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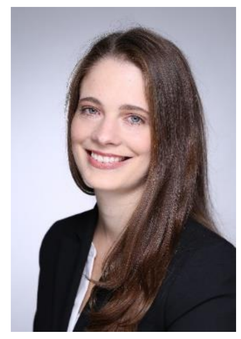
MULTIFUNCTIONAL 2D CARBON NITRIDES FOR GREEN HYDROGEN PRODUCTION & DIRECT SOLAR ENERGY STORAGE

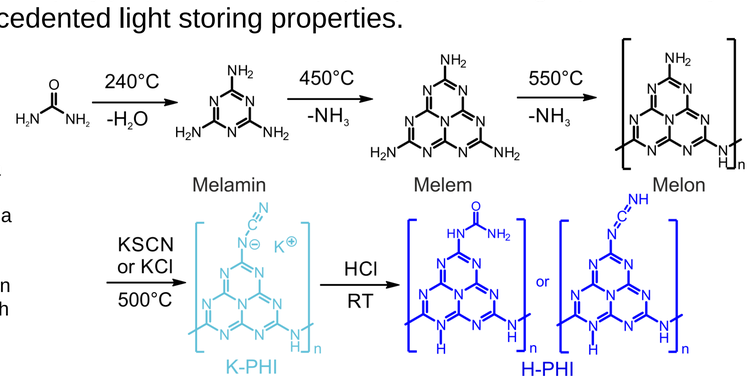
J. Kröger[1,2*], F. Podjaski[1], H. Schlomberg[1,2], and B. V. Lotsch[1,2]

[1] Max Planck Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany.
[2] Department of Chemistry, University of Munich (LMU), Butenandtstr. 5-13, 81377 Munich, Germany.
* Corresponding author. e-mail: j.kroeger@fkf.mpg.de



Synthesis and structural analysis [1-5]

Sunlight is the most sustainable energy source, offering different ways of energy harvesting and transformation. To expand direct energy storage possibilities, we investigate organic photocatalytic materials like carbon nitrides that can produce high value chemicals or solar fuels. Carbon nitrides (CN_x) are environmental friendly, chemically robust, cost efficient and easy to synthesize. Especially our recently discovered 2D carbon nitride poly(heptazine imide) (PHI) shows high photocatalytic efficiencies and has unprecedented light storing properties.



Scheme 1: Synthesis of the 2D CN_x poly(heptazine imdie) (PHI) from urea in a furnace, without using solvents. The first step of the synthesis leads via melamine and melem to melon, a 1D CN_x. Heating up melon in a salt melt with KSCN e.g. results in the formation of K-PHI. Acid treatment of K-PHI with 1M HCl transforms it to H-PHI.

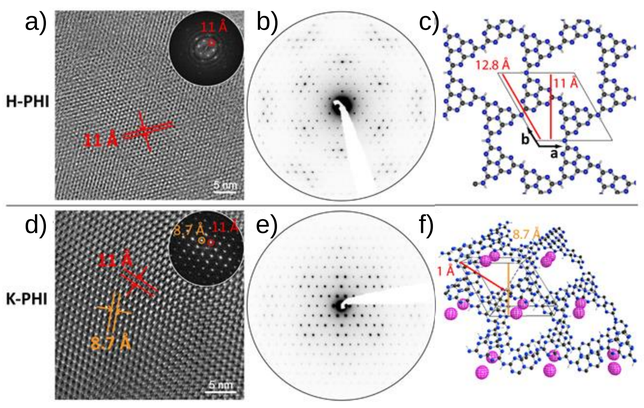
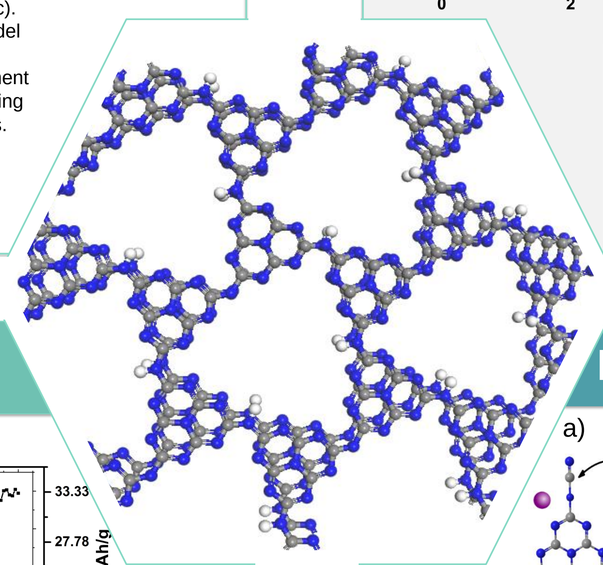


Figure 1: TEM analysis of highly crystalline H-PHI and K-PHI. a) and d) TEM images of H-PHI and K-PHI. Insets show the FFT. b) and e) SAED patterns of H-PHI and K-PHI. Trigonal cell models are depicted in c). f) Structural model obtained from Rietveld refinement for K-PHI including water molecules.



Photocatalytic and "dark" hydrogen evolution [3-6]

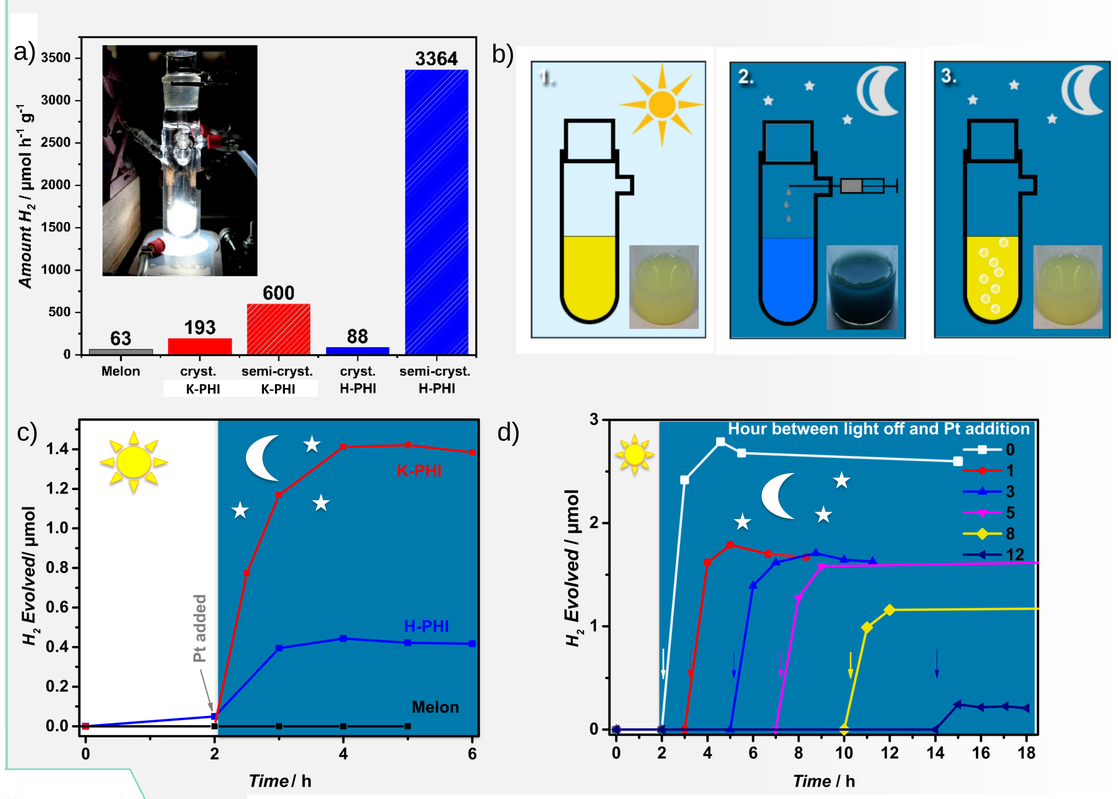


Figure 2: a) Photocatalytic hydrogen evolution reaction (HER) rates of different CN_x: 1D melon, 2D K-PHI and H-PHI (crystalline and semi-crystalline) in presence of 10 vol% methanol and optimized Pt loading, illuminated with AM 1.5 G conditions (100 mW cm^{-2}). Inset shows the photo-reactor used for photocatalysis tests. b) Depiction of the concept of „dark photocatalysis" for time delayed hydrogen evolution. c) „Dark photocatalysis" of melon, K-PHI and H-PHI in presence of phosphate buffer and 4-methylbenzylic alcohol. A Pt nanoparticle suspension (50 uL) is added in the dark after 2 h of illumination to trigger the HER after light charging. d) Hydrogen evolution with increasing delay times of Pt addition after illumination.

PHI as solar battery electrode [7]

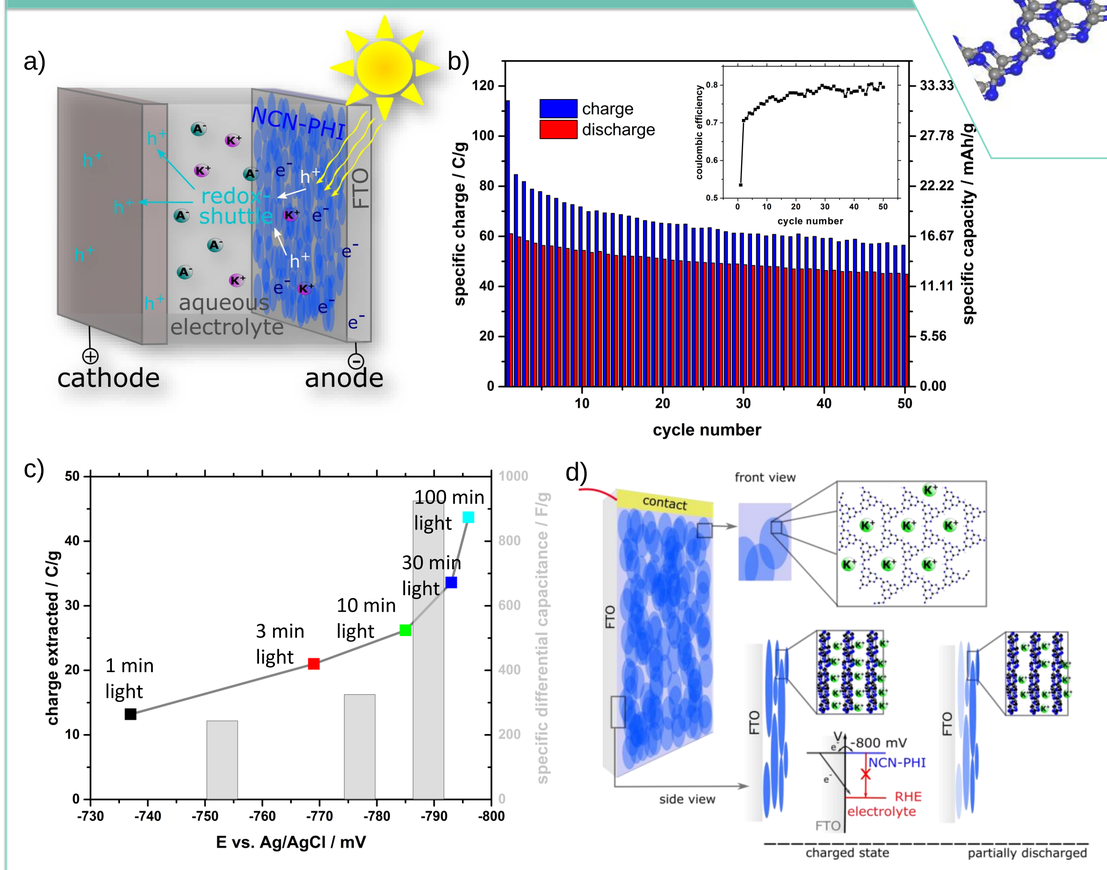


Figure 3: a) Illustration of the mechanisms at a light absorbing and charge storing photoanode with K-PHI deposited on fluorin doped tin oxide (FTO). b) Dark electrochemical performance of the aqueous anode during galvanostatic charging and discharging. c) Extractable charge and differential capacitance of photoanode with increasing illumination durations. d) Schematic depiction of discharging mechanism of K-PHI at FTO after illumination (AM 1.5 G, 100 mW cm^{-2}).

Interfacial modifications boosting HER [8]

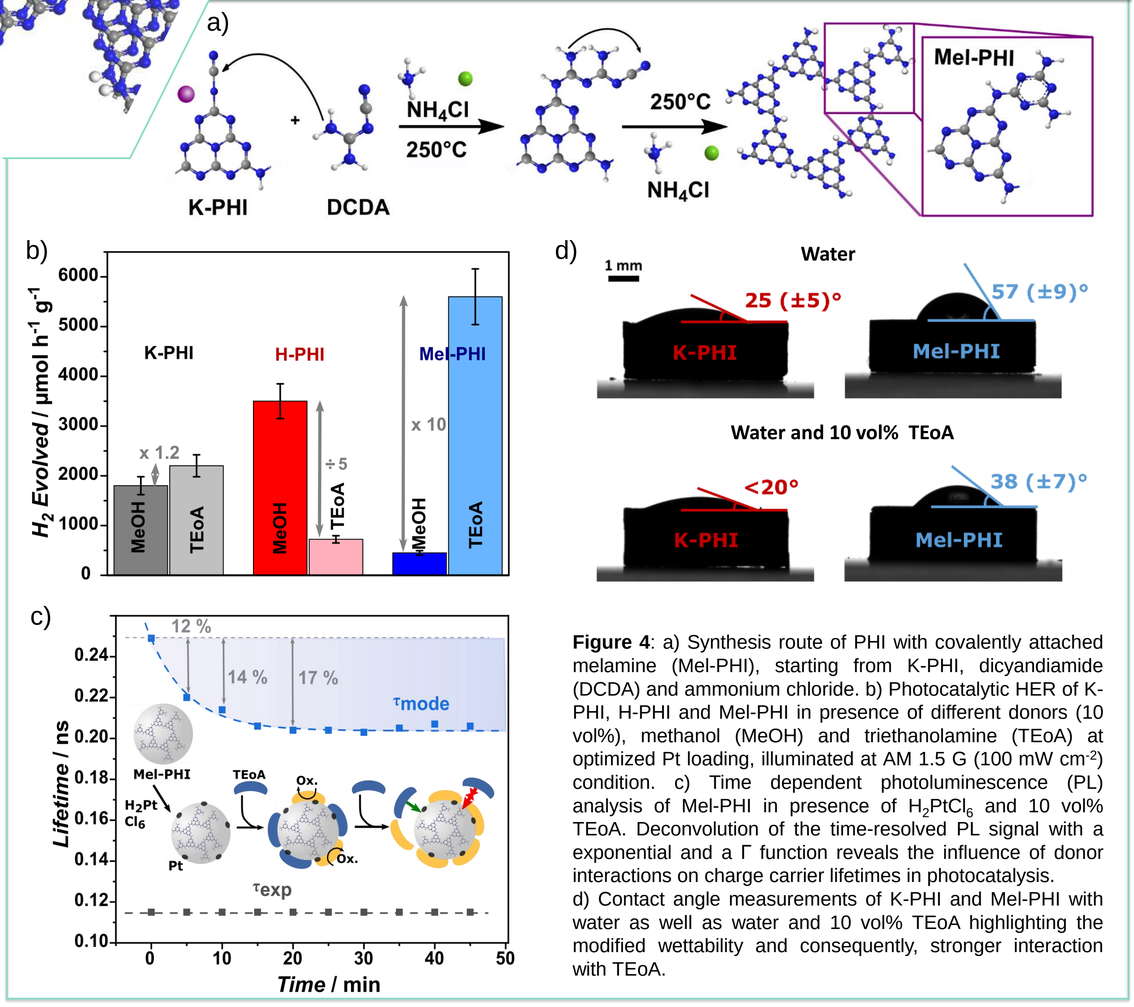


Figure 4: a) Synthesis route of PHI with covalently attached melamine (Mel-PHI), starting from K-PHI, dicyandiamide (DCDA) and ammonium chloride. b) Photocatalytic HER of K-PHI, H-PHI and Mel-PHI in presence of different donors (10 vol%), methanol (MeOH) and triethanolamine (TEoA) at optimized Pt loading, illuminated at AM 1.5 G (100 mW cm^{-2}) condition. c) Time dependent photoluminescence (PL) analysis of Mel-PHI in presence of H_2PtCl_6 and 10 vol% TEoA. Deconvolution of the time-resolved PL signal with a exponential and a Γ function reveals the influence of donor interactions on charge carrier lifetimes in photocatalysis. d) Contact angle measurements of K-PHI and Mel-PHI with water as well as water and 10 vol% TEoA highlighting the modified wettability and consequently, stronger interaction with TEoA.

Conclusion

Due to PHI's unconventional optoelectronic properties, this organic based material enables highly efficient photocatalytic hydrogen evolution and light-induced, long term electron storage, which can be used for „dark photocatalysis" or the fabrication of solar batteries. Our material study can provide design concepts for future photocatalyst, which also can store solar energy to overcome the problem of fluctuating renewable energy supply. We anticipate that PHI can also be used for other, highly desired light-induced reactions, such as CO_2 reduction, N_2 fixation or high value chemical synthesis.

References & Acknowledgements

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