

## Supplementary information

### **Synthesis and structural properties of high-entropy nanoalloys made by physical and chemical routes**

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## Detailed information on the chemical synthesis protocols

### List of abbreviations:

OA: Oleic Acid

HDiol: 1,2 Hexadecane Diol

OAc: Oleic Acid

OAm: Oleyl Amine

TOP: TriOctylPhosphine

BE: Benzyl Ether

### *Synthesis of CoNiPt HENA.*

Compounds	Molecular Weights (g.mol <sup>-1</sup> )	amount (mmol)	Amount (weight or volume)	Relative stoichiometry*
Co(acac) <sub>2</sub>	257.15	0.11	28mg	0.33
Ni(acac) <sub>2</sub>	256.91	0.11	28mg	0.33
Pt(acac) <sub>2</sub>	393.29	0.11	43mg	0.33
HDiol	258.44	0.39	100mg	1.18
OAc	282.46	1.27	0.4mL	3.85
OAm	267.46	1.22	0.4mL	3.70
BE	198.26	180.71	40mL	548

\*: The sum of all the metallic precursors accounts for 1 equivalent.

### Protocol:

a 100mL three-necked round-bottomed flask connected to a vacuum line is loaded with OAm, OAc and BE under argon flushing. This solution is heated at 100°C, and the system is submitted to three vacuum / argon cycles, to remove any volatiles (oxygen and water). The temperature is

then raised to 300°C. In parallel, the three metallic precursors and the reducing agent (HDIol) are dissolved in 2mL of BE under gentle heating (50°C).

This solution is then rapidly injected into the main one, kept at 290°C, and the particles are allowed to grow for 2 minutes. The initially clear, colorless solution turns black.

The flask is then tempered into ambient temperature water, to immediately stop the growth of the NPs.

The NPs are then precipitated in ethanol (3 volumes of ethanol for one volume of the BE solution of NPs), and centrifuged at 10000 rpm for 20 mins. The ethanol supernatant is then discarded.

This precipitation/centrifugation cycle is repeated 2 more times. The resulting purified NPs are redispersed in dichloromethane for analyses.

### ***Synthesis of CoNiPtCu HENA***

Compounds	Molecular weights (g.mol <sup>-1</sup> )	amount (mmol)	Amount (weight/volume)	Relative Stœchiometry*
Co(acac) <sub>2</sub>	257.15	0.0825	21mg	0.25
Ni(acac) <sub>2</sub>	256.91	0.0825	21mg	0.25
Pt(acac) <sub>2</sub>	393.29	0.0825	32mg	0.25
Cu(acac) <sub>2</sub>	181.63	0.0825	15.43mg	0.25
HDiol	258.44	1.55	400mg	4.70
OAc	282.46	1.27	0.4mL	3.85
OAm	267.46	1.22	0.4mL	3.70
BE	198.26	180.71	36.3mL	3012
TOP	370,64	1,50	0,5mL	4,10

\*: The sum of all the metallic precursors accounts for 1 equivalent.

Protocol:

Note:

- 1) To insure an efficient reduction of the metallic precursors, a larger excess of reducing agent proved to be necessary.
- 2) TOP was used as an auxiliary ligand.

A 100mL three-necked round-bottomed flask connected to a vacuum line is loaded with OAm, OAc TOP and BE under argon flushing. This solution is heated at 100°C, and the system is submitted to three vacuum / argon cycles, to remove any volatiles (oxygen and water). The temperature is then raised to 300°C. In parallel, the four metallic precursors and the reducing agent (HDiol) are dissolved in 2mL of BE under gentle heating (50°C). This solution is then rapidly injected into the main one, kept at 290°C, and the particles are allowed to grow for 2 minutes. The initially clear, colorless solution turns black. The flask is then tempered into ambient temperature water, to immediately stop the growth of the NPs. The NPs are then precipitated in ethanol (3 volumes of ethanol for one volume of the BE solution of NPs), and centrifuged at 10000 rpm for 20 mins. The ethanol supernatant is then discarded. This precipitation/centrifugation cycle is repeated 2 more times. The resulting purified NPs are redispersed in dichloromethane for analyses.

### *Synthesis of CoNiPtCuAu HENA*

Componds	Molecular weights (g.mol <sup>-1</sup> )	Amounts (mmol)	Amounts (weight or volumes)	Relative stœchiometry*
Co(acac) <sub>2</sub>	257,15	0,0825	16mg	0,2
Ni(acac) <sub>2</sub>	256,91	0,0825	16mg	0,2
Pt(acac) <sub>2</sub>	393,29	0,0825	50mg	0,2
Au(acac) <sub>3</sub>	294,30	0,0825	19mg	0,2
Cu(acac) <sub>2</sub>	181,63	0,0825	12mg	0,2
HDiol	258,44	1,55	400	4,7
BE	198,26	180,71	36,5	3012
TOP	370,64	1,5	0,24	4,1
OAm	267,46	1,22	0,4	3,7

\*: The sum of all the metallic precursors accounts for 1 equivalent.

Protocol:

Note:

- 1) to insure an efficient reduction of the metallic precursors, a larger excess of reducing agent proved to be necessary.
- 2) TOP was used as an auxiliary ligand.

A 100mL three-necked round-bottomed flask connected to a vacuum line is loaded with OAm, OAc TOP and BE under argon flushing. This solution is heated at 100°C, and the system is submitted to three vacuum / argon cycles, to remove any volatiles (oxygen and water). The temperature is then raised to 300°C. In parallel, the five metallic precursors and the reducing agent (HDiol) are dissolved in 2mL of BE under gentle heating (50°C). This solution is then rapidly injected into the main one, kept at 290°C, and the particles are allowed to grow for 2 minutes. The initially clear, colorless solution turns black. The flask is then tempered into ambient temperature water, to immediately stop the growth of the NPs. The NPs are then precipitated in ethanol (3 volumes of ethanol for one volume of the BE solution of NPs), and centrifuged at 10000 rpm for 20 mins. The ethanol supernatant is then discarded. This precipitation/centrifugation cycle is repeated 2 more times. The resulting purified NPs are redispersed in dichloromethane for analyses.

**Additional data:**

	All NPs	NPs with size < 8 nm	NPs with size > 8 nm
at% of Co	29 ± 3.8	28.3	29.5
at% of Ni	37 ± 6.9	35.3	36.7
at% of Pt	33 ± 6.2	36.3	33.5

**Table S1. Average composition of individual CoNiPt NPs prepared by PLD**

	All NPs	NPs with size < 5 nm	NPs with size > 5 nm
at% of Co	28 ± 11.5	25.7	35.6
at% of Ni	29 ± 6.9	28.0	32.0
at% of Pt	23 ± 6.1	24.9	17.8
at% of Au	19 ± 7.4	21.4	14.6

**Table S2. Average composition of individual CoNiPtAu NPs prepared by PLD**

	All NPs	NPs with size < 4 nm	NPs with size > 4 nm
at% of Co	31 ± 11.9	24.6	43.8
at% of Ni	22 ± 9.9	17.0	30.4
at% of Cu	29 ± 13.0	36.8	16.1
at% of Pt	17 ± 7.8	21.5	9.7

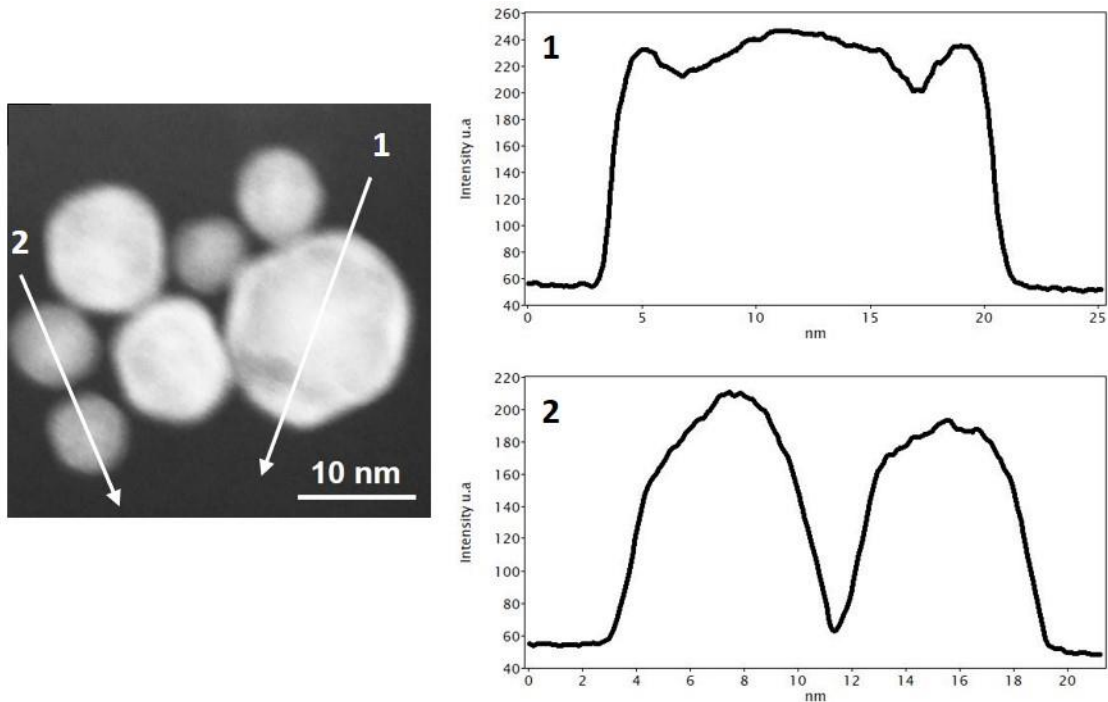
**Table S3. Average composition of individual CoNiPtCu NPs prepared by PLD**

	All NPs	NPs with size < 4 nm	NPs with size > 4 nm
at% of Co	30 ± 9.1	23.9	33.9
at% of Ni	22 ± 5.8	17.7	24.8
at% of Cu	18 ± 7.7	24.0	14.3
at% of Pt	13 ± 4.0	15.6	11.3
at% of Au	17 ± 4.8	18.8	15.7

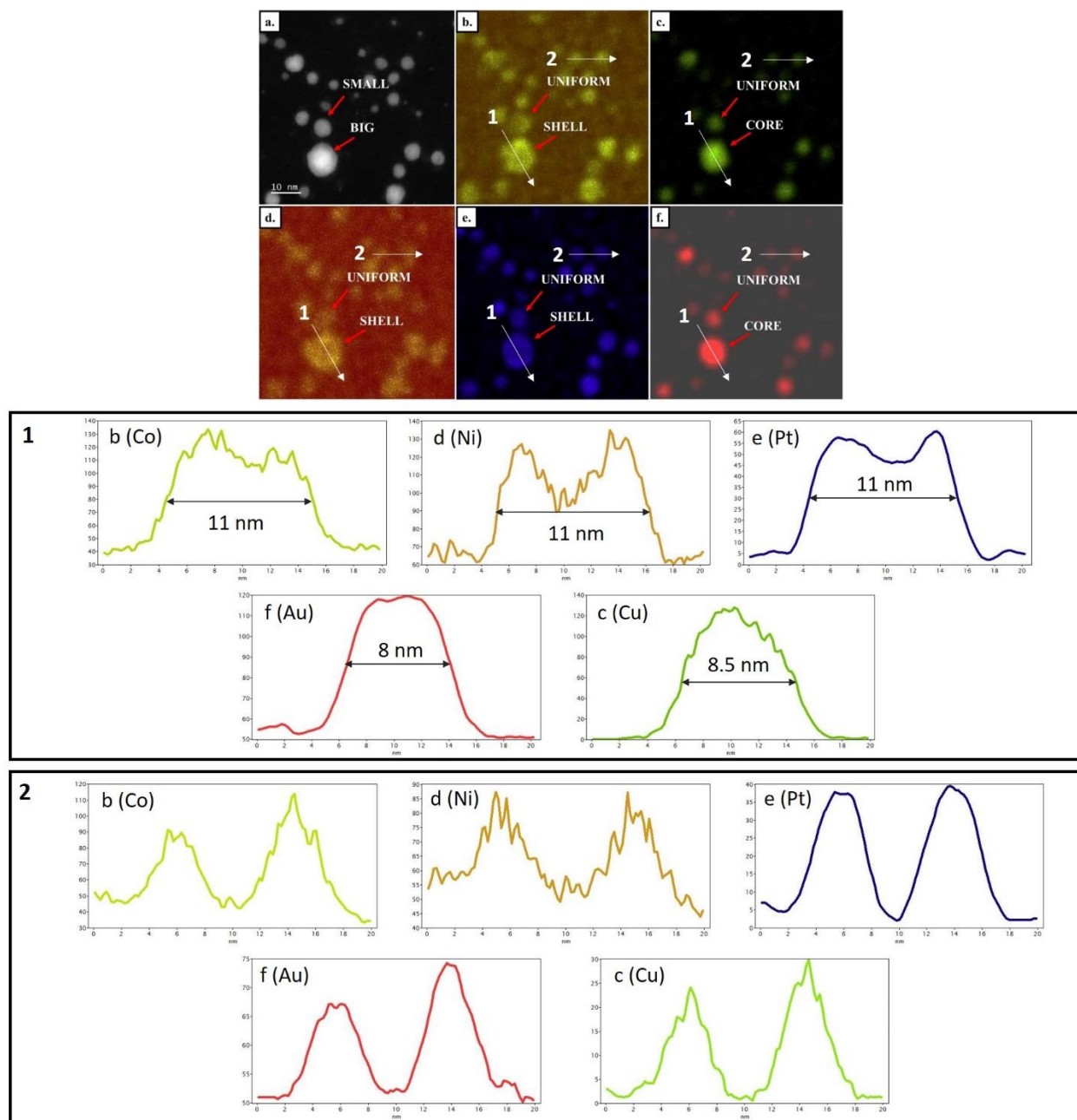
**Table S4. Average composition of individual CoNiPtAuCu NPs prepared by PLD**

	All NPs	NPs with size < 6 nm	NPs with size > 6 nm
at% of Co	11 ± 4.3	13.8	8.7
at% of Ni	20 ± 5.1	19.3	19.8
at% of Cu	26 ± 5.9	21.7	29.1
at% of Pt	25 ± 6.1	29.2	21.9
at% of Au	18 ± 6.5	16.0	20.4

**Table S5. Average composition of individual CoNiPtAuCu NPs prepared by chemical method**



**Figure S1.** (Left) STEM HAADF image of chemically prepared CoNiPtCu HENA. (Right) Line intensity profile measured on a large core-shell NP (profile 1) showing a clear contrast enhancement at the edge of NPs and two small NPs (profile 2) showing no composition inhomogeneity. The arrows in the image indicate the position and direction along which the line intensity profiles were measured.



**Figure S2.** Top: **a.** STEM-HAADF image of CoNiPtAuCu prepared by chemical method. Chemical mapping of **b.** Co (K edge), **c.** Cu (K edge), **d.** Ni (K edge), **e.** Pt (L edge) and **f.** Au (L edge) performed on the same area. Middle: Line intensity profiles measured on the Co, Ni, Pt, Au and Cu mappings. The arrows number 1 in the images indicate the position and direction along which the line intensity profiles were measured (i.e. on a large core shell NPs). The Co, Ni and Pt are more present in the shell of the NPs whereas Au and Cu are more present in the core. Bottom: Line intensity profiles measured on the Co, Ni, Pt, Au and Cu mappings. The arrows number 2 in the images indicate the position and direction along which the line intensity profiles were measured (i.e. on two small NPs). All the elements are homogenously distributed within the two NPs.