



# **Synthesis of Copper Nickel bimetallic nanocrystals**

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## Abstract

The increasing concentration of carbon dioxide (CO<sub>2</sub>) in the atmosphere has presented to be a significant environmental challenge. Fighting this increase in concentration has proven to be a challenge due to its very stable nature. Using technologies that transform CO<sub>2</sub> into more economically viable molecules, such as fuels, through carbon dioxide reduction reaction (CO<sub>2</sub>RR) can be used. The challenge with this method is to find a cheap and reliable catalyst to use in this reaction. Non-noble bimetallic nanocrystals (NCs) have been explored due to their abundance and low-cost. Most notably, Copper-based nanocrystals (NCs) have showed good performances for this reaction. 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.

## Introduction

Solving the environment impact of carbon dioxide (CO<sub>2</sub>) has been a challenge for numerous scientists and engineers. One possibility to fight against this increase of atmospheric CO<sub>2</sub> consists of transforming it into more economically viable molecules while also closing the carbon cycle<sup>[1]</sup>. These molecules could have uses in multiple industries such as energy, pharmaceuticals and cosmetics. Carbon dioxide being such a stable molecule can't easily be reduced into other products. Using catalysts to lower the activation energy of such a reaction has proven to be successful.<sup>[2]</sup> The advantages from this type of catalyst is the conversion of carbon dioxide into other more economically viable molecules such as ethylene, methane, ethanol, methanol, etc.<sup>[3]</sup> Non-noble metals have been explored for this purpose since they are cheap and could add great value to certain industries, especially to replace important but expensive catalyst composed of gold, platinum or silver.

The most promising non-noble metal seems to be copper due to its low cost, non-toxicity and capacity to produce hydrocarbons. Indeed, it has been shown that polycrystalline Copper generates over 16 products<sup>[4]</sup>. Nevertheless, in order to use such reaction for a real application, catalysts that are selective for one product and stable for long time must be developed. Recently it has been shown that copper nanocrystals (NCs) with specific size and shape can aid to increase selectivity.<sup>[5,6]</sup> Indeed, it has been shown that copper cubes can generate ethylene with high efficiency instead copper octahedra generate methane.<sup>[7,8,9]</sup> This is due to the facet expression of each of these geometries.<sup>[10]</sup> However, the synthesis of these NCs is still achieved through trial and error. This implies that controllable synthesis of highly active and cost-effective catalyst remains a challenge. Developing synthetic methods towards the controlled production of these materials could prove to be more efficient for the development of this technologies.

One challenge that need to be mention is that copper NCs degrade after short period during the electrochemical CO<sub>2</sub> reduction reaction.<sup>[11]</sup> One way to increase its stability is to alloy the copper with other metals. For example, in a recent work it has been demonstrated that when Ga is alloyed with Cu the stability can be increased while preserving selectivity for methane.<sup>[12]</sup> This motivates research towards alloying copper with other metals. Through the effort of multiple groups, there are already established methods on achieving copper-based bimetallic NCs containing noble metal.<sup>[13-16]</sup> This is not the case for purely non-noble bimetallic NCs which are generally inexpensive and relatively safe. Alloying this metal with an inexpensive and non-noble metal would be ideal. Nickel seems to follow these criteria. Some papers suggest that achieving Copper-Nickel (CuNi) bimetallic NCs could enhance both selectivity<sup>[17]</sup> and stability<sup>[18]</sup>

during CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR), although with limited insights into the fundamental parameters driving performance.

Despite the few successful report of CuNi NCs synthesis, their synthesis remains both misunderstood and sensitive to multiple parameter such as temperature, atmosphere, reaction time and concentration of precursors. Here we report the synthesis of CuNi bimetallic nanospheres with controllable size and composition as well as CuNi bimetallic trigonal bipyramidal.

## **Experimental part**

### ***Synthesis of CuNi nanospheres***

CuNi nanospheres were synthesized by following a previously reported work.<sup>[19]</sup> To begin the synthesis of Cu<sub>50</sub>Ni<sub>50</sub> nanosphere, 0.5 mmol of copper acetylacetonate (Cu(acac)<sub>2</sub>) and nickel acetylacetonate (Ni(acac)<sub>2</sub>) as well as 10 mL of oleylamine were poured in a 50 mL flask under inert atmosphere, here N<sub>2</sub>. After degassing at room temperature, the mix is brought to 120°C under vacuum for 30 minutes. After these 30 minutes, under inert atmosphere, 1 mmol of trioctylphosphine (TOP) was quickly injected using a syringe. The reaction is then heated to 180°C. Once this temperature is reached, the solution is left for 4 hours, after which the product is naturally cooled to room temperature and transferred to a centrifugal tube. To wash this product, a 2 to 1 ratio of toluene and ethanol was poured in the tube and placed in a centrifuge at 13000 rpm for 10 minutes. The NCs were then collected with toluene and characterised.

### ***Synthesis of CuNi trigonal bipyramidal nanocrystals***

In order to synthesize CuNi trigonal bipyramidal nanocrystals, the same ratio of Cu(acac)<sub>2</sub> and Ni(acac)<sub>2</sub> were added to a 50 mL flask along with oleylamine. This mix was then degassed at room temperature and placed under vacuum. The solution was then heated to 120°C for 40 minutes, then under inert atmosphere heated to 240°C for 2 hours. After these 2 hours, the solution is cooled naturally to room temperature and the product is transferred into a centrifuge tube. To wash this product, a 4 to 1 ratio of toluene and ethanol was poured in the tube and placed in a centrifuge at 13000 rpm for 15 minutes. The NCs were then collected with toluene and characterised.

### ***Characterization***

The characterization of the NCs was done through Transmission electron microscopy (TEM) imaging, X-Ray diffraction (XRD) and scanning electron microscopy coupled with energy dispersive spectroscopy (STEM-EDX). The first was used to understand the morphology (size and shape) of the NCs, XRD to gain understanding on the NCs structure. A typical XRD spectrum is characterized by specific peaks characteristic of each material. These peaks are used to identify the material structure and composition through available database. The width of those peaks is directly related to the NC size. Smaller the NC, broader the peak. Therefore, NCs smaller than 7nm cannot be easily characterized by XRD. Finally, STEM-EDX was used to characterize the NC composition in a single nanocrystal. Image-Jay was used to measure the average size of the synthesized NCs and to estimate their percentage yield.

## Results and discussion

### *CuNi nanospheres*

Fig. 1a shows a typical STEM image of the synthesized CuNi with 50:50 Cu:Ni ratio. The obtained CuNi nanospheres appear to be monodisperse with a size of  $16.2 \pm 2.6$  nm. The EDX map in Fig. 1b shows that Cu and Ni coexist in one particle. By performing EDX map quantification the expected ratio of 50:50 is measured. Finally, a XRD spectrum was obtained, as shown by Fig.1c. The XRD spectrum of the obtained CuNi is compared with the one of Cu and Ni NCs. If an CuNi alloy is obtained, the corresponding peaks will shift compared to the monometallic spectra. Here we notice a slight shift which seems to suggest the presence of an alloy. Nevertheless, one can also notice an asymmetry of the peaks, this could be due to a presence of a core and a shell on these NCs, which seems to once again agree with what we can observe on the EDX map on Fig. b. Overall, these results prove that this method is successful to achieve the targeted characteristics.

In the work of J. Liu et al.<sup>[14]</sup>, it is reported that changing the quantity of TOP added to the reaction should affect the sizes of the nanospheres. We then performed a set of experiment where the amount of TOP was systematically increased and as shown in Fig. 1d, CuNi with increasing diameter can be achieved without affecting their size dispersity and composition. Indeed, we managed to obtain nanospheres ranging from  $6.6 \pm 0.4$  nm to  $19.4 \pm 1.4$  nm. It's important to notice that for 1 mmol of added TOP, the average size doesn't fit the curve and it's standard deviation is very high, therefore this experiment must be repeated to be confirmed.

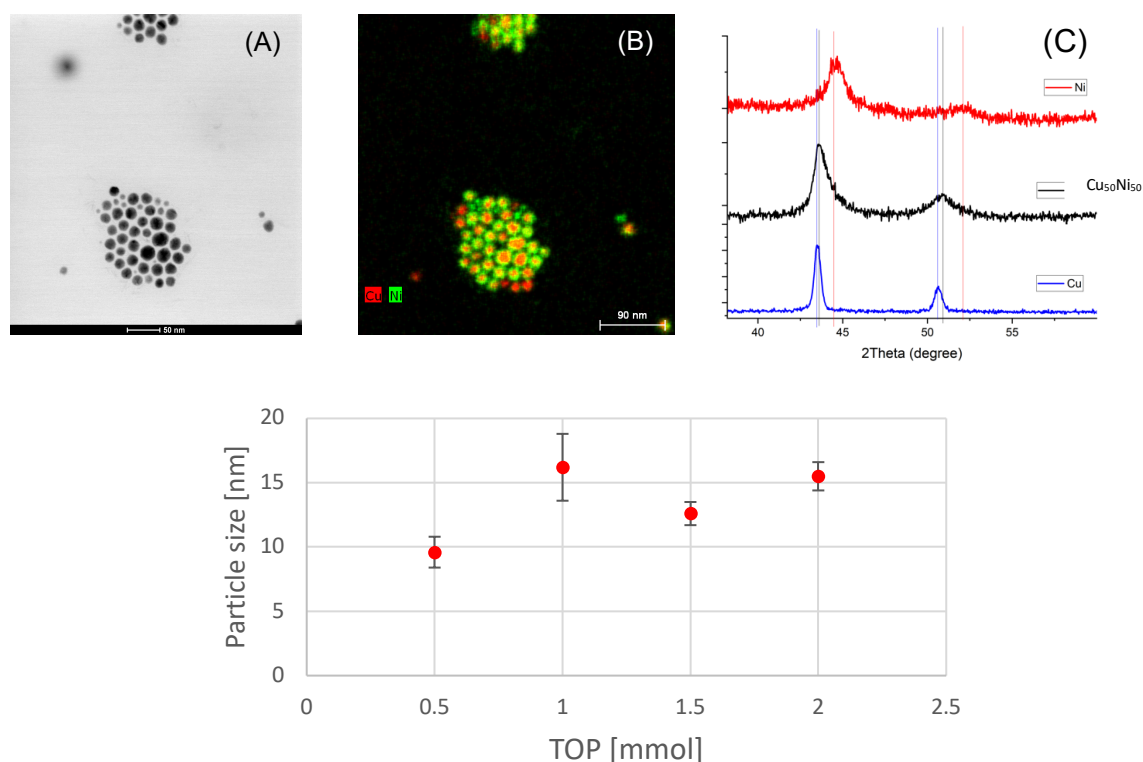


Fig.1 Characterization of CuNi bimetallic nanospheres with 1 mmol of TOP. (A) TEM image (B) EDX map of Cu and Ni for the synthesized  $\text{Cu}_{50}\text{Ni}_{50}$  nanosphere (C) Corresponding XRD spectrum compared with the spectrum of Cu and Ni NCs (D) Effect of TOP on the diameter of CuNi nanospheres. The error bars was calculated by measuring the size of around 200 NCs with image-jay software.

Since control over size was achieved, the focus shifted over to the control of composition. This was achieved by changing the ratio of  $\text{Cu}(\text{acac})_2$  and  $\text{Ni}(\text{acac})_2$  added into the reaction flask. As shown by the STEM images and corresponding EDX maps and quantification reported on Fig 2., the theoretical CuNi ratio could be obtained in the final NCs. All of these samples were synthesized with the same amount of TOP. Despite this constant quantity of TOP, the sizes of the NCs seem to change, as shown by Fig. 3. One reason for this could be related to the difference in the atomic radius of Cu and Ni. Indeed, the atomic diameter of copper is 0.256 nm while for nickel has an atomic diameter of 0.248 nm. However, further investigation is needed to understand the mechanism of nanosphere formation, which remains an open question. Moreover, having learned that TOP can aid to increase the size of those NCs, in the future experiments with higher amount of TOP could help to obtain CuNi with different composition and same size.

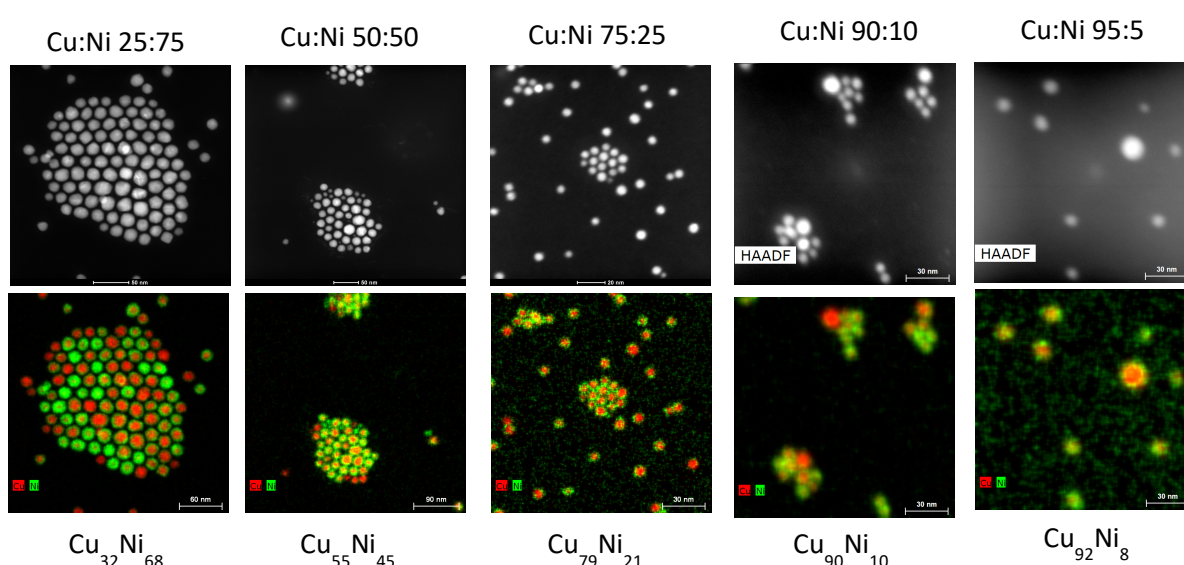


Fig. 2. STEM images (top) and EDX maps (below) of nanospheres with different composition. On the top the theoretical Cu:Ni ratio is reported, instead below the one measured by EDX map quantification.

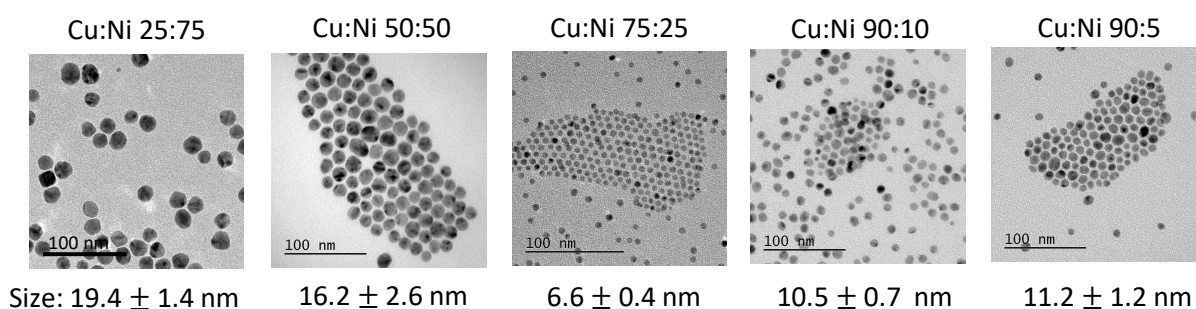


Fig. 3. TEM images of nanospheres with different composition and their average size.

We have then taken a closer look at the STEM-EDX map of a single NCs, to better understand how Cu and Ni are distributed within one NC. As shown by Fig 6 this method allows us to take an image of the sample while also being able to differentiate metals. With these types of images one can then perform a line scan to better understand the distribution of metals on the NC. From this analysis, we learn that in

the core Cu and Ni overlap with the same intensity ratio, instead the exterior part or shell is nickel rich. These results suggest that during this synthesis, copper NCs form first, then Ni diffused in the Cu NCs to form CuNi alloy, but ultimately Ni continue growing on the exterior part, so finally we form CuNi with a shell of Ni that we call CuNi@Ni NCs. Considering that during CO<sub>2</sub>RR, the reaction occurs mostly on the surface, this could pose a problem, since it's possible that only nickel will be involved in the reaction and would therefore produce mostly H<sub>2</sub>. This point will need to be investigated in the future.

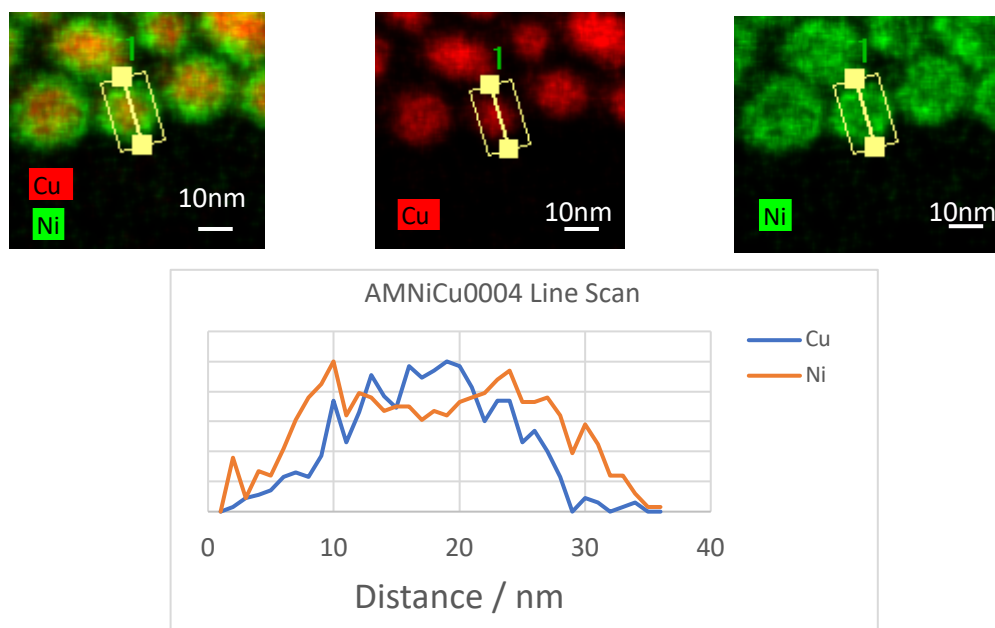


Fig. 6. EDX maps of the synthesized nanosphere showing a CuNi core and a Ni rich shell. On the bottom, the line scan of a single NC for Cu and Ni is reported.

### ***CuNi trigonal bipyramidal nanocrystals***

By modifying the synthetic method for spheres, trigonal bipyramidal NCs were obtained along with some nanospheres as shown by Fig. 7. Specifically, the removal of TOP, increasing temperature and time were investigated. Through multiple screenings, it was found that by removing TOP from the reaction and increasing the temperature from 180°C to 260°C we could obtain trigonal bipyramidal NCs with a yield of ~60% to ~70%. It was also revealed that reaction time doesn't seem to affect this geometric proportion.

As for the characterisation of nanospheres, TEM-imaging, XRD and STEM-EDX were used. From the TEM images, we found that the NCs were on the order of 10 nm big if you measure from the base to the peak. By tilting the sample by 30° we managed to verify the shape of the NCs, as shown by Fig. 8, that we assign to be trigonal bipyramidal (TBP). Whether this NCs are bimetallic was verified through STEM-EDX images, Fig. 9. From these images, one can once again notice that the core contain

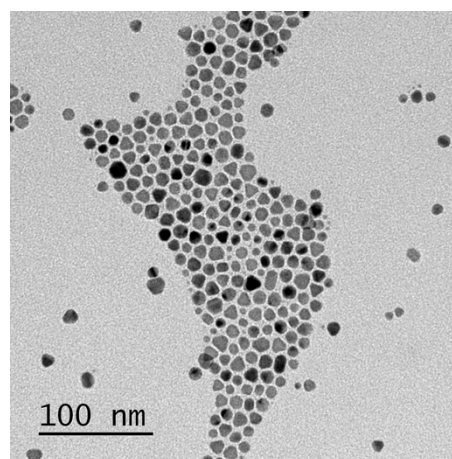


Fig. 7. TEM image of trigonal bipyramidal CuNi NCs.

Cu and Ni instead the shell is Ni rich. This seems to indicate once again that copper is nucleating faster than nickel. The line scan seems to also support this, indeed on the exterior Ni signal is more intense compared to Cu, Graph 3. Since the shell is Ni rich, one can assume that the trigonal bipyramidal shape comes from it.

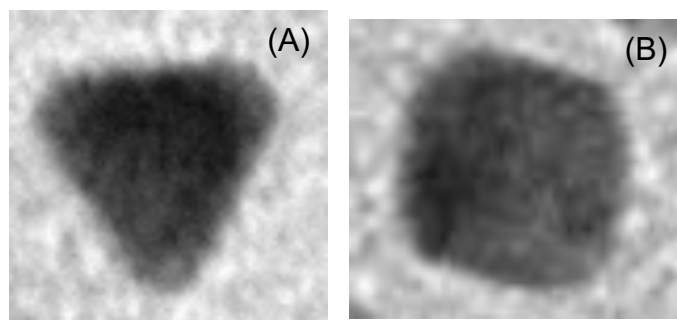


Fig. 8. TEM images of a single Trigonal bipyramidal NC rotated of a) 0 degree and b) 30 degree

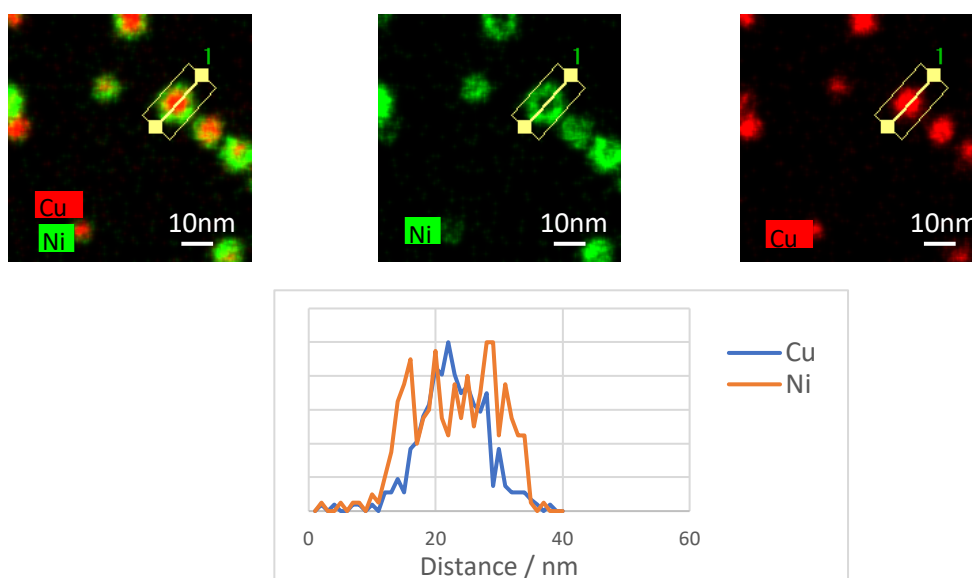


Fig. 9. EDX images of trigonal bipyramidal CuNi nanocrystals Graph 3. Line scan of the CuNi nanocrystal

By inspiring oneself on the nanosphere synthesis, we decided to change the ratio of Cu and Ni precursors, expecting control over the NCs elemental ratio. This method was not successful as shown by the images on Fig. 10. When a higher ratio of copper was added, one can notice that big crystals dispersed shapes as well as small monodispersed nanospheres were produced. From the STEM-EDX images on Fig. 11, one could say that we once again obtained CuNi nanospheres with a copper to nickel ratio of 78 to 22. If more nickel is added to reach a copper to nickel ratio of 28 to 72, the crystals seem to be closer in size. Despite their

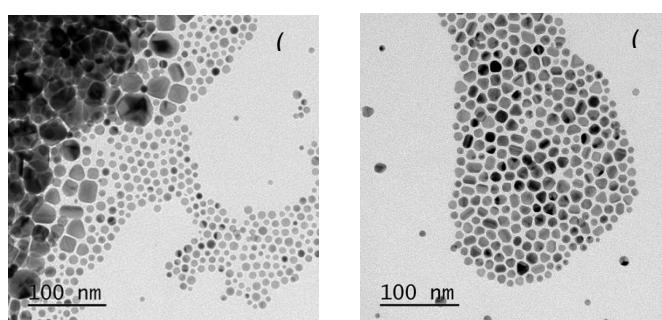


Fig. 10. Synthesis of trigonal bipyramidal with different ratio. (A)  $\text{Cu}_{75}\text{Ni}_{25}$  (B)  $\text{Cu}_{25}\text{Ni}_{75}$

resemblance in size, the shape of these NCs is polydisperse which is not ideal for CO<sub>2</sub>RR studies.

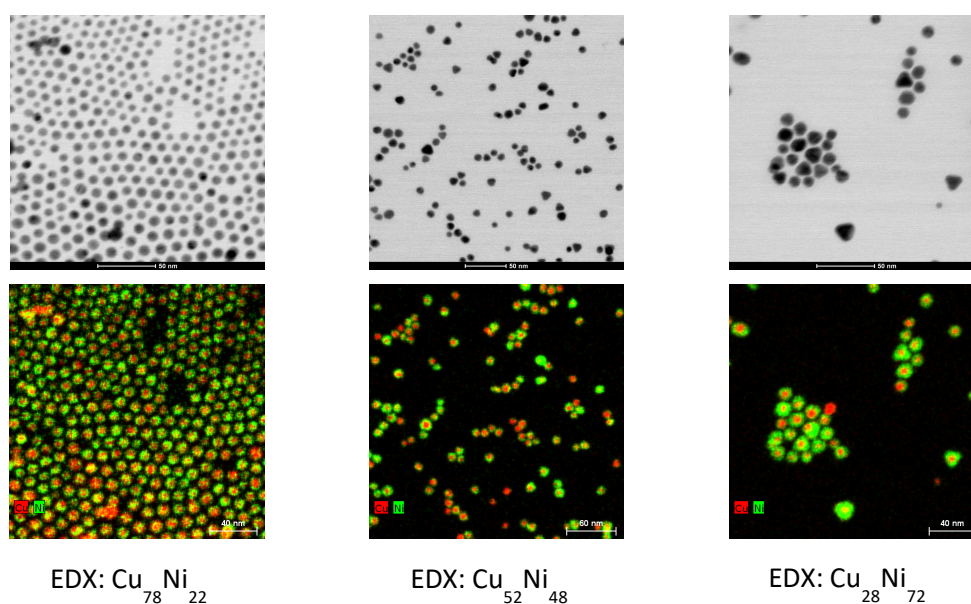


Fig. 11. EDX maps of the product of the trigonal bipyramidal synthesis with different elemental ratio

## Conclusion

In summary, we have synthesized both CuNi nanospheres and trigonal bipyramidal. With the nanospheres we managed to gain control over the size through TOP addition and elemental ratio by controlling the ratio of the two metals during the synthesis. How TOP interacts with the nanospheres still remains an open question. We found that by changing a crystals copper to nickel ratio will affect its final size. This is important because to properly compare which ratio is better for CO<sub>2</sub>RR one would need the same sizes. It was also determined that the bimetallic nanospheres had a nickel rich shell. As stated above, this is important due to the fact that CO<sub>2</sub>RR is a surface reaction. More experiments would have to be to achieve alloyed nanospheres with same size. We then tried to synthesize more complex shapes and achieved to produce a 7 to 3 ratio of trigonal bipyramidal to spheres NCs. It was found that increasing the temperature, also increased the ratio in favour of trigonal bipyramidal NCs. From the TEM images we found that these crystals were on the order of 10 nm. We also determined through XRD and STEM-EDX images that we once again obtain a nickel rich shell, which could be a problem for CO<sub>2</sub>RR. It was also determined that this shape doesn't belong to any basic crystal system. Some kind of distortion could have allowed the formation of these crystals but their synthetic mechanism still remains an open question.

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