



# Leveraging templated growth technique to synthesize Cu based metastable, bimetallic phosphide nanoparticles

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ACKNOWLEDGEMENTS



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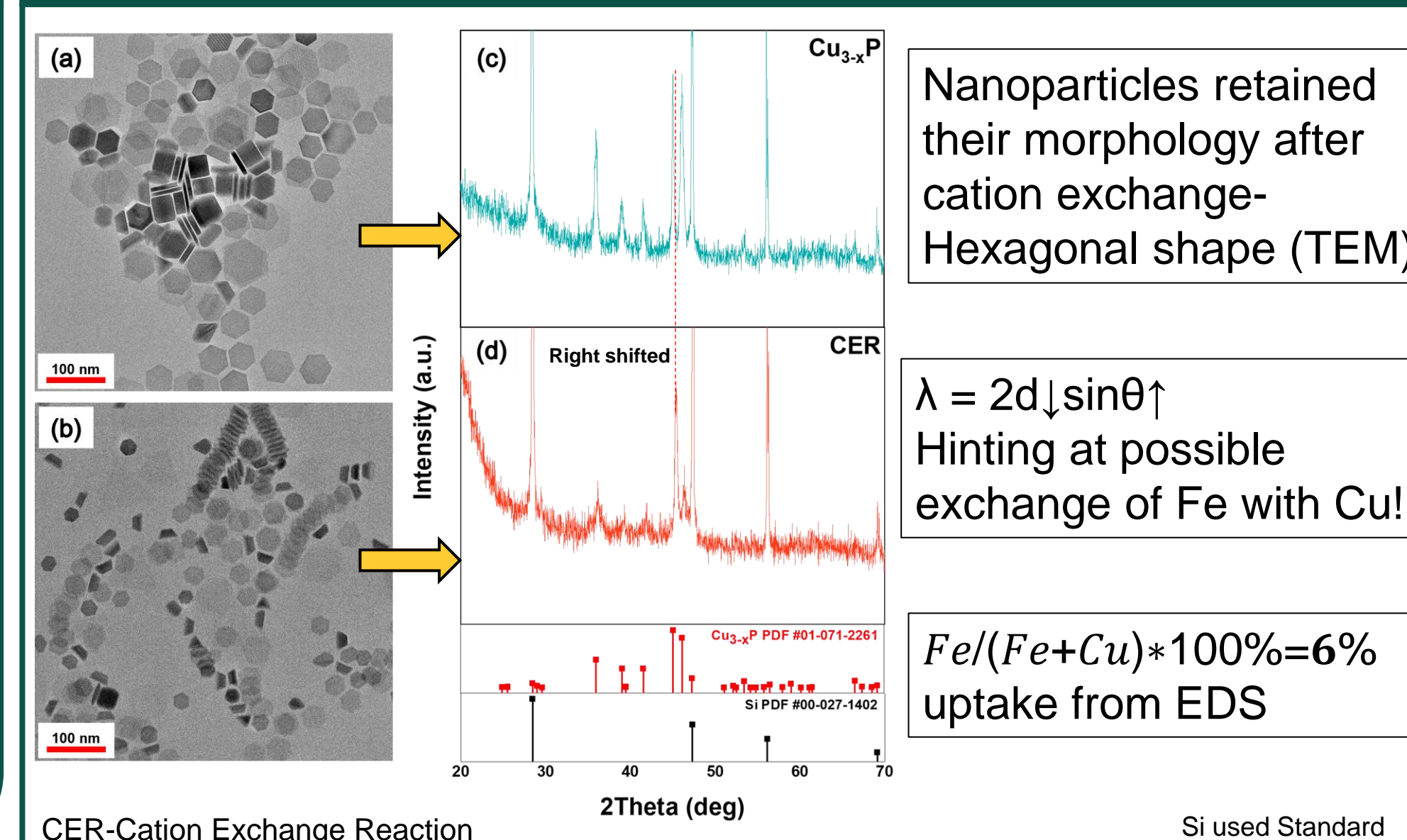
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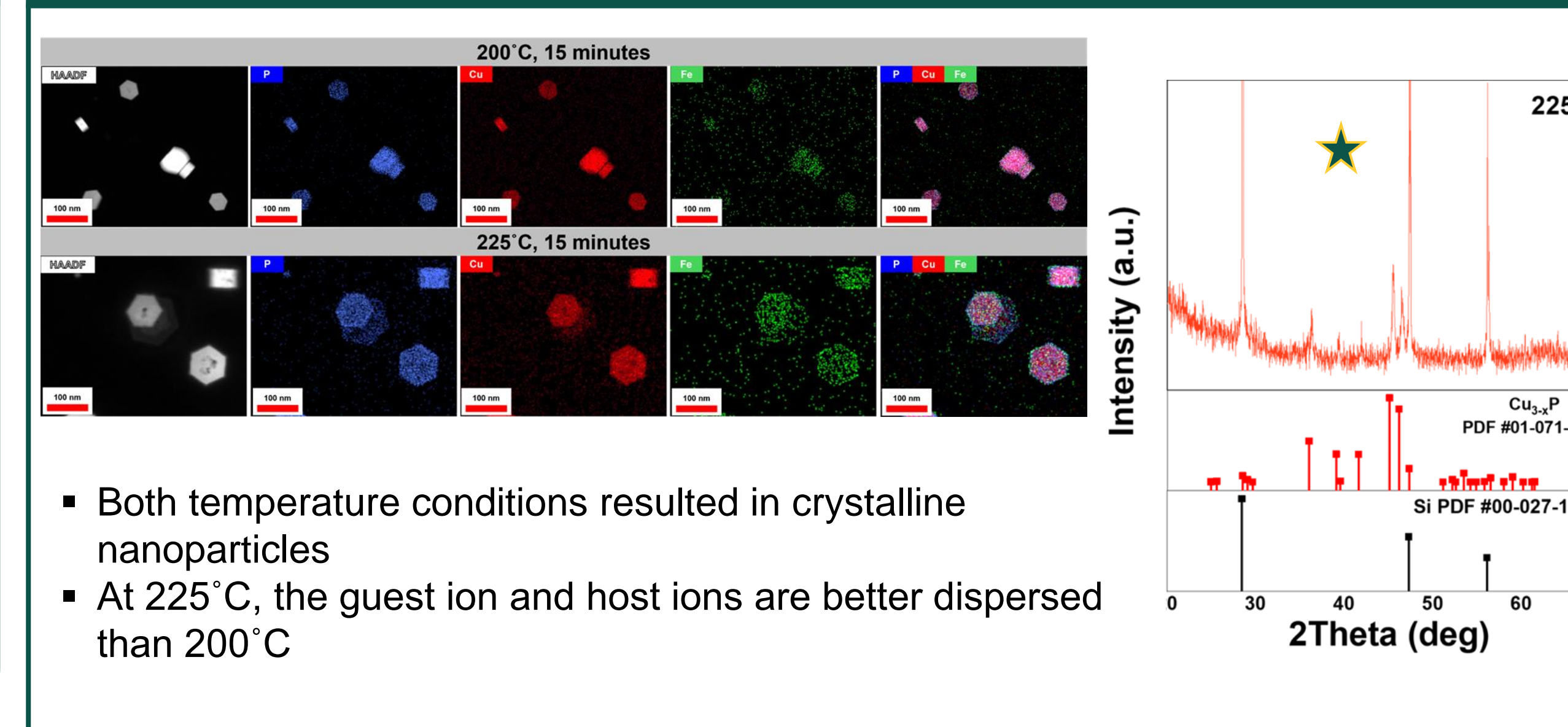
## MOTIVATION

- Transition metal phosphide (TMP) nanoparticles are known as active water splitting catalysts – both for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER)
- Bimetallic phosphides exhibit higher catalytic activity compared to their monometallic counterparts
- $Cu_{3-x}P$  is also an active catalyst for HER and OER, e.g., for copper phosphide microsheets,  $\eta_{HER}$  is 130 mV, whereas  $\eta_{OER}$  is 290 mV
- No known Cu based bimetallic phosphide phases exist with the other late, first row transition metals, M = Fe, Co and Ni in bulk or nano regime, to the best of our knowledge
- Can we synthesize these bimetallic CuMP phases?

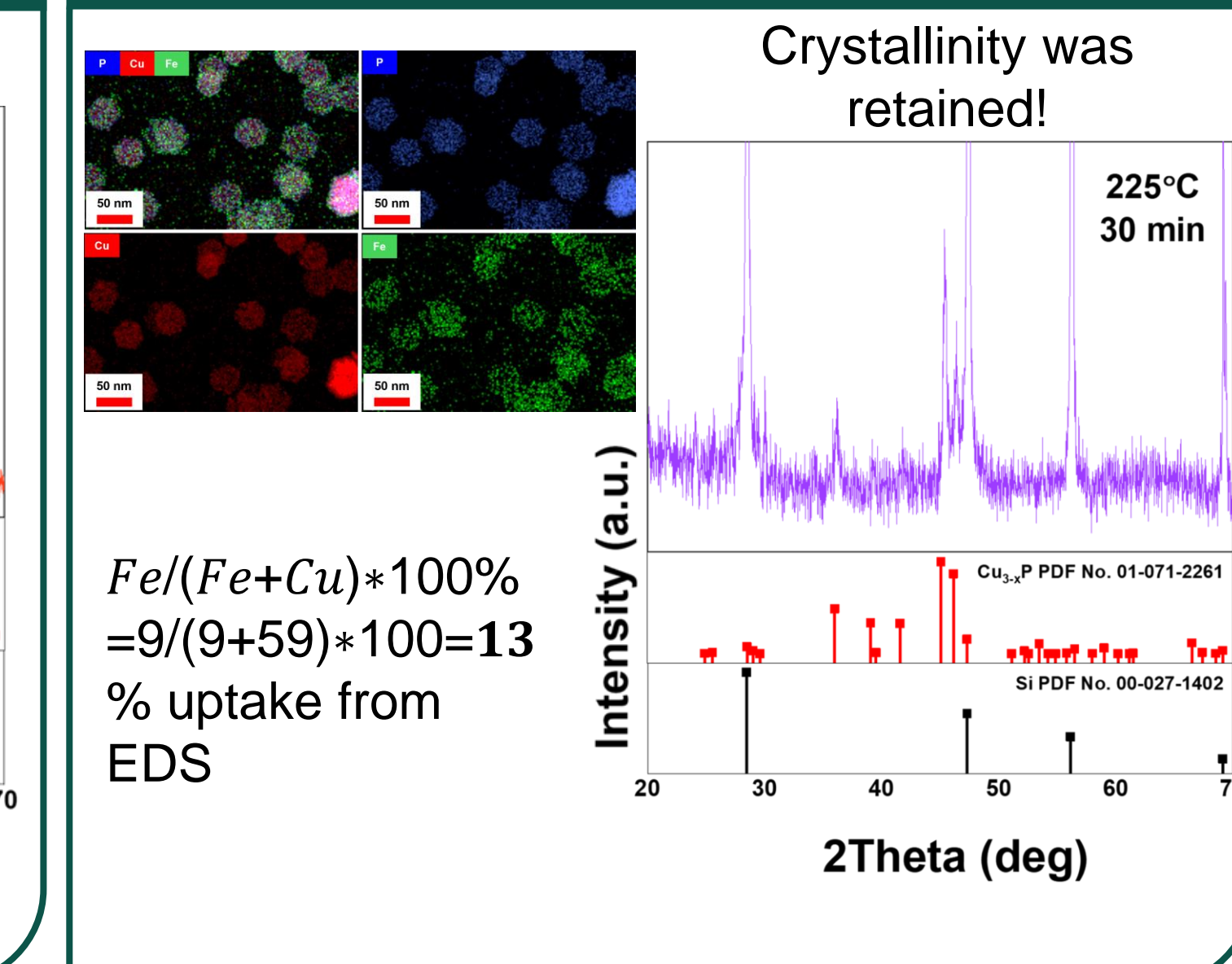
## BEFORE AND AFTER CATION EXCHANGE



## Effect of temperature (Using 1.5 mL TOP, t = 15 minutes)



## MOST OPTIMIZED CONDITION



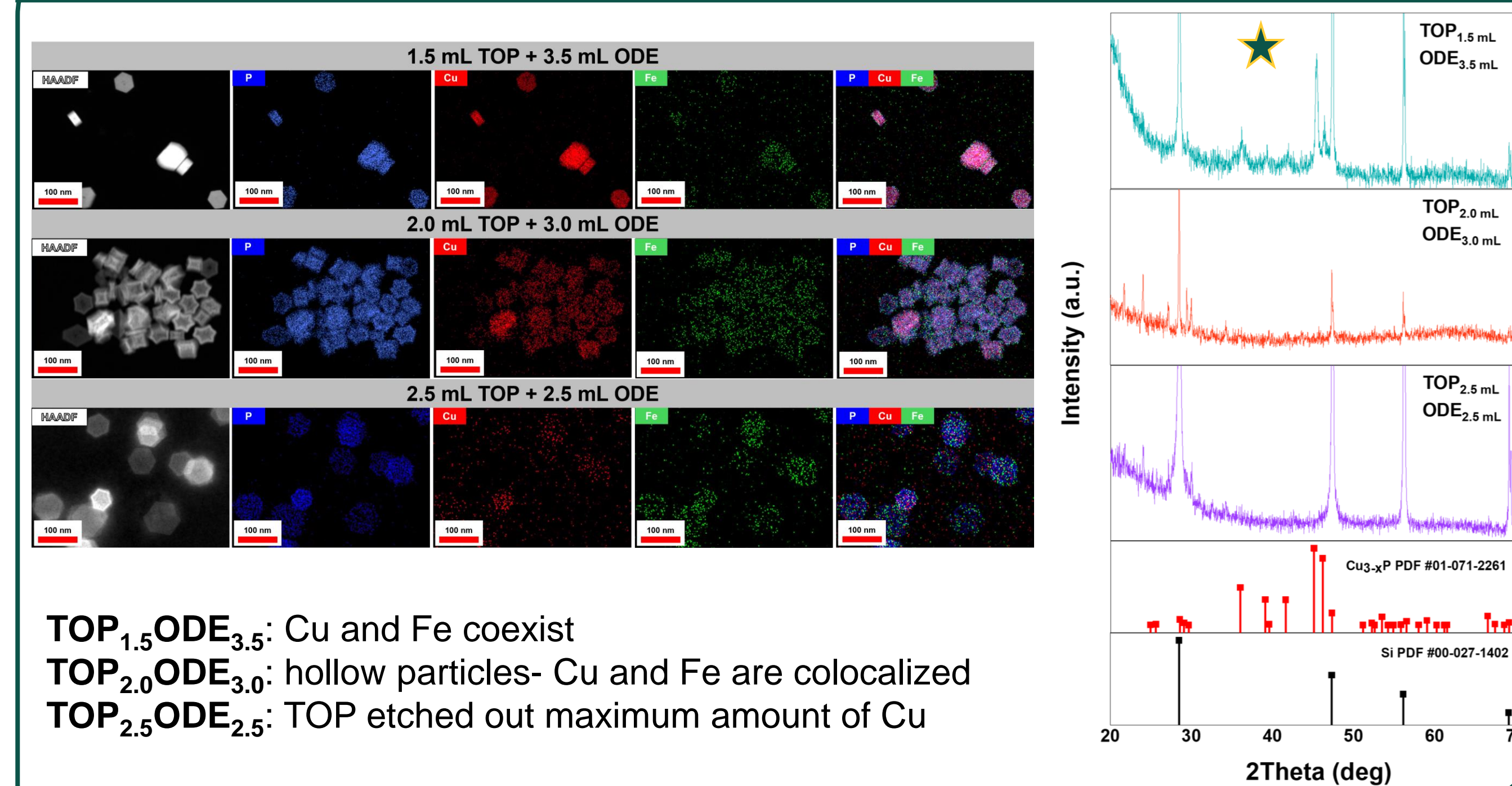
## BACKGROUND

- $Cu_{3-x}P$  nanoparticles can undergo cation exchange with  $In^{3+}$  forming metastable, wurtzite  $InP$  crystalline products
- Cation exchange is not common for metal pnictides, exception-copper phosphide ( $Cu_{3-x}P$ )
  - Inherent vacancies in the  $Cu_{3-x}P$  crystal structure
  - Partial ionic character enabling cation mobilization
- $Cu_{3-x}P$  might be leveraged as a template to perform cation exchange with other host metal ions

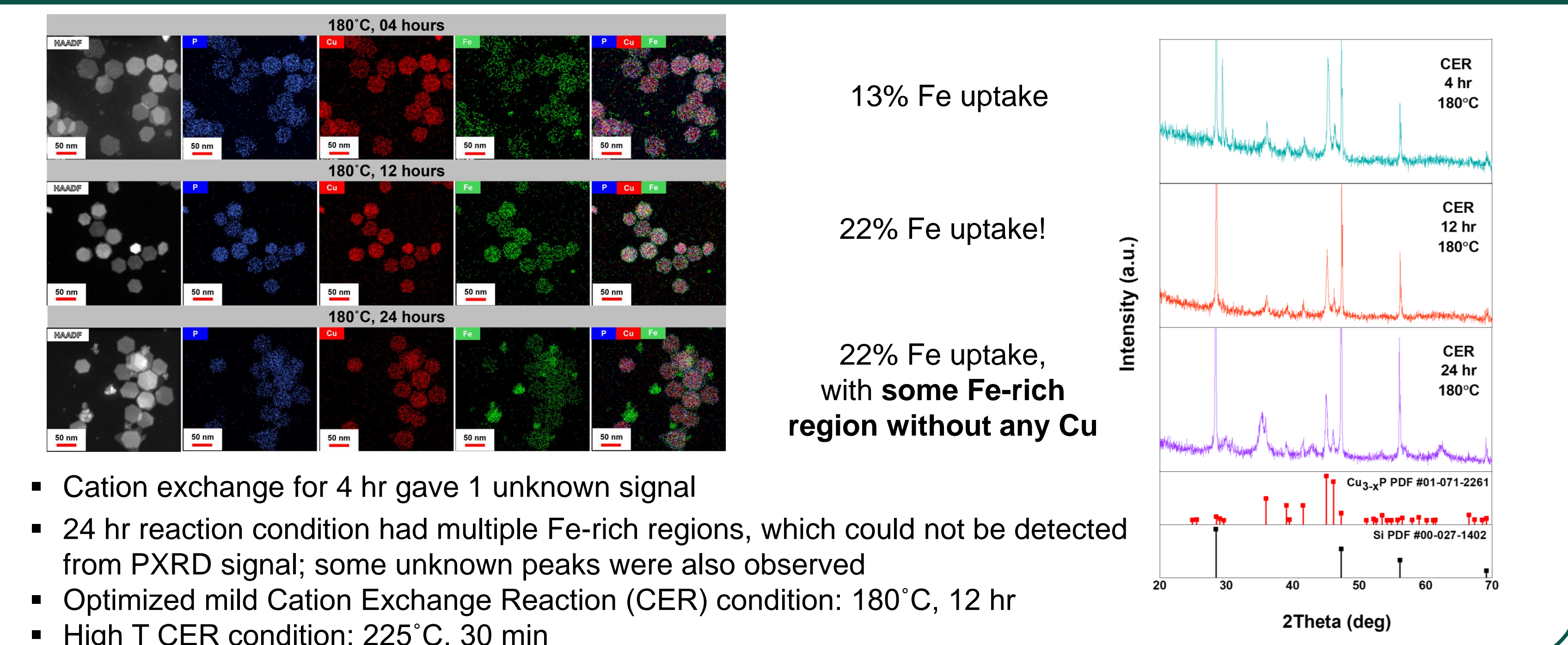
## GOALS OF THIS STUDY

- Evaluate exchangeability of  $Cu_{3-x}P$  with guest metal ion, Fe as a function of temperature and time and solvent composition
- Mapping out the extent of Fe uptake as well as establishing a useful "phase diagram" for the synthesis of copper-containing multimetallic phosphides

## OPTIMIZING THE AMOUNT OF SOLVENT, TOP AND ODE



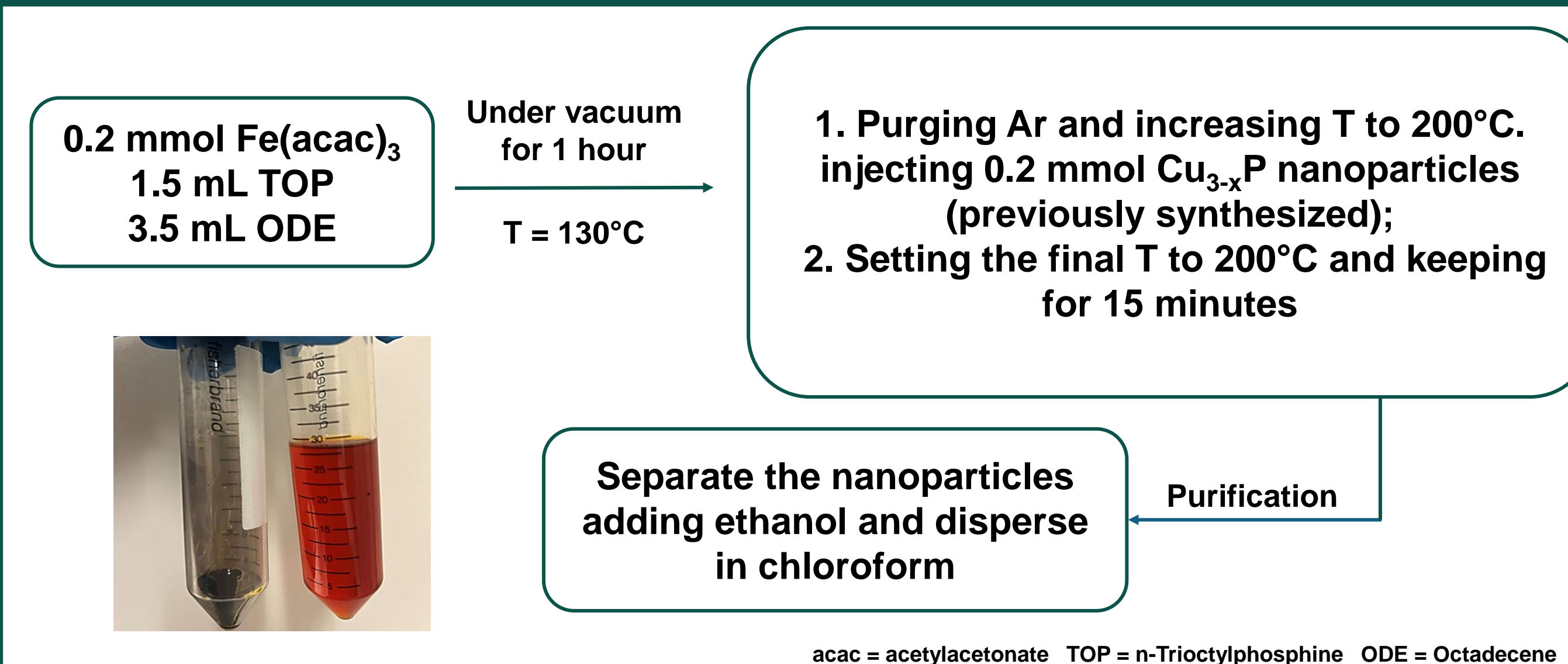
## CATION EXCHANGE OF $Cu_{3-x}P$ IN LOWER T (Temperature), LONGER t (TIME)



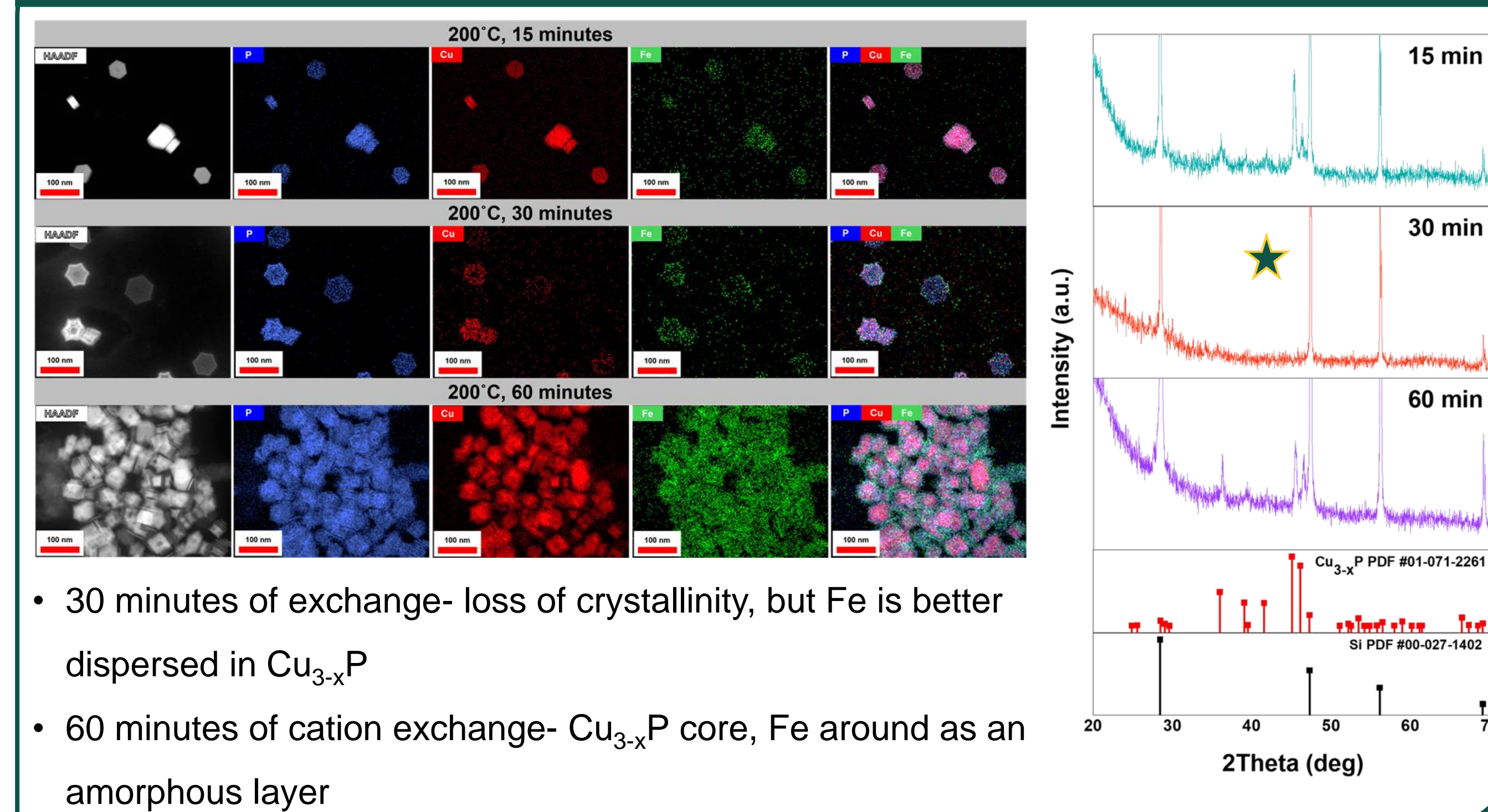
## PRELIMINARY INVESTIGATION

$Fe^{III}$  exchange with  $Cu_{3-x}P$ , where  $x = 0.2-0.3$  (No exchange observed for  $Ni(II)$  or  $Co(II)$  precursors)  
**Hypothesis:** Exchange reaction might be mediated as well as augmented via a redox mechanism as,  
 $Fe^{3+} + Cu^+ \rightleftharpoons Cu^{2+} + Fe^{2+}$ , which is opposed to  $In^{3+}$  cation exchange in  $Cu_{3-x}P$  template as  $In^{3+}$  is difficult to reduce  
**Prediction:** Unit cell dimension might change due to different ionic radii of the incoming and outgoing ions; PXRD data might be shifted as  $\lambda = 2d \sin\theta$ ; changes in  $2\theta$  positions would be indicative of changes in d values

## GENERAL REACTION SCHEME



## Effect of time (Using 1.5 mL TOP, T = 200°C)



## REFERENCES

- De Trizio, Luca, et al, Chemistry of Materials 27.3 (2015): 1120-1128
- Greeley, Jeff, et al, Nature materials 5.11 (2006): 909-913
- Li, Junzhi, et al, Journal of materials chemistry A 5.28 (2017): 14828-14837

## FUTURE WORKS

- Understanding the cation exchange mechanism, working hypothesis for exchange is-  $Fe^{3+} + Cu^+ \rightarrow Fe^{2+} + Cu^{2+}$ 
  - Conducting cation exchange without TOP to see the Fe uptake
  - Instead of taking  $Fe^{3+}$  precursor,  $Fe(acac)_2$  can be used
- Confirming Cu-deficiency after vacancy modulation via LSPR peak position

THANKS FOR VISITING THE POSTER!

## MAPPING Fe UPTAKE LIMIT via VACANCY MODULATION

