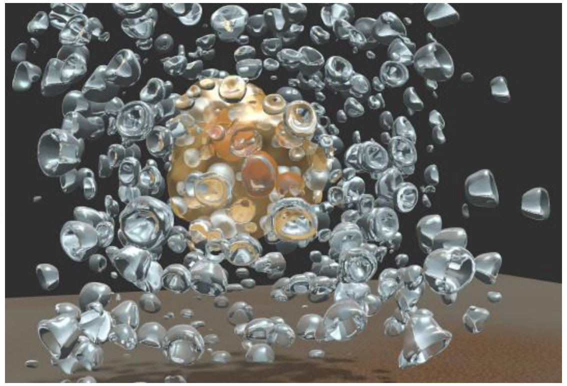
SONOCHEMISTRY & SONOCATALYSIS: Towards a Sustainable Approach to Oxidation & Hydrogenation Reactions at Mild Conditions



Dr. Prince Nana AMANIAMPONG

CNRS Researcher, Univ. Of Poitiers

SCF- Chimie Durable

17th January 2023

Seminar Series

Laboratory

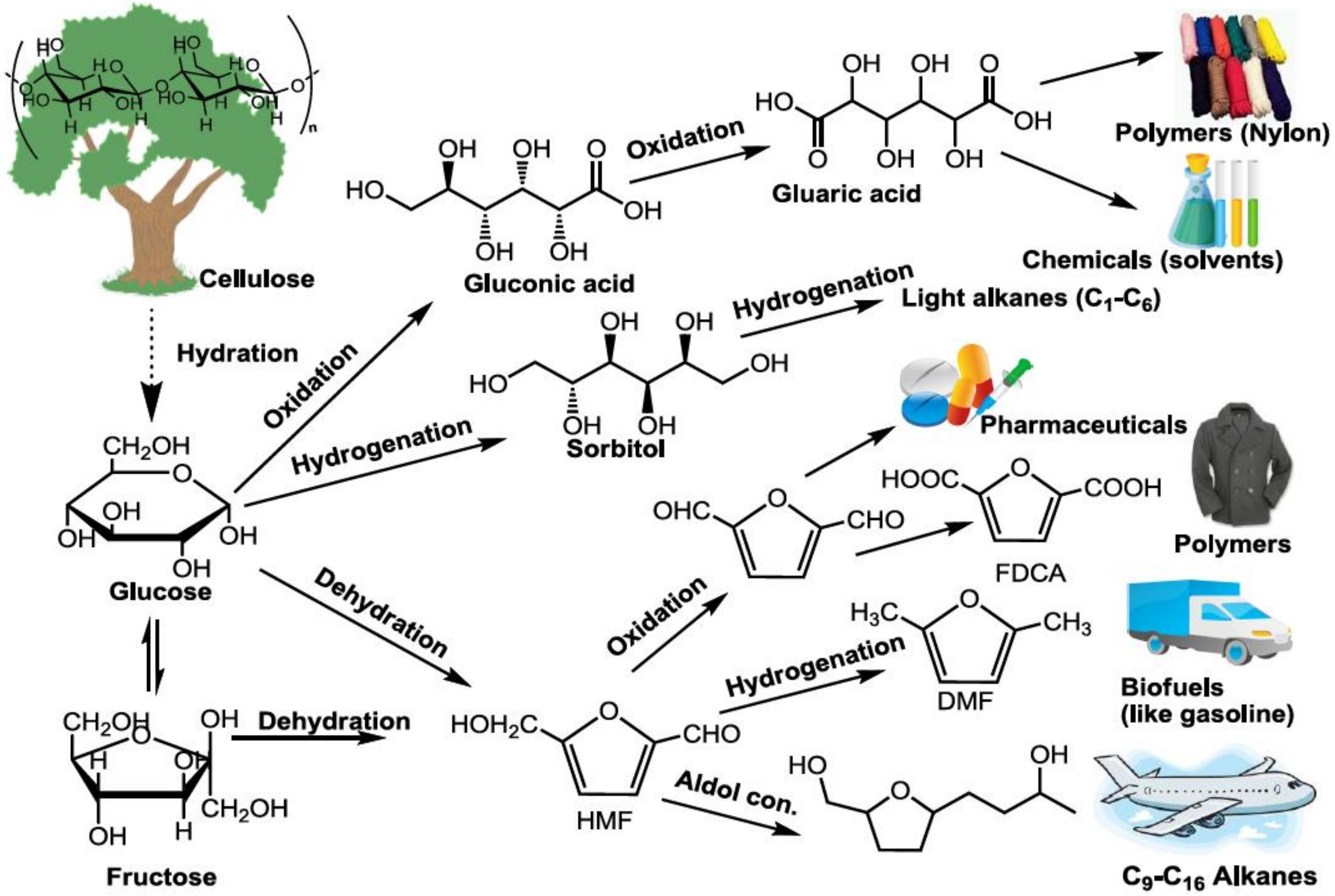
Institut de Chimie des Milieux et Matériaux de Poitiers

UMR CNRS-University of Poitiers 7285

CONTENTS

1. Sonochemical Activation of H_2O towards the Oxidation of Sugars
2. Sonochemical Activation of NH_3 towards N_2H_4 Synthesis
3. Sonochemical Activation of NH_3 towards the Hydrogenation of Alkenes

CONVERSION OF BIO-BASED SUBSTRATES



Can we do Chemistry

- Assisted catalysis?
- At low temperature?
- Convenient reactions conditions
- Reusable and highly selective catalysts

Biological Catalysts:

- ✓ High selectivity
- ✓ Expensive
- ✓ Stringent process parameters
- ✓ Complicated downstream process

Heterogeneous Catalysts:

- ✓ Activity need to be improve
- ✓ Mechanism is unknown
- ✓ High selectivity, catalyst is reusable
- ✓ Convenient reaction conditions and products separation

CONTRIBUTION OF NON-THERMAL TECHNOLOGIES

NON THERMAL TECHNOLOGIES

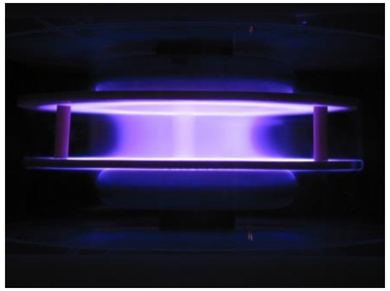
Hurdles

- Reaction mechanism
- Energy consumption
- Scale-up

Non-thermal technologies: non-thermal technologies do not involve an external source of heating and the chemical reaction can be activated either by the action of a pressure, electric or magnetic field, waves, light, to mention a few

Microwave

Ultrasound

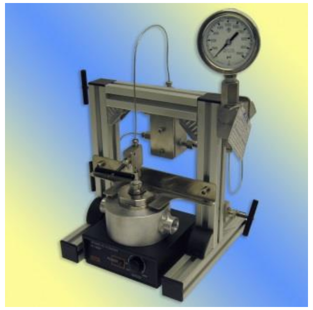


Plasma

Milling

Photochemistry

Electrochemistry



Supercritical fluids

Can we convert biomass

- Without any solvent?
- Without any catalyst?
- At low temperature?

?

Research Vision for the Concept of Assisted-Catalysis Using Sonochemistry @ IC2MP

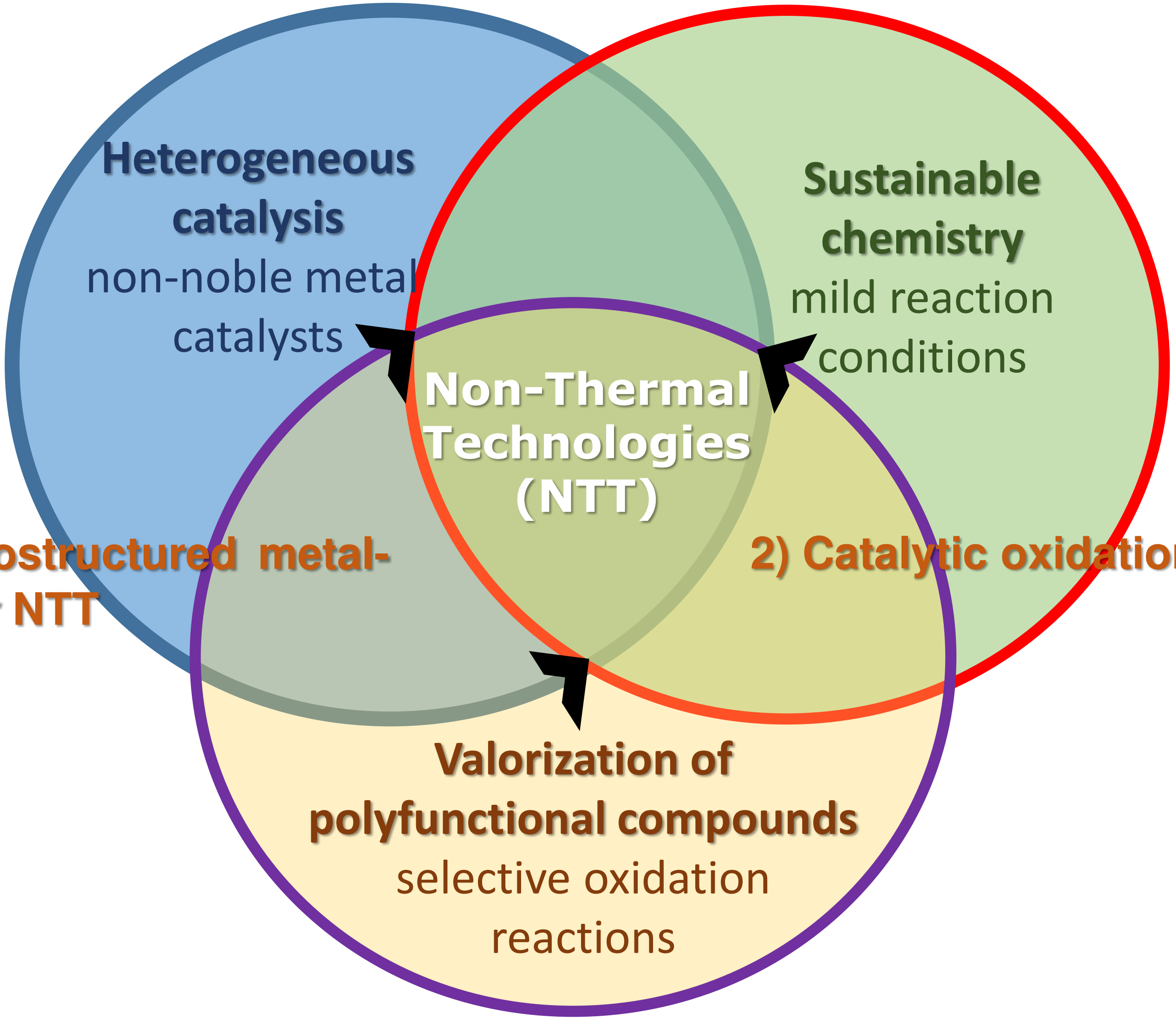
A Activate small molecules (CH_4, CO_2, NH_3, H_2O, etc) with high BDE at low temperatures.

B Perform challenging catalytic reactions at low temperatures with improved atom and energy efficiency.

C Novel and efficient routes for catalysts synthesis

D Novel Strategies for improving existing catalytic reactions

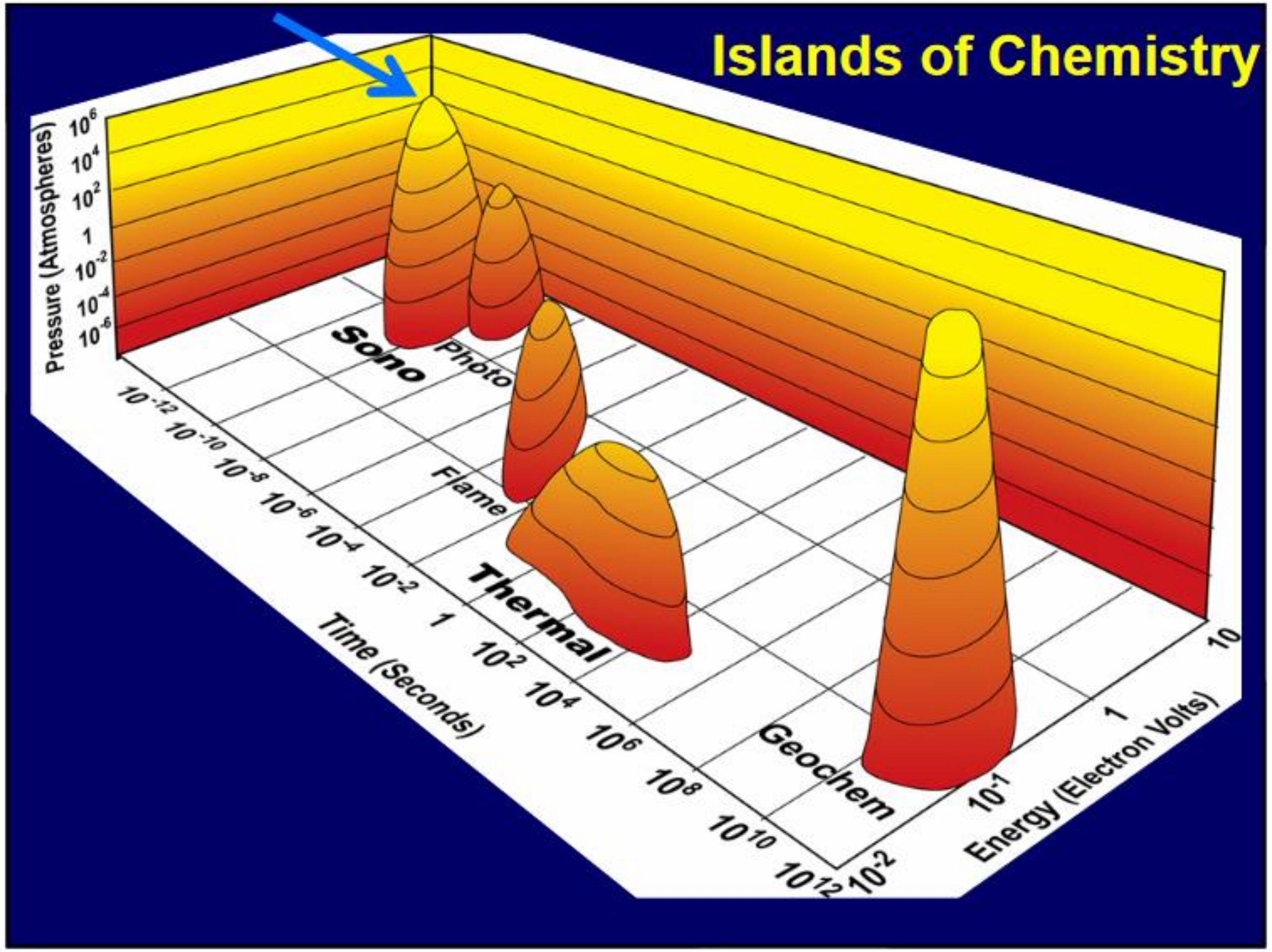
CONTRIBUTION OF NON-THERMAL TECHNOLOGIES



1) Preparation of nanostructured metal-oxide catalysts under NTT

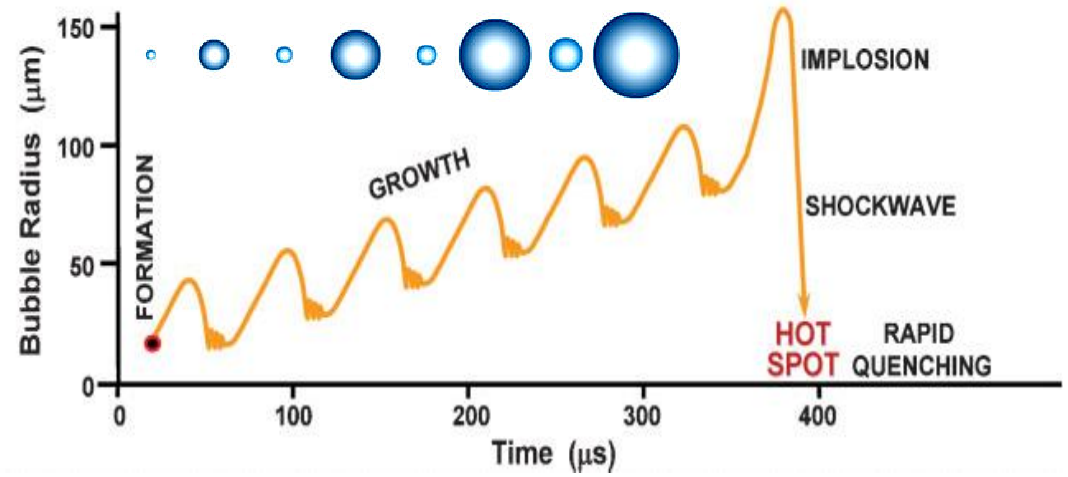
2) Catalytic oxidation of bio-based substrates

ISLANDS OF CHEMISTRY

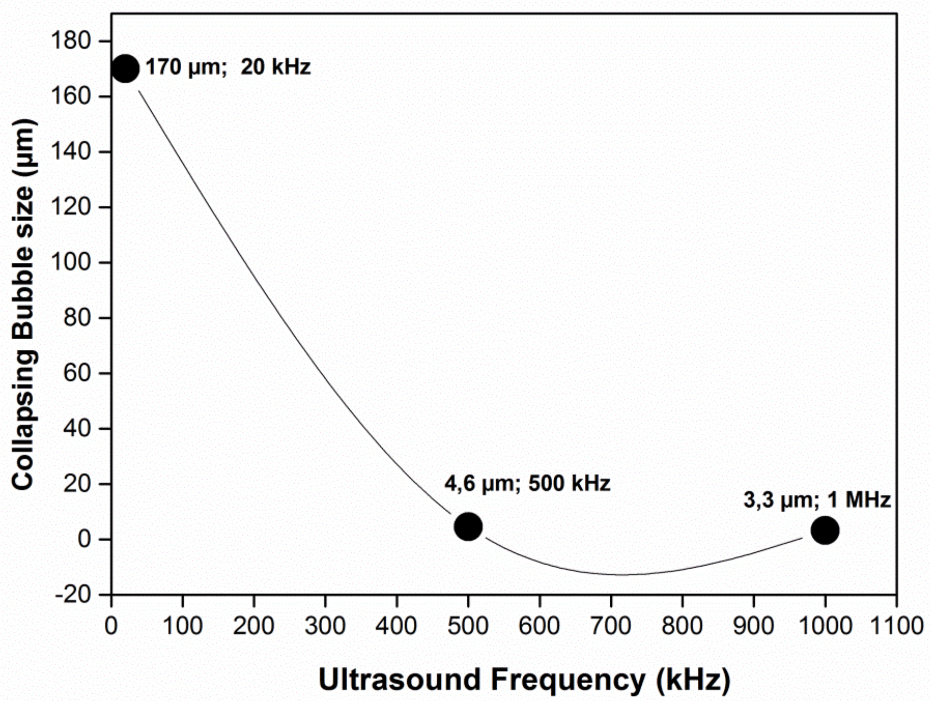


Chemistry: the interaction of energy and matter. The three axes represent **duration of the interaction**, **pressure**, and **energy per molecule**. The labeled islands represent the nature of the interaction of energy and matter in various different kinds of chemistry.

CAVITATION BUBBLE DYNAMICS



Collapsing Bubble Size as a Function of Frequency



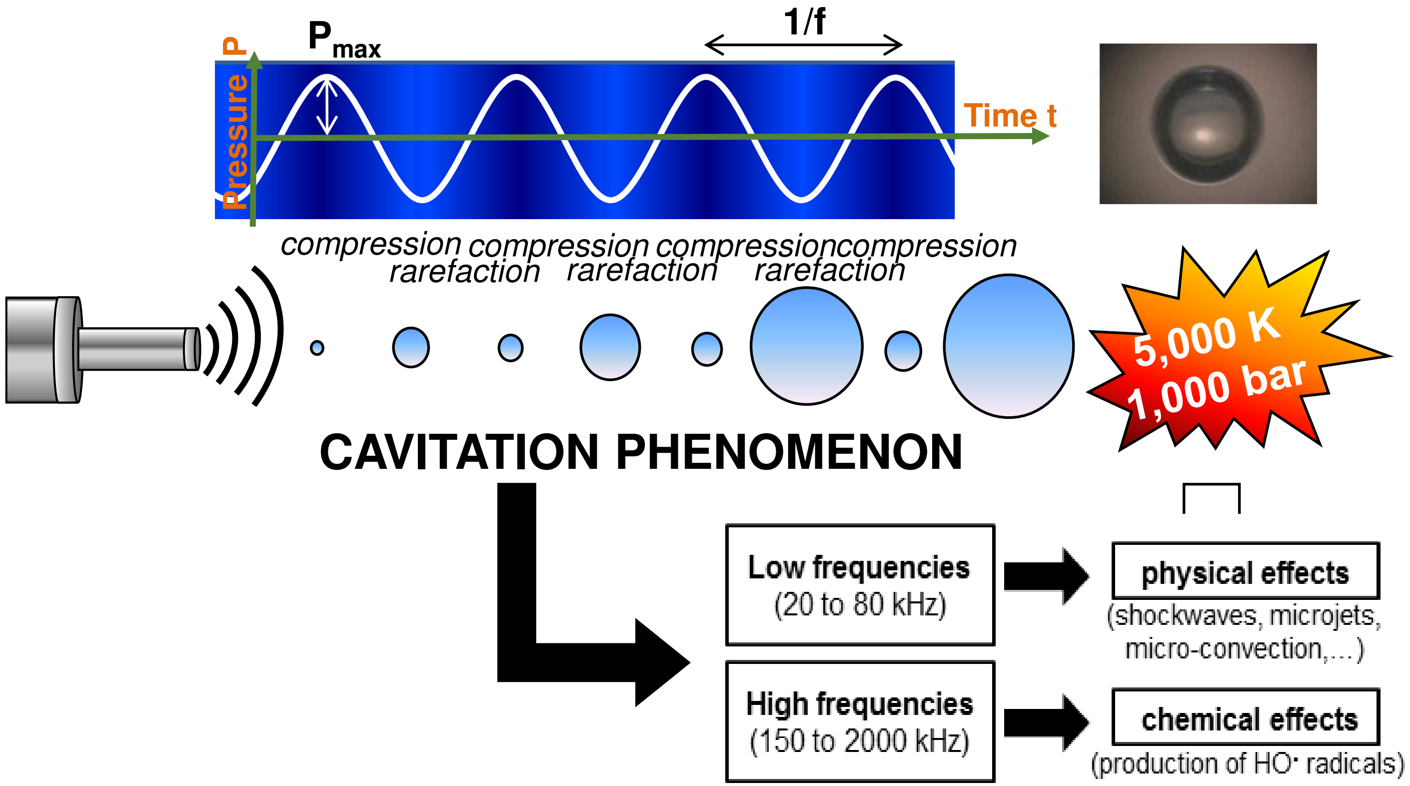
Symmetric Implosion of Cavitation Bubble

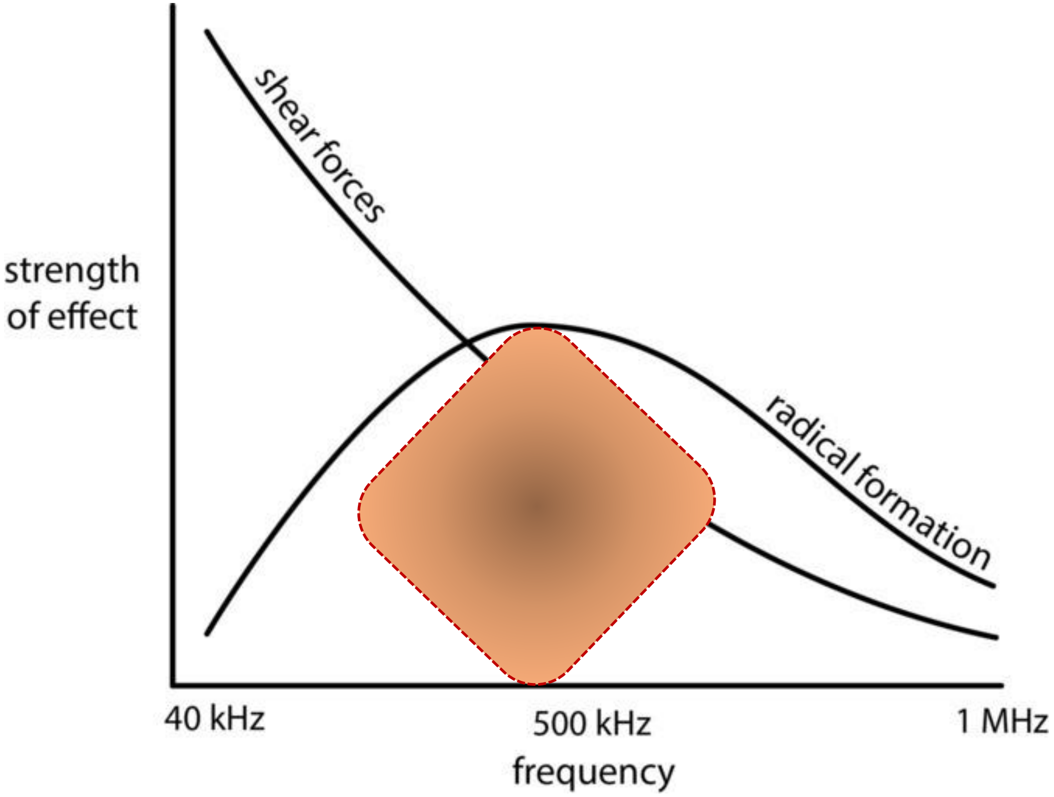
$$\tau = 0,915 . R_{max} . \sqrt{\frac{\rho}{P_m} . \left(1 + \frac{P_V}{P_m}\right)}$$

$P_m = P_A + P_h$

P_V= Vapour Pressure of the liquid

CAVITATION BUBBLE DYNAMICS

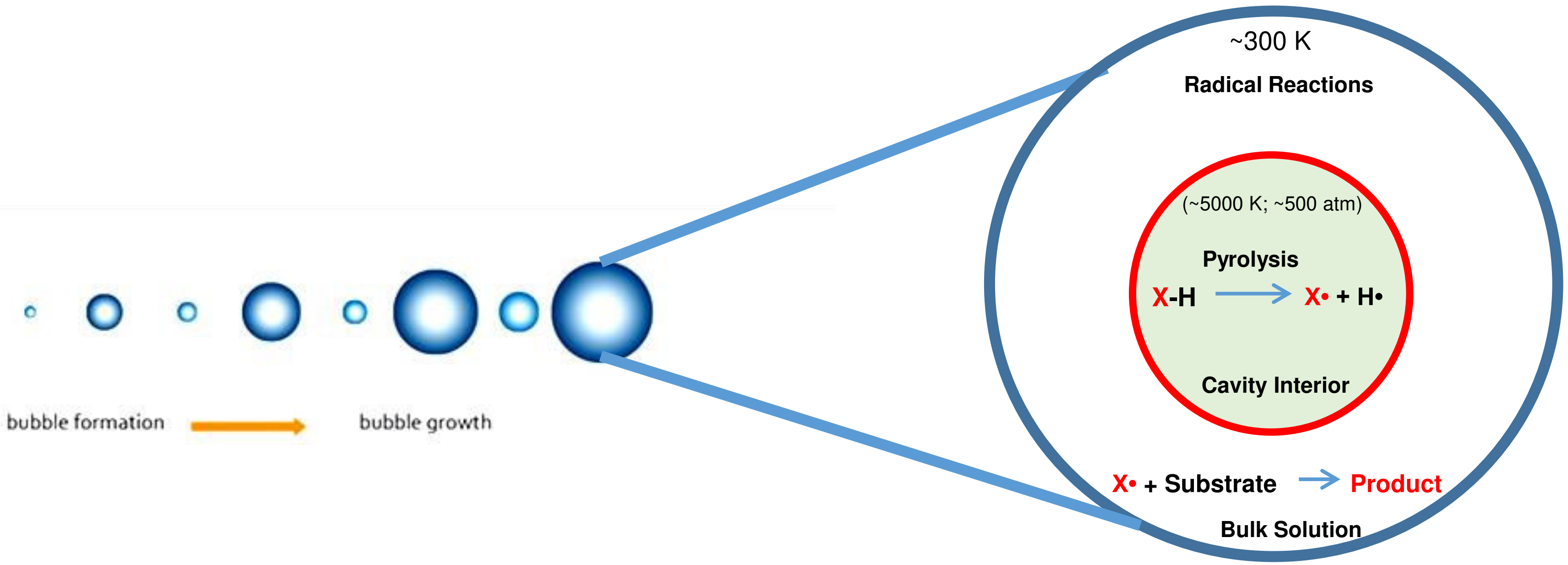




ChemSusChem, **2014**, *7*, 2774

Green Chem, **2016**, *18*, 3903

CAVITATION BUBBLE AS A MICRO-REACTOR



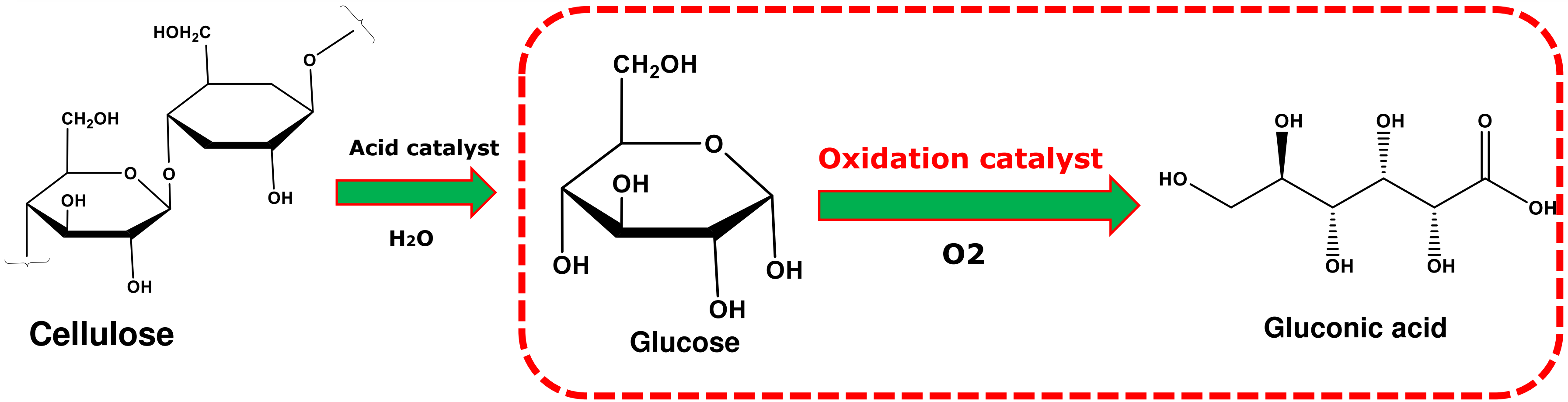
$$T_{max} = \frac{T_0 P_a(\gamma - 1)}{P_v}$$

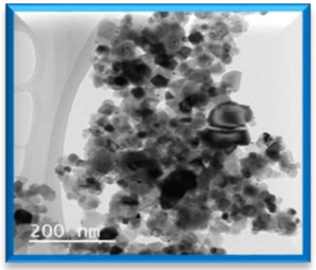
$$P_{max} = P_v \left\{ \frac{P_a(\gamma - 1)}{P_v} \right\}^{[\gamma / \gamma - 1]}$$

Reaction Zone 1: Pyrolysis

Reaction Zone 2: Radical Reaction

CATALYTIC GLUCOSE OXIDATION: Conventional Approach

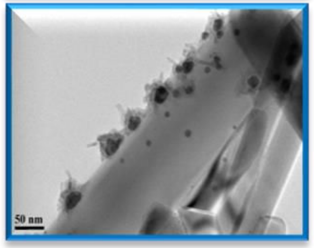




Au/TiO2
reduced in H2
@ 700 °C

✓ Selective | ✓ Active | 82 % Gluconic acid yield

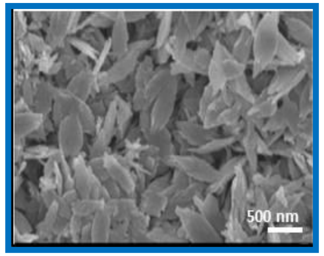
Amaniampong et. al., ChemCatChem (2014) 6 (7) 2015-2114



Au-Cu/TiO2 Nanowires
reduced in H2
@ 700 °C

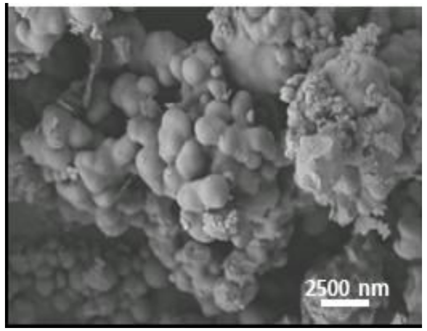
✓ Selective | ✓ Improved stability | 92 % Gluconic acid yield

Amaniampong et. al., Catalysis Sci & Tech.(2015) 5 (4) 2393-2405
Amaniampong et. al., Applied Catalysis A: General **(2015)**505:16-27



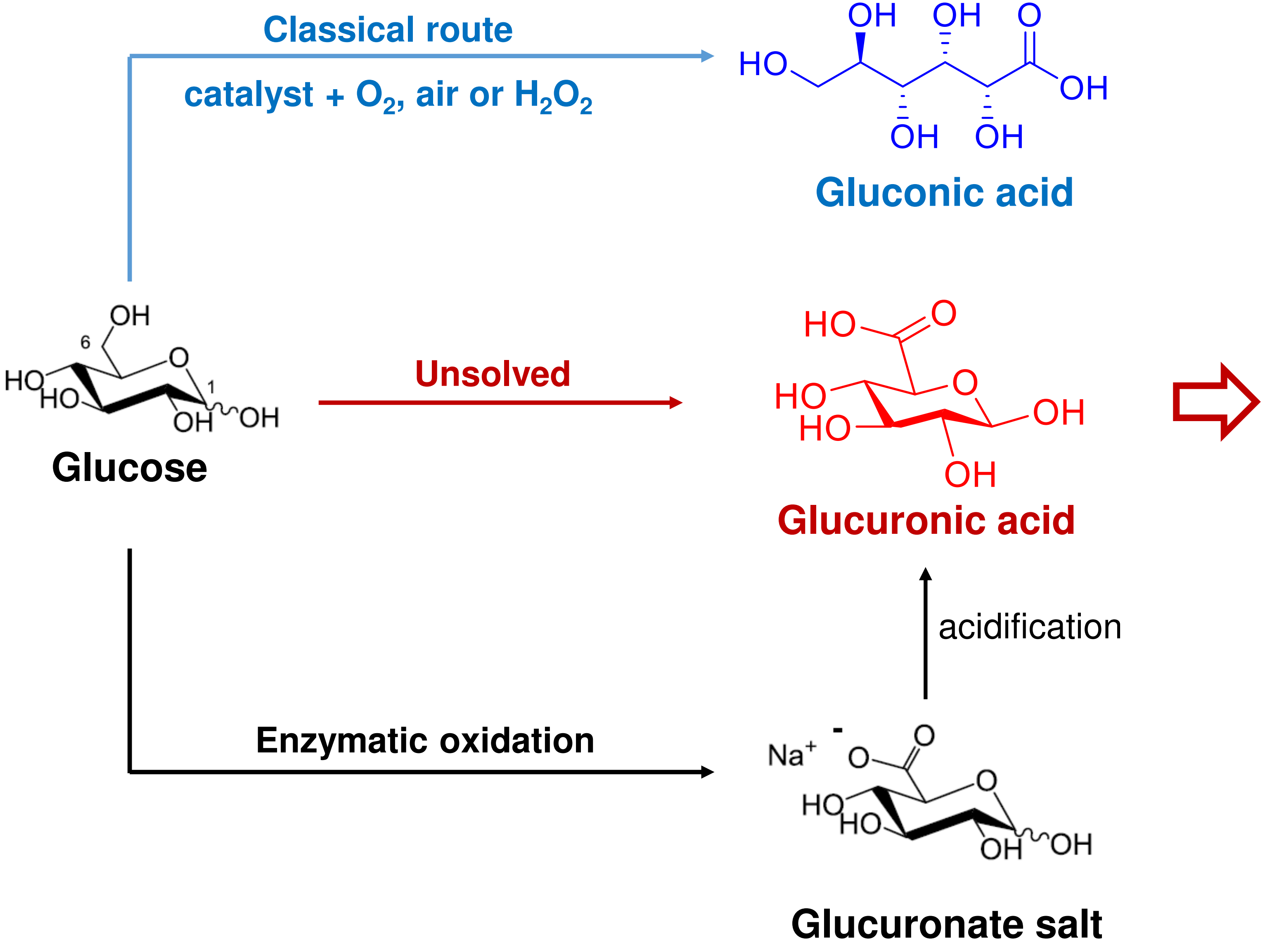
CuO
Nanoleaves

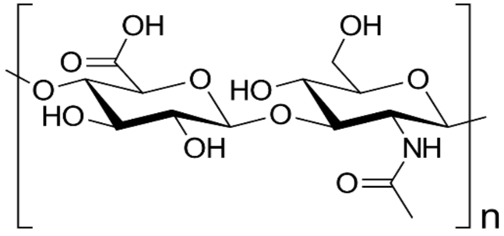
✓ No external O2 | X Poor stability | ✓ Selective | ✓ Active | 59 % Gluconic acid yield



Amaniampong et. al., Angew. Chemie Int. Ed (2015), 54: 8928–8933

SONOCHEMICAL OXIDATION OF BIO-BASED SUBSTRATES: GLUCOSE OXIDATION





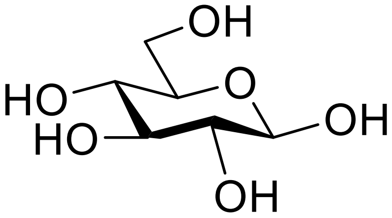
Hyaluronic acid

Market value > $ 1 Billion

SONOCHEMICAL OXIDATION OF BIO-BASED SUBSTRATES: GLUCOSE OXIDATION

$$2\,HO^{\bullet} \xleftarrow[25°C,\ ½\ O_2]{550\ kHz} H_2O \xrightarrow[25°C,\ Ar]{550\ kHz} HO^{\bullet} + H^{\bullet}$$

BDE of HO-H= 497 KJ/mol

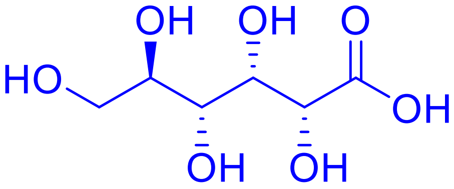


< 10 wt%

Ar

550 kHz

H_2O, 120 min, 25°C, 0,36 W.mL^{-1}



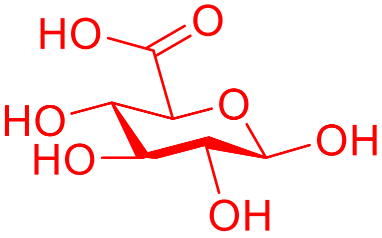
Gluconic acid

50 % yield

O_2

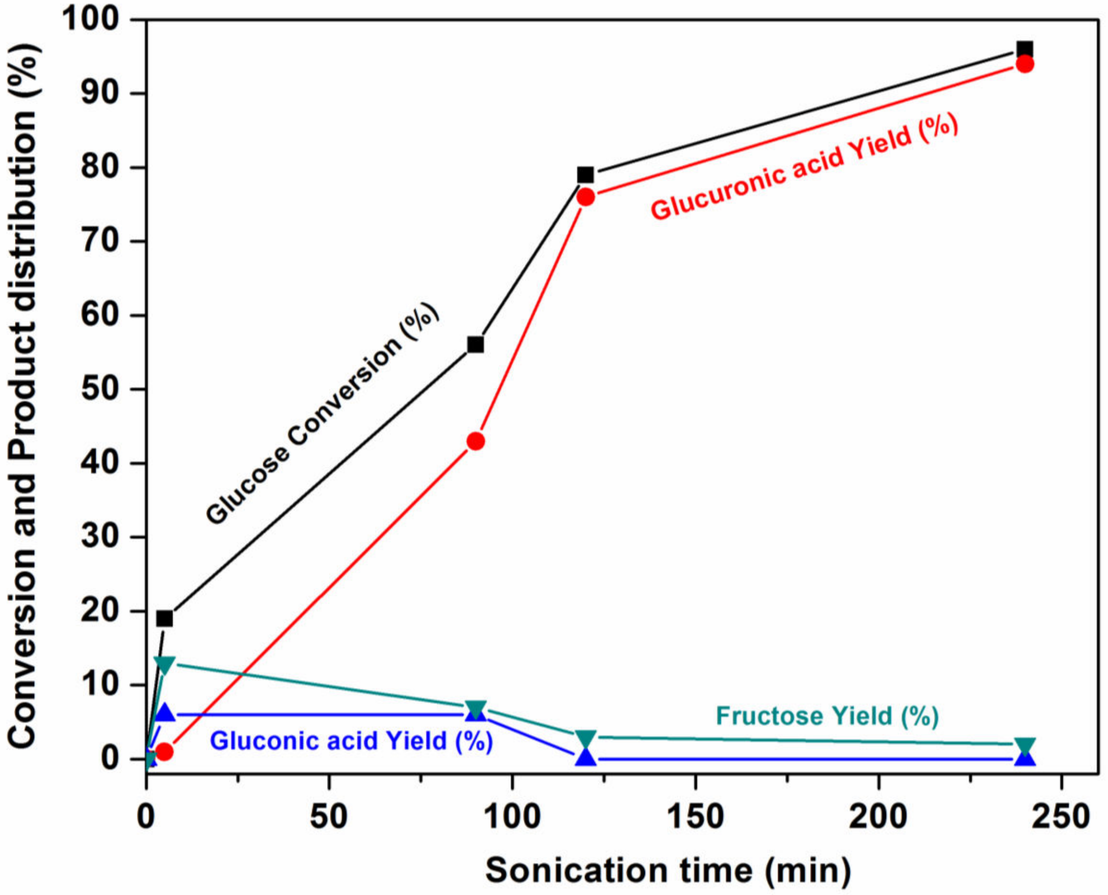
550 kHz

H_2O, 240 min, 25°C, 0,36 W.mL^{-1}



Glucuronic acid

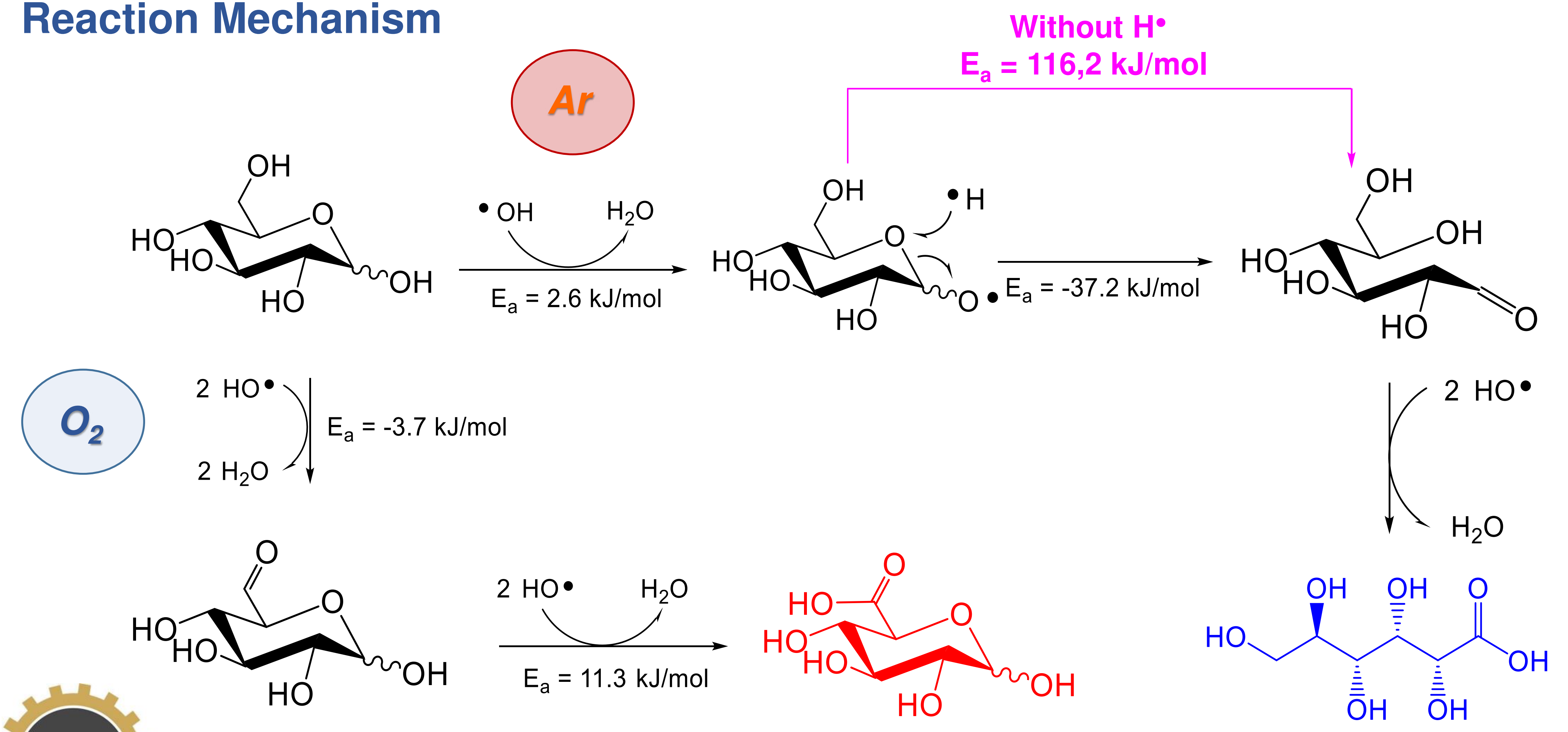
94% yield



Amaniampong et al., Scientific Report, **2017**, 7, 40650

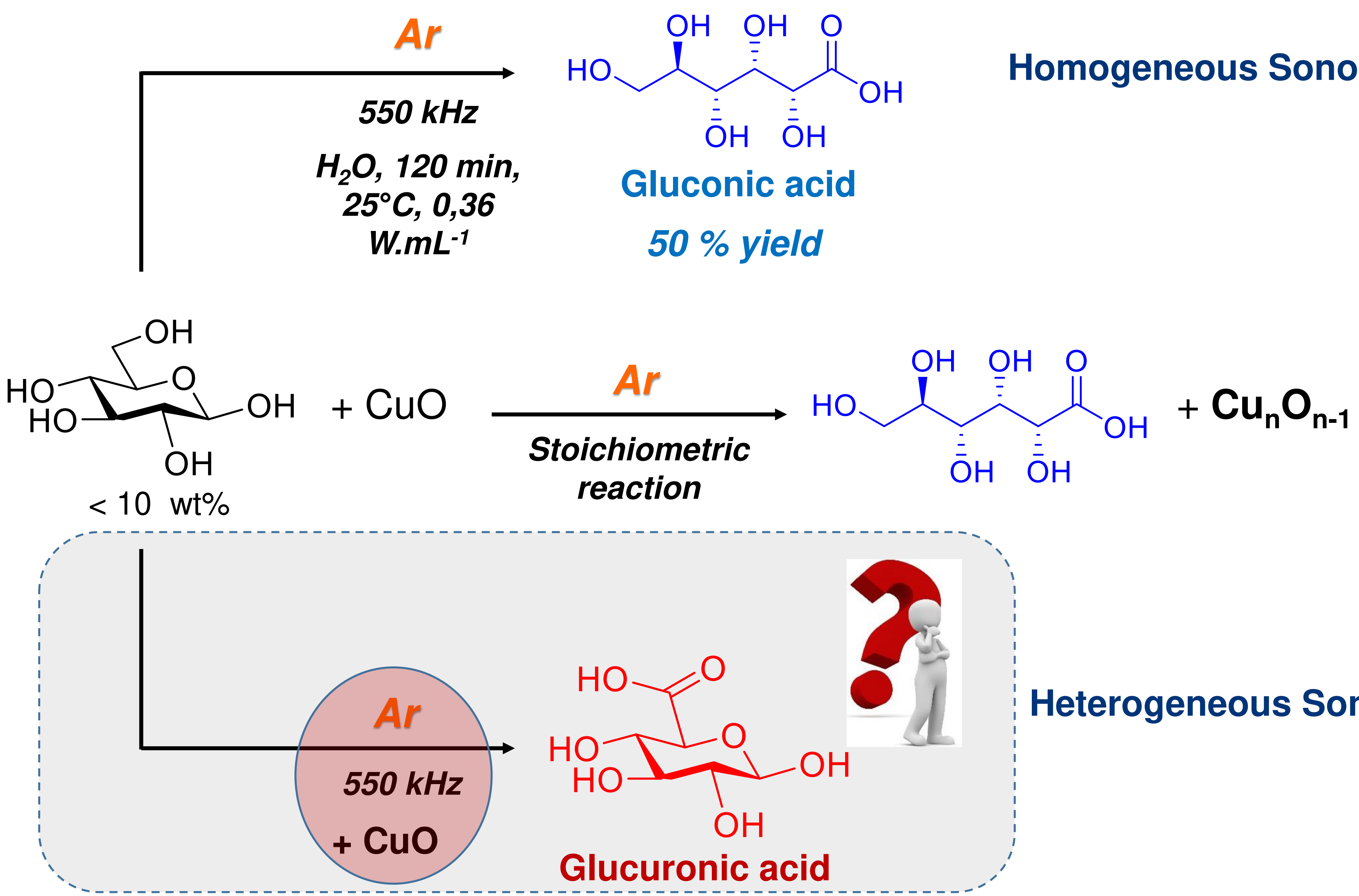
SONOCHEMICAL OXIDATION OF BIO-BASED SUBSTRATES: GLUCOSE OXIDATION

Reaction Mechanism



Amaniampong et al., Scientific Report, **2017**, 7, 40650

SONOCHEMICAL OXIDATION OF BIO-BASED SUBSTRATES: SONOCATALYSIS - GLUCOSE OXIDATION

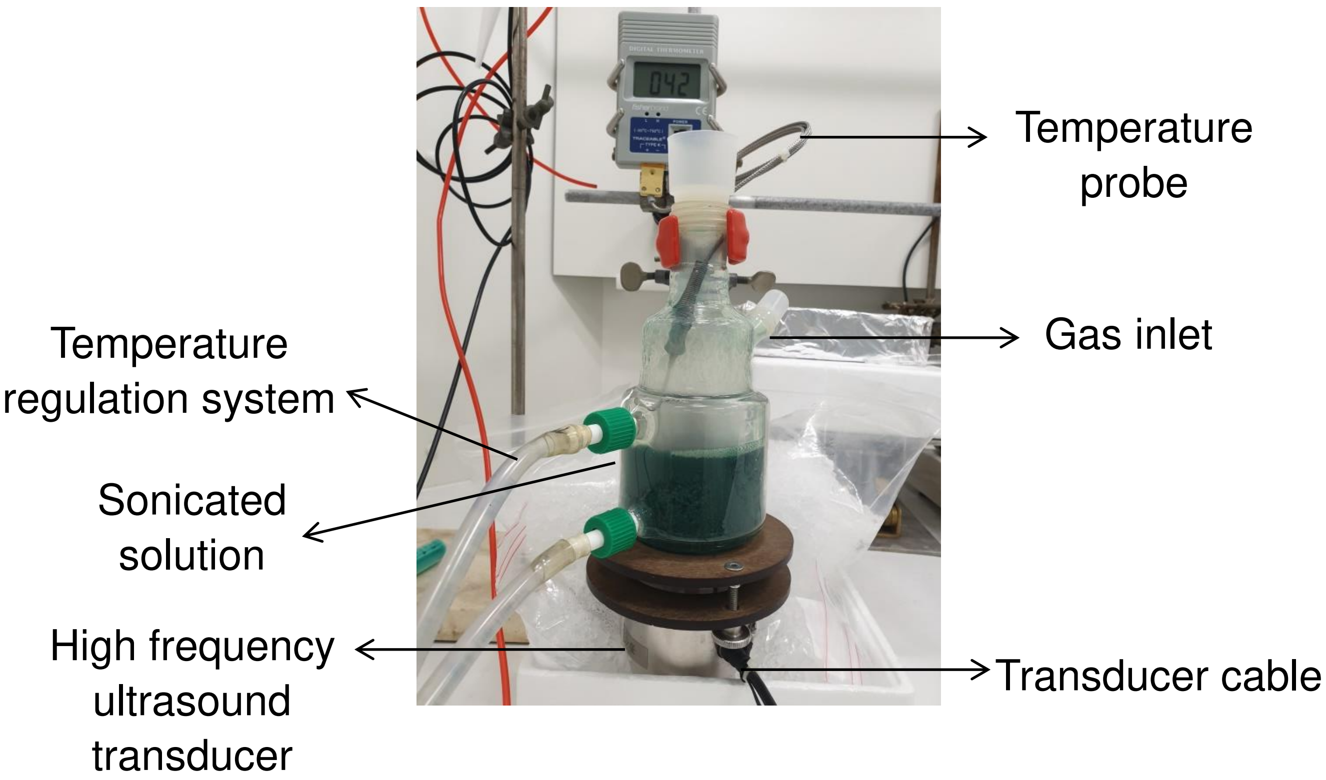


Homogeneous Sonochemical Oxidation Reaction

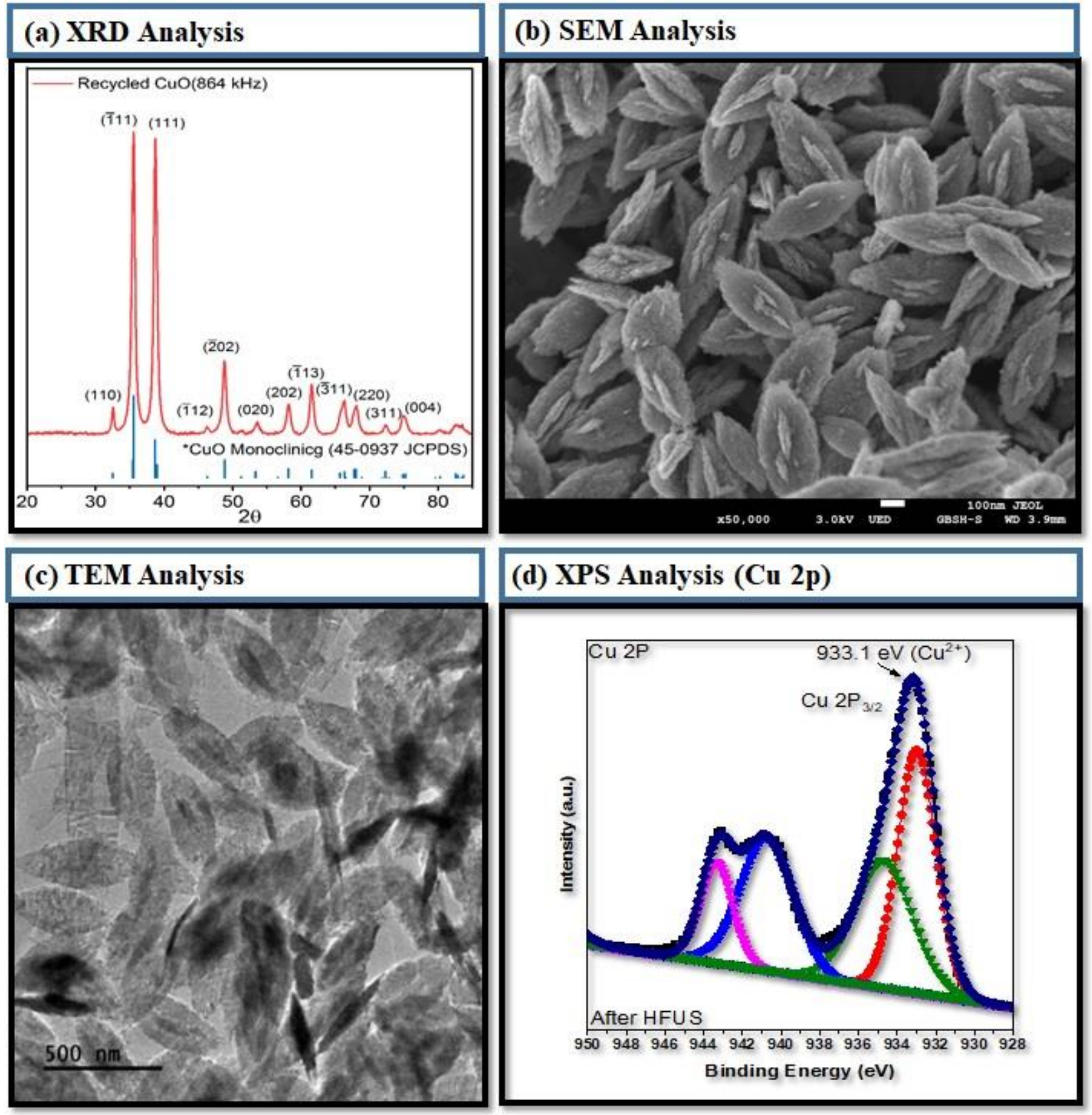
Classical Oxidation Reaction

Heterogeneous Sonochemical Oxidation Reaction

➢ Sonochemical synthesis of CuO (HFUS):



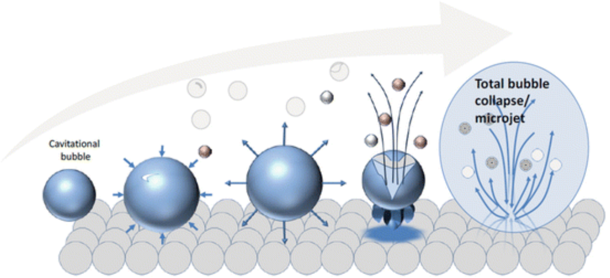
- Triple transducer (total of 75 W)
- P_0 = 13.9 W
- P_{elect} = 70.4 W
- $P_{acoust.vol}$ = 0.44W mL^{-1}

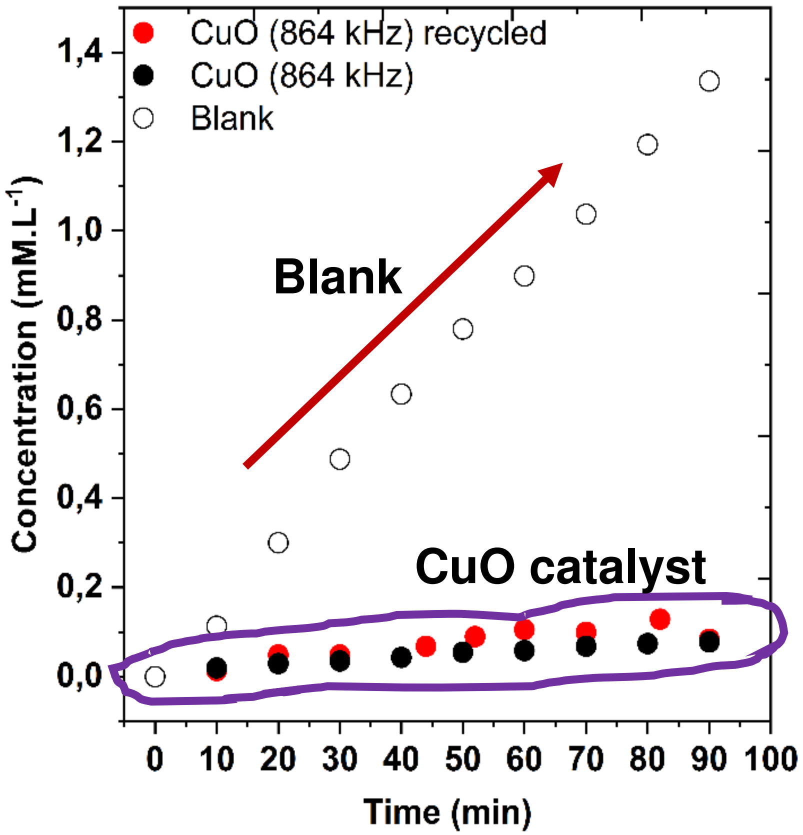


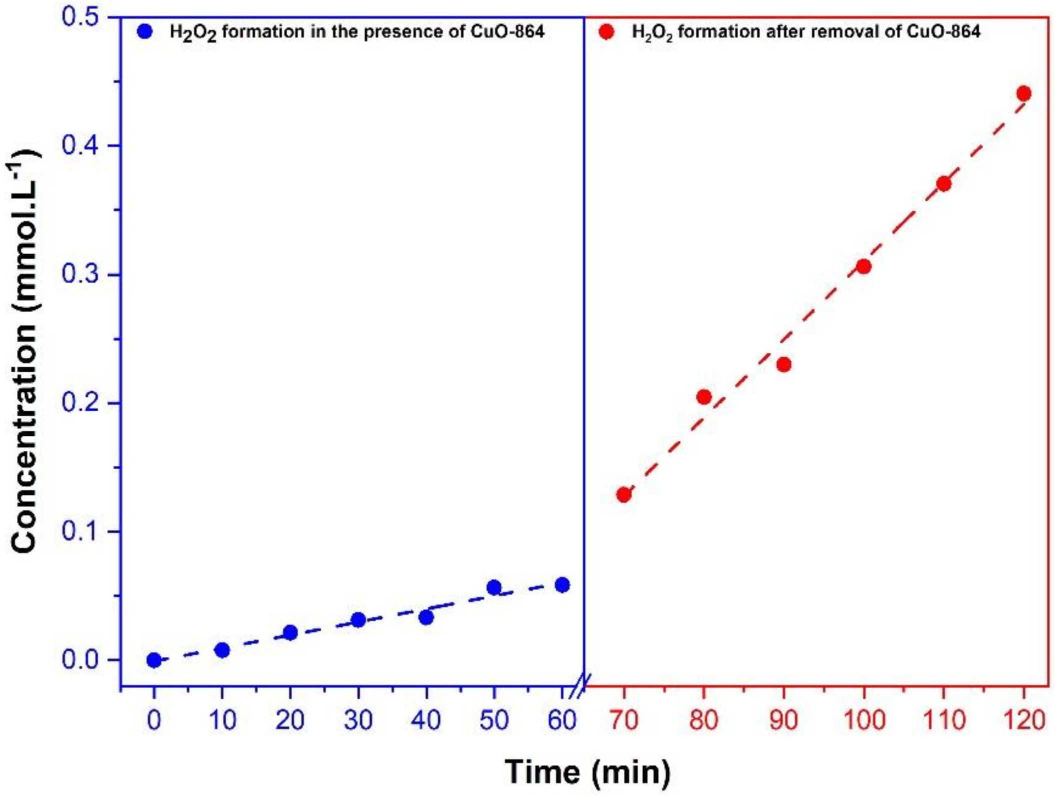
Hydrogen peroxide Quantification

H_2O_2 formation in the presence Fresh and Recycled catalyst

Dr. Teseer Bahry
Postdoc







Ultrasound frequency 578 kHz, Amplitude 100 %, temperature 25 °C

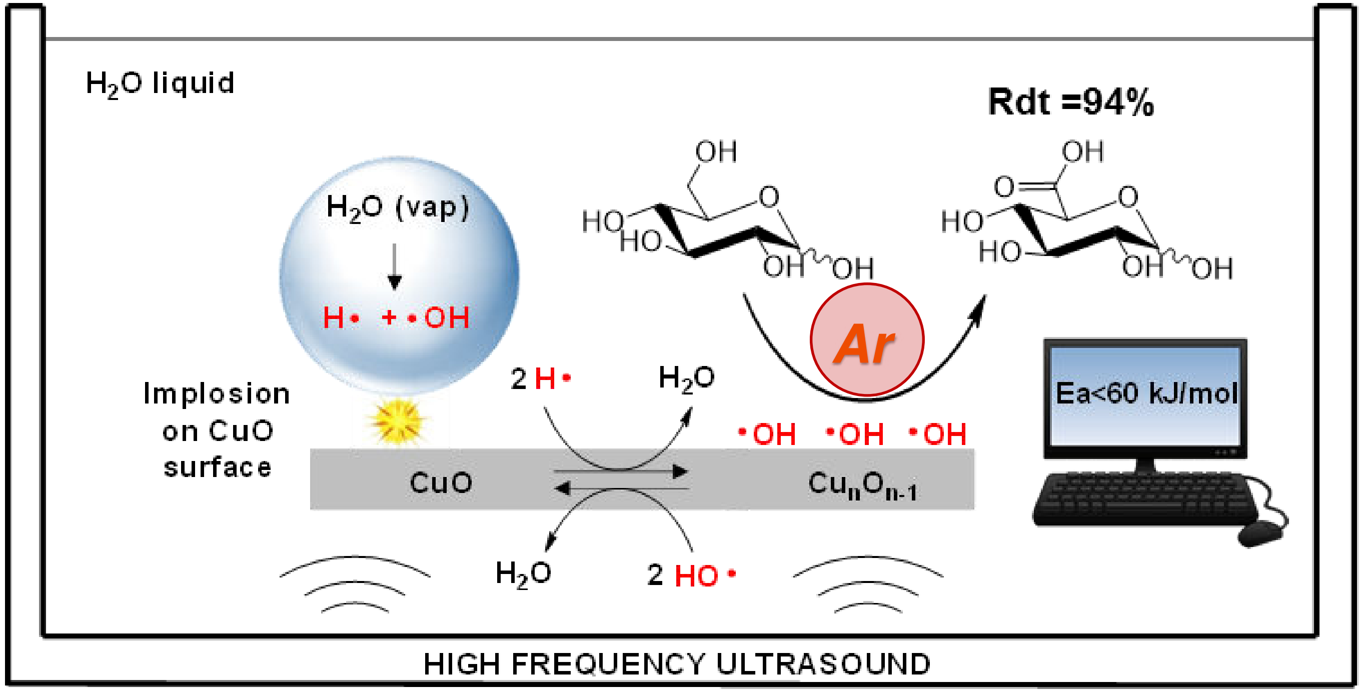
SONOCHEMICAL OXIDATION GLUCOSE OVER CuO CATALYST

➢ DFT calculations

- Without assistance of H•, the ring-opening of glucose is less favorable energetically
  - ⇒ Can we suppress H• during the sonolysis of water?
  - ⇒ **Our approach**: combining CuO catalyst with HFUS to *in situ* trap H•
- DFT: Under HFUS conditions, the surface of CuO is covered by HO•

⇒ **The surface lattice oxygen of CuO traps H•**, leaving a high coverage of HO• on the CuO surface

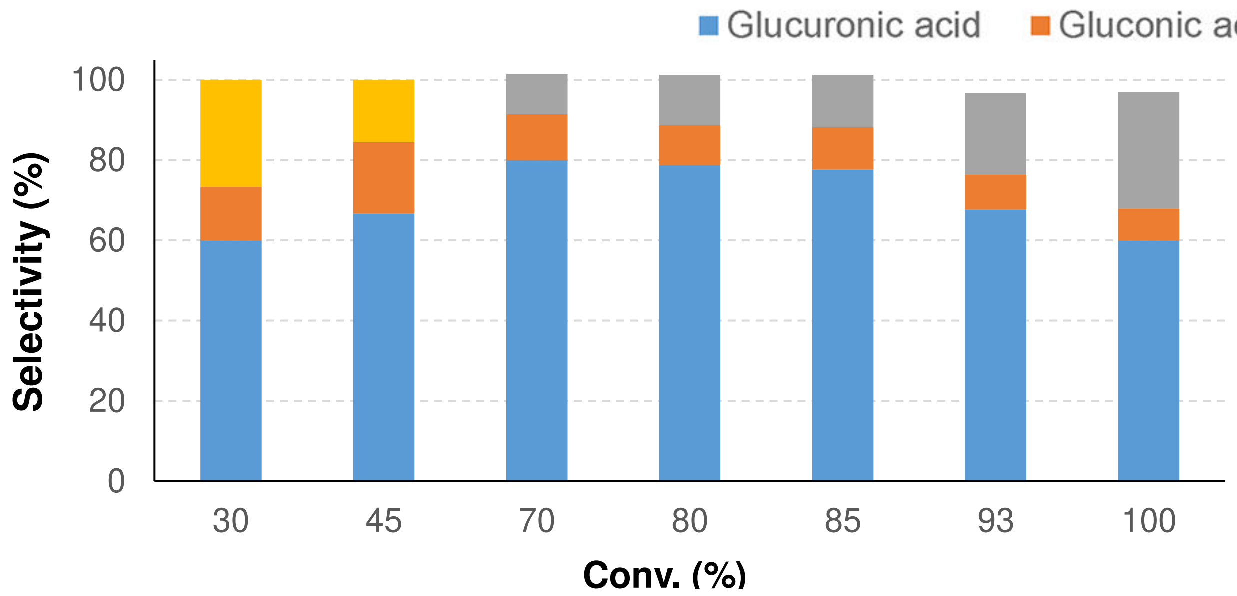
⇒ **The HO• produced in water can replenish the lattice vacancies** created on the surface of the catalyst



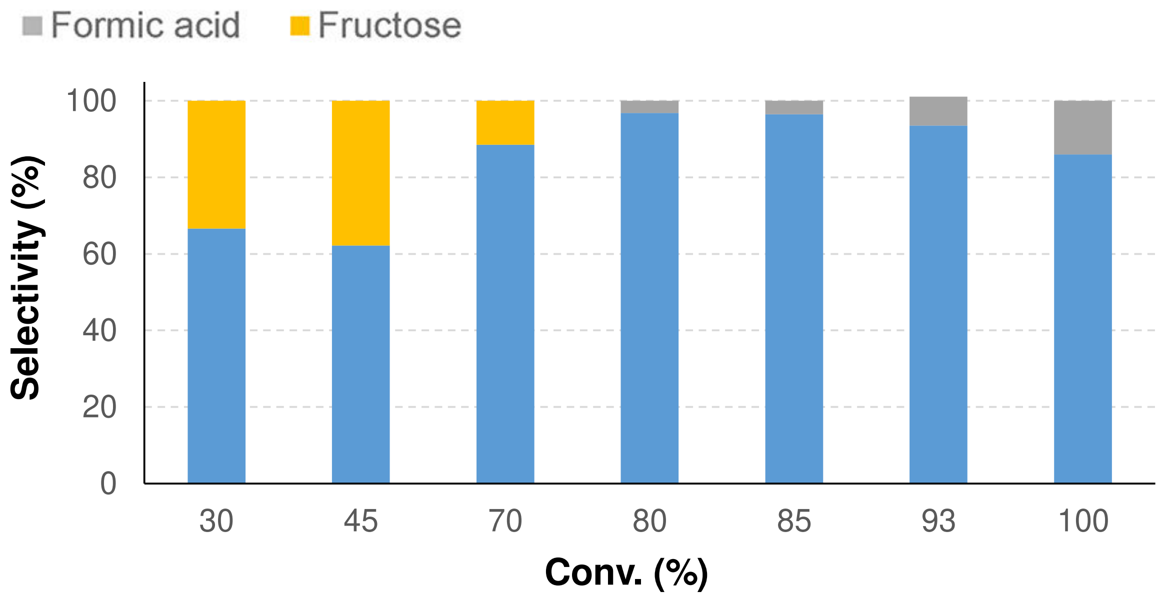
550 kHz
80°C
10 wt % CuO
glucose oxidation 20 g L^{-1}
P_{acoust} = 0.36 W mL^{-1}

Amaniampong et. al., *J. Am. Chem. Soc.* 2019, 141, 37

SONOCHEMICAL OXIDATION GLUCOSE OVER CuO CATALYST



CuO (LFUS): 10-24 µm



CuO (HFUS): 3.5-4.7 µm

(80°C, 550 kHz, 10 wt % CuO, glucose oxidation 20 g L^{-1}, P_{acoust} = 0.36 W mL^{-1})

- Selectivity to glucuronic = 82% (at 80% conv.) with CuO (LFUS)
- The heterogeneous nucleation of cavitation bubbles on a material surface is affected by the particle size *

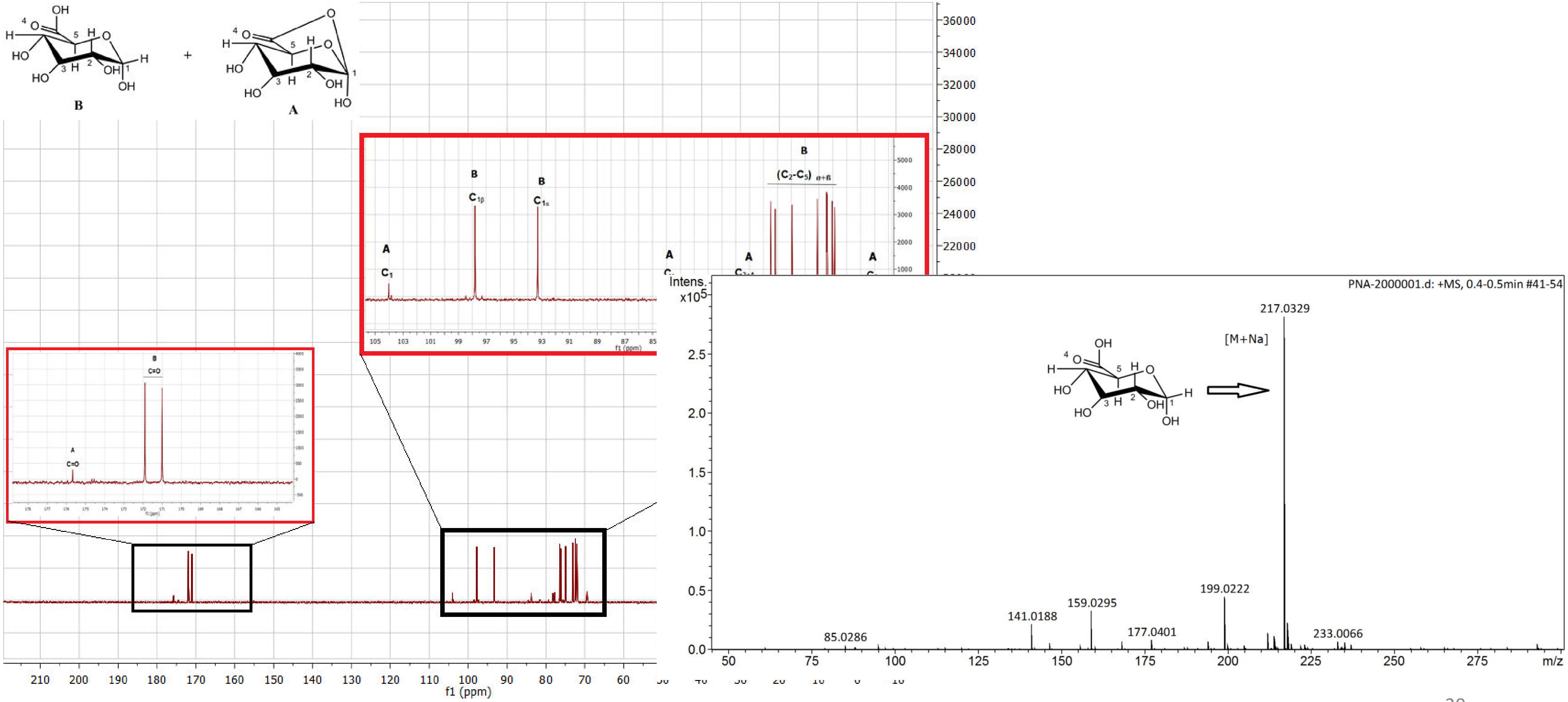
Lower particle size ⇒ enhanced cavitation bubble-solid particles contact angles

- Over **CuO (HFUS)** : switch of the selectivity! ⇒ **selectivity to glucuronic = 95% (at 93% conv.).**

⇒ **Enhanced interactions of the radicals and the surface of the catalyst**

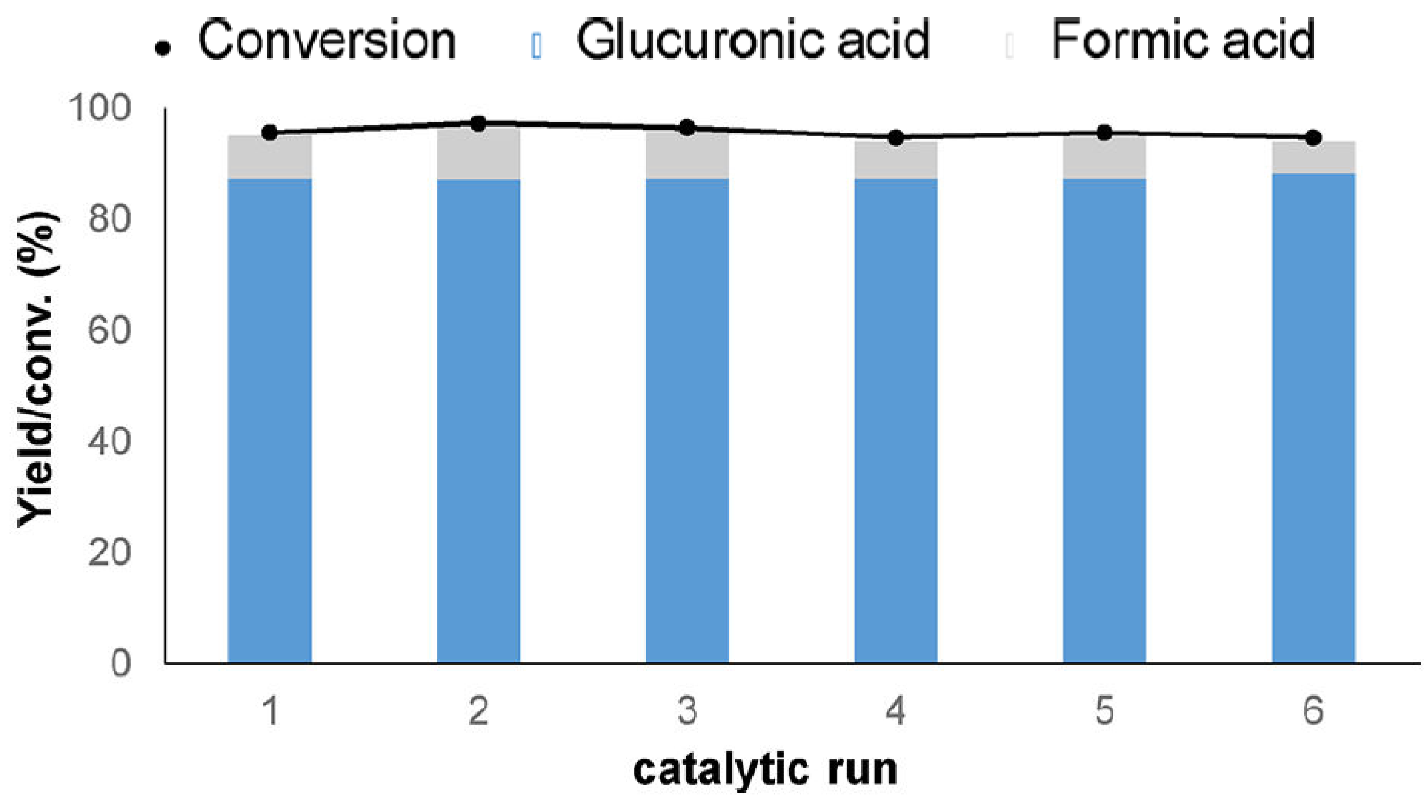
* *Chem. Mater.*, **2014**, 26, 2244

NMR & MS ANALYSIS OF CRUDE REACTION PRODUCT



SONOCHEMICAL OXIDATION GLUCOSE OVER CuO CATALYST

➢ Recycling of the CuO (HFUS) 3.5-4.7 µm



(80°C, 550 kHz, 10 wt % CuO_{HFUS}, glucose oxidation 20 g L^{-1}, P_{acoust} = 0.36 W mL^{-1})

⇒ **CuO (HFUS) stable**

⇒ **Abrasion drastically limited under HFUS** (confirmed by SEM)

Challenge: Direct synthesis of hydrazine from ammonia

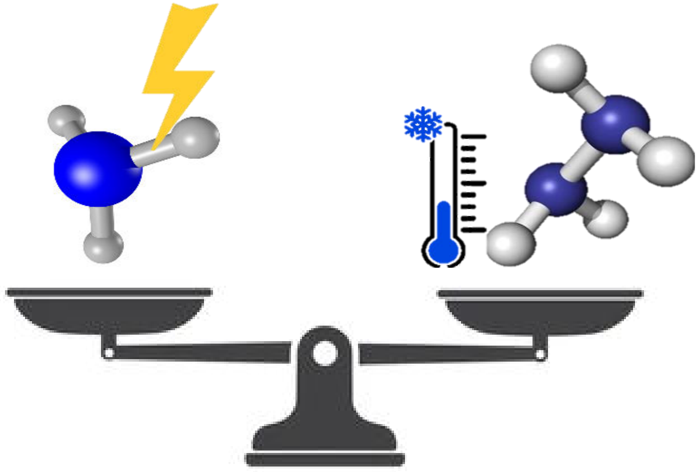
$$NH_3 \xrightarrow[\Delta G = 16{,}5\ kJ.mol^{-1}]{?} N_2H_4$$

Major hurdles:

High N-H bond dissociation energy of ammonia (435 $kJ.mol^{-1}$)

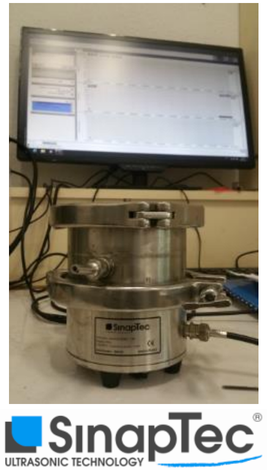
Low thermal stability of hydrazine (ΔG=-150 $kJ.mol^{-1}$)

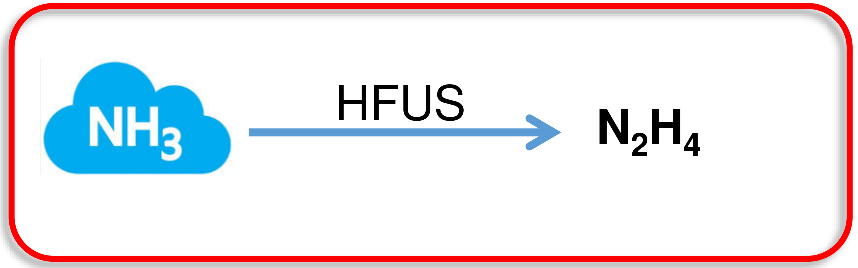
Catalyst able to activate NH_3 will inevitably decompose hydrazine



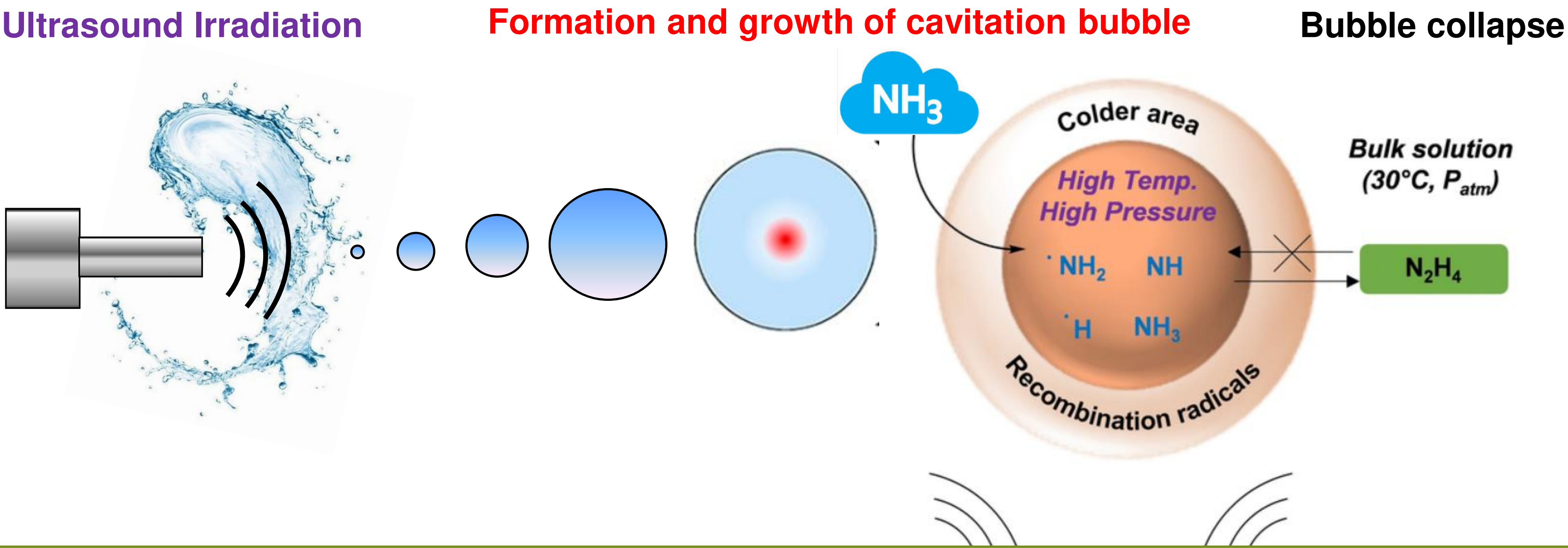
Is it possible to replace a chemical activation by a physical activation of NH_3?

Dr. Anaelle Humblot

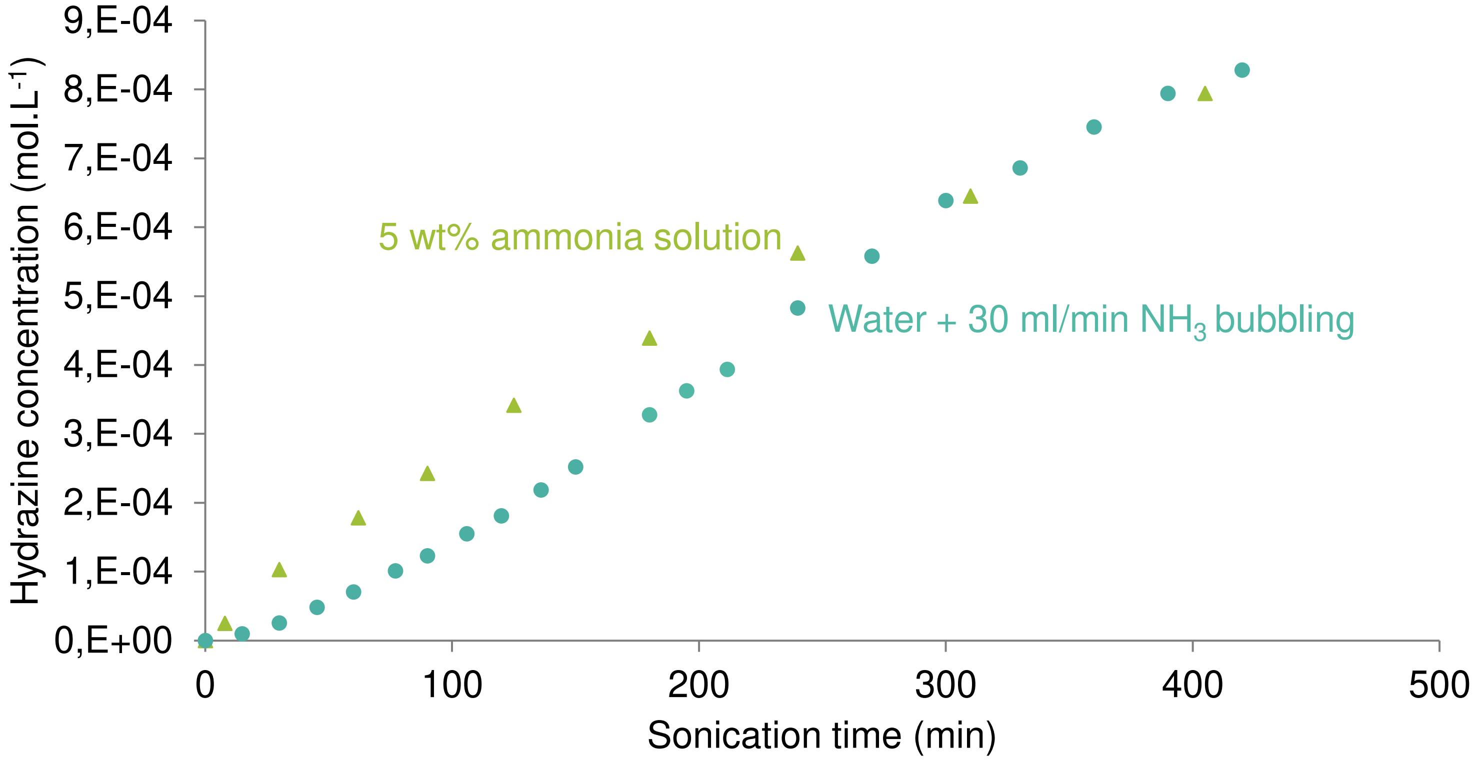




100 ml of 5 wt% ammonia solution
or
100 ml of water + NH_3 bubbling
30°C
High frequency ultrasound 525 kHz



Hydrazine production from ammonia

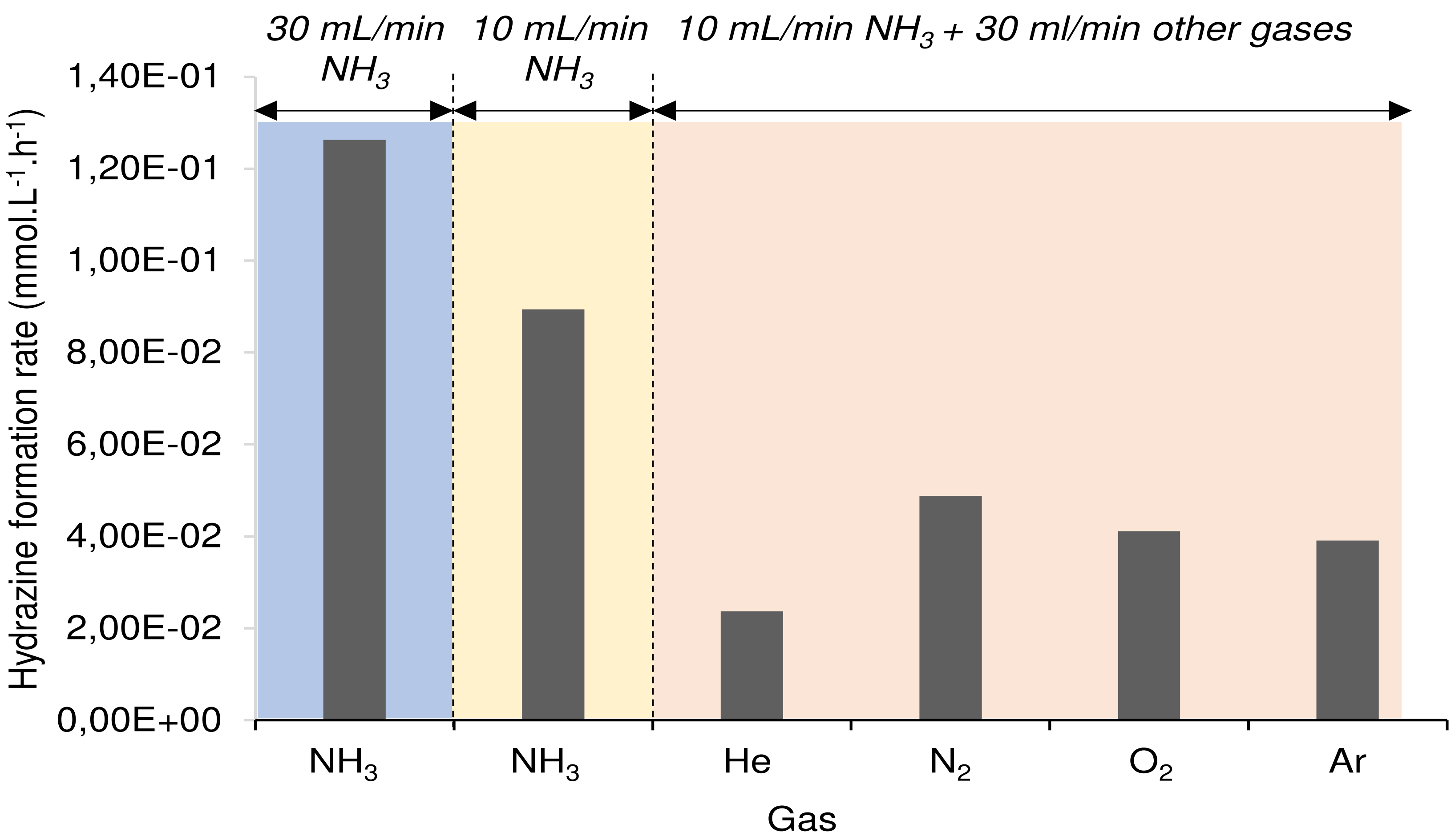


Hydrazine production rate 0,1 $mmol.L^{-1}.h^{-1}$

Continuous production of hydrazine over time in ammonia solution or with ammonia bubbling

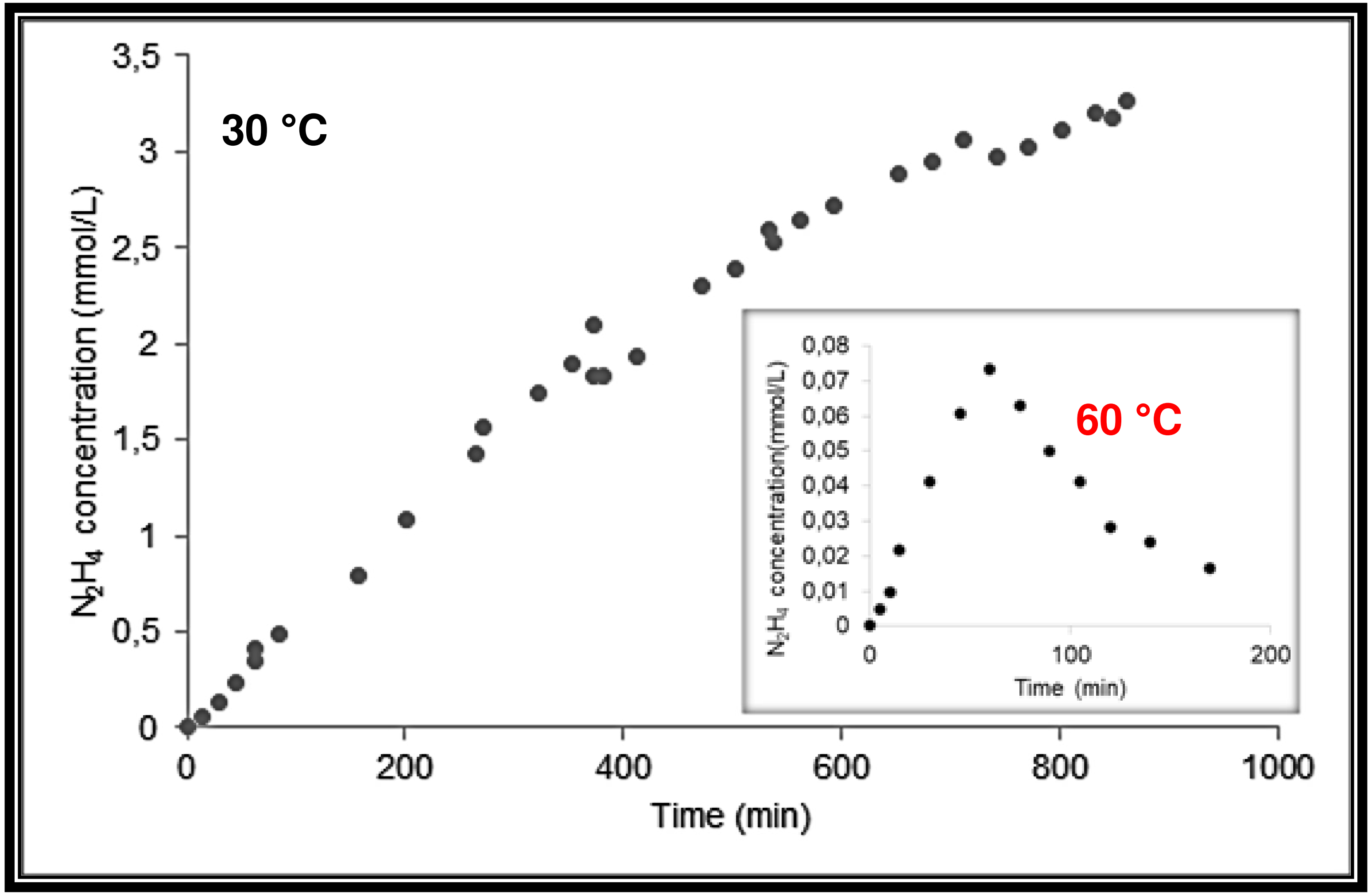
N_2H_4 formation rate > decomposition rate

Effect of Gas flow



Influence of gases on the initial formation rate of N_2H_4 (10 ml/min NH_3 + 20 ml/min gas, 525 kHz, 0.17 W/mL, 30°C). All reactions were conducted at atmospheric pressure

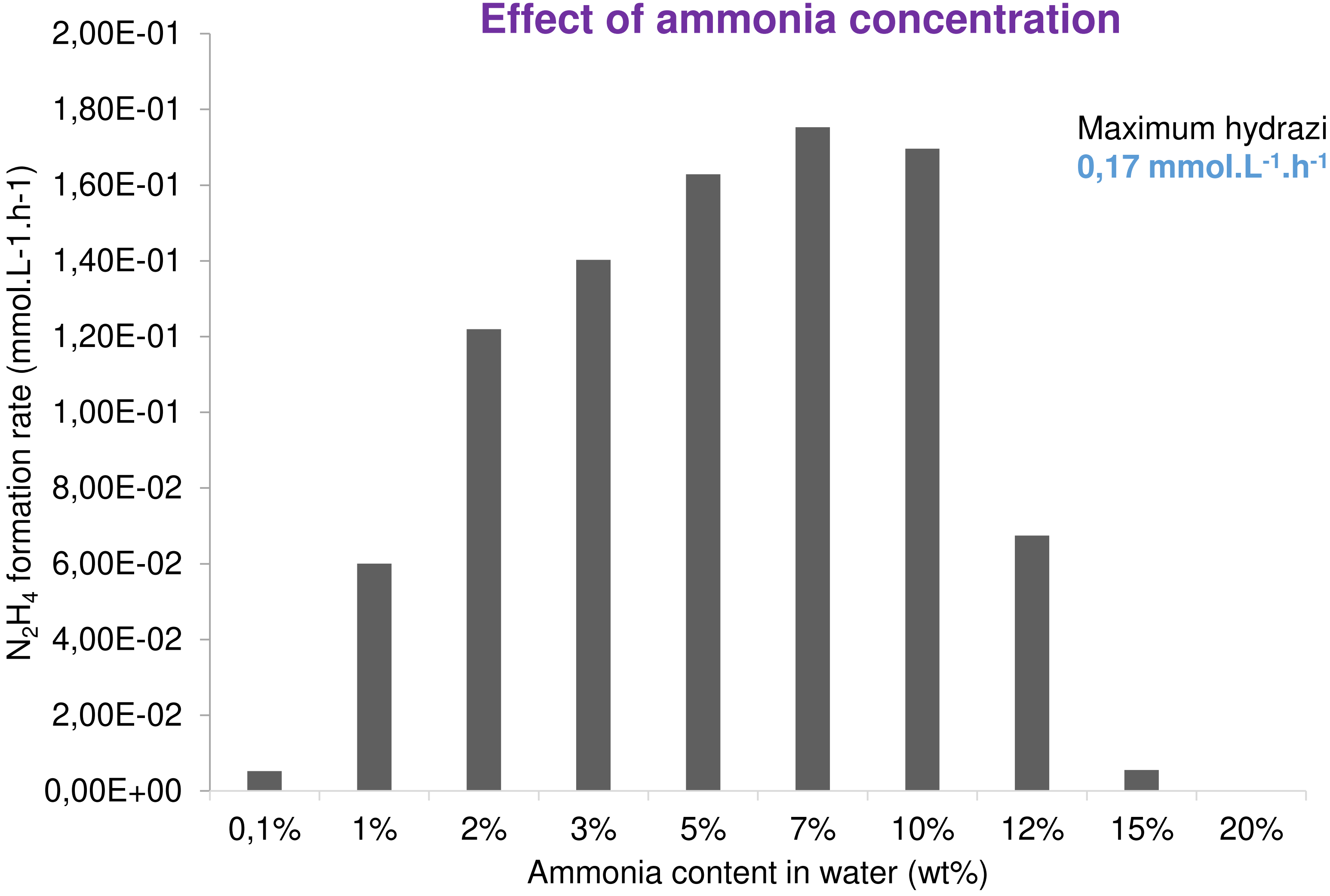
Effect of reaction bulk temperature



Concentration of hydrazine as a function of the reaction time (bubbling of NH_3 at 30 ml/min, 525 kHz, 0.21 W/mL) at 30° C and 60 ° C. 0.17 W/mL at 60° C

ACTIVATION OF NH3 TOWARDS HYDRAZINE FORMATION

Effect of ammonia concentration

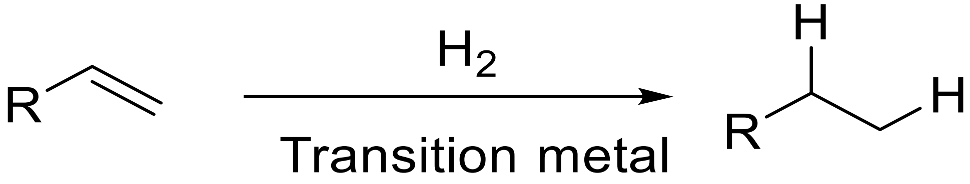


Maximum hydrazine production rate:
0,17 mmol.L^{-1}.h^{-1} N_2H_4 in **7 wt%** ammonia solution

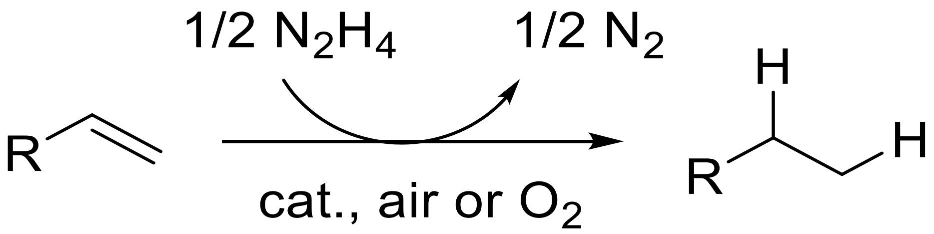
A. Humblot, L. Grimaud, A. Allavena, P.N. Amaniampong, K. De Oliveira Vigier, T. Chave, S. Streiff and F. Jérôme, ***Angew. Chem***. *Int. Ed.* **2021**

DIRECT NH3 ACTIVATION FOR THE SELECTIVE REDUCTION OF ALKENES

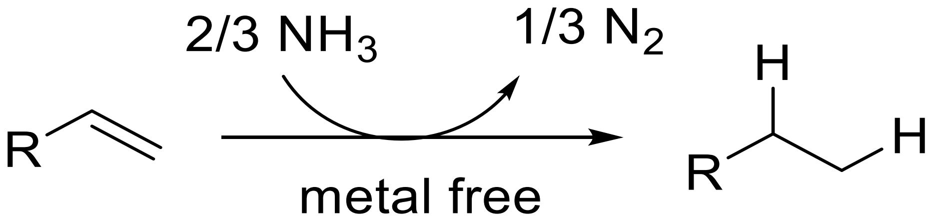
1) Catalytic reduction of alkenes with H_2



2) Reduction of alkenes with N_2H_4

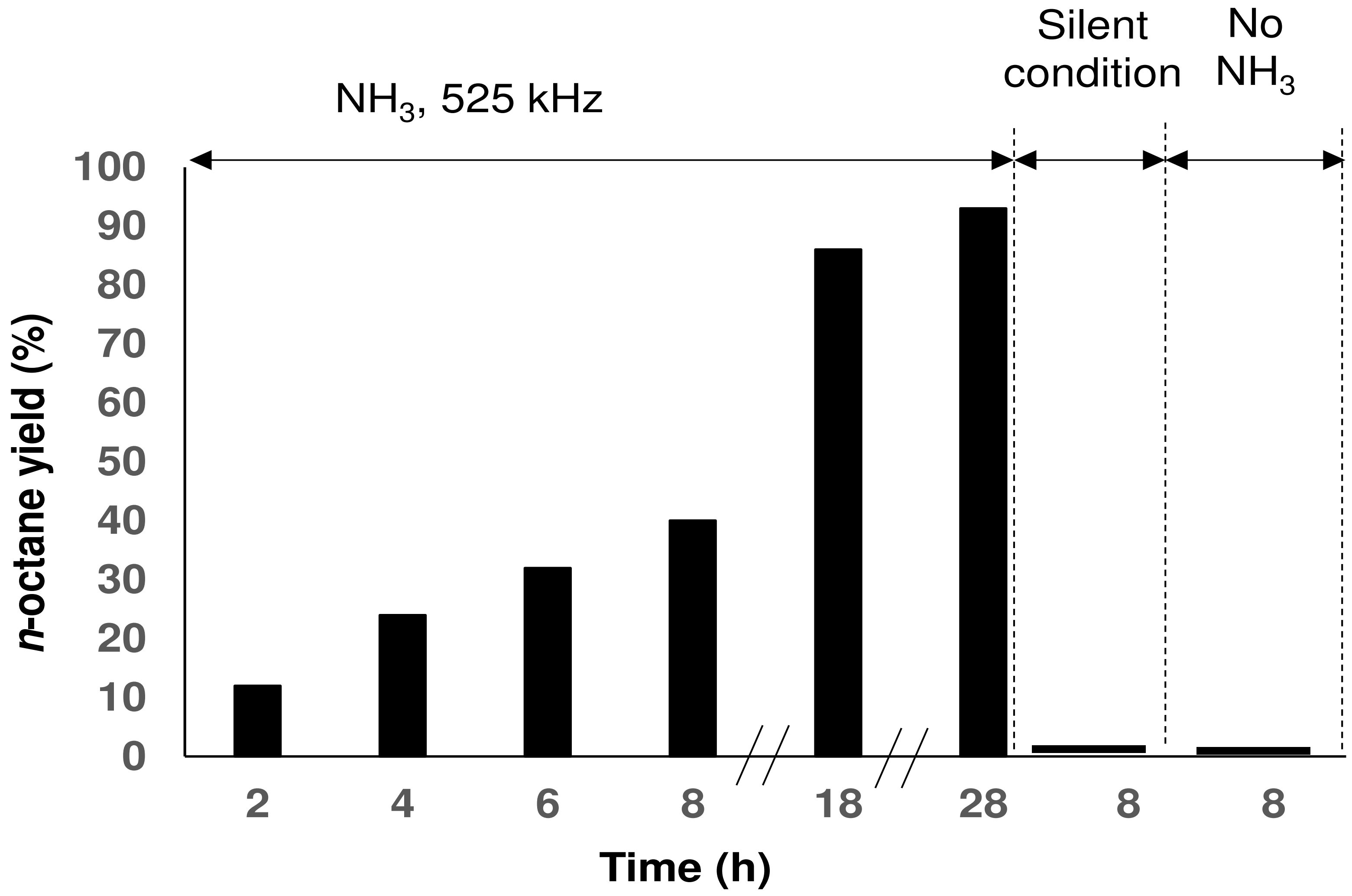


3) This work



Anaelle HUMBLOT
PhD Student

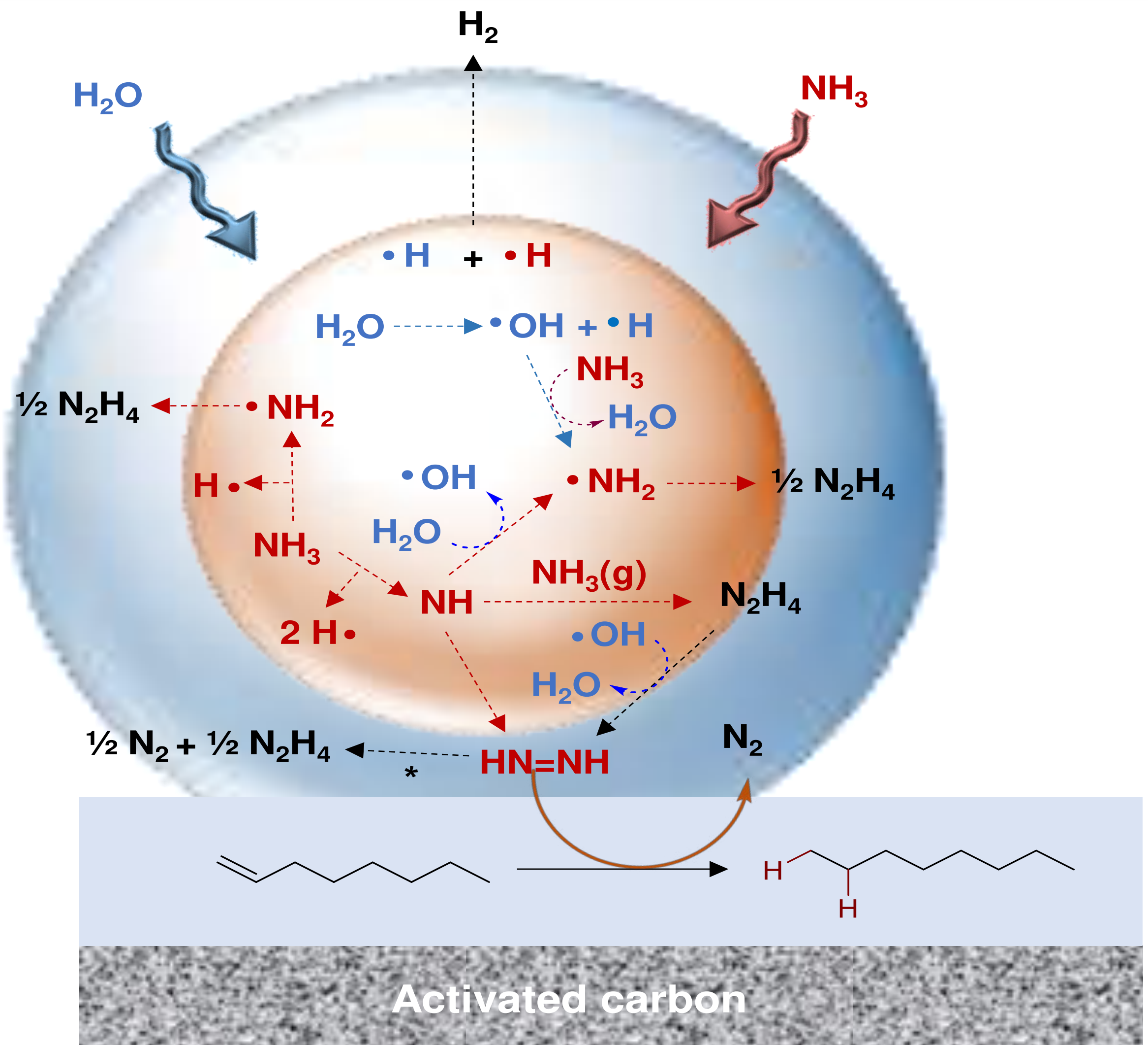
Hydrogenation of 1-Octene in an Aqueous solution of NH_3 (5 wt%)



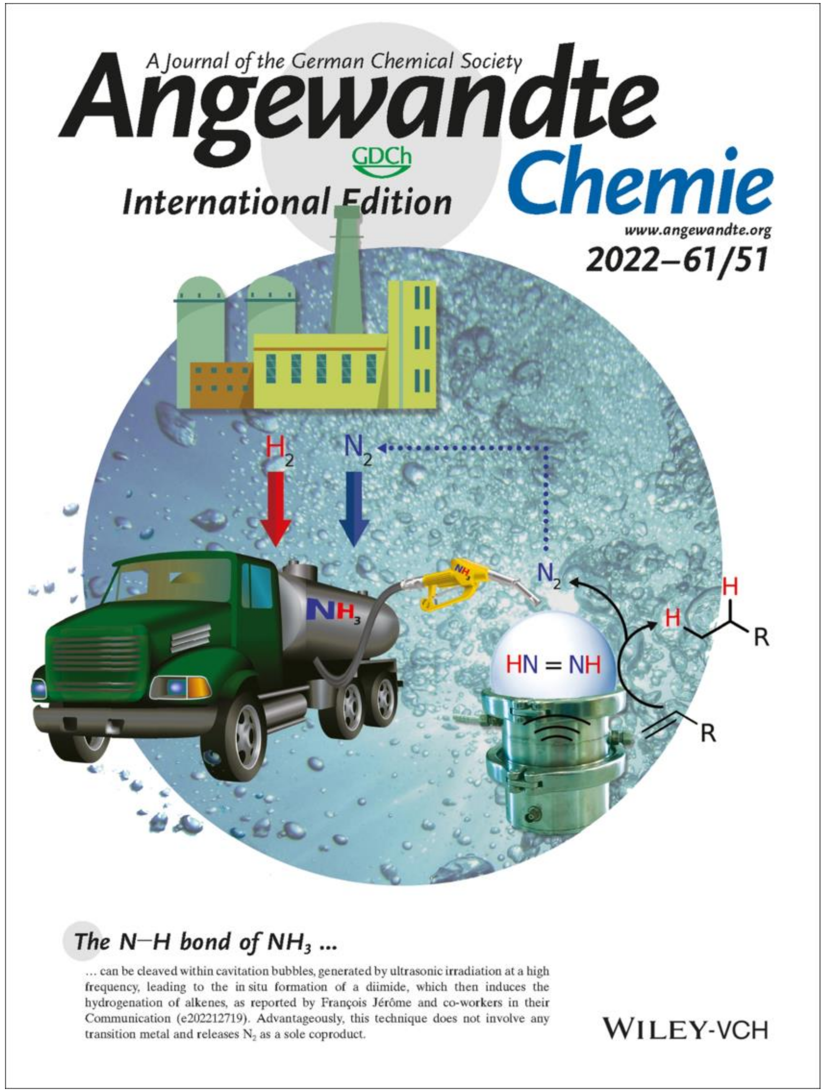
kinetic profile and blank experiments (30°C, 525 kHz, NH_3 5 wt%, under air)

A. Humbot, P.N. Amaniampong, T. Chave, S. Streiff, F.Jerome. ***Angew. Chem.*** *Int. Ed. 2022*

Hydrogenation of 1-Octene in an Aqueous solution of NH_3 (5 wt%)

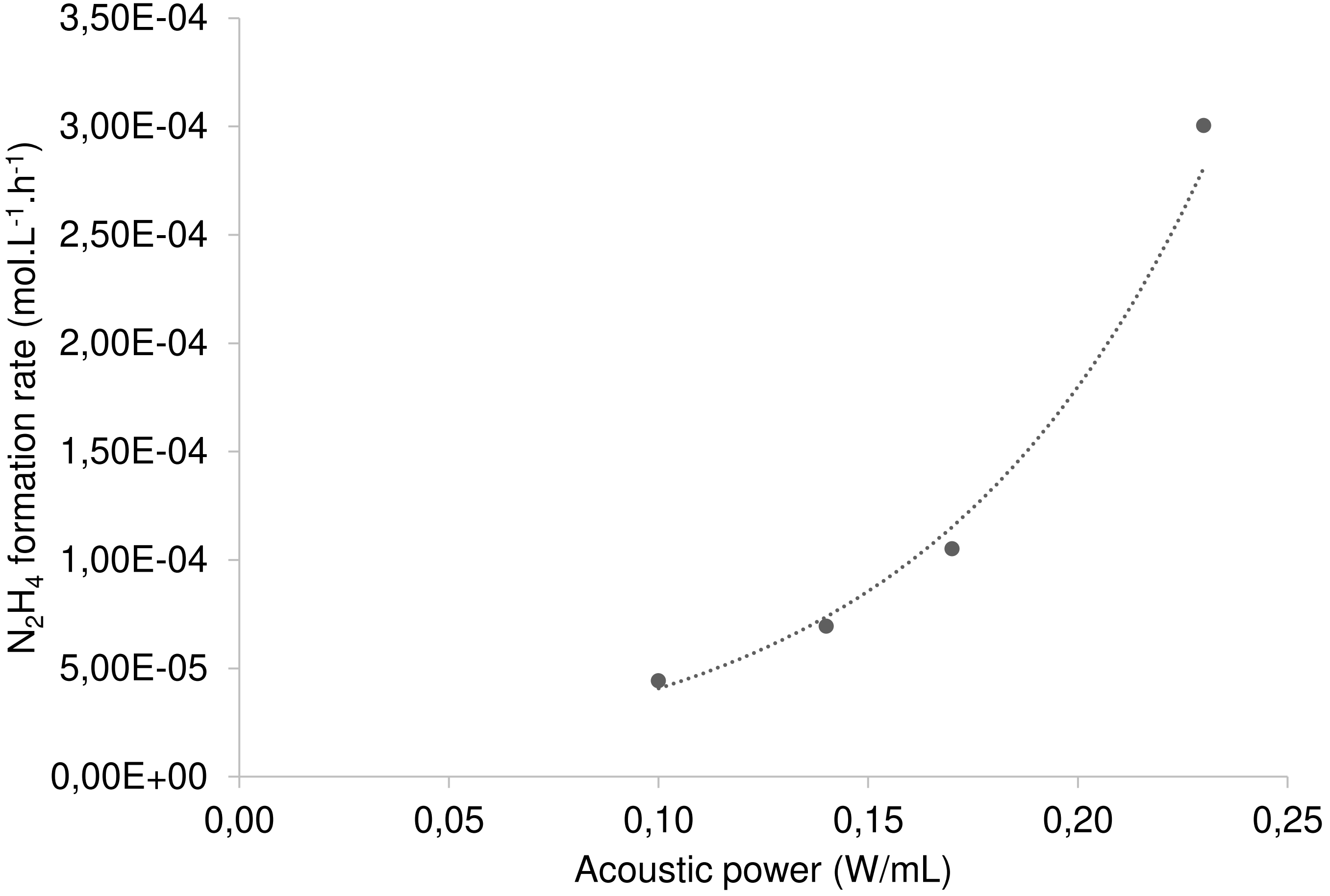


* = disproportionation



Proposed reaction mechanism illustrating the implosion of aqueous NH_3 filled cavitation bubbles on the surface of activated carbon coated with 1-octene and associated reactions

Direction for future studies



The formation rate of hydrazine increases exponentially when increasing the acoustic power

→ Development of a continuous ultrasonic reactor to increase the acoustic power and the production of hydrazine

ACKNOWLEDGEMENT

RESEARCH GROUP MEMBERS
Anaelle HUMBLOT - Former PhD Student
Teseer BAHRY – Postdoc

IC2MP France
Dr Francois JEROME – DR CNRS
Prof. Karine Vigier

COLLABORATORS
Dr. Tony Chave – CNRS France
Dr. Gregory Chatel- Univ Savoie
Dr. Thang Quang Trinh – IHPC A*STAR Singapore
Prof. Jithin John Varghese – IIT Madras India
Dr. Matthew Sherbune – Berkeley
Yingqiao Wang - Berkeley
Dr. Duy Quang Dao – Duy Tan Univ. Viet Nam
Dr. Ngoc Han Tran – NUS Singapore

Merci pour votre attention

prince.nana.amaniampong@univ-poitiers.fr