Materials design for photo and electrochemical reactions

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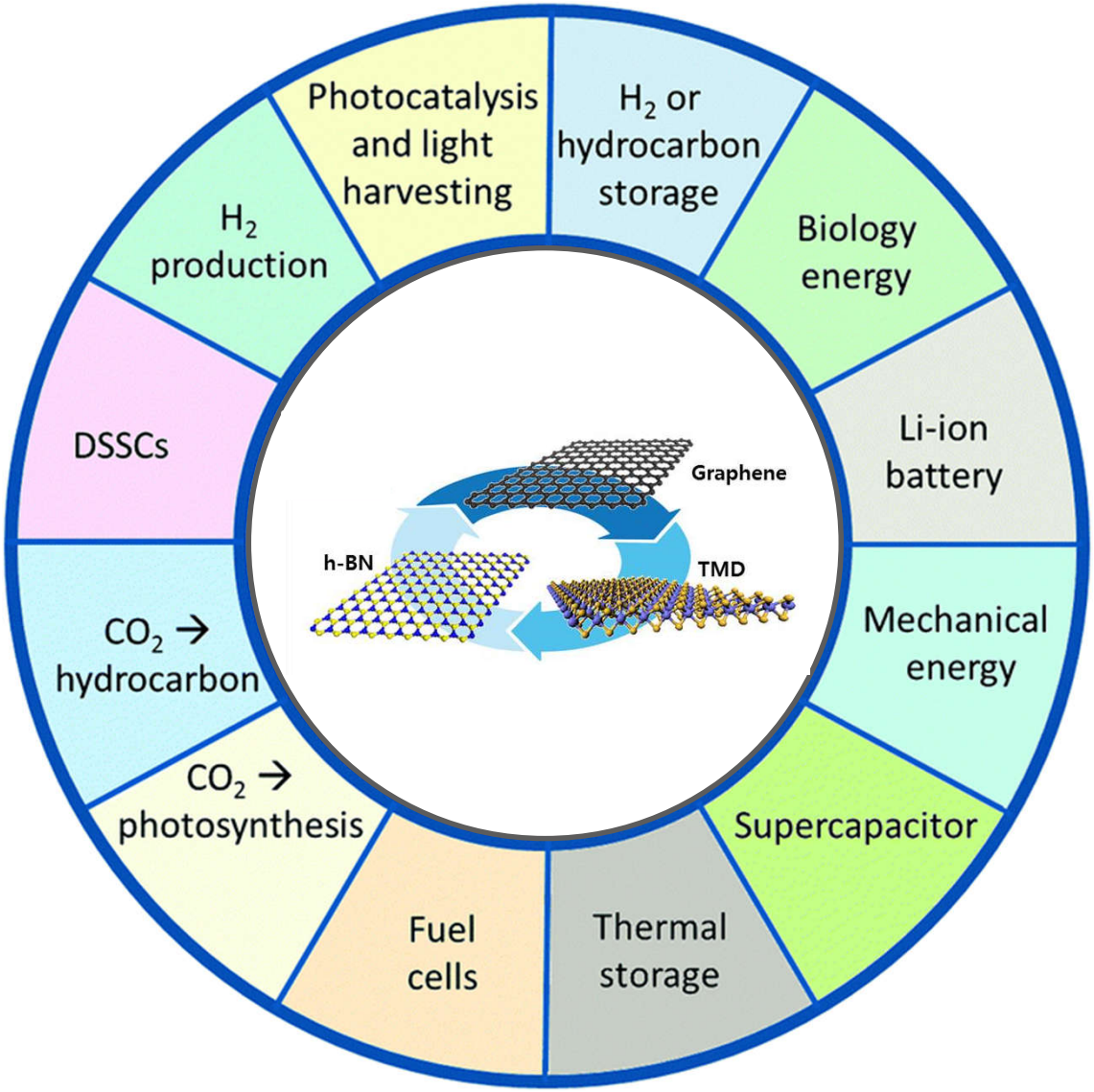
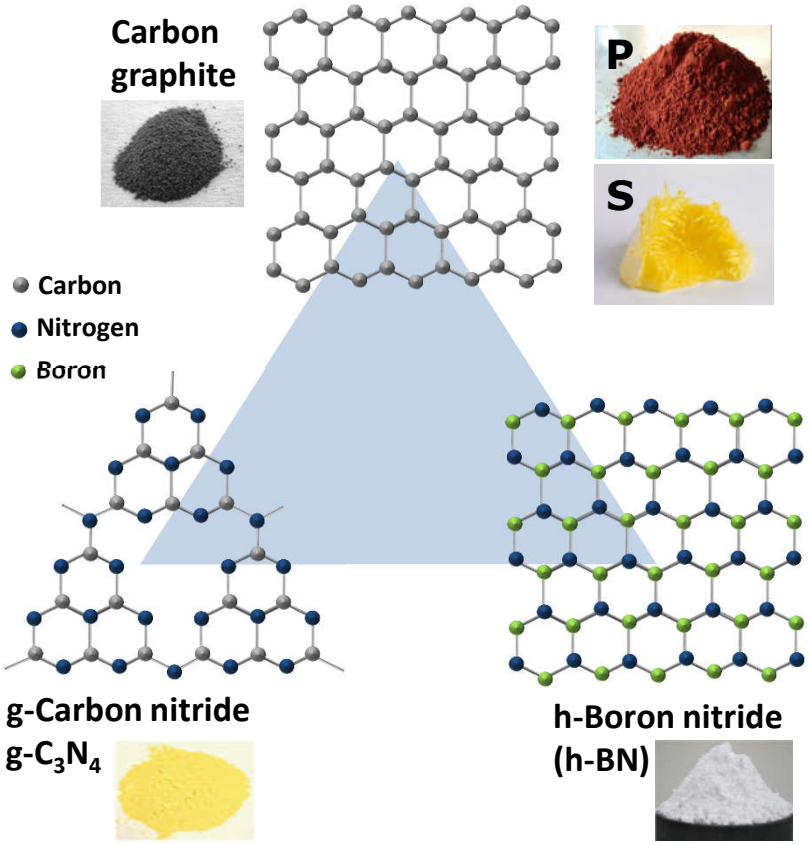
2D Materials for Energy



N. Linares, A. M. Silvestre-Albero, E. Serrano, J. Silvestre-Albero, J. García-Martínez, *Chem. Soc. Rev.* **2014**, *43*, 7681.

Metal-free materials



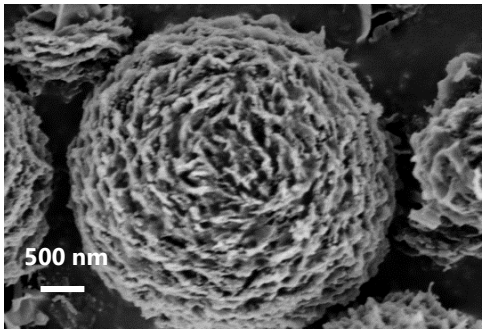
Light, cheap, environmentally-friendly and tunable

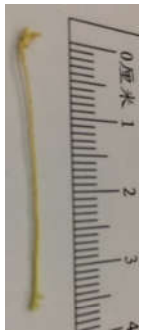
Carbon - Semimetal, Conductive
Electronic device
g-Carbon nitride – Semiconductor,
N content ~60 wt%,
Photo(electro)catalysis
Heterogeneous catalysis
h-Boron nitride - Insulator,
thermal and chemical stability
Lubricant, ceramic, plastics, rubbers

We aim to overcome the traditional solid state chemistry limitations and to obtain new materials that are not known yet.
To study their optical, chemical, catalytic properties as a function of their composition, etc…
Carbon/Boron/sulfur phosphorous nitride…

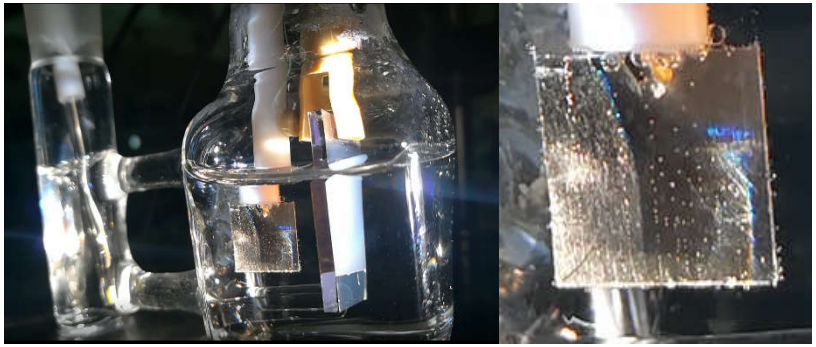
Materials design for photo and electrochemical reactions

Carbon nitride materials for photochemical reactions

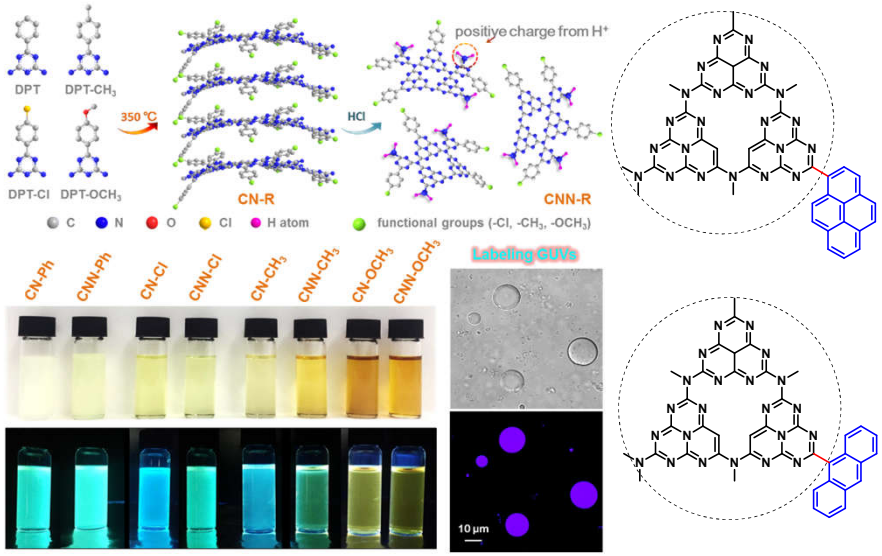




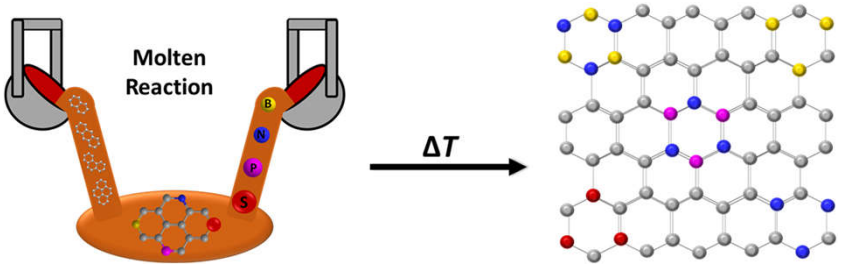
Carbon nitride layers for photoelectrochemical reactions



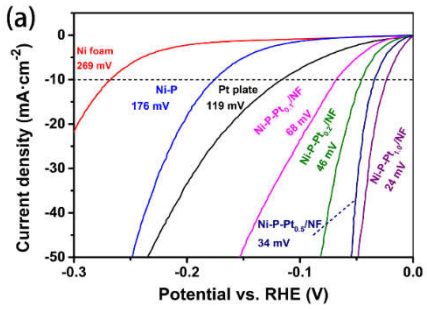
Carbon nitride materials as fluorescence probes

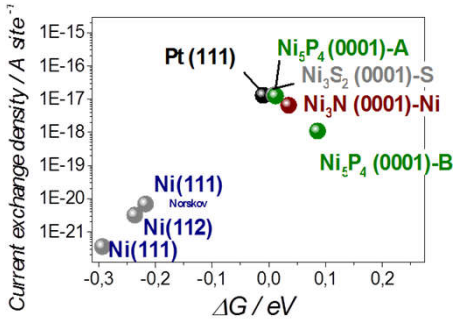


New metal-free materials (C-N-B-P-S-O)

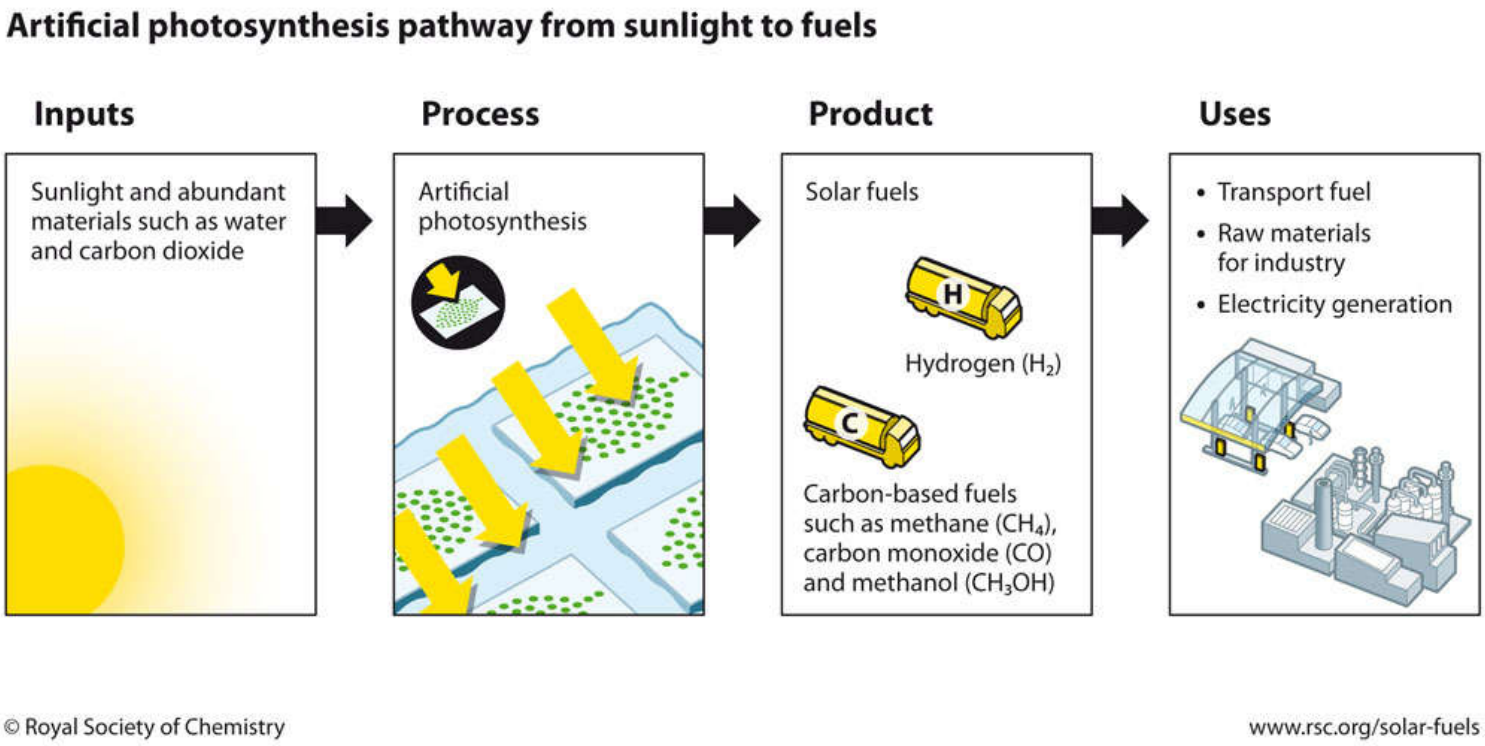


Metal nitrides, phosphides and carbides as efficient electrocatalysts





Solar fuel

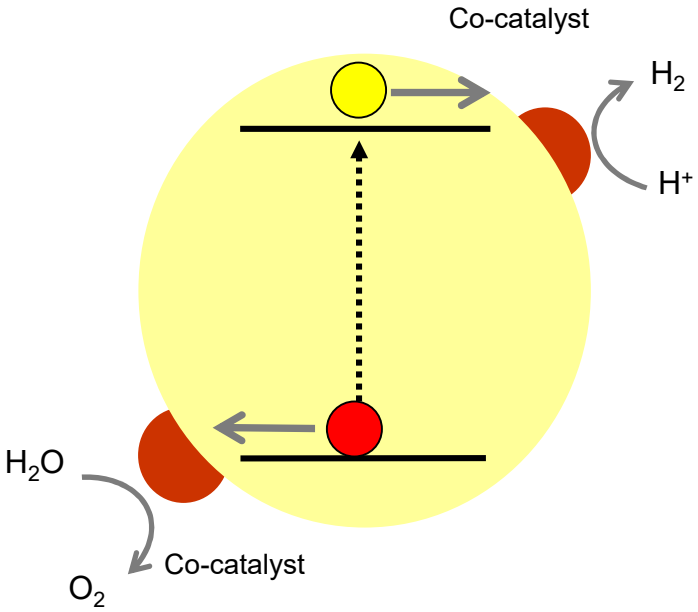


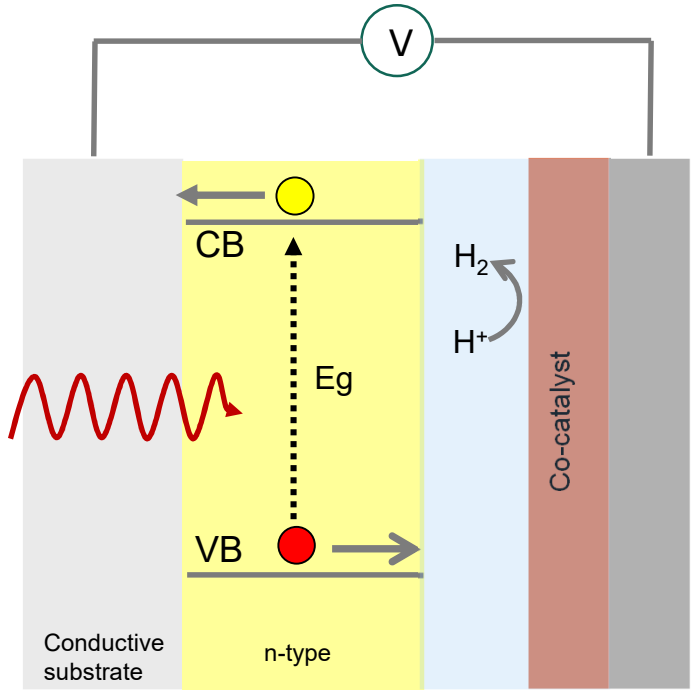
Solar cell – electrical energy
Sun to fuel – chemical energy

Alternative source of energy for replacing fossil fuels

Artificial photosynthesis

Replace metal-based photoelectrocatalysts



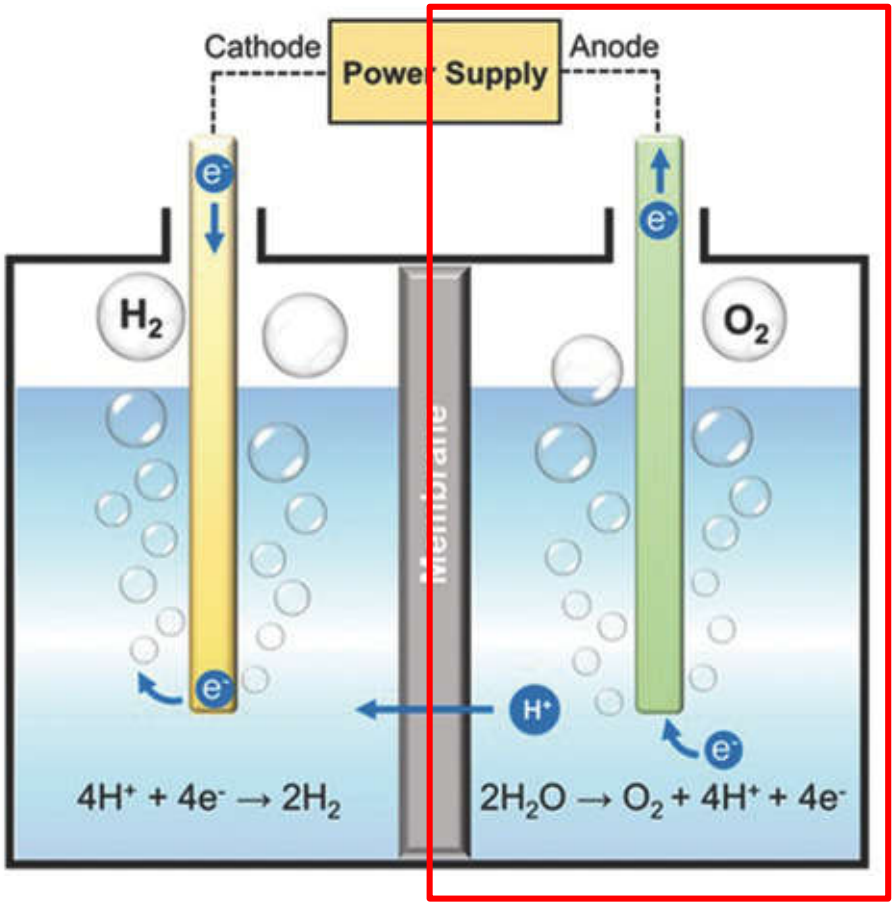


Photoactive materials for sunlight-driven reactions: photocatalyst, absorber layer in photoelectrochemical and solar cells

Electrocatalyst : water splitting and CO_2 reduction

Unique (photo)electronic properties :
Light-emitting diodes and other electronic devices

Electrochemical Water Splitting



Water splitting, nitrogen reduction reaction and organic molecules oxidation

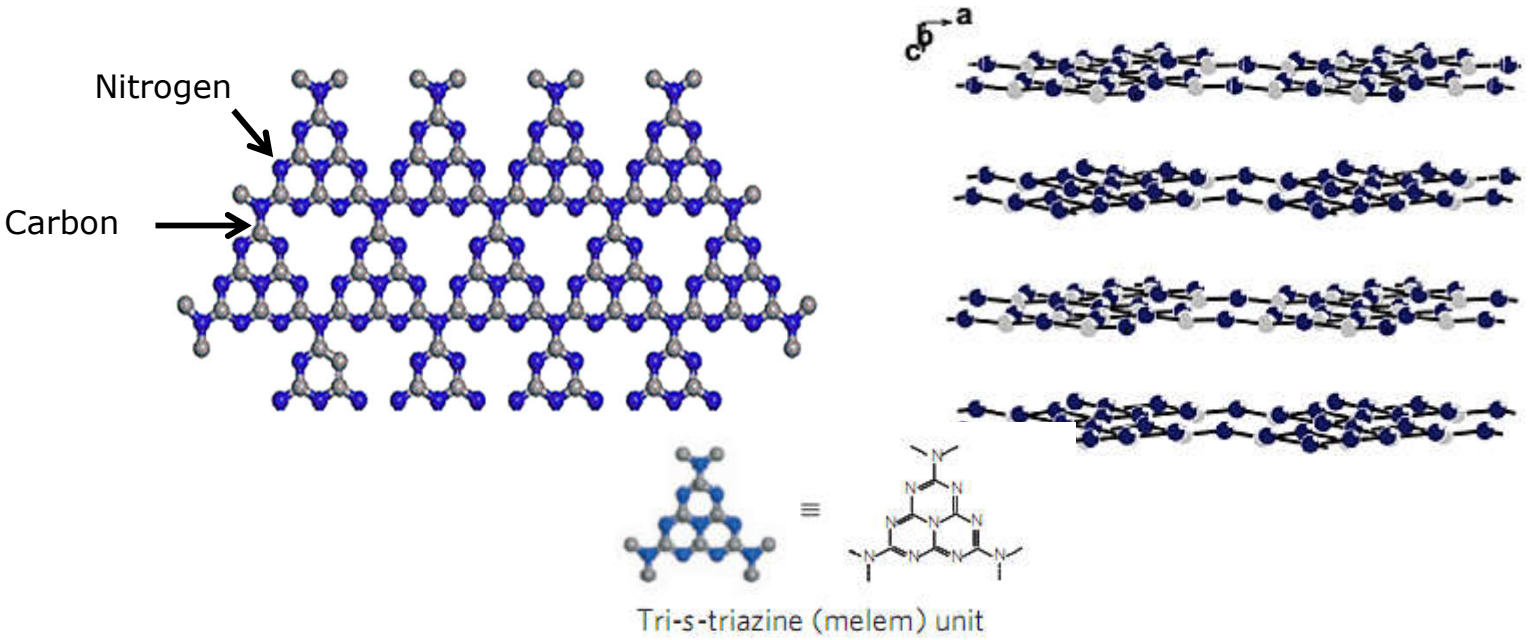
Possible catalysts –

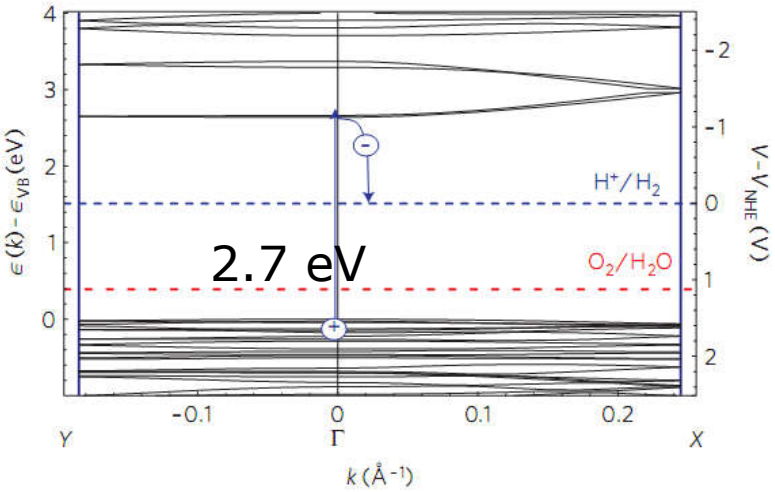
- Precious metal based IrO_2, RuO_2
- Non-precious metals NiFe, NiS, Fe_xO_y
  - ✓ Nanomaterials
  - ✓ Single-atom

Metal nitrides, phosphides and carbides as well as metal-free materials as efficient electrocatalysts

Yang, M.-Q., Wang, J., Wu, H., Ho, G. W., *Small* **2018**, 14, 1703323.

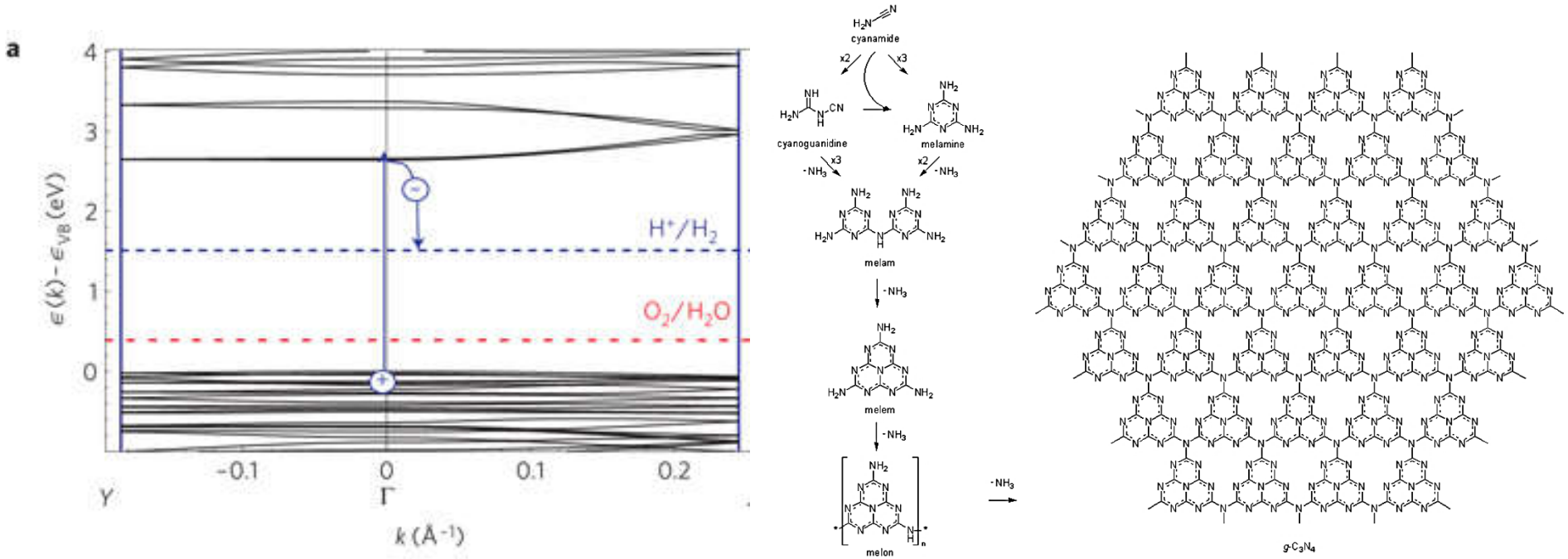
Graphitic carbon nitride (g-C_3N_4) materials





Nature Materials 2009. 8, 76 . J. Am. Chem. Soc. 2014, 136, 1730. J. Phys. Chem. C. 2014, 46, 26479. Energy Environ. Sci., 2012, 5, 6717. Chem. Commun., 2012,48, 3430

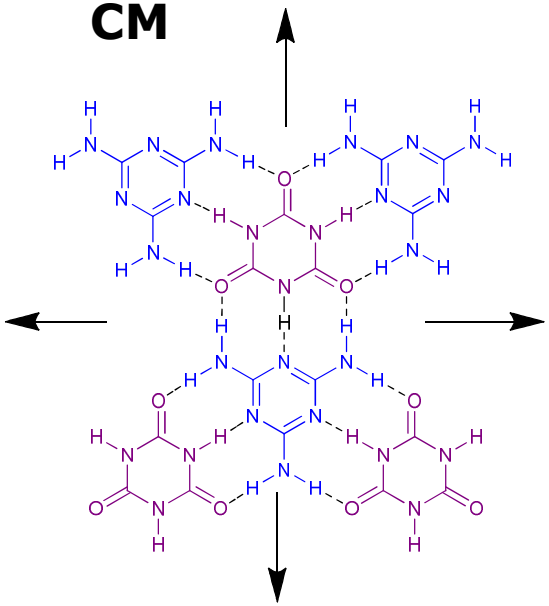
Why carbon nitride materials?



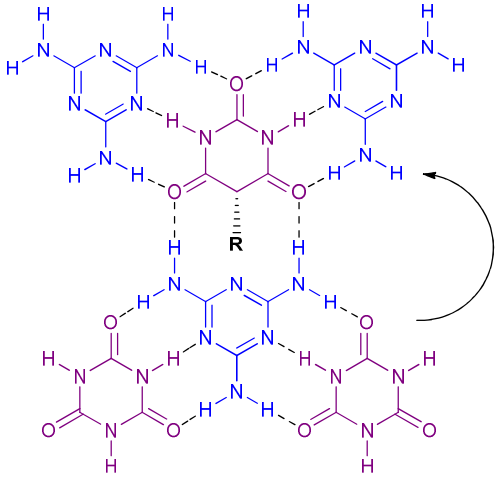
- ***We can't control the chemical and the photophysical properties***
- ***Poor charge separation***
- ***Wide band gap***
- ***Low photoactivity***

Supramolecular structures

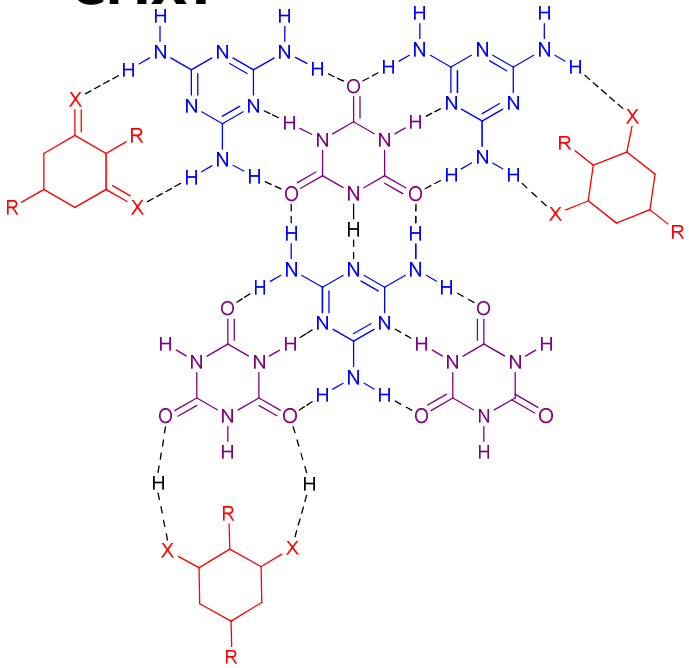
CM



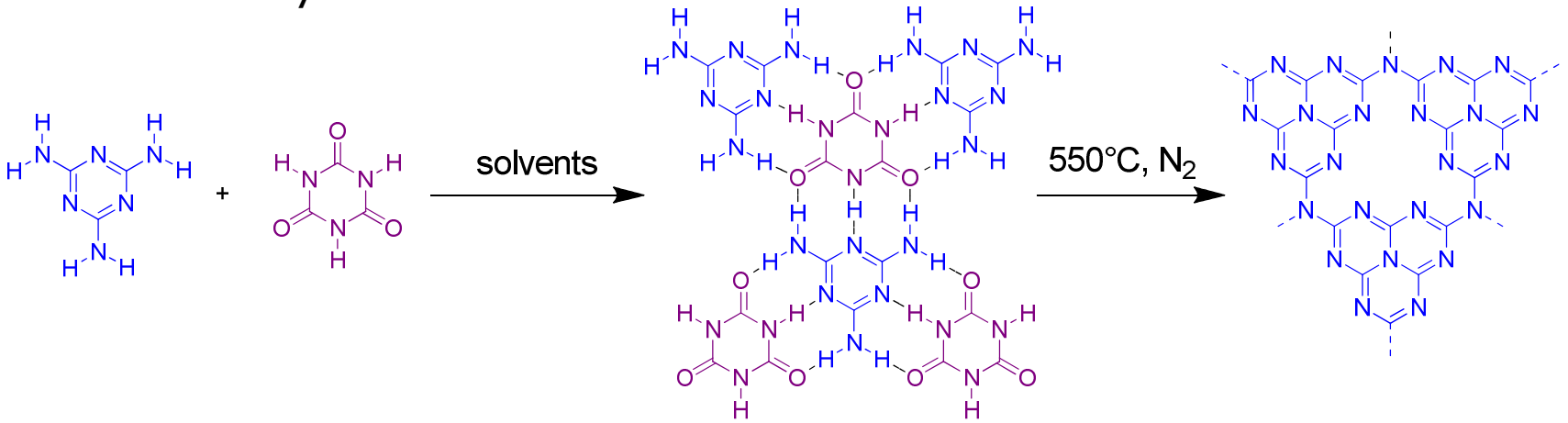
CMB



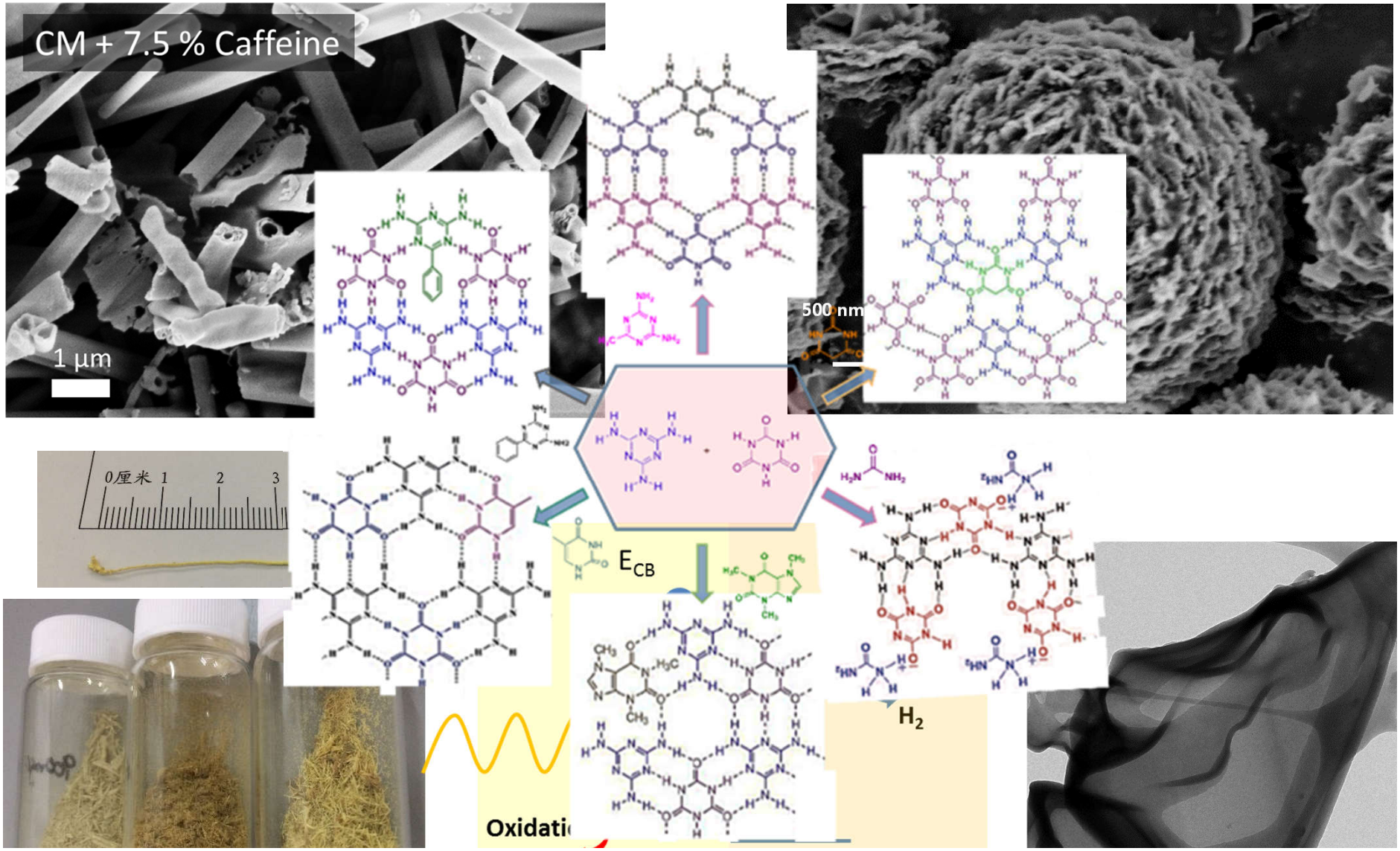
CMX?



Solid state synthesis



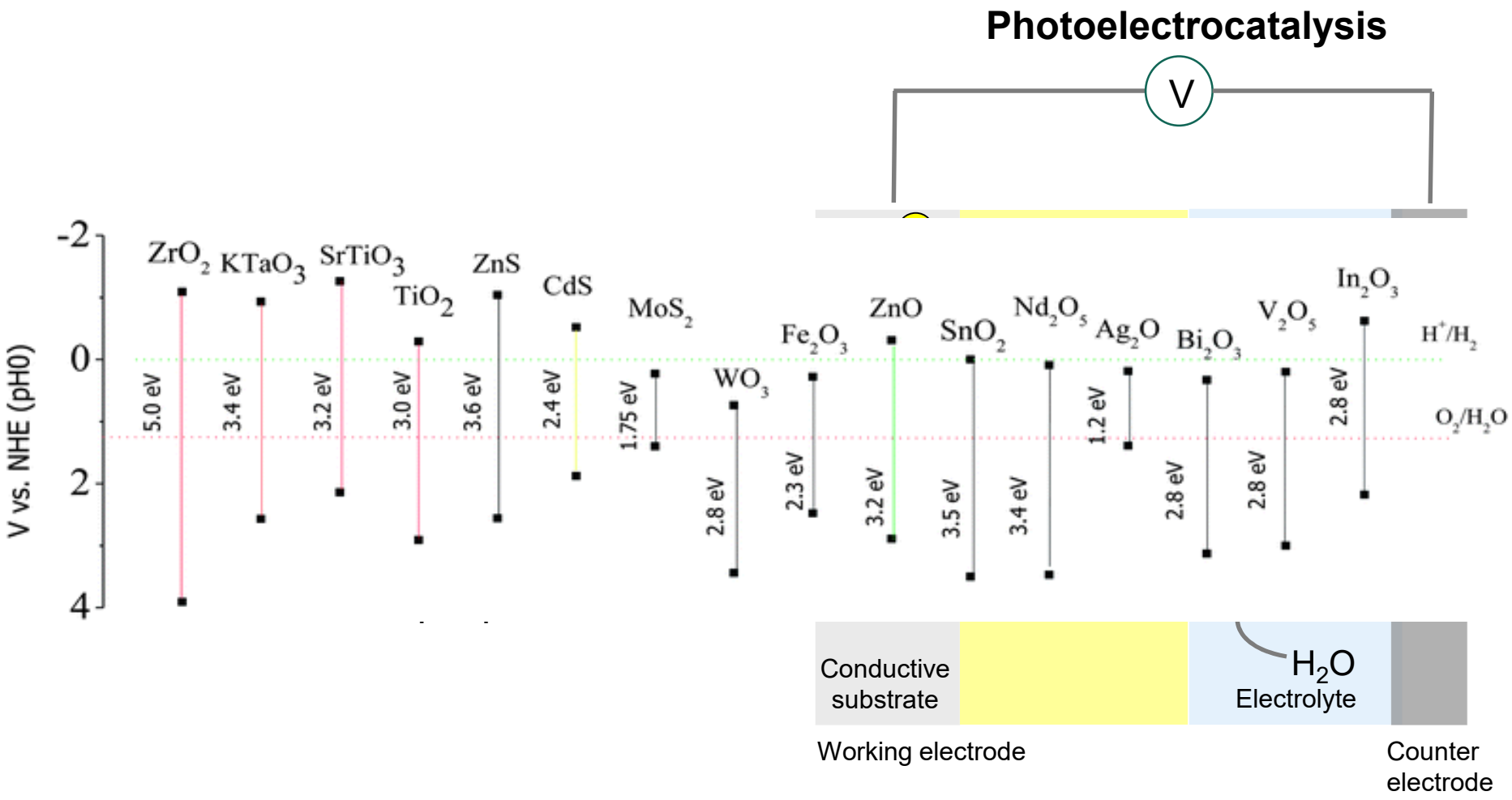
A gallery of carbon nitride materials



Barrio, J. and Shalom, M. (**2018**), Rational Design of Carbon Nitride Materials by Supramolecular Preorganization of Monomers. *ChemCatChem*. doi:10.1002/cctc.201801410.

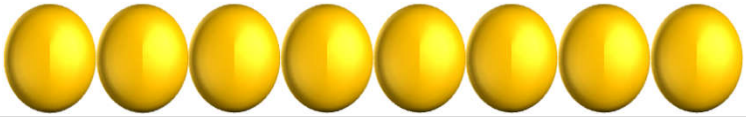
Semiconductor requirements in PEC

Solar fuel production – converting solar to chemical energy



From powder to substrate - the challenges

- Spin coating
- Doctor Blade techniques
- Physical methods
(CVD, sputtering…)



Different substrates
(Glass, FTO, Metal oxides….)

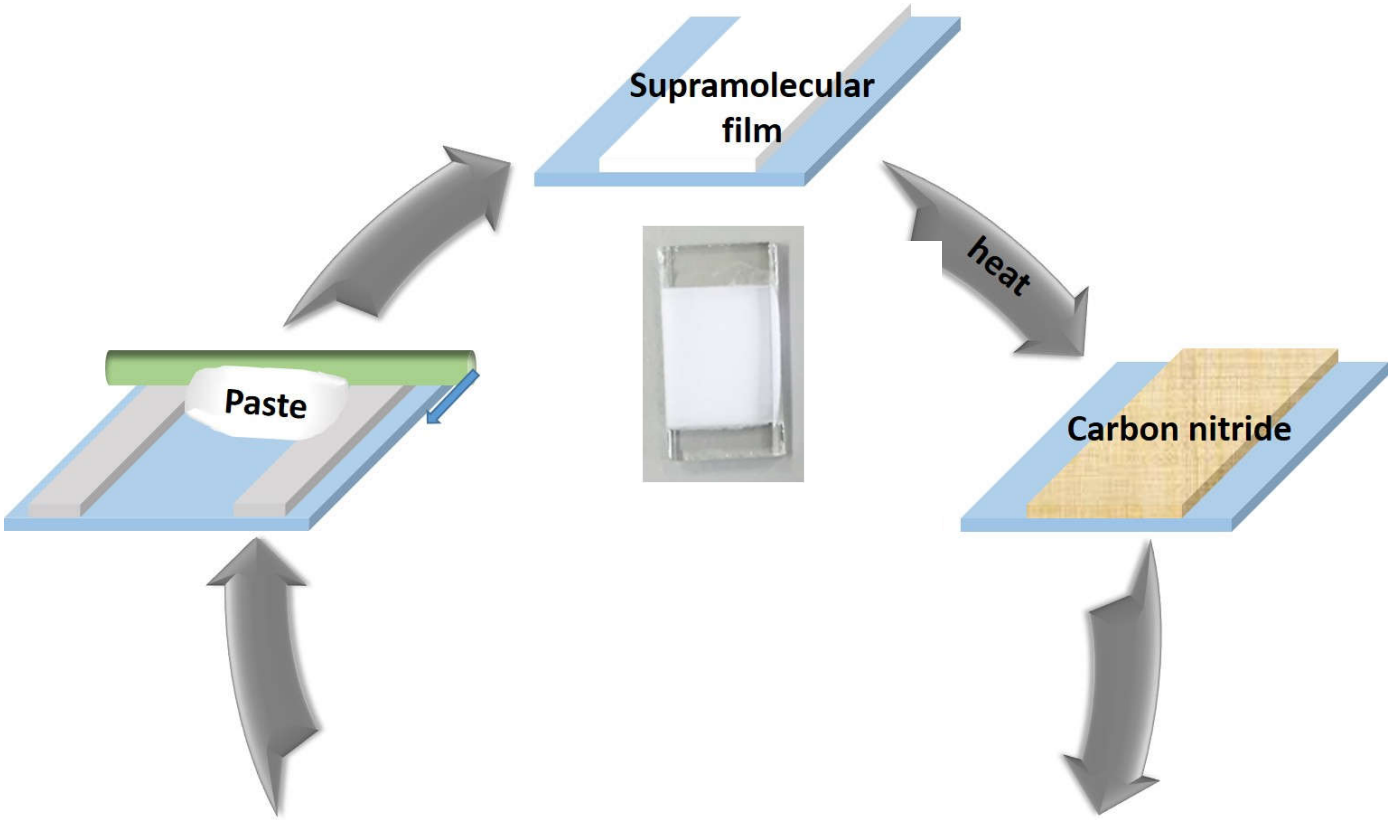
Different substrates
(Glass, FTO, Metal oxides….)

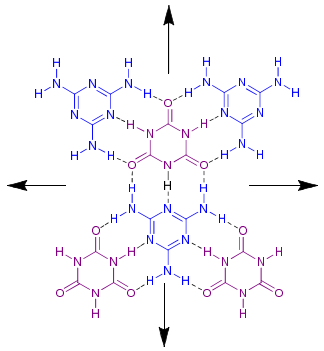
There was no convenient and efficient method to deposit carbon nitride on substrates

Poor charge separation and transfer

Not fully suitable band gap

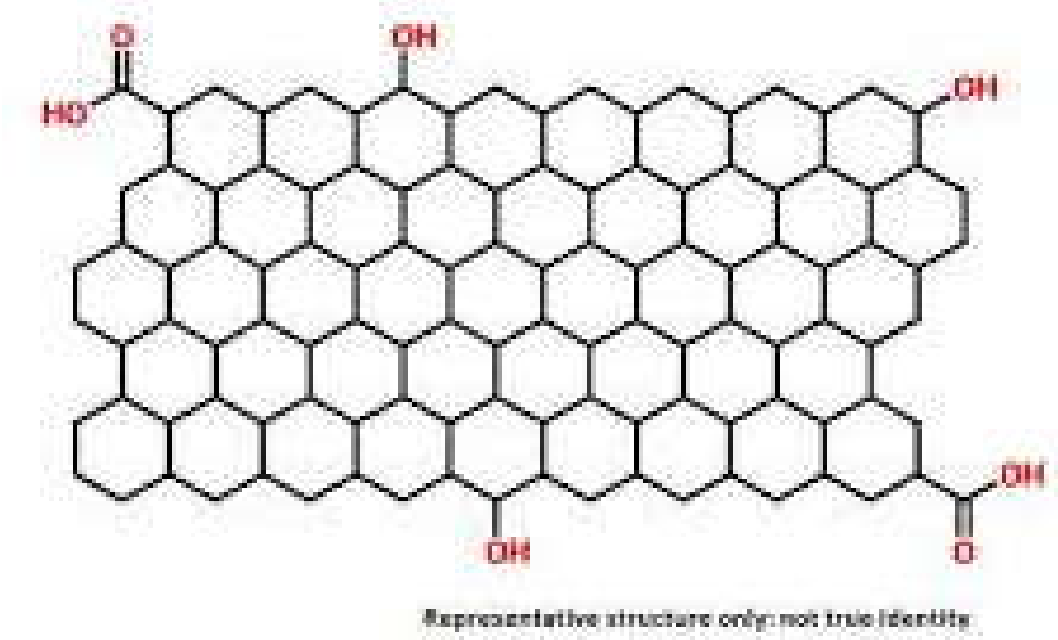
Can we transfer all the gained knowledge from the powder chemistry to electrode?

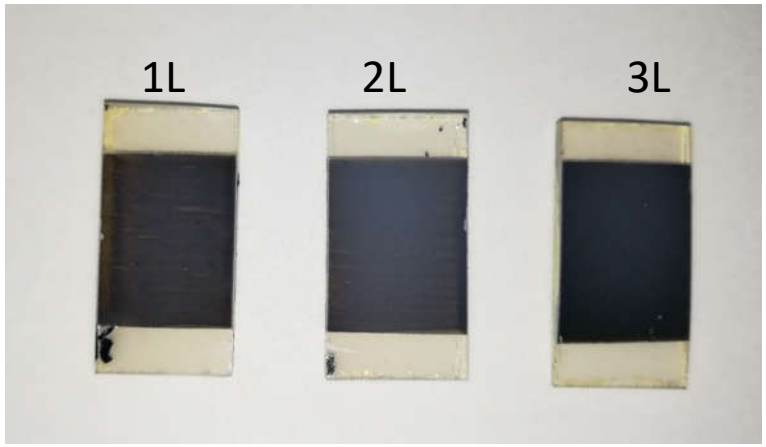


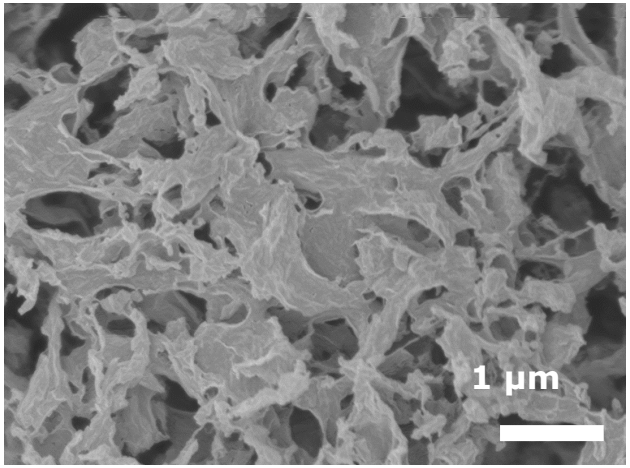


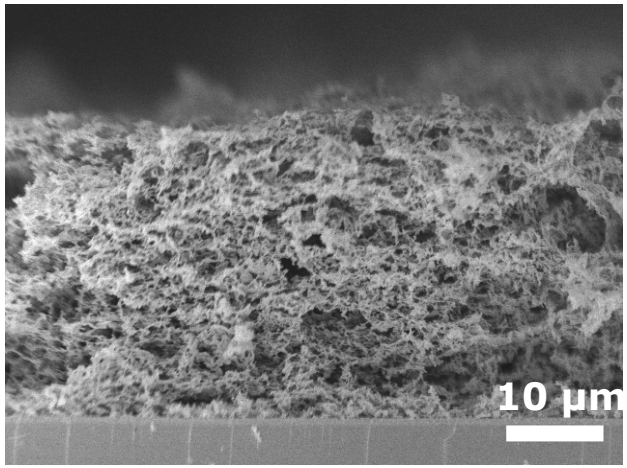
G. Peng, L. Xing, J. Barrio, M. Volokh, M. Shalom, *Angew. Chem. Int. Ed.* **2018**, *57*, 1186.
Selected as Hot paper

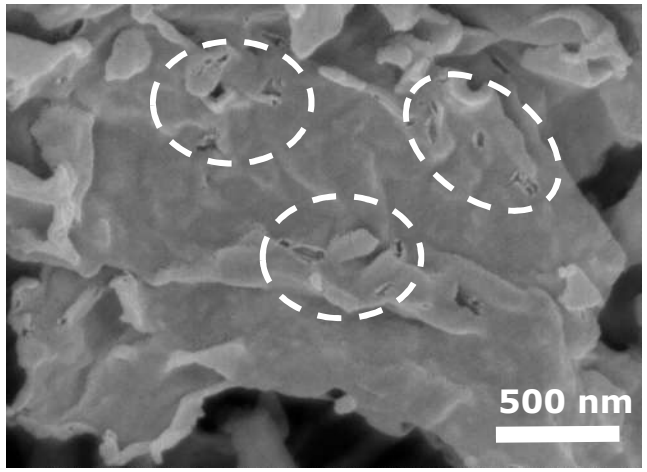
Highly-Porous reduced graphene oxide/CN films as an efficient PEC



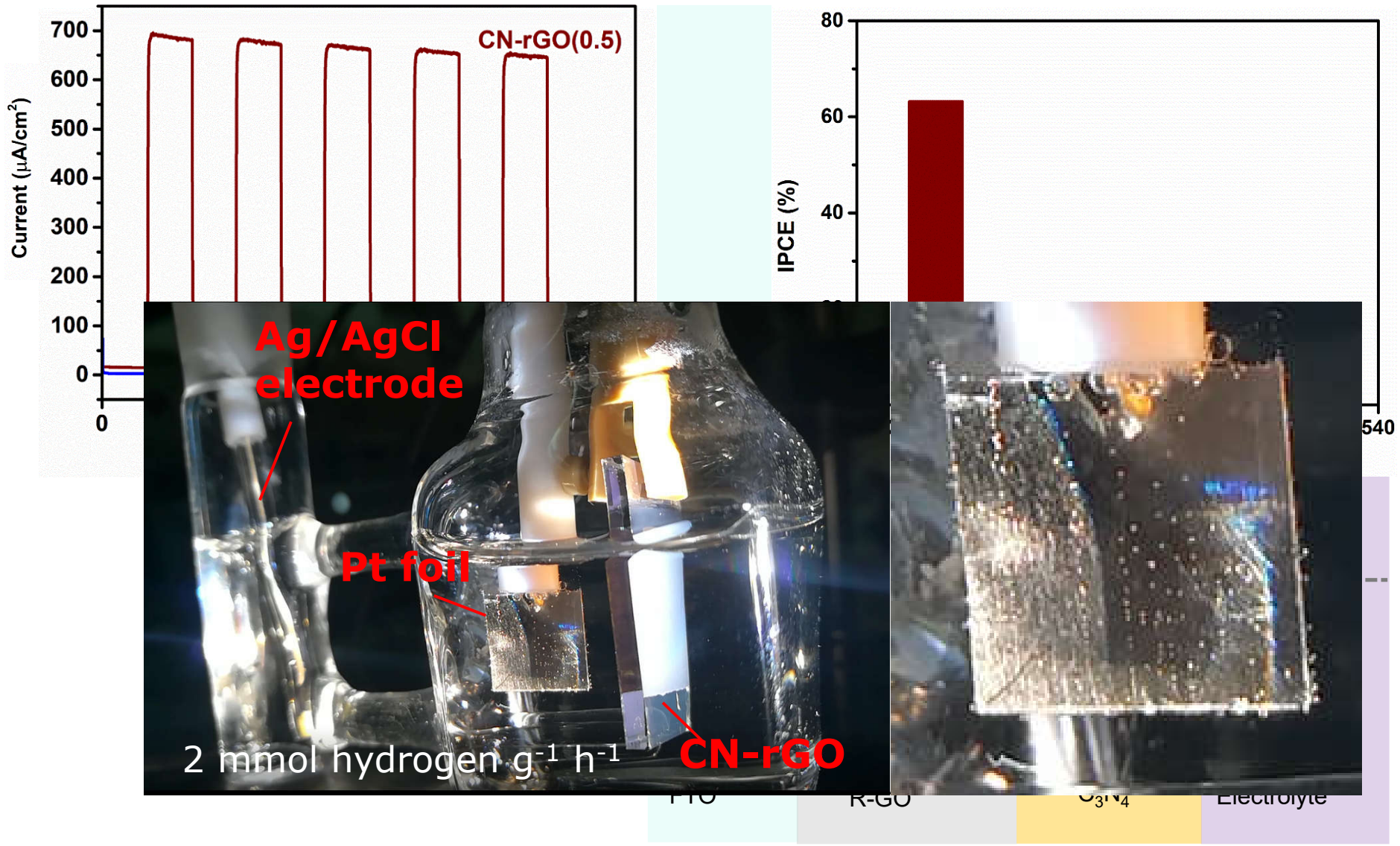






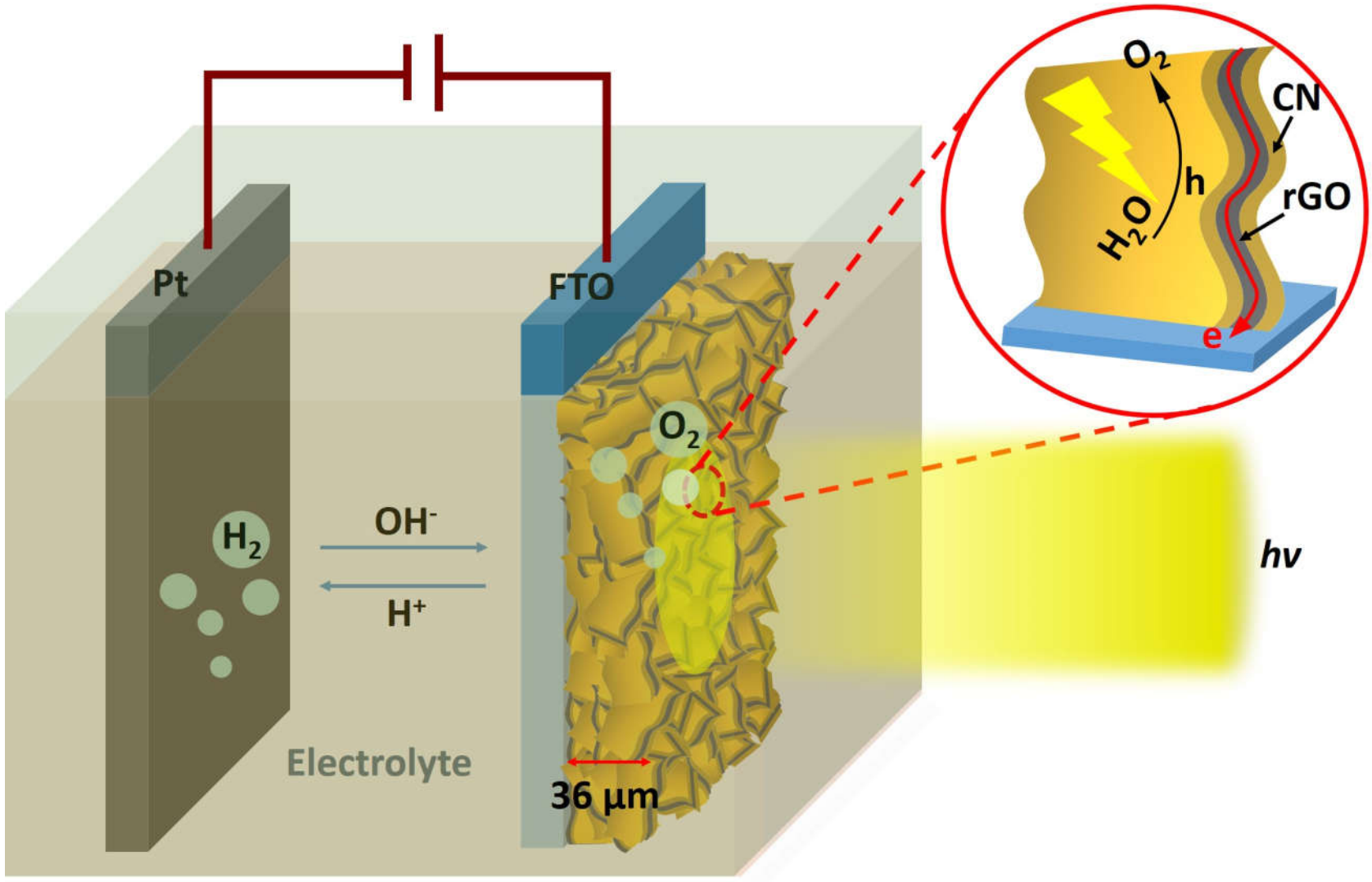


PEC measurements with hole scavenger



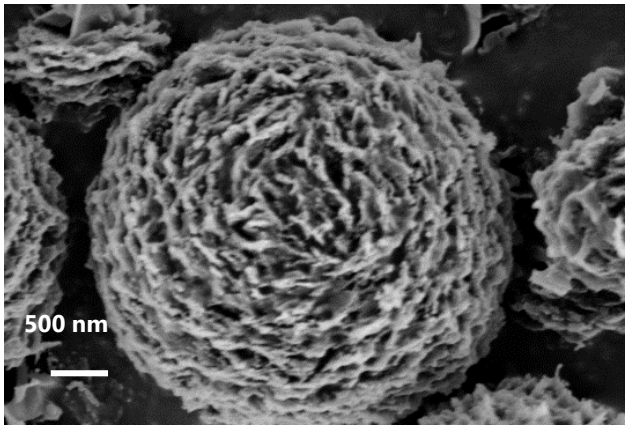
G. Peng, J. Volokh, Tzadikov, M. Shalom, *Adv. Energy Mater.* **2018**, 8, 1800566.

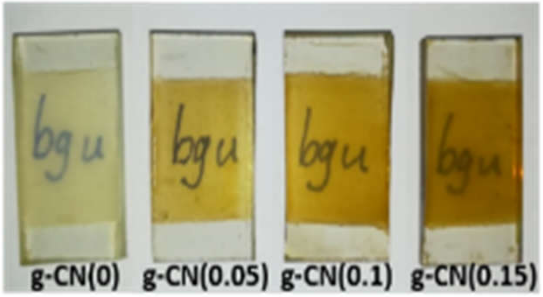
Electrode proposed structure

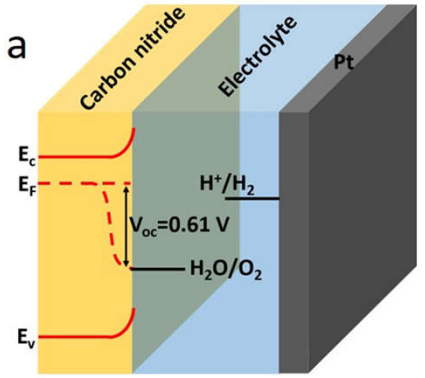


Conclusions

- Controlling the chemical, (photo)electronic and catalytic properties of carbon nitride by supramolecular chemistry
- We can transfer the wide knowledge from the traditional solid state chemistry of carbon nitride into films with different substrates
- We envision that carbon nitride can be used as efficient photoelectrocatalyst -
- The electronic and catalytic properties can be tuned by changing the reaction condition
- It is still required to improve understanding of fundamental processes such as charge separation (excitation lifetime, diffusion length and more)







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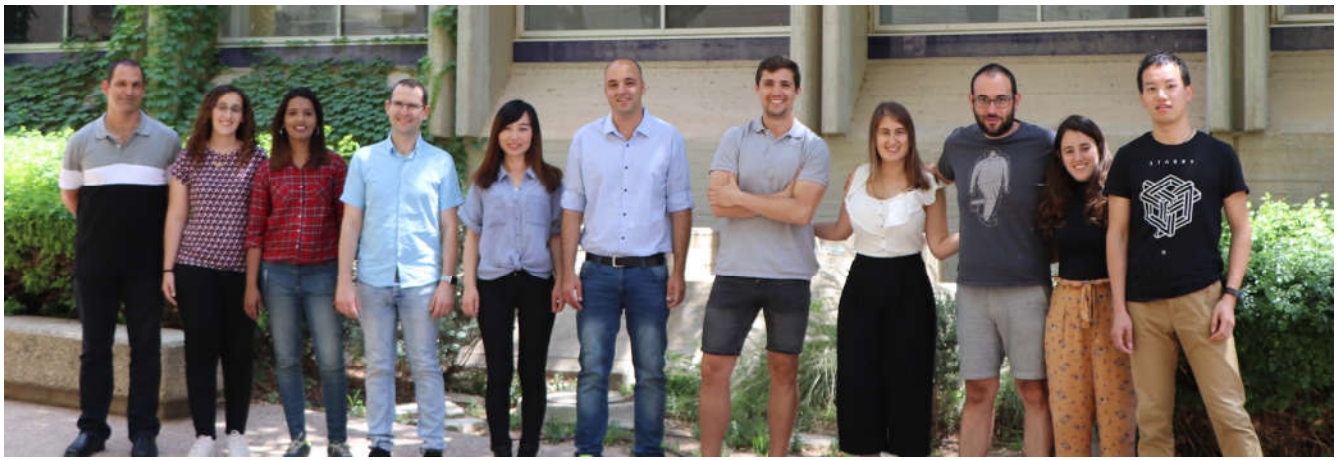

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erc Starting Grants

Thank you for your attention!