

Supporting Information

1,2,4-Triazoles-based approach to noble-metal-free visible-light driven water splitting over carbon nitrides

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Materials

Lithium chloride (99%), potassium chloride (99%), molybdenum (V) chloride (95%), and cobalt chloride hexahydrate (98%) were purchased from Sigma Aldrich, 3-amino-1,2,4-triazole-5-thiol (98%) and triethanolamine (TEOA, 98%) were purchased from Alfa Aesar, ammonia 32% aq. solution was purchased from Merck. All the chemicals were used without further purification.

General synthesis procedure

Lithium chloride, potassium chloride and the corresponding precursors were ground together in a glove-box (mBraun Unilab, O₂ < 0.1 ppm, H₂O < 0.1 ppm) under an argon atmosphere. Typically, 1g of 3-amino-1,2,4-triazole-5-thiol and 5g of LiCl/KCl mixture were used. The weight ratio between lithium chloride and potassium chloride was 9:11 corresponding to their eutectic composition. The amounts of added MoCl₅ were 0, 5, 10, 20, 50, 100 and 200 mg to prepare 0.0, 0.5, 1.0, 2.0, 5.0, 10 and 20 wt. % composites, respectively. The amount of Co₃[3,5-diamino-1,2,4-triazole]₆ was 50 mg or 5 wt.% relative to the amount of 3-amino-1,2,4-triazole-5-thiol. Reaction mixtures (~5–10 g) were transferred into porcelain crucibles and covered with lids. Crucibles were placed in the oven and heated under a constant nitrogen flow (15 L/min) with a heating rate of 2.3 K/min up to the final temperature (550 or 600 °C), held at this T for 6 hours, then allowed to cool down naturally. The crude products were removed from the crucibles and washed with deionized water (50–100 mL). MoS₂/PHI composites were additionally washed with 1 M HCl solution (50–100 mL). Each washing step was carried out for 15 hours. The final products were isolated by filtration, then thoroughly washed on the filter with deionized water (500 mL) until neutral pH, and finally dried in a vacuum oven at 50 °C for 15 h.

Synthesis of Co₃[3,5-diamino-1,2,4-triazole]₆ was carried out according to the modified literature procedure.¹ A mixture of 3,5-diamino-1,2,4-triazole (0.2 g, 2.0 mmol), CoCl₂ · 6H₂O (0.285 g, 1.2 mmol) and aqueous ammonia (32%, 3.0 mL) was placed in a 23 mL glass tube of 45 mL Teflon liner; 4 mL of ethanol and 12 mL of water were then added. The resulting suspension was stirred for 5 min and was then sealed in a Parr autoclave. The autoclave was placed in a programmable furnace and heated to 160 °C. The temperature was held for 3 days, and then, the reactant mixture was allowed to cool down. Bundled violet needles were isolated in 48 % yield. Anal. Calculated (wt. %) for C₁₂H₂₄N₃₀Co₃: C, 18.83; H, 3.16; N, 54.91. Found (EA): C, 18.92; H, 3.20; N, 53.81%. EDS showed absence of oxygen and chlorine in the product. FTIR-ATR (cm⁻¹): 3445 (m), 3410 (w), 3368 (m), 3317 (br, m), 3184 (br, m), 1608 (s), 1544 (s), 1471 (br, s), 1373 (s), 1127 (w), 1101 (m), 1046 (br, s), 842 (m), 765 (s,) 707 (br, w), 672 (w).

Characterization

Powder X-Ray diffraction patterns were measured on a Bruker D8 Advance diffractometer equipped with a scintillation counter detector with CuK α radiation (λ = 0.15418 nm) applying 2 θ step size of 0.05° and counting time of 4s per step. The solid-state NMR ¹³C{¹H} CP/MAS (cross-

polarization magic angle spinning) measurements were carried out using a Bruker Avance 400 spectrometer operating at 100.6 MHz using a Bruker 4 mm double resonance probe-head operating at a spinning rate of 10 kHz. ^1H composite pulse decoupling was applied during the acquisition. ^{13}C chemical shifts were referenced externally to tetramethylsilane (TMS) using adamantane as a secondary reference. Nitrogen adsorption/desorption measurements were performed after degassing the samples at 150 °C for 20 hours using a Quantachrome Quadrasorb SI-MP porosimeter at 77.4 K. The specific surface areas were calculated by applying the Brunauer-Emmett-Teller (BET) model to adsorption isotherms (N_2 at 77.4 K) for $0.05 < p/p_0 < 0.3$ using the QuadraWin 5.05 software package. Elemental analysis (EA) was accomplished as combustion analysis using a Vario Micro device. Optical absorbance spectra of powders were measured on a Shimadzu UV 2600 equipped with an integrating sphere. The emission spectra were recorded on LS-50B, Perkin Elmer instrument. The excitation wavelength was 350 nm. Scanning electron microscopy (SEM) images were obtained on a LEO 1550-Gemini microscope. Transmission electron microscopy (TEM) was performed on a CM200FEG (Philips) microscope, operated at 200 kV. Samples were prepared by depositing a drop of a suspension of particles in ethanol onto the amorphous carbon film. Energy-dispersive X-ray spectroscopy (EDS) investigations were conducted on a Link ISIS-300 system (Oxford Microanalysis Group) equipped with a Si (Li) detector and an energy resolution of 133 eV. X-ray photoelectron spectroscopy (XPS) was performed on a Multilab 2000 (Thermo) spectrometer equipped with Al $\text{K}\alpha$ anode ($h\nu = 1486.6$ eV). All spectra were referenced to the C 1s peak of adventitious carbon at 284.8 eV. For quantification purposes, survey spectra at pass energy of 50 eV and high-resolution spectra at pass energy of 20eV were recorded and analysed by XPS Peak 4.1 software (written by Raymond Kwok). The spectra were decomposed assuming line shapes as sum functions of Gaussian (80%) and Lorentzian (20%) functions. Raw areas determined after subtraction of a Shirley background were corrected according to the corresponding sensitivity factors.²

Photocatalytic tests

Water reduction reaction. 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) 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, $\lambda > 410$ 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 J/mol*K] and T temperature [298 K].

To confirm that the evolved gas is hydrogen, the headspace of the reactor was analyzed by 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.

Water oxidation reaction. Reactions were carried out in a closed three-neck side irradiation reaction vessel. For each reaction, 50 mg of catalyst were well dispersed in an aqueous solution (20 mL) containing AgNO_3 (90 mg) used as an electron acceptor and La_2O_3 (0.1 g) as a pH buffering agent. The reaction solution was purged with argon for several hours to completely remove oxygen, and then irradiated with a 300 W Xenon lamp using a 420 nm UV cut-off filter. The temperature of the reaction solution was maintained constant by a flow of cooling water during the reaction. Photocatalytic O_2 evolution was monitored by an oxygen probe (PreSens Precision Sensing GmbH, Fibox 3 fiber optic oxygen transmitter). Before illumination, the oxygen probe was calibrated with temperature compensation by standard calibration solution 0 (oxygen-free water) and calibration solution 100 (air-saturated water). More details about the set up are available in the literature.³

wt.% MoCl ₅ used	N, wt.%	H, wt.%	C, wt.%	C/N	Mo, wt.%	O, wt.%	S, wt.%	Cl, wt.%	K, wt.%	Yield, %	BET s.a., m ² /g
0	49.1	3.2	31.0	0.63	0.0	16.0	0.0	0.0	0.0	17	40
0.5	48.3	3.1	30.1	0.62	0.0	17.7	0.2	0.3	0.3	20	33
1	46.3	3.2	28.3	0.61	1.6	17.8	2.2	0.4	0.2	23	18
2	44.3	3.2	28.1	0.63	2.0	20.2	2.0	0.2	0.0	18	40
5	45.2	3.0	28.2	0.62	3.2	17.6	2.1	0.5	0.2	18	30
10	40.4	2.8	25.6	0.63	8.8	16.2	5.9	0.3	0.0	26	39
20	35.7	2.7	22.9	0.64	14.9	13.1	10.3	0.4	0.0	25	85

Table S1. Elemental composition, yields and BET surface areas of the products prepared from 3-amino-1,2,4-triazole-5-thiol in LiCl/KCl at 550 °C using different amounts of MoCl₅ (relative to the amount of 3-amino-1,2,4-triazole-5-thiol) added to the reaction mixture.

wt.% MoCl ₅ used	N, wt.%	H, wt.%	C, wt.%	C/N	Mo, wt.%	O, wt.%	S, wt.%	Cl, wt.%	K, wt.%	Yield, %	BET s.a., m ² /g
0	46.6	3.2	28.6	0.61	0	21.6	0.0	0.0	0.0	10	47
1	46.0	3.2	28.5	0.62	0.9	20.6	0.2	0.2	0.4	19	30
2	45.0	3.1	28.3	0.63	2.2	19.8	0.8	0.3	0.5	12	29
5	41.2	3.0	26.6	0.65	4.4	21.9	2.3	0.6	0.0	15	71
10	37.5	2.7	25.6	0.68	7.9	17.0	8.3	0.7	0.3	18	61

Table S2. Elemental composition, yields and BET surface areas of the products prepared from 3-amino-1,2,4-triazole-5-thiol in LiCl/KCl at 600 °C using different amounts of MoCl₅ (relative to the amount of 3-amino-1,2,4-triazole-5-thiol) added to the reaction mixture.

MoCl₅, wt. %*		0.5	1	2	5	10	20
Mo, wt.%	550 °C	0.3	1.6	2.0	3.2	8.8	14.9
	600 °C	-	0.9	2.2	4.4	7.9	-
Mo in MoS₂, wt.%	550 °C	0.3	1.6	1.2	2.6	6.9	11.6
	600 °C	-	0.6	1.7	3.9	6.9	-
Mo in MoO₃, wt.%	550 °C	0	0	0.8	0.6	1.9	3.3
	600 °C	-	0.3	0.5	0.5	1.0	-
MoS₂ loading, wt.%	550 °C	0.5	2.7	2.0	4.3	11.5	19.4
	600 °C	-	1.0	2.8	6.5	11.5	-

Table S3. Overall Mo content, Mo content in MoS₂ and MoO₃, and final MoS₂ loading in the products prepared at 550 and 600 °C depending on the amount of MoCl₅ used, as estimated from the results of EA, EDS and ICP. *Amount of MoCl₅ is relative to the amount of 3-amino-1,2,4-triazole-5-thiol.

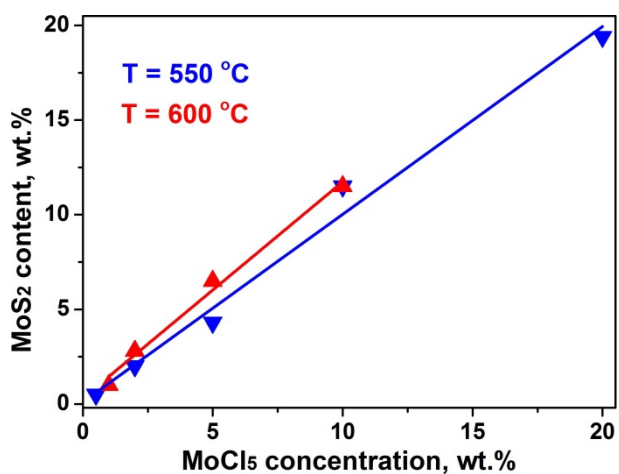


Figure S1. Dependence of MoS₂ loading in the products prepared at 550 and 600 °C on the MoCl₅ concentration in the reaction mixture (related to the amount of 3-amino-1,2,4-triazole-5-thiol).

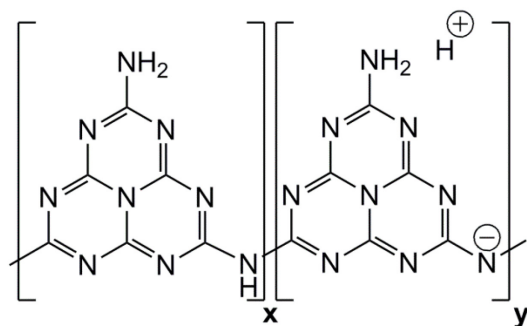


Figure S2. Structure of partially negatively-charged poly(heptazine imide).

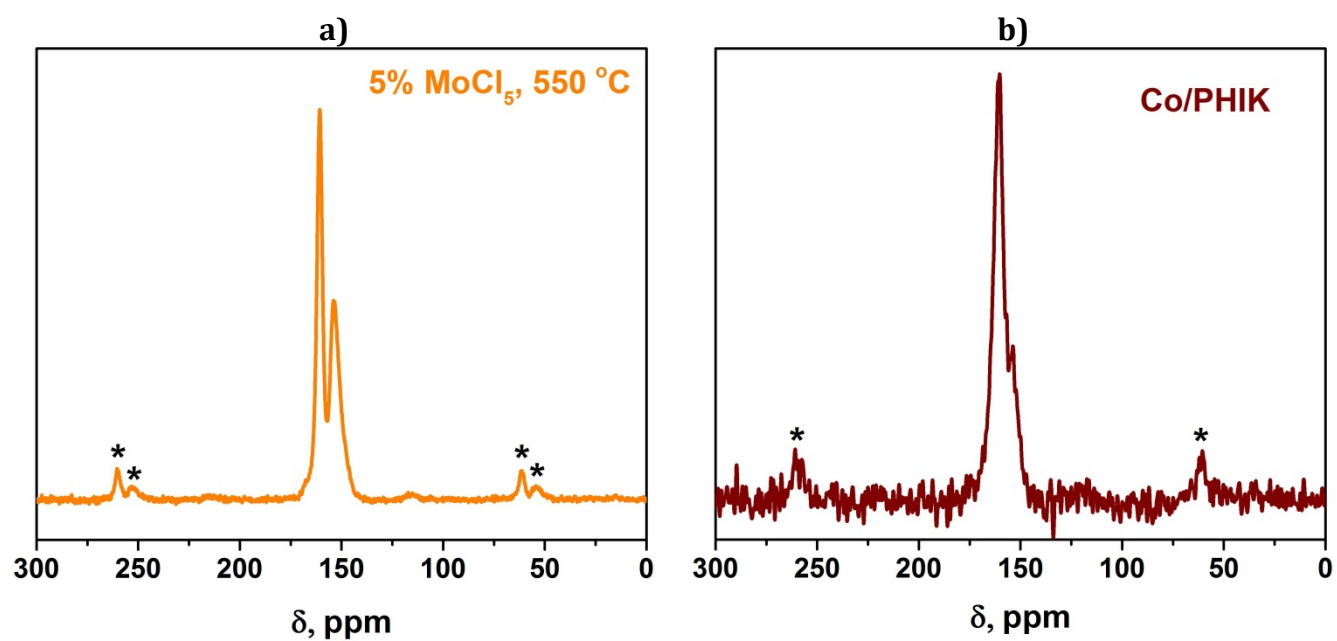
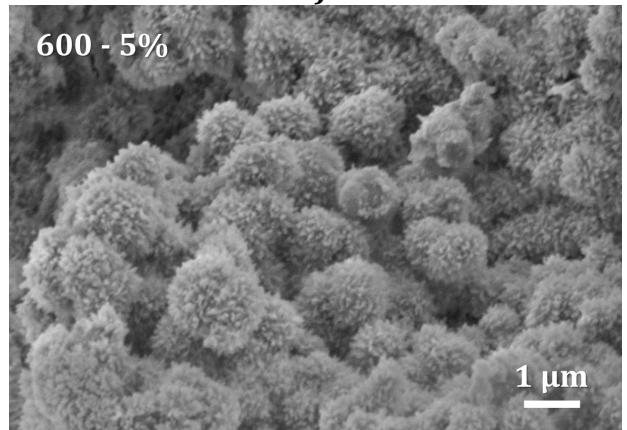
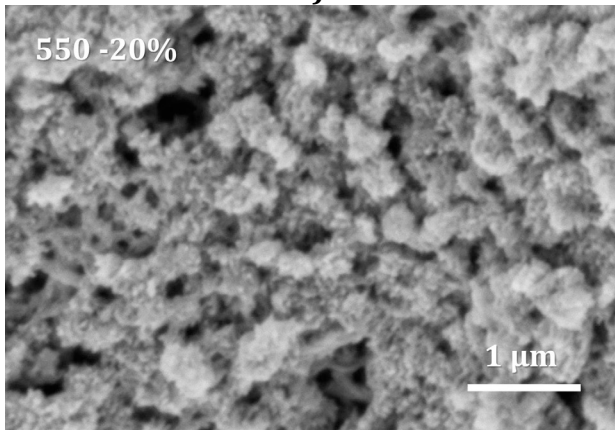
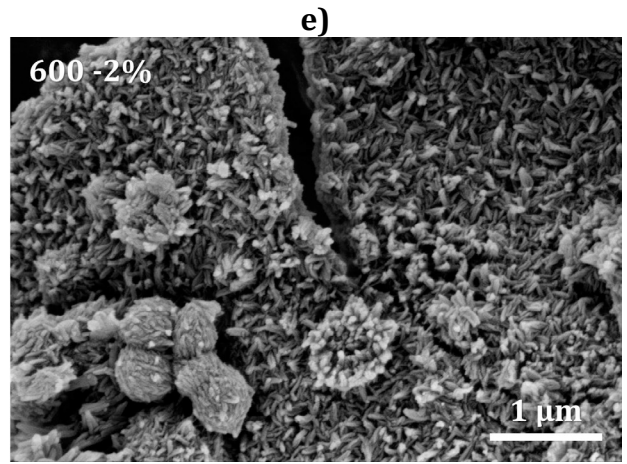
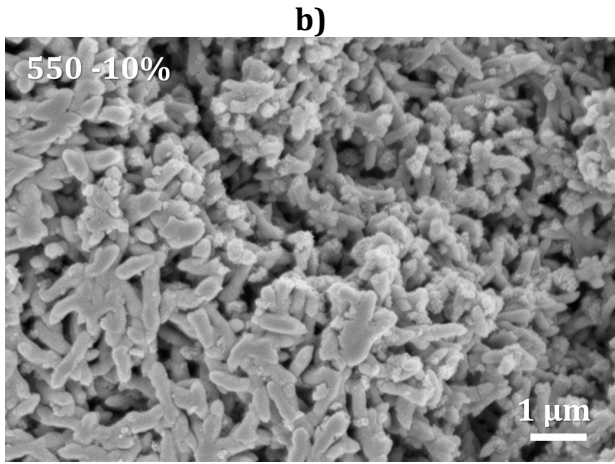
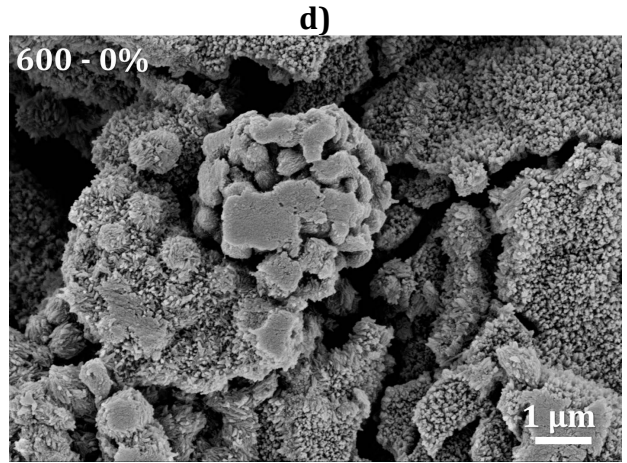
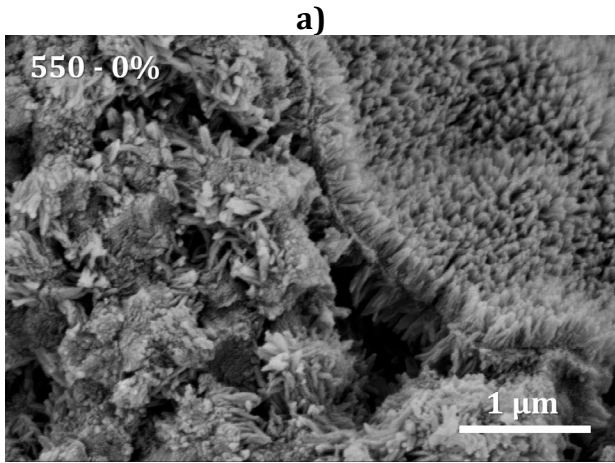


Figure S3. Solid state $^{13}\text{C}\{^1\text{H}\}$ CP/MAS NMR spectra of the products prepared at 550 °C using 5 wt.% MoCl_5 as a dopant (a) and using 5 wt.% $\text{Co}_3[3,5\text{-diamino-1,2,4-triazole}]_6$ complex as a dopant (b) in LiCl/KCl salt melt. Asterisks indicate spinning side bands in the ^{13}C spectra.



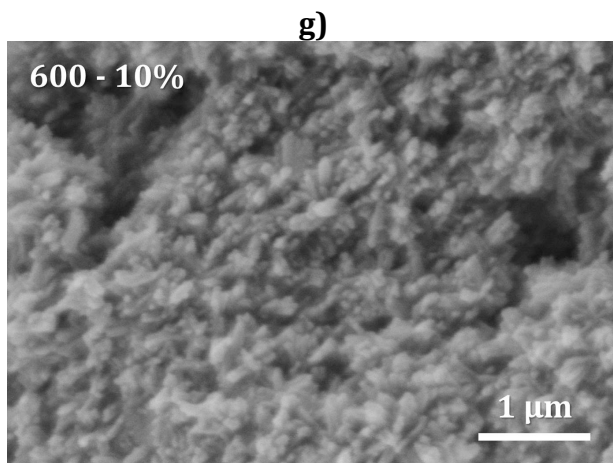


Figure S4. Selected SEM images of the composites prepared at 550 (a-c) and 600 °C (d-g) using 0% (a, d), 2% (e), 5% (f), 10% (b, g) and 20% (c) of MoCl₅ relative to the amount of 3-amino-1,2,4-triazole-5-thiol.

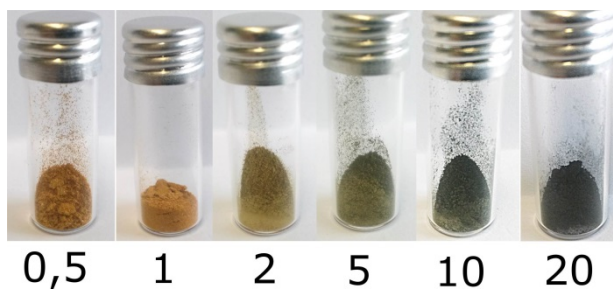


Figure S5. Digital photos of the composites prepared at 550 °C using the indicated amounts of MoCl_5 (relative to the amount of 3-amino-1,2,4-triazole-5-thiol).

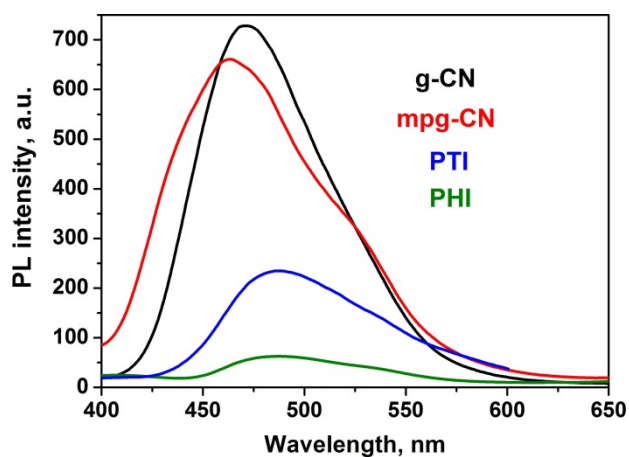


Figure S6. Comparison of steady-state photoluminescence of the reference carbon nitride materials (mesoporous graphitic carbon nitride, mpg-CN, graphitic carbon nitride, g-CN and poly(triazine imide), PTI) with the emission of poly(heptazine imide).

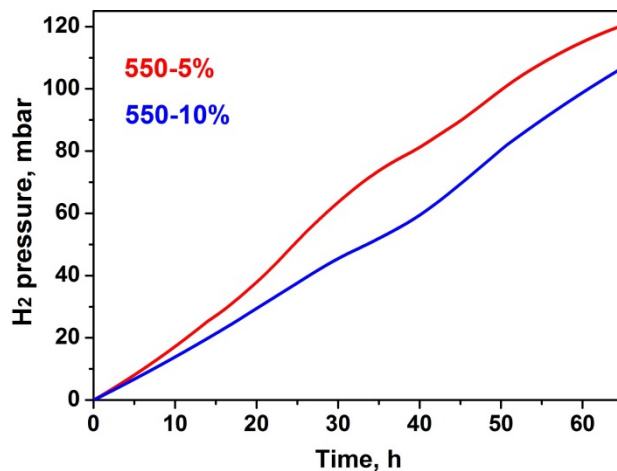


Figure S7. Sustained hydrogen evolution over the selected MoS₂/PHI composites upon visible light irradiation (50 W white LED) using triethanolamine as a sacrificial agent.

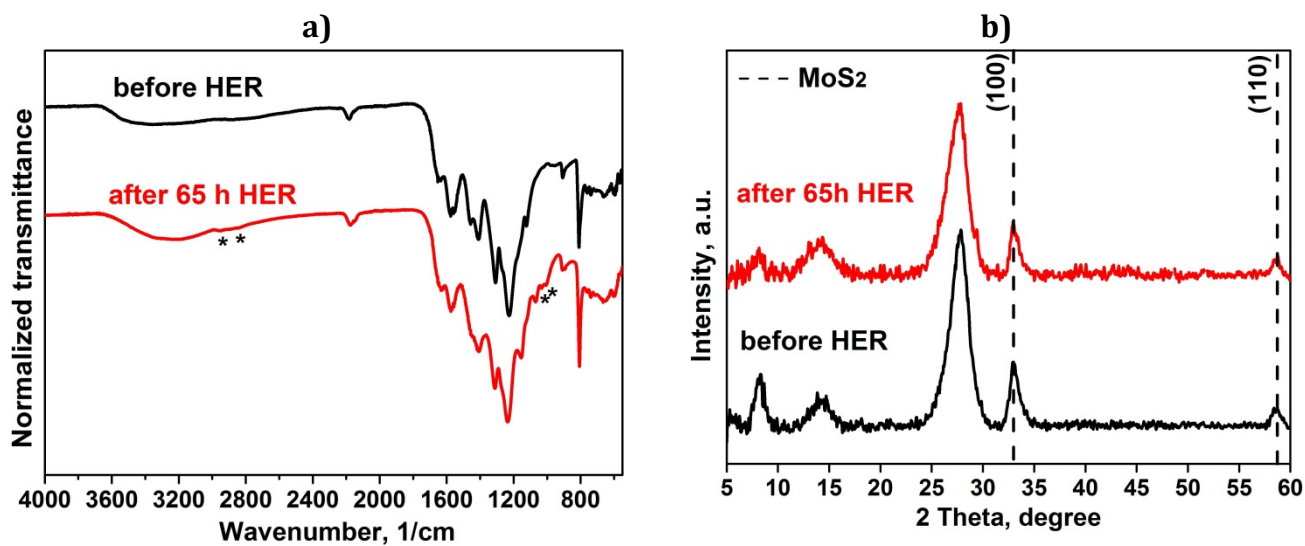


Figure S8. FTIR spectra (a) and PXRD patterns (b) of a sample catalyst (550-10%) before and after 65 hours of hydrogen evolution. In (a), asterisks mark the absorption bands of triethanolamine strongly adsorbed at the surface of the photocatalyst. In (b), the slight intensity decrease of the reflection at $2\theta = 8^\circ$ is attributed to the loss of the smallest catalyst particles during isolation step, in which this reflection is more pronounced.

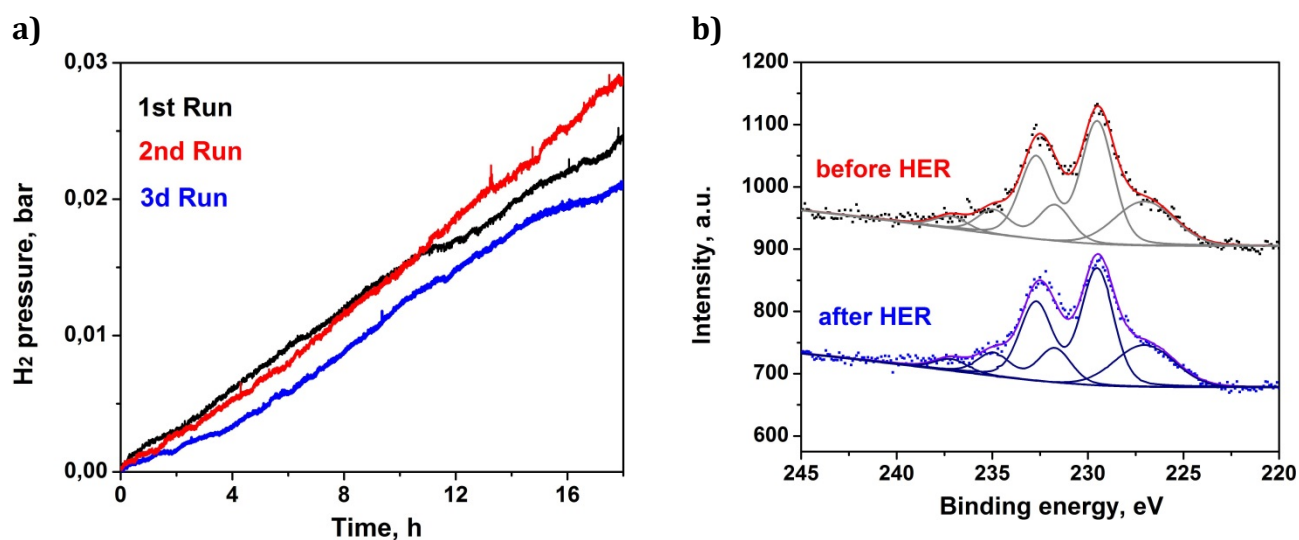


Figure S9. (a) Repeated hydrogen evolution over MoS₂/PHI composite prepared at 550 °C at 10 wt.% MoCl₅ concentration, upon irradiation with visible light (50 W white LED) using TEOA as a sacrificial hole scavenger. The composite was recovered between the runs as explained below. The reaction mixture was collected after the test; the catalyst was collected by centrifugation (7.000 rpm), repeatedly (5-7 times) washed with DI water until neutral pH, then collected by centrifugation (7.000 rpm), sonicated for 5 min in 10 mL of DI water and freeze-dried to prevent aggregation. Operation under inert atmosphere and lower centrifugation speeds are desirable to prevent leaching of MoS₂. (b) Mo3d XPS spectrum of a composite prepared at 550 °C using 10 wt.% MoCl₅ relative to the amount of 3-amino-1,2,4-triazole-5-thiol, before and after hydrogen evolution experiment.

Entry	Product	C, wt. %	N, wt. %	O, wt. %	S, wt. %	K, wt. %	Mo, wt. %	Cl, wt. %	Co, wt. %	Ag, wt. %
1	5 wt.% MoCl ₅ – 550 °C	29.1	46.6	18.1	2.2	0.21	3.3	0.5	-	-
2	5 wt.% MoCl ₅ – 550 °C, after 20 hours of HER	28.4	43.4	23.0	2.0	0.20	3.0	0	-	-
3	5 wt.% MoCl ₅ – 550 °C, after 20 hours of HER	29.3	44.0	22.6	1.5	0.1	2.3	0.2	-	-
4	5 wt.% Co complex– 550 °C	30.9	47.9	7.0	-	12.5	-	-	1.64	-
5	5 wt.% Co complex– 550 °C, after OER	21.4	32.7	11.2	-	0	-	-	1.13	33.5

Table S4. Elemental composition of the products before and after HER and OER as analyzed by EDS. During OER, large amount of Ag is photodeposited on the polymer surface that causes apparent decrease of C, N and Co content, but their relative content remains the same. Besides, silver ions replace K⁺ ions in the polymer structure by ion exchange mechanism that explains zero K content in the photocatalyst after OER.

Product	C, wt. %	N, wt. %	C/N	H, wt. %	O, wt. %	S, wt. %	K, wt. %	Co, wt. %	Mo, wt. %
Co/PHIK	30.1	46.7	0.645	2.6	6.8	0	12.2	1.6	0
MoS ₂ /Co/PHIK	28.9	46.9	0.616	2.4	6.3	2.4	9.7	0.9	2.5

Table S5. Elemental composition of Co/PHIK and MoS₂/Co/PHIK composites as determined by EA, EDS and XPS.

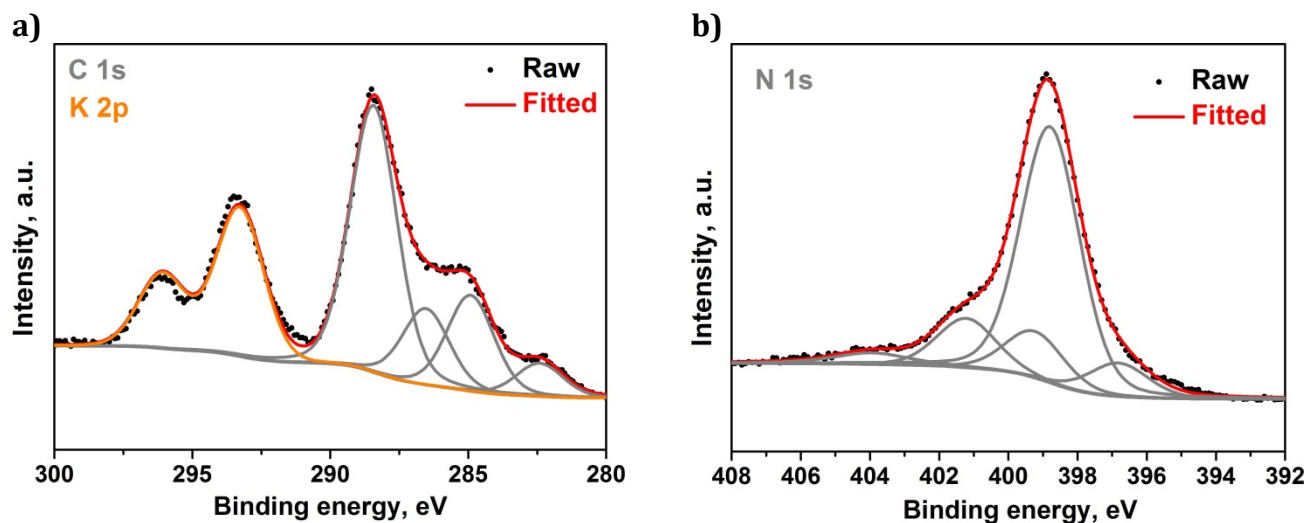


Figure S10. C1s and K2p (a) and N1s (b) XPS spectra of Co/PHIK composite.

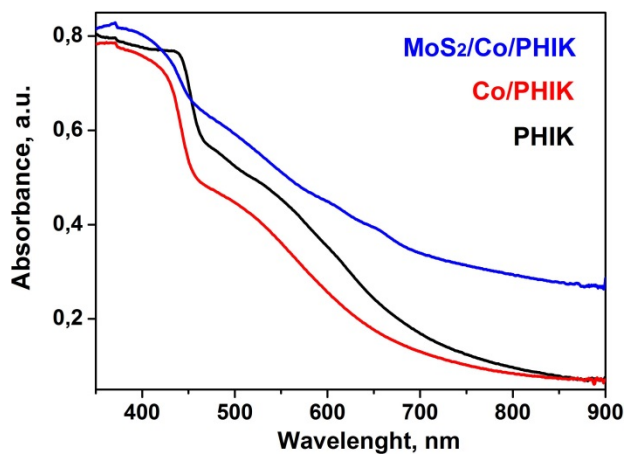


Figure S11. UV-Visible light absorption spectra of PHIK, Co/PHIK and MoS₂/Co/PHIK.

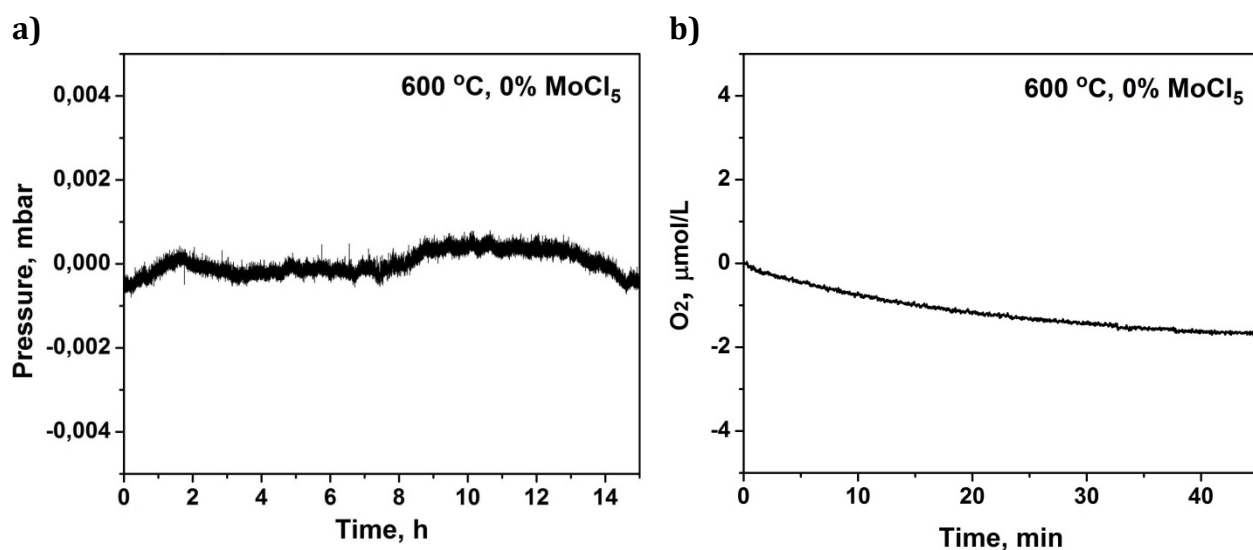


Figure S12. Photocatalytic hydrogen (a) and oxygen (b) evolution over poly(heptazine imide) prepared at 600 °C. Conditions: (a) irradiation with visible light (50 W white LED), TEOA was used as a sacrificial hole scavenger; (b) irradiation with visible light (300 W Xe lamp, 420 nm cut-off filter), AgNO₃ was used as a sacrificial electron scavenger.

1. Zhang, R.-B.; Li, Z.-J.; Qin, Y.-Y.; Cheng, J.-K.; Zhang, J.; Yao, Y.-G. Synthesis, Structure, and Physical Properties of a New Anions-Controlled Cd(II)-Guanazole (3,5-Diamino-1,2,4-triazole) Hybrid Family. *Inorg. Chem.*, **2008**, 47, 4861–4876.
2. Wagner, C. D.; Davis, L. E.; Zeller, M. V.; Taylor, J. A.; Raymond, R. H.; Gale, L. H. Empirical Atomic Sensitivity Factors for Quantitative Analysis by Electron Spectroscopy for Chemical Analysis. *Surf. Interface Anal.* **1981**, 3, 211–225.
3. Yang, X.; Tang, H.; Xu, J.; Antonietti, M.; Shalom, M. Silver Phosphate/Graphitic Carbon Nitride as an Efficient Photocatalytic Tandem System for Oxygen Evolution. *ChemSusChem*, **2015**, 8, 1350–1358.