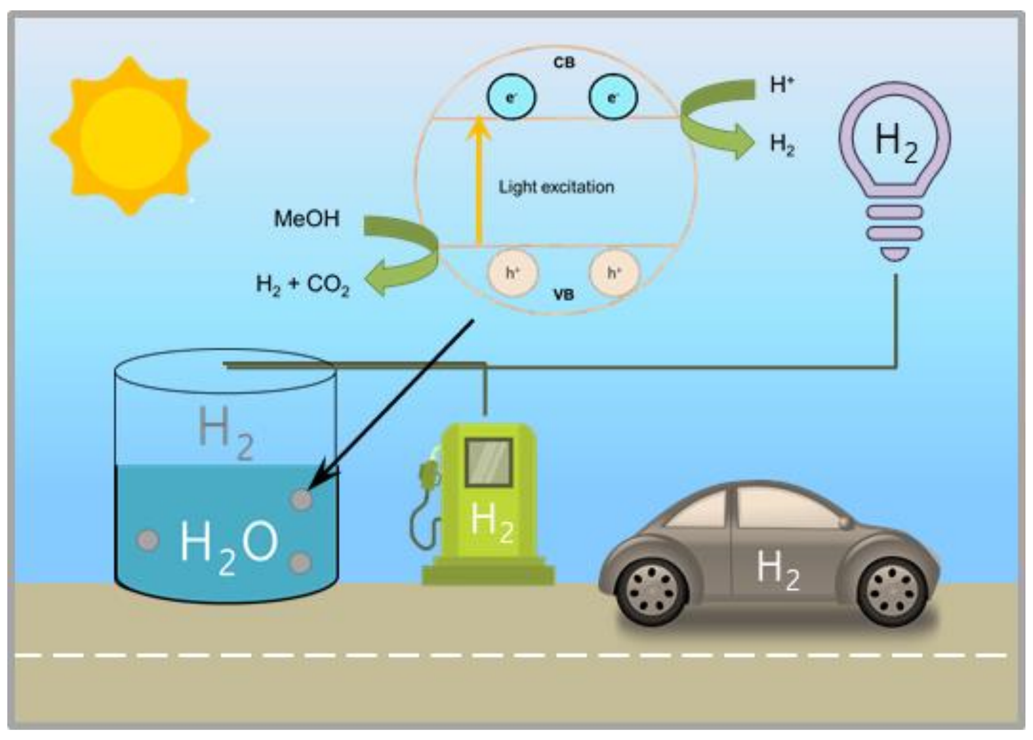
HKUST-1/TiO_2 immobilization into chitosan beads for H_2 generation by photocatalysis

Marie Le Pivert[1*], **Alisha Khan[1]**, **Mireille Benoît[1]**, **Johnny Deschamps[2]**, **Hynd Remita[1]**

[1] Institut de Chimie Physique, UMR 8000 CNRS, Université Paris-Saclay, F-91405 Orsay, France

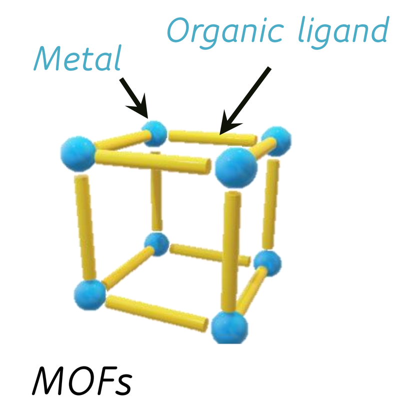
[2] Unité Chimie et Procédés (UCP), ENSTA, Institut Polytechnique de Paris, F-91120 Palaiseau, France

*corresponding author: marie.le-pivert@universite-paris-saclay.fr



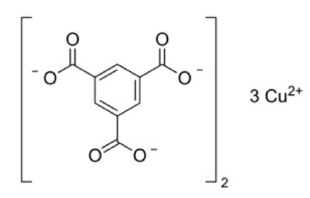
I. Introduction

- 2030 Agenda for sustainable development and net zero emissions by 2050 : green and renewable fuels are required
- Hydrogen (H_2) from water splitting produced by photocatalysis : green fuels with zero emission
- Challenge : new efficient photocatalysts development for H_2 production by photocatalysis
  - Hybrid nano-heterostructured multi-phase materials as efficient photocatalysts such as MOFs/TiO_2. MOFs are hybrid (organic/inorganic) micro- or meso-porous ordered solids with high porosity
  - Efficient supported photocatalysts development for easy collection and reuse



II. Selection of the most efficient photocatalyst

Based on our team work (A. Khan PhD), HKUST-1/TiO_2 (1:20) appeared as promising photocatalyst for H_2 production.



a) Well-know photocatalyst for composite development

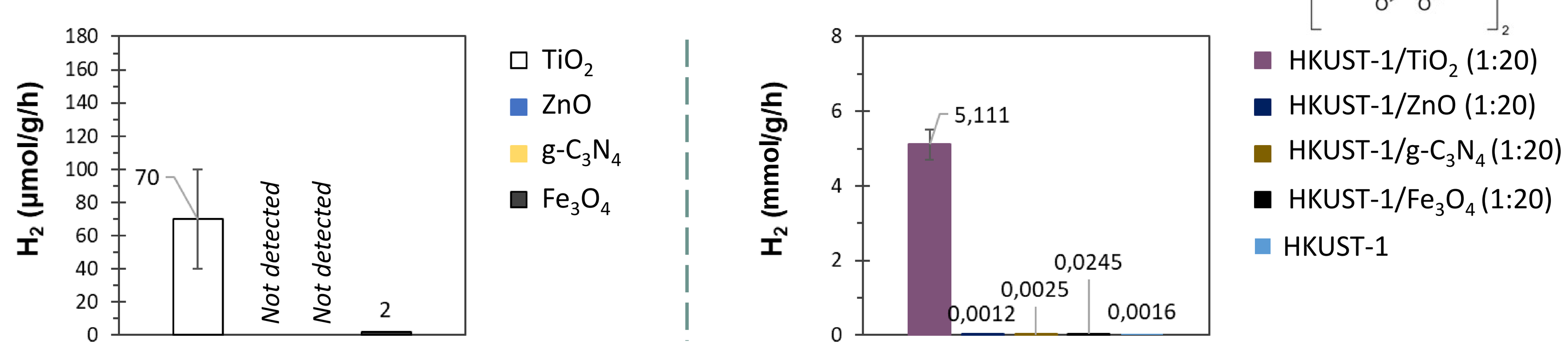


Fig. 2. H_2 production rate as a function of the photocatalyst and the composite (Xenon lamp 300W, 20ml MeOH/H_2O (1:3) agitation).

- TiO_2 is more relevant for H_2 production than ZnO, g-C_3N_4 and Fe_3O_4.
- HKUST-1/TiO_2 (1:20) is very promising for green H_2 production.

b) Ternary composite development

HKUST-1/TiO_2 (1:20) is promising for H_2 production. Nevertheless, it mainly absorbs in UV light. The aim is then to develop ternary composites.

- TiO_2/HKUST-1/g-C_3N_4: influence of the synthesis and the ratio

Synthesis 1: Catalysts stirring in 5mL of methanol (Samples named as a function of the catalysts addition order).
Synthesis 2: Melamine and TiO_2 → 550°C for 4 h (10°C/min) → powdered → 500°C for 2 h (5°C/min) → powdered → catalysts addition and stirring over one night.

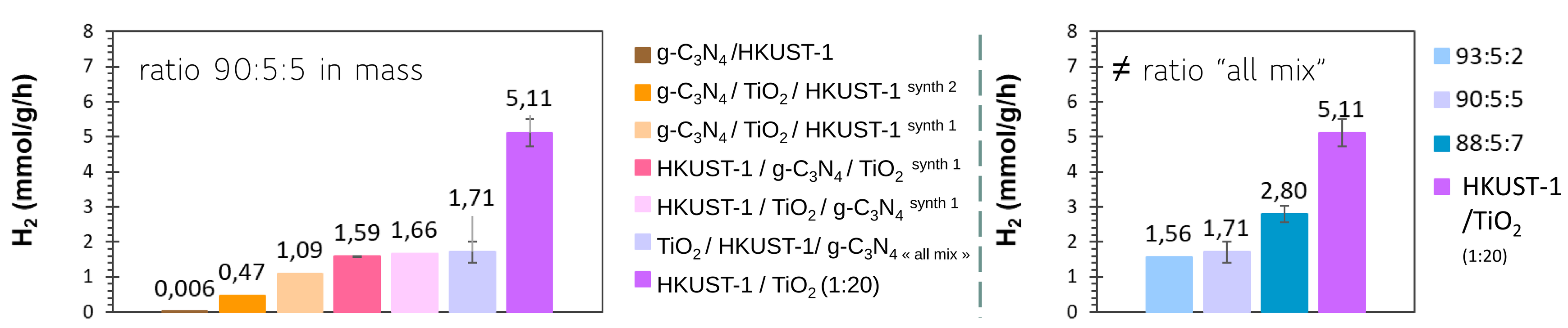


Fig. 3. H_2 production rate as a function of the composite: different synthesis and ratio (Xenon lamp 300W, 20ml MeOH/H_2O (1:3) agitation).

- The binary system (HKUST-1/TiO_2) is more efficient than the ternary system (TiO_2/HKUST-1/g-C_3N_4).

- TiO_2/HKUST-1/Ni-MOF-74: influence of the ratio

- Ni-MOF-74 seems neither unfavorable nor beneficial for H_2 production in the ternary composite (TiO_2/HKUST-1/Ni-MOF-74).

H_2 production rate (mmol/g/h):
HKUST-1/TiO_2 (1:20): 5,11 ± 0,40
TiO_2/HKUST-1/Ni-MOF-74 (93:5:2): 4,88 ± 0,63
TiO_2/HKUST-1/Ni-MOF-74 (92:5:3): 5,43 ± 0,15
TiO_2/HKUST-1/Ni-MOF-74 (92:5:3): 5,05 ± 0,08

III. Photocatalyst beads development

Beads based on chitosan, which is a biopolymer, was selected to encapsulate photocatalyst as a promising solution for easy collection and reuse.

a) Composite beads synthesis

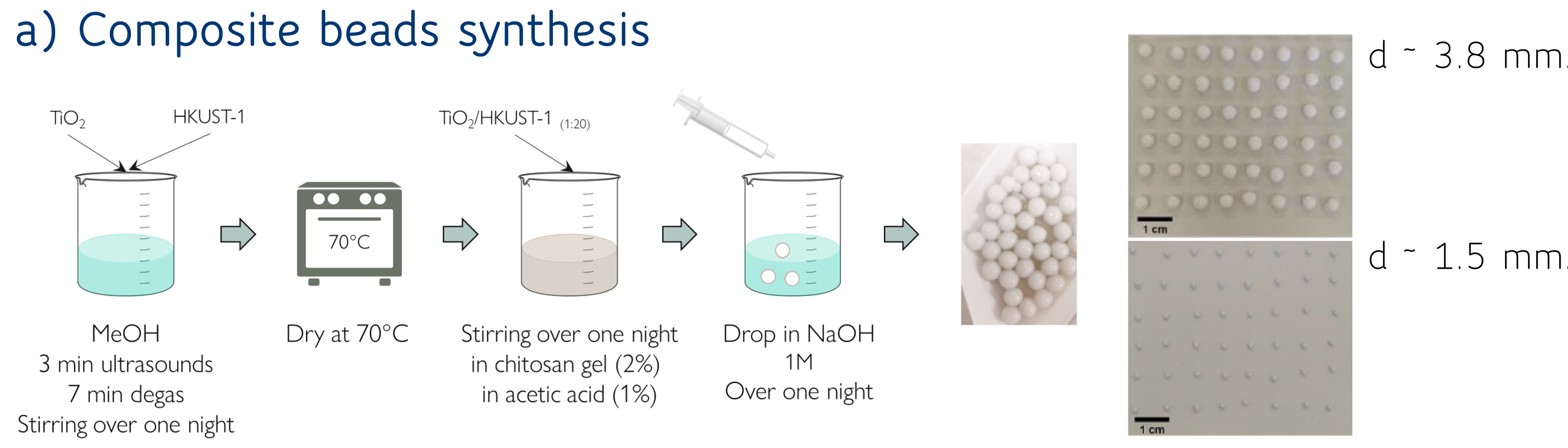


Fig.4. Schematic experimental set-up for synthesis of beads nanocomposite of TiO_2/HKUST-1 (1:20).

- Fresh and humid beads could be easily destroyed and smashed into powder. In contrast, dried beads are electrostatic and very solid, making them resistant to manual destruction.

b) Beads characterization

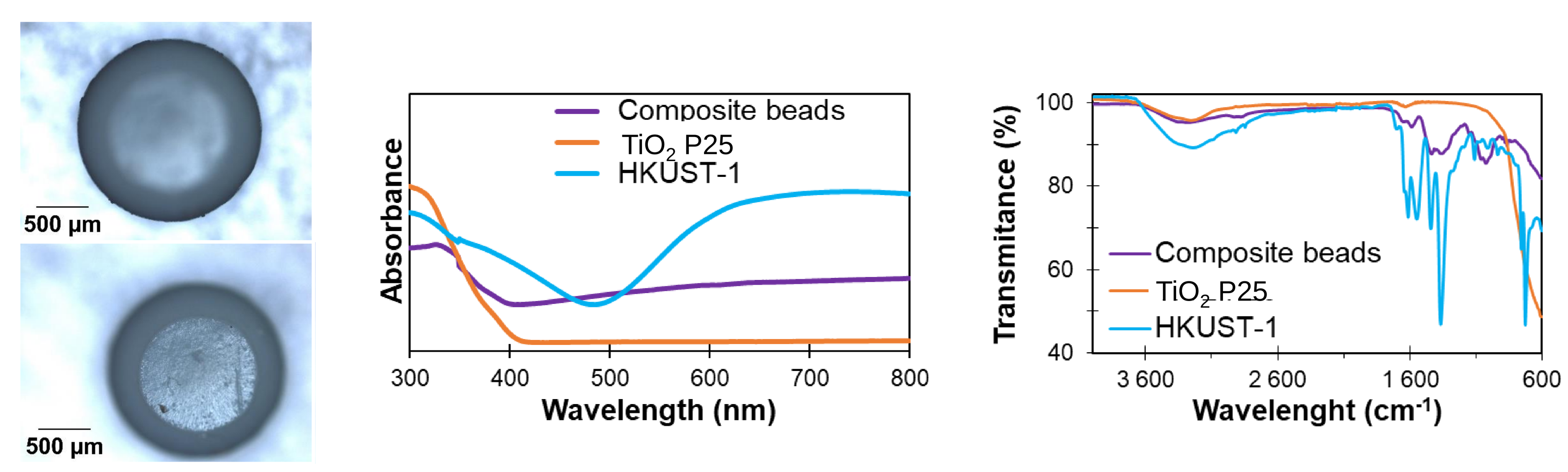


Fig.5. Optic images of composite dried beads; UV-visible absorbance spectra and FT-IR spectra of composite beads, TiO_2 and HKUST-1.

- The obtained HKUST-1/TiO_2 CS beads have a good spherical appearance and uniform size.
- The HKUST-1/TiO_2 composite exhibits good stability throughout the bead synthesis process and shows resistance to both acidic and basic pH levels used during the process.
- No Time Resolved Microwave Conductivity (TRMC) signal was recorded for the smashed HKUST-1/TiO_2 composite beads, probably due to the low amount of photocatalyst in comparison to the amount of chitosan.

IV. H_2 production by photocatalysis

a) Influence of the HKUST-1/TiO_2 concentration

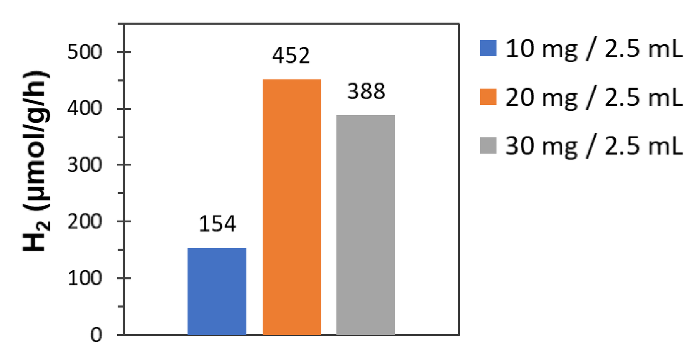


Fig. 6. H_2 production as a function of the HKUST-1/TiO_2 composite amount insert in the beads (2,5 mL CS gel) (Mercury lamp 150W, 20ml MeOH/H_2O (1:3), eq. 5 mg of photocatalyst insert).

- The HKUST-1/TiO_2 CS beads, produced by inserting 20 mg of composite into 2.5 mL of gel, exhibit the highest efficiency

b) Influence of the drying

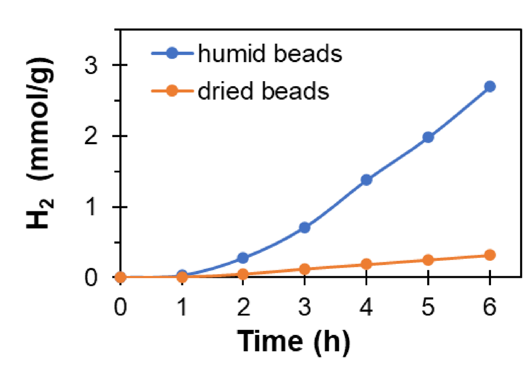
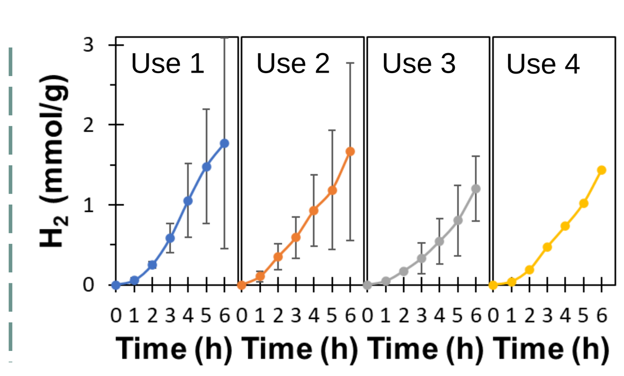


Fig. 7. H_2 production as a function of the HKUST-1/TiO_2 CS beads: humid vs dried (Mercury lamp 150W, 20ml MeOH/H_2O (1:3), eq. 20 mg of photocatalyst insert).

- The humid beads exhibit the highest efficiency against dried beads.

c) Recycling test



Beads crack

Fig. 8. H_2 production as a function of the cycle of use of the composite beads (Mercury lamp 150W, 20ml MeOH/H_2O (1:3), 20 mg of photocatalyst insert).

Conclusion and prospects on PhotoStor2 Project

TiO_2 is more relevant to produce **H_2 by photocatalysis** compared to other well-known photocatalysts, such as **ZnO**, **g-C_3N_4** and **Fe_3O_4**. TiO_2 coupling with MOFs is promising for green fuels generation with a production rate of **5.1 mmol/g/h** for **HKUST-1/TiO_2 (1:20)**. **Ternary composite based on HKUST-1/TiO_2**: not added value with Ni-MOF-74 and adverse effect with g-C_3N_4. **Beads based on chitosan** to embed photocatalysts, which are at nanometer scale, are promising for a **sustainable H_2 generation with easy reuse but need optimization to avoid cracks**. Porous bead development could be an answer to the cracking problems observed.