Supporting Information

HCP Cobalt Nanocrystals with High Magnetic Anisotropy prepared by Easy One-Pot Synthesis

Lynda Meziane,[a] Caroline Salzemann,[a] Corinne Aubert,[b] Hélène Gérard,[c] Christophe Petit[a*] and Marc Petit[b*]

[a] Sorbonne Universités, UPMC Univ Paris 06, MONARIS, UMR CNRS 8232, Case 229, 4 Place Jussieu, 75252 Paris Cedex 05, France. [b] Sorbonne Universités, UPMC Univ Paris 06, Institut Parisien de Chimie Moléculaire, UMR CNRS 8232, Case 229, 4 Place Jussieu, 75252 Paris Cedex 05, France. [b] Sorbonne Universités, UPMC Univ Paris 06, Laboratoire de Chimie Théorique, UMR CNRS 7616, 4 Place Jussieu, 75252 Paris Cedex 05, France.

List of the Contents of the Supporting Information

Supporting Information

I. General information

Samples Characterization: A 100 kV transmission electron microscope (TEM, JEOL JEM-1011 with a digital camera Gatan) was used to characterize cobalt nanocrystals and their assemblies (low magnification bright and dark field picture, Selected Area Electron Diffraction, SAED). A 200 kV transmission electron microscope (TEM, JEOL JEM 2010 with a digital camera Gatan) was used for High Resolution TEM picture.

To observe the nanoparticles, 10 µl of the solution containing dispersed nanoparticles in toluene were deposited on a TEM grid, followed by evaporation of solvent in order to form a nanoparticle film.

Hysteresis Loops at 3 K and 300 K of the Cobalt NCs magnetization were measured with a commercial SQUID magnetometer (Cryogenic S600) with applied fields up to 4 T. nanomaterials are either in a cells containing a liquid solution (isolated case) or aggregates on on a adhesive polymeric tape (schotch tm)

II. Synthesis of $ClCo(PPh_3)_3$

$ClCo(PPh_3)_3$ is commercially available but depending on the commercial source the quality could be different.

On 9.6 g of $CoCl_2.6H_2O$, (40 mmoles) and 32.0 g of triphenylphosphine (122 mmoles) were added 600 ml of degassed ethanol. The resulting heterogeneous solution was stirred vigorously at 60-70°C for 30 minutes environ to form *in situ* the complex $Cl_2(PPh_3)_2Co(II)$ as a bright blue powder. The mixture was then cool down to 30°C and 1.28 g of sodium borohydride were added (34 mmoles) in 10 portions every 10 minutes. The color of the mixture changed from bright blue to dark green-brown. After 2 hours the brown-green precipitate was filtrated and washed sequentially with ethanol, water, ethanol and finally diethyl ether. The brown-green solid was dried under vaccum to give 26 g of the desired $Cl(PPh_3)_3Co(I)$ complex with 75% yield.

III. Synthesis of the 9.2 nm hcp-Co spheres

In a glove-box under Nitrogen atmosphere 10 ml of degassed oleylamine were mixed with 221 mg (0.25 mmoles) of $Cl(PPh_3)_3Co(I)$ in a 25 ml vial caped with a septa

pierced by a pipette (to provide overpressure). The solution was stirred and heated using a 50 ml « *drysyn* » filled with sand. The mixture was heated by increasing the temperature by 5°C every minutes to reach 190°C, and then was kept at 190 °C for 1 hour. Then the solution was cool down to room temperature and the nanoparticles were washed by adding 20 ml of ethanol and then centrifuged during 5 minutes at 2500 rpm. The resulting black solid was then dispersed in toluene.

IV. Variation of the optimal conditions

A-Variation of the reducing reagent at room temperature

Figure S1A (Entry 3, Table 1) shows Cobalt NPs obtained from chemical reduction at room temperature of $CoCl(PPh_3)_3$ using sodium triethylhydroborate as reducing reagent. The synthesis takes place in a glove box to prevent oxidation. 0,062 mmol of cobalt complex were dispersed in 12mL of toluene and 410µL of oleylamine. Then 200µl of a 1M solution of $NaB(Et)_3H$ in toluene were added under stirring. A color change was observed from green to black indicating the formation of Co(0). The solution was washed with ethanol centrifuged and the black precipitate containing the NPs has been dispersed in toluene for TEM analysis.

Figure S1B (Entry 4, Table 1) shows Cobalt NPs obtained from chemical reduction at room temperature of $CoCl(PPh_3)_3$ using sodium triethylhydroborate as reducing reagent. The synthesis takes place in a glove box to prevent oxidation. 0,123 mmol of cobalt complex were dispersed in 15 mL of toluene. 400 µl of a 1M solution of $NaB(Et)_3H$ in toluene and 714mg of acid oleic were added and the mixture was stirred for 3h. The solution has been washed by ethanol and the black precipitate containing the NPs has been dispersed in toluene for TEM analysis.

Figure S1C (Entry 4, Table 1) shows Cobalt NPS obtained from chemical reduction at room temperature of $CoCl(PPh_3)_3$ using sodium borohydride as reducing reagent. 0,25 mmoles of cobalt complex were dispersed in 10mL of toluene in presence of 144 mg of oleic acid (passivating agent). Then 10 mL of a 0.05 M $NaBH_4$ aqueous solution were added to the organic media under stirring. In order to favors the contact between the two phases, the mixture is kept under stirring for 3h. The colorless aqueous phase was removed and the organic phase was washed by ethanol and

centrifuged. The black precipitate containing the NPs has been redispersed in toluene for TEM analysis

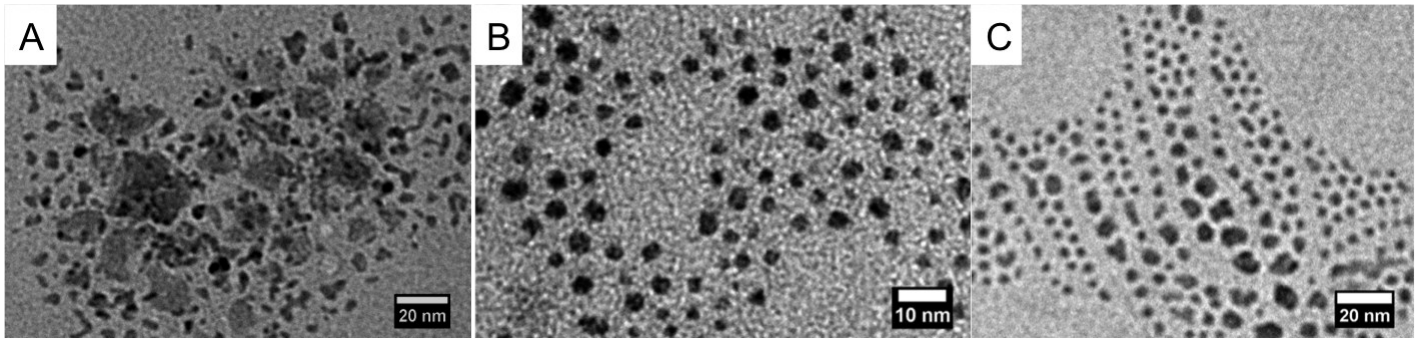


Figure S1 : Co NPs obtained by chemical reduction at room temperature of $CoCl(PPh_3)_3$ by Sodium triethylhydroborate as reducing agent in presence of (A) oleylamine or (B) oleic acid as passivating agent or by sodium borohydride in presence of oleic acid (C).

B-Variation of the concentration

Synthesis of the 7.8 nm hcp-Co spheres

In a glove-box under Nitrogen atmosphere 10 ml of degassed oleylamine were mixed with 110 mg (0.125 mmoles) of $Cl(PPh_3)_3Co(I)$ in a 25 ml vial caped with a septa pierced by a pipette (to provide overpressure). The solution was stirred and heated using a 50 ml « *drysyn* » filled with sand. The mixture was heated by increasing the temperature by 5°C every minutes to reach 190°C, and then was kept at 190 °C for 1 hour. Then the solution was cool down to room temperature and the nanoparticles were washed by adding 20 ml of ethanol and then centrifuged during 5 minutes at 2500 rpm. The resulting black solid was then dispersed in toluene.

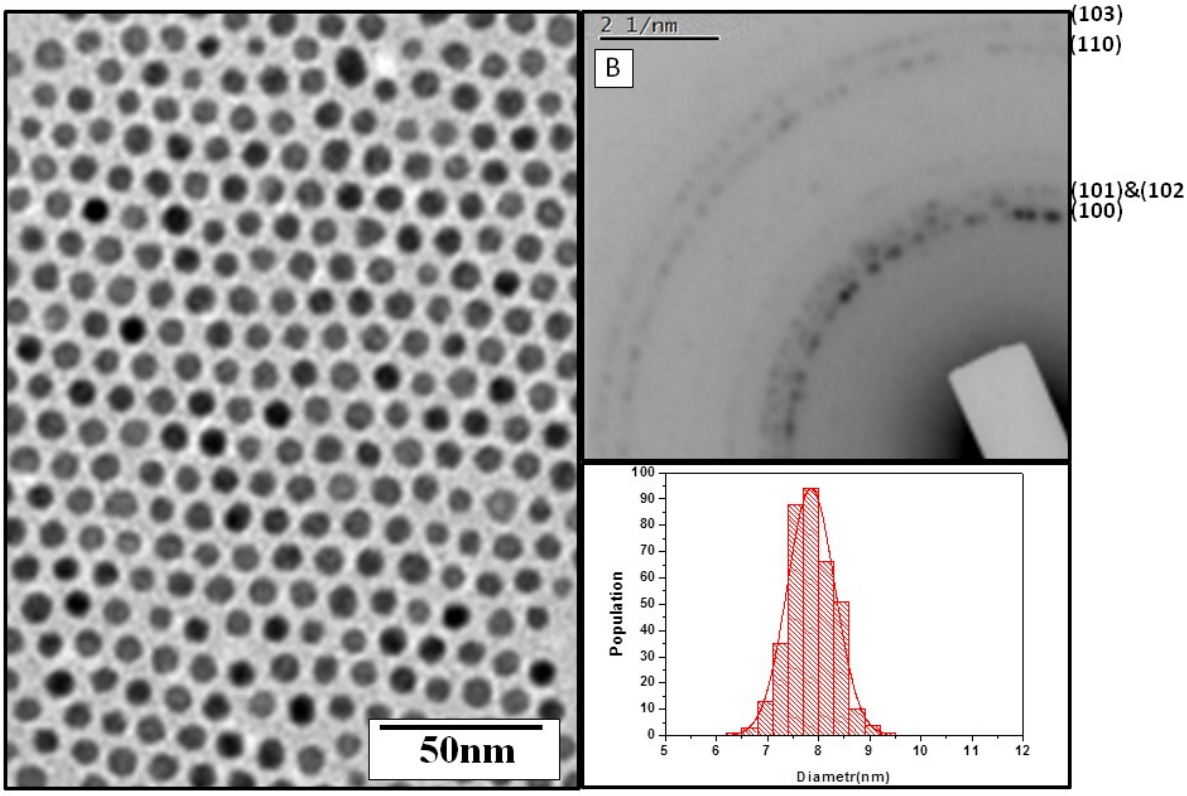


Figure S2 : 7.8 nm Co NPs obtained NPs obtained in oleylamine at 190°C with a concentration of $CoCl(PPh_3)_3$ divided by a factor 2.

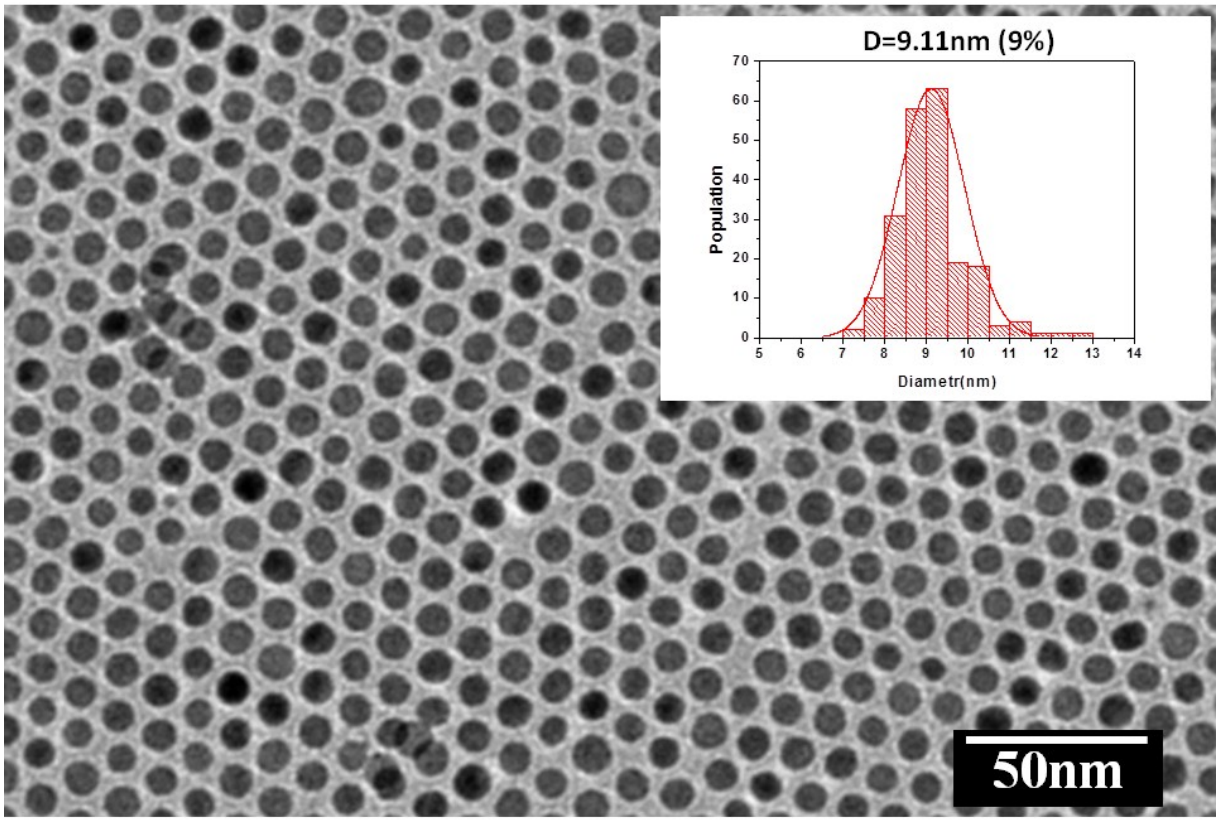
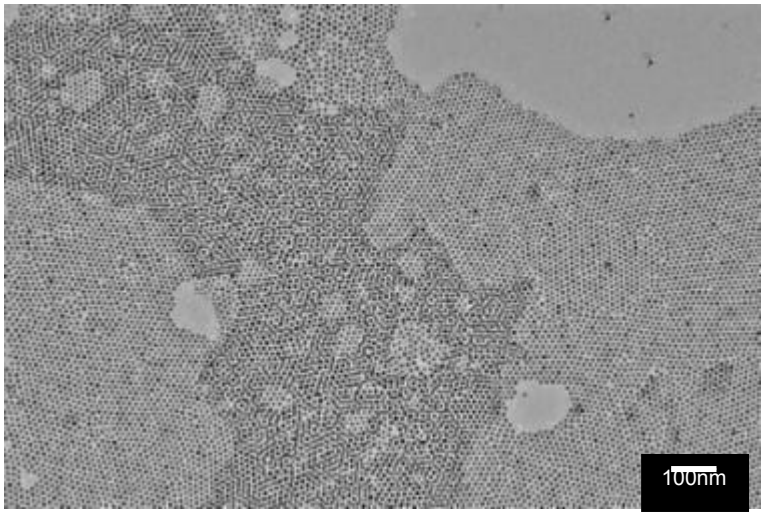


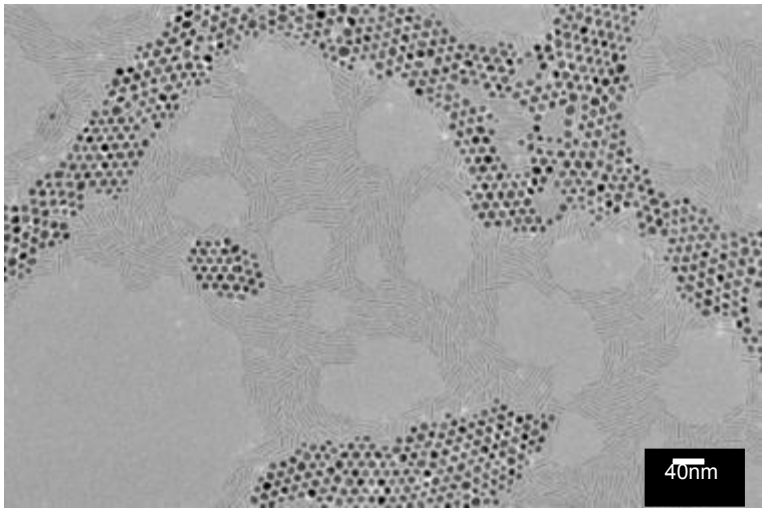
Figure S3 : 9.2 nm NPs obtained NPs obtained in oleylamine at 190°C with a concentration of $CoCl(PPh_3)_3$ increased by a factor 2 .

C-Variation of the reaction time

Synthesis of the hcp-Co rods

In a glove-box under Nitrogen atmosphere 10 ml of degassed oleylamine were mixed with 221 mg (0.25 mmoles) of $Cl(PPh_3)_3Co(I)$ in a 25 ml vial caped with a septa pierced by a pipette (to provide overpressure). The solution was stirred and heated using a 50 ml « *drysyn* » filled with sand. The mixture was heated by increasing the temperature by 5°C every minutes to reach 190°C, and then was kept at 190 °C for 9 hour. Then the solution was cool down to room temperature and the nanoparticles were washed by adding 20 ml of ethanol and then centrifuged during 5 minutes at 2500 rpm. The resulting black solid was then dispersed in toluene.





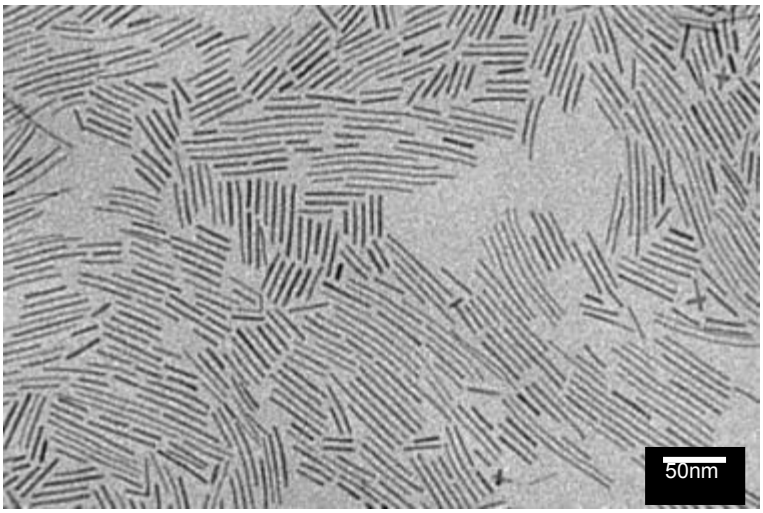


Figure S4 : Kinetics of the Morphological transition of Co NPs at 190°C from $CoCl(PPh_3)_3$ in oleylamine: t=1h (**A**), 220 min (**B**), 540 min (**C**)