Oleylamine and low valency organic precursor : a facile route to of metallic and multicomponent Nanocrystals

Christophe Petit[1], Rabah Benbalagh[3], Suzanne Giorgio[4], Arthur Moisset[1], Marc Petit[2], Alexandre Sodreau[2], Anthony Vivien[1,2], Caroline Salzemann[1], Francois Rochet[3].

[1] Sorbonne Université, CNRS, MONARIS, UMR 8233, 75005 Paris, France

[2] Sorbonne Université, CNRS, IPCM, UMR 8232, 75005 Paris, France

[3] Sorbonne Université, CNRS, LCP-MR, UMR 7614, 75005 Paris, France

[4] Université d'Aix-Marseille, CINAM, UMR 7325, 13288 Marseille, France

Corresponding author email: christophe.petit@sorbonne-universite.fr

Metallic nanoparticles will initiate important development in nanotechnologies due to their specific chemical and physical properties (*i.e.* in catalysis, magnetism, optics, etc..) and new development in sustainable energy. It is well known that these properties are mainly controlled by the fine tuning of structural parameters such as the size, shape, crystallinity and composition. However, the understanding of the mechanical steps leading to the shape control of these objects still remains challenging. Recently our group developed a one-pot synthesis of metallic or bimetallic spherical NPs with only two reagents: $MCl(PPh_3)_3$ and Oleylamine (M= Co or Ni).[1-3] This method showed many advantages like the reproducibility, the low size dispersity and well crystalline NPs.[2-3] This synthesis allows also the formation of transition metal phosphorus (TMP) nanorods starting from pure metallic spherical NPs. Herein, we propose a mechanism for the morphological transition from spherical cobalt NPs to Co_2P NRs over time in a mixture of $[CoCl(PPh_3)_3]$ and oleylamine (OAm) heated at 190°C.[4] The crucial role of oleylamine in the transition was also confirmed by X-ray photoelectron spectroscopy (XPS) but it discloses also the significant involvement of the organo-phosphorus ligand of the Co(I) precursor during the spheres to rod transition yielding to Co_2P nanorods formation. Interestingly this model could be extended to multicomponents NPs as CoNiP. Lastly, the novel synthesis, which produces Co_2P nanorods at a relatively low temperature (∼190 °C), compared to the standard process (∼330 °C), is a notable finding, given the promising applications of this material, particularly in electrocatalytic water splitting.

References

1- L. Meziane, et al., *Nanoscale*, 2016, 8, 18640.

2-A. Vivien, et al. *Chem. Mater.*, 2019, 31, 960–968.

3-A. Moisset, et al. *Nanoscale*, 2021, 13, 11289–11297.

4- R. Benbalagh, et al. *The Journal of Physical Chemistry C*, 2024, 128, 3408-3422.