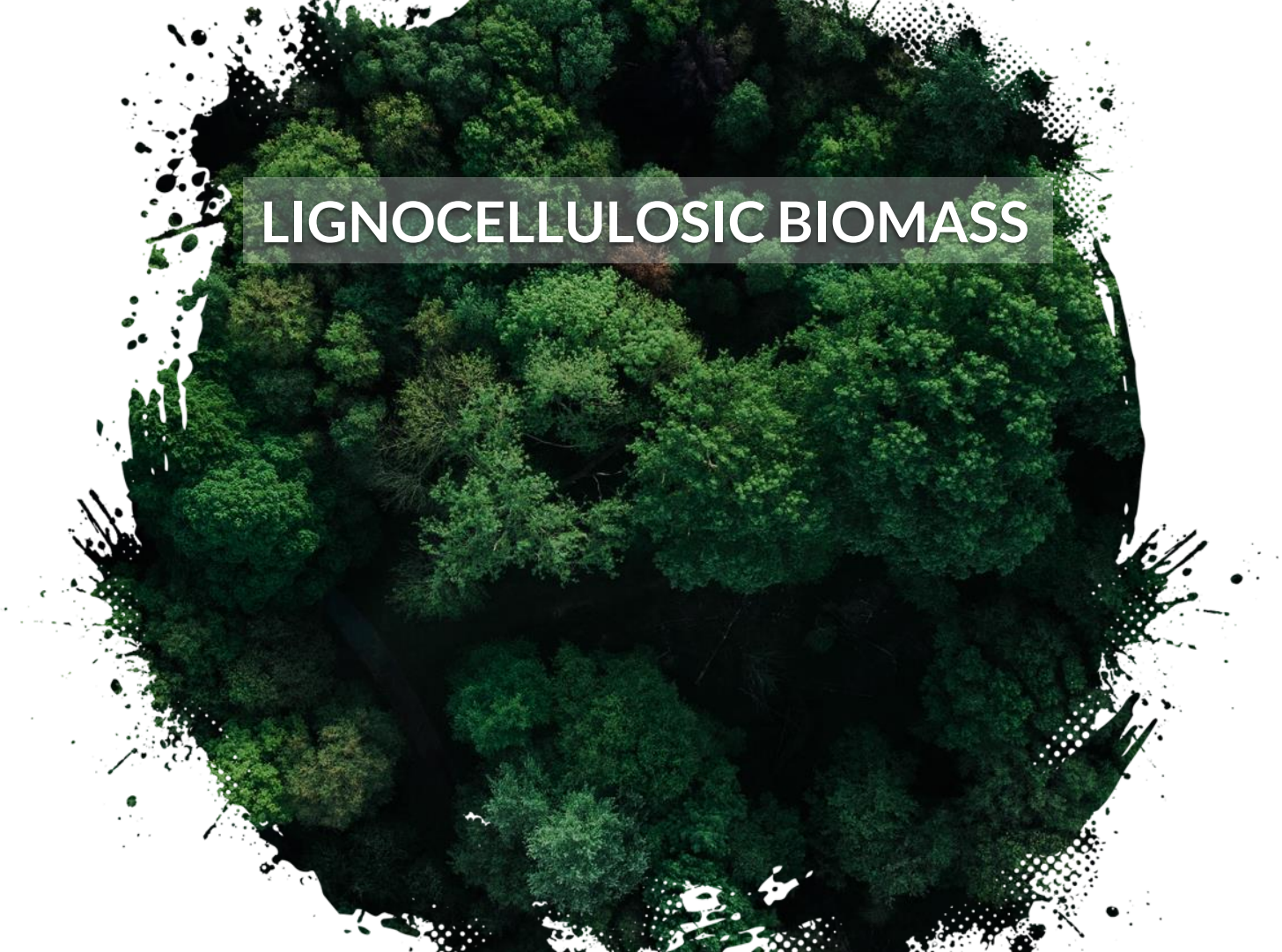
PhD student: Eleonora Monti
Department of Industrial Chemistry "Toso Montanari"-
Alma Mater Studiorum-University of Bologna
Prof. Fabrizio Cavani, Prof. Nikolaos Dimitratos

Investigation of gold-based catalysts for liquid phase oxidation of glucose to glucaric acid


LIGNOCELLULOSIC BIOMASS

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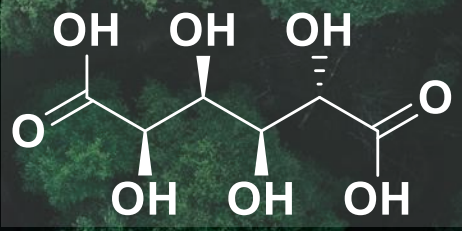
Top 12 value added chemical

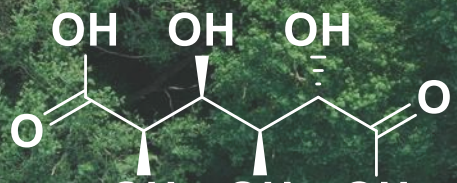
GLUCARIC ACID



Anti-corrosion additives

Phosphate-free detergents and biodegradable cleaners

GLUCARIC ACID



Adhesive and coating

Intermediate in the production of biobased adipic acid

STATE OF ART

Oxidation of Glucose to Glucaric acid (GA) by **HNO_3**, giving a yield of **43%** of Glucaric acid (GA)

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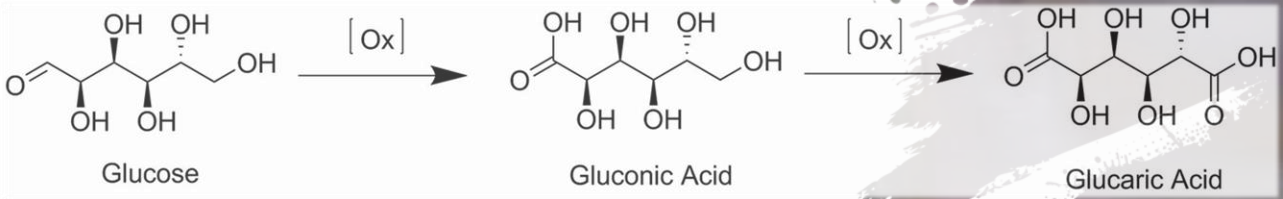
T.S. Moon et al.: **Biochemical conversion** with *Recombinant E. Coli* using a glucose solution 0,05M at 30°C

Rennovia Inc. : alloy **Au-Pt/TiO_2** gave **64%** yield GA for 5 h under 5 bar O_2 at 90°C neutral pH conditions

Derrien et al. : alloy **Au-Pt/ZrO_2** yield of **50%** of GA for 10 h under 40 bar of air at 100°C with a Glucose:metal molar ratio of 80:1 in neutral conditions

Solmi et al. : **Au-Bi/AC** yield of **31%** of GA for 3 h under 10 bar O_2 at 60°C with a Glucose:metal:NaOH molar ratio of 500:1:1500

MAIN GOAL



Optimization of reaction parameters

5% wt Glucose solution, 10 bar of O_2
Quantitative analysis by HPLC

- Stirring rate
- Glu:Au molar ratio
- Time on line

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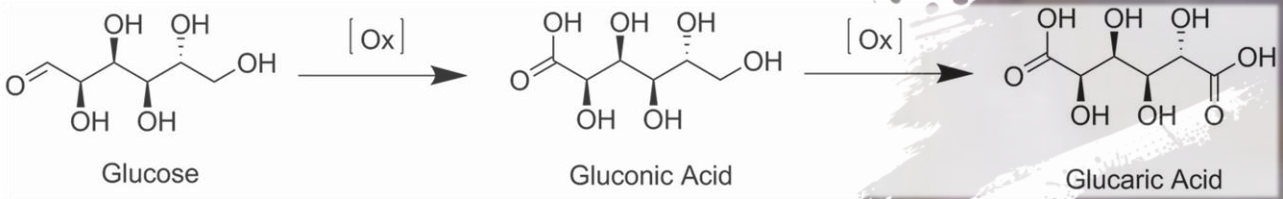

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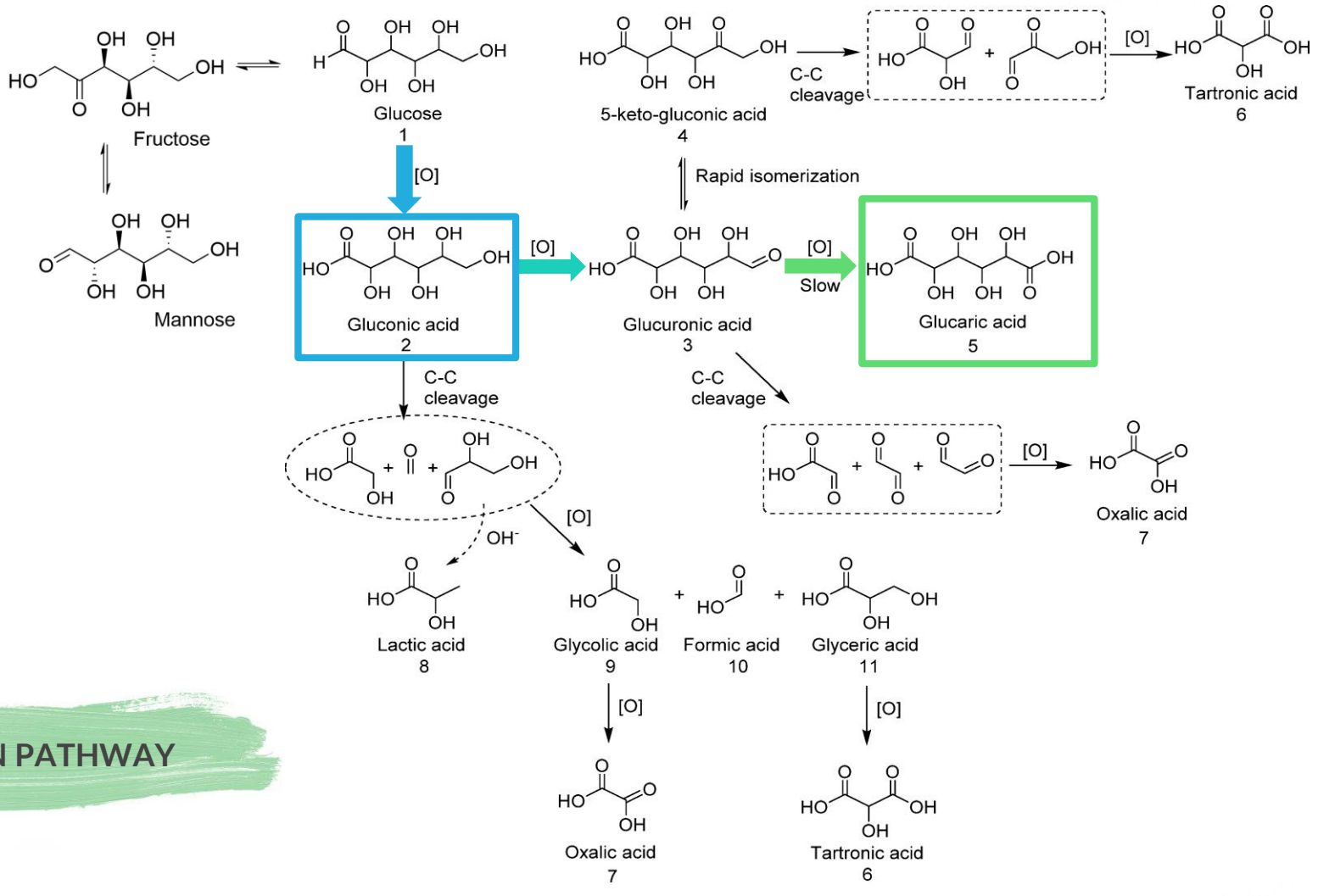
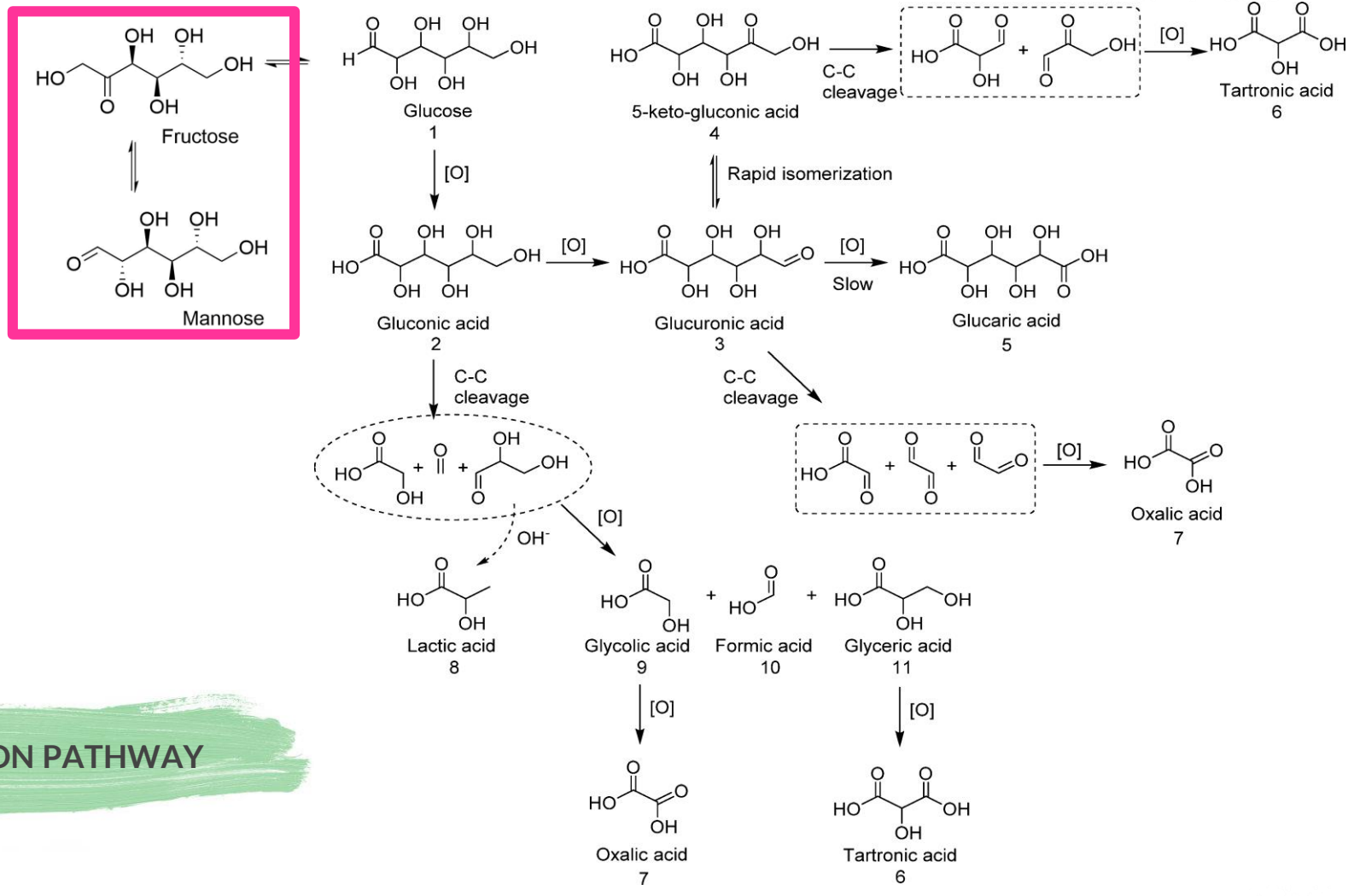
Synthesis of Au based catalysts

Sol immobilization technique
Metal loading 1% wt Au/AC

- Tunning of nanoparticle size
- Effect of heat treatment for removal of protective ligands



REACTION PATHWAY



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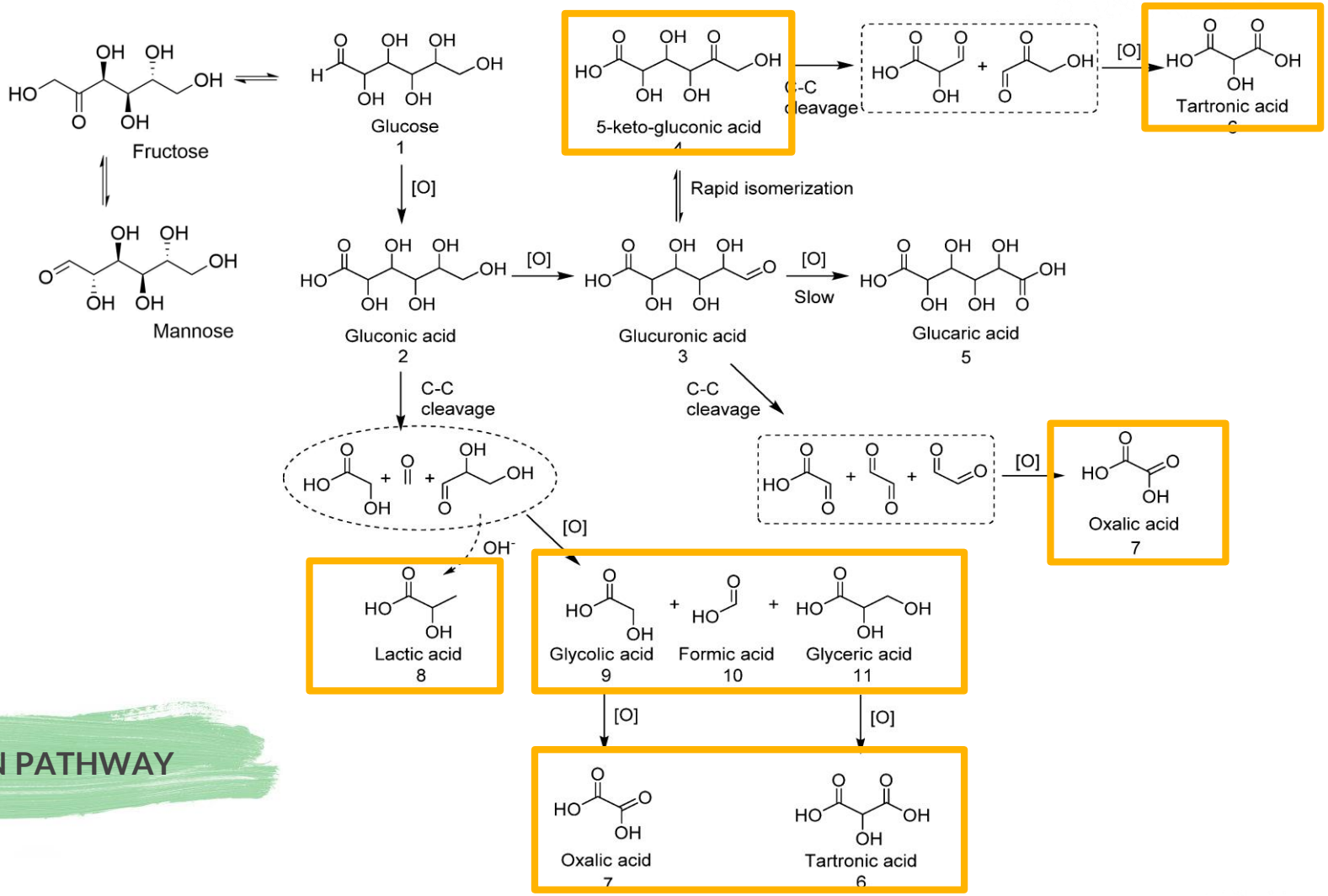
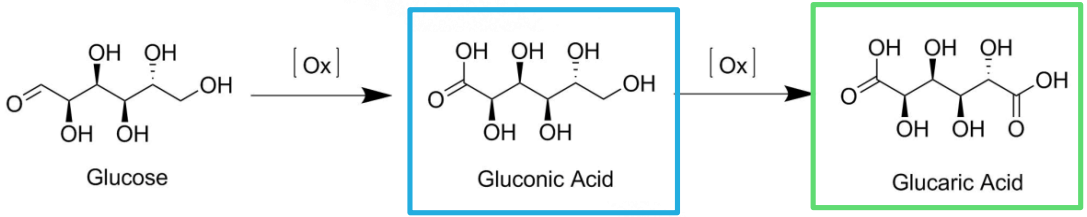
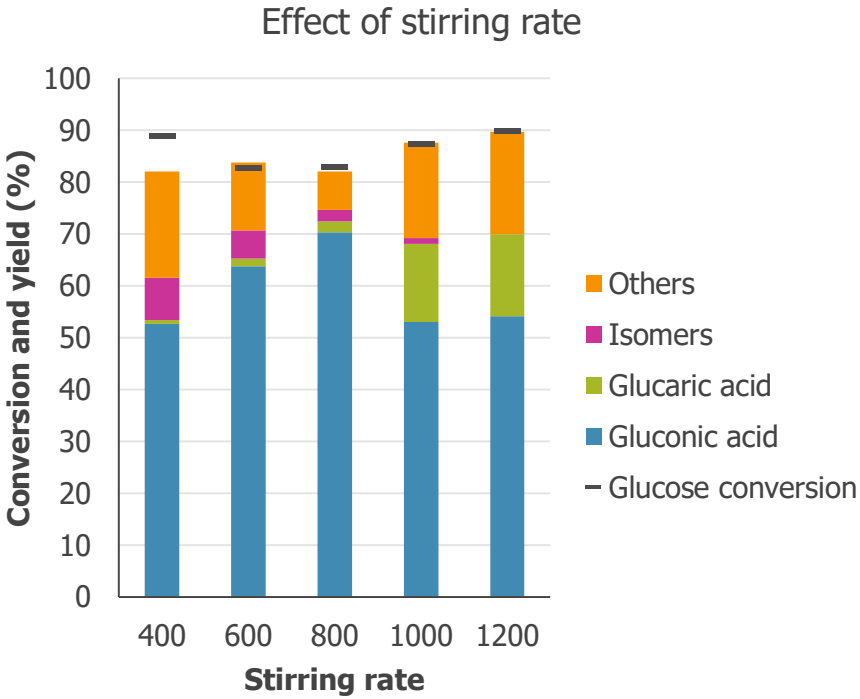


OPTIMIZATION OF REACTION PARAMETERS





Reaction conditions: 15 min, 60°C, 10 bar O_2,
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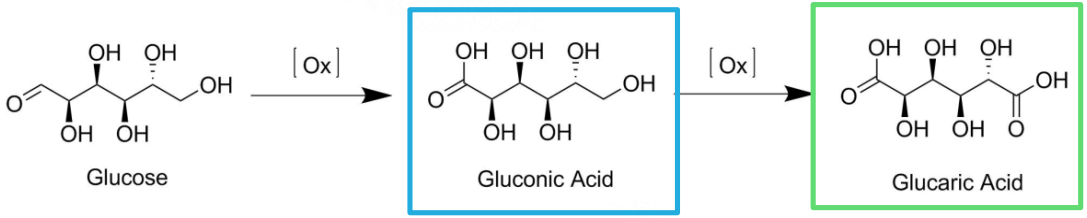

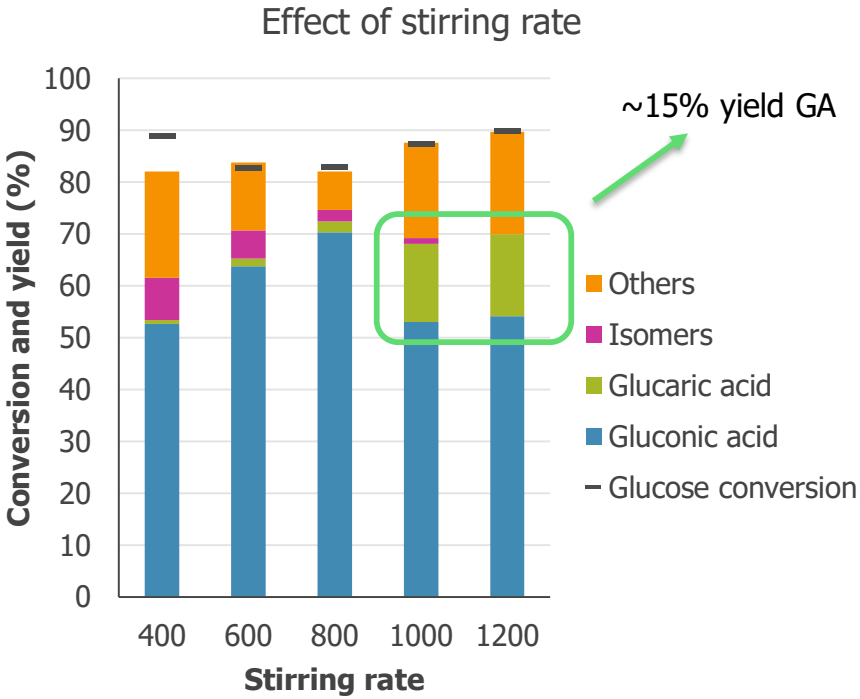

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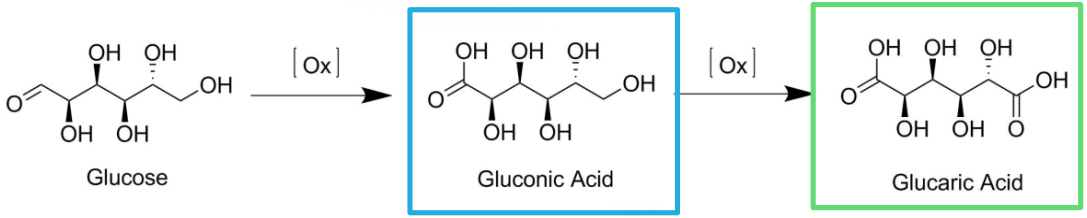
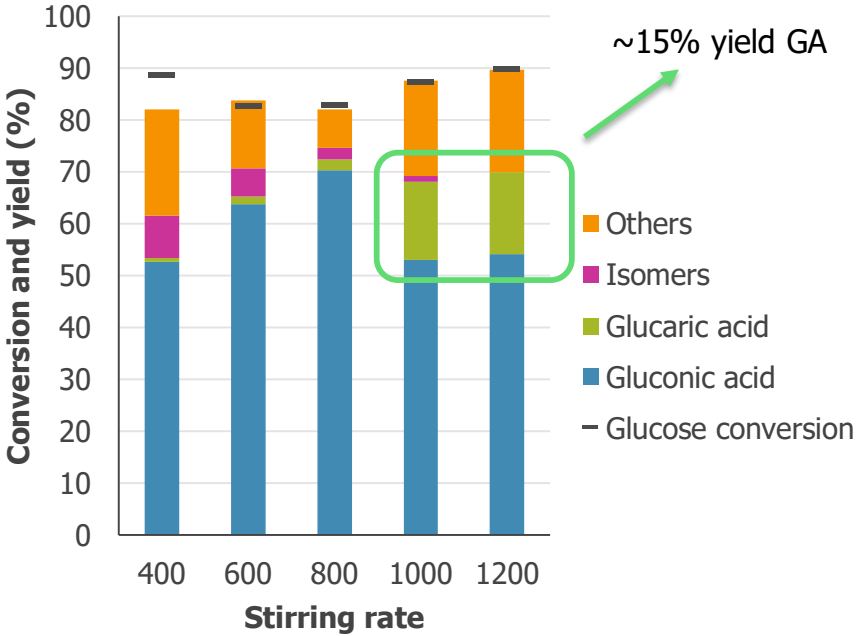


Effect of stirring rate



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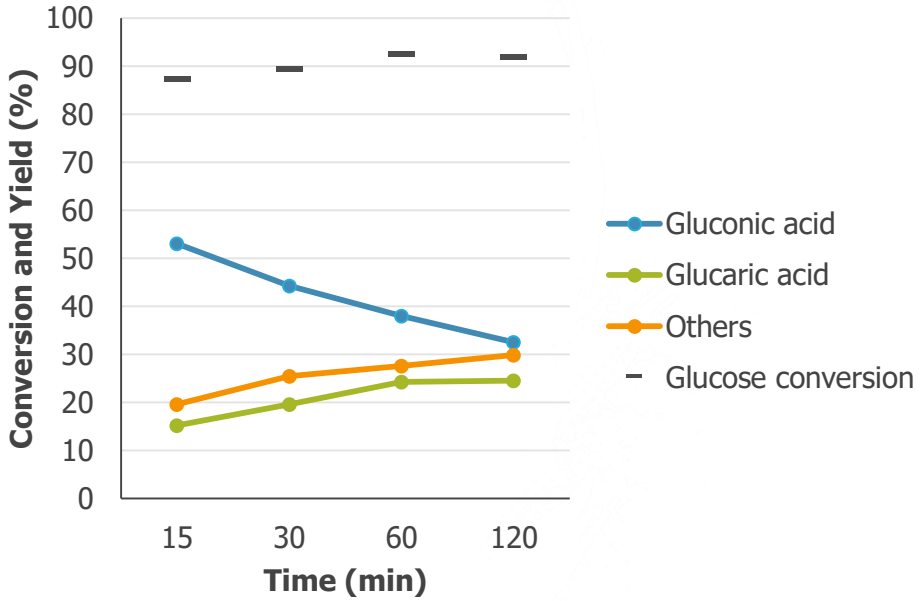
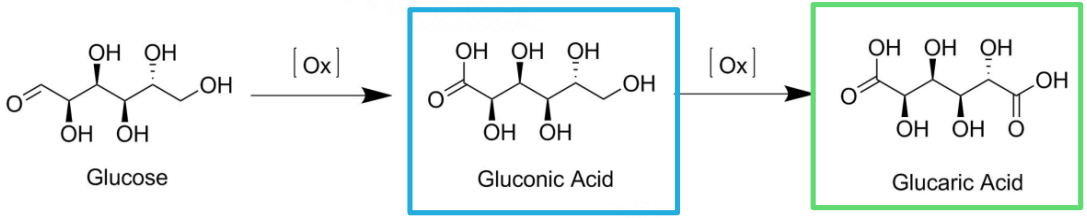
Study time on line



Reaction conditions: 60°C, 1000 rpm, 10 bar O_2,
Glu:Au:NaOH molar ratio of 1000:1:3000

OPTIMIZATION OF REACTION PARAMETERS



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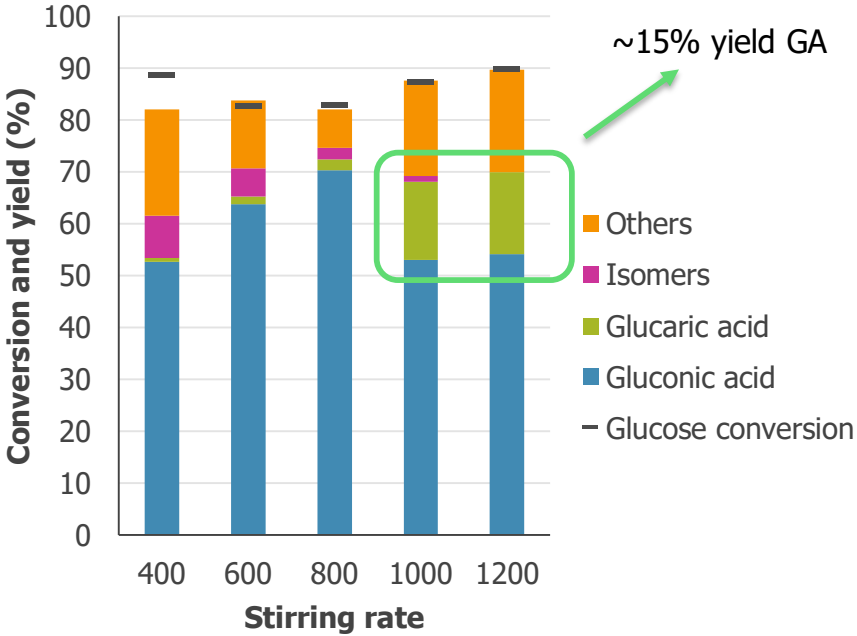

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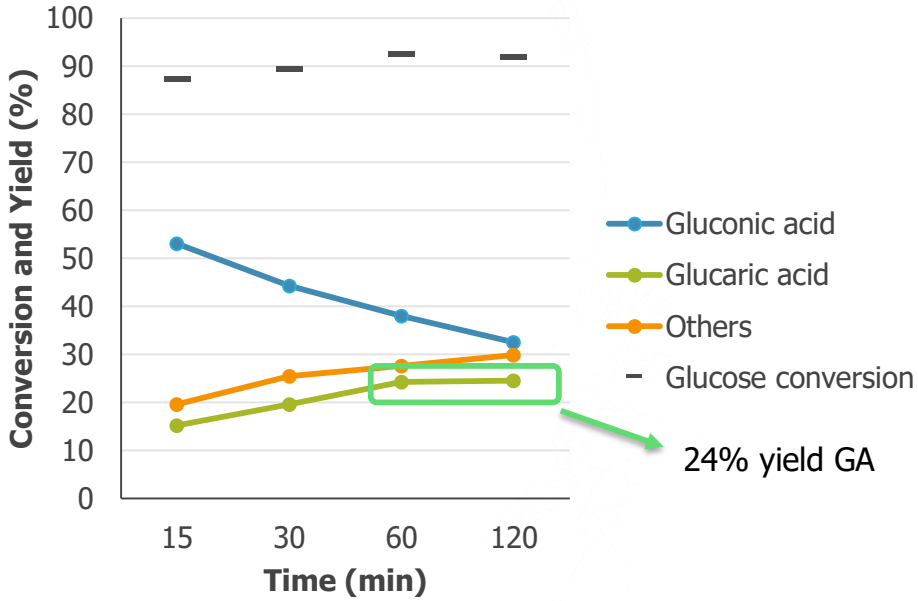

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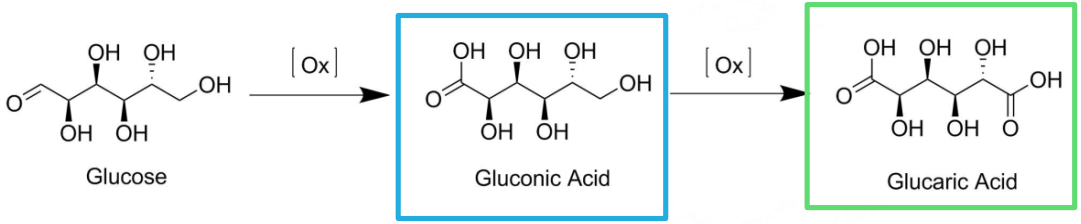
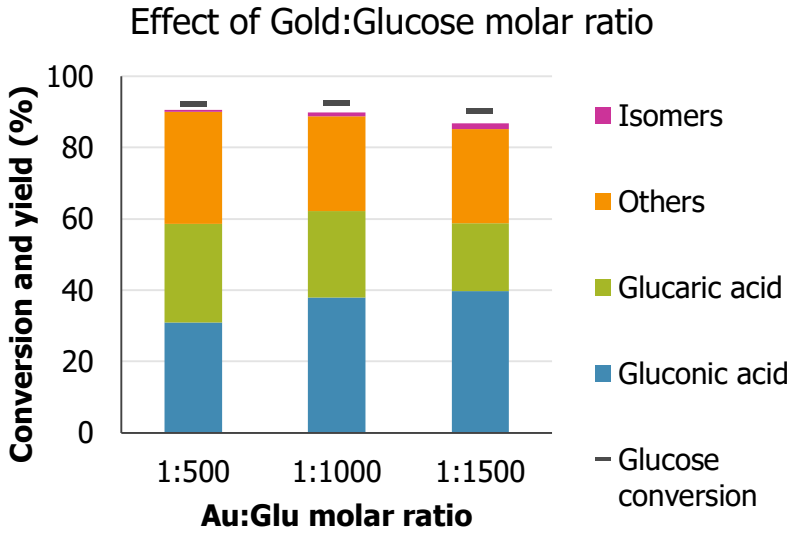
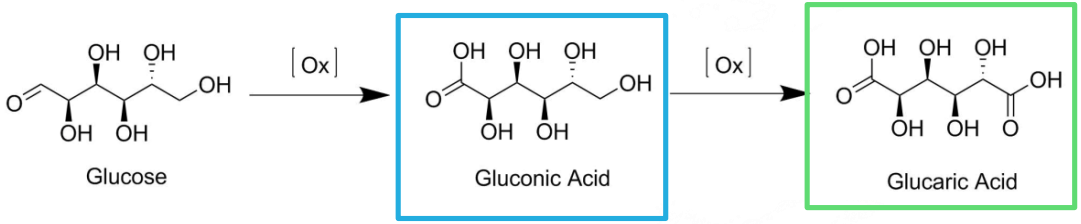
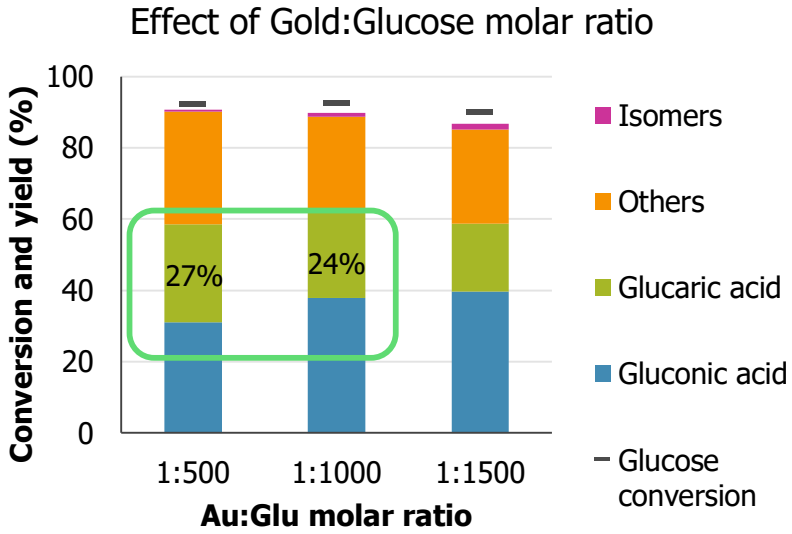




Reaction conditions: 1 h, 60°C, 1000 rpm, 10 bar O_2,
Glu:NaOH molar ratio of 1:3

OPTIMIZATION OF REACTION PARAMETERS





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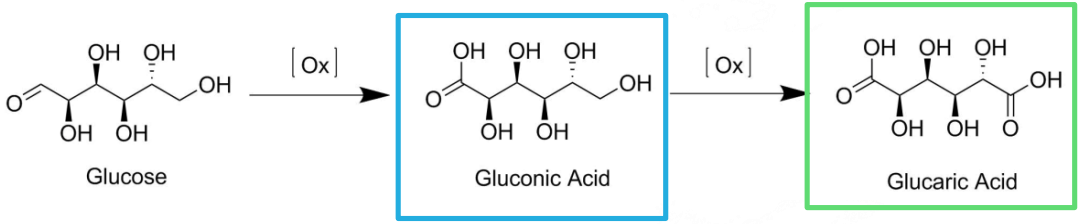

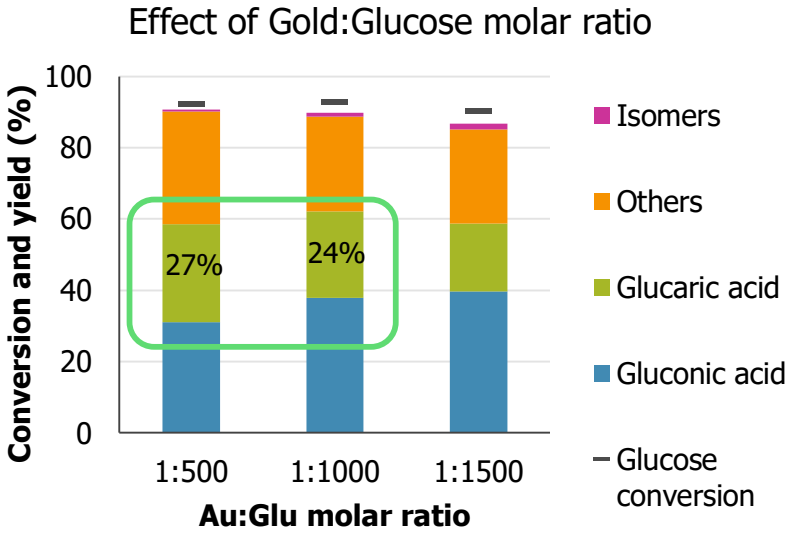

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Au NPS SYNTHESIS-
SOL IMMOBILIZATION METHOD

Au precursor
$HAuCl_4 *3H_2O$
+PVA

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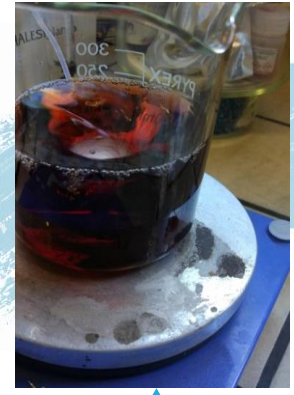

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$NaBH_4$
solution

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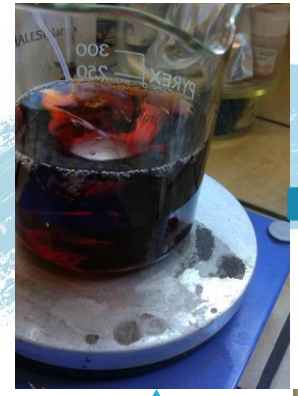

Activated carbon

$NaBH_4$ solution

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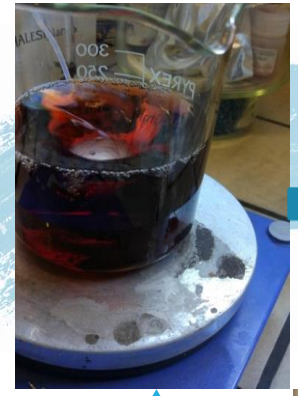

Activated
carbon

Filtration

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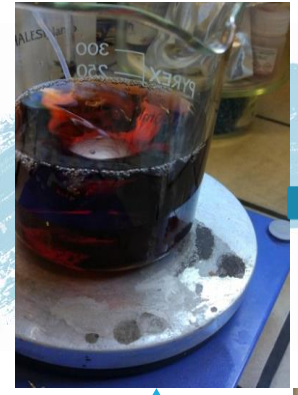
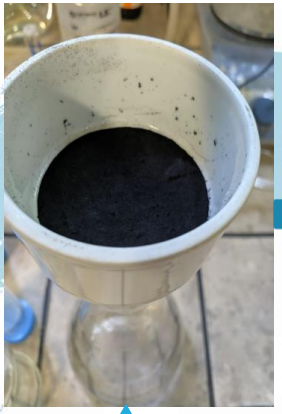


Activated
carbon

Filtration



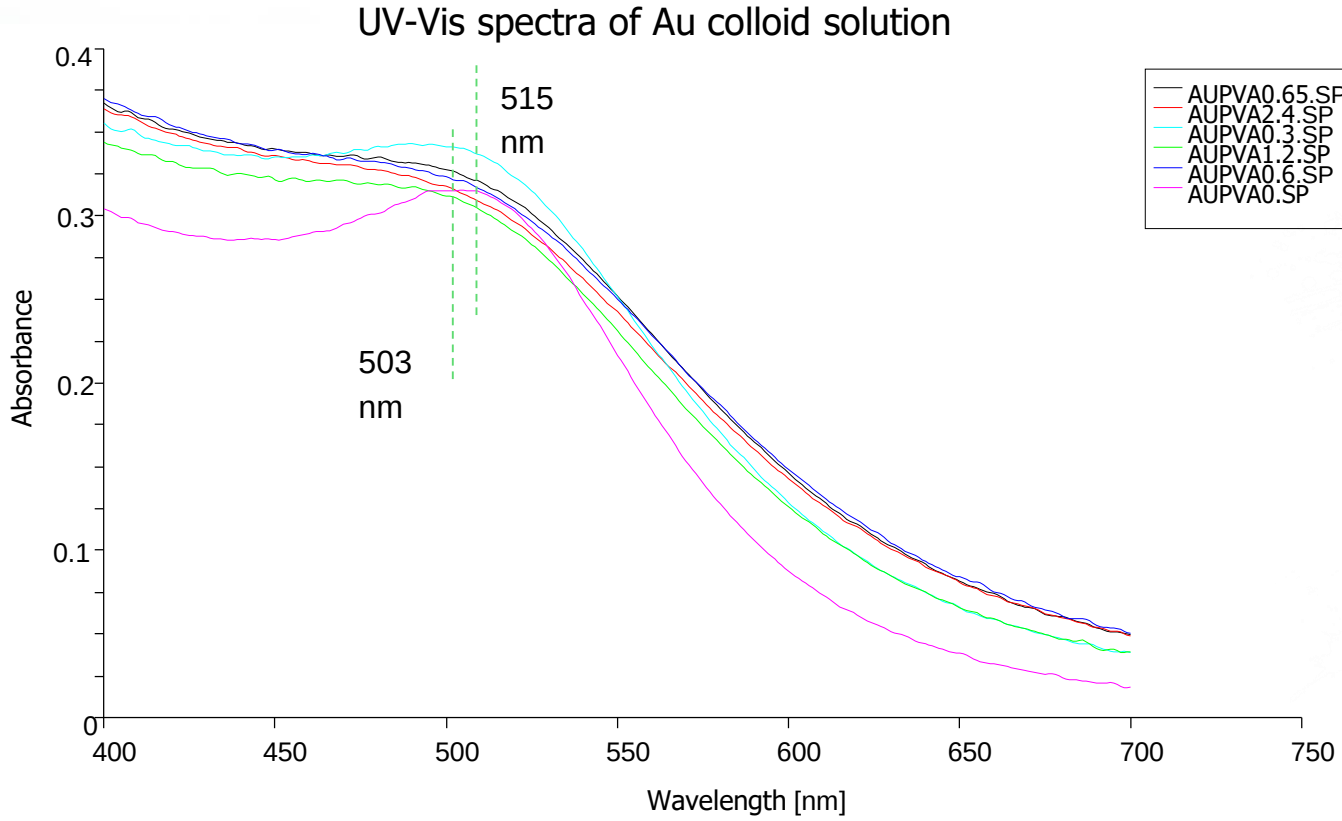
Dry @ 80°C
for 4h

INFLUENCE OF PVA:Au WEIGHT RATIO

PVA:Au weight ratio
0:1
0.3:1
0.6:1
1.2:1
2.4:1

- Study effect of PVA in Au nanoparticles size
- Study the presence of PVA on the surface of the catalyst

INFLUENCE OF PVA:Au WEIGHT RATIO



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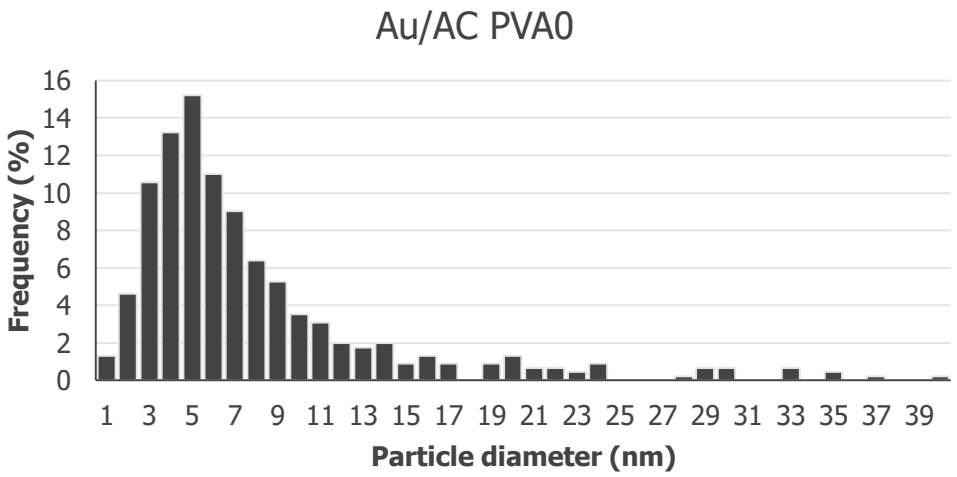
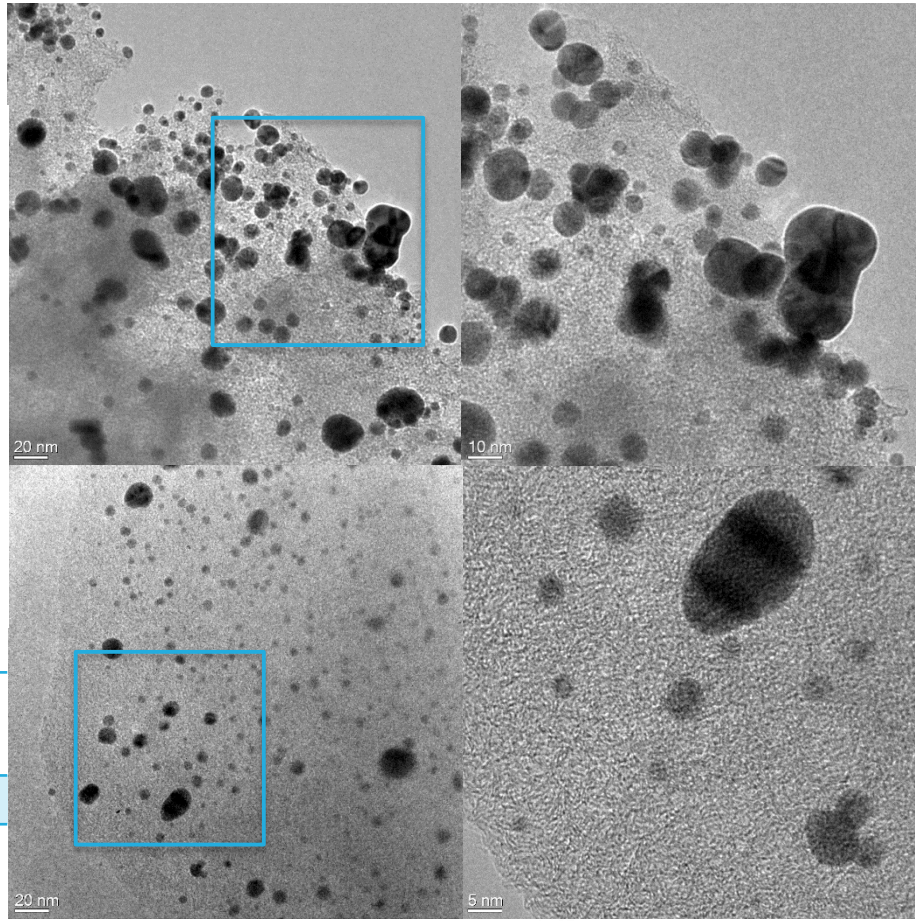


Catalyst	Average particle diameter (nm)	Standard deviation (nm)
Au/AC PVA0	6.6 (particles <20 nm)	3.8



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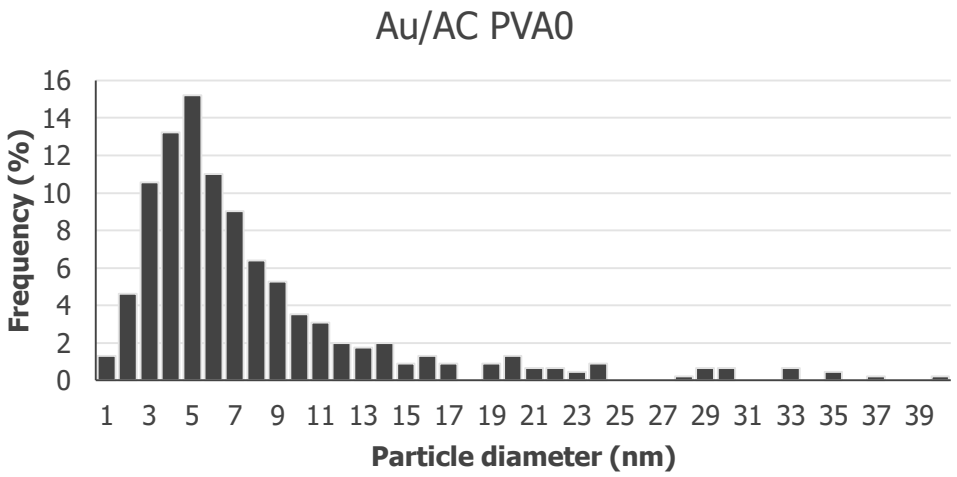
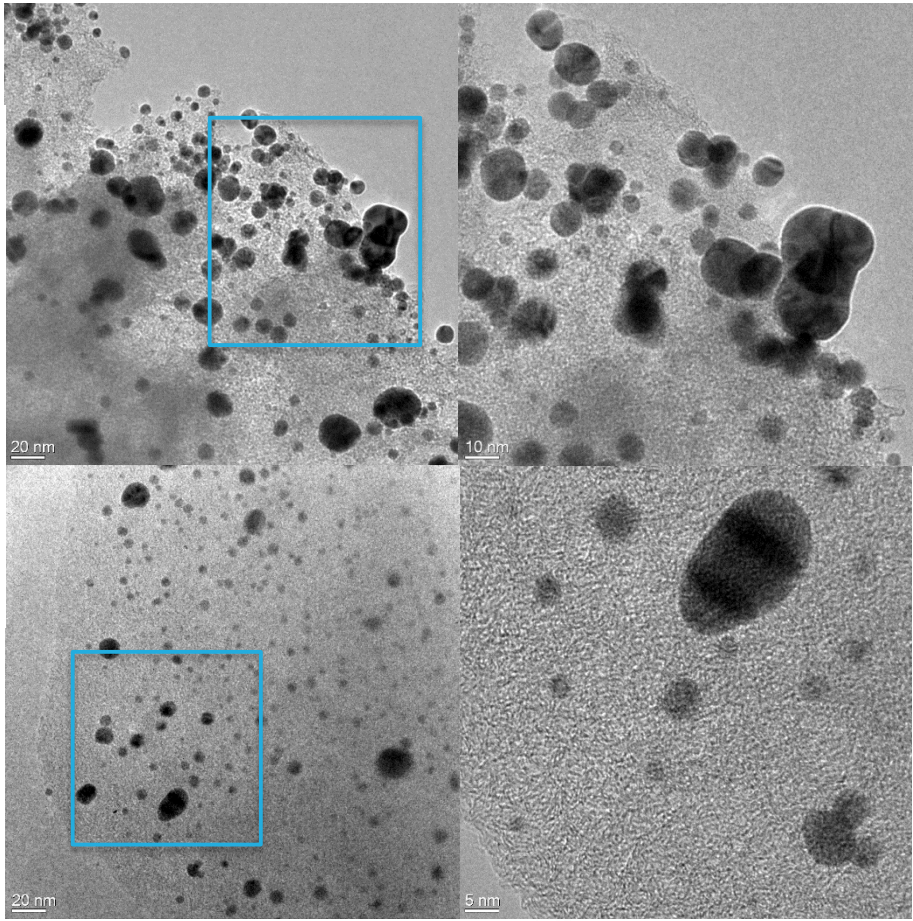
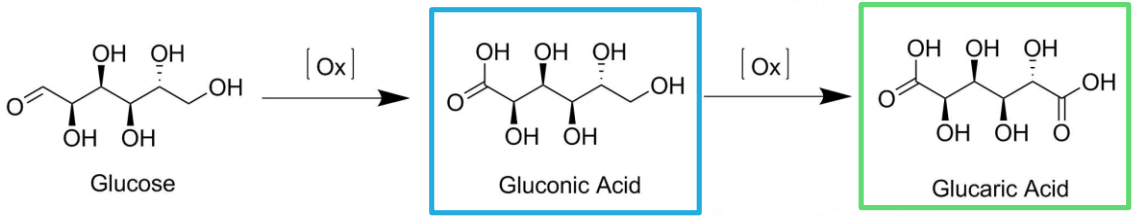
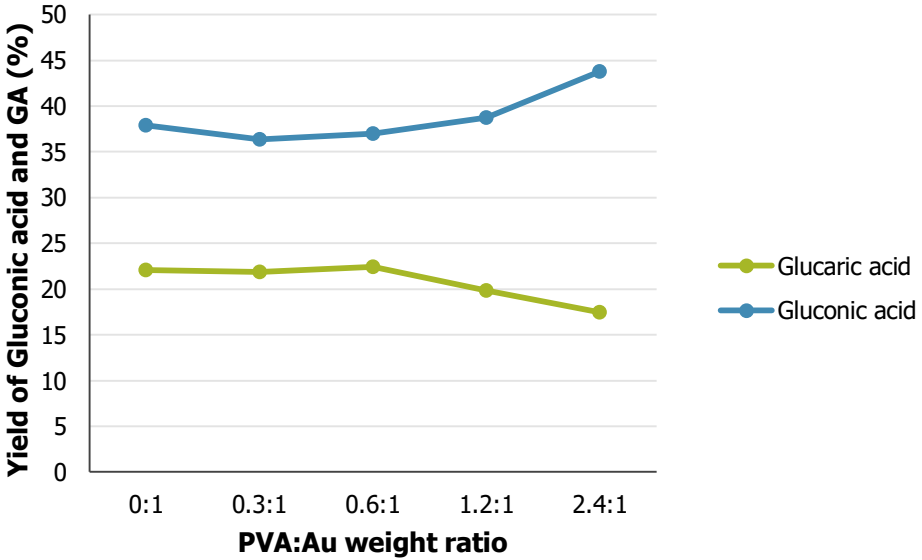


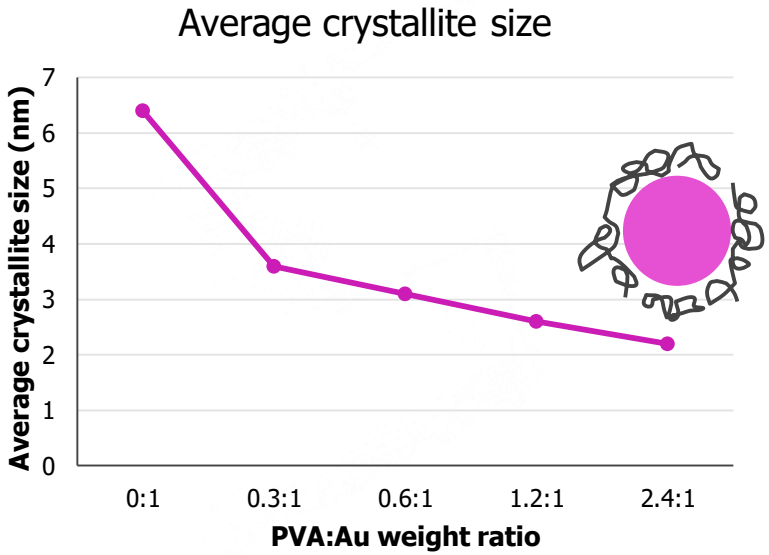
Catalyst	Average crystallite size (nm)
Au/AC PVA0	6.4
Au/AC PVA0.3	3.6
Au/AC PVA0.6	3.1
Au/AC PVA1.2	2.6
Au/AC PVA2.4	2.2



INFLUENCE OF PVA:Au WEIGHT RATIO



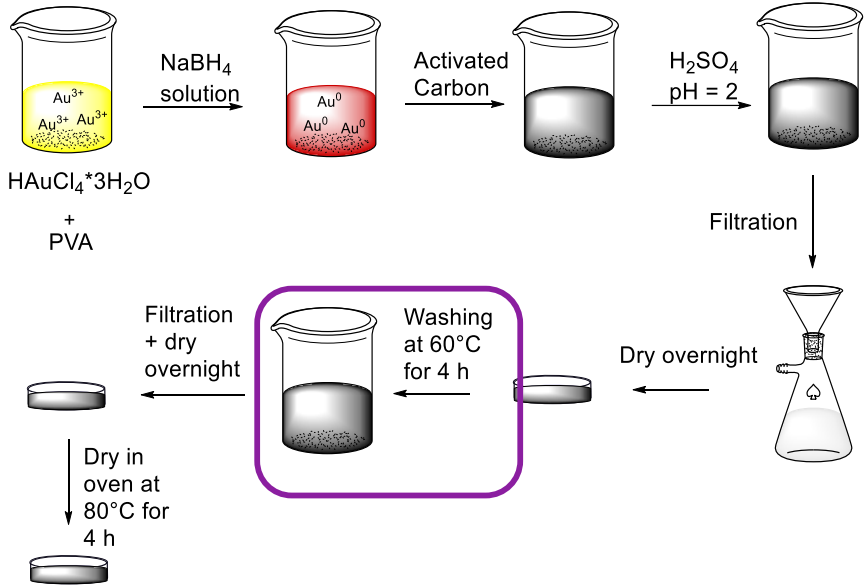




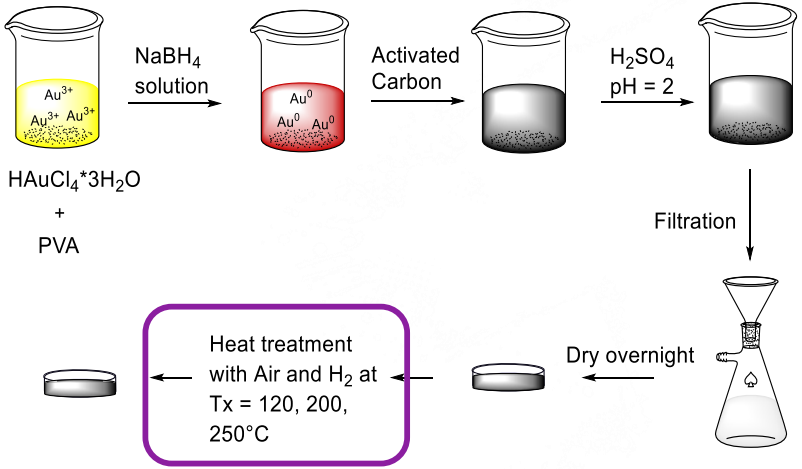
Reaction conditions: 1 h, 60°C, 1000 rpm, 10 bar O_2,
Glu:Au:NaOH molar ratio of 1000:1:3000

PVA REMOVING: WASHING vs HEAT TREATMENT

Washing

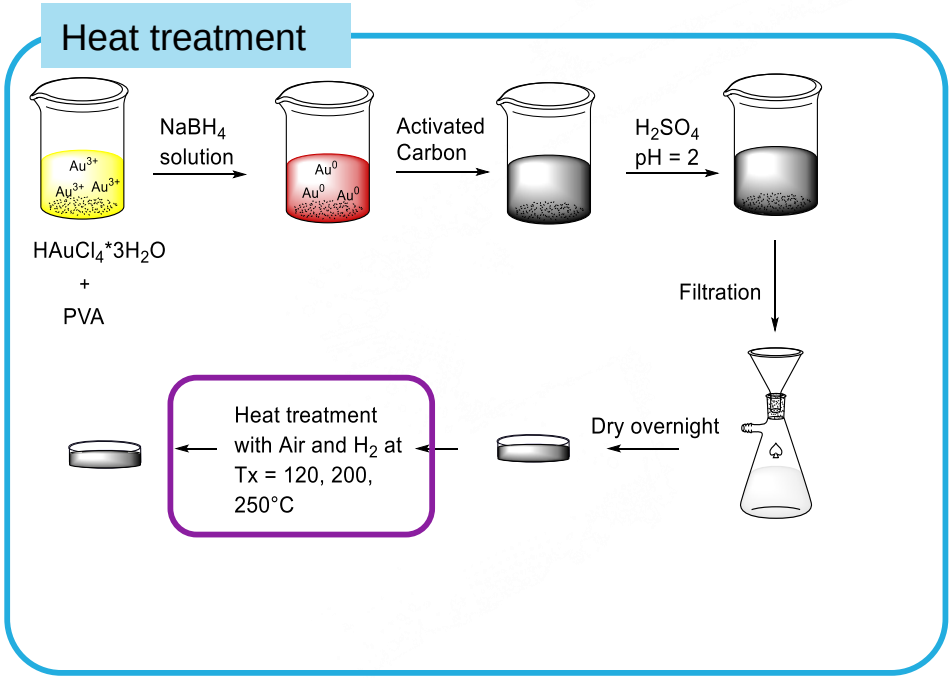


Heat treatment



PVA REMOVING: WASHING vs HEAT TREATMENT

Catalyst	Average crystallite size (nm)
Au/AC HT120°C	2.9
Au/AC HT200°C	4.1
Au/AC HT250°C	7.5



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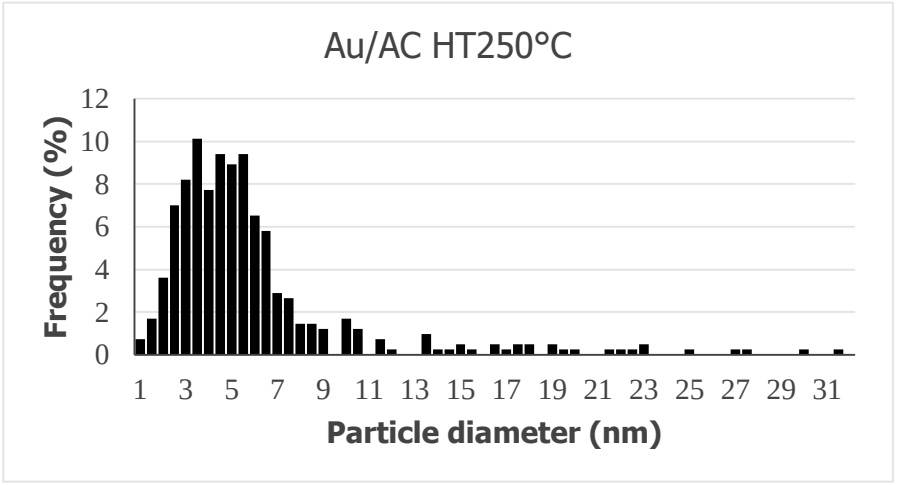
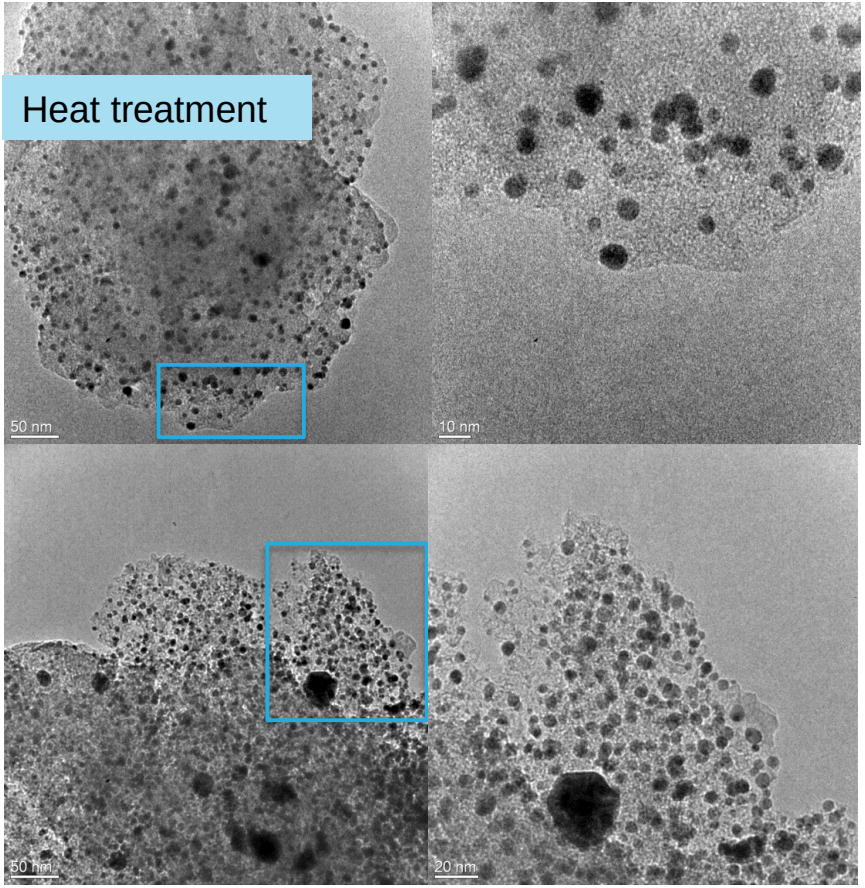


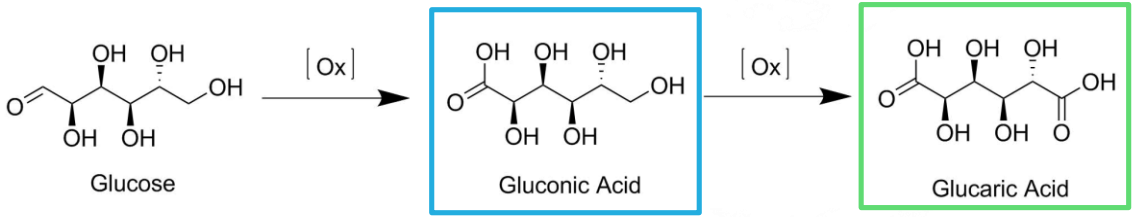
Catalyst	Average particle diameter (nm)	Standard deviation (nm)
Au/AC HT250°C	5.0 (particles <15 nm)	2.4

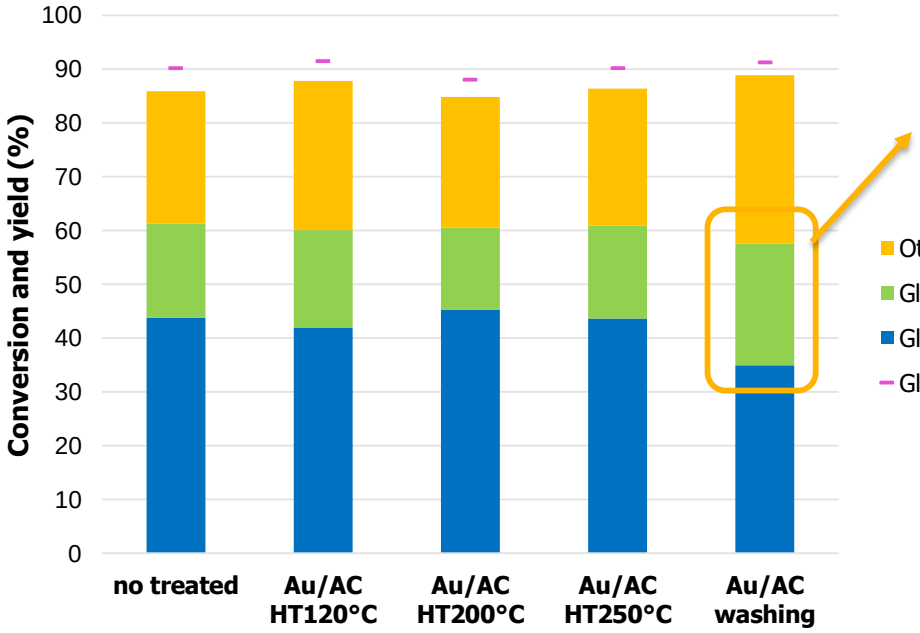
TEM images

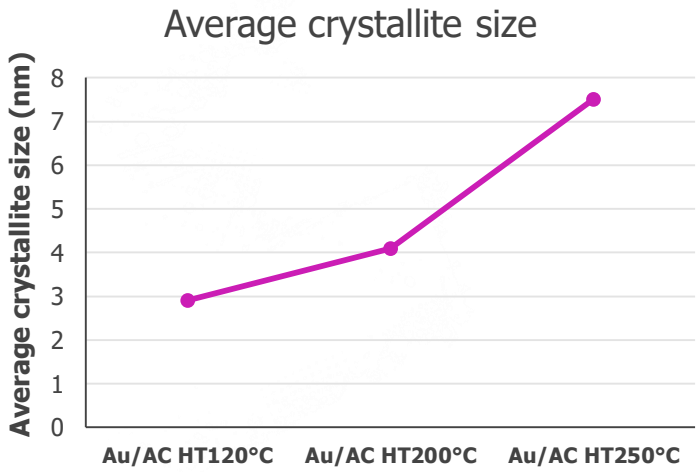


Au/AC HT250°C

PVA REMOVING: WASHING vs HEAT TREATMENT



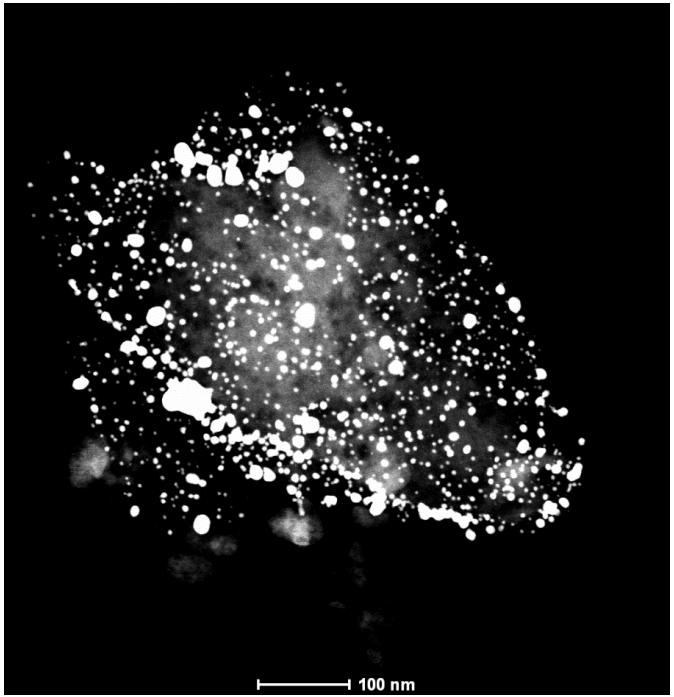




Reaction conditions: 1 h, 60°C, 1000 rpm, 10 bar O_2,
Glu:Au:NaOH molar ratio of 1000:1:3000

EFFECT ON THE DISPERSION

STEM-HAADF images



Au/AC PVA0
Without PVA

Au/AC HT250°C
With PVA

CONCLUSION

Study of reaction: kinetic regime
stirring rate ≥1000 rpm, Au:Glu molar ratio 1:1000, for 1 h of reaction (**24% yield GA**)

Higher PVA concentration in the preparation of Au NPs results in smaller size
Au/AC PVA0, Au/AC PVA0.3 and Au/AC PVA0.6 resulted in the highest formation of GA
(**22% yield GA**)

Method of removal of stabilizing agent:
Washing with water at 60°C (**23% yield GA**)






Thank you for your kind attention