

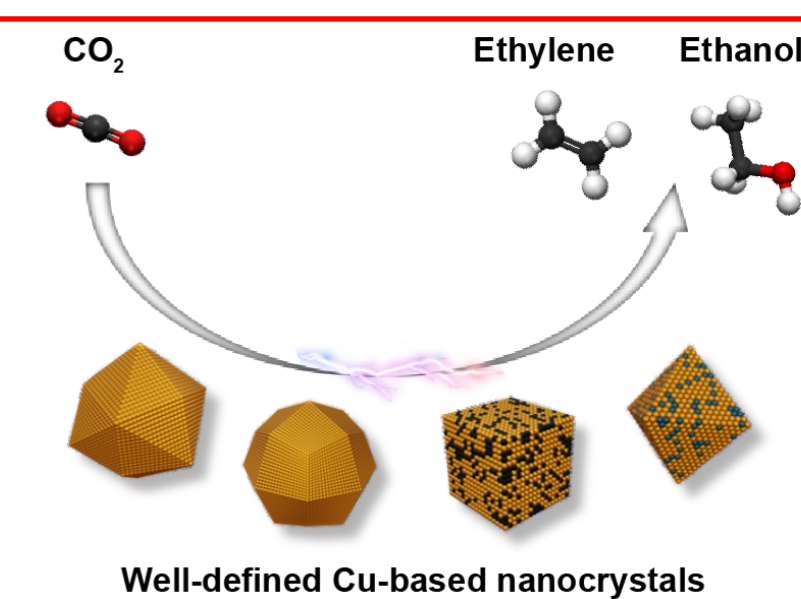
Synthesis of Copper Nickel bimetallic nanocrystals

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Abstract

Rising concentration of carbon dioxide (CO₂) in the atmosphere has to considerable environmental catastrophe^[1]. Fighting this increase in concentration has proven to be a challenge do its very stable nature. In a race against time, multiple technologies are being developed to control our carbon dioxide emissions. One of these technologies consists of transforming CO₂ into more economically viable molecules, such as fuels, through carbon dioxide reduction reaction (CO₂RR).

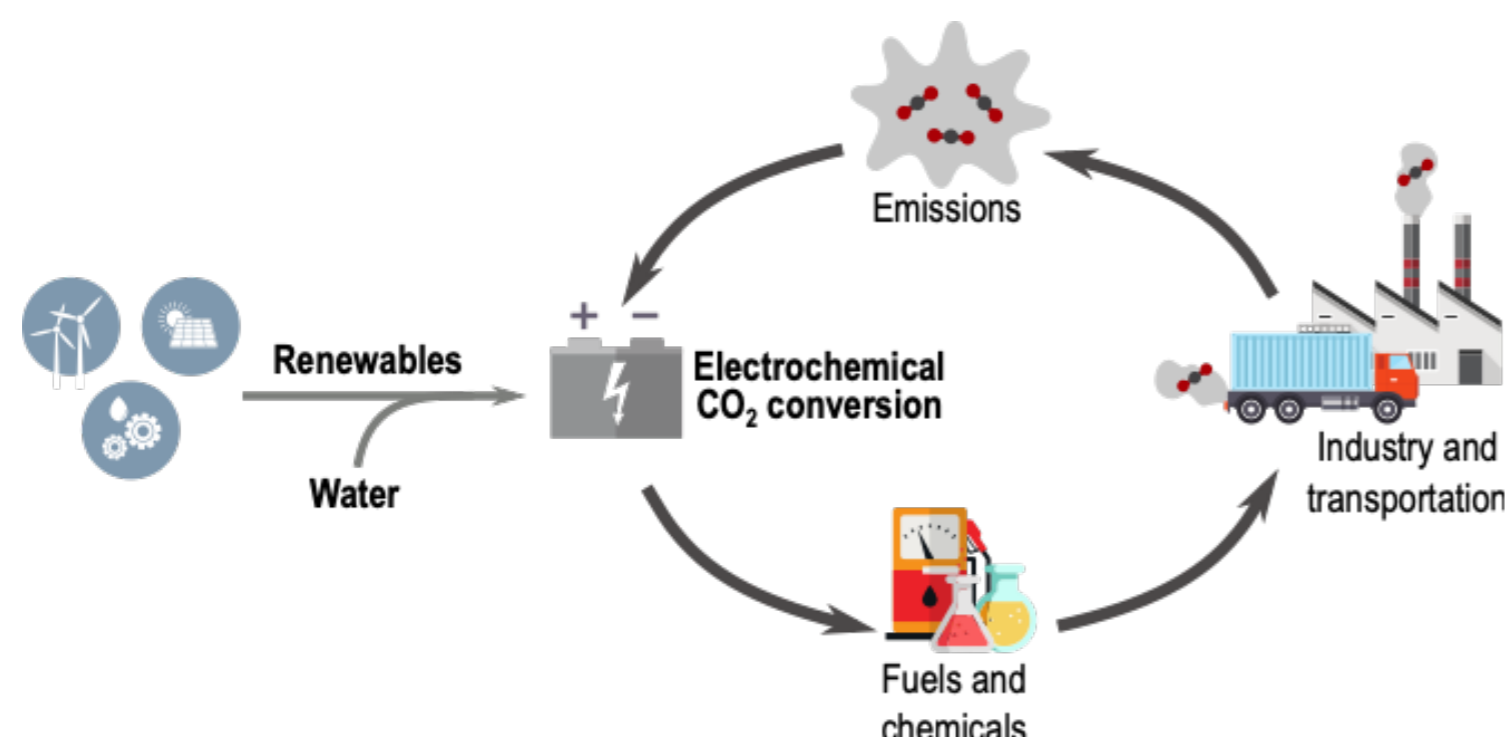
The challenge with this method is to find a cheap and reliable catalyst to use in this reaction. Possible catalysts are Copper-based nanocrystals (NCs) which allow to obtain molecules interesting for industry, with varying selectivity based on its characteristics^[2]. However, the synthesis of these NCs remains a process of trial and error. During my summer project, I aimed to better understand how to synthesize Copper-Nickel NCs with controllable size, shape and composition.



What is CO₂RR?

CO₂RR is the transformation of CO₂ into more useful and economical viable molecules (such as ethylene, methane, ethanol, etc.). These molecules can be used in many industries such as fuels, medicine and cosmetics. **The challenge is to find a catalyst that can enable this reaction with high selectivity and stability.**

Sustainable production of fuels and chemicals from CO₂RR

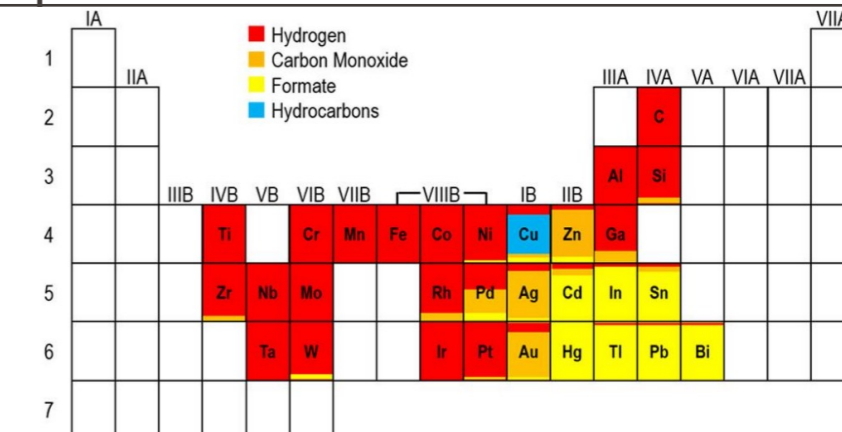


Copper Nickel NCs as CO₂RR catalyst

Why add Nickel (Ni)?

- Could enhance selectivity^[6] and stability^[7]
- Also has a relatively low carbon footprint from its extraction

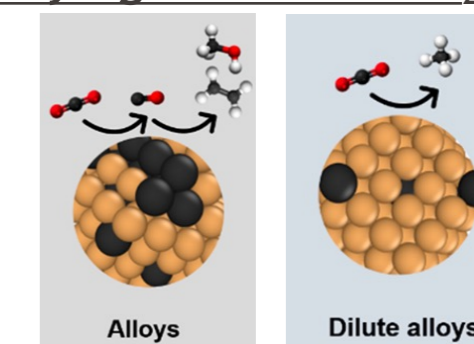
Major products from each element after CO₂RR^[8]



Open questions:

- Achieving controllable shapes, composition and size
- Understanding the formation of this bimetallic nanocrystals

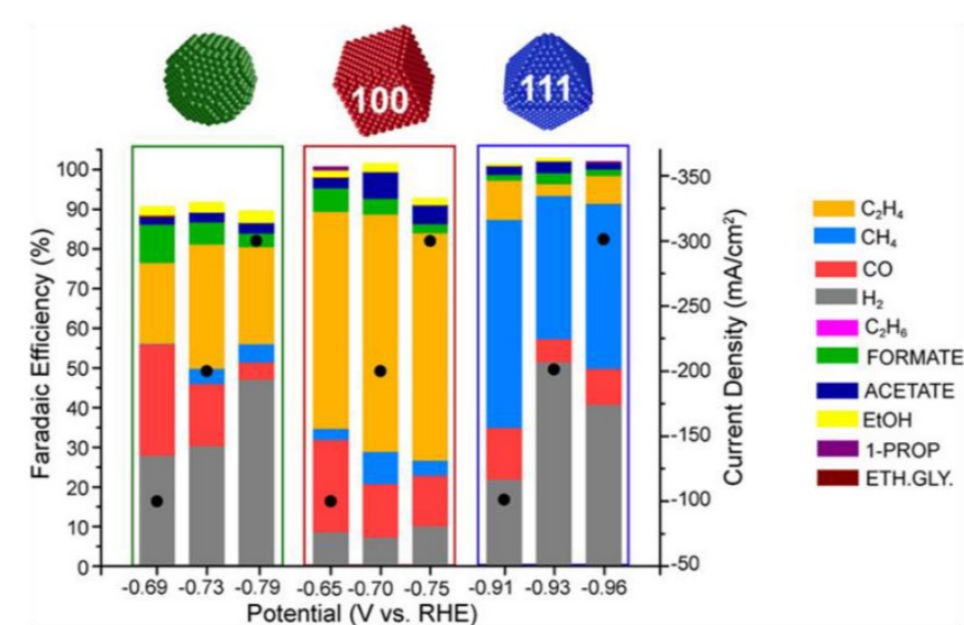
Alloying effect on CO₂RR^[2]



Why nanocrystals as possible solution?

Copper (Cu) is the only metal able to transform CO₂ into hydrocarbon products.^[3] However simple Cu foil shows very low selectivity during CO₂RR, indeed up to 16 different products are obtained!^[2]

Shape effect on CO₂RR selectivity^[4]



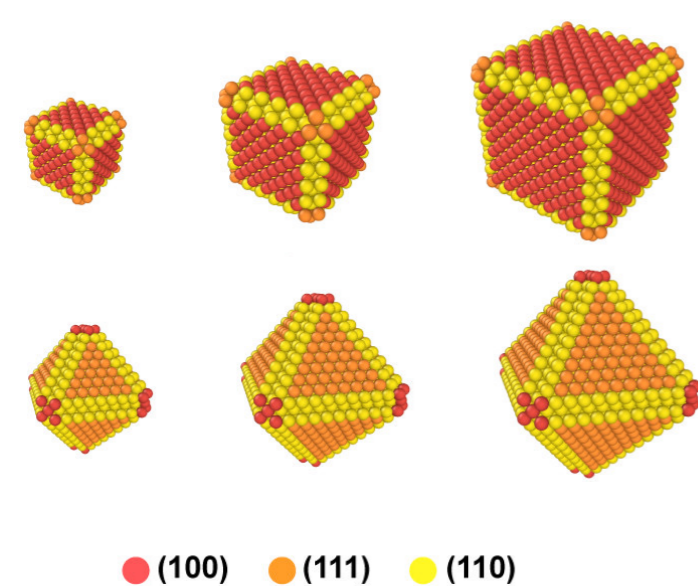
Buonsanti's group has demonstrated that to increase selectivity, NCs can be used. Indeed, cubes generate mostly ethylene and octahedra mostly methane. ^[2,4]

Yet, selectivity and stability of those catalyst needs to be improved for real application.

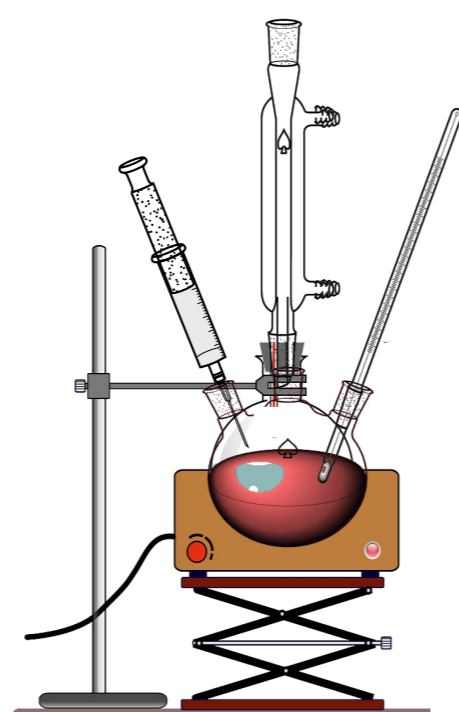
Colloidal chemistry to synthesize NCs:

Just like a chef mixing ingredients at the right temperature to make their perfect dish. We use different molecules and temperatures to try and obtain our NCs. By changing these variables, we can obtain different NCs.

How NCs change with size and shape^[5]



Typical set-up for colloidal chemistry

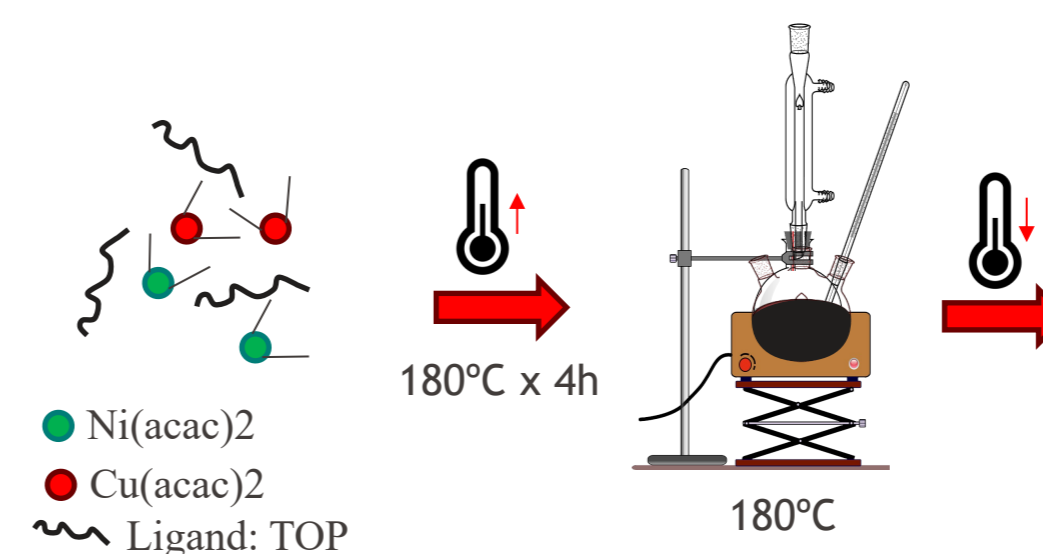


References

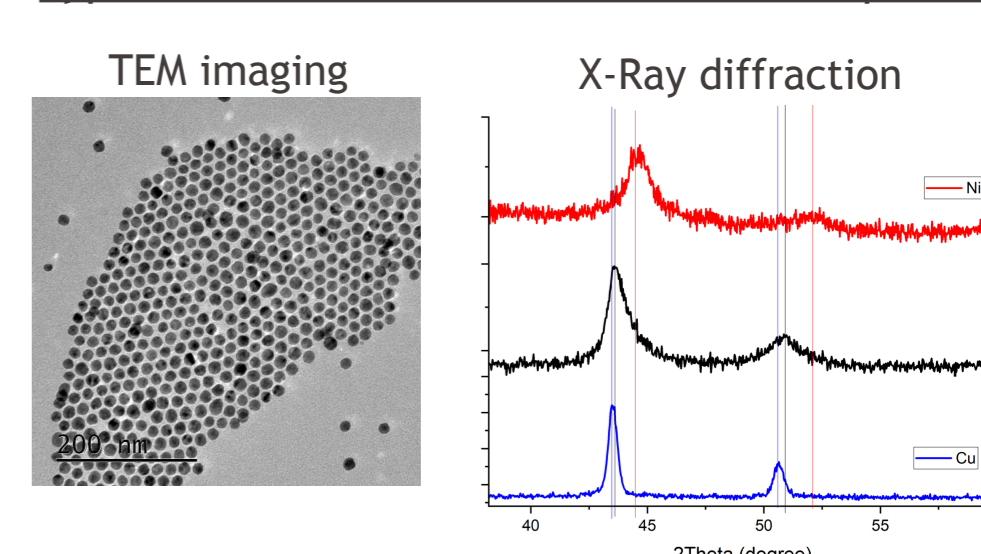
- NOAA Global Monitoring Laboratory, "Green House gases continue to increase rapidly in 2022", 2023. Available: <https://www.noaa.gov/news-release/greenhouse-gases-continued-to-increase-rapidly-in-2022> [Accessed 19 September 2023]
- L. Zaza, K. Rossi, R. Buonsanti, *ACS Energy Lett.*, 2022, 7, 4, 1284-1291.
- J.L. White, M.F. Baruch, J.E. Pander III, Y. Hu, I.C. Fortmeyer, J.E. Park, T. Zhang, K. Liao, J. Gu, Y. Yan, T.W. Shaw, E. Abelev, A.B. Bocarsly, *Chem. Rev.* 2015, 115, 23, 12888-12935.
- G.L. De Gregorio, T. Burdyny, A. Loiudice, P. Iyengar, W.A. Smith, R. Buonsanti, *ACS Catal.* 2020, 10, 9, 4854-4862.
- K. Rossi, R. Buonsanti, *Acc. Chem. Res.* 2022, 55, 5, 629-637.
- T.M. Suzuki, T. Morikawa, *Chem. Commun.*, 2020, 56, 15008-15011.
- Y. Yan, Z. Zhao, Y. Xu, Y. Zhao, W. Tang, J.-M. Lee, *ACS Materials Lett.* 2021, 3, 8, 1143-1150.
- J.L. White, Y. Hu, I.C. Fortmeyer, J. Gu, A.B. Bocarsly, *Chem. Rev.* 2015, 115, 23, 12888-12935.
- J. Liu, Y. Zheng, S. Hou, *RSC Adv.*, 2017, 7, 37823-37829

Results

Protocol used to obtain CuNi nanospheres^[9]

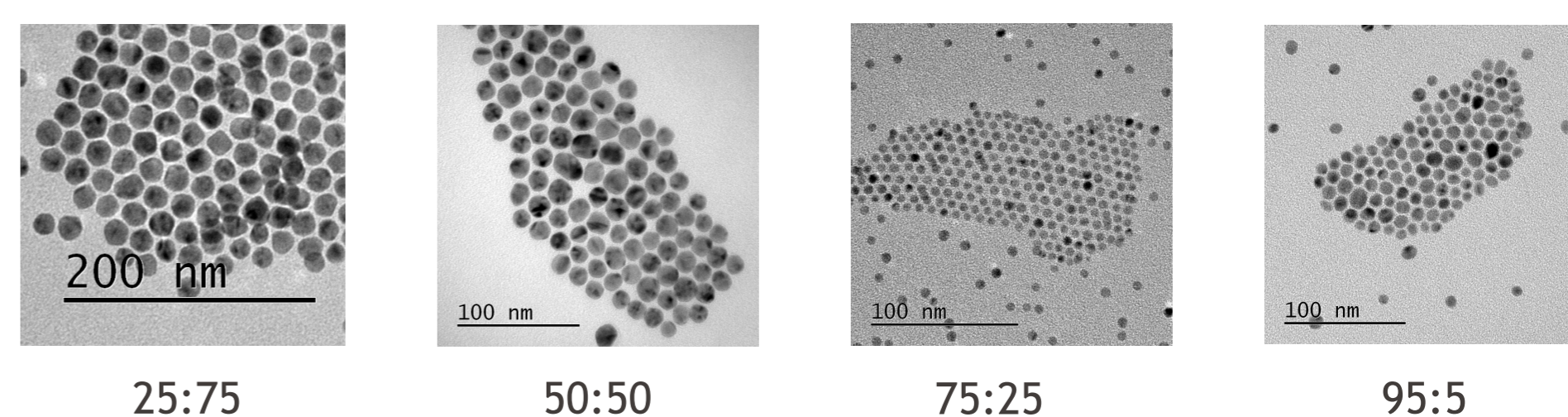


Typical characterisation of CuNi nanospheres



Electron microscopy characterization of CuNi NCs at different composition

Increasing Cu content



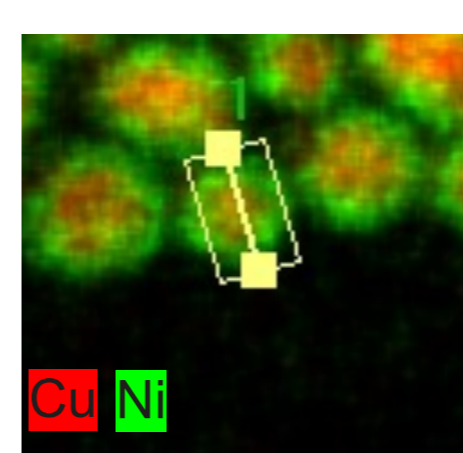
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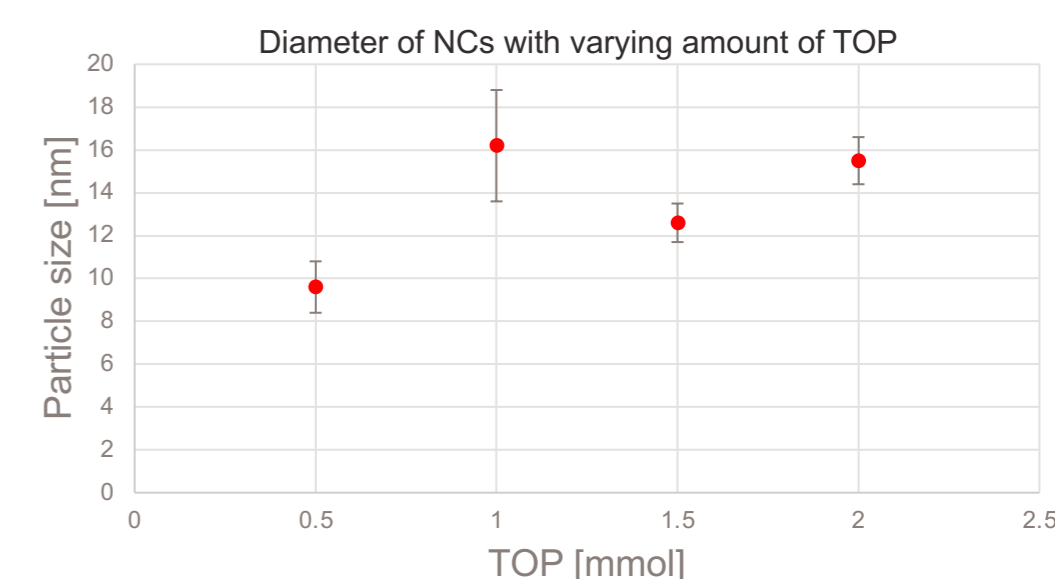
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Single NCs analysis reveal a Nickel rich surface

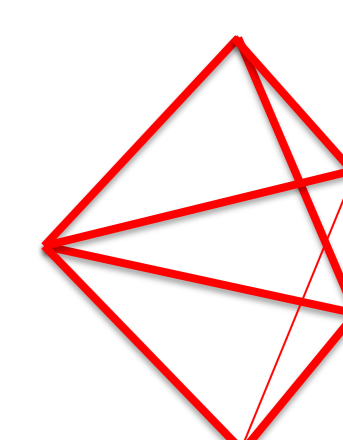
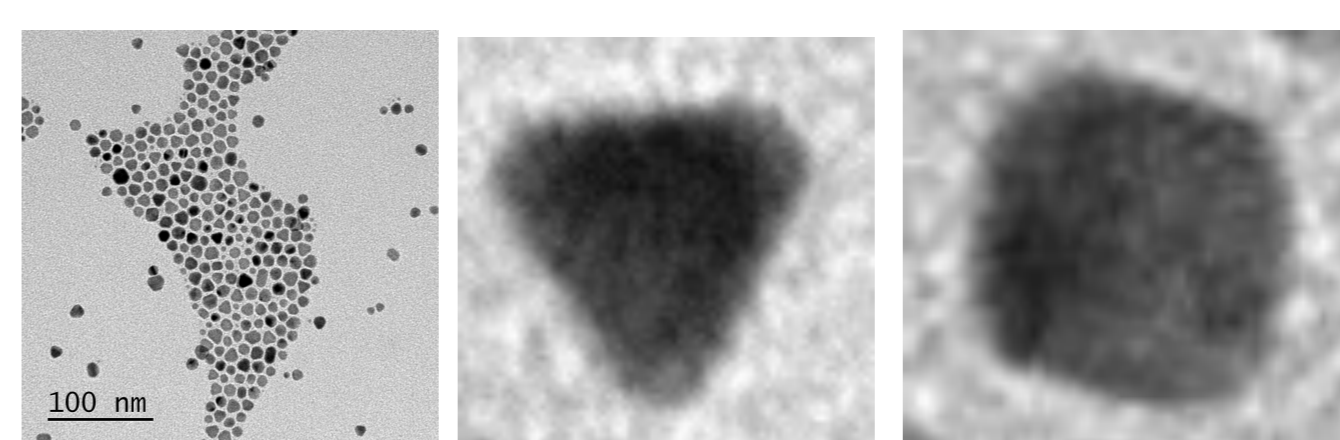


A relation between TOP amount and sphere size was established.



Trigonal bipyramidal (TBP) CuNi bimetallic NCs were also obtained. However, its formation mechanism is still unknown!

Images of CuNi TBP



Conclusion and outlook

- Copper Nickel nanosphere with different composition and size were successfully synthesised.
- Shaped nanocrystals were obtained but a proper understanding of its synthetic mechanism is still missing.
- Formation mechanism of nanosphere and TBP are still open questions.