2016 IEEE Nanotechnology Materials and Devices Conference (NMDC)

Controlled synthesis of core-shell Fe@Au faceted Nanoparticles*

P. Benzo, M. Benoit, N. Tarrat, C. Langlois, R. Arenal, B. Pécassou, A. Le Priol, N. Combe, A. Ponchet and M. J. Casanove

Abstract - **Core-shell Fe@Au crystalline NPs, particularly suitable for biomedical applications, have been successfully synthesized by sequential deposition from two elemental targets in a ultrahigh vacuum sputtering device. The size of the NPs, in the 8-15 nm range, is controlled by the deposited Fe volume. The obtained NPs adopt an original polyhedral core-shell morphology in which a Fe nanocube core acts as a nanosubstrate for the epitaxial growth of gold islands with a truncated pyramid shape. The morphological, structural and chemical properties of the NCs are studied through advanced TEM based techniques (HREM, STEM-HAADF, EDX) down to the atomic scale.**

I. INTRODUCTION

An important attention has been paid in the last decade to nanomaterials including segregated domains such as core-shell nanoparticles (NPs), which preserve the respective properties of the core and the shell while favoring interactions between them. Such heterostructures are indeed expected to favor multi-functionality, to generate fully new properties or more simply to provide an efficient way of preserving the core material from oxidation.

Today, a new step must be taken to better target the properties and applications of core-shell nanoparticles and this comes with an effective control of their morphology. Indeed, numerous properties of functional core-shell nanoparticles depend on their morphology and in particular on the presence of crystalline facets which conditions the surface electronic and crystallographic structures. This obviously matters in the case of catalytic reactivity [1,2] - including photo-catalysis - or electrical conductivity, but also in the biological field, for providing suitable anchoring sites for organic molecules. For example, the preferential anchoring of proteins on {100} facets compared to {110} facets has been recently demonstrated in $SrTiO_3$ polyhedral nanocrystals (Dong et al., *Facet-Specific Assembly of Proteins on $SrTiO_3$ Polyhedral Nanocrystals* **Sci. Rep. 4: 5084** (2014) [3]).

The core-shell chemical configuration is required in biological applications when the biocompatibility of active but toxic elements has to be ensured. This is the case for Fe@Au core-shell nanoparticles, which combine a toxic ferromagnetic Fe core with a biocompatible, chemically inert and easily functionalized Au shell.

Magnetic materials are already used in many medical applications as they can be easily manipulated or heated by an external field. Despite their much lower magnetic properties compared to pure iron, iron oxides are used until now for these applications because of their low toxicity. However, Fe@Au nanoparticles should display much more interesting, as they will take full advantage of the properties of each metal in its crystalline state: magnetization and anisotropy of the iron core, ability of the well-defined crystalline facets of the biocompatible Au shell to provide well-controlled anchoring sites for attaching targeting molecules. Some potential biomedical applications of FeAu NPs are Magnetic resonance imaging contrast enhancement, hyperthermia treatment or directed drug delivery (*see [4] D. Huber, Small 1, 482 (2005) for a review on biomedical applications of iron-based nanoparticles*).

Here, we report the successful synthesis of Fe−Au bimetallic crystalline NPs adopting an original polyhedral core−shell morphology in which a Fe nanocube core acts as a nanosubstrate for the epitaxial growth of gold islands with a truncated pyramid shape.

II. METHODS

Fe-Au NPs were grown by sequential deposition from two elemental targets in an ultrahigh vacuum sputtering device. A NaCl (100) crystal was used as a substrate and covered by a 5 nm thick amorphous alumina layer. The deposition temperature of the two metals was optimized in order to assure the three dimensional growth. After metal deposition, the temperature was slowly decreased to room temperature and maintained at this temperature to deposit a 5 nm thick alumina cover layer.

Accurate determination of morphological, structural and chemical parameters in individual nano-crystals have been obtained through advanced TEM based techniques, down to the atomic scale. In particular, Cs-corrected (objective lens) HREM, and Cs-corrected probe STEM-HAADF and STEM-EDS techniques have been used [5].

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*Research supported by the NEXT Laboratory under the disruptive project FUN.

P. Benzo, M. Benoit, N. Tarrat, B. Pécassou, A. Le Priol, N. Combe, A. Ponchet and M. J. Casanove are with *CEMES, CNRS UPR 8011 and Université de Toulouse, 29 rue Jeanne Marvig, F-31055 Toulouse cedex4, France (*corresponding author email: benzo@cemes.fr)

C. Langlois was with *CEMES, CNRS UPR 8011 and Université de Toulouse, 29 rue Jeanne Marvig, F-31055 Toulouse cedex4, France.*
He is now with MATEIS, INSA Lyon, 7, Avenue Jean Capelle, F-69621 Villeurbanne Cedex, France.

R. Arenal is with *L.M.A., Instituto de Nanociencia de Aragon, Universidad de Zaragoza, C/Mariano Esquillor s/n, 50018 Zaragoza, Spain.*

978-1-5090-4352-1/16/$31.00 ©2016 IEEE

III. RESULTS AND DISCUSSION

Figure 1a-b shows a Bright Field TEM general view of the as-deposited NPs. Due to the high deposition temperature (600°C), no post-deposition annealing was necessary to obtain the NPs growth. The size of the NPs was controlled by varying the nominal thickness of the Fe layer. The mean diameter of the obtained NPs increases from 8 to 14 nm when the Fe nominal thickness increases from 1 to 2 nm (the nominal thickness of Au was fixed at 1nm) (Figure 1c).

Figure 1d shows an high resolution HAADF-STEM image of a single nanoparticle oriented along the [00-1] direction of Fe. Thanks to the Z-contrast, available in HAADF-STEM mode, the dark-core/bright-shell distribution observed can be undoubtedly attributed to an Fe-rich core and a Au-rich shell, respectively. Moreover, this NP display a well-defined morphology with a cubic Fe core and a shell formed of Au pyramidal islands.

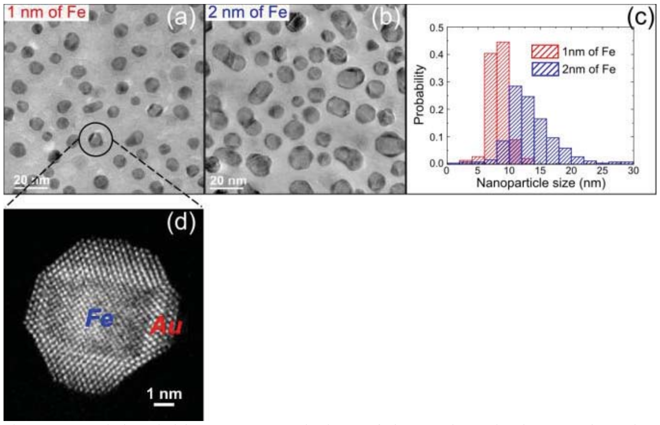

Figure 1. Bright Field TEM general view of the as-deposited NPs when the Fe nominal thickness increases from (a) 1 to (b) 2 nm (the nominal thickness of Au was fixed at 1nm) with (c) the corresponding size distributions. (d) HAADF-STEM image of a single Fe−Au NP.

The HAADF-STEM image displayed in Figure 1d clearly reveals the existence of two different crystal lattices (one in the core region and one in the surrounding pyramids). In order to go further in the structural analysis, and in particular to clearly identify the two different lattices, the NPs were also studied in Cs-corrected high-resolution TEM (HREM). A typical HREM image of a suitably oriented NP is displayed in Figure 2. The analysis of the diffractograms corresponding to the core and the pyramids confirms that both regions are formed by nanocrystals (not shown). The Fe nanocrystal, in its bcc phase, is observed along a [001] axis and displays a nanocube shape exposing {100} facets. The measured lattice parameters of the core well correspond with the theoretical ones of pure Iron. This indicate that the core is made of pure Fe (not oxidized) and that it is fully protected by the Au shell. The fcc Au nanocrystals, observed along their $[01\bar{1}]$ axis, present a truncated pyramid morphology with top and bottom bases parallel to (100) planes and lateral facets parallel to (111) planes. The scheme in Figure 2 sums up this structural and morphological analysis.

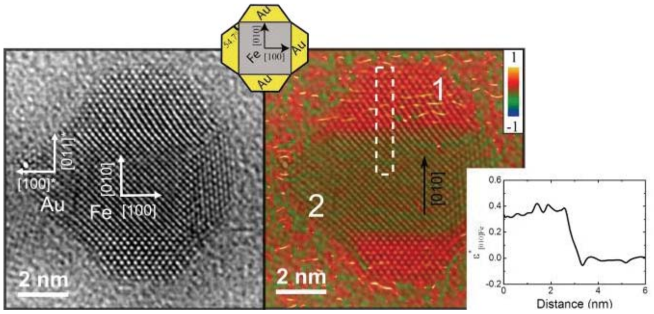

Figure 2 Left: HREM micrograph of a core−shell NP and corresponding scheme. Right: same micrograph superimposed to the map of $\varepsilon^*[100]$ measured by geometrical phase analysis. The line profile along the [010] Fe axis (black arrow), taken from the rectangular region, is plotted in the inset.

The lattice parameter in the Au pyramids was better determined using the geometrical phase analysis method (GPA). In this method, the analyzed region, here the Au pyramid, is considered as a strained version of the reference region, chosen in the Fe region in our case. The colored map superimposed to the HREM image in Figure 2 displays the variation ($\varepsilon^*_{[010]}$) of the lattice plane spacing in a given region compared to the (100) lattice plane spacing in the center of the iron core. The line profile along the [010] Fe axis, displayed in inset, shows an abrupt increase of $\varepsilon^*_{[100]}$, around 40%, when crossing the interface from the Fe core to pyramid 1. This measured variation well agrees with the important relative change in lattice parameters $(a_{Au} - a_{Fe})/a_{Fe}$, indicating that the top of the Au pyramid is fully relaxed. In pyramid 2, which is differently oriented relatively to the Fe lattice, the measured lattice spacing corresponds to the spacing of a {110}* Au plane family (the * referring to the Au lattice). The absence of contrast at this interface clearly reveals the coherent epitaxial growth of the Au pyramids over the Fe cube facets under a slight biaxial compressive stress.

IV. CONCLUSION

In summary, we achieved the synthesis of a new kind of core−shell Fe−Au NPs by a physical vapor deposition method. The TEM analysis of these highly faceted NPs demonstrated the epitaxial growth of strained Au pyramids on {100} Fe nanocube facets, ensuring an efficient protection of the core.

ACKNOWLEDGMENT

Part of this work was supported by the NEXT Laboratory (in Toulouse) under project FUN.

REFERENCES

[1] Yang, C.-W., Chanda, K., Lin, P.-H., Wang, Y.-N., Liao, C.-W., & Huang, M. H. (2011). *Fabrication of Au-Pd Core-Shell Heterostructures with Systematic Shape Evolution Using Octahedral Nanocrystal Cores and Their Catalytic Activity*. **Journal of the American Chemical Society**, 133(49), 19993-20000.

[2] Wang, D., Xin, H. L., Hovden, R., Wang, H., Yu, Y., Muller, D. A., et al. (2013). *Structurally ordered intermetallic platinum-cobalt core-shell nanoparticles with enhanced activity and stability as oxygen reduction electrocatalysts*. **Nature Materials**, 12(1), 81-87.

[3] Dong, L., Luo, Q., Cheng, K., Shi, H., Wang, Q., Weng1, W. & Han, W.-Q. (2014). *Facet-Specific Assembly of Proteins on $SrTiO_3$ Polyhedral Nanocrystals*. **Scientific Reports** 4: 5084

[4] Huber D. (2005). *Synthesis, Properties, and Applications of Iron Nanoparticles.* **Small** 1, 482.

[5] Langlois, C., Benzo, P., Arenal, R., Benoit, M., Nicolai,J., Combe, N., Ponchet, A. and Casanove M. J. (2015). *Fully Crystalline Faceted Fe−Au Core−Shell Nanoparticles*. **Nano Letters**, 15, 5075−5080.