Morphology Control in 2D Carbon Nitrides: Impact of Particle Size on Optoelectronic Properties and Photocatalysis

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Abstract
The carbon nitride poly(heptazine imide), PHI, has recently emerged as a powerful 2D carbon nitride photocatalyst with intriguing charge storing ability. Yet, insights into how morphology, particle size and defects influence its photophysical properties are virtually absent. Here, ultrasonication is used to systematically tune the particle size as well as concentration of surface functional groups and study their impact. Enhanced photocatalytic activity correlates with an optimal amount of those defects that create shallow trap states in the optical band gap, promoting charge percolation, as evidenced by time-resolved photoluminescence spectroscopy, charge transport studies, and quantum-chemical calculations. Excessive amounts of terminal defects can act as recombination centers and hence, decrease the photocatalytic activity for hydrogen evolution. Re-agglomeration of small particles can, however, partially restore the photocatalytic activity. The type and amount of trap states at the surface can also influence the deposition of the co-catalyst Pt, which is used in hydrogen evolution experiments. Optimized conditions entail improved Pt distribution, as well as an enhanced wettability and colloidal stability. A description
of the interplay between these effects is provided to obtain a holistic picture of the size–property–activity relationship in nanoparticulate PHI-type carbon nitrides that can likely be generalized to related photocatalytic systems.

**Introduction**

Graphitic carbon nitrides (g-C₃N₄), of which the archetype material is known since the 19th century as the heptazine-based polymer “melon”, have recently re-entered the stage as an earth-abundant semiconductor system with potential application ranging from photo/electrochemical redox catalysis for environmental remediation to chemical sensing.[¹] These applications are based on the material’s favorable properties, including chemical and thermal stability, an optical band gap in the visible range and energy levels appropriately positioned for a number of key photocatalytic reactions, including water splitting.[²] The class of carbon nitrides comprises triazine- and heptazine-based polymers, the dimensionality of which being determined by the synthesis procedure: whereas 1D heptazine-based polymers are obtained by heating the precursors in a solid state reaction, ionothermal synthesis results in the 2D network poly(heptazine imide) (PHI) or poly(triazine imide) (PTI).[³-⁵] For example, using a KSCN melt as a reaction medium, the PHI structure is obtained with hydrated potassium ions incorporated from the melt (K-PHI) and possessing cyanamide groups as defects; the potassium ions can be subsequently exchanged e.g. by protons, forming H-PHI.[³, 6, 7] Besides high photocatalytic hydrogen evolution rates,[⁶, ⁷] PHI exhibits the unusual ability to stabilize photo-generated electrons after the holes are quenched by suitable electron donors. This can be exploited afterward to temporally decouple for hours the absorption of sunlight from its transformation into chemical fuels such as hydrogen.[³, ⁸] This long-lived photo-reduced state can also be harvested for time-delayed electrical discharge after illumination in an aqueous solar battery anode.[⁹] Unveiling the full potential of such “light-storage” properties necessitates a more thorough understanding of the structure–property–activity relationships in PHI. Even though the atomic-level structure of K- and H-PHI has recently been resolved,[³] little is known about the impact of morphology, particle size, and surface terminations on the photocatalytic properties. In particular, surface terminations were recently described to have a significant impact on the photocatalytic behavior of PHI by enhancing its interaction with reactants.[¹⁰]
For melon-type carbon nitrides, it was reported that morphology tuning, e.g. by exfoliation, can change the optical and electronic properties of the material, which then results in enhanced photocatalytic activity. Different reasons for this enhancement were listed, including increased surface area, higher amount of beneficial defects or surface functional groups for attaching the co-catalyst as well as higher porosity, leading to enhanced light absorption and charge transport, which results in a reduction of the recombination rate of photo-generated charges. This demonstrates the importance of morphology and surface properties for photocatalytic reactions and the need to understand their correlations. However, there are not only reports about enhanced photocatalytic behavior by reducing the particle size, but also about reduced charge carrier lifetimes in exfoliated carbon nitride, which then lead to a reduced hydrogen evolution rate. Consistent with these findings, a more efficient charge carrier separation with longer lifetimes of photoinduced charges was reported for carbon nitrides, since the excitons were found to dissociate across the layers rather than within one layer, posing the question of whether excitons in carbon nitrides are inter- or intralayer excitons, or both. The above highlights the controversial nature and a lack of understanding of the size–activity relationship in carbon nitrides, which is influenced by many parameters. One possible explanation for these conflicting results may be found in the differences in synthesis and exfoliation of melon, the latter carried out e.g. by sonication, thermal treatment, mechanical treatment, ion intercalation, or chemical exfoliation by sulfuric acid. During the exfoliation process, defects or vacancies can be generated, and new surface terminal groups may develop on the carbon nitride backbone. On the one hand, defects are discussed as facilitators in photocatalysis. They can form electronic states in the optical band gap, which can enhance visible light absorption and influence charge carrier transfer at the interface. On the other hand, defects can act as recombination centers or deep trap states, reducing the charge carriers’ mobility and driving force for photocatalytic reactions, which counteracts photocatalytic performance. A recently published work highlights the effect of functional groups and defects in melon-type carbon nitride being beneficial only up to a particular concentration, which also strongly depends on the type of functional group or defect. This ambiguity of structure and defect types warrants an in-depth analysis of the interplay and influence of morphology and structural changes on different optoelectronic properties and, consequently, photocatalytic activity. As photocatalysis is a complex process relying on intertwined structural, optoelectronic, and morphological properties, many of which are associated with different time...
scales, disentangling these factors is essential for understanding the overall photocatalytic activity.

Here, we study the effect of ultrasonic particle size reduction of K- and H-PHI on the photocatalytic hydrogen evolution reaction (HER) by analyzing multiple parameters. Central to our study is the size separation of PHI particles, based on differential centrifugation velocities. By breaking apart agglomerates, functional surface groups and defects are generated and, comprehensively analyzed by various techniques. With decreasing particle size and the correspondingly increase in surface area, the number of functional groups increases (especially NH\(_2\), OH, and -C=O), while at the same time, light absorption is slightly shifted to longer wavelengths. Besides, we find that with increasing amounts of functional groups, the distribution of photo-deposited Pt, used as co-catalyst for HER, becomes more uniformly distributed, and the Pt particle size is reduced. Simultaneously, the suspension stability is enhanced, which is beneficial for high photocatalytic activity, provided that the particles are not smaller than 180 nm. On the other hand, the amount and depth of trap states increases with the number of functional groups, influencing the accessibility of photo-excited electrons for transfer to the surface. Intriguingly, we observe that re-agglomeration of those particles causes a significant increase of the hydrogen evolution rate (up to 35%). This might be correlated with an enhanced crystallite interaction in the particle when the amount of functional groups increases, enabling better charge carrier separation. Photoluminescence (PL) and conductivity measurements hint to a multiple trapping and release model (MTR)\(^{[28]}\) for the electron transfer in PHI. This observation points to opposing effects of reduced charge carrier separation and enhanced dispersion stability with decreasing particle size. Therefore, hydrogen evolution as a function of particle size is found to be an interplay of all these parameters. Optimal performance is found for 2 h sonicated samples with particle sizes above 180 nm, ideally in a re-agglomerated material. Importantly, we find that the contribution of each parameter, depending on the particle size, is not as unambiguous as often reported in the literature.

**Results and Discussion**

**Morphology and structural analysis**

Particle size reduction by an ultrasonication route involved the sonication of PHI in water for an extended duration of 2 h, followed by fractionated centrifugation of the aggregates. This yields a colloidal solution with a concentration of around 5 mg mL\(^{-1}\) (**Figure 1a**), akin to procedures
The first precipitate (P1) contains the largest particles (P1: 300-1500 nm), the second precipitate (P2) contains medium particle sizes (P2: 100-400 nm), with the third precipitate (P3) containing the smallest particles down to 40 nm (Figure S1-S3, Table S4, Supporting Information). The particle sizes were analyzed by a combination of dynamic light scattering (DLS), atomic force microscopy (AFM), transmission electron microscopy (TEM), and scanning electron microscopy (SEM), as well as Brunauer–Emmett–Teller (BET) surface area analysis (Figure S1-S10, Supporting Information). To reduce the particle sizes even further, H-PHI was sonicated for 24 h, and the supernatant (P4) was separated and precipitated at 500 relative centrifugal force (RCF) (Table S1, Supporting Information). The resulting particle sizes are in the range of 20-350 nm (Figure S3, S6, Supporting Information). Since K-PHI is protonated when storing in water for a long time, forming H-PHI, this 24 h sonication process was only performed on H-PHI (Figure S44, Supporting Information). The suspension of PHI with small particles (below 200 nm) remained colloiddally stable in water for months, with no indication of settling. This is also evident by their large zeta-potential (-23 mV to -45 mV) across all pH values measured for H-PHI sheets (Figure S9, Table S2 Supporting Information). The colloidal suspensions can be dried to isolate PHI for further characterization (notated as “PHI re-agglomerate”).

The primary crystallite size obtained by TEM analysis of pristine particles is only in the range of 20-45 nm (Figure S4, Supporting Information) when compared to SEM and AFM analysis, which show that larger particles are agglomerates of smaller crystallites. After 24 h sonication (P4), the primary crystallite size is reduced to 5-25 nm, as shown by TEM (Figure 1b, Figure S5, Supporting Information). In AFM, a minimal thickness of 3–5 nm (Figure 1c, d) for P4 particles could be measured. Based on the interlayer separation of 3.16 Å resulting from the PXRD analysis (vide infra), this corresponds to 9 to 16 PHI layers in the stacking direction. Crystallite sizes can also be estimated from PXRD data (Figure 2a) by using the Scherrer equation (Table S4, Supporting Information), which gives a more representative value of the average domain size compared to the local information gained from TEM or AFM. For particles being sonicated for 24 h, the crystallite size is only slightly reduced (by 15% to 22 (±1) nm in the vertical direction) with respect to the pristine material (lateral: 14 (±1) nm and vertical: 26 (±1) nm), proving that primary crystallites remain intact during sonication, but that the agglomerates break apart, forming smaller agglomerates or even single crystallite particles.
The measurement of the hydrodynamic diameter of the particles, estimated by DLS (Figure S10, Table S3, Supporting Information), is in reasonable agreement with particle sizes of K-PHI and H-PHI obtained by microscopy techniques (Table S4, Supporting Information). However, since DLS analysis assumes perfectly spherical particles, a direct relationship between the results of microscopy and DLS for 2D materials is yet to be accurately determined. Nevertheless, DLS measurements were used in the following for particle size estimation, since this measurement allows for fast and quantitative particle analysis.

The analysis of BET surface area and pore volume reveals a type IV isotherm, associated with condensation processes in mesopores, most probably located between agglomerated particles as textural pores (Figure S11, Supporting Information). The surface area is slightly increased for H-PHI P4 (70 cm$^3$ g$^{-1}$) in comparison to the pristine material H-PHI (60 cm$^3$ g$^{-1}$) (Table S5, Supporting Information). This finding is in line with the assumption of particles consisting of agglomerated crystallites, where the big agglomerated particles break apart during sonication, forming smaller agglomerates or even single crystallites.

![Diagram](image.png)

Figure 1: Morphology and particle size analysis of PHI. a) Schematic illustration of PHI sonication for breaking apart agglomerated particles, followed by stepwise centrifugation for particle size separation (blue: nitrogen, grey: carbon, white: hydrogen, red: oxygen). b) TEM image of H-PHI P4 (24 h sonicated), the inset showing a magnification of single P4 particles with the Fast Fourier Transformed (FFT) image showing the characteristic distances in PHI. c) AFM image of single H-PHI P4 particles (24 h sonicated). d) Corresponding height profiles.

Although considered a mild dispersion technique, acoustic bubbles formed by ultrasound are hot and can generate highly reactive radicals. Thus, the absence of chemical changes to the investigated materials must be ascertained. To verify that the sonicated materials are chemically
identical to the pristine PHI and to study the surface termination of small particles, the colloidal solution was evaporated to dryness. The residual powder was structurally characterized by $^{13}$C and $^{15}$N magic angle spinning solid state nuclear magnetic resonance spectroscopy (MAS NMR), Fourier transform infrared spectroscopy (FT-IR), powder X-ray diffraction (PXRD), elemental analysis, and X-ray photoelectron spectroscopy (XPS).

As stated above, the primary crystallite size is almost unchanged when the particle size is reduced by sonication. Therefore, in PXRD no significant changes are observed. The *in-plane* ($\bar{1}10$) and *out-of-plane* (001) reflections are at $7.9^\circ$ (11.10 Å) and $27.9^\circ$ to $28.3^\circ$ 2$\theta$ (3.19 Å for H-PHI and 3.16 Å for K-PHI), respectively, with the key difference being the slight isotropic broadening of the interlayer stacking reflection (Figure 2a, S12, S13, Supporting Information) in smaller particles.[3]

The FT-IR spectra of the colloidal H-PHI and K-PHI are basically identical to the pristine sample, showing all the signals corresponding to the heptazine moiety (Figure S14, S15, Supporting Information). This points clearly to an intact PHI polymer network, which is further proven by elemental analysis (Table S8, Supporting Information) as well as $^{13}$C and $^{15}$N {H} CP MAS NMR spectroscopy (Figure 2b, c). The signal positions in $^{13}$C NMR at 157 ppm to 158 ppm (heptazine-ring carbon) and 163 to 164 ppm (heptazine-ring carbon next to imide bridge) remain at the same position, but broadening of $^{13}$C signals can be seen in all sonicated materials, likely due to surface functionalization or increased water interaction. The same trend can be observed in $^{15}$N {H} CP NMR for the two main signals around -176 to -190 ppm (heptazine-ring nitrogen atoms) and -237 to -244 ppm (imide bridges). The peaks at 166 ppm in the $^{13}$C NMR and -267 ppm in the $^{15}$N NMR of K-PHI P1 are more pronounced than those in the pristine material, which also hints to an increase in NH$_2$ groups, consistent with the literature[21] (Figure 2b, c S24, Supporting Information). Additionally, an enhanced water interaction is visible in $^{15}$N NMR, especially in smaller particles, which is observed by a shift of the NH-bridge nitrogen peak at -240 ppm to -238 ppm,[3, 4, 32] in agreement with quantum-chemical calculations (Figure S20-S23, Supporting Information). In line with this, the FT-IR analysis shows an increase in the O-H/N-H bond vibration at 3680-2220 cm$^{-1}$ in atmospheric conditions (up to 47% in P4) with decreasing particle size, being more pronounced when the average particle size gets smaller than 200 nm (Figure 2d, S14-S18, Table S6-S7, Supporting Information).
Figure 2: Characterization of structural defects of pristine PHI and small particles of PHI after sonication. a) PXRD of pristine KPHI and K-PHI P1 as well as pristine H-PHI and H-PHI P4. b) $^{13}$C ($^1$H) CP MAS NMR experiments of pristine K-PHI and K-PHI P1 as well as pristine H-PHI and H-PHI P4. c) $^{15}$N ($^1$H) CP MAS NMR experiments of pristine K-PHI and K-PHI P1 as well as pristine H-PHI and H-PHI P4. d) Relative area of NH and OH vibrations (related to the heptazine vibration at 805-811 cm$^{-1}$) of FT-IR of H-PHI as a function of particle size. R of carboxyl functionality = OH or NH$_2$. e) XPS analysis of pristine H-PHI (average particle size 1500-1000 nm) and H-PHI particles after 2 h (P2 with average particle size 400-350 nm) and 24 h sonication (P4 with average particle size around 79 nm) e) C 1s spectrum, and f) N 1s spectrum. Grey areas depict bonds in the heptazine ring, blue areas the NH$_2$ or OH bonds, and orange the NO or CO bonds.

XPS analysis of pristine H-PHI and a 2 h and 24 h sonicated sample was used to confirm the functional groups introduced into the system by sonication. In C 1s spectra, besides the typical heptazine ring signals two distinct signals are observed at 286.4 and 288.9 eV, which can be correlated to C-N(H$_2$) or C-O(H) (blue area) and C=O (orange), respectively, where the latter is assigned either to a carboxylic acid or (NH$_2$)$_x$C=O moiety (Figure 2e). The formation of vacancies due to sonication can be excluded or considered insignificant (Chapter 5.4, Table S9, Supporting Information). To disentangle the C-N(H)$_x$ and C-O(H) signals, N 1s and O 1s spectra were analyzed as well (Figure 2f, Figure S19, Supporting Information). The relative portion of NH$_x$ (blue area in the N 1s XPS spectrum) increases by up to 13% with decreasing particle size (Chapter 5.4, Supporting Information), akin to FT-IR and NMR analysis. However, the signal in the O 1s spectrum at 531.8 eV (OH groups, blue area) is reduced with decreasing particle size (to 64%), probably caused by evaporation of structural water in the vacuum chamber of XPS, which is more likely to happen for smaller particles.
In addition, a slight increase of N-O (orange) (up to 20%, extracted from N 1s spectrum) and C=O bonds (orange) (up to 8%, estimated from C 1s spectrum) can be found with decreasing particle size. The presence of these groups is also confirmed by O 1s XPS spectra, although here, contributions from the substrate may have a small influence (Chapter 5.4, Supporting Information). The concentration of N-O bonds is only around 10% of the C=O concentration (in COOH or CO(NH)x)y, so that FT-IR spectroscopy shows a slight increase of C=O vibrations but no clear trend for N-O (Figure S16-S18, Table S7, Supporting Information). Furthermore, a small peak in 13C NMR at 170 ppm (Figure 2b, S23, Supporting Information) and additional vibrations at 2100 cm⁻¹ in FT-IR (Figure S15-S18, Supporting Information) hint to a meagerly increased amount of C≡N in sonicated samples. In comparison to the other functional groups, the concentration of N-C≡N groups in all fractions (pristine-P4) is small and does not significantly change with the particle size.

From these characterizations, we conclude that the ultrasound treatment is sufficiently mild such that the pristine and sonicated PHI are chemically identical in terms of their polymer backbone after sonication. Besides, the particle size reduction with increasing sonication time, the de-agglomeration of PHI crystallites in ambient to humid environment increases especially the amount of terminal OH and NH₂ groups (up to 47% in P4 compared to the pristine material). Besides C=O groups, which rise up to 20% by particle size reduction from pristine PHI to P4, a small amount of C≡N and NO defects are formed, which are not severely affected in their concentration by particle size reduction.

**Influence of functional groups on photocatalytic hydrogen evolution**

Next, we investigated photocatalytic hydrogen evolution to study the influence of morphological and structural modifications induced by sonication. First, the effects of particle size on the absorption edge of the samples were analyzed. In the pristine material, the optical band gap for K-PHI is 2.73 (±0.01) eV, whereas for H-PHI a value of 2.92 (±0.01) eV was obtained. A slight increase in the optical band gap is observed for particle sizes below 200 nm by 0.09 (±0.01) eV (K-PHI) and 0.03 (±0.01) eV (H-PHI), respectively (Figure S25-S28, Table S10, Supporting Information). When reducing the particle size, a pronounced Urbach tail is visible in the UV-Vis spectra. This is likely caused by excitations below the band gap, due to emerging intermediate
states in the band gap associated with defects, in line with the findings of increasing amounts of surface groups.[36]

All PHI materials were tested for the photocatalytic activity in hydrogen evolution reaction (HER) in a 1 mg mL\(^{-1}\) suspension containing 10 vol% methanol as an electron donor and an optimized Pt loading of 2 wt% for H-PHI and 8 wt% for K-PHI,[3, 6, 7] photo-deposited from hexachloroplatinic acid during illumination with simulated sunlight (AM 1.5 G). For pristine H-PHI, a maximum activity of 31 µmol h\(^{-1}\) was measured, which increases to 35-41 µmol h\(^{-1}\) (by 13-25%) when the average particle sizes are reduced down to 500-180 nm (P1, P2) (Figure S29, Supporting Information). A further reduction in particle size causes a monotonous decrease in HER activity by 97% (1 µmol h\(^{-1}\)) for the 24 h sonicated particles P4 with an average size of 75 nm (Figure 3a, S27, Supporting Information). Interestingly, the photocatalytic performance of P4 particles can be increased upon re-agglomeration prior to photo-deposition of Pt, which also works for re-agglomerated P1 particles (Figure 3a, S29-S31, Supporting Information), vide infra. Due to drying, P4 particles agglomerate randomly, similar to the coiling process described for carbon nitrides in the literature.[37] The enhanced photocatalytic activity is contrary to the expectation that high dispersity and/or smaller particle sizes lead to a better catalytic rate.[38] For K-PHI, initially, a similar trend is observed (Figure 3b, S30, S33, Supporting Information), although K-PHI is not stable during photocatalysis and transforms into H-PHI, which is assumed to take place faster for smaller particles, causing an increase in photocatalytic activity for small particles again (Figure S32-S34, S45, Supporting Information). For this reason, the following analysis will mainly concentrate on the H-PHI results.

Next, we investigated the influence of particle size on the distribution, size, and loading of the Pt co-catalyst, which typically is a “blind spot” in most reported photocatalytic experiments with carbon nitrides. As a general trend, we observe a decrease in the size of Pt nanoparticles, when the PHI particle size is reduced (Figure S37-S43, Supporting Information). At the same time, the Pt particles are more homogeneously distributed (Figure 3c-e). For pristine H-PHI, the Pt particle size was estimated by SEM to be in the range of 8-38 nm (Figure 3c, Figure S37, S40, Supporting Information) while it increases in P1 up to 40-68 nm. When decreasing the particle size further to P2-P4, the Pt particle size is reduced to 1-5 nm (Figure 3d, e, S37-S40, Supporting Information). The different Pt particle sizes likely correlate with the nature and number of PHI functional groups:
with decreasing particle size, the number of surface functional groups increases, which can act as Pt coordination-centers and nucleation sites (Figure S40-S43 Supporting Information). In addition, the more Pt nucleation sites are present, the more homogeneous the Pt coverage, which has a positive effect on the photocatalytic activity, as has also been reported for melon-based carbon nitrides, since charge carrier migration distances are very limited.[2, 39] In line with this, a shift by 0.40-0.45 eV to lower binding energies can be observed for the Pt 4f XPS signals correlated with Pt\(^{2+}\) for P4 in comparison to pristine H-PHI, which is likely caused by stronger metal-support interactions via surface NH, OH, and CO groups (Figure S19, Chapter 5.4, Supporting Information).[6, 15, 40] The stronger the metal-carbon nitride interaction, the better the local charge transfer.[15, 41] In addition, the XPS spectra showed a decreasing Pt\(^{2+}\)/Pt\(^{0}\) ratio up to 20% for decreasing particle sizes (pristine material: 1.70; P4: 1.37) (Table S9, Supporting Information), which points to an incomplete Pt reduction for bigger particles, possibly due to less efficient overall charge transfer.[42]

![Figure 3](image)

Figure 3: Photocatalytic hydrogen evolution of H-PHI and K-PHI in the presence of the electron donor methanol (10 vol%) and co-catalyst Pt (2 wt% for H-PHI and 8 wt% for K-PHI). a) Hydrogen evolution in the presence of H-PHI pristine and P4 (24 h sonication) as well as re-agglomerated P4 as a function of average particle size in batch (20 mg of catalyst were used). b) Hydrogen evolution of K-PHI pristine, P1, P1 re-agglomerated, P2 and P3 (5 mg of catalyst were used). SEM images of H-PHI after photocatalysis (left) and back-scattered electron image with brighter spots displaying Pt (right) c) for pristine H-PHI, d) for 2 h sonicated (P2) H-PHI and e) for 24 h sonicated (P4) H-PHI.

Regarding the Pt loading, we found that with decreasing particle size (down to a particle size of ~250 nm), more Pt was photo-deposited on the material. While 2 wt% added Pt were deposited on
particles of 250 nm in size, only 1 wt% Pt was found on pristine particles after photocatalysis (Table S11, Supporting Information). At smaller sizes below 250 nm the Pt amount decreases again (1.4 wt% at 79 nm particle size) (Table S11, Figure S41-S44, Supporting Information). The fact that less Pt is deposited on smaller particles despite the larger amount of functional groups and enhanced local metal-carbon nitride interaction points to a faster recombination process of photo-generated charges in smaller particles. Such enhanced recombination rates are detrimental for HER (Figure S36, S44 Supporting Information) as observed for particle sizes < 180 nm, which are probably influenced by the amount and type of surface functional groups (especially NH₂, OH and C=O) (Figure S35, Supporting Information). In the pristine material, however, the bulk-based charge separation across the 2D layers[12, 17] appears to be hindered by the long diffusion lengths of the photo-generated charges to reach the catalytic surface, leading to decreased activity. The charge diffusion might be enhanced in re-agglomerated particles due to the nature and density of functional groups at their surface or interface,[12, 43] which is resulting in an enhanced photocatalytic activity.

**Figure 4:** Photoluminescence (PL) analysis of H-PHI in degassed water. a) Deconvolution of the PL signal of H-PHI P1 based on two Gaussian functions to describe also shallow and deep states in the band gap. b) The optical band gap of H-PHI and PL signal deconvolution by two Gaussian functions depending on the particle size. Re-agglomerated particles are denoted as “re-ag.”. c) Time-dependent PL analysis of H-PHI P1, which is fitted with one exponential and a Γ function. d) Contribution of the exponential and Γ-decay to the overall lifetime decay (errors included) as a function of the average batch particle size.
To study the influence of the surface functional groups and their possible role as trap states, which have already been suggested to be present by UV-vis spectroscopy, we used photoluminescence (PL) spectroscopy. PL experiments were performed on the pristine material in degassed water, degassed water and electron donor and under the same conditions as photocatalysis experiments, i.e. in the presence of an electron donor and co-catalyst (Figure S46, Supporting Information). Figure 4a shows a representative emission spectrum of H-PHI P1 in degassed, O₂–free water, excited at 370 nm, where the maximum is located at around 450 nm (2.7 eV). The broad PL signal can be deconvoluted into two Gaussian contributions, similar to carbon nitride materials reported in the literature, located at around 2.75 eV, stemming from the bulk, and at 2.45 eV, corresponding to mostly (surface) trap states (Figure 4a, S46-S49, Supporting Information). Both emission peaks are smaller than the optical band gap of 2.9 eV for all studied environments, indicating that emissions are caused by states in the band gap. Although their spectral positions slightly vary with the particle size investigated, their energetic shifts are constant relative to the band gap, as shown in Figure 4b.

In order to extract more information about the influence of the trap states, time-resolved photoluminescence (TRPL) measurements were carried out, which contain information on both radiative and non-radiative decay types. These were fitted by a combination of an exponential and a Γ-function (Figure 4c, S50, Supporting Information). A priori, both recombination types can show a distribution decay nature according to a Γ function. However, the best fit obtained in all cases is an exponential function attributed to the faster decay in the bulk (<0.15 ns). The distribution function (Γ), which accounts for all decays on longer time scale, is assigned to trap states induced by surface terminations. The respective weight factors of both processes are compared for their contribution to the excited charge carrier decay process as a function of particle size (Figure 4d, S50, Table S12, Supporting Information). In aqueous suspension, where the intrinsic properties are best visible (Figure 4b, d), an increase in the relative weight attributed to the traps (orange) is observed as PHI is sonicated. This finding is consistent with an increase of functional groups on the particle’s surface that can act as trap states. Additionally, shorter lifetimes were observed with smaller particle sizes (Table S12, Supporting Information), probably due to enhanced formation and population of such trap states, yielding a higher degree of charge recombination or capturing the charges on longer timescales exceeding the time scale of the PL
measurement. Under the conditions in which the photocatalysis experiments take place, i.e. donor presence and photo-deposited Pt, the relative PL trends for the surface based processes are preserved (Figure S51, S52, Supporting Information). However, the absolute numbers are changing. Charge trapping and recombination in the bulk is not affected by the addition of Pt.

The re-agglomeration of P4 particles prolongs the lifetime compared to that of the pristine material, significantly (Table S12, Supporting Information). The relative weight of the PL fit functions reaches similar values to that of the pristine material (Figure 4d). This can be rationalized by an enhanced exciton separation in the agglomerates.\[12\] The transfer between crystalline areas might even be enhanced in the re-agglomerated samples due to more or different functional groups at the interface and hence possible hydrogen bonding between the agglomerated particles.\[28, 48\] As evidenced by electrochemical impedance spectroscopy, a grain-boundary based electron transport process is likely to be present, which hints to a multiple-trapping-and-release model (MTR)-like process in PHI (Figure S53, Supporting Information). The electrons are transported across the layers in the crystallites, and once reaching an edge of the crystallite, charge hopping becomes necessary. The hopping is enhanced by shallow trap states formed at the interface and improves with well-interconnected interfaces.\[28\] Similar results were reported for a melon-type carbon nitride, where enhanced exciton dissociation was reported at the interface between ordered and disordered carbon nitride structure.\[49\]

To better estimate the energetics of the functional groups (NH$_2$, OH, NHC≡N and NHCOOH or NHCONH$_2$) and hence, trap states for different particle sizes, quantum-chemical calculations were performed, which provide insights into the nature of the trap states and their energetic depth. Three different model systems for PHI were designed as size-increasing computational models, consisting of 1, 7, and 19 pores to approach the different particle sizes that are actually observed under experimental conditions (Figure S54 Supporting Information). When comparing the localization of HOMO and LUMO, no significant difference was found for the localization as a function of the size of the model system or functional group (Figure S55-S61, Table S13 Supporting Information). Independent of the size of the pore model, orbitals are rather localized at single hepatize units than being delocalized over the entire system (Figure S55-S57, Table S13, Supporting Information), hence revealing contributions from functional groups at the pore edges. Changes in orbital contributions by functional groups are also reflected in the calculated optical
band gaps, where the largest values were found for primary amine terminations with 4.35 eV, followed by NHCONH₂ (4.31 eV), hydroxyl (4.30 eV), NHC≡N (4.27 eV) and NHCOOH groups (4.25 eV), successively decreasing the band gap (Table S14, Supporting Information). The smaller the experimentally analyzed PHI particles are, the more significant the influence of the functional groups. However, it is likelier that the functional groups form trap states, rather than a homogenous shifts of the band edges. This is reflected by both the Urbach tail seen in the UV-Vis spectra (Figure S26, Supporting Information) and by spectral PL deconvolution (Figure S47, Supporting Information). In addition, calculated ionization potentials (E_IP) and electron affinities (E_EA) for different model systems (Chapter 6.6 Supporting Information) were identified as proxies for the functional group contribution and band edge energies (Figure S62-S66, Supporting Information).

Akin to the literature, it was found that relative to terminal NH₂ groups, the OH groups change the E_IP (by 0.60 eV) and E_EA (by 0.63 eV) in a similar way such that only shallow trap states are formed.

Figure 5: Quantum-chemical calculations of electron affinity (E_EA) and ionization potential (E_IP) of the one-pore PHI model system obtained on PBE-D3/def2-TZVP[50]/RI-PBE-D3/def2-TZVP[51] level of theory. Comparison of different terminal groups (NH₂, OH, NHCOOH, NHCONH₂ and NHC≡N), with values referenced to the NH₂ terminal group.
close to the LUMO (Figure 5, S67, Supporting Information).\cite{23, 52} C=O and C≡N containing terminal groups reduce the optical band gap the most, which is also visible in a more pronounced shift of the \( E_{EA} \) in comparison to \( E_{IP} \) relative to the \( \text{NH}_2 \) terminated system (Figure S68-S70, Supporting Information). This might be consistent with the formation of trap states that are located deeper in the optical band gap than for \( \text{NH}_2 \) and \( \text{OH} \) groups.\cite{22-24} For this reason \( \text{NHCOOH} \), \( \text{NHCONH}_2 \) and \( \text{NHC≡N} \) groups might influence the charge carrier energetics, and therefore the photocatalytic activity, most profoundly.

The higher the concentration of functional groups in general, the higher the amount of detrimental deeper trap states that would enhance recombination and hence reduce the hydrogen evolution rate.\cite{24, 47} In agreement with photocatalysis experiments and PL data, the highest photocatalytic activity was measured for P1 and P2 samples, with a slight higher but not excessive amount of functional groups as evidenced by structural analysis. Based on these findings, we conclude that it is possible to tune the light absorption properties and the amount and depth of trap states by introducing different functional groups intentionally, which has a pronounced influence on the availability of charge carriers for HER.

Figure 6: Overview of different contributions to hydrogen evolution, including the concentration of functional groups (i), suspension stability (ii), Pt particle size and distribution (iii), light absorption (iv), exciton separation and transport (v), and amount and depth of trap states (vi). With different effects on hydrogen evolution, a combination of those contributions is responsible for the observed hydrogen evolution trend.
Taking together the results for sonicated PHI and their effects on photocatalysis, it can be stated that photocatalysis is a process with multiple interwoven parameters. They act together on the hydrogen evolution activity in different and partly opposing ways. By changing the size of the photocatalyst, e.g. by sonication, the amount of functional groups, the particle dispersibility, the size, distribution and loading of the Pt co-catalyst, light absorption, exciton or charge separation, as well as the amount and depth of trap states are all changed, as summarized in Figure 6. Contrary to most published results, a non-linear trend for the actual measured photocatalytic activity as a particle size function was obtained. This is caused by an increased amount of functional groups (especially OH, NH₂, and C=O) at the surface with decreasing particle sizes (i), which leads to enhanced polarity/wettability and suspension stability (ii). As a result, the Pt deposition is more homogeneous, and the Pt particle size is reduced for smaller PHI particles (iii). However, the band gap increases for very small particles (iv), and the charge or exciton separation is decreased with too small particles due to restrictions in layer number and, therefore, carrier diffusion length (v). Higher levels of deep trap states are observed in smallest size regime due to a larger number of surface defects (vi). These deep lying surface defects reduce the hydrogen evolution activity, as long as bulk recombination is not the limiting factor for large particles. Although a complex interplay of these factors determines the effective photocatalytic activity, the increase in HER rate for particle sizes in the range of 180-500 nm suggests that tuning individual parameters is indeed possible. This way, beneficial properties become exposed while limiting effects become less detrimental. This approach provides a general template for future catalyst design.

Conclusion
In this work, we have used ultrasonication as a route to systematically study correlations between morphology-related properties and photocatalytic hydrogen evolution rates in the 2D carbon nitride poly(heptazine imide). By reducing the particle size of PHI down to 20 nm by de-agglomeration, this technique successfully yields stable colloidal solutions while preserving the structural integrity of the PHI primary crystallites in the in-plane as well as the out-of-plane directions. A combined structural analysis by NMR, FT-IR, PXRD, TEM, and XPS revealed that the polymer backbone remains unchanged when reducing particle size, and that the number of functional groups (mainly NH₂, OH, and C=O bearing) located at the periphery increases. As a result, the Pt distribution becomes more homogeneous. This highlights the intertwined effects resulting from size reduction and their impact on charge carrier localization, co-catalyst
attachment, and consequently, charge transfer for HER. TRPL measurements in combination with electrochemical analysis and quantum-chemical calculations suggest that the increasing amount of functional groups creates trap states, which are only beneficial for photocatalytic hydrogen evolution as long as their influence is not excessive. Thus, an optimum activity is reached for 2 h sonicated samples with a particle size of 180-500 nm and re-agglomerated samples of those particles. The functional groups formed are also beneficial for charge transport at particle interfaces, consistent with a multiple-trapping-and-release (MTR) model known for semi-crystalline organic semiconductors. If particles are too small, an excess amount of recombination centers are introduced, likely caused by defects lying deep in the band gap. These trap states reduce the efficiency for Pt deposition and hence charge transfer, resulting in lower photocatalytic activity as evidenced by quantum-chemical calculations of ionization potentials and electron affinities. For particles below 180 nm, large optical band gaps and deep trap states adversely affect photocatalysis, whereas the remaining effects of size reduction such as increased wettability enhance photocatalytic efficiency. The results presented here are not only instrumental in the context of PHI thin film and device fabrication, but they might also help to tune the properties of photocatalytic carbon nitride based microswimmers or solar battery applications. Disentangling the interdependent structural, morphological, and optoelectronic variables, which together define light-induced charge transport and transfer reactions is key to understand, address and optimize general photocatalyst design.

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Tuning the particle size of the 2D carbon nitride poly(heptazine imide) enables optimization of photocatalytic hydrogen evolution. We show that changes in the particle size affect the overall photocatalytic process in different ways, and we trace back the individual contributions of size-related variables on the photocatalytic activity. This multi-parameter analysis offers design strategies for next-generation photocatalysts.
Supporting information

“Morphology Control in 2D Carbon Nitrides: Impact of Particle Size on Optoelectronic Properties and Photocatalysis”

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1. Instrumental details

A Philips CM30 ST (300 kV, LaB$_6$ cathode) was used for transmission electron microscopy (TEM). The samples were suspended in n-butanol and drop-cast onto a lacey carbon film (Plano). Electron diffraction patterns were simulated from the crystal information reported in a previous paper of our group.\cite{1}

Scanning electron microscopy (SEM) was performed on a Zeiss Merlin electron microscope. The samples were drop-cast onto a Si substrate after cleaning with acetone and isopropanol.

Diffusive light scattering (DLS) and zeta-potentials were measured with a Malvern Zetasizer Nano ZS. DLS measurements were performed at concentration of 0.25 mg mL$^{-1}$ for the suspensions. The amount of big particles >3000 nm was not quantifiable due to an upper limit of measurable particles sizes by the DLS instrument. For zeta-potential measurements the carbon nitride sample was suspended at concentration of 10 µg mL$^{-1}$ in aqueous solutions of various pH adjusted by HCl or NaOH, with the ionic strength maintained at 10 mM using NaCl.

AFM was performed with an Asylum Research (Oxford Instruments) MFP-3D AFM in tapping mode with an Olympus cantilever with a resonance frequency of $\approx$300 kHz. The colloidal sample was drop-cast onto a Si/SiO$_2$ substrate that had been cleaned with acetone and isopropanol.

Powder X-ray diffraction (PXRD) patterns were collected at room temperature on a laboratory powder diffractometer in Debye-Scherrer geometry (Stadi P-Diffraktometer (Stoe), Cu-K$_{\alpha1}$ radiation from primary Ge(111)-Johann-type monochromator, triple array of Mythen 1 K detectors (Dectris)). The samples were sealed in 0.5 mm diameter borosilicate glass capillaries.

The lateral and vertical sizes of PHI-materials were determined from the powder patterns by using the Scherrer-equation\cite{2}

$$\tau = \frac{K \cdot \lambda}{\beta \cdot \cos \theta}$$

with $\tau$ as the mean size of the ordered domains, $K$ as a dimensionless shape factor, $\lambda$ as the wavelength of the diffractometer, $\beta$ as the diffraction line broadening, and $\theta$ as the Bragg angle. The instrumental profile was determined by refining the instrumental function, described by the fundamental parameter approach\cite{3-4} using a diffraction pattern of the Si640d NIST standard and fixed for crystallite size analysis. The lateral crystallite size was determined by a single line fit in the 2$\theta$ range of 6.5–8.7$^\circ$ of the 110 reflection using the Jana2006 software.\cite{5} As the 110 reflection overlaps with the anisotropically broadened 010 reflection, a 2$^{nd}$ peak was included into the refinement and refined independently. The background was modeled with Chebychev polynomials.
of 2\textsuperscript{nd} order. For the estimation of the vertical crystallite size, a single line fit of the 001 reflection in a 2\(\theta\) range of 26.5–29.5\(^\circ\) was performed. The complex background of the diffraction patterns, that is governed by diffuse scattering, and the overlap with anisotropically broadened reflections causes an increased analytical error (\(\approx 10\%\)), that is far larger than the analytical error, which is to be expected for a crystallite size determination using a high resolution laboratory X-ray powder diffractometer (\(\approx 1–2\%\)).

Fourier transformed infrared (FT-IR) spectra were performed with a PerkinElmer UATR TWO spectrometer equipped with a diamond crystal.

Diffuse reflectance UV and visible light (UV-Vis) spectra were collected on a Cary 5000 spectrometer (referenced to PTFE or barium sulfate) and the spectra in percentage reflectance were converted using the Kubelka Munk function. These data are plotted in a Tauc plot, with the assumption of a direct optical band gap, to estimate the optical band gap.

C, H, N elemental analyses were performed with a UNICUBE (Elementar Analysensysteme GmbH). Other elements were quantified with a Vista Pro Simultaneous ICP-OES Spectrometer combined with axially plasma system as excitation source and echelle polychromator with CCD detector (Varian Darmstadt). Calibrations were carried out by standard addition and the data were analyzed by the ICP-Expert software. Samples were digested in concentrated HNO\(_3\) at 185 °C for 25 min in a microwave (Discover SP-D, CEM GmbH).

Sorption measurements were acquired on a Quantachrome Autosorb iQ gas sorption analyzer using argon as the sorbent at 87.45 K. To activate and outgas the samples, they were left in vacuum (10\(^{-7}\) mbar) overnight at 150 °C. The surface area was calculated from the adsorption isotherm by using the Brunauer–Emmett–Teller (BET) theory.

For X-ray photoelectron spectroscopy (XPS), the powder samples were pressed into an indium foil. The spectra were collected on an Axis Ultra (Kratos Analytical, Manchester) X-ray photoelectron spectrometer equipped with a monochromatized Al K\(_a\) X-ray source and charge neutralization. The spectra were processed with the software CasaXPS 2.3.16 and referenced with the adventitious carbon 1s peak at 284.80 eV.\(^{[6-7]}\) For the Pt 4f\(_{7/2}\) and Pt 4f\(_{5/2}\) the area ratio was constrained to 4:3 and the binding energy separation to 3.33 eV.\(^{[8]}\) The comparison of binding energies was performed with the NIST Standard Reference Database 20 (Version 4.1) unless otherwise specified. For quantification the spectra were corrected by the transmission function and the relative transmission functions given by the instrument manufacturer were used.

Solid-state \(^1\)H, \(^{13}\)C and \(^{15}\)N nuclear magnetic resonance (NMR) experiments were performed on a Bruker Avance-III 400 MHz instrument at frequencies of 400, 100.61 and 40.53 MHz, respectively (\(B_0 = 9.4\) T). Chemical shifts for \(^1\)H and \(^{13}\)C are referenced to tetramethylsilane (TMS, \(\delta(^1\)H, \(^{13}\)C) = 0.0 ppm), while \(^{15}\)N is referenced to nitromethane (\(\delta = 0.0\) ppm). Magic Angle Spinning (MAS) with spinning rates ranging between 10 and 12.5 kHz was used in all experiments on solids. \(^{13}\)C
and $^{15}$N spectra with cross-polarization (CP) were recorded with a ramped polarization mixing and SPINAL-64 proton decoupling ($^1$H RF field of 50 kHz).\textsuperscript{9,10}

Photoluminescence (PL) spectra were collected on a double monochromator spectrofluorometer (Edinburgh FLS980) at an excitation wavelength of $\lambda = 370$ nm. Prior to every measurement the suspension (0.25 mg mL$^{-1}$) was degassed with a constant flow of Ar. Different conditions of each samples were measured starting with 0.25 mg mL$^{-1}$ aqueous suspension, methanol was added as a sacrificial donor and an optimized amount of hexachloroplatinum acid used for photo-depositing Pt before measurements, similar to photocatalysis experiments. Time-dependent lifetime measurements were performed with a 5 nm spectral window, which was centered at $\lambda = 480$ nm. The decay signal was fitted with a combination of a $\delta$ function and a $\Gamma$ function, as it was described in a previous paper of our group\textsuperscript{11}:

$$I(t) = \int_0^\infty p(k)e^{-kt}dk = \frac{A_{\Gamma mean}}{(1+\beta t)^{\alpha+1}} + A_{exp}e^{-kt}$$

where the first term corresponds to the $\Gamma$-distribution, defined by the $\alpha$ and $\beta$ parameters, and the second one describes an exponential decay. In this manner, $A_{\Gamma mean}$ and $A_{exp}$ show the relative weight of each contributions. To prevent agglomeration or sedimentation, the suspensions were stirred during the measurement.

2. Experimental details

Material synthesis: K-PHI and H-PHI were prepared as reported previously.\textsuperscript{1,12-13} Melamine (5.0 g; Carl Roth > 99%) was heated at 550 °C for 12 h at 5 °C min$^{-1}$ ramp rate under argon to yield melon as a yellow solid (2.0–2.4 g), which was ground to a fine powder before further processing. K-PHI was prepared by heating a finely ground mixture of melon (1.5 g) and KSCN (3.0 g, dried at 150 °C in vacuum; Carl Roth 99%) under argon at 400 °C for 1 h, then 500 °C for 30 min, both under maximum ramp rate. The resulting yellow solid was dispersed in water, centrifuged to isolate the product, and then repeatedly washed with water to remove all trace of KSCN. After drying at 60 °C in a vacuum oven, K-PHI was isolated as a yellow solid (1.0–1.3 g). H-PHI was prepared by stirring K-PHI (1.0 g) in HCl (100 mL, 1 M) overnight. The off-white solid was isolated by centrifugation, washed repeatedly with water until the supernatant was neutralized, then dried at 60 °C in a vacuum oven to afford H-PHI as an off-white solid (700–900 mg).

Sonication procedure: Colloidal solution of H-PHI (P4) was prepared by subjecting an aqueous suspension of H-PHI at concentration of 10 mg mL$^{-1}$ to ultrasonication for 24 h. The resulting dispersion was then centrifuged at RCF 500 to precipitate out the aggregates and the supernatant was collected as the colloidal solution. For solid state characterization and determination of the
colloid concentration, a known volume of the solution was taken and dried on a weighed petri dish on a hot plate at no more than 60 °C overnight.

The particle size separation for H-PHI and K-PHI was performed by sonicating 300 mg of the powder in 100 mL deionized water for 2 h while frequently shaking of the suspension, similar to literature.\textsuperscript{[14-15]} To prevent heating the sonication bath was cooled with an ice bath. To separate the particles according to their size, three centrifugation steps were used. The precipitate of the first step at 353 RCF for 25 min gained P1 particles. The supernatant was further centrifuged at 795 RCF for 40 min to obtain smaller precipitated particles (P2) and the smallest particles (P3) were obtained by centrifugation of the supernatant again at 35329 RCF for 90 min (Table S1).

| Sample name          | Synthesis conditions                               |
|----------------------|---------------------------------------------------|
| K/H-PHI pristine     | No sonication                                      |
| K/H-PHI P1           | 2 h sonication                                     |
|                      | Particle separation:                               |
|                      | Precipitate of centrifuging at 353 RCF            |
| K/H-PHI P1 re-       | K/H-PHI P1 dried in vacuum                        |
| agglomerated         |                                                    |
| K/H-PHI P2           | 2 h sonication                                     |
|                      | Particle separation:                               |
|                      | Precipitate of centrifuging at 795 RCF after P1 is removed |
| K/H-PHI P3           | 2 h sonication                                     |
|                      | Particle separation:                               |
|                      | Precipitate of centrifuging at 35329 RCF after P2 is removed |
| H-PHI P4             | 24 h sonication                                    |
|                      | Particle separation:                               |
|                      | Supernatant of centrifugation at 500 RCF           |

**Photocatalytic hydrogen evolution:** Photocatalytic experiments were performed in a double-walled glass reactor, where the outer compartment is circulated with thermostated water (25 °C), as previously described.\textsuperscript{[12-13]} The reactor was top-irradiated through a quartz window with a xenon lamp (Newport, 300 W) equipped with a water filter and a full spectrum mirror (2000 nm > \( \lambda \) > 200 nm). An air mass (AM) 1.5 G filter was used unless specified different and the light intensity was 100 mW cm\(^{-2}\). The catalyst powder (5, 10 or 20 mg) was suspended in a solution of water (4.5 mL, 9 mL or 19 mL), methanol (0.5 mL, 1 mL or 2 mL) and dihydrogen hexachloroplatinic (8 wt% aqueous solution, Aldrich, optimized volume as previously reported\textsuperscript{[12-13]}), which forms the platinum co-catalyst from its in-situ reduction. Colloidal suspension of PHI were diluted with water to reach an equal concentration as in the experiments with powder samples. The total volume of the diluted suspension was 18, 9 or 4.5 mL, where 2, 1 or 0.5 mL methanol respectively (10 vol%) and an optimized amount of dihydrogen hexachloroplatinic were added. The headspace was subjected to several cycles of evacuation and argon backfill prior to the experiment. The headspace of the reactor was periodically sampled and hydrogen was quantified by gas chromatography
(Thermo Scientific TRACE GC Ultra) equipped with a TCD detector using argon as the carrier gas.

**Electrochemical characterization:** The pellets (diameter of 5 or 6 mm) for impedance measurements were pressed in a uniaxial press with 1.5-2 bar of the respective powder.

The impedance spectra were recorded in a frequency range of 1x10⁶ -1x10⁴ Hz with a Metrohm (Autolab PGSTAT302N) single potentiostat. As measurement cell, a Swagelok cell with steel electrodes was used. Galvanostatic DC polarization experiments were performed with a Keithley 2604B Source Meter by applying 2 nA current to the pressed pellets in a Swagelok cell.

### 3. Quantum-chemical calculations

The optimization of atom positions and lattices of all periodic structures was performed on RI-PBE-D3/def2-TZVP[16-19] level of theory using an acceleration scheme based on the resolution of the identity (RI) technique and the continuous fast multipole method (CFMM[20-22]) implemented[23-24] in Turbomole version V7.3.[25-26]

Structures of the molecular compounds were optimized on PBE0-D3/def2-TZVP[17-18, 27-28] and RI-PBE-D3/def2-TZVP[16-19] level of theory. To ensure all minima to be true minima on the potential energy hypersurface subsequent frequency calculations were performed on the same level of theory.

The same level of theory was used for spin densities, starting from the optimized ground state geometry with a subsequent single-point calculation. An additional electron was added to yield a radical-anionic state as a model for the reduced state and an additional hole to yield a radical cationic state as a model for the oxidized state. Differences of total energies were used to calculate Electron Affinities and Ionization Potentials accordingly.

NMR chemical shifts were calculated on B97-2/pcS-2[29-30] level of theory using the FermiONs++[31-32] program package. NMR chemical shifts were calculated as differences of calculated NMR chemical shielding with respect to Nitromethane and Tetramethylsilane computed on the same level of theory.

Optical band gaps were calculated as lowest singlet excitation energies on TD-PBE0/def2-TZVP// RI-PBE-D3/def2-TZVP level of theory.

Single Point energies on XTB[33-35] level of theory were performed with the XTB program package in Version 6.2 RC2 (SAW190805).
4. Particle size and morphology analysis

4.1. Scanning electron microscopy (SEM)

Figure S1: SEM images of K-PHI pristine, P1, P2 and P3 (from top left to bottom right).

Figure S2: SEM images of K-PHI pristine, P1, P2 and P3 with higher resolution (from top left to bottom right).
4.2. Transmission electron microscopy (TEM)

Figure S4: TEM images of pristine H-PHI (left) and K-PHI (right).
Figure S5: TEM of H-PHI P4 after 24 h sonication (left) and electron diffraction image measured (middle) and simulated (right) based on the structure of H-PHI described in a previous publication. Inset on the left shows the Fast Fourier Transformed (FFT) image. [1]

4.3. Atomic force microscopy (AFM)

Figure S6: AFM images of H-PHI P4 and height profile of bigger particles after 24 h sonication. Measurements were performed with a double tip, which might lead to slight bigger measured particle sizes.

Figure S7: AFM image of pristine H-PHI and height profile of the particles.
Figure S8: AFM images (left) of K-PHI P2 (top) and P3 (bottom) and their height profiles (right). Smaller particles cannot be resolved from background, so that only bigger particles are measured here as an upper limit for particle sizes in P3.
4.4. Zeta-potential

![Graph showing Zeta-potential at different pH values for H-PHI pristine and P4.](image)

Figure S9: Zeta-potential at different pH values for H-PHI pristine and P4.

Table S2: Zeta-potential of two different batches of H-PHI pristine and P4 as well as K-PHI pristine, P1, P2 and P3 at pH=6.3.

| Sample          | Zeta Potential [mV] |
|-----------------|---------------------|
| H-PHI pristine 1| -28.3 (±2.0)        |
| H-PHI P4 1      | -37.5 (±3.0)        |
| H-PHI pristine 2| -17.3 (±2.1)        |
| H-PHI P4 2      | -22.9 (±2.0)        |
| K-PHI pristine  | -33.8 (±1.0)        |
| K-PHI P1        | -32.9 (±1.2)        |
| K-PHI P2        | -35.1 (±1.0)        |
| K-PHI P3        | -35.1 (±1.0)        |

The zeta-potential measurements clearly show, that with decreasing particle size the suspension stability is increasing for H-PHI. In Table S2, the zeta-potentials of two different batches of H-PHI pristine with their respective P4 particles are compared. For H-PHI P4 1 the average particle size was decreased down to 75 nm, whereas in H-PHI P4 2 the average particle size was around 120 nm, which might be a reason for the different values. However, it has to be stated, that there is a batch to batch variance of the pristine H-PHI particles already, which has to be taken into account. For K-PHI also an increase in suspension stability with decreasing particle sizes can be observed.
4.5. Diffuse light scattering (DLS)

Figure S10: DLS measurement of H-PHI pristine and P4 depicting the hydrodynamic radius (particle size is twice the radius).

Table S3: Average particle sizes estimated by DLS measurement and polydispersity index (PDI) of some H-PHI samples from different batches. Although all H-PHI P4 batches were synthesized analogous slightly different average particle sizes were obtained, which allows a detailed particle size dependent study in a wide particle size range.

| Sample          | Average particle size [nm] | PDI  |
|-----------------|---------------------------|------|
| H-PHI pristine 1| 810                       | 0.55 |
| H-PHI pristine 2| 1300                      | 0.81 |
| H-PHI P4 1      | 70                        | 0.36 |
| H-PHI P4 2      | 79                        | 0.27 |
| H-PHI P4 3      | 147                       | 0.40 |
| H-PHI P4 4      | 160                       | 0.48 |
| H-PHI P4 5      | 165                       | 0.42 |
| H-PHI P4 6      | 178                       | 0.41 |

Table S4: Average particle size measured by DLS, SEM, AFM, TEM analysis and estimated from PXRD via the Scherrer equation (in-plane × vertical expansion).

| Sample          | Particle size according to DLS [nm] | Particle size according to SEM [nm] | Particle size according to AFM [nm] | Crystallite size according to PXRD [nm] | Crystallite size according to TEM [nm] |
|-----------------|--------------------------------------|-------------------------------------|--------------------------------------|------------------------------------------|----------------------------------------|
| K-PHI pristine  | 200-3000                             | 30-1500                             | -                                    | 18 (±1) × 17 (±1)                         | 25-40                                  |
| K/H-PHI P1      | 300-1500                             | 20-900                              | -                                    | 17 (±1) × 17 (±1)                         | -                                     |
|                 |                                       |                                     |                                     | 16 (±3) × 27 (±1)                         | -                                     |
| K/H-PHI P1      | 250-1500                             | 20-750                              | -                                    | 17 (±1) × 17 (±1)                         | -                                     |
| re-aggregated   |                                       |                                     |                                     |                                         |                                       |
| K/H-PHI P2      | 100-400                              | 18-200                              | 60-500                               | 16 (±1) × 15 (±3)                         | -                                     |
| K/H-PHI P3      | 40-100                               | 10-200                              | 40-300                               | 14 (±2) × 13 (±3)                         | -                                     |
| H-PHI pristine  | 600-3000                             | 60-2500                             | 200-3000                             | 14 (±1) × 26 (±1)                         | 20-45                                  |
| H-PHI P4        | 20-200                               | 20-350                              | 25-2500                              | 13 (±1) × 22 (±1)                         | 10-45                                  |
Although all batches were synthesized in an analogous way, for each extracted fraction (P1, P2, P3 or P4) slightly different average particle sizes were obtained, which are caused by batch to batch variations. Therefore, for every fraction a particle size range is given, which was obtained from analyzing different batches (by DLS and SEM) of each fraction. Nevertheless, this variation in average particles sizes for the different fractions, allows a detailed particle size dependent study in a wide particle size range. In the following for each batch the average particle size is given, which was obtained, from several measurements (mostly DLS) of the same sample.

### 4.6. BET analysis

![BET analysis](image)

Figure S11: Isotherm of H-PHI pristine and P4 H-PHI. The fitting is use to extract BET surface area.

| Sample       | BET by DFT analysis [cm$^3$ g$^{-1}$] |
|--------------|---------------------------------------|
| H-PHI pristine | 60                                    |
| H-PHI P4      | 70                                    |
5. Structural analysis

5.1. Powder XRD

Figure S12: PXRD of K-PHI P1 and P3 particles, showing slightly more diffuse background in P3 and broader peaks, pointing to more disorder (left). PXRD of K-PHI pristine, P1, P2 and P3 showing a stepwise increasing peak width and a shift of the stacking peak to lower 2θ values (right, see grey arrow in the insets).

Figure S13: PXRD of H-PHI pristine, P1 and P4 with particle size of 160 nm and 145 nm.
5.2. FT-IR measurements

Figure S 14: FT-IR spectra of H-PHI pristine, P1, P2 and P4 (left) and K-PHI pristine and P1-P3 (right).

Figure S15: FT-IR spectra of H-PHI pristine, P1, P2 and P4 (left) and K-PHI pristine, P1-P3 (right) normalized to signal at 810 cm\(^{-1}\), to extract the relative amount of overlaying NH and OH vibrations.

Table S6: Comparison of the area of the NH/OH- (~3670-2220 cm\(^{-1}\)) and C≡N- (~2220-2110 cm\(^{-1}\)) bands in FT-IR for K-PHI.

| Sample          | Area between 3669-2223 cm\(^{-1}\) | Area between 2217-2107 cm\(^{-1}\) |
|-----------------|-----------------------------------|-----------------------------------|
| K-PHI pristine  | 1.00                              | 1.00                              |
| K-PHI P1        | 1.06                              | 0.77                              |
| K-PHI P2        | 1.23                              | 1.06                              |
| K-PHI P3        | 1.23                              | 1.11                              |
Figure S16: FT-IR of K-PHI with highlighted areas of vibrations analyzed in the following. The heptazine vibration is used to normalize the spectra. Based on literature the NH and OH vibration might be distinguishable, where OH vibrations in carbon nitrides are rather located at 3450 cm\(^{-1}\), whereas NH vibrations can be found at 3100 cm\(^{-1}\).\(^{[36]}\) However, since the distinction is difficult here, NH and OH vibrations are discussed together.

Table S7: Average amount of functional groups normalized to the pristine material depending on the particle size for H-PHI (pristine, P1, P2 and P4) estimated by FT-IR.

| Particles     | NH/OH vibration | N≡C vibration | CO vibration | NO vibration |
|---------------|-----------------|----------------|--------------|--------------|
| H-PHI pristine| 1.00            | 1.00           | 1.00         | 1.00         |
| H-PHI P1      | 1.20 (±0.01)    | 2.07 (±0.30)   | 1.75 (±0.10) | 1.02 (±0.02) |
| H-PHI P2      | 1.27 (±0.03)    | 2.70 (±0.37)   | 2.06 (±0.18) | 0.98 (±0.07) |
| H-PHI P4      | 1.47 (±0.11)    | 1.42 (±0.19)   | 2.27 (±0.16) | 0.91 (±0.07) |

Figure S17: Correlation of particle size and sonication duration of H-PHI with the relative amount of C≡N, CO and NO vibrations observed in FT-IR.
Figure S18: Relative peak area of NH/OH, NC, CO and NO vibrations of K-PHI and H-PHI as a function of particle size. FT-IR spectra were normalized to heptazine out-of-plane vibration at 805-811 cm\(^{-1}\). Red and blue shaded areas illustrate the trend depending on the particle size to guide the eye.

### 5.3. Elemental analysis

Table S8: Elemental analysis in weight percentage of H-PHI P1, P2 and P4 compared to its pristine counterpart. Different batches were measured, to also include the batch to batch variance.

|                  | C [wt\%]       | N [wt\%]       | Residual weight [wt\%] | C:N molar ratio |
|------------------|----------------|----------------|------------------------|-----------------|
| H-PHI pristine (batch 1) | 28.9 (±0.3)    | 48.2 (±0.2)    | 19.6                   | 0.698 (±0.007)  |
| H-PHI P4 (batch 1)    | 28.3 (±0.1)    | 47.1 (±0.5)    | 21.8                   | 0.701 (±0.005)  |
| H-PHI pristine (batch 2) | 28.1 (±0.2)    | 46.7 (±0.3)    | 25.2                   | 0.601 (±0.008)  |
| H-PHI P4 (batch 2)    | 27.3 (±0.1)    | 46.0 (±0.1)    | 26.7                   | 0.594 (±0.003)  |
| H-PHI pristine (batch 3) | 28.8 (±0.1)    | 47.5 (±0.1)    | 23.7                   | 0.607 (±0.003)  |
| H-PHI P1 (batch 3)    | 28.7 (±0.1)    | 47.3 (±0.2)    | 24.0                   | 0.606 (±0.005)  |
| H-PHI P2 (batch 3)    | 28.6 (±0.2)    | 46.4 (±0.2)    | 25.0                   | 0.616 (±0.007)  |
## 5.4. XPS analysis

Table S9: Comparison of relative areas of XPS signals of H-PHI pristine and smaller particles after 2 h and 24 h sonication. The number in () describes the error of the values given in %. The signal intensities were determined by relative sensitivity factors and detector function. Numbers in green denote the % change relative to the pristine material.

| XPS Signal | Corresponding binding conditions | H-PHI P4 (24 h sonication) | H-PHI P2 (2 h sonication) | H-PHI pristine 1000-1500 nm |
|------------|---------------------------------|-----------------------------|---------------------------|-----------------------------|
| C 1s 1 (284.8 eV) | C-C | 488.9 (8.57) | 559.4 (4.5) | 1174.6 (8.8) |
| C 1s 2 (286.4 eV) | C-O(H) / C-N(H)x | 252.4 (4.43) | 402.1 (3.2) | 515.7 (3.8) |
| C 1s 3 (288.4 eV) | N-C=N | 3375.2 (59.2) | 3117.6 (24.9) | 3236.9 (24.1) |
| C 1s 4 (288.9 eV) | C=O | 1117.7 (19.6) | 1131.2 (9.1) | 1043.6 (7.8) |
| N 1s 1 (398.9 eV) | C-N=C | 3614.6 (50.7) | 3531.0 (50.2) | 3519.5 (26.2) |
| N 1s 2 (400.6 eV) | NHx / N-C3 | 2544.0 (35.7) | 2372.7 (33.8) | 2224.2 (16.6) |
| N 1s 3 (404.2 eV) | NO | 198.1 (2.8) | 176.6 (2.5) | 163.3 (1.2) |
| N 1s 4 (406.0 eV) | π-π* excitation | 275.2 (3.9) | 188.4 (2.7) | 184.4 (1.4) |

| Ratio C-O(H)/N-C=N | 0.075 | 0.129 | 0.159 |
|---------------------|------|------|------|
| Ratio C=O/N-C=N | 0.331 | 0.363 | 0.322 |
| O 1s 1 (531.7 eV) | OH | 306.4 (4.3) | 302.4 (4.3) | 479.2 (3.6) |
| O 1s 2 (533.6 eV) | NO / O-C=O | 192.5 (2.7) | 127.1 (1.81) | 133.2 (1.0) |
| O 1s 3 (536.1 eV) | N(H)-C=O / O2 | - | 47.0 (0.67) | 85.0 (0.63) |
| Pt 4f 1 (71.2 eV) | Pt^0 | 32.0 (0.56) | 57.8 (0.82) | 72.4 (0.54) |
| Pt 4f 2 (73.0 eV) | Pt^{2+} | 43.7 (0.77) | 116.8 (0.93) | 123.2 (0.92) |
| Ratio Pt^{2+}/Pt^0 | 1.37 | 1.46 | 1.70 |
| Ratio Pt/N | 0.012 | 0.029 | 0.033 |

In most of the XPS spectra also a residual indium signals from the support material are visible. Contaminations of the indium surface by carbon or/and oxygen bearing groups could possibly contribute to the signals attributed to PHI, so that their contribution was estimated by XPS measurements on bare indium. From this measurements, we find that the substrate induced signals of carbon and oxygen bearing groups are in the range of 45 at% (carbon) and 24 at% (oxygen), with 30 at% indium signal. A significant substrate contribution to the PHI C 1s signals can be excluded, since the In signal intensity in the PHI samples reaches maximally 1.4 at% of the total.
material amount. However, for O 1s signals, where the intensity in the PHI on In measurement is low, a partial contribution of InOₓ and In(OH)ₓ cannot be ruled out. Based on the In signal in the PHI sample and assuming a constant proportion of the substrate induced oxygen peaks, their relative contribution was estimated to be at maximum 25% of the overall O 1s signal.

![Figure S19: XPS analysis of pristine H-PHI (particle size 1500-1000 nm) and H-PHI particles after 2 h (P2, particle size 400-350 nm) and 24 h sonication (P4, particle size around 79 nm) O 1s und Pt 4f spectrum.](image)

The N 1s XPS spectra show two major signals at 398.9 and 400.6 eV, which can be assigned to C-N=CN=C (grey area) and overlapping NHₓ (blue are) and N-C₃, respectively (Figure 2f). The smaller the particle size, the bigger the area of the signals of NHₓ and N-C₃ (increases 14 %), whereas the C-N=C amount is not changed. Since no evidence of changes in the N-C₃ concentration could be found, this enhancement is probably mainly caused by increasing amounts of NHₓ.

The formation of nitrogen vacancies due to sonication can be excluded. By elemental analysis an increase in C/N ratio should be observed, when nitrogen vacancies are formed. This trend might be observed for samples with longer sonication treatment (pristine: C/N =0.601 (±0.008); P4: C/N = 0.594 (±0.003)), however those changes are within the measurement error (Table S8). The XPS analysis can also be used for vacancy formation analysis, where the ratio of C-N=C/ N-C₃ would be decreasing when vacancies are formed. Since the N-C₃ and the NHₓ signal cannot be deconvoluted easily, the exact estimation of vacancies is not possible. By just taking the ratio of C-N=C/ N-C₃ and NHₓ signal, it appears that a low amount of nitrogen vacancy formation is possible, for smaller particles below 200 nm. The C-N=C/ N-C₃ and NHₓ ratio of 1.58 in the pristine material is reduced to 1.43 in the 24 h sonicated sample, which might hint to a small vacancy formation during sonication, resulting from increasing amounts of terminal groups. However, since no clear trend in elemental analysis or FT-IR is visible and the deconvolution of the N-C₃ and NHₓ signal is not possible here, it can be assumed that the nitrogen vacancy formation is not significant.
Besides, two additional, small signals in the N 1s XPS spectra at 404.1 and 405.9 eV can be caused by N-O groups\cite{[42-45]} and π-excitation or charging,\cite{[37,46-47]} respectively (Figure 2f). In comparison to the O 1s spectra, the signal at a binding energy of 533.6 eV can be attributed to N-O bonding, chemisorbed water\cite{48} or O-C=O\cite{49-50}. A third small signal in O 1s at 536.1 eV can be assigned to adsorbed oxygen or C=O bonding in urea \cite{42-43,51-52}, which is in good agreement with C 1s and N 1s spectra, where also C=O or N-O groups were observed.

Pt analysis

In addition, different Pt loading can be observed by XPS for H-PHI pristine, P2 and P4. In literature, the ratio of Pt:N is used to describe the coverage of the carbon nitride surface with Pt after photocatalysis. For the pristine material, a value of 0.033 was measured (Table S8). However, when comparing this result to elemental analysis, assuming a loading of 2 wt% Pt and 46 wt% N atoms, which results in an atom ratio of 0.01 Pt/ 3.29 N, a ratio of 0.003 is obtained. This is in line with literature reported values, for a similar material, estimated by elemental analysis with a ratio of 0.0012.\cite{[13]} From this it can be clearly seen that XPS is a surface sensitive method.\cite{[53]} Due to the inhomogeneous surface coverage of H-PHI pristine material with Pt clusters (Figure S37-S40), the amount of detected Pt by XPS depends on the measured spot. Therefore, elemental analysis is preferred to determine the overall Pt deposition in different materials, rather than XPS.

Different ratios of $\text{Pt}^{2+}/\text{Pt}^0$ can be seen in XPS for pristine, P2 and P4 particles. It was described in literature that a higher amount of $\text{Pt}^{2+}$ can be found when more functional groups are present (as a result of nitrogen vacancies), since those are stabilizing the $\text{Pt}^{2+}$ oxidation state.\cite{[54]} Furthermore, it was described that $\text{Pt}^0$ and $\text{Pt}^{2+}$ are important in the hydrogen evolution reaction, since both are responsible for different reactions. $\text{Pt}^0$ acts as electron trap centers and catalyzes the hydrogen formation, whereas $\text{Pt}^{2+}$ prevents the back-oxidation of the formed hydrogen.\cite{[55]} However, it was also reported that the $\text{Pt}^{2+}/\text{Pt}^0$ ratio changes during the first 4-6 h of illumination\cite{[56]}. Although. Each sample was illuminated for the same time, a different amount of $\text{Pt}^{2+}$ and $\text{Pt}^0$ in our case here can also just arise from different reactivity, as it was seen in photocatalytic hydrogen evolution. As a result, the comparison of the amount of different oxidation states of Pt is difficult, especially since defect concentration as well as efficiency of charge transfer influences the $\text{Pt}^{2+}/\text{Pt}^0$ ratio. It was described that the shape and size as well as the amount of Pt and Pt clusters affects the hydrogen evolution rate more significantly than their oxidation state.\cite{[56-57]}
5.5. NMR measurements and quantum-chemical calculations

Figure S20: Calculated NMR chemical shifts of Melem and urea functionalized Melem, obtained on B97-2/pcsSeg-2//PBE0-D3/def2-TZVP level of theory (blue: N-atoms, grey: C-atoms, red: O-atoms, white: H-atoms).

Figure S21: Calculated NMR chemical shifts of a single PHI pore filled with 7 water molecules, obtained on B97-2/pcsSeg-2//PBE0-D3/def2-TZVP level of theory.
NMR could not be used to verify the findings of NO and C=O groups, since the $^{13}$C NMR signal of a COOH and urea group is expected at around 180 ppm and to be of relatively low intensity.$^{[58]}$ Similar to the detection limit of low concentrations of C=O in PHI, the N-O signal (expected around -20 ppm)$^{[59]}$ in $^{15}$N NMR cannot be detected.
Figure S24: Direct $^{13}$C NMR of K-PHI P1. The “shoulder” depicts an additional signal, which is not as pronounced in the pristine material. This shoulder might be caused by a relative increased amount of functional groups at the heptazine units.

6. Photocatalysis and optical characterization

6.1. UV-Vis spectroscopy

Figure S25: UV-Vis spectrum of H-PHI P4 (average particle size of 20-40 nm) and P4 (average particle size of 38-255 nm) in aqueous suspension.
Figure S26: Tauc plot of H-PHI pristine, P1 and P2 in aqueous suspension (left) and in presence of 10 vol% methanol with photo-deposited Pt (right). Band gaps are averaged over different fittings and measurements (errors are given accordingly).

Figure S27: Tauc plot of K-PHI pristine, P1, P2 and P3 of the solid powder.

Table S10: Optical band gap of K-PHI pristine, P1, P2 and P3 and H-PHI pristine, P1, P2, P4 and P4 re-agglomerated (re-ag.) in aqueous suspensions (susp.), in presence of methanol or methanol and photo-deposited Pt.

| Compound       | Band gap in aqueous susp. [eV] | Band gap in aqueous susp. with methanol [eV] | Band gap in aqueous susp. with methanol, Pt [eV] |
|----------------|--------------------------------|-----------------------------------------------|-----------------------------------------------|
| K-PHI pristine | 2.79                           | 2.79                                          | 2.85                                          |
| K-PHI P1       | 2.82                           | 2.82                                          | 2.89                                          |
| K-PHI P2       | 2.90                           | 2.90                                          | 2.90                                          |
| K-PHI P3       | 2.88                           | 2.88                                          | 2.90                                          |
| H-PHI pristine | 2.92                           | 2.92                                          | 2.91                                          |
| H-PHI P1       | 2.91                           | -                                             | 2.90                                          |
| H-PHI P2       | 2.92                           | -                                             | 2.91                                          |
| H-PHI P4       | 2.95                           | 2.95                                          | 2.94                                          |
| H-PHI P4 re-ag. | 2.95                          | 2.96                                          | 2.95                                          |
Figure S28: Optical band gap obtained from Tauc plots of K-PHI and H-PHI in suspension and as solid depending on particle size (left). Relative change of the optical band gap of K-PHI and H-PHI (obtained from solid and suspension measurements and normalized to the pristine material) depending on the particle size (right). Colored lines were included to guide the eye.

6.2. Photocatalysis

Figure S29: a) Photocatalytic hydrogen evolution of H-PHI pristine and P4, with different particle sizes. b) and c) Dependence of photocatalytic hydrogen evolution on particle size. Besides the average particle size the width of the distribution of the particle size is also important, which might be the reason for scattering of the data points. The blue line in c) is included to guide the eye. The grey line depicts the average activity of the pristine material.
Figure S30: Photocatalytic hydrogen evolution of suspensions of H-PHI P4 freshly prepared (blue) and H-PHI P4 after 2 years of storage (orange). After 2 years the particles agglomerate partially, which then enhances the photocatalytic activity. This points to a certain particle size, which is ideal for efficient charge separation.

Figure S31: Photocatalytic hydrogen evolution of H-PHI pristine, P4 and P4 re-agglomerated with visible light illumination (> 420 nm) and H-PHI P4 full spectrum illumination of a Xe 300 W lamp (100 mW cm$^{-2}$).
Figure S32: Photocatalytic hydrogen evolution of K-PHI depending on particle size (pristine, P1, P1 re-agglomerated, P2 and P3) with Pt (8 wt%) and MeOH (10 vol%) as donor, however K-PHI is transformed to H-PHI during photocatalysis experiments.

Figure S33: Dependence of photocatalytic hydrogen evolution of K-PHI on particle size. Smaller particles tend to protonate faster than bigger particles and form H-PHI (see below in PL part). For this reason, the particle size dependent analysis was only performed with H-PHI in the following and no clear trend was observed for K-PHI.
Figure S34: FT-IR of dried K-PHI pristine, P1-P3 after photocatalytic hydrogen evolution in presence of Pt and MeOH as donor. Grey areas depict vibrations of remaining methanol and blue the changes due to protonation of the K-PHI backbone.

Figure S35: Comparison of photocatalytic hydrogen evolution and amount of defects (a) HN/OH, b) C≡N, c) CO, d) NO) with particle size of H-PHI. The defect amount was estimated by FT-IR by normalizing the defect vibrations to the heptazine vibration at 805-811 cm⁻¹. No clear correlation could be observed for the amount of C≡N or NO vibration modes with respect to the particle size.
6.3. Analysis of PHI after photocatalysis

Figure S36: Photocatalytic hydrogen evolution of H-PHI pristine and P4. For H-PHI P4 the HER rate is depicted for different Pt amounts used for photo-deposition from H$_2$PtCl$_6$.

Table S11: Amount of Pt photo-deposited after photocatalysis experiments with H-PHI measured with elemental analysis. For photocatalysis experiments 2 wt% Pt (photo-deposition of H$_2$PtCl$_6$) and 10 vol% methanol were used. No clear trend can be observed besides a Pt amount increase for particles sizes at around 200 nm.

| Average particle size [nm] | Pt amount deposited [wt%] |
|---------------------------|---------------------------|
| 1270                      | 1.37 (±0.01)              |
| 890                       | 1.43 (±0.01)              |
| 650                       | 0.93 (±0.01)              |
| 250                       | 2.01 (±0.01)              |
| 200                       | 2.10 (±0.11)              |
| 165                       | 0.99 (±0.01)              |
| 160                       | 1.06 (±0.01)              |
| 79                        | 1.38 (±0.01)              |
Figure S37: SEM images of H-PHI particles after photocatalysis for H-PHI pristine (grey), 2 h (blue) and 24 h (yellow) sonicated. Left side of each box depicts normal SEM images on the right side back-scattered images are shown, for better imaging of Pt deposition (bright spots).

Figure S38: SEM images of K-PHI particles after photocatalysis. Left side depicts the secondary electron SEM images on the right side back scattered images are shown for better imaging of Pt deposition (bright spots).
Figure S39: Correlation of particle size of H-PHI with average photo-deposited Pt particle size (estimated from SEM images) and hydrogen evolution rate.

Figure S40: Average Pt particle size (estimated from SEM images) after photocatalysis on H-PHI depending on defect amount of NH, OH, C≡N, CO and NO.

Figure S41: Correlation of particle size of H-PHI with average photo-deposited Pt particle sizes (estimated from SEM images), photo-deposited Pt amount after photocatalysis (analyzed with elemental analysis) and NH/OH vibration intensity in FT-IR (normalized to the heptazine vibration at 805-811 cm$^{-1}$). The photocatalytic experiments were performed with 2 wt% H$_2$PtCl$_6$ acid and 10 vol% methanol.
Figure S42: Correlation of particle size of H-PHI with average photo-deposited Pt particle size (estimated from SEM images), photo-deposited Pt amount after photocatalysis (analyzed with elemental analysis) and C≡N and CO vibration intensity in FT-IR (normalized to the heptazine vibration at 805-811 cm⁻¹). The photocatalytic experiments were performed with 2 wt% H₂PtCl₆ acid and 10 vol% methanol.

Figure S43: Correlation of particle size of H-PHI with average photo-deposited Pt particle size (estimated from SEM images), photo-deposited Pt amount after photocatalysis (analyzed with elemental analysis) and NO vibration intensity in FT-IR (normalized to the heptazine vibration at 805-811 cm⁻¹). The photocatalytic experiments were performed with 2 wt% H₂PtCl₆ acid and 10 vol% methanol.
Figure S44: Correlation of deposited Pt amount with photocatalytic hydrogen evolution of H-PHI.

6.4. PL analysis

Figure S45: PL emission spectra of K-PHI in aqueous suspension. The transformation of K-PHI to H-PHI can be seen over time, by a reduction of the overall PL count as well as the increasing contribution of an additional emission peak around 510 nm. For K-PHI mainly on emission peak (centered at 450 nm) is observed.
Figure S46: PL emission spectra of H-PHI pristine, P1, P2, P4 and P4 re-agglomerated in aqueous suspension, aqueous suspension with methanol and aqueous suspension with methanol and Pt.

Figure S47: Comparison of PL contributions (convoluted of two Gauss functions) of H-PHI pristine, P4, P4 re-agglomerated, P1 and P2 in aqueous suspension, aqueous suspension with methanol and aqueous suspension with methanol and Pt.

From the spectral analysis of PL contributions, it is not possible to extract the relative contribution of traps, since these give rise to both radiative and non-radiative decays (such as charge transfer). When methanol as a hole quencher and the co-catalyst Pt were present during the PL measurement, an expected quenching of photoluminescence intensity up to 50% was observed in all the measured samples (Figure S46-S49). These results are consistent with literature about Pt deposition on
melon-type carbon nitride$^{[60]}$, where the presence of an electron donor and acceptor can cause efficient exciton dissociation and charge transfer at the expense of radiative decay.

Figure S48: PL contributions for different H-PHI materials, plotted with their main energy in presence of MeOH (left) and MeOH and Pt (right). Blue signs depict the center of the Gauss function corresponding to the PL deconvolution at higher energies and orange signs depict the center of the Gauss function corresponding to the PL deconvolution at lower energy.

Figure S49: PL emission spectra of K-PHI pristine, P1, P1 re-agglomerated, P2 and P3 in aqueous suspension, aqueous suspension with methanol and aqueous suspension methanol and Pt.
Figure S50: Time-resolved PL analysis of H-PHI in aqueous suspension for pristine, P1, P2, P4 and P4 re-agglomerated.

Figure S51: Relative contribution of the exponential and $\Gamma$ function in the fit for time-resolved PL analysis of H-PHI in presence of MeOH (left) and MeOH and Pt (right). The particle sizes of are: pristine H-PHI (810 nm), P4 re-ag. H-PHI (300 nm), P1 H-PHI (500 nm), P2 H-PHI (230 nm) and P4 H-PHI (around 75 nm).
Table S12: Fitted lifetimes ($\tau_{\text{exp}}$ and $\tau_{\text{mode}}$) and their weighing factors (A) for time-dependent PL measurements of H-PHI with different particle sizes (pristine, P1, P2, P4 and P4 re-agglomerated (re-ag.)) and environments (white: aqueous suspension; light grey: water with 10 vol% MeOH; dark grey: water, MeOH and Pt).

| Sample       | $\tau_{\text{exp}}$ [ns] | $A_{\text{exp}}$ | $\tau_{\text{mode}}$ [ns] | $\tau_{\text{mean}}$ [ns] | $A_{\Gamma}$ | Average size [nm] |
|--------------|--------------------------|------------------|---------------------------|---------------------------|-------------|------------------|
| H-PHI pristine | 0.42 (± 0.03)            | 0.77 (± 0.01)    | 1.73 (± 0.09)             | 5.22 (± 0.43)             | 0.23 (± 0.01) | 810              |
| H-PHI P1     | 0.54 (± 0.05)            | 0.62 (± 0.01)    | 1.38 (± 0.73)             | 4.34 (± 1.49)             | 0.38 (± 0.01) | 500              |
| H-PHI P4     | 0.52 (± 0.04)            | 0.75 (± 0.01)    | 2.05 (± 0.10)             | 5.73 (± 0.43)             | 0.25 (± 0.01) | 300              |
| H-PHI P2     | 0.39 (± 0.04)            | 0.59 (± 0.01)    | 1.13 (± 0.05)             | 3.88 (± 0.26)             | 0.41 (± 0.01) | 230              |
| H-PHI P4     | 0.43 (± 0.04)            | 0.65 (± 0.01)    | 1.32 (± 0.24)             | 4.98 (± 1.33)             | 0.35 (± 0.01) | 75               |
| H-PHI pristine | 0.35 (± 0.02)            | 0.76 (± 0.01)    | 0.92 (± 0.05)             | 4.67 (± 0.52)             | 0.24 (± 0.01) | 810              |
| H-PHI P1     | 0.47 (± 0.04)            | 0.58 (± 0.01)    | 1.13 (± 0.84)             | 4.05 (± 1.81)             | 0.42 (± 0.01) | 500              |
| H-PHI P4     | 0.49 (± 0.03)            | 0.78 (± 0.01)    | 1.91 (± 1.02)             | 5.85 (± 1.48)             | 0.22 (± 0.01) | 300              |
| H-PHI P2     | 0.40 (± 0.04)            | 0.59 (± 0.01)    | 1.08 (± 0.19)             | 3.90 (± 0.78)             | 0.41 (± 0.01) | 230              |
| H-PHI P4     | 0.31 (± 0.04)            | 0.54 (± 0.02)    | 0.68 (± 0.03)             | 3.72 (± 0.34)             | 0.46 (± 0.02) | 75               |
| H-PHI pristine | 0.49 (± 0.03)            | 0.79 (± 0.01)    | 1.63 (± 0.09)             | 4.76 (± 0.42)             | 0.21 (± 0.01) | 810              |
| H-PHI P1     | 0.46 (± 0.05)            | 0.58 (± 0.01)    | 1.05 (± 0.05)             | 3.63 (± 0.25)             | 0.42 (± 0.01) | 500              |
| H-PHI P4     | 0.42 (± 0.03)            | 0.77 (± 0.01)    | 1.41 (± 0.08)             | 3.92 (± 0.33)             | 0.23 (± 0.01) | 300              |
| H-PHI P2     | 0.42 (± 0.03)            | 0.64 (± 0.01)    | 0.93 (± 0.04)             | 3.41 (± 0.27)             | 0.36 (± 0.01) | 230              |
| H-PHI P4     | 0.40 (± 0.04)            | 0.65 (± 0.01)    | 1.07 (± 0.05)             | 4.27 (± 0.34)             | 0.35 (± 0.01) | 75               |

Figure S52: Lifetime attributed to the $\Gamma$-function (measured in presence of methanol and photo-deposited Pt) of H-PHI in comparison to photocatalytic hydrogen evolution activity depending on particle size.
6.5. Electrochemical measurements

The electrochemical impedance spectroscopy as well as electrochemical polarization experiments were performed with pressed pellets in between of two steel electrodes. Out of this reason, only re-agglomerated particles could be analyzed. The charge transfer abilities of H-PHI pristine, P1, P2 and P4 were studied by impedance spectroscopy, to analyze the effect of different particle sizes and an increasing amount of functional groups on the electronic and ionic conductivity behavior within the material. With decreasing particle size, the amount of grain boundaries is increasing. Since the conductivity is slightly increasing with decreasing particle size, the conductivity might be based on grain boundary transport. Due to the shape of response in the electrochemical polarization experiments a rather electron based conductivity can be assumed and ionic motions can be neglected.\cite{61-62} In combination with the particle size dependent conductivity measurements this points to an enhanced electron transfer between re-agglomerated particles (grain sizes), if more functional groups are present at the interface (e.g. in P4).

Figure S53: Electrochemical characterization of H-PHI pellets (pristine, P1-P3 re-agglomerated (re-ag.)) between two steel electrodes by impedance spectroscopy (top left) and DC polarization experiments with the grey area depicting the 2 nA applied current (top right). To fit the impedance spectroscopy data a resistance in series with a constant phase element and a resistance in parallel was used. From DC measurements, a mainly electron driven charge transport can be assumed. Button: Conductivity depending on particle size.

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6.6. Quantum-chemical calculations

Figure S54: Designed PHI model systems with 1, 7 and 19 pores. Structures were obtained as cut-outs from a 2D periodic optimization of H-PHI.

In general, orbital contributions are rather localized on heptazine units, with negligible contribution of the NH bridge, between two heptazine units.

Figure S55: HOMO (left) and LUMO (right) of the 1 pore model system, obtained on RI-PBE/def2-SVP//RI-PBE-D3/def2-TZVP level of theory
Figure S56: HOMO (left) and LUMO (right) of the 7 pore model system, obtained on RI-PBE/def2-SVP//RI-PBE-D3/def2-TZVP level of theory.

Figure S57: HOMO (left) and LUMO (right) of the 19 pore model system, obtained on RI-PBE/def2-SVP//RI-PBE-D3/def2-TZVP level of theory.

Table S13: HOMO and LUMO energies of the model systems of PHI with 1, 7 and 19 pores obtained on RI-PBE/def2-SVP//RI-PBE-D3/def2-TZVP level of theory.

| Model system | HOMO energy [eV] | LUMO energy [eV] |
|--------------|------------------|------------------|
| 1 pore       | -5.65            | -3.06            |
| 7 pores      | -5.77            | -3.71            |
| 19 pores     | -5.74            | -3.80            |
Figure S58: HOMO (left) and LUMO (right) of the 1 pore model system with 6 NHC≡N termination groups, obtained on PBE-D3/def2-TZVP//PBE-D3/def2-TZVP level of theory. The functional group is highlighted in orange.

Figure S59: HOMO (left) and LUMO (right) of the 1 pore model system with 6 OH termination groups, obtained on PBE-D3/def2-TZVP//PBE-D3/def2-TZVP level of theory. The functional group is highlighted in orange.

Figure S60: HOMO (left) and LUMO (right) of the 1 pore model system with 6 NHCOOH termination groups, obtained on PBE-D3/def2-TZVP//PBE-D3/def2-TZVP level of theory. The functional group is highlighted in orange.
Figure S61: HOMO (left) and LUMO (right) of the 1 pore model system with 6 NHCONH₂ termination groups, obtained on PBE-D3/def2-TZVP//PBE-D3/def2-TZVP level of theory. The functional group is highlighted in orange.

Table S14: Optical and fundamental band gaps and HOMO and LUMO energies, obtained on RI-PBE-D3/def2-TZVP//PBE-D3/def2-TZVP level of theory using the 1 pore model system with different functionalization.

| Functionalization | Optical band gap [eV] | Band gap [eV] | HOMO energy [eV] | LUMO energy [eV] |
|-------------------|----------------------|---------------|------------------|------------------|
| NH₂               | 4.35                 | 2.63          | -5.81            | -3.18            |
| OH                | 4.30                 | 2.58          | -6.40            | -3.82            |
| NHCOOH            | 4.25                 | 2.55          | -6.36            | -3.81            |
| NHCONH₂           | 4.31                 | 2.59          | -6.52            | -3.93            |
| NHC≡N             | 4.27                 | 2.57          | -6.76            | -4.19            |

Calculations on XTB level of theory using the 1 pore model for OH edge defects revealed large absolute errors in comparison to PBE/def2-TZVP level of theory (see Methods for details). Referencing these calculations on edge defect models relative to calculations without any edge defects, the methodological errors are reduced significantly. Calculations on larger model systems as the 7 and 19 pore model system were carried out on XTB level of theory only.

Figure S62: Spin density of the radical cation (left) and radical anion (right) of the 1 pore model system with NH₂ functionalization, obtained on PBE-D3/def2-TZVP//PBE-D3/def2-TZVP level of theory. The functional group is highlighted in orange.
Figure S63: Spin density of the radical cation (left) and radical anion (right) of the 1 pore model system with NHC≡N functionalization, obtained on PBE-D3/def2-TZVP//PBE-D3/def2-TZVP level of theory. The functional group is highlighted in orange.

Figure S64: Spin density of the radical cation (left) and radical anion (right) of the 1 pore model system with NHCOOH functionalization, obtained on PBE-D3/def2-TZVP//PBE-D3/def2-TZVP level of theory. The functional group is highlighted in orange.

Figure S65: Spin density of the radical cation (left) and radical anion (right) of the 1 pore model system with NHCONH$_2$ functionalization, obtained on PBE-D3/def2-TZVP//PBE-D3/def2-TZVP level of theory. The functional group is highlighted in orange.
Figure S66: Spin density of the radical cation (left) and radical anion (right) of the 1 pore model system with OH functionalization, obtained on PBE-D3/def2-TZVP//PBE-D3/def2-TZVP level of theory. The functional group is highlighted in orange.

Figure S67: Comparison of XTB (blue) and PBE-D3/def2-TZVP (grey) electron affinities ($E_{EA}$) and ionization potentials ($E_{IP}$) of different surface functionalization on the 1 pore model system, relative to NH$_2$ functional groups.
Figure S68: Comparison of ionization potential ($E_{IP}$) and electron affinity ($E_{EA}$) for the 1 pore model system, obtained on PBE-D3/def2-TZVP and XTB level of theory. 1 pore model with NH$_2$ terminations, stepwise substitution of NH$_2$ groups with OH groups, relative to the fully OH terminated system.

Figure S69: Comparison of electron affinity ($E_{EA}$) and ionization potential ($E_{IP}$) normalized on the system with NH$_2$ termination groups. Stepwise substitution of NH$_2$ functional groups by NHC≡N on the 1 pore model (yellow), 7 pore model (blue) and 19 pore model (red). Calculations were performed on XTB level of theory.
Figure S70: Comparison of electron affinity ($E_{EA}$) and ionization potential ($E_{IP}$) normalized on the system with NH$_2$ termination groups. Stepwise substitution of NH$_2$ functional groups by NHCOOH (top) or OH (bottom) on the 1 pore model (yellow), 7 pore model (blue) and 19 pore model (red). Calculations were performed on XTB level of theory.

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