

Thermodynamically driven Oxidation-induced Kirkendall Effect in Octahedron-shaped Cobalt Oxide Nanocrystals

Miguel A. Ramos-Docampo, Beatriz Rivas-Murias, Benito Rodríguez-González and
Verónica Salgueiriño*

Departamento de Física Aplicada and CACTI, Universidade de Vigo 36310, Vigo (Spain)

* vsalgue@uvigo.es

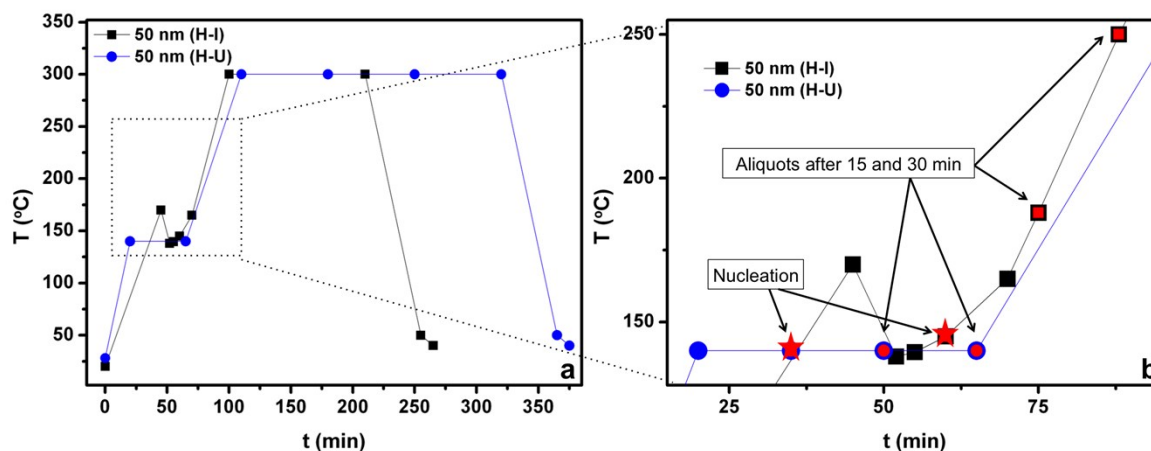


Figure S1. Temperature profile of the H-I and H-U processes followed to obtain 50 nm edge octahedron-shaped nanoparticles. On the right graph, the red stars indicate the time and temperature at which nucleation took place and the red dots and squares are related to the time (15 and 30 min after nucleation) and temperature at which the aliquots were extracted.

Progression	Solution color	Species formed through the reaction
1	Deep purple	Co ²⁺ ions in solution
2	Pink slurry	Co-amine species in solution
3	Red	Co(OH) ₂ present in solution
4	Black	Residual red cobalt hydroxide and cobalt oxide species. (Formation of the CoO nuclei)
5	Dark brown	Cubic CoO

Table S1. Table describing the changes in colour observed and associated to the different steps of the synthetic process.

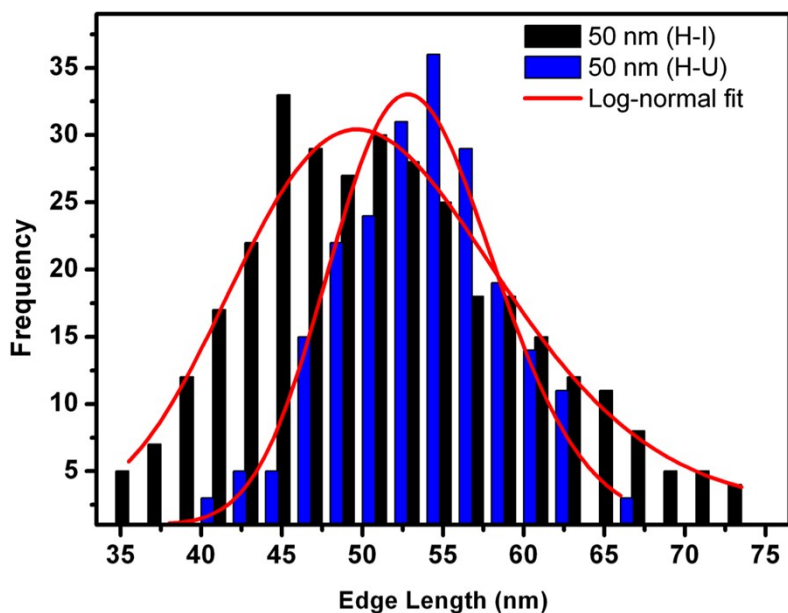


Figure S2. Size distribution analysis using the edge length of the octahedra obtained using H-I or H-U synthetic approaches, fitted to a log-normal (in red).

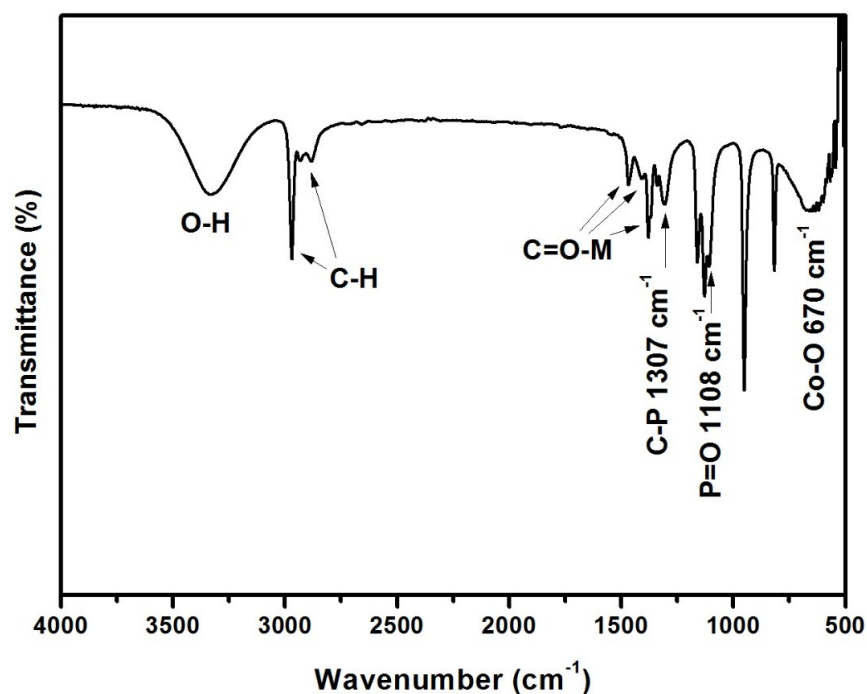


Figure S3. FTIR spectra of a sample of cobalt oxide octahedra.

From the FTIR spectrum in figure S1, we can conclude there is no clear evidence of the presence of oleylamine derivatives in the surface of the CoO nanocrystals. Although the band centered at approximately 1280 cm^{-1} can be correlated to C-N stretching modes, no bands at 1620 , and/or 3360 and 3440 cm^{-1} , which are very significant in primary and secondary amine species, appear. A possible explanation would indicate the lower affinity of amines to the surface of the initially formed CoO nanoparticles. Perez de Berti *et al.* and Li *et al.* have described a similar situation when synthesizing metal oxide nanoparticles in the presence of both amines and carboxylates.^{1,2} On the other hand, residual TOPO species were found (see bands at 1108 and 1307 cm^{-1} , indicative of the P=O and C-P stretching modes, respectively). Additionally, bands centered at 1127 and 1160 cm^{-1} can correlate to TOPO dimers and free TOPO molecules, respectively.³ When assigning these later bands to TOPO dimers and free TOPO, the band at 1108 cm^{-1} matches to TOPO molecules coordinated to the CoO surface (please note that the band at 670 cm^{-1} corresponds to Co-O vibrational modes).

Cobalt atoms, however, are not coordinated only to TOPO, but to carbonyl groups as well. Carbonyl vibrational modes usually appear between 1500 and 1700 cm^{-1} . Indeed, the fact of a

shifting appearing below 1500 cm^{-1} implies the coordination of the carbonyl group with a metallic atom, stemming from a decrease of the vibrational energy ($E_{vib} = hc\bar{\nu}$). Therefore, the overtones shown from, roughly, 1300 to 1500 cm^{-1} can be assigned to metal-carboxylate species. A similar feature was already confirmed by Pérez de Berti et al., who found out a similar IR profile when investigating the formation of magnetite nanoparticles in the presence of oleic acid.¹ Our approach requires the oleic acid molecules attached at the CoO surface facets of the growing nanocrystals, and indeed, the distances between peaks, which also give a piece of information about the coordination mode, indicate monodentate ligands (distances $< 200\text{ cm}^{-1}$), bidentate ligands (distances $> 100\text{ cm}^{-1}$) or bridge ligands (distances between $140 - 200\text{ cm}^{-1}$). In our case, the spectrum indicates bidentate ligands.

There is a broad band at 3333 cm^{-1} that correlates to stretching O-H vibrations, stemming from either carboxylic species or environmental water (moisture). However, considering the broad but with a lower intensity band always associated to water, we can discard the possibility of moisture in our sample and assign this 3333 cm^{-1} band to carboxylic species. Finally, the bands between 2870 and 2971 cm^{-1} can be assigned to the sp^3 C-H stretching modes present in the organic molecules already described.

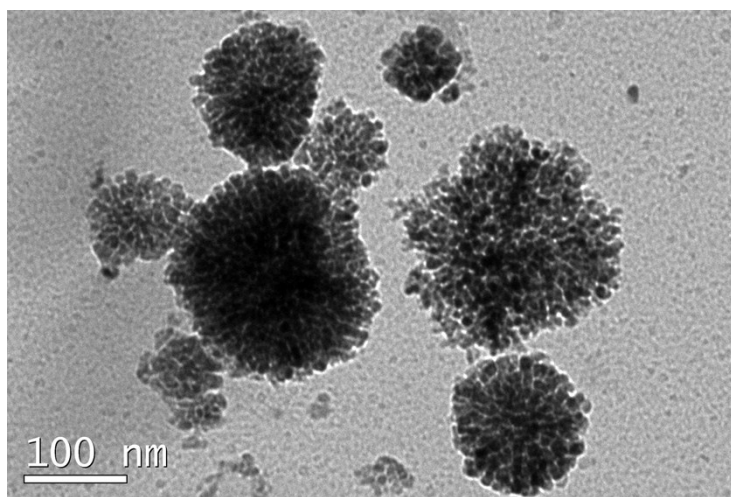


Figure S4. TEM image of spherical aggregates of CoO from an intermediate stage in the H-U strategy.

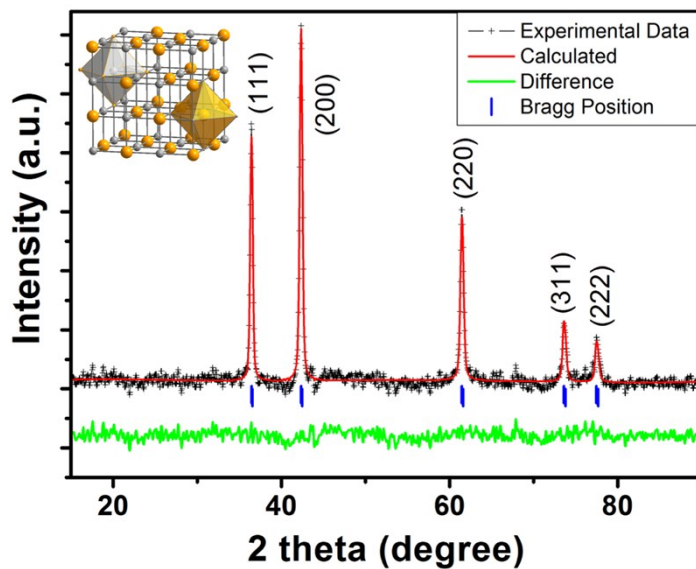


Figure S5. XRD pattern of the sample of octahedra obtained using H-I synthetic approach including the Rietveld refinement.

The Rietveld refinement has been performed considering the presence of the CoO and Co₃O₄ phases. However, the secondary Co₃O₄ phase (observed by HRTEM) is screened in the XRD pattern, due to the fact that its more intense peak (311) is very close to the second more intense peak of the CoO phase (the 111 peak).

References

1. I. O. Pérez de Berti *et al.*, *Nanotechnology* 2013, **24**, 175601.
2. Y. Li *et al.*, *J. Mater. Chem.* 2006, **16**, 2175.
3. C. Yang *et al.*, *Journal of Material Science* 2015, **50**, 3103.