Hydrothermal Synthesis of Euhedral Co$_3$O$_4$ Nanocrystals via Nutrient-Assisted Topotactic Transformation of the Layered Co(OH)$_2$ Precursor under Anoxic Conditions: Insights into Intricate Routes Leading to Spinel Phase Development and Shape Perfection

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**ABSTRACT:** Euhedral cobalt spinel cubes, octahedra, and cuboctahedra with narrow size dispersions have been synthesized in a one-pot hydrothermal reaction, using cobalt(II) nitrate and sodium hydroxide at variable concentrations as the only reagents, while their ratio was kept constant at $c_{Co^{2+}}/c_{OH^−} = 2.7$. Three main reaction stages, including parent reactive template (PRT) formation, nutrient-mediated topotactic nucleation (NTN), and morphogenesis of nanocrystals (MNC), were distinguished. In the NTN step, the primary spinel grains development occurs with the [100] and [111] directions of the Co$_3$O$_4$ facets inheriting the [1−11] direction of the elongated PRT plates (formation of cubes) or the [001] direction of the hexagonal PRT plates (formation of octahedra). In an anoxic environment, the excess nitrate anions play a critical role as the Co$^{2+}$ to Co$^{3+}$ oxidants and oxygen donors required to attain the Co$_3$O$_4$ stoichiometry. The nucleated Co$_3$O$_4$ primary nanocrystals are spontaneously assembled into sub-micrometer spinel mesocrystals via imperfectly oriented attachments and then consolidated into euhedral bulk nanocrystals by a hydrothermal treatment (nanocubes) or via dissolution and reentrant recrystallization processes (octahedra and cuboctahedra).

**1. INTRODUCTION**

A major advantage of the well-faceted (euhedral) nanocrystal catalytic materials over traditional heterogeneous catalysts of ill-defined shapes and broad distribution of particle sizes arises from their favorable structural and morphological uniformity.$^{1}$ Such materials allow for unparalleled insight into the quantitative structure–reactivity relationships under more realistic pressure and temperature conditions, in contrast to macroscopic single crystals used in surface science studies.$^{2,3}$ A comprehensive in-depth understanding of the nanocrystal growth with controlled shapes is then of vital importance to master the reproducible large-scale production of high-quality photo/electro/catalytic nanomaterials.

Numerous experimental investigations supported by computational modeling have established that the performance of an oxide catalyst for a given reaction can be considerably enhanced by controlling the dimension and morphology of the grains.$^{4−7}$ Such studies are made possible owing to considerable progress in the development of adoperative bottom-up synthetic methods,$^{8}$ nanocrystal modeling$^{9−12}$ and recent advances in the imaging of nanoobjects by electron microscopy.$^{13−15}$ The last allows retrieving the requisite structural and morphological information, depending on the size and particular features of the investigated specimens.$^{16−19}$

Cobalt spinel is one of the most explored oxides with a remarkable record of widespread applications.$^{20−25}$ Depending on the type and location of the introduced cations, the physical and chemical properties of doped Co$_3$O$_4$ can be tuned over a wide range of compositions without altering the overall spinel crystallographic structure.$^{24−26}$ With regard to the particular structure of the exposed planes with disparate concentrations of the active sites, another possibility of the photo/electro/catalytic reactivity regulation stems from the remarkable ability of Co$_3$O$_4$ for shape modification.$^{2,7−29}$ Those features make nanostructured spinel catalysts very attractive benchmark systems to explore their unique redox properties and the resultant reactivity in relation to the size- and shape-induced effects.

Among the many available methods for the liquid-phase synthesis of nanospinel catalysts of uniform morphology, the hydrothermal method is one of the most expedient
approaches. When it is sensibly designed, it allows attaining clear-cut polyhedral nanocrystals with a low extent of agglomeration. For this purpose, various organic capping and shape-directing reagents are often used, which have to be carefully removed prior to any sensible studies of the obtained nanocrystals. Typically, calcination in oxygen or air at moderate temperatures is used for this purpose, but this process is often not easy to fully accomplish under mild conditions. Enhancement of the temperature to favor combustion of the organic part may lead to undesired sintering of nanocrystals and their contamination by the residual carbon deposit. Hence, it is essential to optimize simple preparation methods for synthesis of polyhedral spinel nanocrystals with the desired shape and size by the sole adjustment of the synthesis conditions, but without the use of any auxiliary organic agents or exogenous oxidants that may contaminate the final product.

There have been several works and review articles devoted to the hydrothermal synthesis of bare and doped cobalt spinels of predefined morphology. Yet, the mechanism of the consecutive transformations of the involved intermediate phases that appear in the course of the synthesis is not comprehensively understood. So far, the most common model of the topotactic (111) Co$_3$O$_4$|[(001)] Co(OH)$_2$, transformation of cobalt hydroxide into cobalt spinel under thermal and hydrothermal conditions, valid only in an aerobic environment, has been based on structural similarities between both of these terminations, supported by an analysis of the corresponding electron diffraction patterns.[24−30]

Detailed investigations into the growth process of nanocrystals and the parameters that govern the growth mechanism reveal an important role of the oriented attachment (OA) in the shape development. The oriented attachment of nanoparticles is associated with their coalescent growth, where the primary crystallites spontaneously stick together according to a common crystallographic orientation of the facets.[30] Such processes are often involved in the hydrothermal synthesis of nanomaterials, leading to the formation of sub-micrometer mesocrystals, which may next be transformed into bulk single crystals.[31−34] Another important mechanism that is widely involved in oxide materials synthesis consists of a topotactic transformation of layered double hydroxide (LDH) precursors directly into the spinel phase.[35,36] In such a phase transition the two crystalline materials, the hydroxide precursor and the spinel oxide, exhibit distinct crystallographic relationships, which have a strong influence on the morphology of the burgeoning material.

In the present work we investigate systematically the principal steps of the hydrothermal synthesis of Co$_3$O$_4$ nanocrystals with a well-controlled morphology, using cobalt nitrate and sodium hydroxide as the sole precursor reagents. Several complementary experimental techniques such as XRD, RS, IR, TEM, and SEM were applied to monitor the synthesis progress, leading to the development of euhedral spinel nanocrystals of the required shape. The proposed mechanistic model of cobalt spinel formation was supported by DFT shape modeling with application of the Wulff construction. Despite the widespread use of the cobalt nanospinel and its derivatives as electro/photo/catalysts, there have been only a few papers devoted explicitly to the hydrothermal synthesis of Co$_3$O$_4$ nanocrystals, and none of them have dealt with the elucidation of an intimate mechanism of the spinel phase formation and shape perfection of the produced nanocrystals into euhedral bulk solids.

2. EXPERIMENTAL SECTION

2.1. Synthesis. The Co$_3$O$_4$ nanoparticles with controlled polyhedral shape were synthesized by a hydrothermal method. In the standard procedure, specific amounts of Co(NO$_3$)$_3$·6H$_2$O and NaOH precursor compounds, with a constant Co$^{2+}$ to OH$^-$ ratio equal to 2.7, were dissolved in 18 mL of demineralized water. The obtained mixture was stirred for 5 min and then transferred into a 20 mL Teflon lined stainless steel reactor and heated at 180 °C for 0.5, 1, 3, 5, and 8 h to provide the intermediate and final products. The obtained black spinel precipitate was separated from the supernatant by centrifugation at 3000 rpm for 5 min and washed with distilled water. The washing procedure was repeated at least five times. Finally, the synthesized Co$_3$O$_4$ nanocrystals were dried at 60 °C overnight.

2.2. Characterization. X-ray patterns were recorded with a Bruker D8-advance diffractometer, using Cu Kα radiation (λ=1.540598 Å). The diffractograms were recorded in the range of 2θ = 10−70° with steps of 0.02°/s. Raman spectra were recorded in the range 100−900 cm$^{-1}$ with 1 cm$^{-1}$ resolution by means of a Renishaw InVia spectrometer, using the wavelength excitation of 785 nm and nine scans for each measurement. The infrared ATR spectra were registered by means of a Nicolet 6700 spectrometer with a liquid-N$_2$-cooled MCT detector. The spectra were recorded in the wavenumber range of 550−3900 cm$^{-1}$ with an accumulation of 64 scans. SEM imaging of the gold-coated spinel nanocrystals was carried out on a Tescan instrument at a 20 kV acceleration voltage. A more detailed analysis was performed by transmission electron microscopy (TEM), using an FEI Tecnai Osiris microscope equipped with an X-FEG Schottky field emitter (200 kV) and a high angle annular dark field (HAADF) detector. The samples deposited on lacey-carbon-coated copper grids were imaged using a beryllium double-tilt low-background holder.

2.3. TEM Image Simulations. The constructed structural models of Co$_3$O$_4$|[(001)] Co(OH)$_2$, transformation of cobalt hydroxide into cobalt spinel under thermal and hydrothermal conditions, valid only in an aerobic environment, has been based on structural similarities between both of these terminations, supported by an analysis of the corresponding electron diffraction patterns.[24−30]

2.4. DFT Modeling. The quantum-chemical calculations were performed with the VASP code 5.4.4 (Vienna Ab initio Simulation Package), which utilizes the PAW method to reconstruct the all-electron wave function. Methfessel−Paxton smearing[32] with σ = 0.1 eV was used. The bulk lattice constant was calculated by fitting the E/V values to the Birch−Murnaghan equation of state.[33] The following optimization criteria were used: 10$^{-5}$ eV for the SCF, 10$^{-3}$ eV/Å for the geometry optimization, and a basis set cutoff energy of 500 eV. The value of the Hubbard U parameter was selected to be 4.4 and 6.7, for Co$^2+$ and Co$^3+$, respectively. The DFTsol methodology, implemented in the VASPsol code, was used for a description of the solvation effects.[37] The effective dielectric constant of water at T = 180 °C and p = 15 bar was set to ε = 39.1.[38]

3. RESULTS AND DISCUSSION

3.1. Morphology of Co$_3$O$_4$ Nanocrystals: Influence of the Synthesis Conditions. In order to keep the minimum number of reactants for the synthesis of the Co$_3$O$_4$ nanocrystals (NCs), we selected cobalt nitrate and sodium hydroxide as the sole precursors. In both cases the residual counterions (NO$_3^-$ and OH$^-$), possibly retained on the spinel surface, can be easily eliminated by calcination even under mild conditions, without leaving any persistent remains. Such precursors have been used previously for the synthesis of
cobalt spinel nanocubes by the precipitation method and subsequent aging at ~100 °C under reflux under aerobic conditions. A similar protocol of the cobalt spinel hydrothermal synthesis has also been used elsewhere; however, the principal mechanistic steps of the intricate pathways of Co2+/OH formation and growth have not been comprehensively revealed and clarified. Herein, we demonstrate that by variation of only the concentrations of the Co(NO3)2 and NaOH reactants, while the Co2+/OH ratio is kept constant, it is possible to obtain spinel nanocrystals of various well-defined polyhedral morphologies under hydrothermal treatment at 180 °C under anoxic conditions. In preliminary experiments we tested various Co2+/OH− ratios, ranging from 2.7 to 3, 3.5, 4, and 4.5, and found that for the subsequent mechanistic studies Co2+/OH− = 2.7 is the most appropriate.

In Table 1 different compositions of the synthesis mixtures are shown, which lead to particular morphologies of the cobalt spinel nanocrystals, revealed by SEM imaging (Figure 1).

| morphology   | cCo2+ (mol dm−3) | cOH− (mol dm−3) | cCo2+/cOH− | ΔcCo2+ (mol dm−3) |
|--------------|-----------------|-----------------|-------------|-------------------|
| cubic        | 1.31            | 0.49            | 2.7         | 1.07              |
| cuboctahedral| 2.69            | 1.00            | 2.7         | 2.19              |
| octahedral   | 4.09            | 1.52            | 2.7         | 3.33              |

“cCo2+” and “cOH−” indicate the initial concentrations of cobalt nitrate and sodium hydroxide, respectively, whereas ΔcCo2+ stands for change in the Co2+/OH− concentration in the mother liquor after precipitation of the parent cobalt hydroxide.

Generally, all of the examined spinel NCs exhibit well-developed polyhedral shapes with an apparent high flatness of the exposed surfaces. SEM observations of several distinct nanocrystals at different tilt angles allow for the preliminary assignment of the exhibited shapes to the most fitted polyhedral benchmark (see below).

As it is illustrated in Figure 1a, the average particle diameter of the cubic (hexahedral) nanocrystals enclosed by the six {100} planes is equal to dsub = 780 ± 60 nm (gauged by the body diagonal). The 14-faceted polyhedral particles terminated by 8 {111} and 6 {100} planes are slightly larger, dsub-act = 830 ± 100 nm. Upon a move to nanocrystals of octahedral morphology exhibiting only the 8{111} planes and an average diameter of dact = 820 ± 100 nm, the particle size distribution becomes somewhat broader.

The accurate shapes of the observed 14-faceted polyhedra can be assessed using the (100)-(110)-(111) morphodrome of the P63/mmc spinel NCs, reported elsewhere. The shapes enclosed by the two types of planes, (100) and (111), with the abundance ratio of R(111)/R(100) give rise to a truncated hexahedron for 0 < R < 1/2, a cuboctahedron for R = 1/2, and a truncated octahedron for 1/2 < R < 1. Thus, the obtained nanocrystals, with 0.42 < R < 0.64, can be assigned to specific nearly cuboctahedral to truncated octahedral morphologies (Figure 1). For the sake of conciseness they will jointly be called hereafter as a cuboctahedral shape, although in contrast to spinel cubes and octahedra their faceting is not as well developed and the corners still remain quite rounded. All nanocrystals of cobalt spinel are rather uniform in the size with a low degree of agglomeration, providing excellent model materials for sensible structure—activity investigations. The specific surface areas of the three kinds of Co3O4 NCs was measured by the Brunauer—Emmett—Teller (BET) method. The obtained values for Co3O4 cubes, cuboctahedra, and octahedra are equal to 2.26, 1.97, and 1.90 m2 g−1, respectively.

The obtained results indicate that the actual morphology of the Co3O4 nanocrystals depends primarily on the amount of the Co(NO3)2 and NaOH precursors used in the synthesis, and not just on their molar ratio as has been suggested previously. As already mentioned, the latter quantity was kept constant at [Co(NO3)2]/[NaOH] = 2.7, with a purposeful stoichiometric excess of the cobalt cations with respect to the hydroxyl groups (see Table 1). The Co2+aq ions left in the mother liquor after precipitation of the precursor β-Co(OH)2 phase play an important role in its subsequent transformation into cobalt spinel under anoxic conditions (see below). For a low amount of the reactants, at a cobalt nitrate concentration of 1.31 mol dm−3, the cobalt spinel nanocrystals are produced in the form of well-cut cubes (Figure 1a). When the amount of Co(NO3)2 (and accordingly NaOH) was enhanced to reach 2.69 mol dm−3, the shape of the Co3O4 changed into a cuboctahedron (Figure 1b). With a further increase in the amount of cobalt nitrate to 4.09 mol dm−3, the obtained spinel nanocrystals show an octahedral habit (Figure 1c). In all cases the initial pH of the reaction mixture was in the range of 6.2—6.5, the reaction temperature was T = 180 °C, and the overall pressure was p = 15 bar.

In order to clarify the mechanism of the Co3O4 nanocrystal formation, and to unravel the chemical background for the observed phenomena, we examined the evolution of the phase composition and morphology of all the identified intermediate species by means of TEM, XRD, IR, and RS techniques at various time intervals. The initial green α-Co(OH)2 precipitated upon mixing of the reactants, was spontaneously transformed into a more stable pink β-Co(OH)2 identified by the characteristic XRD diffraction pattern (JCPDS card #30-443). The results collated in Figure 2 show that, upon 1 h of the hydrothermal reaction, crystalline submicrometric sheets of the β-Co(OH)2 phase, present exclusively at the beginning of the reaction, are still dominant (Figure 2a1). The position along with narrow shape of the (001) and other diffraction lines imply the formation of the well-crystalline β-Co(OH)2 plates with a regular interlayer registry. Yet, multiple bands in the range 1000—1500 cm−1 observed in the IR spectra (Figure 2a2), apart from the O—H vibrations at 3642 cm−1 and Co—
OH at 628 cm$^{-1}$ due to $\beta$-Co(OH)$_2$, 61 reveal the presence of NO$_3^-$ anions ($\nu_2 = 1322$ cm$^{-1}$, $\nu_4 = 1442$ cm$^{-1}$, $\nu_1 = 1045$ cm$^{-1}$) of the local $C_{2v}$ symmetry, associated with the cobalt centers. 62−64 The band at 1632 cm$^{-1}$ is characteristic for the $\delta$H$_2$O−H vibrations of water molecules. Its presence is consistent with an appreciable bathochromic tailing of the intense and narrow peak at 3642 cm$^{-1}$, attributed to the stretching mode of the hydroxyl groups in the brucite-like layers, implying that some scarce water admolecules may be present in the interlayer gallery or on the external surface. These results indicate that on the surface and within the interlayer space of cobalt hydroxide some nitrate anions are trapped, according to the following reaction

$$\text{(1)} \quad (1 - x)\text{Co}^{2+} (\text{OH})_2 + 2x\text{NO}_3^- + x\text{Co}^{2+} + x\text{H}_2\text{O}$$

$$\rightarrow [\text{Co}^{2+}_{1-x}\text{Co}^{3+}_x (\text{OH})_2] (\text{NO}_3)_{x} + x\text{NO}_2$$

leading to the appearance of a transient layered double hydroxide (LDH) phase. 63 This process is particularly favored just upon precipitation of cobalt hydroxide, when it is still in its incipient $\alpha$-Co(OH)$_2$ polymorph with an expanded interlayer space. Since a residual dissolved oxygen is probably acting here as an oxidant, this phase is of minor abundance. A main pathway of the nitrate capture can occur in a nonredox fashion, via an anion exchange in the brucite-type layers when the framework hydroxyls are replaced by the nitrate anions

$$\text{(2)} \quad (2 - x)\text{Co}^{2+} (\text{OH})_2 + 2x\text{NO}_3^- + x\text{Co}^{2+}$$

$$\rightarrow 2[\text{Co}^{2+} (\text{OH})_{2-x} (\text{NO}_3)_{x}]$$

bringing about a steady development of cobalt hydroxide nitrates, which at the next stages of the hydrothermal reaction are seen in XRD quite clearly. Both reactions are made possible due to the presence of the abundant residual cobalt and nitrate ions in the solution, left upon the precipitation of Co(OH)$_2$ (Table 1). The LDH entities containing NO$_3^-$ are expected to exhibit larger interlayer spacings, 63 yet their distinction by XRD in the case of the simultaneous presence of other cobalt hydroxide nitrate phases is difficult because many diffraction lines are overlapping. However, upon inspection of the narrow region, recorded in the range $2\theta = 15-30^\circ$ after 2 h of the reaction, the appearance of the $[\text{Co}^{2+}_{1-x}\text{Co}^{3+}_x (\text{OH})_2] (\text{NO}_3)$ species with the outer-sphere NO$_3^-$ was inferred from the clearly resolved discrete diagnostic peak at $2\theta = 23.53^\circ$, along with the akin Co(OH)(NO$_3$)$^-$ and Co$_2$(OH)$_2$(NO$_3$)$^-$ phases, containing nitrate anions in the first coordination sphere and the divalent cobalt alone (Figure 2a1 insert). It is probably worth noting here that the latter phase can be formulated alternatively as $\text{Co}(\text{OH})_{1/2}(\text{NO}_3)$$_{1/2}$, with a fourth of the OH$^-$ groups in the brucite-like layer replaced by the NO$_3^-$ anions.

More detailed information about the phase composition of this aliquot sample was obtained from Raman spectra shown in Figure 2a$_2$, where in addition to the bands at 255 (E$_g$), 429
bands of the coordinated nitrate species (999, 1050, 1306, and 1482 cm\(^{-1}\)) reveal the presence of the Co\(_3\)O\(_4\) phase alone. For the sake of clarity enlarged XRD, RS, and IR spectra are also reproduced. In Figures S8–S19 in the Supporting Information.

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An analysis of the spectroscopic data of the specimens examined after 5 h of the hydrothermal reaction reveals progress in the evolution of the phase composition of the reaction mixture. In the XRD pattern, except for the characteristic lines due to Co\(_3\)O\(_4\) (JCPDS card #41-0836), the diffraction patterns (a) and (b) correspond to the regions marked by pink and yellow squares (a\(_1\)), respectively. They confirm the coexistence of the Co\(_3\)(NO\(_3\))(OH)\(_2\) (a\(_2\), pink dots), CoOOH (a\(_3\), green dots), and Co\(_3\)O\(_4\) (a\(_4\), yellow dots) phases. Electron diffraction patterns (b\(_1\), b\(_2\), b\(_3\)) corresponding to the regions b\(_1\), b\(_2\), and b\(_3\) (yellow hexagon), respectively, reveal the presence of the Co\(_3\)O\(_4\) phase alone. For the sake of clarity enlarged XRD, RS, and IR spectra are also reproduced in Figures S8–S19 in the Supporting Information.

Figure 3. Main stages of the synthesis of octahedral cobalt spinel nanocrystals. XRD, IR, RS, and TEM data collected after 1/2 h (a\(_1\)-a\(_2\)), 1 h (b\(_1\)-b\(_2\)), and 5 h (c\(_1\)-c\(_2\)) of the hydrothermal reaction. The XRD patterns are assigned to \(\beta\)-Co(OH)\(_2\) (\(\blacktriangle\)), Co(NO\(_3\))(OH)\(_2\)·H\(_2\)O (\(\blacklozenge\)), Co\(_2\)(NO\(_3\))\(_3\)(OH)\(_2\)·H\(_2\)O (\(\blacklozenge\)), Co\(_3\)O\(_4\) (\(\blacklozenge\)), CoOOH (\(\blacklozenge\)), and Co\(_3\)O\(_4\) (\(\blacklozenge\)) phases. The FFT diffraction patterns (a\(_3\)) and (a\(_4\)) correspond to the regions marked by pink and yellow squares (a\(_1\)), respectively. They confirm the coexistence of the Co\(_3\)(NO\(_3\))(OH)\(_2\) (a\(_4\), pink dots), CoOOH (a\(_3\), green dots), and Co\(_3\)O\(_4\) (a\(_4\), yellow dots) phases. Electron diffraction patterns (b\(_1\), b\(_2\), b\(_3\)) corresponding to the regions b\(_1\), b\(_2\), and b\(_3\) (yellow hexagon), respectively, reveal the presence of the Co\(_3\)O\(_4\) phase alone. For the sake of clarity enlarged XRD, RS, and IR spectra are also reproduced in Figures S8–S19 in the Supporting Information.

Co\(_3\)(NO\(_3\))(OH)\(_2\) (a\(_4\), yellow dots) phases. Electron diffraction patterns (b\(_1\), b\(_2\), b\(_3\)) corresponding to the regions b\(_1\), b\(_2\), and b\(_3\) (yellow hexagon), respectively, reveal the presence of the Co\(_3\)O\(_4\) phase alone. For the sake of clarity enlarged XRD, RS, and IR spectra are also reproduced in Figures S8–S19 in the Supporting Information.
CoO$_4$ nanocubes separated from the solution by the TG/MS analysis revealed a small loss of the sample mass ($\Delta m \approx 0.035$ mg, 0.61%), associated with removal of the residual surface hydroxyl and nitrate adspecies.

Analogous physicochemical investigations were performed for the synthesis of the octahedral CoO$_4$ nanocrystals, and the results are collated in Figure 3.

Inspection of the data collated in Figure 3 shows that, in comparison to the synthesis of the spinel cubes, all stages of the reaction are now substantially accelerated. In the XRD pattern of the sample examined after a few minutes upon mixing of the reactants, a combination of Co$_2$(NO$_3$)(OH)$_3$, Co(NO$_3$)(OH)$_2$$\cdot$H$_2$O, and CoOOH (JCPDS card #01-073-1213) phases along with the parent $\beta$-Co(OH)$_2$ phase were found. The first phase becomes dominant after 30 min of the hydrothermal treatment (Figure 3a$_1$). The IR and RS spectra (Figure 3a$_2$,a$_3$) are consistent with the XRD results, yet the appearance of the distinct F 2g and A 1g Raman peaks characteristic of cobalt spinel indicates that at this stage some incipient CoO$_4$ grains were already formed. The CoO$_4$ nanocubes (100) and (111) terminations of cobalt spinel, covered with OH$^-$ (a), 2OH$^-$ (b), 4OH$^-$ (c), NO$_3^-$ (d), 4NO$_3^-$ (e), OH$^-$/NO$_3^-$ in configuration 1 (f), and OH$^-$/NO$_3^-$ species in configuration 2 (g), along with the corresponding equilibrium shapes of the CoO$_4$ nanocrystals predicted by means of Wulff construction using the values reported in Table 2. The orange balls represent the default Na$^+$ counterions. A more detailed version of this picture is given in Figures S20–S22 in the Supporting Information.
corresponding TEM pictures reveal the morphology of the sub-micrometre plate-shaped particles (Figure 3a$_{a,b,c}$), which are decorated by the embedded small (3−5 nm) Co$_3$O$_4$ crystallites. The FFT diffraction patterns (Figure 3a$_{a,b,c}$), taken from the regions marked by pink and yellow squares in Figure 3b$_3$, justify the simultaneous presence of the Co$_2$(NO$_3$)$_3$(OH)$_3$ (pink dots), CoOOH (green dots), and Co$_3$O$_4$ (yellow dots) phases in the interior of the plates (Figure 3a$_6$), whereas at the edge of the examined plate, the CoOOH phase with some Co$_3$O$_4$ contribution dominates (Figure 3a$_7$).

The changes in the phase composition of the reaction mixture after 1 h of the synthesis progress are shown in Figure 3b$_1$−$b_5$. The XRD pattern is now governed by the Co$_3$(NO$_3$)$_3$(OH)$_3$ and CoOOH reflections with a clearly enhanced Co$_3$O$_4$ contribution. Accordingly, the intensity of the nitrate multiplet in the IR spectrum decreases significantly (Figure 3b$_7$), whereas in the RS spectrum only the Co$_3$O$_4$ bands are visible (Figure 3b$_6$), illustrating nicely the lucid complementarity of the both vibrational spectroscopies for probing different aspects of the phase heterogeneity of such complex materials. The plates of the coexisting Co$_2$(NO$_3$)(OH)$_3$/CoOOH phases are around 100 nm in diameter (Figure 3b$_2$) and are densely intergrown with the preponderant small spinel crystallites (see below), the diagnostic FFT diffraction pattern of which is shown in Figure 3b$_3$. The magnified fragments of the TEM pictures and the corresponding FFT patterns (Figure 3b$_{a,b,c}$) reveal the polyhedral (most commonly truncated octahedral) shape of these primary Co$_3$O$_4$ nanocrystals with dimensions of 3−5 nm. The obtained results imply that during the hydrothermal treatment an important fraction of the Co$^{2+}$ ions associated with the nitrate ligands was endogenously oxidized into Co$^{3+}$ species for the successful formation of Co$_{12}$$^{2+}$(Co$_{18}$O$_{44}$) entities out of the initially precipitated β-Co$_{3}$(OH)$_2$ phase, despite the anoxic conditions. The resultant primary spinel nanocrystallites tend to aggregate spontaneously into sub-micrometre mesocrystals of cobalt spinel with an apparent subhedral shape and a markedly rough external surface (see Figure 3b$_{10}$ and the inset). A more detailed inspection of the corresponding TEM images reveals that the large (~0.1−0.5 μm) subhedral spinel grains are composed of much smaller congested truncated octahedra (5−50 nm), which are nucleated and grow out of the CoOOH and Co$_2$(NO$_3$)(OH)$_3$ phases. Due to a much higher concentration of the nutrient (in comparison to the cubes), the enhanced supersaturation of the nutrient solution promotes a higher nucleation rate, giving rise to the appearance of a much larger amount of the prime cobalt spinel nanocrystals. Their subsequent growth and coalescence lead to an immediate crowding and the formation of a fairly dense texture of the resultant sub-micrometre grains, seen in Figure 3b$_{a,b,c}$. This process is favored by an enhanced ionic strength of the solution, which facilitates the nanocrystal agglomeration by attenuating the interparticle repulsion. Examination of the XRD, IR, RS, and TEM results recorded after 5 h (Figure 3c$_1$−c$_7$) reveals the spontaneous smoothing of the initially coarse surface (cf. Figure 3b$_{10}$), whereas spinel nanocrystals of transient subhedral and eventual octahedral shapes found in the batch are shown in Figure 3c$_{a,b,c}$ (magnified fragment) and Figure 3c$_7$, respectively. An IR feature below 1500 cm$^{-1}$ indicates that some nitrate adspecies are still present on the surface of the obtained spinel octahedral nanocrystals (Figure 3c$_7$). Indeed, in comparison to the nanocubes, in the case of the octahedral crystallites the TG/MS analysis showed a larger weight loss of Δ$m ≈ 0.094$ mg (1.81%), due to removal of the residual surface NO$_3^−$ and OH$^−$ species, which is caused by the stronger attachment of those anions to the (111) termination than to the (100) plane (see Table S2 in the Supporting Information).

The obtained results document clearly that polyhedral, low-agglomeration spinel nanocrystals of a uniform size and controlled shape can be obtained from the sole cobalt nitrate and sodium hydroxide precursors by a mere variation of their concentration, while the concentration ratio and the reaction temperature are kept constant. The synthesized spinel nanocrystals are shown by XRD and RS to be free of the contaminant spurious phases; therefore, in contrast to the spinel NCs obtained previously from the same precursors, subsequent purification in HCl, recommended therein, is not needed.

### 3.2. DFT Surface Energy Calculations and Shape Modeling

Molecular modeling of surface energies in conjunction with the Wulff construction allowed us to predict the equilibrium shape of the primary Co$_3$O$_4$ nanoparticles under the investigated hydrothermal conditions, as well as providing a suitable background to explain the observed morphological

| coverage | $\gamma_{100}$ (J m$^{-2}$) (Δ%) | (100) surface abundance (%) | $\gamma_{111}$ (J m$^{-2}$) (Δ%) | (111) surface abundance (%) |
|----------|-----------------|-----------------|-----------------|-----------------|
| bare surface | 1.27 (0) | 1.70 (0) |
| OH$^−$ | 1.09 (14) | 1.37 (19) | 23 |
| 2OH$^−$ | 0.95 (25) | 1.41 (17) | 5 |
| 3OH$^−$ | 0.74 (42) | 1.22 (28) | 1 |
| 4OH$^−$ | 0.43 (66) | 1.04 (39) | 0 |
| 5OH$^−$ | 1.00 (100) | 1.22 (28) | 0 |
| 6OH$^−$ | 1.00 (100) | 0.99 (42) | 0 |
| NO$_3^−$ | 0.91 (28) | 1.44 (15) | 2 |
| 2NO$_3^−$ | 0.93 (27) | 1.48 (13) | 2 |
| 4NO$_3^−$ | 1.28 (−1) | 1.33 (22) | 54 |
| 5NO$_3^−$ | 67 | 1.50 (12) | 33 |
| OH$^−$/NO$_3^−$ (conf 1) | 1.12 (12) | 1.85 (−9) | 31 |
| OH$^−$/NO$_3^−$ (conf 2) | 0.39 (69) | 1.40 (18) | 2 |

$\Delta%$ defines changes in the surface energies in comparison to the $\gamma$ values for the bare surfaces.
changes. We calculated the surface energies of the key (100), (111), and (110) terminations covered by hydroxyls, nitrates, and mixed OH\(^-\)/NO\(_3^-\) species, using Na\(^+\) left in the mother liquor as a default counterion. Because in all of the examined surface coverage scenarios the appearance of the (110) facet was scarce and was always much smaller than the two other facets, for the sake of simplicity this termination was excluded from further consideration. The optimized structures of the exposed facets covered with representative combinations of the OH\(^-\) and NO\(_3^-\) adspecies are collected in Figure 4, whereas all other examined attachment modes (adsorption configurations) are shown in Figures S23 and S24, respectively, in the Supporting Information.

An inspection of Figure 4 shows that hydroxyl species are bound in a terminal fashion on both surfaces. The nitrates on the (100) facet are attached in a monodentate way, whereas they are attached on the (111) termination in mono- and bidentate forms with the O atom acting as a donor center. Adsorption energies of all the examined adsorption configurations of the OH\(^-\) and NO\(_3^-\) adspecies are collated in Table S2 in the Supporting Information. For the OH\(^-\) and NO\(_3^-\) anions there are substantial differences in the adsorption energies between the (100) and (111) facets, revealing a strong preference of the OH\(^-\)/NO\(_3^-\) species for attachment to the (111) plane, especially at low coverages. As the amount of the surface-trapped anions increases, the adsorption energy decreases, and this effect is of particular importance for the (100) plane. The corresponding values of the surface energies, \(\gamma_{AD}\), for both terminations are collected in Table 2.

From a quick inspection of the results it is clear that, generally, the stabilization effect of the hydroxyls is smaller than that of the nitrate anions for the (100) facet, whereas for the (111) plane this difference is evidently attenuated. In all cases the covered (111) facet exhibits distinctly higher surface energies in comparison to the (100) termination. This effect is most pronounced for the planes containing mixed OH\(^-\)/NO\(_3^-\) adspecies in configuration 2. The highest coverages by the hydroxyls correspond to four (three species attached to the surface, one OH\(^-\) group stabilized by the solvation cavity) and five (111) (four species attached to the surface, one NO\(_3^-\) group stabilized by the solvation cavity) NO\(_3^-\) adspecies. The mixed OH\(^-\)/NO\(_3^-\) configurations are distinctly more stable than the 2OH\(^-\)/2NO\(_3^-\) configurations.

The calculated \(\gamma_{100}\) and \(\gamma_{111}\) values for various surface coverages can next be used in conjunction with the Wulff construction to reveal the equilibrium morphology of the corresponding spinel nanocrystals. The resultant polyhedra expose the prime (100) and (111) facets at various abundances (Figure 4), depending on the actual surface coverage. The attachment of OH\(^-\) enhances the development of the (100) termination, and the truncated cubes are predicted for the surface covered by one, two, and three OH\(^-\) groups. Above the coverage by three hydroxyls, the equilibrium shape of Co\(_3\)O\(_4\) is thoroughly cubic (Figure 4c3). The adsorbed nitrates show an opposite tendency, with enhancement of the number of the adsorbed NO\(_3^-\) anions. The initially nearly cubic morphology, dominant at the coverage by one or two nitrate molecules, evolves into a cuboctahedral shape when the coverage is above three molecules per the surface unit cell (Figure 4e3). In the case of mixed ligands configuration 1 gives rise to cuboctahedral nanocrystals, whereas in configuration 2 a cubic shape is preferred (Figure 4f3, respectively).

Generally, the results show a strong thermodynamic tendency toward cube or truncated cube morphologies of the primary cobalt spinel nanocrystals. The shapes close to the completely octahedral shape were never predicted in the examined conditions. Surface coverage by the NO\(_3^-\) anions seems to be favorable for the synthesis of cuboctahedral nanocrystals, whereas enhanced surface hydroxylation apparently favors cubes. The predicted shapes were taken as the reference morphologies for mechanistic considerations of the Co\(_3\)O\(_4\) nanocrystal formation and faceting. It should be noted, however, that the final morphology of the synthesized spinels is also a matter of mechanistic and space confinement factors, which are addressed below in more detail by mechanistic considerations.

3.3. Mechanistic Pathways of Spinel Morphogenesis and Development of Specific Faceting. An analysis of the results collated in Figures 2 and 3 revealed that the cubic and octahedral nanocrystals were clearly produced along different routes and at different rates. Whereas the progress of the
octahedral NC formation is rather prompt (the synthesis is fully accomplished within 3 h), in the case of the cubes it is distinctly more sluggish and takes 8 h to be completed (see also a full sequence of the collated XRD, IR, and RS spectra measured during the reaction progress in Figures S25 and S26). The spinel phase in the XRD-detectable amounts appears after 4 and 0.5 h of the reaction, respectively. The proper sequential arrangement of the identified starting, intermediate, and final phases (Figure 5) and an analysis of the evolution of the grain morphologies allowed the discovery of a pronounced difference in the formation and growth mechanisms of the specifically faceted cobalt spinel nanocrystals.

Figure 6. TEM pictures documenting topotactic transformation of the parent reactive \( \text{Co}^{2+}(\text{OH})_x(\text{NO}_3)_x \) template into \( \text{Co}_3\text{O}_4 \) cubes. The PRT plates with the (1−11) basal planes (a1), top view (a2) and side view (a3) and a selected plate viewed along the [1−11] direction and the corresponding FFT pattern (a4). Random nucleation of spinel phase and coalescence of the grains (b, c), formation of meso-crystalline cubes via oriented attachment of the nanosized cuboidal building blocks (d, e) and FFT patterns of the regions marked by yellow and red squares revealing the [100][1−11] topotactic relationship between the \( \text{Co}_3\text{O}_4 \) crystals and the \( \text{Co}^{2+}(\text{OH})_x(\text{NO}_3)_x \) template (e1, e2), a sub-micrometer \( \text{Co}_3\text{O}_4 \) cubic crystal with a malformed edge due to an uncompleted process of the surface wrapping (f), and a single crystal of cobalt spinel decorated by precipitated entities during its growth via 2D attachment mechanism (g). An atomistic model of the \( \text{Co}^{2+}(\text{OH})_x(\text{NO}_3)_x \) plate (h), the \( \text{Co}^{2+}(\text{OH})_x(\text{NO}_3)_x \) template with the nucleating spinel phase (i), and the corresponding TEM image (j) with the simulated fragment delineated by a yellow rectangle (insert).
In the case of the cube-shaped nanocrystals during the hydrothermal treatment, in contact with the residual Co(NO\textsubscript{3})\textsubscript{2} solution (see Table 1), the starting $\beta$-Co(OH)\textsubscript{2} phase (blue curve) is gradually transferred in parallel into the dominant Co\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}(OH)\textsubscript{4}\textsuperscript{+} (green) and lesser Co(NO\textsubscript{3})\textsubscript{2}·(OH)·H\textsubscript{2}O (red) intermediate phases

$$\text{2Co(OH)}_2 + \text{NO}_3^- + \rightarrow \text{Co}_2(\text{OH})_3(\text{NO}_3)^+ + \text{OH}^-$$  

(3)

$$\text{2Co(OH)}_2 + 2\text{NO}_3^- + \text{Co}^{2+}$$

$$\rightarrow \text{Co}_2(\text{OH})_3(\text{NO}_3)^+ + \text{Co}($$/OH$$/)(\text{NO}_3)^-$$  

(4)

They exhibit relative content maxima at about 2–3 and 3–4 h of the reaction progress, respectively (Figure 5a). Apparently the process of OH\textsuperscript{−}/NO\textsubscript{3}\textsuperscript{−} ligand exchange (eqs 3 and 4) is more likely to occur than the alternative much more reluctant Co(OH)\textsubscript{2}, which are incorporated next to produce the double hydroxide [Co\textsubscript{2}+\textsubscript{3}−(OH)\textsubscript{4}]\textsuperscript{+} (blue curve) is gradually transferred in parallel into the Co\textsubscript{3}O\textsubscript{4} crystals along with the dissolved Co\textsubscript{2+(aq)} cations are released. At is discussed below, the autogenously produced nitric acid plays an important role in hydrothermal etching of the produced spinel in its immature meso-crystal state.

For the sake of conciseness, a Co\textsuperscript{2+}(OH)\textsubscript{2}·(NO\textsubscript{3})\textsubscript{2} formulation is used hereafter (when needed) for designation of both distinct Co\textsubscript{2}(OH)\textsubscript{2}(NO\textsubscript{3})\textsubscript{2} and Co(OH)(NO\textsubscript{3})\textsubscript{2} phases detected during the reaction course, with $x = 1/2$, 1, respectively, as they jointly constitute a parent reactive template (PRT) for spinel phase formation. In accordance with these reaction schemes, the acidity of the solution decreased from the initial value of pH 6.5 to pH 2.1 due to the release of the hydronium ions. Such processes may occur in a rather gross fashion concurrently with the prerequisite Co\textsuperscript{2+} oxidation to Co\textsuperscript{3+}, since formation of a distinct Co\textsuperscript{3+}OOH phase was not observed in this case (Figure 5a). Nonetheless, an analogous reaction can also be envisioned to proceed in restricted areas for the cobalt hydroxyl nitrate entities with insufficient NO\textsubscript{3}\textsuperscript{−} ligands (x < 1/2 on average), already at the early stages of the reaction as a minor pathway. Indeed, once the critical Co\textsuperscript{2+}/Co\textsuperscript{3+}O\textsubscript{2} ratio of at least an imperfect spinel stoichiometry is achieved locally, random nucleation and subsequent growth of the nascent Co\textsubscript{3}O\textsubscript{4} crystals are made possible, as revealed in Figure 2a. Apparently, oxidation of Co\textsuperscript{2+} to Co\textsuperscript{3+} provides an intrinsic incentive for the nucleation of nascent spinel kernels. The nitrate anions trapped from the solution along with the dissolved Co\textsuperscript{2+}(aq) cations are gradually consumed with the progressing development of the spinel phase, and an equivalent amount of the protons is released. At is discussed below, the autogenously produced nitric acid plays an important role in hydrothermal etching of the produced spinel in its immature meso-crystal state.

A more in depth insight into the structural aspects of the proposed mechanism of the spinel formation can be inferred from an analysis of the series of TEM images collated in Figure 6. The key mechanistic indication here is provided by the presence of the hydrothermally produced elongated hexagonal Co\textsuperscript{2+}(OH)\textsubscript{2}·(NO\textsubscript{3})\textsubscript{2} plates exhibiting the (111) basal plane (Figure 6a). The shape of these plates is features the characteristic angles of 131 and 107° observed typically in TEM images (Figure 6a–a\textsubscript{1}), along the diffraction spots of clearly uneven intensities (Figure 6a\textsubscript{2}), corresponding to the (111) basal plane. Such plates have been observed previously\textsuperscript{70} and they should be not misidentified with the often reported akin regular hexagonal $\beta$-Co(OH)\textsubscript{2} crystallites. The latter exhibit the (001) basal plane,\textsuperscript{71,72} and feature all angles equal to 120°, together with even intensities of all the diffraction spots (see Figure S27 in the Supporting Information). The thickness of the cobalt hydroxyl nitrate plates varies from 12 to 20 nm (Figure 6a\textsubscript{2}), indicating that they are composed of 15–25 sheets.

The indexed FFT pattern shown in Figure 6a\textsubscript{2} unequivocally validates the [111] orientation of these plates. The TEM image presented in Figure 6b eventually confirms that the spinel nucleation occurs randomly within the Co\textsuperscript{2+}(OH)\textsubscript{2}·(NO\textsubscript{3})\textsubscript{2} template and that the appearing nanosized cuboidal Co\textsubscript{3}O\textsubscript{4} crystallites exhibit a nearly common vertical orientation imposed by the topotactic features of this process. An example of the resultant alignment of the spinel grains along the common [100] director is shown in Figure 6c.
Formation of the separated Co₃O₄ domains in Figure 6b,c is in line with the conjecture that the layered reactive template → spinel transformation takes place according to spontaneous nucleation and growth processes with the vital participation of the dissolved cobalt nitrate and is extended in time. Apparently, the nucleation rate is sensitive to fluctuations in the concentration of the Co(NO₃)₂ nutrient in the mother liquor. The emerging Co₃O₄ domains grow further at the expense of the PRT matrix and/or via coalescence. Once the substrate of the reactive template becomes virtually devoured, subsequent mesoscale self-assembly of the produced primary 2–3 nm crystallites to larger aggregates leads to the formation of approximately rectangular meso-crystals of ~50–100 nm size (Figure 6d,e). Since the spinel domains are produced from a single Co₂⁺(OH)₂−x(NO₃)ₓ plate, the ensuing Co₃O₄ crystallites inherit the common crystallographic orientation of the parent template due to the [100]Co₃O₄∥[1−11]−Co₃⁺(OH)₂−x(NO₃)ₓ topotactic relationship, as implied by the FFT patterns for the regions marked by the red and yellow squares (Figure 6e,f,g). The structural compatibility of both the square (100) and (1−11) frameworks (see Figure S28a in the Supporting Information) facilitates the topotactic character of this transformation. It probably explains also why the resultant primary Co₃O₄ nanocuboids can maintain the initial thickness of the precursor plates and thereby a uniform size to large extent. Since the preliminarily spinel cuboids have similar native dimensions, their consecutive merging via imperfect oriented attachment into spinel mesocrystals of a submicrometer size is greatly facilitated (Figure 6d,f–l).

The TEM image presented in Figure 6f shows some nuances of the late stage of the sub-micrometer spinel cube growth, where at one of the corners some building blocks are apparently still missing. The final compact (euhedral) submicron cubes of cobalt spinel are shown in Figure 6g. The visible fine entities decorating the surface are characteristic of the residual classic 2D surface growth mechanism, which proceeds until an equilibrium with the surrounding solution is reached. As a result, the Co₃O₄ cubic nanocrystals are produced via the nutrient-mediated topotactic nucleation and crystallization with their [100] directions inheriting the [1−11] direction of the Co²⁺(OH)₂−x(NO₃)ₓ PRT plates. An atomistic model of the parent hexagonal hydroxyl nitrate platelet and the incipient spinel domains nucleated out of this template are shown in Figure 6h,i. It should be noted, however, that the number density of the cobalt atoms in Co₃O₄ (~45 nm⁻³) is almost 2 times higher than in the parent Co³⁺(OH)₂−x(NO₃)ₓ template phase (~24 nm⁻³). Such a volumetric misfit gives rise to local disorder in the intergrain region and even to partial disruption of the PRT plates, while the spinel framework integrity is maintained. At an extreme, it may also lead to the appearance of hollow patches, observed for example upon vigorous thermal decomposition of β-Co(OH)₂ under aerobic conditions, reported previously.

The diffusionless topotactic transformation is mainly engaging the Co cations within the brucite-like sheets that are oxidized and relocated in the new spinel 16d positions. It also entails incorporation of the O²− anions produced upon NO₃⁻ decomposition along with the capture of the solvent Co³⁺(aq) cations (at 8a sites) required to build up the ultimate spinel lattice. The volumetric disparity of both frameworks leads to considerable structural disorder in the interfacial region, which is nicely revealed by the corresponding TEM picture, interpreted quantitatively by the image simulation (Figure 6j), using the model shown in Figure 6i. The experimental image fits quite well the simulated TEM picture (insert), speaking in favor of the presence of disordered interfacial zones around the nascent spinel grains. As a result, the intimate mechanism of the Co²⁺(OH)₂−x(NO₃)ₓ → Co₃O₄ conversion can be treated as a topotactic process mediated by the dissolved cobalt nitrate, contributing in concert to the spinel framework formation. The proposed scenario is an alternative account to the surface-wrapping mechanism of spinel cube formation, suggested previously elsewhere. The resultant 5–10 nm primary cubic nanocrystals (Figure 6c), being arranged in a certain crystallographic registry in the course of hydrothermal treatment, are assembled into larger Co₃O₄ mesocrystals (Figure 6d,e), following the imperfect oriented attachment mechanism.

In such sub-micrometer grains, still without coherent material linking the assembled building blocks, the precursor and solvent molecules may be located within the space between the aligned crystallites. They are next used as binding species in the hydrothermal recrystallization step, where the formed mesocrystals are gradually consolidated into the compact well-cut sub-micrometer cubes shown in Figure 6f,g. Prior formation of a mesocrystal, as a requisite midway step of the latter process, has been suggested previously.

In the case of the hydrothermal synthesis with a high concentration of the nitrate precursor, the OH⁻ ligand exchange by nitrates in the precipitated β-Co(OH)₂ layers is quick, and within 0.5 h the Co₂(NO₃)(OH)₃ phase dominates the reaction mixture (Figure 5b). Subsequent oxidation of the divalent cobalt cations in the Co²⁺(NO₃)²−(OH)⁻H₂O phase by the ligated NO₃⁻ anions leads to immediate (within 1 h) formation of the CoOOH precursor containing only Co²⁺:

$$\text{Co}^{2+}(\text{NO}_3^-)(\text{OH})^-\cdot\text{H}_2\text{O} \rightarrow \text{Co}^{3+}\text{OOH} + \text{NO}_2^- + \text{H}_2\text{O}$$  \hspace{1cm} (7)

In parallel, CoOOH may also be formed at the expense of Co₂(NO₃)(OH)₃ in a more involved reaction:

$$\text{Co}_2(\text{NO}_3)(\text{OH})_3^+ + \text{NO}_3^- + \text{H}_2\text{O}^+ \rightarrow 2\text{Co}^{3+}\text{OOH} + 2\text{NO}_2 + 2\text{H}_2\text{O}$$  \hspace{1cm} (8)

Then, the resultant Co³⁺OOH, along with Co²⁺(OH)₂−x(NO₃)ₓ, can be converted readily into cobalt spinel with participation of the residual Co²⁺(aq) cations, following the reaction

$$2\text{Co}^{3+}\text{OOH} + \text{Co}^{2+} + 2\text{H}_2\text{O} \rightarrow 2\text{Co}^{2+}\left[\text{Co}^{3+}\right]_{2}\text{O}_4^- + 2\text{H}_2\text{O}^+$$  \hspace{1cm} (9)

The resultant drop of the pH value to 3.7 is smaller than in the case of the spinel cubes synthesis (pH 2.1), as the formation of CoOOH is accompanied by consumption of protons (eq 8). As a result, owing to an abundance of nitrates, the cobalt oxidation and spinel nucleation processes become substantially accelerated. Indeed, the synthesis of the Co₃O₄ octahedra, which proceeds with concurrent involvement of the cobalt oxhydroxide and hydroxyl nitrate phases, is shortened from 8 to 3 h in comparison to the cube synthesis (cf. Figure 5a,b).

Mechanistic details of the genesis of cobalt spinel octahedra can be deduced from analysis of the TEM data collated in Figures 3 and 7. Inspection of Figure 7a shows that the plates of the parent reactive template, in contrast to the spinel cube synthesis, exhibit a hexagonal shape with the edges subtending
only the 120° angles. The corresponding FFT pattern shows that such plates are composed of a mixture of the Co₃(NO₃)(OH)₉, CoOOH, and nascent Co₃O₄ phases, which exhibit a [111] Co₃O₄||[001] CoOOH, Co₃(NO₃)(OH)₉ topotactic relationship. The latter favors formation of the (111) facets by the incipient spinel crystallites, facilitated by the topological compatibility of the hexagonal (111) and (001) frameworks (see Figure S28b in the Supporting Information). As a result the Co₃O₄ crystallites are preferentially exposing the (111) facets (Figure 7b,c). An atomistic model of the nascent Co₃O₄ crystallites grown out of the Co₂(NO₃)(OH)₂/CoOOH template is shown in Figure 7b1 and was used to simulate the TEM images (seen in the insets in Figure 7b), reproducing well the observed pattern of the lattice fringes and the characteristic contrast features resulting from the coexistence of the Co₃O₄/CoOOH (lighter contrast) and Co₂(NO₃)(OH)₂ (dark contrast) regions as well. With the progress of the reaction the spinel crystallites form a compact texture, stemming from the competition for space with the growing progress (Figure 7c). The observed changes in the image contrast result from a slight mutual disorientation of the spinel crystallites due to an imperfect attachment mechanism being involved. A model of such a texture, shown in Figure 7c1, was used for the image simulation, satisfactorily imitating the essential traits of the observed TEM picture (Figure 7c with both simulated inserts). When the higher concentration of the nutrient left in the mother liquor (Table 1) and the adsorption energies reported in Table S2 are taken into account, the surface of the primary crystallites should be decorated mainly by NO₃⁻ adspecies. Such conditions are predicted to be thermodynamically favorable for the appearance of cuboctahedral crystallites (Figure 4e–e), nicely corroborating the experimental TEM observations and substantiating the model used for the image simulation as well (Figures 3b,b and 7c,c1).

At the late stage of the hydrothermal reaction, the congested spinel polycrystallites are finally transformed into a single crystal with the (111) plane primarily exposed (see Figure 7d,d for the magnified fragment showing the interplanar distance of d(111) = 4.66 Å with the corresponding simulation). Successful annihilation of the intergrain boundaries in the hydrothermally consolidated bulk Co₃O₄ single crystal is clearly documented in Figure 7d, yet some remnant irregularities of the exposed surface, reflecting its implicated origin, are still visible.

The whole series of molecular, structural, and morphological events leading to the formation of the bulk euhedral Co₃O₄ nanocrystals of a given polyhedral shape is collated in Figure 8. It can be divided into three stages: parent reactive template (PRT) formation, nutrient-assisted topotactic nucleation (NTN), and nanocrystal morphogenesis (NCM). The sequence of the consecutive phase changes β-Co(OH)₂ → [Co₂(NO₃)(OH)₉]ₙ Co(OH)₉(NO₃⁻)·H₂O, Co₃(OH)₉(NO₃⁻)·nH₂O → CoOOH leads to the development of the parent reactive template. The Co₃(OH)₉(NO₃⁻)·nH₂O species of the LDH structure play an important role in the presence of only an exogenous oxidant. Under the anoxic conditions LDH can appear as a merely spurious phase, since an endogenous oxidation of Co²⁺ to Co³⁺ mediated by the coordinated NO₃⁻ (produced in the prior OH⁻/NO₃⁻ ligand exchange step) plays the crucial role here (Figure 8, top left). The shape of the PRT plates, dictated by the concentration of the nutrient in the mother liquor, governs the nutrient-assisted topotactic nucleation of the spinel crystallites. The PRT plates produced at a low concentration...
of the nutrient exhibiting preferentially the (1−11) planes provide the template for the Co₃O₄ nucleation in the form of cubes, whereas at higher concentrations the plates with the (001) basal plane (enriched in CoOOH) are involved in the topotactic nucleation of the truncated octahedra, in line with the DFT predictions. The required intimate displacements of the cobalt ions from the atomic positions occupied in the brucite-like layer and incorporation of the Co²⁺(aq) cations into 16d (Co³⁺) and 8a (Co²⁺) sites in the spinel framework are shown in Figure 8 (top right).

The primary nanocubes of Co₃O₄ evolve from the nucleated 3−5 nm nanograins through subsequent growth and coalescence. In this stage, owing to their topotactic origin, they attain a fairly good crystallographic alignment, despite distinct spatial separation from one another. The primary Co₃O₄ nanoparticles are next self-assembled to produce mesocrystals, and their fairly uniform cuboidal shape and size plays a beneficial role in this process (NCM stage), since evenly sized building units are needed to develop the bulk cubic architecture over a wide size range. Subsequent hydrothermal recrystallization and framework consolidation gives rise to the formation of euhedral cubic Co₃O₄ crystals of sub-micrometer dimensions. Due to the low concentration of the nutrient the whole process of the hydrothermal synthesis, slowed down particularly in the PRT and NCM stages where the NO₃⁻ and Co²⁺(aq) species are explicitly involved, is rather sluggish (8 h).

In the case of the octahedral crystals, the course of the morphogenensis is distinctly different. Owing to the higher concentration of the nutrient a more vigorous nucleation gives rise to incipient agglomeration of the abundant nascent crystallites, which adopt a truncated-octahedral shape, also predicted by the DFT modeling. Their self-assembly leads to the formation of subhedral mesocrystals with a rough external surface. Yet, such a malformed morphology still exposes distinct facets, crinkled only by steps, kinks, and other
topologic irregularities. Since depletion of the nutrient stops the nucleation process, further shape evolution occurs via hydrothermal etching in the autogenously produced nitric acid, together with the re-entrant growth. After 3 h of reaction time, their joined action leads to spectacular surface flattening with preferential development of the (111) facets. Upon final hydrothermal consolidation of the crystal structure, clear-cut single-crystal octahedra are formed. At a medium concentration of the nutrient, the shape evolution ceases at the stage where both (111) and (100) planes are exposed, and the resultant spinel assumes an approximate cuboctahedral habit.

4. CONCLUSIONS

A detailed mechanism of the anoxic hydrothermal synthesis of euhedral Co3O4 nanocrystals with narrow size distribution, under a constant $c_{\text{Co}^{2+}}/c_{\text{OH}^-}$ ratio and varying concentration of the Co(NO3)2 and NaOH precursors, was established. At a nutrient concentration of 1.31 mol dm$^{-3}$ regular cubic ($780 \pm 60$ nm), at 2.69 mol dm$^{-3}$ nearly cuboctahedral (830 $\pm$ 100 nm), and at 4.09 mol dm$^{-3}$ octahedral (820 $\pm$ 100 nm) cobalt spinel nanocrystals are formed. The NO3$^-$ anions play the key roles of an oxidant, an oxygen donor, and, by controlling the surface energy, a shape-directing agent for the spinel formation. The shape of the nascent Co3O4 crystallites is primarily governed by the crystallographic constraints imposed by the nutrient-assisted in situ topotactic transformation. The spinel random nucleation occurs with the [100] or [111] direction of the Co3O4 facets inheriting the [111] direction (formation of cubes) or [001] direction (formation of octahedra) of the PRT PLT. Sub-micrometer bulk cubic single crystals are produced via a mesocrystal stage, owing to an imperfectly oriented attachment of the primary cuboidal building nanoblocks. Bulk Co3O4 octahedra are formed by spontaneous self-assembly of the prime truncated octahedral nanocrystals into compact agglomerates of a malformed polyhedral shape. Surface smoothing and preferential development of the (111) termination occurs via hydrothermal etching and reentrant growth. High concentrations of the nutrient favor an octahedral shape, whereas a medium concentration favors a cuboctahedral shape.

This study also provides useful guidelines for a general synthetic approach to the rational hydrothermal production of other nanosized metal oxides, where not only the nature of the nutrient but also its concentration in the mother liquor play a decisive role.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.cgd.0c01031.

Parameters for TEM image simulation of models presented in Figure 6 and 7, adsorption energies of OH$^-$ and NO3$^-$ species attached to (100) and (111) terminations of cobalt spinel facets, XRD data collected after 1 h of cubic cobalt spinel nanocrystal hydrothermal synthesis, XRD data collected after 2 h of cubic cobalt spinel nanocrystal hydrothermal synthesis, XRD data collected after 5 h of cubic cobalt spinel nanocrystal hydrothermal synthesis, Raman data collected after 1 h of cubic cobalt spinel nanocrystal hydrothermal synthesis, Raman data collected after 5 h of cubic cobalt spinel nanocrystal hydrothermal synthesis, XRD data collected after 0.5 h of octahedral cobalt spinel nanocrystal hydrothermal synthesis, XRD data collected after 1 h of octahedral cobalt spinel nanocrystal hydrothermal synthesis, XRD data collected after 5 h of cubic cobalt spinel nanocrystal hydrothermal synthesis, IR data collected after 0.5 h of octahedral cobalt spinel nanocrystal hydrothermal synthesis, IR data collected after 5 h of cubic cobalt spinel nanocrystal hydrothermal synthesis, IR data collected after 5 h of cubic cobalt spinel nanocrystal hydrothermal synthesis, IR data collected after 1 h of cubic cobalt spinel nanocrystal hydrothermal synthesis, IR data collected after 1 h of octahedral cobalt spinel nanocrystal hydrothermal synthesis, IR data collected after 5 h of cubic cobalt spinel nanocrystal hydrothermal synthesis.

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Notes
The authors declare no competing financial interest.

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