Universität Berlin

Institut für Chemie

Sekr. TC 2

Englische Straße 20

10587 Berlin, Germany

General Information

Synthesis conditions. Total amount of oxygen originating from N₂ flow (3 ppm, 15 L/min) that passes through the oven of ~1L volume during at least 10 hours of synthesis (this is a minimal duration of “molten state” of the reaction mixture) is:

$$\frac{15[\text{L/min}] \cdot 600[\text{min}] \cdot 3 \cdot 10^{-6}}{22.4[\frac{\text{L}}{\text{mol}}]} = 1.205 \text{ mmol.}$$

Hydrogen evolution set up and measurement procedure.

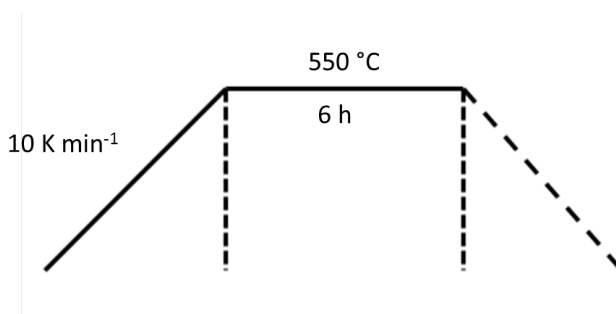
All catalytic experiments were carried out under argon atmosphere. The double walled and thermostatically controlled reaction vessel was connected to a digital pressure sensor (Type-P30, DP =_0.1%, WIKA Alexander Wiegand SE & Co. KG, Germany) to monitor the pressure increase due to hydrogen evolution. 25 mg of sample was placed inside the reactor; then the reactor was evacuated and refilled with argon for several times. Water and TEOA were pre-treated before use. Water was first degassed for 1 h under vacuum in an ultrasonic bath followed by purging with argon for 1 h. TEOA was separately purged for 1 h with argon. The solvent mixture (total volume 38 mL) composed of water and triethanolamine (TEOA) in the ratio of 9/1 (v/v) and 19.7 μL H₂PtCl₆ solution (corresponds to theoretical Pt loading of 3 wt. % onto the catalyst), were added in the reactor. The temperature in the reactor was maintained at 25 °C by a thermostat. After stirring for 10 min to reach thermal equilibrium, the reaction was started by switching on 50 W white LED array (Bridgelux BXRA-50C5300, λ > 410 nm) or 12 W blue LED array (Osa Opto Light, OLM-018 air, λ = 420 nm). The amount of evolved gas was continuously monitored as time-

dependent pressure increase. The hydrogen evolution rate was calculated according to the ideal gas law:

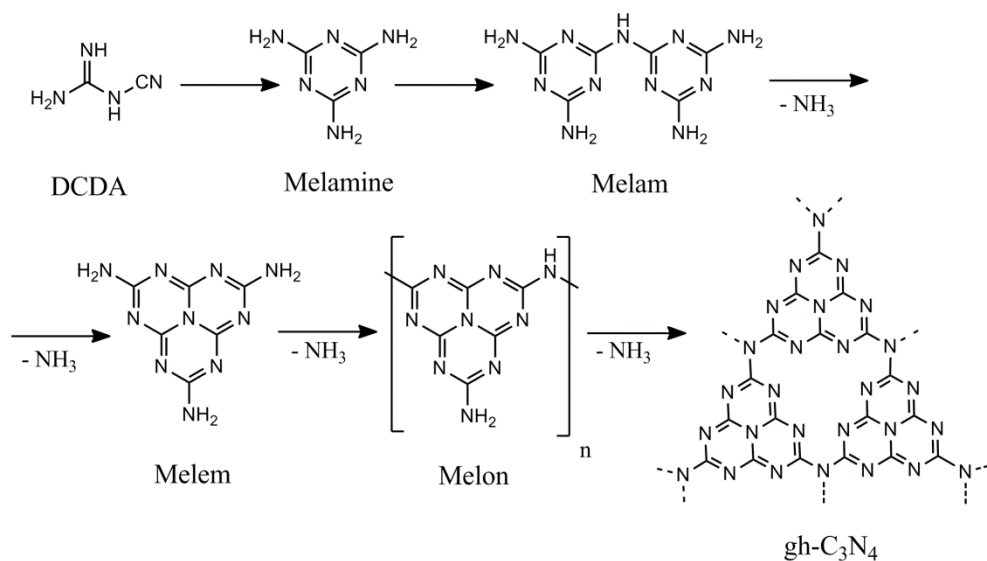
$$\dot{n} = \frac{n}{t} = 10^5 \frac{\Delta p \cdot V}{R \cdot T \cdot t}$$

where \dot{n} is hydrogen evolution rate [$\mu\text{mol/h}$], n moles hydrogen [μmol], t illumination time [h], Δp pressure increase [bar] during irradiation time t , V volume of the headspace above the reaction mixture, R universal gas constant [$8.314 \text{ J/mol}\cdot\text{K}$] and T temperature [298 K].

To confirm that the evolved gas is hydrogen, the headspace of the reactor was analyzed by mass spectrometry (Pfeiffer Vacuum ThermoStar GSD 301 T gas analyzing system; using argon as carrier gas) and GC-MS after the test. GC-MS analysis was performed using a Shimadzu GCMS-QP2010 equipped with a capillary column (HP-Plot/Q, 30 m, 0.25 mm, 20 μm). The measurement was running under isothermal conditions at 40 °C column temperature. Helium was used as a carrier gas; before injection of the headspace sample, the sample loop was purged with argon.



Scheme S1. Heating program used for the synthesis of composites in SnCl_2 -containing salt melts.



Scheme S2. Condensation scheme of dicyandiamide (DCDA) to hypothetical s-heptazine-based fully condensed C₃N₄¹⁻³.

Salt mixture A/B	A content, wt. %	B content, wt. %	Melting Point, °C
SnCl ₂	100	-	247
LiCl/SnCl ₂ *	20	80	220
NaCl/SnCl ₂	12.6	87.4	183
KCl/SnCl ₂	19.9	80.1	180
CsCl/SnCl ₂	15.4	84.6	174
ZnCl ₂ /SnCl ₂	36.1	63.9	171

Table S1. Composition and melting points of eutectic salt mixtures figuring in this paper.

*LiCl and SnCl₂ do not form an eutectic, the melting point was determined by DSC method as the onset of the first melting step.

Melt	N, wt. %	C, wt. %	H, wt. %	C/N	100-C-N- H	Yield*, %	Color	S _{BET} , m ² /g
LiCl/SnCl ₂	46.2	28.8	2.92	0.63	22.1	70.1	beige	32
NaCl/SnCl ₂	46.2	28.3	2.70	0.61	22.8	63.8	beige	218
KCl/SnCl ₂	40.5	25.7	2.72	0.63	31.1	80.8	beige	170
CsCl/SnCl ₂	45.5	27.8	2.76	0.61	23.9	71.2	beige	113
ZnCl ₂ /SnCl ₂	45.9	26.8	3.26	0.58	24.0	74.1	orange	30
SnCl ₂	27.7	17.4	1.23	0.63	53.7	116.8	black	27
ref.-CN	60.1	35.0	2.06	0.58	2.8	63	yellow	10

* Given yields are based on the amounts of the precursor (DCDA); S_{BET}: Surface area values from BET method.

Table S2. Elemental analysis data, yields, colors and calculated BET surface areas of composite materials synthesized in different salt melts containing SnCl₂.

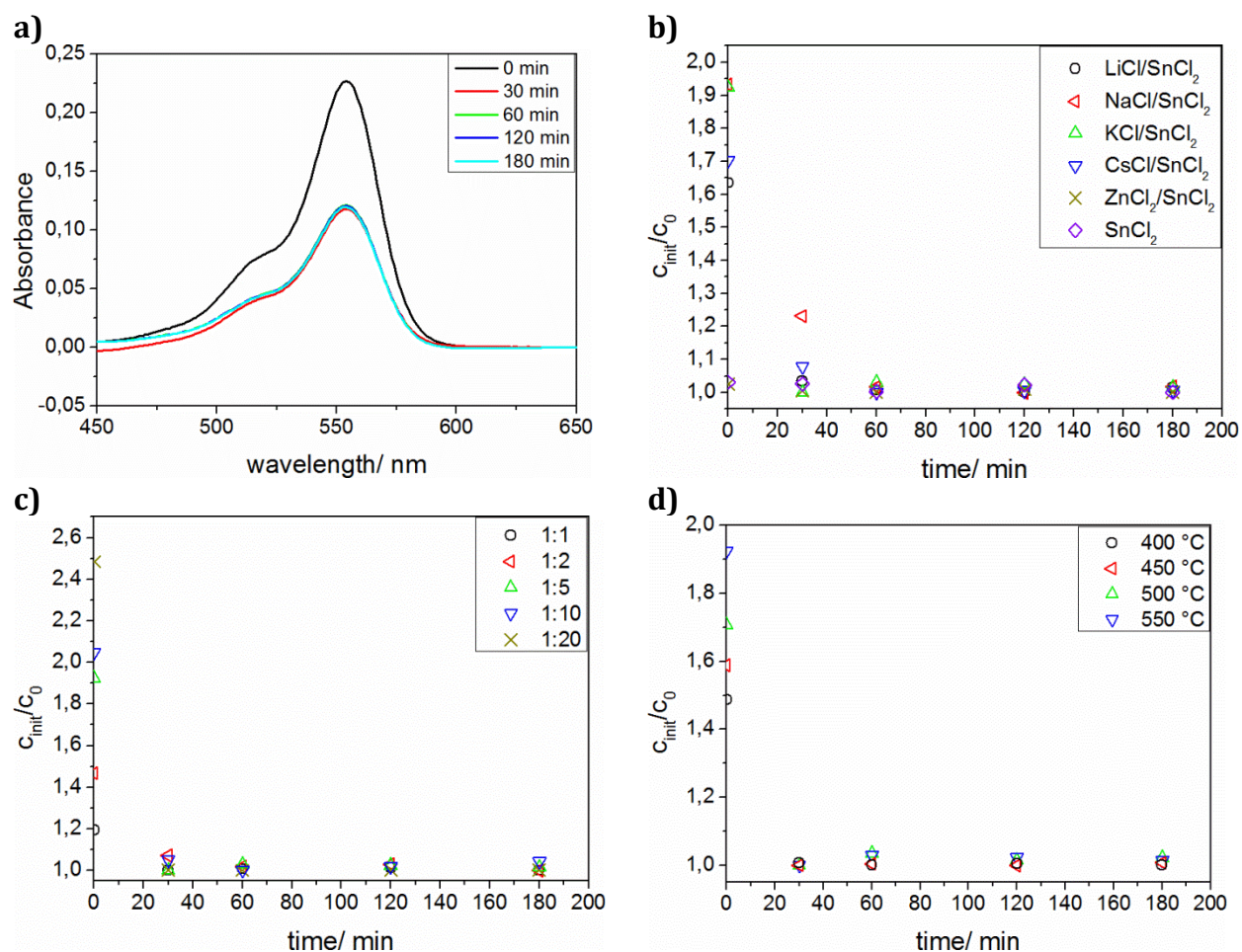


Figure S1. Stabilization of the concentration of RhB with time in the dark by reaching adsorption-desorption equilibrium: a) original UV-Vis spectra of RhB solutions containing KCl/SnCl₂-product as a function of time; ratios of initial dye concentration (C_{init}) to concentration just before the irradiation is switched on (C_0) in the presence of composites prepared b) in different salt melts (at 550 °C, at 1:5 precursor to salts ratio), c) at different precursor to salts ratios (at 550 °C, in KCl/SnCl₂ melt) and d) at different synthesis temperatures (in KCl/SnCl₂ melt, at 1:5 precursor to salts ratio).

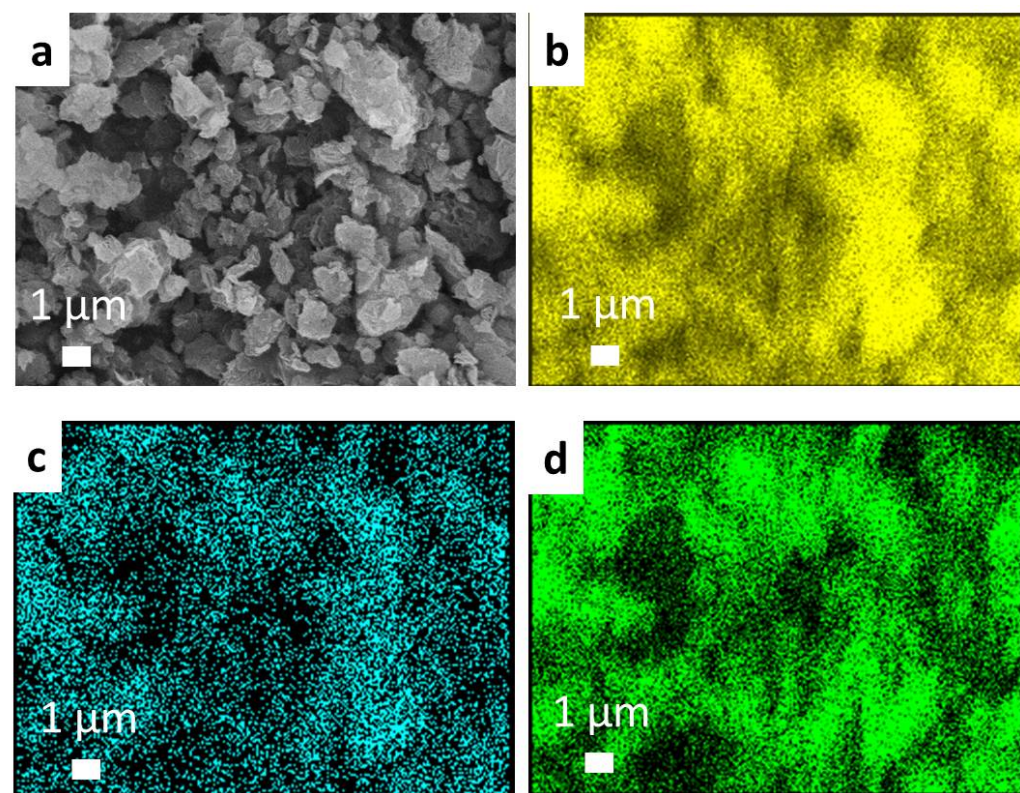


Figure S2. SEM (a) and corresponding elemental mapping images of Sn (b), Cl (c) and O (d) in KCl/SnCl₂-composite.

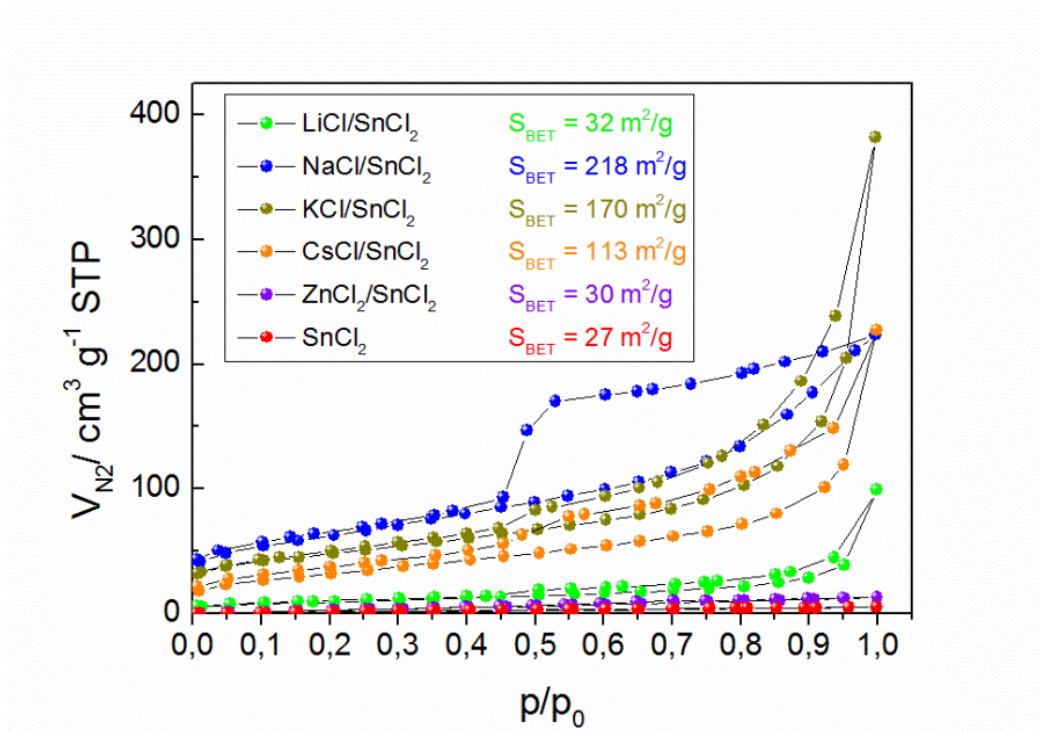
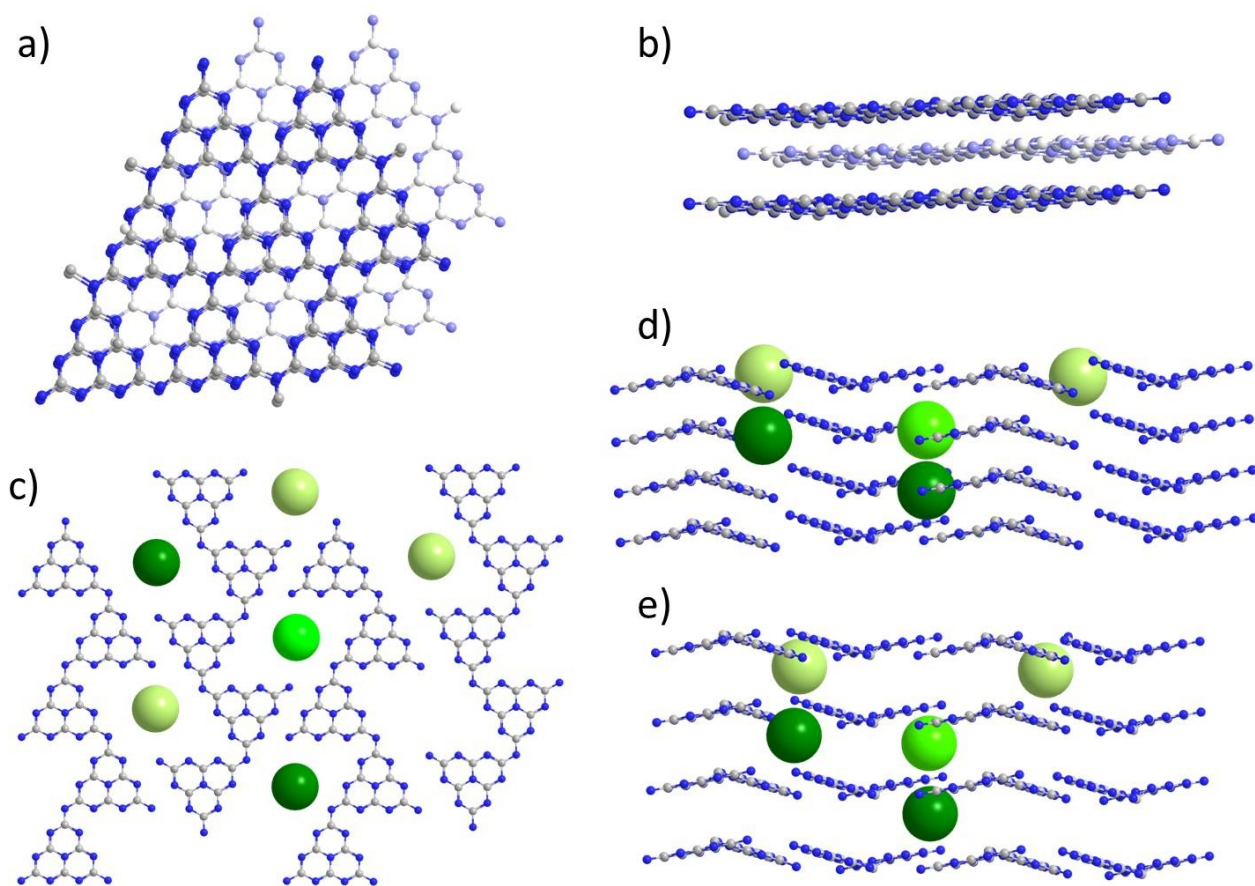


Figure S3. N₂ sorption isotherms of products prepared in SnCl₂ containing salt mixtures. Observed hysteresis (H3-type) is caused by agglomeration of plate-like particles that give rise to slit-shaped pores in products prepared in LiCl/SnCl₂, KCl/SnCl₂ and CsCl/SnCl₂. H2-type hysteresis for the product prepared in NaCl/SnCl₂ indicates rather undefined pore shapes.⁴



Scheme S3. Simplified (for clarity of view) schematic representation of layer stacking in idealized heptazine-based C_3N_4 (gh- C_3N_4) and in suggested Phases I and II intercalated with tin species: schematically shown top (a) and side (b) view of a perfect AB stacked carbon nitride; c) schematically shown top view of a perfect AA stacked 1D-melon zig-zag polymer intercalated with tin species, general representation of Phases I and II; d) and e) side views of Phases I and II, respectively, illustrating that all melon units are tilted. Tin ions are shown as green spheres with different color intensities illustrating different distances to these ions (more intense color – closer distance, while more pale color – further distance). Oxygen and chlorine counter-ions are omitted for clarity. Nitrogen atoms are marked in blue, carbon atoms – in grey, hydrogen atoms are omitted for clarity.

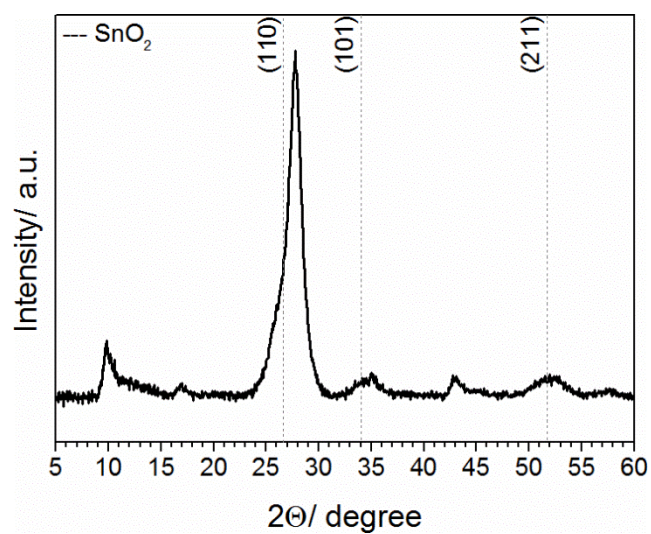


Figure S4. WAXS pattern of NaCl/SnCl₂-derived product. The three main SnO₂ reflections are marked as vertical dotted lines.

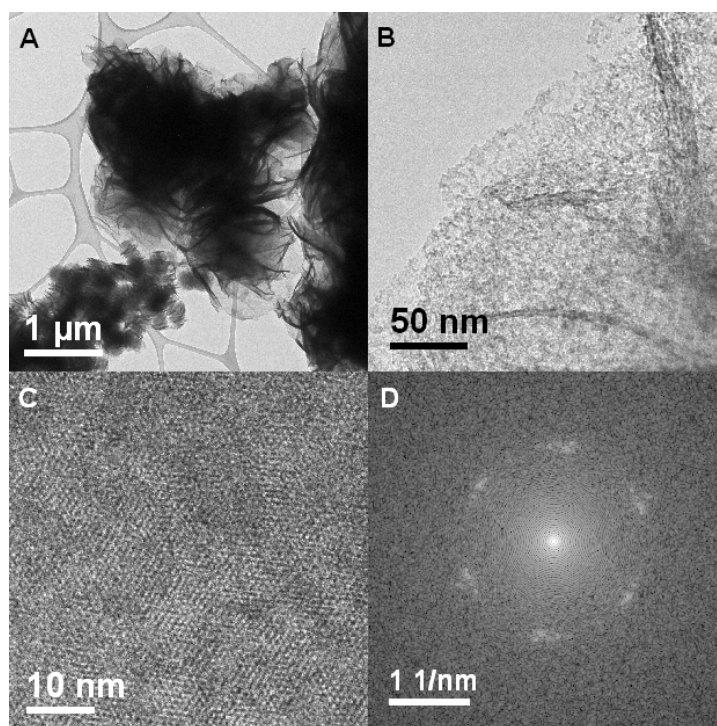
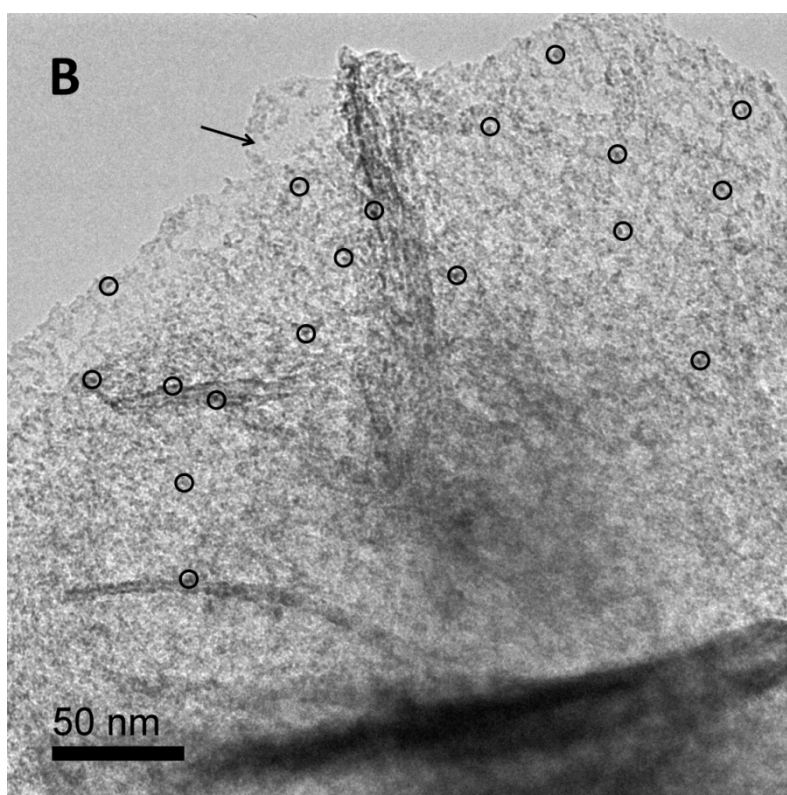
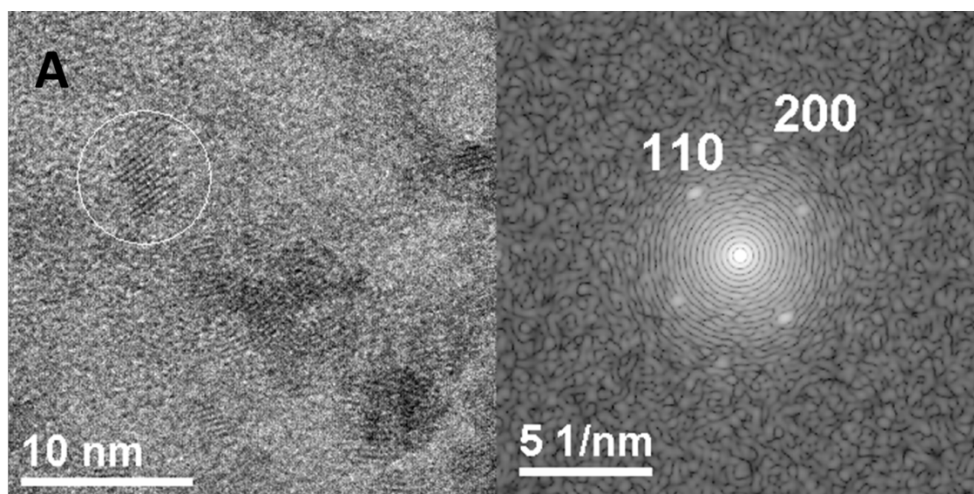
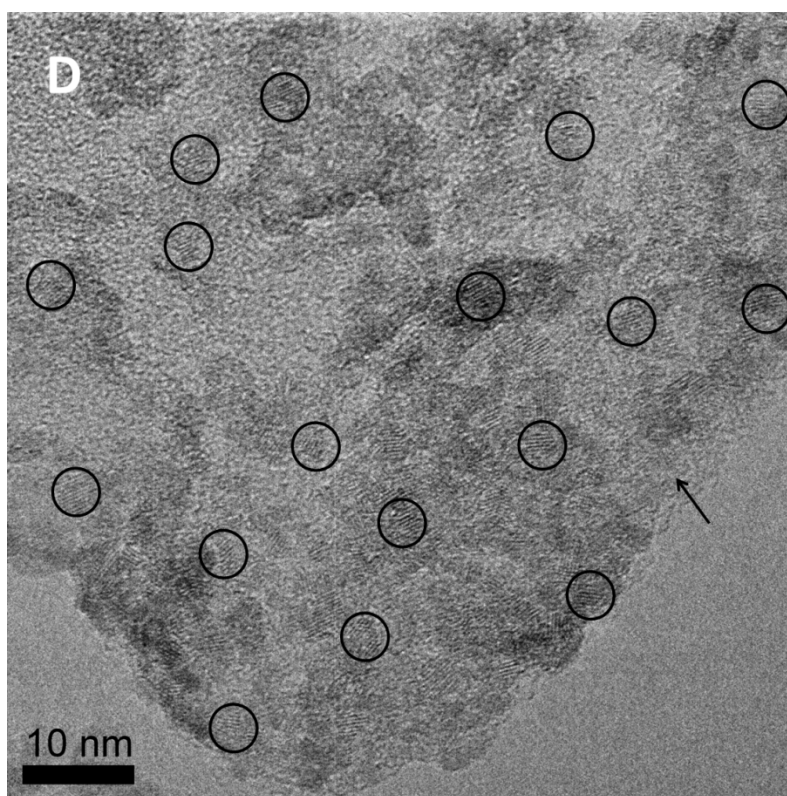
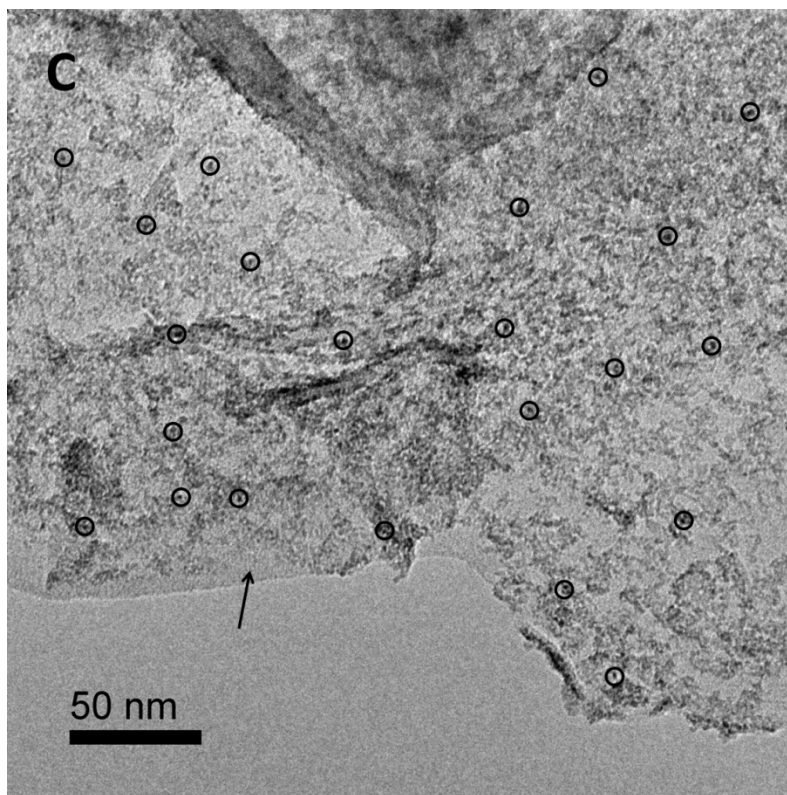


Figure S5. TEM overview images of KCl/SnCl₂-derived composite (A, B); HR-TEM image of the carbon nitride sheets (C) with the corresponding fast Fourier transform (FFT) image (D).





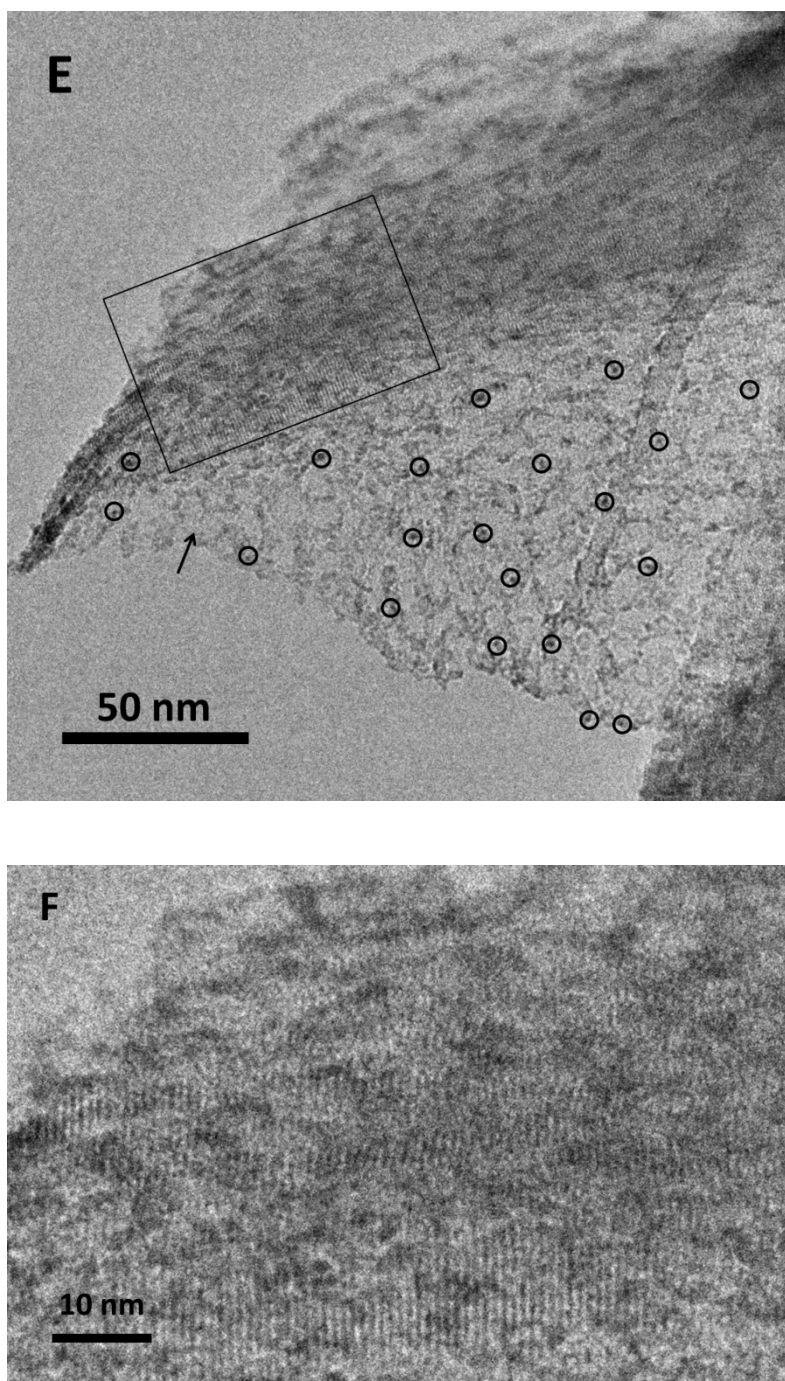


Figure S6. A) HR-TEM image and the corresponding fast Fourier transform (FFT) image ($d_{200}= 2.37$, $d_{110}= 3.37$, zone axis $[001]$) of a SnO_2 particle from the KCl/SnCl_2 composite; B- E) TEM images of CN-polymer sheets (indicated by arrows) decorated with SnO_2

nanoparticles (dark dots, some of them are marked by circles); F) magnification of rectangular area of E) showing lattice fringes of CN-polymer .

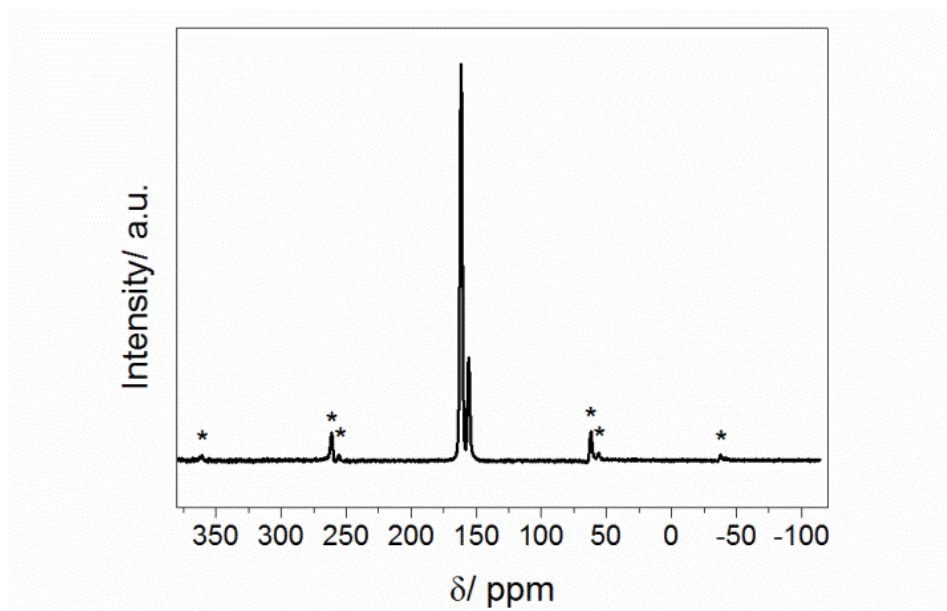


Figure S7. $^{13}\text{C}\{^1\text{H}\}$ CP/MAS NMR of $\text{KCl}/\text{SnCl}_2\text{-CN}$. * indicate the spinning side bands in the ^{13}C -spectra.

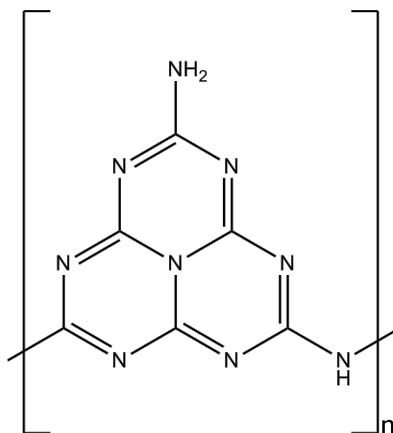


Figure S8. Repeating unit of melon.

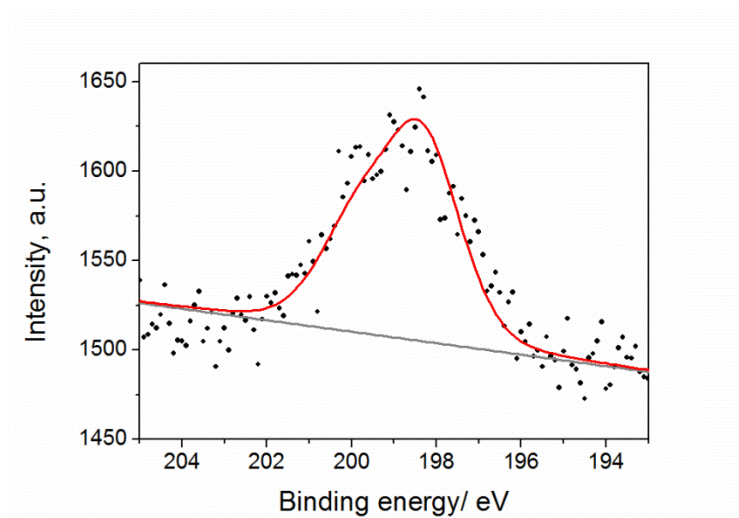


Figure S9. Cl2p XPS spectrum of KCl/SnCl₂-CN.

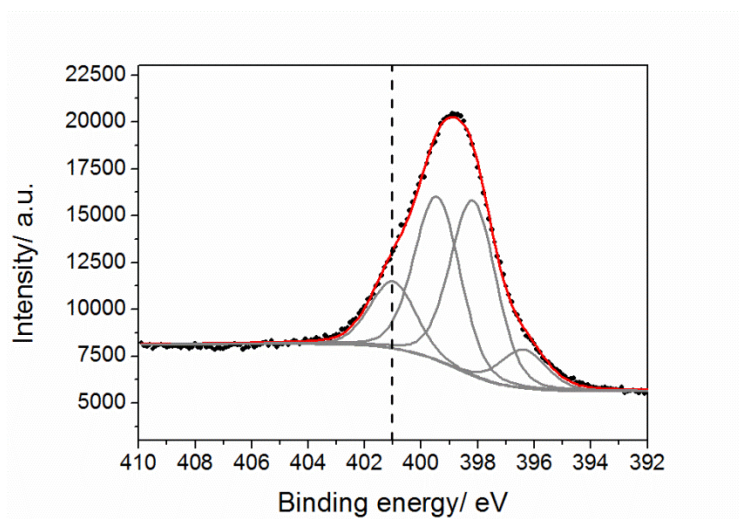


Figure S10. N1s XPS spectrum of KCl/SnCl₂-CN after Ar ion bombardment, dashed line marks peak of amino nitrogen which is shifted to 401.0 eV due to coordination to Sn.

Temperature °C	N, wt. %	C, wt. %	H, wt. %	C/N ratio	100-C-N-H
400	41.8	25.1	2.89	0.60	30.2
450	44.5	27.6	2.96	0.62	24.9
500	48.1	30.3	2.82	0.63	18.8
550	40.5	25.7	2.72	0.63	31.1

Table S3. Composition of products prepared in KCl/SnCl₂ eutectic at different synthesis temperatures, according to EA data.

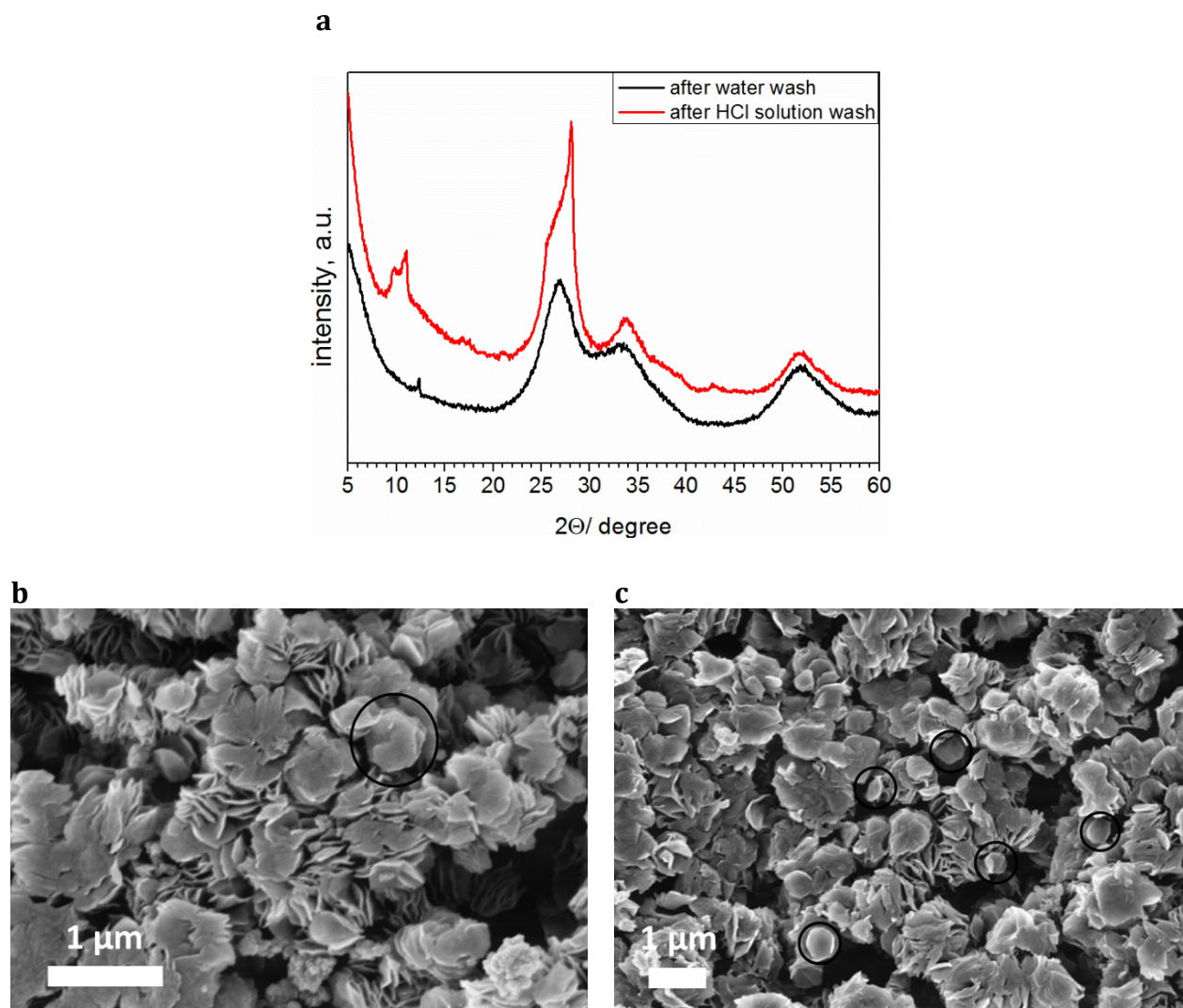


Figure S11. a) WAXS patterns of product synthesized in KCl/SnCl₂-melt at 400 °C at 1:5 precursor to salt ratio after water wash and after HCl solution wash illustrating the absence of crystallized low molecular weight salts such as melonates after water washing step, b) c) SEM images of KCl/SnCl₂-derived composite illustrating the presence of hexagonal-shape nano-sheets after acid-washing step.

DCDA : Salts weight ratio	N, wt. %	C, wt. %	H, wt. %	C/N	100-C-N-H	S_{BET}, m²/g
1:1	46.6	28.2	2.57	0.61	15.8	139
1:2	50.8	30.4	2.64	0.60	16.2	38
1:5	40.5	25.7	2.72	0.63	31.1	170
1:10	41.5	25.5	2.69	0.61	30.3	138
1:20	27.5	18.5	2.67	0.67	51.3	295

Table S4. Composition of products prepared in KCl/SnCl₂ eutectic at different precursor to salts weight ratios, according to EA data, and calculated BET surface areas of products.

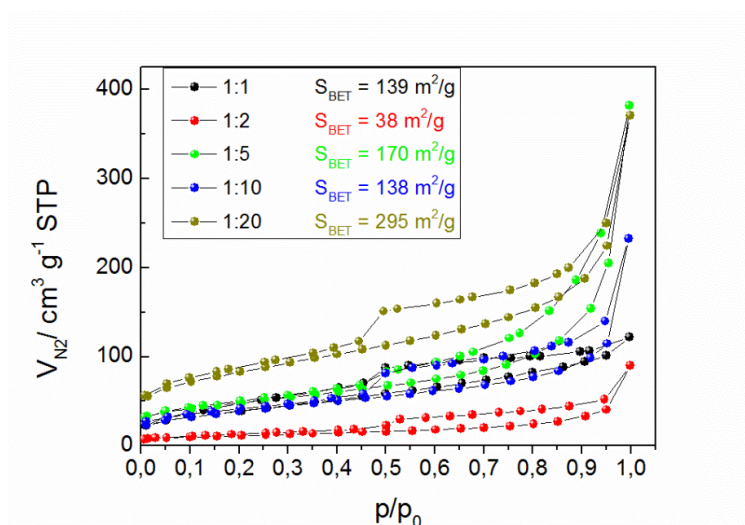


Figure S12. N₂ sorption isotherms of products prepared at different precursor to salt melt (KCl/SnCl₂) ratios.

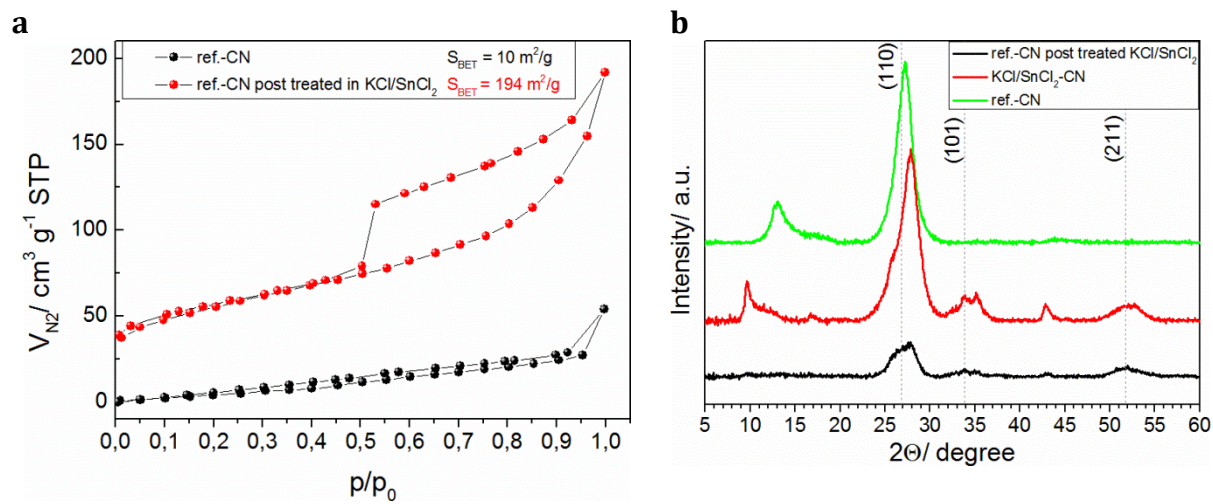


Figure S13. a) N_2 sorption isotherms of ref.-CN before and after post-treatment using KCl/SnCl₂ eutectic and b) WAXS patterns of ref.-CN before and after post-treatment using KCl/SnCl₂ eutectic, and of KCl/SnCl₂-derived composite. The three main SnO₂ reflections are marked as vertical dotted lines.

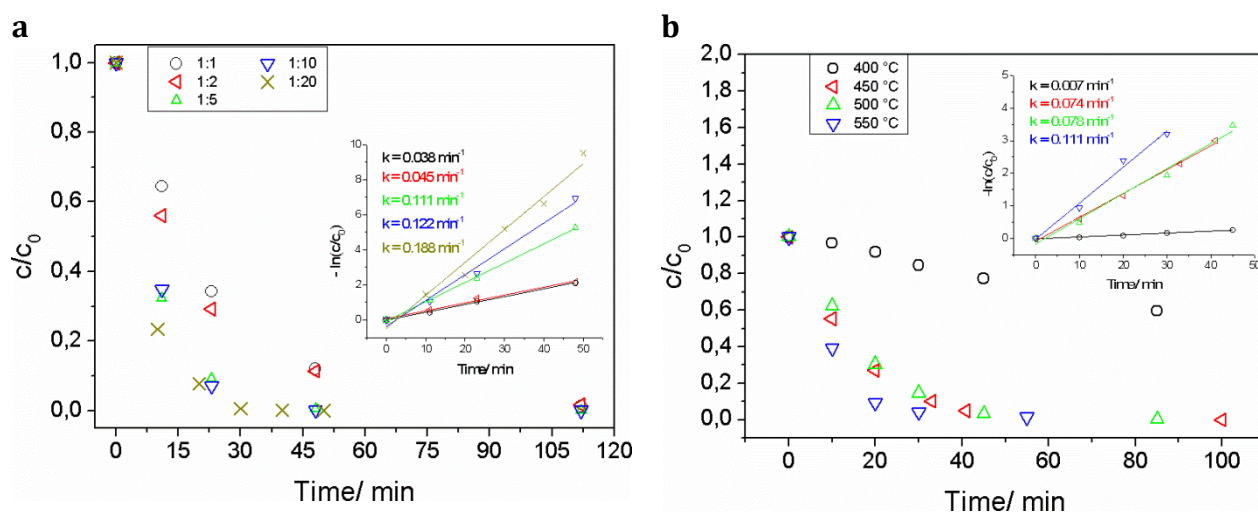


Figure S14. Dependence of Rhodamine B relative concentration (C/C_0) on irradiation time in the presence of photocatalysts prepared in KCl/SnCl₂ melt a) at different precursor to

salts weight ratios, b) at different synthesis temperatures. The insets show the linearly fitted dependences of $[-\ln(C/C_0)]$ on irradiation time and the reaction rate constants calculated as the slopes of these linear fits.

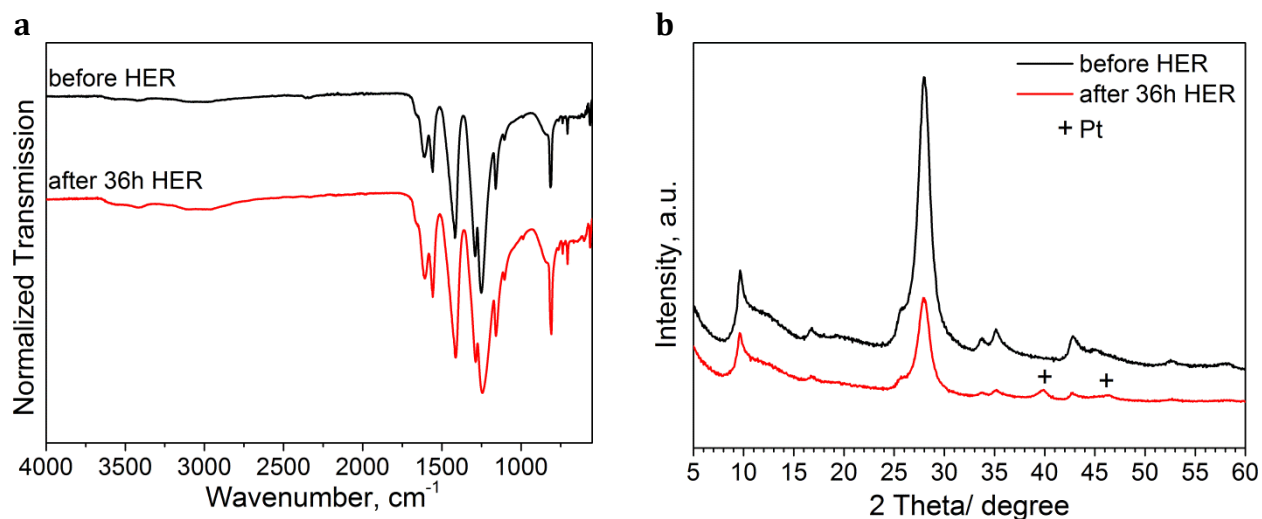


Figure S15. a) FTIR spectra and b) WAXS patterns of KCl/SnCl₂-product before and after 36 hours of HER illustrating chemical and structural stability of the composite during HER. During operation, a partial exfoliation of the photocatalyst likely takes place, which is observed as the decrease of the intensity of $2\theta = 27^\circ$ peak, while the intensity of $2\theta = 10^\circ$ peak remains almost unchanged. The exfoliation is likely due to the presence of triethanolamine which acts as a stabilizing agent for the newly created surface. This newly created surface must be stabilized chemically, e.g. by formation of terminal amino-groups and surface-adsorbed water molecules, which is observed in the corresponding FTIR spectrum as a slight increase of the broad absorption band between 3600-2800 cm^{-1} .

SnCl ₂ /KCl-product	C, wt. %	N, wt. %	H, wt. %	Sn, wt. %	O, wt. %	Cl, wt. %	Pt, wt. %
before HER	25.7	40.5	2.7	10.0	20.1	1.0	-
after HER	26.0	39.7	3.0	9.9	20.1	1.0	0.3

Table S5. Elemental composition (according to EA and EDX data) of KCl/SnCl₂-product before and after 36 hours of HER illustrating chemical stability of product during HER.

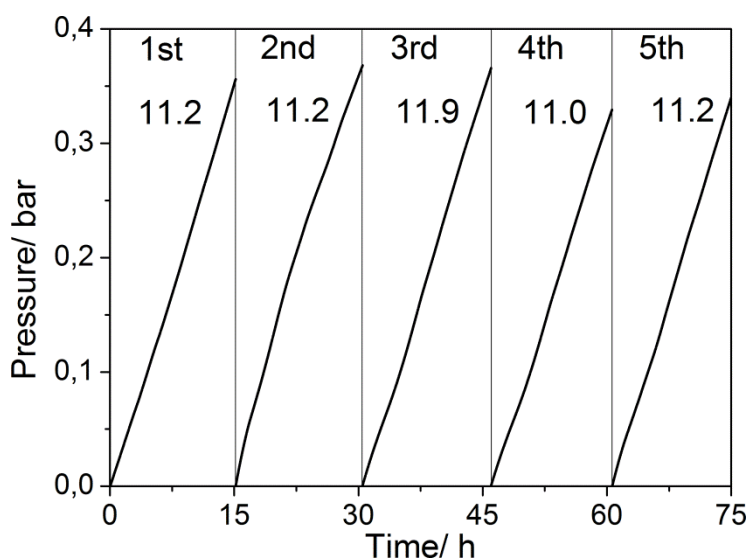


Figure S16 . Photocatalytic activity of KCl/SnCl₂-derived composite in HER upon recycling which was performed after each 15 hours of HER. Numbers indicate the calculated hydrogen evolution rate in μmol/h. Between the runs, the composite was separated by centrifugation, washed with deionized water until neutral pH (3 times) and then the activity test was repeated.

1. B. V. Lotsch and W. Schnick, *Chem. Eur. J.*, 2007, **13**, 4956-4968.
2. E. Kroke, *Angew. Chem. Int. Ed.*, 2014, **53**, 11134-11136.
3. A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J.-O. Muller, R. Schlogl and J. M. Carlsson, *J. Mater.Chem.*, 2008, **18**, 4893-4908.
4. K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol and T. Siemieniewska, *Pure & Appl. Chem.*, 1985, **57**, 603-619.