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Experimental and theoretical evidence for oriented aggregate crystal growth of CoO in a polyol

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Supporting information

About the intermediate solid phase formed during the polyol process

The precipitation of CoO particles in polyol is preceded by the formation of an intermediate solid phase, which was successfully isolated and identified as a layered hydroxyl-acetate cobalt salt [1] (see Figure SI.1). Interestingly, this solid exhibits a voil-like morphology, far from the popcorn-like morphology of the final cobalt oxide solids (Figure SI.2). This loss of morphology memory agrees with the fact that the intermediate solid phase serves as cation reservoirs, which dissolution controls the concentration in the reaction medium of the metal cation solute on which nucleophilic substitution and condensation reactions proceed leading to the desired oxide,

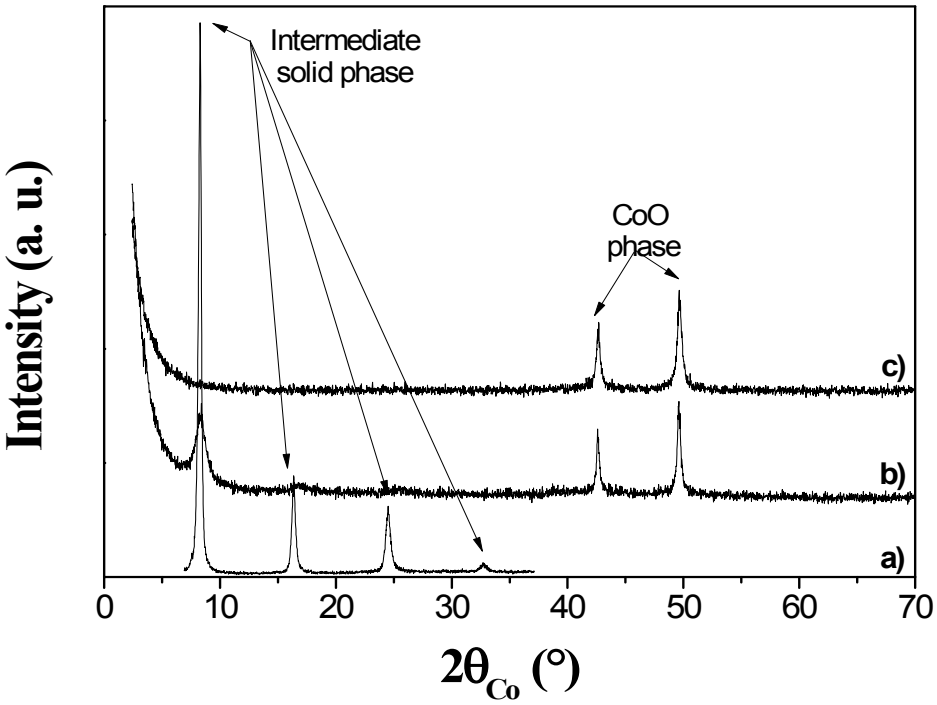

Figure SI.1. XRD patterns recorded on the powders isolated from the DEG reaction solution after different heating times (the temperature being fixed to 180°C) and corresponding respectively to a) the layered hydroxy-acetate cobalt salt, b) a mixture of that and the cobalt oxide and c) the cobalt oxide alone.

[1] L. Poul, N. Jouini, F. Fiévet, *Chem. Mater.* 2000, **12**, 3123.

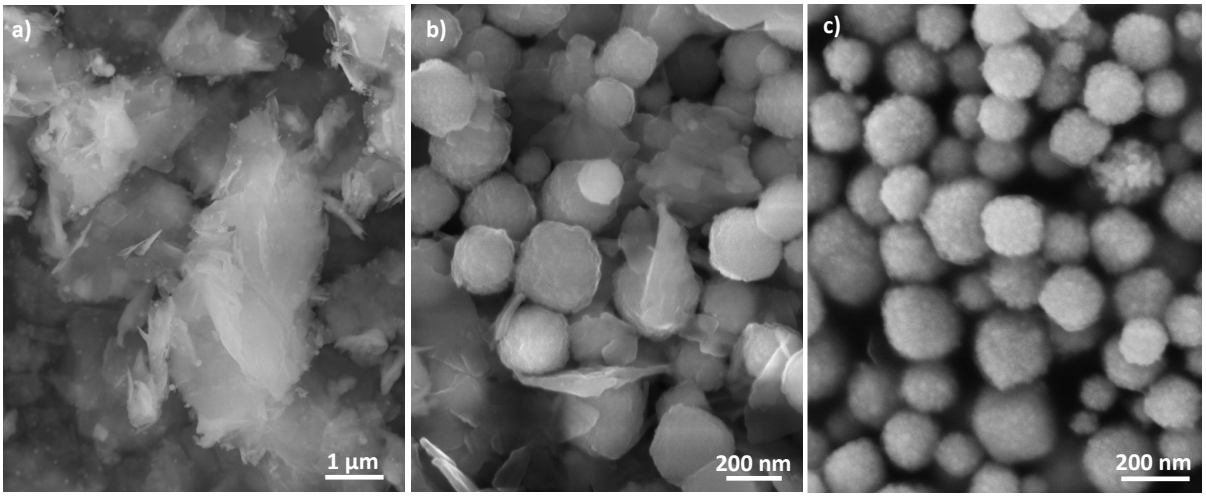

Figure SI.2. SEM micrographs recorded on the powders recovered from the DEG reaction solution after different heating times (the temperature being fixed to 180°C) corresponding to a) the layered hydroxy-acetate cobalt salt alone, b) a mixture of that and the cobalt oxide and c) the cobalt oxide alone.

XRD Texture factor

X-ray diffraction, through the calculation of the texture factor T_{hkl} defined as follows, could be an interesting tool to evidence a texture in a crystalline matter. It allows comparing the experimental diffraction line intensity for a given diffracting family of reticular planes (hkl) to the tabulated for non-textured reference:

$$T_{hkl} = \frac{\left(\frac{A_{norm.hkl}^{exp.}}{I_{norm.hkl}^{theo.}}\right)}{\frac{1}{n}\sum_{\{h\,k\,l\}}\left(\frac{A_{norm.h'k'l'}^{exp.}}{I_{norm.h'k'l'}^{theo.}}\right)}$$

In practice, $A_{norm.hkl}^{exp.}$ measures the observed intensity (peak area) of the (hkl) diffraction line normalized with the experimental area of the peak expected to be theoretically the most intense, while $I_{norm.hkl}^{theo.}$ corresponds to the normalized intensity of the same (hkl) line of a randomly oriented sample corresponding to the tabulated bulk CoO (JPDS n° 98-000-9865) and n to the number of reflexion.

T_{hkl} was calculated for a DEG-made representative CoO nanopowder. Its value was systematically found to be very close to 1 (see Table SI.1), meaning that the constituting quite isotropic in shape grains were statistically orientated on the sampling holder, preventing thus the evidence of any texture effect.

DEG-made CoO nanopowder						
(hkl)	**2θ (°)**	**d (Å)**	$A_{hkl}^{exp.}$ **(Cts.s^{-1}.°)**	$A_{norm.hkl}^{exp.}$	$I_{norm.hkl}^{theo.}$	**T_{hkl}**
(111)	42.540(2)	2.466	8578.9	56.8	65.5	0.90
(200)	49.581(1)	2.133	15098.1	100.0	100.0	1.04
(220)	72.726(3)	1.509	8471.9	56.1	52.5	1.11
(311)	88.058(8)	1.287	3094.7	20.5	21.1	1.01
(222)	93.130(10)	1.232	2016.3	13.3	14.7	0.94

Table SI.1. Details of the calculation of the T_{hkl} values for a DEG-made representative CoO nanopowder, as inferred from its XRD pattern (λ = 1.7889 Å).

Intermolecular DEG interactions

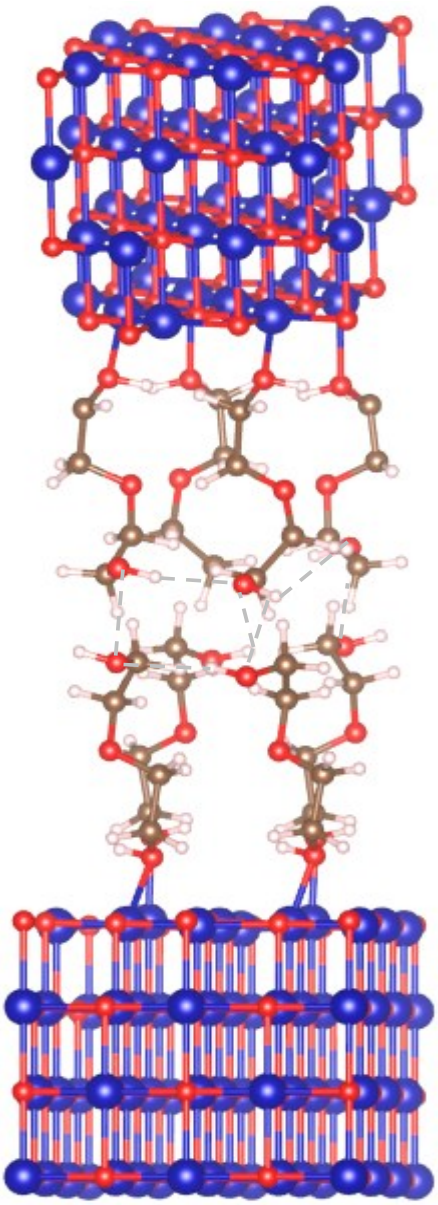

Figure SI.3. Illustration of the Hydrogen bonds (see dashed lines) between DEGs adsorbed one two neighbour CoO nanocrystals. (Oxygen atoms appear in red).

Replacing DEG solvent by TrEG

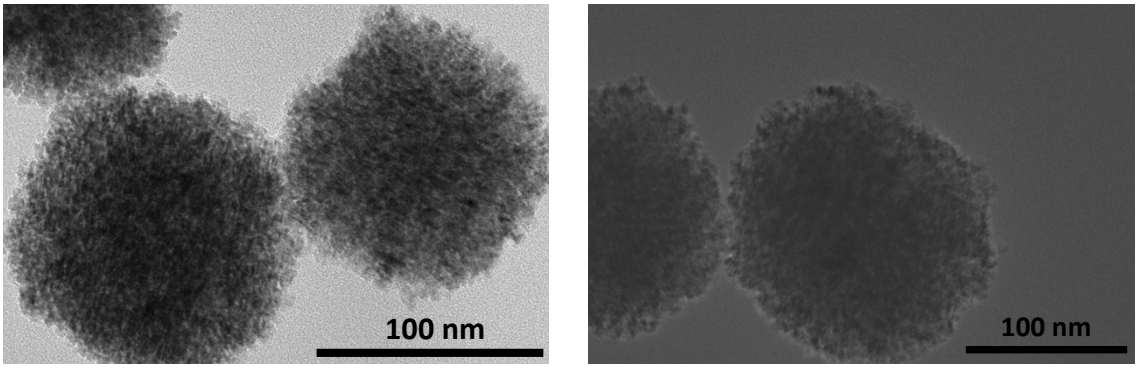

Figure SI.4. TEM images of textured sub-micrometer sized CoO particles produced in DEG (left) and in TrEG (right)