Supporting Information

Spontaneous Formation of Hollow Cobalt Oxide Nanoparticles at Room Temperature at the Water/Air Interface

Oxidation Process of CoO Hollow Nanoparticles

When the Co NPs are exposed to air, the formation of a first thin oxide layer on the Co surface is very rapid, even at RT. Colloidal Co NPs solutions processed in air-free conditions, but subsequently exposed to the atmosphere, gave different thicknesses of oxide shell depending on the exposure time. This process occurs up to passivation or full oxidation, depending on the oxidizing environment and the stability of the NP (high crystalline and homogeneous coating), to form homogeneous CoO layers that effectively protect the Co core from oxidation.

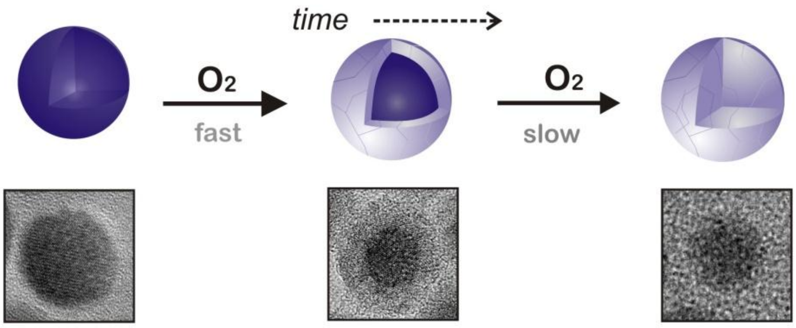

***Figure S1**: Schematic diagram illustrating the different oxidation processes observed for Co NPs in contact with air. Scheme not drawn to scale.*

Recovery Process of CoO Hollow Nanoparticles

The maximum volume of water was removed from the bottom part of the Petri dish with the help of a syringe. Afterwards, the remaining solution was mixed with an equal volume of MeOH. The mixture was shaked with the aim of favor the precipitation of the particles, and then centrifuged at 6000 rpm during 20 min. After remove the supernatant, 2 mL of MeOH were added and the centrifugation process repeated. Finally, the supernatant was removed and the particles redispersed in a small volume of DCB (~0.5 mL).

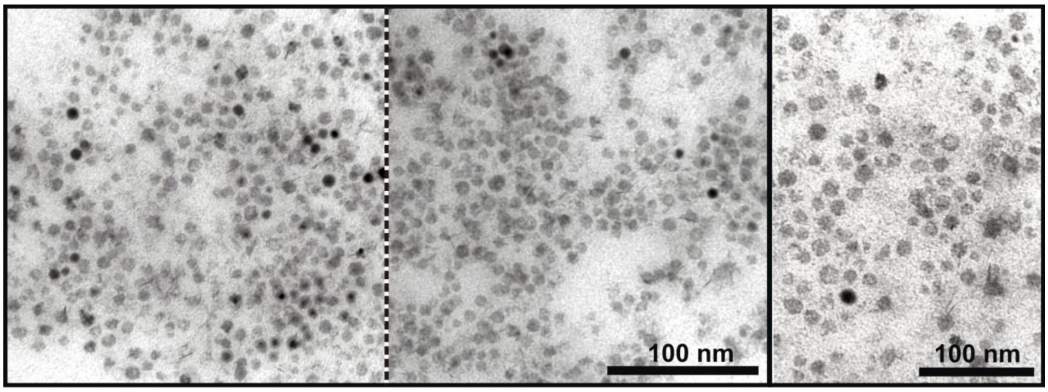

Figure S2: *TEM images of the hollow Co NPs recovered after 5 h of exposure onto distilled water.*

Magnetic Measurements

AC susceptibility curves as a function of the AC frequency in a temperature range close to the observed T_B of the hollow particles are shown in the inset of Figure 4B. The observed frequency dependence is indicative of a blocking process. However, attempts to fit the experimental data using the Arrhenius law end up always in values of the microscopic relaxation time $\tau_0 \sim 10^{-40}$ (it is expected to be around 10^{-11} for superparamagnetic NPs[26]).

Besides, a quite accurate fit of the experimental data taking reasonable values of τ_0 ($\sim 10^{-9}$ - 10^{-10}) can be obtained by using the Vogel-Fulcher law ($\tau = \tau_0 \exp(A/(T-T_0))$) with a T_0 value of about 40 K. This gives a T_B' slightly below 10 K, which is very close to that obtained for residual disintegrated CoO NPs. Thus, the scenario is that hollow particles are polycrystalline and consist of tiny antiferromagnetic CoO grains.

Pourbaix diagram

A useful way to study the relation of potential to corrosion is with an electrochemical equilibrium diagram-called the Pourbaix Diagram. Pourbaix Diagrams are thermodynamic plots of potential vs. pH. An interpretation of the cobalt Pourbaix diagram would indicate that the exposure of cobalt to water may lead to corrosion, especially if it is not dried immediately. Nevertheless, there are corrosion inhibitors used as an effective way to reduce metal corrosion. The inhibitor in our experiment, i.e. the surfactant layer, acts by adsorbing onto the metal surface, thus providing a barrier to the corrosive environment.

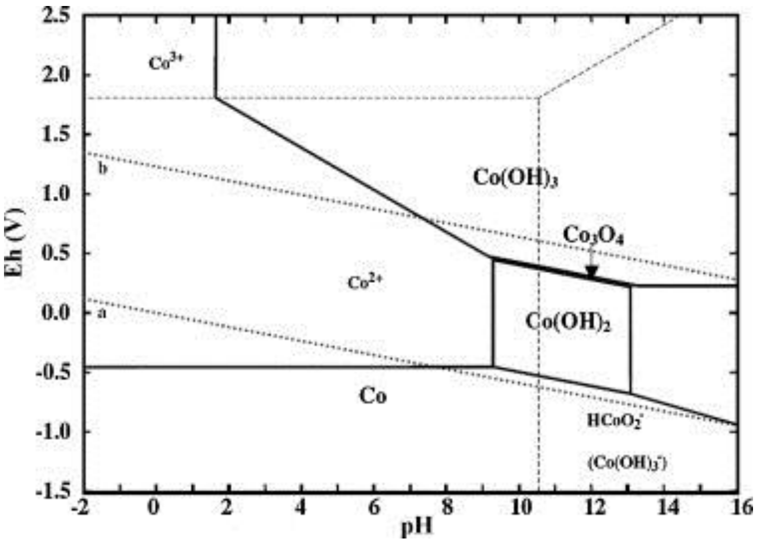

Figure S3. *Pourbaix diagram for cobalt*