









Master Program in NANOTECHNOLOGIES FOR ICTs and QUANTUM DEVICES

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Internship Report

Synthesis and Structural Analysis of High-Entropy Nano-Alloys

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I. Introduction

High Entropy Alloys (HEA) are 15 years old bulk materials that combine four or more metals in equiatomic composition. Mixing many elements at equiatomic composition in an alloy favors the formation of a solid solution crystallized in a cubic phase (face-centered cubic or centered cubic). Firstly introduced by Yeh and coworkers¹ the term "high entropy alloy" derives from the fact that this solid solution phase is stabilized by the high configurational entropy of the alloys. Indeed, the entropy of mixing of an alloy (ΔS_{mix}) can lower the Gibbs free energy of mixing (ΔG_{mix}) according to the equation:

 $\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix} \quad (1)$

where ΔH_{mix} is the enthalpy of mixing, and T is the temperature of the system.

The values of ΔG_{mix} , determine the crystal phase of the alloy at the thermodynamic equilibrium. If ΔG_{mix} is below the free energies of formation of all possible intermetallic compounds (ΔG_{ic}), a solid solution is formed. On the contrary, if $\Delta G_{mix} > \Delta G_{ic}$ phase separations are observed. However, Yeh and coworkers have shown that ΔS_{mix} depends on the number and the concentration of the elements mixed in the alloy according to:

 $\Delta S_{mix} = -R \sum x_i ln x_i \tag{2}$

where R is the gas constant, x is the molar fraction and i indicates an element of the alloy.

Therefore, in alloy containing at least 5 elements with nearly equitatomic composition, the entropy of mixing is high enough to drive the formation of solid solution at high temperature, at the expense of intermetallic phases.

HEA have become one of the most interesting material classes in the last years in both fundamental and applied material science. This new concept allows the fabrication of many new alloys with promising and tunable mechanical and catalytic properties^{2,3,4}. However research has been focused entirely on bulk HEA, ignoring HEA nanoalloys because of the absence of well controlled methods to synthetize such complex nanoparticles (NPs). In the last three years, some studies have shown that the synthesis of these nanomaterials can be reached using high temperature techniques such as carbothermal shock⁵, mechanical ball milling⁶ or plasma arc discharge⁷, but with a limited control over composition and size. Yet the game is worth the effort, because the development of synthesis methods where elemental composition, particle size, and atomic structure can be precisely controlled could bring about a new repertoire of nanostructures with unprecedented functionalities, notably for mechanical, hydrogen storage, catalytic or corrosion resistant coating applications^{4,6,8,9}.

During this internship, I studied those futuristic nanomaterials in the MEANS team (Microscopie Electronique Avancée et Nano-Structures) of the MPQ laboratory (Matériaux et Phénomènes Quantiques) at the University of Paris. We worked in collaboration with the ICMMO laboratory at the University of Paris Saclay. This collaborative work financed by the MITI of CNRS aims at:

(i) Developing innovative synthesis protocols using both wet chemical and physical routes to obtain good control over the size, shape, composition and structural phase of HEA NPs. I notably work in close collaboration with Abdallah Jaafar (other intern of the MEANS group) on the synthesis of HEA NPs by pulsed-laser deposition at the MPQ lab. Chemical syntheses of HEA NPs based on the hot injection method were performed by Nour Kefane at ICMMO under the supervision of Vincent Huc. I spent one week at Orsay to learn this promising wet chemical protocol.

(ii) Exploiting the multi-functionalities of the last generation transmission electron microscope of the MPQ laboratory (the SUPER TEM) to better understand the structural properties of these new nanomaterials that have never been fabricated in France. I have been deeply involved in the many TEM experiments performed at the MPQ lab (high resolution imaging, diffraction and chemical mapping by EDX spectroscopy) and I performed the data analysis of all the samples presented in this manuscript.

II. Experimental part

II.1 Pulsed Laser Deposition

Pulsed Laser deposition (PLD) is a physical vapor deposition method to synthetize NPs on a substrate. This technique is based on the ablation of metallic targets using a pulsed laser beam (excimer laser that emit in the UV). The interaction between the metal surface and the laser beam generates a plasma that condenses on a heated substrate. Metal ablation is carried out in a vacuum chamber (10⁻⁸ Torr) and the substrate is heated by applying a current in a tantalum wire.

The formation of nanoalloys is performed via the alternating deposition of pure metals. Pure metallic targets are mounted on a rotating holder. This choice allows a better and tunable control of the nanoalloys composition. The parameters used to control the nucleation and growth processes, the composition and the final morphology of NPs are the number of laser pulses on each metallic targets, the frequency (1 Hz and 5 Hz) and energy of the laser (150 to 300 mJ) and the temperature of the substrate (400 °C, 500 °C, 600 °C and 700 °C). The ablation rate of each metal is measured with a quartz balance that gives the thickness of materials deposited in nanometer per laser pulses. In addition, it is possible to perform different sequences of deposition (in which order the different materials are deposited) to change the structural properties of the deposited NPs¹⁰.

II.2 Wet Chemical Synthesis

The wet chemical method used to synthetize HEA NPs exploits a technique that is called "hot injection". It consists in the simultaneous injection of all the metallic precursors in a solution heated up to 300 °C in which they are reduced to induce the nucleation and growth of nanoalloys. This high temperature approach is crucial to overcome the different reduction rates of each metal precursors. Homogenous reduction rates favor the formation of HEA nanoalloys with a cubic structure and avoid phase segregation of metals leading to the formation of core-shell or Janus nanostructures.

To synthetize the NPs, metallic precursors have been used in the form of acetylacetonate, while the reaction media is composed by benzyl ether (high-boiling solvent), hexadecanediol (reducing agent) and oleylamine, oleic acid and trioctylphosphine (surfactants). The surfactants are organic compounds that will coat the NPs, avoiding the aggregation and coalescence.

The synthesis is performed under a magnetic stirring using a coated magnetic stir bar in the solution and under Argon environment to avoid the presence of oxygen¹¹.

II.3 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) is one of the most complete characterization tools for studying nanomaterials. This system exploits the electron-matter interaction in order to overcome the resolution limit of conventional optical microscopes ($d = \lambda/2.8$) (the wavelength of the electrons is very small and tunable depending on their accelerating voltage). Indeed, electrons in the TEM are accelerated at 200 kV that corresponds a wavelength equal to $\lambda = 0.00251$ nm. In this sub-

nanometric wavelength range, the resolution, according to the diffraction limit, is significantly improved¹².

There are two ways to use the TEM: TEM mode (parallel illumination) and Scanning TEM (STEM) mode (focalized beam scanned over the sample).

In this study, the two TEMs of the MPQ lab have been exploited: The Jeol 2100 + with a LaB6 gun and a resolution of 0.2 nm and the JEOL ARM 200F equipped with a cold FEG emission gun and two aberration correctors (for TEM and STEM mode) that ensures sub-angstrom resolution imaging.

The nanoalloys made by PLD are directly fabricated on TEM grids (made of Copper or Molybdenum) covered by a thin film of carbon as a substrate (electrons must pass through the carbon film). Nanoalloys fabricated by chemical routes are deposited on TEM grids by drops casting.

We exploited the following TEM techniques to measure the size, shape, composition and atomic structures of nanoalloys.

II.3.1 Conventional TEM imaging (Figure 1a)

Low resolution TEM collected on a CCD camera obtained by selecting the transmitted beam in the diffraction plane. The contrast of crystalline NPs supported on the amorphous carbon film is due to diffraction phenomena. This kind of images permits to have an overview of the samples and are used to calculate the distribution in size, the density and the coverage ratio of the NPs.

II.3.2 STEM-High Angle Annular Dark Field (HAADF) imaging (Figure 1b)

These images are built point by point by collecting electrons with large scattering angle (the ones that interact with atom nuclei) with a ring-shaped detector. This type of imaging is commonly called Z-contrast imaging, because their contrast is relative to the thickness, density and atomic number of the material. However, we will demonstrate that they also depend on diffraction depending on the camera length used.

II.3.3 High Resolution (HR) TEM imaging (or phase contrast imaging) (Figure 1c)

These images are indirect images of crystal structures produced by the interference between the scattered and the transmitted beam. The contrast is related to phase shifts of the various beams, and it makes possible to have atomic resolution. These images allow the recognition of the NPs crystal structure (atomic planes and defects). In addition, calculating the Fast Fourier Transform (FFT) of these images allows obtaining the diffractogram of the single NP (to study the orientation and the crystal structure).

II.3.4 HR STEM-HAADF imaging (Figure 1d)

These are STEM-HAADF images at very high magnification that gives atomic resolution thanks to the newly installed aberration corrector (it is possible to get the same information as the HRTEM images and the contrast information of the STEM-HAADF mode).

II.3.5 Diffraction (Figure 1e)

A diffraction patterns in TEM correspond to a slice of the reciprocal space of the sample from which we can deduced: the crystal structure and lattice parameter of NPs assemblies.

II.3.6 Energy Dispersive X-Ray Spectroscopy (EDX)

As the electron-matter interaction is very rich, it is also possible to have access to chemical information with TEM. In fact the high energy electron beam can easily eject a core electron from an atom. After this ionization process, the atom comes back to its fundamental state via an electronic transition that generates an X-Ray with an energy that is characteristic of the nature of the ionized atom. The emitted X-Rays are then collected in a photodiode that will produce a spectrum (**Figure 1f**)). In TEM mode is possible to have a spectrum of the global sample, while in STEM mode is possible to have spectra and chemical mapping (**Figure 1g**)) of single NPs.



Figure 1: a. Conventional TEM image of CoNiPtCu NPs; b. STEM-HAADF image of CoNiPt NPs; c. High resolution (HR)TEM image of gold NPs; d. HR STEM-HAADF image of CoNiPt NPs; e. Diffraction pattern of Pt NPs; f. X-Rays Spectrum of CoNiPt NPs; g. Chemical Mapping of CoNiPt NPs.

II.4 Image analysis

The images are analyzed with Digital Micrograph and image J softwares, while the chemical analyses are obtained using the Jeol's softwares Analysis Station and Analysis Program. Lastly, the graphs are made using Matlab.

III. Results

III.1 Synthesis of HEA NPs by PLD

One of the biggest challenges in the synthesis of HEA NPs by PLD is that each element has different ablation rate and mobility on the substrate. These differences in the deposition and growth speeds of metals are a problem if one wants to avoid segregation effects and obtain an equiatomic solid solution. In order to understand the behavior of individual elements and eventually identify problematic elements for the formation of HEA NPs, we have first fabricated CoNiPt NPs, then CoNiPtCu and CoNiPtAu NPs and finally CoNiPtAuCu NPs. In the following it will be clear that the synthesis of ternary, quaternary and quinary nanoalloys is achievable with PLD.

III.1.1 Global TEM analysis

After a calibration step of the quartz balance used to measure the deposition rate of each element in nanometer per laser pulses, metals are deposited on the amorphous carbon film of a TEM grid by using an alternating deposition process. We used short deposition periods of each metals repeated several times to ensure the homogeneity of the nanoalloys. The total thickness of metals deposited on the substrate was always 1 nm. Such a low amount of deposited materials ensure the formation of isolated NPs instead of a continuous film. Figure 1 shows that we successfully fabricated CoNiPt (a), CoNiPtCu (b), CoNiPtAu (c) and CoNiPtAuCu (d) NPs with a mean size below 5 nm by PLD. Global EDX measurements show that the composition measured over large area of the sample is close to the equiatomic composition. Also, from the diffraction patterns, we could demonstrate that each sample has a Face-Centered Cubic (FCC) structure that is the crystal structure expected for this HEA system exclusively made of metals forming FCC structures. From the diffraction patterns, it is possible to extract the lattice parameter knowing that each ring corresponds to a different (h,k,l) plane of the crystal, in particular: first ring is (1,1,1), second ring is (2,0,0), third ring is (2,2,0) and the fourth is (3,1,1). The lattice parameters computed are: $a_{CoNiPt} = 3.716 \pm$ 0.014 Å; $a_{CoNiPtCu} = 3.722 \pm 0.010 \text{ Å}$; $a_{CoNiPtAu} = 3.762 \pm 0.019 \text{ Å}$; $a_{CoPtNiCuAu} = 3.786 \pm 0.047 \text{ Å}$. To make a comparison, from the composition it is also possible to obtain the predicted lattice parameter of the alloys following the Vegard's Law: $a = \sum_i a_i \cdot x_i$; where a is the lattice parameter, x is the molar fraction and *i* is an index that indicates the element in the alloy. Using this formula the lattice parameters are: $a_{CoNiPt} = 3.634 \pm 0.003 \text{ Å}$; $a_{CoNiPtCu} = 3.623 \pm 0.038 \text{ Å}$; $a_{CoNiPtAu} = 3.719 \pm 0.003 \text{ Å}$; $a_{CoPtNiCuAu} = 3.692 \pm 0.039$ Å. The discrepancies between the lattices parameters measured by diffraction and the ones calculated from the composition of the sample measured by EDX reveal that the Vegard Law, which applies to binary nanoalloys (CoPt, CuAu, AuPd...), does not seem to apply in these more complex systems.



Figure 1: TEM image, diffraction pattern, composition and mean size of a. CoNiPt; b. CoNiPtCu; c. CoNiPtAu; d. CoNiPtAuCu.

These first results clearly demonstrate that with the PLD technique it is possible to synthetize good HEA NPs (with equiatomic composition and FCC structure) at least using up to five metals.

III.1.2 Modulate the nucleation and growth processes by PLD

CoNiPt nanoalloys has been used to study the effects of deposition conditions on the size, shape, cover ratio and density of nanostructures. These structural parameters were measured on TEM images by using image processing based on interface-tracking algorithms. In particular, we focused on the effects of the substrate temperature, the frequency of the laser and the deposition sequence.

III.1.2.1 Effect of the temperature

Figure 2 shows four different samples synthetized with the same deposition sequence at 400 °C, 500 °C, 600 °C and 700 °C.



Figure 2: TEM images of CoNiPt NPs deposited at a. 400°C; b. 500°C; c. 600°C; d. 700°C. The inset in the bottom right corner of each image corresponds to the size dispersion of the NPs.

The insets of **Figure 2 - a**, **b**, **c** and **d** reveal two different types of size distributions. The samples synthetized at temperature smaller than 600 °C show a Gaussian distribution with a peak between 3 and 4 nm for both samples. When the temperature is equal or above 600 °C it is clear that the size distributions are no more Gaussian but bimodal with one peak around 1-2 nm and another one around 5 nm. The appearing of these two populations of NPs is due to two coarsening mechanisms that are activated at high temperature: (i) the Ostwald ripening that consists in the growth of the larger NPs at the expense of the small one that shrink; (ii) the coalescence that occurs when two NPs get in contact and their respective orientation allows their merging.

Figure 3 – \mathbf{a} and \mathbf{b} show that increasing the temperature also affects the density and the cover ratio (i.e. ratio between surface covered by the NPs and the total surface of the image) of NPs.



Figure 3: Graphs showing **a**. the density of NPs **b**. the cover ratio of NPs as a function of the substrate temperature measured on TEM images of the CoPtNi samples.

The trend is clear, increasing the temperature of the substrate reduces the density of NPs that goes from $20700 \text{ NPs/}\mu\text{m}^2$ at 400 °C to $11300 \text{ NPs/}\mu\text{m}^2$ at 700°C. However, the density is constant up to 500 °C and drops rapidly between 500 °C and 700 °C. This confirms that the coalescence and the Ostwald ripening mechanisms are thermos-activated phenomena that start affecting the morphology of the NPs film above 500 °C, as previously observed in monometallic and bimetallic NPs¹³.

Similarly, increasing the temperature reduces the cover ratio of NPs (T_c). Quantitatively, $T_c = 0.31$ at 400 °C and $T_c = 0.20$ at 700 °C. However, this reduction is only observed above 600 °C. It is worth noting that the lowering of the cover ratio is not a consequence of the coalescence or the Ostwald ripening, but it is due to a reshaping of nanostructures from flat shapes wetting the substrate to 3D NPs. Our results show that the surface diffusion of metal atoms on the nanostructures that drives these reshaping mechanisms significantly impacts the morphology of NPs at 700°C. To estimate this change in the "tridimensionality" of the NPs, we have measured their average aspect ratio ($\chi = height / diameter in the substrate plane$) that can be computed using this formula:

$$\chi = \frac{3e_n \sum_i a_i^2}{4T_c \sum_i a_i^3}$$
(3)

where e_n is the nominal thickness measured with the quartz balance during the synthesis (i.e. total thickness of deposited metals considering they form a continuous thin film), T_c is the cover ratio and a_i is the radius of a single NP (always approximated with a circle). Using this formula, we found that the aspect ratio is twice as important at 700 °C as at 400 °C.

III.1.2.2 Effect of the laser frequency

Secondly, we studied how the laser frequency can affect the CoNiPt NPs. **Figure 4** shows two samples fabricated with a laser frequency of 1 and 5 Hz and a substrate temperature of 600 °C.



Figure 4: TEM images of CoNiPt NPs deposited with a. $F_{laser} = 1$ Hz; b. $F_{laser} = 5$ Hz. The inset in the bottom right corner of each image corresponds to the size dispersion of the NPs.

Figure 4 clearly shows that changing the laser frequency also affects the size distribution of NPs. In fact, with a frequency of 1 Hz (the same sample of **Figure 2 - c**) we obtain a bimodal distribution, whereas with a frequency of 5 Hz the size distribution is a Gaussian centered around 4 nm. This means that at higher frequency there are not two populations of NPs even if the temperature is high enough to activate the coarsening mechanisms. This result illustrates that the NPs size depends on the competition between the deposition rate and the growth rate driven by coarsening. At first, the fabrication time at high frequency is shorter. Consequently, the annealing time of the NPs where the coarsening is effective, is 5 time shorter than at 1 Hz. Thus, there is not enough time for the NPs to coalesce and be significantly affected by the Ostwald ripening. Moreover, at 5 Hz the deposition speed is much faster than at 1 Hz. Therefore, monomer attachment becomes the driving force in the growth of NPs and overcome the effect of the coarsening processes.

III.1.2.3 Effect of deposition sequence

The deposition sequence also influences the size of NPs. Particularly, we show that the choice of the firstly deposited metal can change the morphology of the NPs film. **Figure 5** shows two samples of CoNiPt NPs fabricated with two different sequences starting with Pt and Co. The quantity of deposited metals, the frequency and the temperature are similar in the two syntheses.



Figure 5: TEM image of CoNiPt NPs deposited by PLD starting with **a**. Pt; **b**. Co. The insets show the size distribution of NPs and deposition sequence with number of laser's shots for each metal.

The size of NPs is significantly bigger (about 2 nm) when we start the deposition sequence with platinum. The size distributions of NPs have a bimodal form, revealing that the coarsening mechanisms contribute to the growth of NPs in both syntheses. In addition, the cover ratio and the density also depend on the firstly deposited metal. Quantitatively, $T_c = 0.31$ and $\rho = 13900 \text{ NPs/}\mu m^2$ when starting with platinum and $T_c = 0.22$ and $\rho = 21000 \text{ NPs/}\mu m^2$ when starting with cobalt. Thus, we can conclude that starting with cobalt leads to the formation of smaller 3D NPs, while more spread nanostructures are formed when starting with Pt. These results reveal the wetting behavior of Pt and the importance of the shape of the first nuclei in the final morphology of the nanoalloys. The increasing of the density is a further proof that the NPs are smaller starting with cobalt (remembering that the quantity of material deposited is always the same). Considering cover ratio, as it is written before, it is possible to make a conclusion about the morphology of the NPs: starting with cobalt the cover ratio is lower so the aspect ratio is bigger and thus the NPs are more 3D.

To conclude, the various parameters of PLD synthesis offer a rather good degree of control over the size, density and morphology of the NPs.

III.1.3 Atomic scale study of ternary nanoalloys

If the nearly equiatomic composition and the FCC structure of our nanoalloys is revealed by global EDX and diffraction analysis, it is necessary to investigate the atomic structure at single NP level to evaluate the possible presence of crystal defects and segregation effects and also confirm that the crystal structure and the composition are homogeneous in all the NPs. The high resolution STEM imaging and the nanoscale EDX analyses performed on the CoNiPt sample fabricated at 600 °C with a frequency of 1 Hz are shown in **Figure 6**.



Figure 6: **a.** High resolution STEM-HAADF image of CoNiPt NPs; **b.** Diffractogram (i.e Fast Fourier Transform) of the NP in the red square in **a** that is oriented along the [1,0,1] zone axis; **c-f.** Chemical Mapping of CoPtNi NPs. **c.** Reference STEM-HAADF image; **d.** Chemical mapping of Co; **e.** Chemical mapping of Ni; **f.** Chemical mapping of Pt; **g.** Graph showing the composition of single CoNiPt NPs as a function of their size.

High-resolution STEM images (**Figure 6 - a**) clearly revealed that the CoNiPt NPs are almost defects free and they present a FCC structure (see diffractogram in **Figure 6 - b**) with a lattice parameter equal to $a_{CoNiPt} = 3.796 \pm 0.046$ Å. Chemical mapping has been performed by STEM-EDX on several NPs. This technique consists in acquiring 1 to 5 EDX spectra at each pixel of the image with an acquisition time in the millisecond range for each spectra. As illustrated in **Figure 6**

- **c-f**, it is clear that all the elements (Co, Ni and Pt) are present and homogeneously distributed inside the NPs, without segregation. To read these maps it is important to know that each map is referred to a single element and the colors of the pixels are an indication of the number of counts detected at a selected X-ray energy (i.e. the K, L or M peak of the analyzed element), starting from black (no X-Rays detected) and going towards hotter colors up to white (saturation). Therefore, the chemical mappings are not quantitative analyses of the local concentration of element, but qualitatively reveals the distribution of the elements at the nanoscale.

Quantitative chemical analysis of single NPs was also performed by measuring EDX spectra with the STEM beam scanning over single NPs for one minute. The high count number detected with this approach allows measuring the relative concentration of elements in nano-size materials. The relative intensity (I) of the peaks used for the quantification is related to the relative concentration of the elements A and B by using the following equation:

$$\frac{c_A}{c_B} = k_{AB} \frac{I_A}{I_B} \quad (4)$$

where k_{AB} is the Cliff-Lorimer coefficient.

Quantitative STEM EDX nanoanalyses revealed that the nearly equiatomic composition is uniform in all the CoNiPt NPs (**Figure 6 - g**). The average composition for all the NPs, for small NPs (below 8 nm) and for big NPs (above 8 nm) are shown in **Table 1**. The dispersion in the concentration does not exceed 7 % and it is 5.6% on average. These excellent results reveal that PLD synthesis allows controlling the formation of ternary nanoalloys with size below 10 nm and nearly equiatomic composition.

	All NPs	NPs with size < 8 nm	NPs with size $> 8 \text{ nm}$
at% of Co	29.03 ± 3.82	28.36	29.54
at% of Ni	37.58 ± 6.92	35.30	36.79
at% of Pt	33.39 ± 6.16	36.34	33.53

 Table 1: Average compositions of single NPs.

III.1.4 How to reveal local variations of the concentration in single NPs?

Phase segregation in nano-objects, like core-shell nanostructures where metals are fully spatially separated, can be detected by TEM. Usually, the superposition of FCC nanocrystals with different lattice parameters generate moiré pattern that are easily recognizable¹⁴. However, detecting local variations of the concentration in multi-element nanostructures crystalized in a FFC structure is more challenging. To tackle is important question for the structural analysis of HEA NPs, we have synthetized a Co₂₆Ni₃₃Pt₄₁ sample with the hope that the higher concentration of Pt will created Ptrich area in the nanostructures. Low resolution STEM-HAADF images of this sample (**Figure 7a**), show many higher intensity areas that could corresponds to Pt-rich area. Indeed, STEM-HAADF images are considered incoherent, showing chemical image contrast (Z-contrast) due to the dominating effect of thermal diffuse scattering when scattered electrons are detected at high angles¹⁵. In a simplified way, the intensity of STEM-HAADF images is given by:

 $I = dt Z^{\alpha} \qquad (5)$

where d, t and Z are the density, the thickness and the atomic number of the sample and α is a constant between 1,5 and 2. However, STEM-HAADF images can also be influenced by channeling effects along the atomic column (also called diffraction contrast) that depends on crystal orientation, making their interpretation less straightforward¹⁶. These additional contrasts are illustrated in the STEM-HAADF images of pure gold NPs seen in **Figure 7 b-d**, in which higher intensity areas due to crystal defects are also observed despite the monoatomic composition of the NPs. As expected, the use of smaller camera length that increases the angle of detection of scattered electrons, reduces the contribution of diffraction contrast to the image¹⁷. Nevertheless, complementary analyses are necessary to confirm the presence of Pt-rich areas in the Co₂₆Ni₃₃Pt₄₁ NPs.



Figure 7: a. STEM-HAADF image of $Co_{30}Pt_{40}Ni_{30}$ NPs b. STEM-HAADF image of gold NPs with camera length of b. 3 cm, c. 8 cm; d. 12 cm.

The STEM-HAADF image in **Figure 8** – **a** shows a nanoalloys with core-shell contrast at high resolution (i.e. the higher intensity of the core could correspond to a Pt-rich area). We calculated the local lattice parameter by measuring the inter-atomic distances along the (200) direction and determined how it varies between the core and the shell of the NPs. As seen in **Figure 8** – **b** the lattice parameter is significantly higher in the core than in the shell of the NPs, but it increases and decreases in a continuous manner at the interfaces between the two areas. The average lattice parameters measured in the core and the shell are 3.88 Å and 3.61 Å, respectively. As the lattice parameter of Pt (3.92 Å) is much larger than the one of Co (3.56 Å) and Ni (3.50 Å), these atomic scale analyses confirm the presence of a Pt-rich core. Using the Vegard Law and considering Co and Ni as a single element of lattice parameter equal to $a_{CoNi} = 3.53$ Å (the average of the two lattice parameters) the atomic percentage of Pt is given by at $%_{Pt} = \frac{(a - a_{CONi})}{(a_{Pt} - a_{CONi})}$. We found that the atomic percentage of Pt in core and the shell of the NP is 88% and 20%, respectively. This quantitative result remains a rough estimation because we have seen that the Vegard law does not

apply well in our ternary alloys.

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Figure 8: a.HR STEM-HAADF image of CoNiPt NPs (inset: intensity profile measured along the white rectangle); b. Variation of the lattice parameter measured inside the yellow rectangle in a.

To further confirm the presence of a Pt-rich core in this CoNiPt NP, EDX mapping was performed on the same nanostructure. The chemical maps in **Figure 9a-c** shows that Co, Pt and Ni are detected in the whole NPs. Intensity profile was measured on these chemical maps along the (200) direction. According to equation (4), the ratio of EDX-peak intensities is directly proportional the concentration ratio of elements. **Figure 9d** shows how the ratio between the intensity of the Pt peak and the cobalt and nickel peaks summed together varies over the NP. From this local EDX analysis, we can see that the Pt/(Co+Ni) concentration ratio is 3 time more important in the core than in the shell of the NPs. In line with the variation of the lattice parameters, EDX mapping confirm the presence of a Pt-rich core.



Figure 9: Chemical mapping of the same CoNiPt NPs than in **Figure 8**. Chemical maps of **a**. Co; **b**. Ni; **c**. Pt. **d**. Evolution of $I_{P/I_{CoNi}}$ ratio measured along the (200) direction on the chemical maps.

To conclude, we have developed a TEM protocol combining high resolution STEM-HAADF imaging and EDX nanoanalysis that allows detecting local variations of the composition in FCC CoNiPt nanoalloys that occurs when the global Pt composition of the sample is above 40%. The local increases in the Pt concentration induce a continuous increase of the lattice parameters of the FCC structure, which makes them different from complete phase separations.

III.1.5 Atomic scale study of quaternary nanoalloys

We have also studied the crystal structure and composition of the four-metal HEA NPs at the single NP level.

III.1.5.1 CoNiPtCu

The structural analysis performed by high resolution STEM-HAADF and the composition of individual NPs measured by STEM-EDX as a function of their size are shown in **Figure 10**. Most NPs present an FCC structure (**Figure 10a-b**). We also note the presence of many single atoms and very small clusters slowly diffusing on the substrate between the well crystalized NPs. In line with the fact that these single atoms and clusters were not observed in the CoNiPt sample, Cu signal was detected by EDX when the electron probe was positioned on the substrate. Additionally, chemically ordered NPs with L1₀ or L1₂ structures were occasionally observed (**Figure 10 d-g**). This result is not surprising given that such chemically ordered structures are found in the phase diagram of NiPt¹⁸, CoPt¹⁹ and CuPt²⁰ binary alloys. Finally we note that we observed, large NPs (> 10 nm) with core-shell structure (**Figure 10 d**). We also note that on average the NPs are smaller than in other samples which explains the diffuse aspect of the circles observed on the global diffraction pattern of the sample (**Figure 1**)



Figure 10: a-d-f. HR STEM-HAADF image of CoNiPtCu NPs; b. Diffractogram of the NP in the red square in a.; c. Graph showing the composition of single CoNiPtCu NPs as a function of their size; e. Diffractogram of the NP in the red square in d.; g. Diffractogram of red square in f.

EDX analysis performed on single NPs shows that the four elements are present in each NP (**Figure 10g**). However, as seen in **Table 2**, the composition from a particle to another is twice as variable as in the CoNiPt NPs (i.e composition dispersion of 10.6 % on average versus 5.6 % in CoNiPt NPs). We can see in **Figure 10g** that small NPs present an excess of Cu and Pt while Ni and Co are more present in large NPs. These results are confirmed in **Table 2**, where the averaged compositions of small (< 4 nm) and large (> 4 nm) NPs are given.

	All NPs	NPs with size $< 4 \text{ nm}$	NPs with size $> 4 \text{ nm}$
at% of Co	31.73 ± 11.94	24.63	43.80
at% of Ni	21.99 ± 9.92	17.05	30.39
at% of Cu	29.16 ± 13.02	36.82	16.15
at% of Pt	17.11 ± 7.80	21.50	9.66

 Table 2: Average compositions of single NPs.

This size-dependent composition of NPs is attributed to an inhomogeneous Ostwald ripening process during the synthesis. Indeed the MeANS group has already demonstrated in several binary nanosystems (CoPt, AuCu and AuPd) that concentration gradients could appear during the synthesis or the annealing of nanoalloys if the metals in the NPs have different mobility¹³. Here, the fact that Ni and Co are in excess in large NPs means that these two elements are more mobile than Cu and Pt. Consequently, they are more prone to reach large NPs during Ostwald ripening process. On the contrary, the low mobility of Cu and Pt make them stay in the small NPs that shrink during coarsening.

This composition variability could notably explain the formation of core shell configurations in large NPs, because the equiatomic composition is essential for the formation of cubic solid solution in HEA alloys. Moreover, it could also explain the formation of chemically ordered structures in some NPs. Further investigations are necessary to correlate the local composition and the presence of chemical ordering in our HEA NPs.

III.1.5.2 CoNiPtAu

The other quaternary nanoalloys successfully synthetized is the same as the one described in the previous section but substituting the copper with gold. Again, the structural analysis performed by high resolution STEM-HAADF and the composition of individual NPs measured by STEM-EDX as a function of their size are shown in **Figure 11**.



Figure 11: a-d. HR STEM-HAADF image of CoNiPtAu; b. Diffractogram of the NP in the red square in a.; c. Graph showing the composition of single CoNiPtAu NPs as a function of their size.; e. Diffractogram of the NP in the red square in d.

As in previous samples, NPs present a FCC structure (**Figure 11a-b**). We did not observe single atoms diffusing between the NPs but the amount crystal defects in the nanostructures was much more important than in the CoNiPt or CoNiPtCu NPs. In particular, many multi-twins nanocrystals were observed (**Figure 11 d-e**). It is worth noting that gold NPs frequently adopt multi-twinned morphology because the formation energy of stacking faults is low in gold. Therefore, it seems that gold brings these peculiar structural properties to the nanoalloys. The presence of many defects explains the diffuse aspect of the circles observed on the global diffraction pattern of the sample (**Figure 1**).

EDX analysis performed on single NPs shows that the four elements are again present in each NP (**Figure 11g**), but interestingly, the composition dispersion of NPs is much lower than in the CoNiPtCu NPs (only 8 % on average, see **Table 3**). We can see in **Figure 11c** and **Table 3** that there are slight excesses of Ni - Co in large NPs and Au - Pt in small NPs. However, this effect is not very strong, which could explain the absence of phase segregation and chemical ordering in this quaternary NPs.

	All NPs	NPs with size $< 5 \text{ nm}$	NPs with size $> 5 \text{ nm}$
at% of Co	28.16 ± 11.53	25.69	35.58
at% of Ni	29.01 ± 6.95	28.00	32.04
at% of Pt	23.10 ± 6.14	24.87	17.79
at% of Au	19.72 ± 7.42	21.43	14.59

Table 3: Average compositions of single NPs.

III.1.6. HEA NPs with five metals: CoNiPtAuCu

Finally, the last sample fabricated is the quinary alloy CoNiPtAuCu. Mixing five metals by PLD is a challenge but we successfully synthetized the quinary HEA NPs. Again, **Figure 12** shows high

resolution STEM-HAADF images, their corresponding diffractograms and the single NPs composition measured by STEM-EDX on this sample.



Figure 12: a-d-f. HR STEM HAADF image of CoNiPtAuCu; b. Diffractogram of the NP in the red square of a.; c. Graph showing the composition of single CoNiPtCuAu NPs as a function of their size; f. Diffractogram of the red square of d.

One more time, most NPs present a FCC structure (Figure 12a-b) and we note the presence of many twin-planes on the NPs as in the CoNiPtAu NPs (Figure 12f). Additionally, as in the CoNiPtCu sample, chemically ordered NPs with $L1_0$ or $L1_2$ structures and large NPs with core shell contrast were occasionally observed (Figure 12 d-e).

EDX analysis performed on single NPs shows that the five elements are present in each NP (**Figure 12c**). The composition dispersion of NPs is small (only 6.3 % on average, see **Table 4**) and as in previous samples, there are slight excesses of Ni - Co in large NPs and Cu-Au -Pt in small NPs. The small dispersion in NPs composition is not in line with the formation of core-shell nanostructures and chemical order. However, we note in **Table 4** that the average composition of all the NPs presents an excess of Co (30%) and Ni (22%). Thus, with the size effect on the composition of NPs. the larger nanostructures present 2 to 3 time more Co - Ni than Cu-Pt-Au. In line with previous observations, we assume that this important deviation from the equiatomic composition leads to the formation of core-shell NPs and local chemical order. To conclude, the structural properties of these CoNiPtAuCu nanoalloys seems to combine the structural features observed in the two quaternary nanoalloys (CoNiPtCu and CoNiPtAu) revealed in the previous sections.

	All NPs	NPs with size $< 4 \text{ nm}$	NPs with size $> 4 \text{ nm}$
at% of Co	29.61 ± 9.07	23.86	33.91
at% of Ni	21.90 ± 5.85	17.71	24.79
at% of Cu	18.38 ± 7.74	24.04	14.26
at% of Pt	13.05 ± 4.03	15.57	11.33
at% of Au	17.06 ± 4.85	18.82	15.72

 Table 4: Average compositions of single NPs.

III.2 Synthesis of HEA NPs by wet chemical method

The other strategy we used to synthetize HEA NPs is the wet chemical method. Our hot injection protocol performed by our collaborators at ICMMO is explained in the experimental section. As with the PLD method, we successfully synthetized ternary, quaternary and quinary nanoalloys.

III.2.1 Global TEM analysis

The low resolution TEM images, global diffraction, composition and average size of CoNiPt, CoNiPtCu and CoNiPtAuCu nanoalloys are shown in Figure 1 - a b and c.



Figure 1: TEM image, diffraction pattern, composition (missing for CoNiPtCu) and mean size of **a**. CoNiPt, **b**. CoNiPtCu and **c**. CoNiPtAuCu.

At first comparing the average size with the physically prepared NPs we can assert that the chemically prepared NPs are always bigger than the one synthetized by PLD. Chemically prepared NPs are also more monodispersed. Indeed in average the polydispersity (defined as: size dispersion over mean size) is 46% in the NPs fabricated by PLD and 33% in the chemically prepared NPs.

TEM images in **Figure 1** show that the NPs are well dispersed over the substrate (there are no aggregates). This is a consequence, as it is shown in the following, not only of the dilution of the solution, but also of the quantity of surfactants used during the synthesis.

Globally, each sample present a FCC structure and good composition (near equiatomic). As for the physically prepared NPs, it is possible to obtain the lattice parameter from the diffraction pattern and to make a comparison with the lattice parameter computed with the composition by using the Vegard's Law. The results are shown in **Table 1**.

SAMPLES	a [Å] (diffraction)	a [Å] (Vegard's Law)
CoNiPt	3.719 ± 0.027	3.641 ± 0.011
CoNiPtCu	3.699 ± 0.031	/
CoNiPtAuCu	$3,832 \pm 0.031$	3.751 ± 0.026

Table 1: Lattice parameters for

As for the HEA NPs prepared by PLD, the lattice parameter obtained from the diffraction pattern is a bit higher with respect to the one calculated with the Vegard law (**Figure 2**). This deviation from the Vegard law observed in both physically and chemically prepared NPs indicates that the lattice distortion induced by the very different size of the atoms in the nanocrystals does not vary linearly with composition in nanoalloys containing more than two elements. As we study very small NPs, we can also assume that size effects on the lattice parameter could also influence this result, but it is worth noting that the Vegard law applies in sub-10 nm binary nanoalloys.



Figure 2: Deviation from the Vegard Law.

III.2.2 Role of surfactants

The surfactants are key components of chemical syntheses. Notably, they coat the NPs preventing the coalescence and keeping each NP isolated. Because they have this effect of "protective" layer that influence the nucleation and growth of the NPs, a logic question is if the concentration of surfactants used during the synthesis can influence the size of the NPs. We have studied this question on the CoNiPt NPs.

Figure 3 shows CoNiPt NPs prepared in the same protocol than the NPs in **Figure 1 a**, except that the quantity of surfactants was halved (oleic acid: 0.2 ml; oleylamine: 0.2 ml).



Figure 3: a. TEM image of CoNiPt; b. Diffraction pattern of CoNiPt.

Figure 3 b reveals that the NPs remain FCC but reducing the surfactants concentration in the synthesis increases a bit the lattice parameter that is equal to 3.745 ± 0.014 Å. This small increase in the lattice parameter can be due to the fact that the NPs, having less surfactants on the surface, are less "compressed" and so the lattice parameter is a bit larger. Reducing the quantity of surfactant did not affect the size of NPs ($d = 6.21 \pm 1.63$ nm vs $d = 5.91 \pm 1.21$ nm in previous synthesis). We also note that the NPs are more aggregated in the last synthesis highlighting the primary role of coating agents: ensuring the colloidal stability of NPs in solution.

III.2.3 Atomic scale study of the CoNiPtCu Nanoalloys

The atomic structure of CoNiPtCu NPs was studied by high resolution TEM and STEM-EDX mapping (**Figure 4**). The chemical mapping (**Figure 4** d) shows that the four metals are present in the NPs. However, two populations of nanostructures were identified in this sample: small NPs with a multi twin structure (**Figure 4 a-b**) and big NPs with a core-shell structures. Indeed, the STEM HAADF images show a clear contrast enhancement at the edge of big NPs (**Figure 4 c**) in line with the increase intensity at the edge of big NPs on the Pt map obtained by EDX (**Figure 4 d**). As illustrated by the Bragg-filtered HRTEM analysis in **Figure 4 e-g**, here, the phase separation is

complete and we observe two different FCC structure in the core and the shell of the large NPs. The lattice parameter in the core and in the shell are 3.481 Å and 3.817 Å, respectively. Given the higher lattice parameter of Pt, this confirms the formation of a Pt rich shell. Bragg-filtered HRTEM imaging performed by selecting one of the two FCC patterns on the diffractogram of the NPs allows revealing the core of the NPs with a small lattice parameter (**Figure 4f**) and the shell of the NPs with a large lattice parameter (**Figure 4g**).



Figure 4: a. HRTEM image of CoNiPtCu; b. Diffrattogram of the NP in the white square of a.; c. STEM-HAAFD image of CoNiPtCu; d. Chemical mapping of CoNiPtCu (high-left corner: Co; high-right corner: Pt; low-left corner: Cu; low-right corner: Ni); e. HRTEM image of CoNiPtCu (White inset: diffractogram of the NP in the white square; Yellow inset: diffractogram of the shell of the NP in the white square; Red inset: diffractogram of the core of the NP in the white square); f. Inverse FFT of the white inset of e. selecting only the reflections of the red inset of e.; g. Inverse FFT of the white square of e. selecting only the reflections of the yellow inset of e.

III.2.4 Atomic scale study of the CoNiPtAuCu Nanoalloys

To successfully synthetize the quinary alloy (CoNiPtAuCu), it has been necessary to change the surfactants, in particular the oleic acid it has been changed with trioctylphosphine. **Figure 5** shows some HR STEM-HAADF images and the composition of individual NPs measured by STEM-EDX as a function of their size, confirming the success in the synthesis of these HEA NPs.



Figure 5: a-d. HR STEM-HAADF image of CoNiPtAuCu; b. Diffractogram of the NP in red square of a.; c. Diffractogram of the NP in yellow square of a.; e. Diffractogram of the NP in red square of d.; f. Graph showing the composition of single CoNiPtCu NPs as a function of their size.

Looking firstly at **Figure 5 a** (NP in the red square), **b** and **f** it is clear that the NPs are well crystallized showing a FCC structure with a low quantity of defects. Moreover, aside from a lack of cobalt, the composition is near equiatomic for the majority of the NPs and the composition dispersion of NPs is low (only 5.6 %, see **Table 2**). As the HEA NPs prepared by PLD, there is a size effect on the composition of NPs, but interestingly the repartition of elements in the small and big NPs is different than in the physical synthesis. Here, small NPs present an excess of Co and Pt while large NPs are richer in Au and Cu. This result highlights the role of the environment (liquid vs vacuum) on the mobility of metals during Ostwald ripening processes. As in the PLD synthesis, this change in the composition goes hand to hand with the apparition chemical ordering (**Figure 5c-e**) and phase segregations (**Figure 5a**). As illustrated in **Figure 6**, chemical mapping shows that all the elements are homogenously distribute in small NPs while large NPs have a core rich in AuCu and shell rich in CoNiPt.

	All NPs	NPs with size $< 6 \text{ nm}$	NPs with size $> 6 \text{ nm}$
at% of Co	10.75 ± 4.26	13.77	8.68
at% of Ni	19.61 ± 5.09	19.31	19.83
at% of Cu	26.13 ± 5.90	21.73	29.14
at% of Pt	24.89 ± 6.13	29.22	21.94
at% of Au	18.62 ± 6.50	15.98	20.42

Table 2: Average composition of single NPs.



Figure 6: a. STEM-HAADF image of CoNiPtAuCu; Chemical mapping of Co (b.), Cu (c.), Ni (d.), Pt (e.) and Au (f.) of a.

IV. Conclusion and perspectives

Considering the obtained results, the synthesis of ternary (CoPtNi), quaternary (CoPtNiCu and CoPtNiAu) and quinary (CoPtNiCuAu) high-entropy nano-alloys is a success. We can assert that concerning the small NPs (in a range between 3 up to 6 nm) we succeeded in the formation of well crystallized solid solutions. In particular, knowing the composition of the single NPs thanks to our STEM-EDX analyses, we conclude that the well crystallization in the FCC phase of the small NPs is a direct consequence of their equiatomic composition. So that, both Pulsed Laser Deposition and the hot injection methods are suitable for the fabrication of HEA NPs and these extraordinary results make already possible further collaborative studies to evaluate and understand the potential of these NPs for catalytic applications.

Concerning the formation of some large core-shell NPs, we clearly identified a size effect on the composition of NPs leading to the phase separation observed only in NPs with a size above 7 nm. Thus, we believe that this phenomenon is due to the Ostwald ripening, a coarsening mechanism that usually produce a size dependent composition of nanoallays¹³. Thus, the composition of the largest NPs deviates from the equiatomic conditions, lowering the entropy of mixing and then favoring the formation of phase segregated nanostructures. Interestingly, this size effect is not the same in the physically prepared NPs and in the chemically prepared NPs, in fact the EDX analyses show an accumulation of different metals in large and small NPs in the two synthesis methods. In particular the large NPs synthetized by the PLD show an increase of Co and Ni, on the other side large NPs prepared by wet chemistry present an excess of Au and Cu. So it is worth says that this effect, that depends on the different mobility of metals, is also medium-dependent because the NPs fabricated by PLD are formed under vacuum on a substrate while the wet chemical method exploits the nucleation and growth in the liquid.

To overcome this issue, in the future it will be possible to exploit the Flash Laser Annealing technique. This technique consists in using the pulsed laser beam of the PLD set up to anneal the NPs. Interestingly, as the absorption cross section of the laser beam increases with NP size, this peculiar annealing process induces an inverse Ostwald ripening in which the small NPs increase in size at the expense of the large ones, up to all the NPs have the same size²¹. The very high temperature reached with this technique could also homogenize the composition of the NPs, so it should permit to eliminate (or at least limit) this unwanted compositional size effect.

For what concern the chemically synthetized NPs, liquid-cell TEM experiments will be necessary to understand what are the growth mechanisms involved in the formation of those large core shell NPs^{22,23,24}. This in situ TEM technique allows observing at single NP level the formation mechanisms of nanocrystals in liquid of controlled composition and temperature and measuring the evolution of their size, shape, atomic structure and composition in real time. Thus, thanks to these liquid-cell experiments it will be possible to develop new protocols to achieve the equiatomic composition of all the NPs chemically synthetized.

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