Supporting Information for:

Colloidal Synthesis of Nanohelices via Bilayer Lattice Misfit

Yang Liu, Yuda Li, Soojin Jeong, Yi Wang, Jun Chen and Xingchen Ye*

Department of Chemistry, Indiana University, 800 East Kirkwood Avenue, Bloomington, IN 47405, USA

Correspondence should be addressed to Prof. Xingchen Ye, email: xingye@indiana.edu.

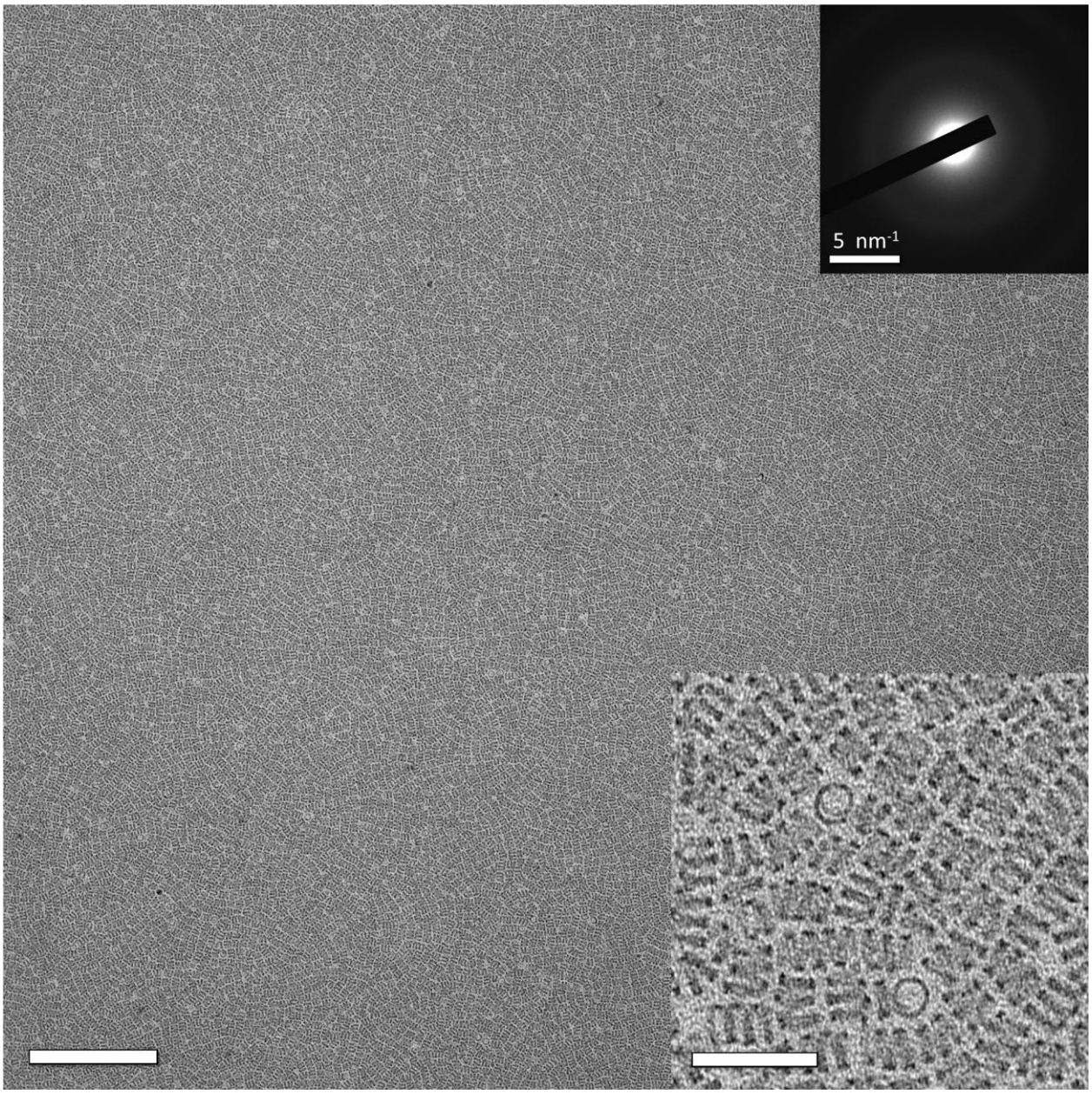

Figure S1. Low-magnification (main panel) and high-magnification (bottom inset) TEM images of Gd_2O_3 nanohelices. Upper inset: Corresponding selected-area electron diffraction (SAED) pattern. Scale bars: (main panel) 200 nm, (bottom inset) 30 nm.

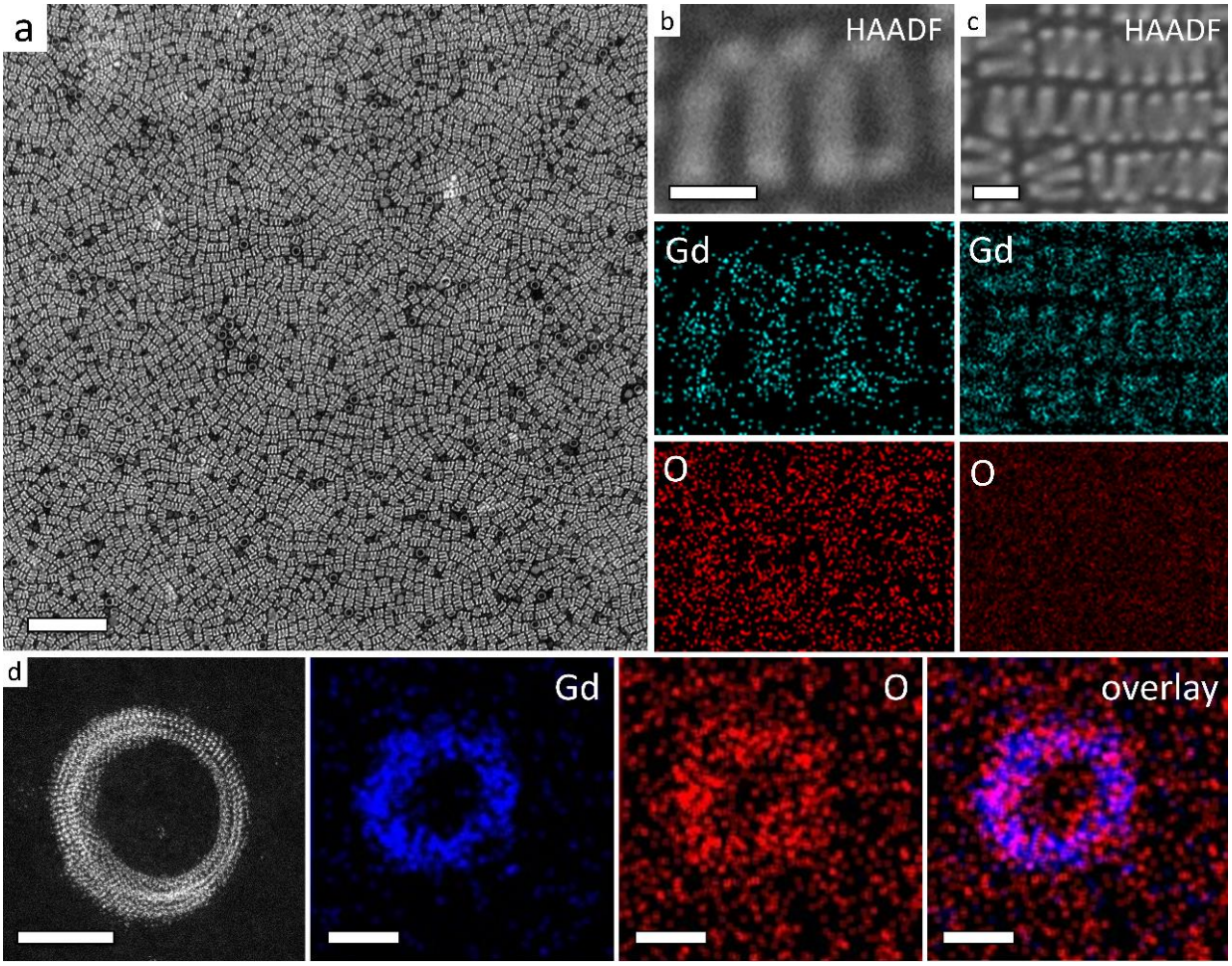

Figure S2. (a) Low-magnification HAADF-STEM image of Gd_2O_3 nanohelices. (b,c) Side-view HAADF-STEM images of (b) a single nanohelix (c) multiple nanohelices and corresponding elemental maps of gadolinium and oxygen. (d) Top-view AC-HAADF-STEM image of a single nanohelix and corresponding elemental maps of gadolinium, oxygen and their overlay. Scale bars: (a) 100 nm, (b-d) 5 nm.

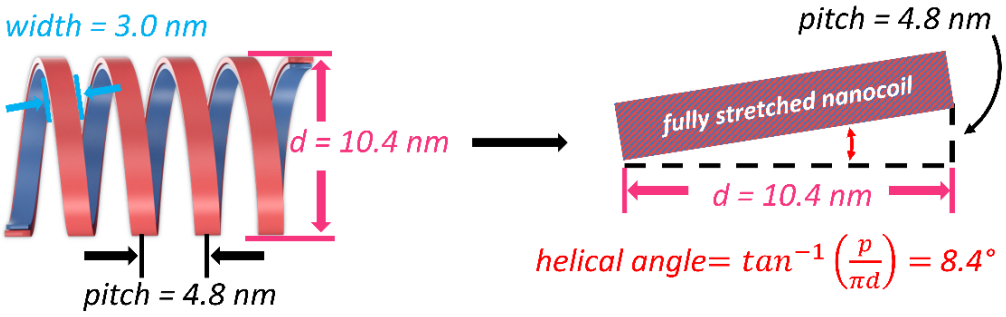

Figure S3. Calculation of the helical angle calculation for a nanohelix.

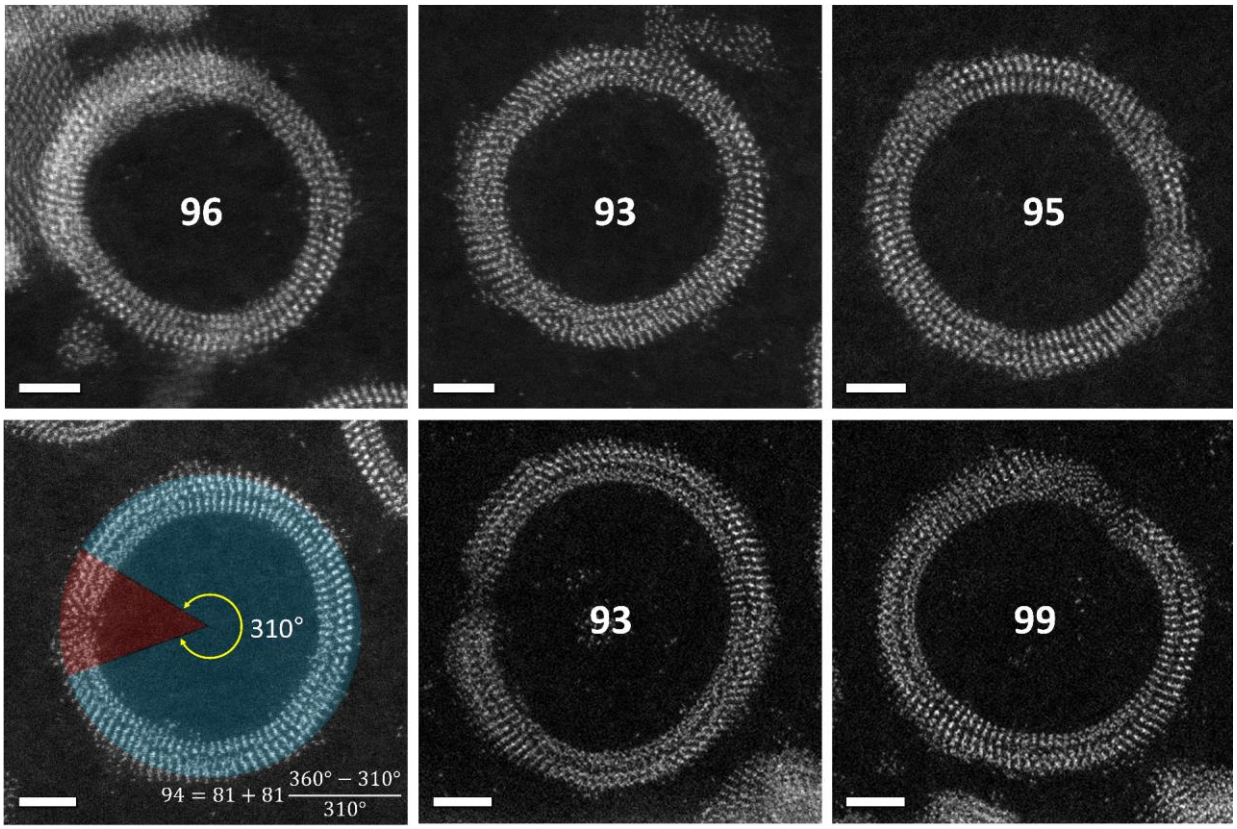

Figure S4. A collage of top-view AC-HAADF-STEM images of individual single-turn nanohelix with a bilayer structure along its radial direction. The estimated number of atomic rows on the circumference of each nanohelix is indicated. For nanohelices showing missing atoms (i.e. below one full turn) or those showing overlapping ends (i.e., contour length exceeding one full turn), we measured the number of atomic planes n_1 from well-defined, clearly discernible region and extrapolated to a full circle based on the total angle spanned by the arc (θ, usually in the range of 300-340º) using $n = n_1 + n_1\frac{360-\theta}{\theta}$. An example is shown on the bottom left image. Scale bars: 2 nm.

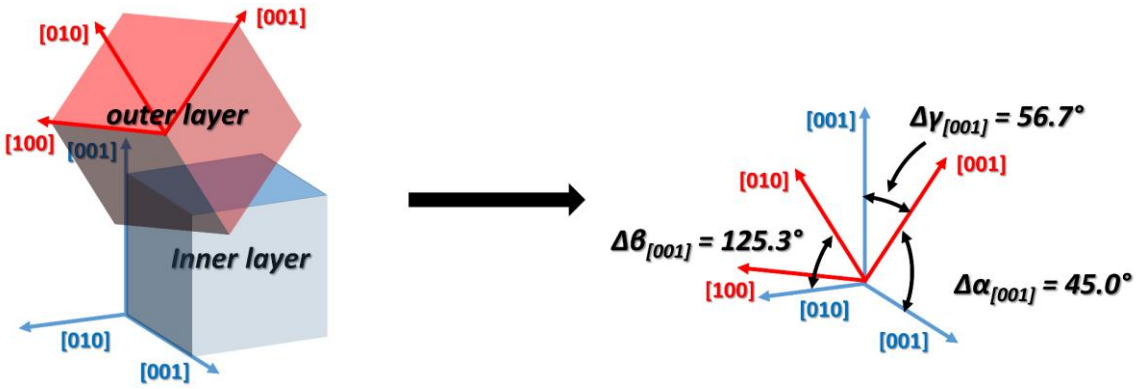

Figure S5. Schematic illustration of the relative orientation between the outer {111} and inner {100} layers. The right panel illustrates the relative orientation between the coordinate systems of outer and inner Gd_2O_3 layers.

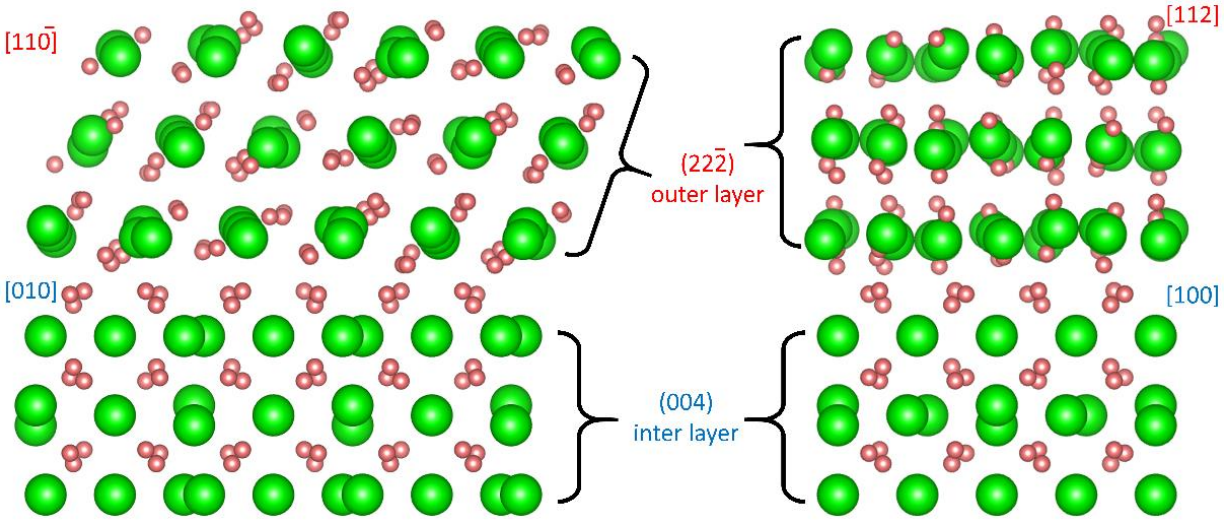

Figure S6. Crystal structure model for the radial bilayer of Gd_2O_3 nanohelices. The same structural models are presented in Figures 2f,g, where the oxygen atoms are omitted for clarity.

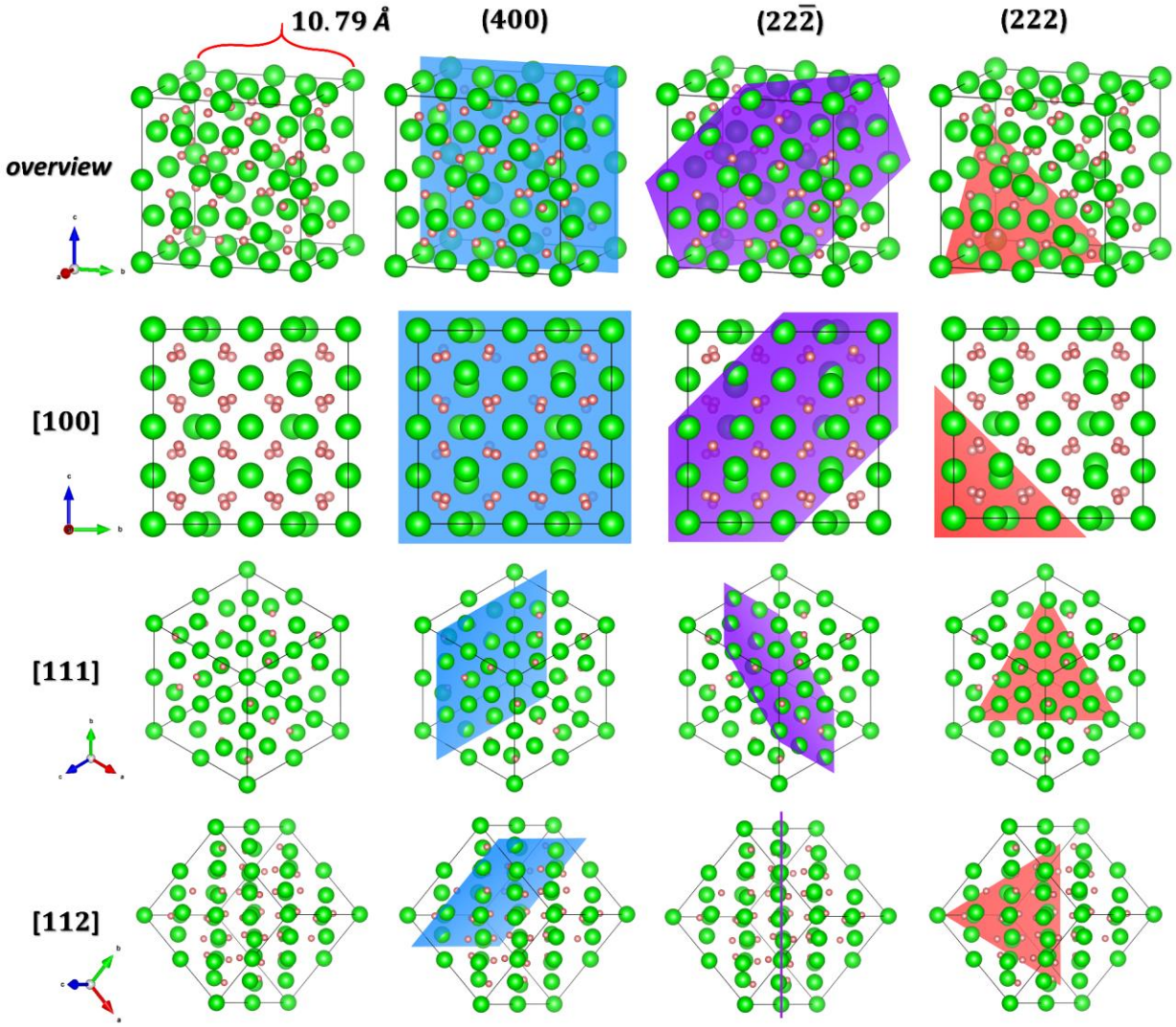

Figure S7. Crystal structure details for cubic-phase Gd_2O_3 (space group: Ia3). The (400), (22$\bar{2}$), (222) crystal planes are shown when unit cell is viewed along [100], [111], and [112] directions.

Table S1. Calculated nanohelix inner diameters based on continuum elasticity theory of strained bilayers.

Parameters	Inner layer thickness, d_{in}	Outer layer thickness, d_{out}	Young's modulus ratio, χ	Poisson's ratio, ν	lattice misfit, ε	Diameter, D_{helix}^{inner}
Method	$d_{in}^{model} + \frac{d_{gap}}{2}$	$d_{out}^{model} + \frac{d_{gap}}{2}$	Isotropic	Ref. 2	$\frac{3.3\ \text{Å} - 2.7\ \text{Å}}{3.3\ \text{Å}}$	Equation 1
Value	6.0 Å	6.8 Å	1	0.25	0.18	75.3 Å
Method	$d_{in}^{model} + \frac{d_{gap}}{2}$	$d_{out}^{model} + \frac{d_{gap}}{2}$	Anisotropic, $\frac{E_{(100)}}{E_{(111)}}$	Ref. 2	$\frac{3.3\ \text{Å} - 2.7\ \text{Å}}{3.3\ \text{Å}}$	Equation 1
Value	6.0 Å	6.8 Å	1.3	0.25	0.18	76.3 Å
Method	$d_{in}^{model} + \frac{d_{gap}}{2}$	$d_{out}^{model} + \frac{d_{gap}}{2}$	Isotropic	Ref. 2	$\frac{2 \times (3.3\ \text{Å} - 2.}{3.3\ \text{Å} + 2.7}$	Equation 1
Value	6.0 Å	6.8 Å	1	0.25	0.20	68.5 Å
Method	$d_{in}^{model} + \frac{d_{gap}}{2}$	$d_{out}^{model} + \frac{d_{gap}}{2}$	Anisotropic, $\frac{E_{(100)}}{E_{(111)}}$	Ref. 2	$\frac{2 \times (3.3\ \text{Å} - 2.}{3.3\ \text{Å} + 2.7}$	Equation 1
Value	6.0 Å	6.8 Å	1.3	0.25	0.20	69.4 Å

Notes: 1. The gap between inner and outer layers d_{gap} was measured to be 1.2 Å based on multiple AC-HAADF-STEM images.

2. Both isotropic and anisotropic Young's modulus for Gd_2O_3's are considered due to different possibilities reported in the literature,[1] which shows that the resulting variations in calculated diameter values are insignificant. The Poisson's ratio of Gd_2O_3 is based on the value reported in previous literature.[2]

3. Two ways of calculating lattice misfit are used.

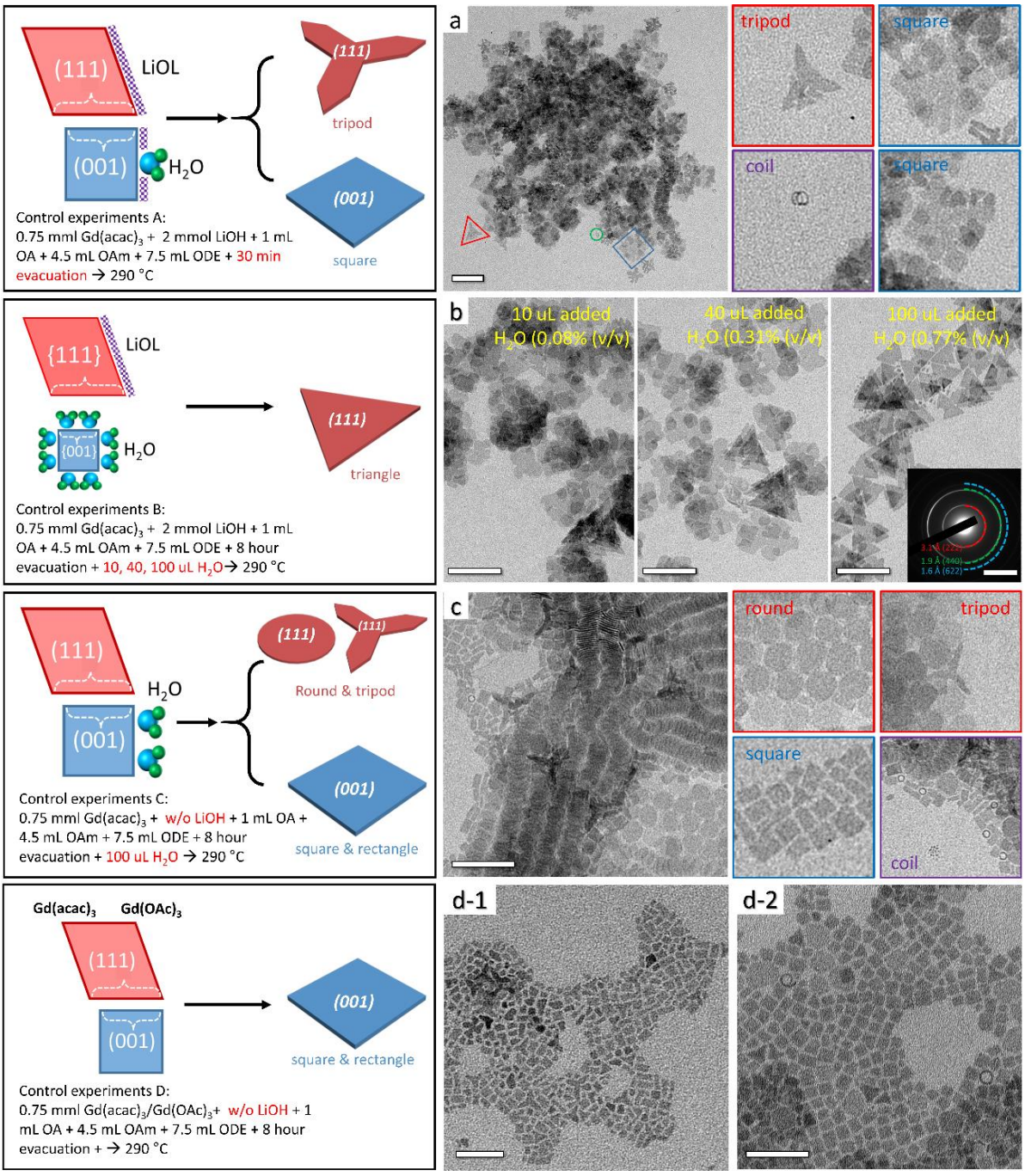

Figure S8. Design of control synthetic experiments and TEM images of resulting reaction products. Inset of (b) shows the corresponding SAED pattern (scale bar: 5 nm^{-1}). Scale bars: (a-c) 100 nm, (d) 50 nm. Panel a shows that a short vacuum degassing such as 30 min is usually insufficient to synthesize nanohelices, which is likely suppressed by the residual water in the reaction mixture produced from the slow reaction of oleic acid and LiOH (sparingly soluble in reaction solvent 1-octadecene). The vital role of water is further supported by experimental results shown in panel b in where controlled amounts of water were deliberately added to the reaction mixture prior to temperature ramp. Further, the results shown in panels c and d indicate that lithium oleate can promote the formation of nanohelices.

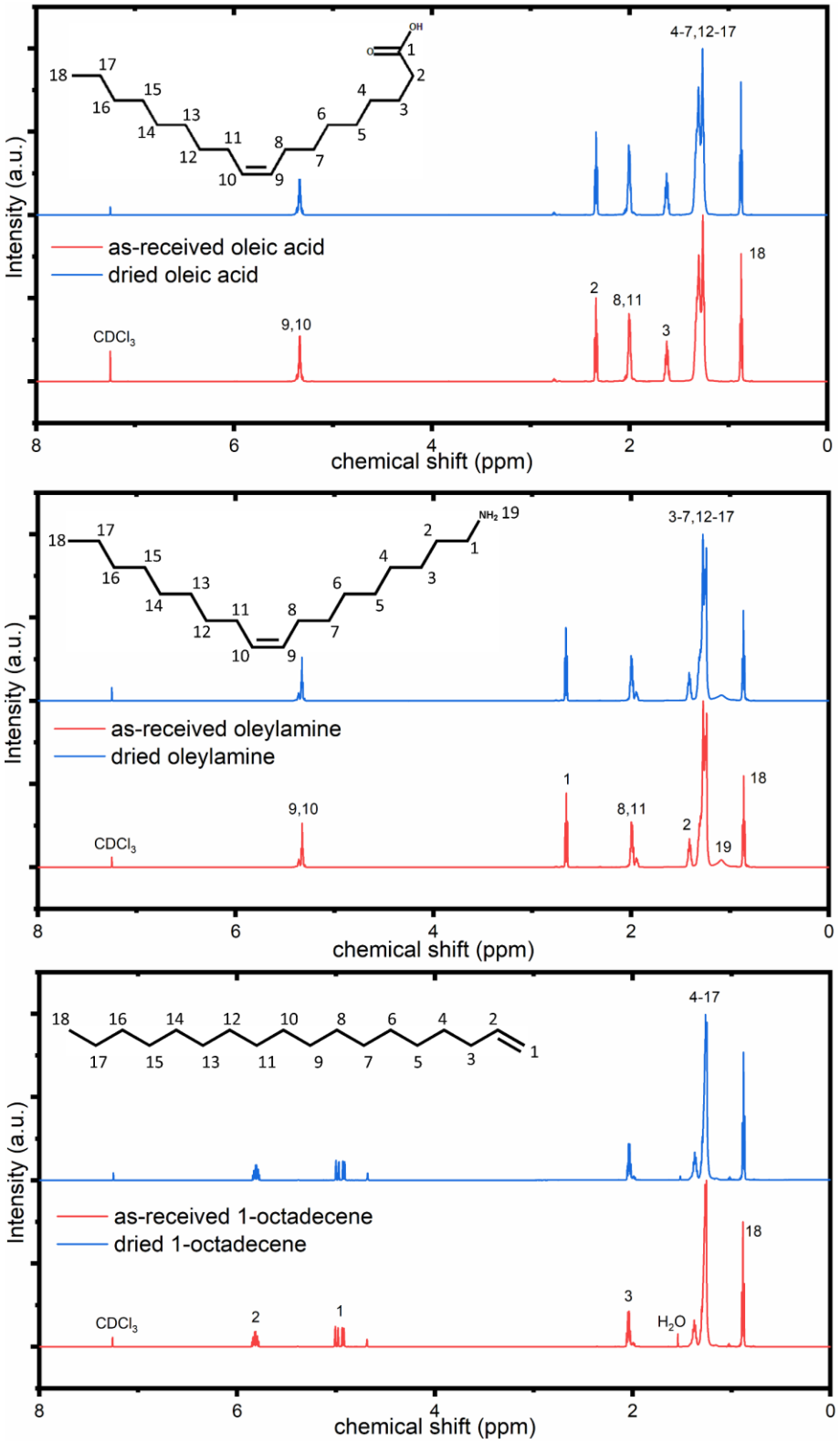

Figure S9. ^{1}H NMR spectra of liquid reagents as-received and after vacuum degassing (below 0.06 Torr) at elevated temperatures (110 °C for OA, 100 °C for OAm and 95 °C for ODE) for at least four hours.

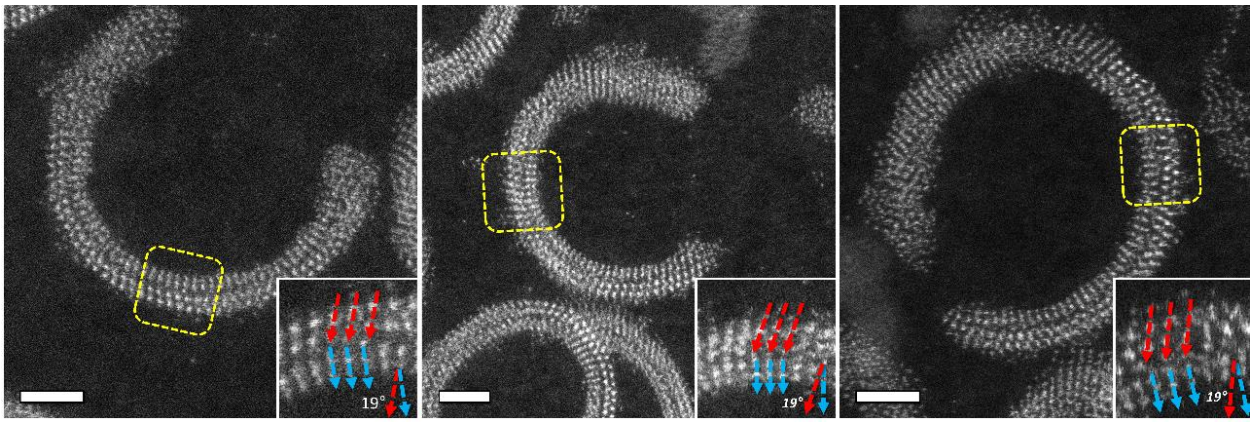

Figure S10. Additional AC-HAADF-STEM images of single- and half-turn nanohelices with a bilayer structure. The bottom inset of each image shows the zoomed-in view of the region outlined by the yellow dashed box. An angle of ca. 19° between the inner and outer layer crystal planes is consistently determined. Scale bars: 2 nm.

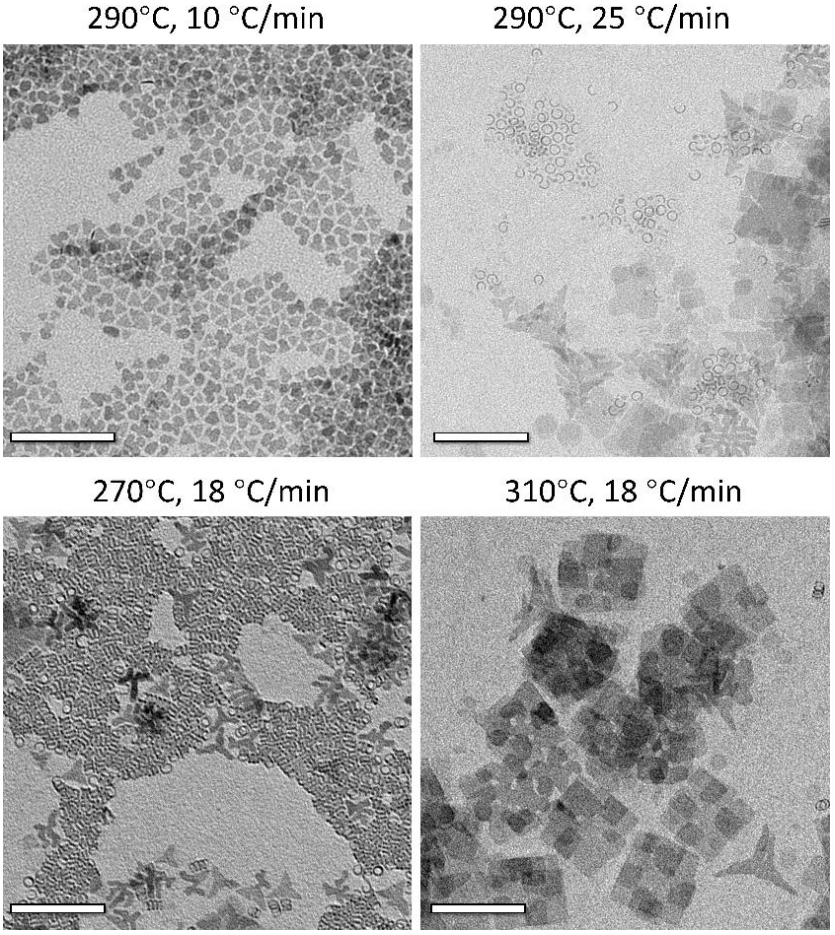

Figure S11. Representative TEM images of reaction products obtained when using different ramp rates and reaction temperatures. Scale bars: 100 nm.

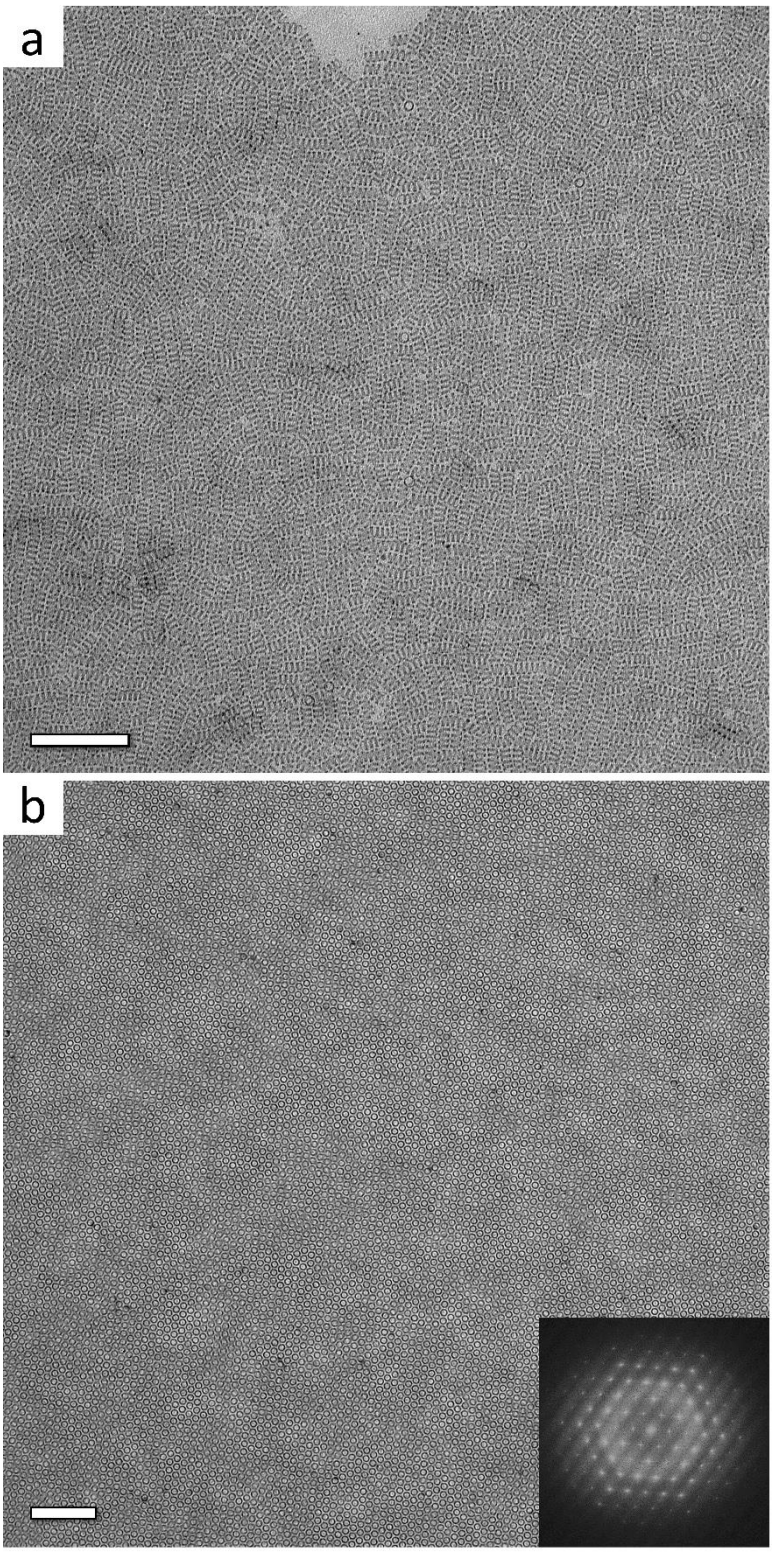

Figure S12. (a) Low-magnification TEM image of a monolayer of horizontally lying nanohelices. (b) Low-magnification TEM image of 2D hexagonal superlattices of vertically standing nanohelices. Inset: Corresponding FFT pattern. Scale bars are 100 nm.

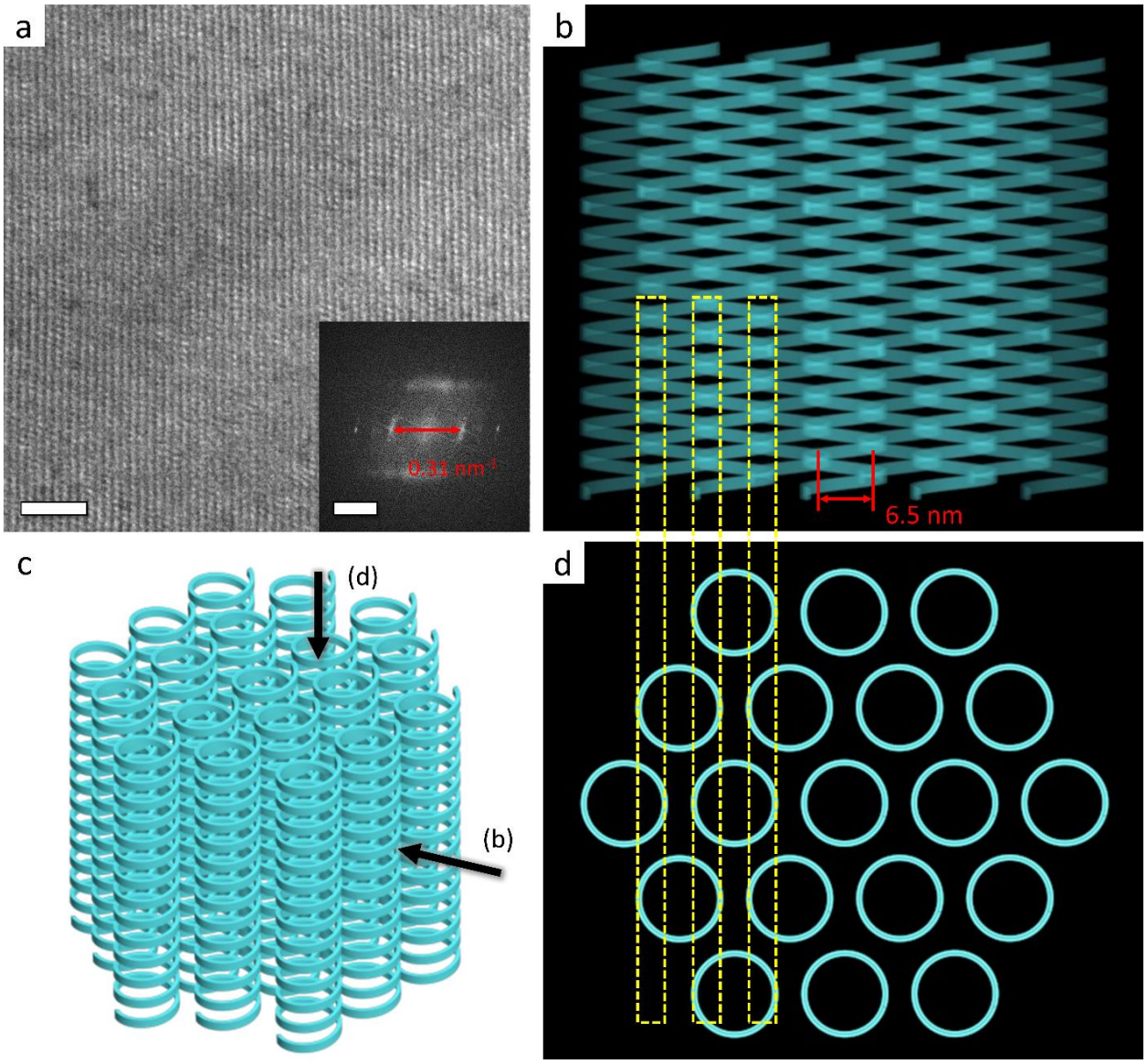

Figure S13. (a) Low-magnification TEM image and (b,c) structural models of 3D self-assembled superlattices of horizontally lying nanohelices. The periodic stripe-like contrast seen in (a) is believed to arise from superimposed rims of adjacent nanohelices, as illustrated in (d), a side-view of the 3D structural model. Scale bars: (a) 50 nm, (inset of a) 0.2 nm^{-1}. From the first-order peak of the FFT pattern, the periodicity of stripes is estimated to be 6.5 nm. This value is smaller than the inner diameter of individual nanohelices (7.5 ± 0.4 nm), further confirming overlapping rims of neighboring nanohelices.

Supplementary References

1. Gaillac, R.; Pullumbi, P.; Coudert, F. X., ELATE: an open-source online application for analysis and visualization of elastic tensors. *J. Phys. Condens. Matter.* **2016,** *28*, 275201.

2. Awin, E. W.; Sridar, S.; Shabadi, R.; Kumar, R., Structural, Functional and Mechanical Properties of Spark Plasma sintered Gadolinia (Gd_2O_3). *Ceramics International* **2016,** *42*, 1384-1391.