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# CuNPs encapsulated in UiO-66(Zr) and UiO-66(Ce/Zr) as catalysts for $CO_2$ conversion

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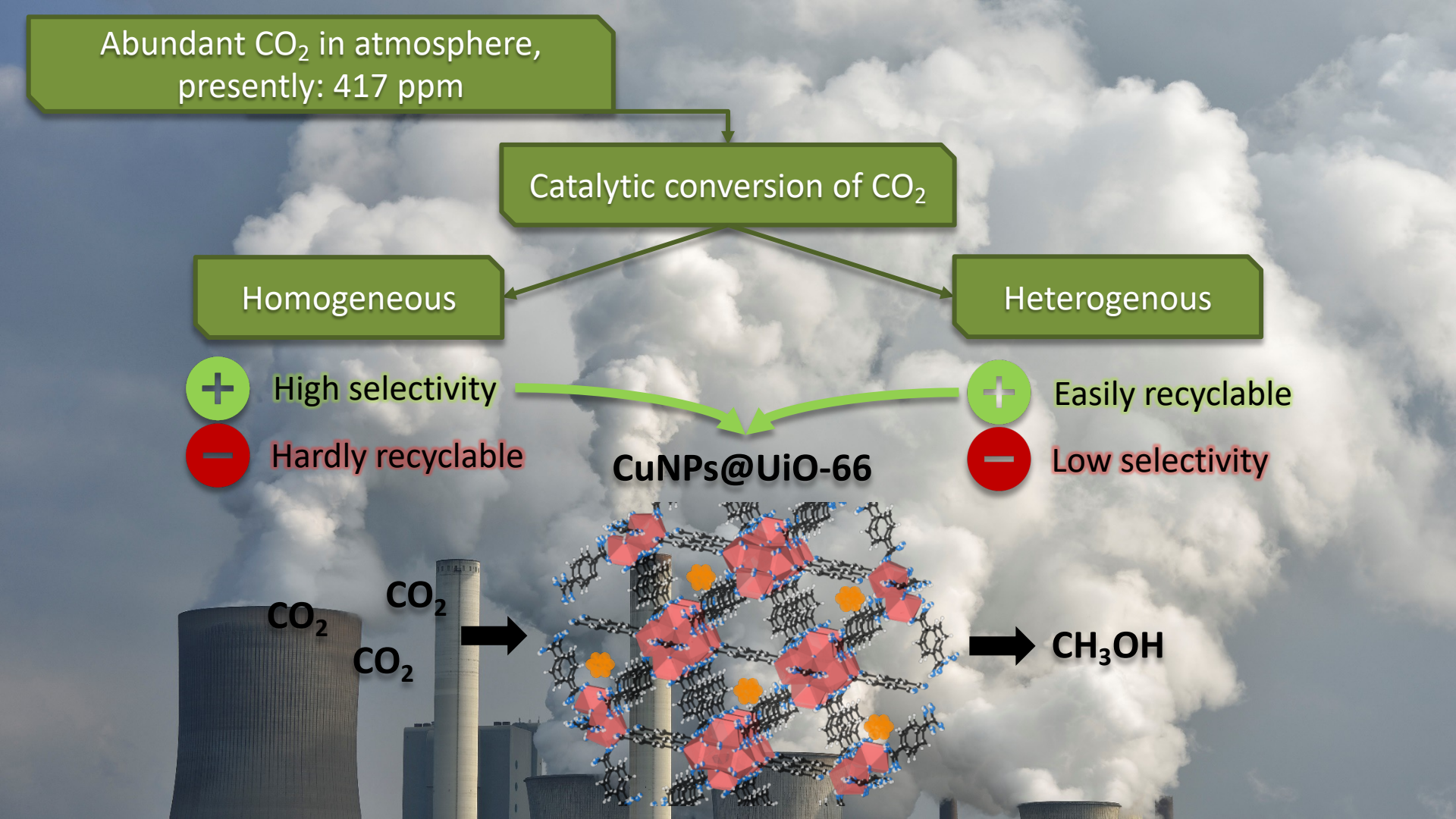

Abundant $CO_2$ in atmosphere, presently: 417 ppm
Catalytic conversion of $CO_2$
Homogeneous
Heterogenous
High selectivity
Hardly recyclable
Easily recyclable
Low selectivity
CuNPs@UiO-66
$CO_2$
$CO_2$
$CO_2$
$CH_3OH$

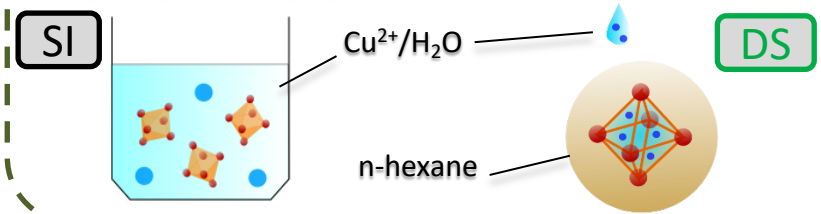
# Preparation of CuNPs@UiO-66 composites

## Ship-in-the-bottle

### Introduction of Cu species

A. Solution infiltration

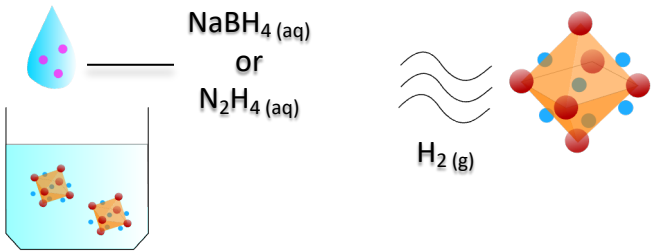
B. Double solvent method




### Reduction of Cu species

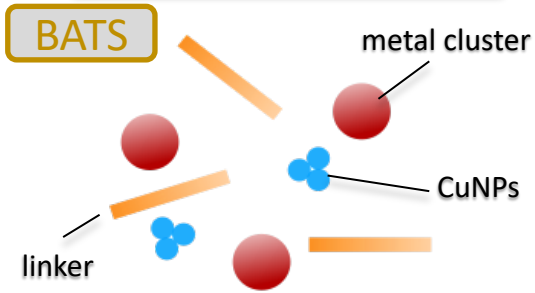
A. In aqueous phase

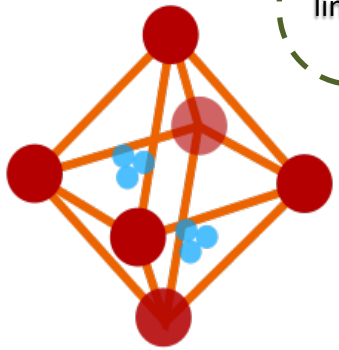
B. In gaseous phase




## Bottle-around-the-ship

### Synthesis with CuNPs

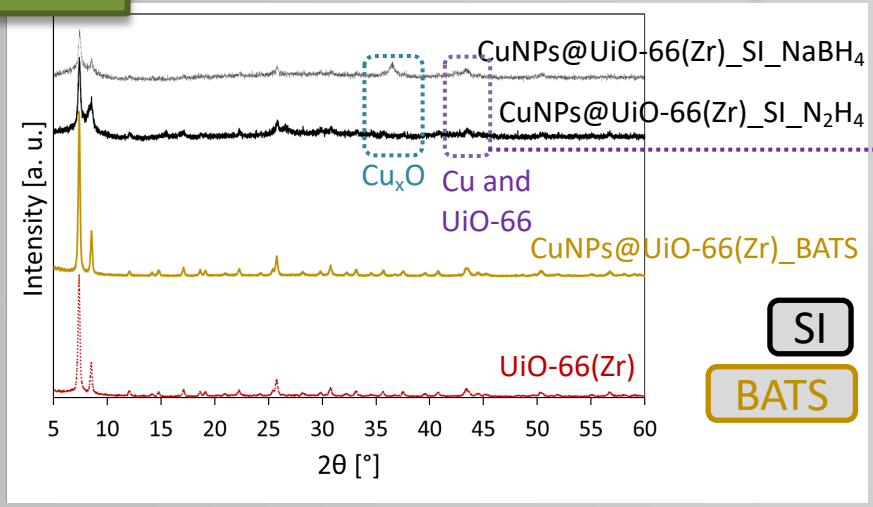


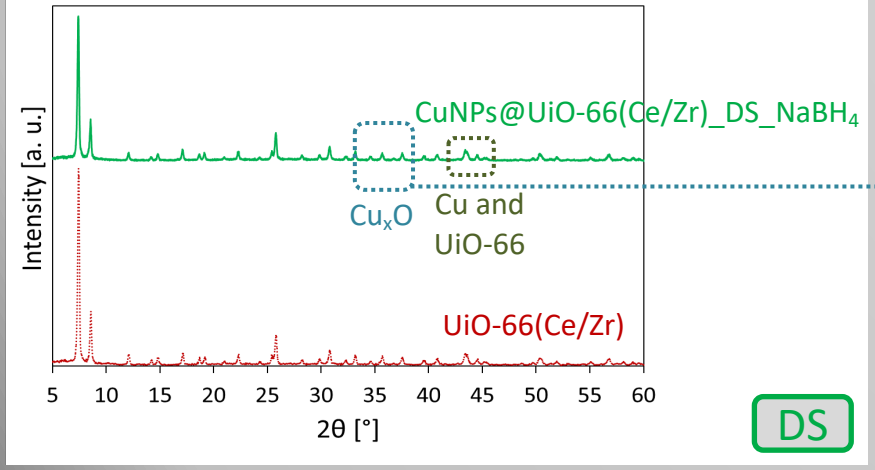



**CuNPs@UiO-66**

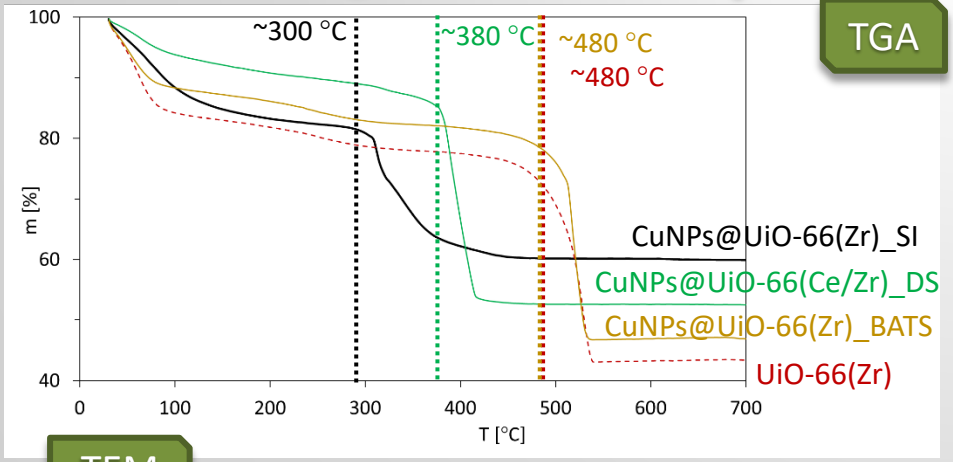
# Properties of CuNPs@UiO-66 composites

PXRD

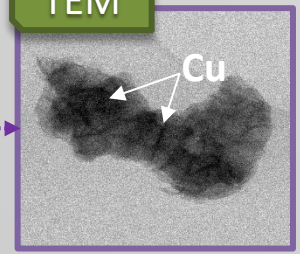


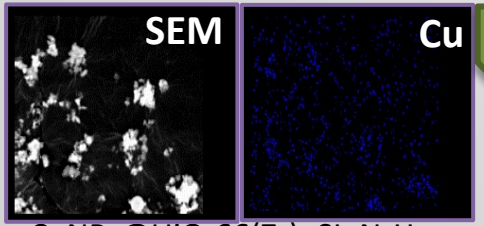

TGA



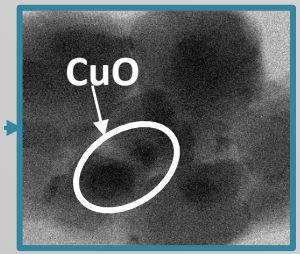

TEM

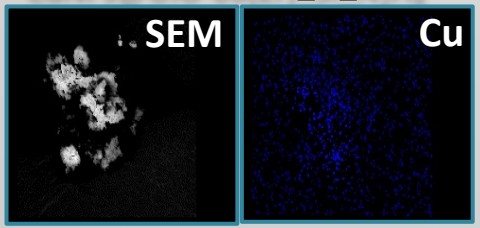



EDS




CuNPs@UiO-66(Zr)_SI_$N_2H_4$



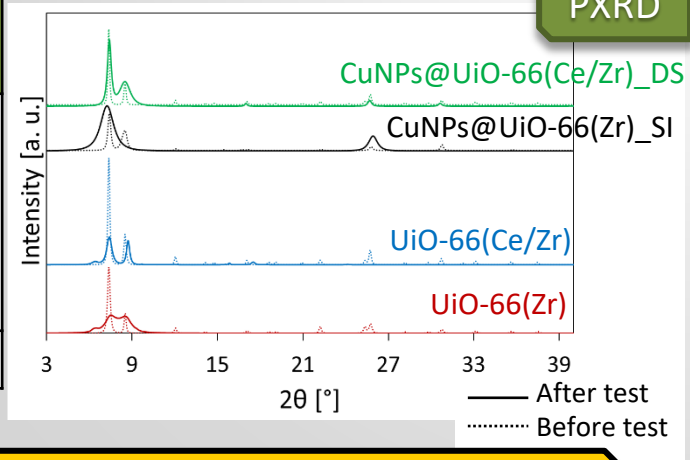

CuNPs@UiO-66(Ce/Zr)_DS_$NaBH_4$

# Catalytic activity of CuNPs@UiO-66 in synthesis of methanol

| Catalyst | Selectivity to MeOH [%] | $STY_{MeOH}$ [μmol $gCu^{-1}$ $h^{-1}$] | T [°C] | p [bar] |
|---|---|---|---|---|
| UiO-66(Zr) | 3,5 | 275 | 200 | 18 |
| UiO-66(Ce/Zr) | 28,7 | 278 | | |
| **CuNPs@UiO-66(Zr)_SI_$NaBH_4$** | **59** | **468** | | |
| **CuNPs@UiO-66(Ce/Zr)_DS_$NaBH_4$** | **56** | **397** | | |
| $Cu/ZnO/Al_2O_3$ [1)] | - | 624 | 230 | 30 |

*200 mg of catalysts, $H_2 : CO_2$ = 3:1, 80 mL/min, t = 25 h, $V_r$ = 300 $cm^3$*

PXRD




| Material | $S_{BET}$ [$m^2g^{-1}$] | |
|---|---|---|
| | Before test | After test |
| UiO-66(Zr) | 1380 | 34 |
| CuNPs@UiO-66(Zr)_BATS | 1435 | - |
| CuNPs@UiO-66(Zr)_SI_$NaBH_4$ | 757 | 217 |
| UiO-66(Ce/Zr) | 1165 | 345 |
| CuNPs@UiO-66(Ce/Zr)_DS_$NaBH_4$ | 647 | 149 |

## Conclusions:

- CuNPs@UiO-66(Zr) synthesized according to bottle-around-the-ship approach, retain crystallinity, thermal stability and SSA of a non-modified UiO-66(Zr).
- Double solvent method has smaller impact on crystallinity and thermal stability of UiO-66 structures, due to use of limited amounts of both impregnating solution and reducing agent.
- Encapsulation of CuNPs in UiO-66 structures significantly rises the catalytic activity of material in reaction of methanol synthesis from $CO_2$, despite the method used to introduce CuNPs.
- After catalytic tests UiO-66 materials maintain crystallinity, however the structure has deteriorated.

1) J. Schumann, T. Lunkenbein, A. Tarasov, N. Thomas, R. Schlogl, M. Behrens, ChemCatChem, 2014, 6, 2889-2897