Direct observation of cation distributions of ideal inverse spinel CoFe$_2$O$_4$ nanofibres and correlated magnetic properties

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1. Analysis of the morphology and diameter of the inverse spinel structure of CFO single-particle-chain nanofibres.

Fig. S1 Morphological characterization of the inverse spinel structure of CFO single-particle-chain nanofibres. (a) Low-magnification SEM image; (b) Magnified SEM image showing the local morphology of the CFO nanofibers; (c) Representative bright-field TEM image. Inset, quantitative analysis of the diameter of a CFO nanofibre; (d) High-
magnification TEM image showing that individual CFO nanofibres consist of single nanoparticles stacked along the nanofibre axis much like a single-particle chain.

The morphology of the CFO nanofibers was characterised by SEM and TEM. Figure S1a, b show two representative SEM images of the CFO nanofibres, revealing that individual CFO nanofibers have a continuous structure and uniform diameter after the calcination process. Nanofibers were approximately 120 μm in length. Figure S1c shows a TEM image of a bundle of CFO nanofibres, which reveals the same morphological features as SEM observation. The quantitative analysis (inset of Fig. S1c) indicated that CFO nanofibres were 60 nm long on average, ranging from 55 nm to 65 nm. The two enlarged CFO nanofibers shown in Figure S1d illustrate that individual CFO nanofibers consist of single nanoparticles stacked along the nanofibre axis much like a single-particle chain.

2. Chemical analysis of the inverse spinel structure of CFO nanofibres.
Fig. S2 Chemical analysis of the inverse spinel structure of CFO single-particle-chain nanofibres. (a) EDX spectrum acquired from a large number of CFO nanofibres; (b) Representative HAADF-STEM image of a single CFO single-particle-chain nanofibre; (c) Cobalt elemental mapping; (d) Iron elemental mapping; (e) Oxygen elemental mapping.

Figure S2a shows an EDX spectrum of bundles of the CFO single-particle-chain nanofibres. Quantitative analysis shows a 1:2 atomic ratio of Co:Fe, inferring chemical composition of CoFe$_2$O$_4$. Figure S2b shows a representative HADDF-STEM image of a single CFO single-particle-chain nanofibre. Figure S2c-e display the corresponding EDX mappings of oxygen ($K_{\alpha}$, 0.52 keV), iron ($K_{\alpha}$, 6.4 keV) and cobalt ($K_{\alpha}$, 7.71 keV) elements, respectively. These three elements O, Fe, and Co appear to be evenly distributed throughout the nanofibre, revealing a uniform chemical phase.

3. The simulated HAADF-STEM images of ideal normal spinel
structures of CFO.

Fig. S3 Simulated HAADF-STEM images and perspective views of ideal normal spinel CFO structure. (a-c) Projected along [001], [011] and [-112] axes, respectively. Right-bottom insets illustrate the corresponding line intensity profiles of the simulated STEM images from the red line ‘7’, ‘8’, ‘9’ individually. (d-f) The relevant perspective views of the unit cells along the three crystal orientations, showing the spatial atom columns at tetrahedral A sites and octahedral B sites, respectively. It is noted that the ball colours have the same meanings as in Figure 1.

Fig. S3 shows the simulated STEM images of ideal normal spinel structure of CFO projected along [001], [011] and [-112] orientations, respectively. Due to the Co$^{2+}$ cations occupying tetrahedral A sites and Fe$^{3+}$ cations occupying octahedral B sites in the normal spinel CFO structure, one can see that the contrast of the atomic columns between the tetrahedral
A sites and octahedral B sites in Fig. S3a are simply the reverse of what we see in experimental Fig. 2a and simulated Fig. 2h when the electron beam is incident along [001] axis. This result well verifies that our STEM observations of full inverse spinel structure in CFO nanofibers are correct. Besides, the large difference in the number of atoms in the atomic columns and the tiny difference in atomic number between Co and Fe causes the simulated HAADF-STEM images of the normal spinel structures to be the same when the images were taken along the [011] and [-112] axes, i.e., both exhibit the same contrast distribution of atomic columns (Fig. S3b and Fig. S3c), which is confirmed by relative intensity differences of line intensity profiles as shown in right-bottom insets.

4. **Structural characterization of the inverse spinel structure of CFO nanofibres.**
Fig. S4 Structural characterization of the inverse spinel structure of CFO nanofibres. (a) TEM image of the CFO nanofibre. (b) CBED pattern detected from the area marked by a red circle in (a); (c) CBED pattern detected from the area marked by a green circle in (a); (d) XRD spectrum detected from a large number of CFO single-particle-chain nanofibres synthesized at 900°C, revealing their spinel structure.

Figure S4b and S4c show two CBED patterns detected from the area delineated with red and green circles in Fig. S4a, revealing [013] and [1-10] orientations, respectively. This result further proves that individual CFO nanofibres are composed of single nanocrystallites, stacked along the nanofibre axis, such that each crystallite has a random crystal orientation. Figure S4d shows a typical XRD spectrum of a mass of the CFO single-
particle-chain nanofibres, of which peaks can be indexed to (220), (311), (222), (400), (422), (511), (440), (533) and (731) planes of the cubic spinel structure. This result is consistent with the crystal characterization observed using TEM.

5. Distorted surface layers of nanoparticles in the CFO nanofibres.

Fig. S5 (a) and (b) HRTEM images, showing that there are 2~5 distorted atomic layers covered on the surface of individual CFO single-particle-chain nanofibres.