XMCD and XMCD-PEEM Studies on Magnetic-Field-Assisted Self-Assembled One-Dimensional Nanochains of Spherical Ferrite Particles

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Study of X-ray-magnetic-circular-dichroism (XMCD) and XMCD in photoemission-electron-microscopy (XMCD-PEEM) is for the first time performed on magnetic-field-assisted self-assembled quasi-one-dimensional (1D) nanochains of spherical ferrite particles, with a homogeneous particle size of about 200 nm and chain length of micrometers. Supported by theoretical analysis, the XMCD provides direct evidence for the distributions of the Fe$^{2+}$ $O_h$, Fe$^{3+}$ $T_d$ and Fe$^{3+}$ $O_h$ cations and the preferential occupation of the dopant ions. A non-monotonic $H_{assist}$-dependence of the cation distribution is revealed, consistent with that of the saturation magnetization, while discrepant with that of the magnetic anisotropy. Unlike bulk ferrites, where the magnetism is predominantly determined by the crystal chemistry, in nanoscale ferrites the external synthetic conditions and shape effects play a nontrivial role as...
well. At $H_{\text{assist}} = 2500 \text{ Oe}$, the nanochains exhibit a high saturation-magnetization approaching the bulk value and relatively large magnetic anisotropy induced by the chain-like shape, which makes it a good candidate for magnetic 1D-nanodevices. XMCD-PEEM is performed on these nanochains, showing the precise trapping of magnetic domain walls in a single chain. Cobalt and zinc dopants are also incorporated to tailor the magnetic properties of these nanochains for future device applications serving diverse demands.

1. Introduction

One-dimensional (1D) magnetic nanostructures, such as nanowires, nanotubes, and nanorods, exhibit novel magnetic properties, differing from those of their bulk counterparts.$^{[1,2]}$ By virtue of their potential applications in areas widely ranging from cancer therapy to quantum computing, these nanostructures have attracted tremendous interest.$^{[3-5]}$ For instance, a so-called nanoconveyer, consisting of patterned 1D magnetic zigzag nanowires, is demonstrated to facilitate the transport of multiple individual nanostructures by utilizing the magnetic force of the magnetic domain walls (DWs) trapped at the kink of the nanowires.$^{[6]}$ Different kinds of nanoparticles can be manipulated in this way, and thus the nanoconveyer-belt technology could affect broad fields, including nanoassembly, biomechanics, nanomedicine, and nanofluidics. On the other hand, the proposed racetrack memory technology, storing digital data in the magnetic DWs of 1D nanowires, promises to yield information storage devices with high reliability, performance, and capacity. As one of the most popular and reliable alternatives to the magnetic disk drive, this racetrack implementation is extremely flexible and can cover a range of applications from ultrafast to ultradense memory-storage devices.$^{[7,8]}$

Interestingly, operation of the abovementioned 1D nanodevices relies on the magnetic DWs, which are usually produced by fabricating various kinds of artificial pinning sites — e.g., notches and kinks$^{[9-11]}$ — utilizing micro-patterning techniques such as electron-beam and
focused-ion-beam lithography. Here, we introduce a type of quasi-1D nanochains, composed of spherical magnetite (Fe₃O₄) particles, where the boundaries between the particles form natural pinning sites for the DWs. These nanochains, prepared by a growth strategy of magnetic-field-assisted self-assembly, have their dimensions not relying on any of those micro-patterning techniques and are easily controlled by the value of the assisted magnetic field (hereafter called $H_{\text{assist}}$). [12] Compared to patterned nanowires, where the shape effect usually prevails, these ferrite nanochains have one extra important factor influencing their magnetic properties — namely the cation distribution of the spinel structure — given the fact that magnetic properties of the spinel oxide are strongly related to their crystal chemistry and structure. [13,14] This, on the one hand, provides a great opportunity for adjusting the magnetism of the nanochains, e.g., by introduction of foreign dopants; On the other hand, unlike bulk ferrites, the inversion degree of the inverse spinel structure at the nanoscale can significantly diverge depending on the adopted synthetic conditions, [15,16] which urges us to investigate the $H_{\text{assist}}$-dependent crystal chemistry and its influence on the magnetic properties of the ferrite nanochains. So far, no direct evidence of the nanochains’ crystal chemistry has been demonstrated, partly because of the limitations of conventional characterization methods, such as Mössbauer spectroscopy, which cannot distinguish between the Fe²⁺ and Fe³⁺ octahedral ($O_h$) sites. In this respect, X-ray magnetic circular dichroism (XMCD) provides a powerful and vigorous tool for tackling this issue, as this technique can distinguish the different Fe sites, i.e., Fe²⁺ $O_h$, Fe³⁺ tetrahedral ($T_d$), and Fe³⁺ ($O_h$) in the ferrites [17-19].

In this work, we carry out a thorough study of the cation distribution in 1D nanochains of spherical ferrite particles, by taking advantage of element-specific XMCD spectroscopy combined with a theoretical modeling of the these spectra. The trend in the cation distribution, varying with $H_{\text{assist}}$, is unraveled and compared to those of the saturation magnetization and magnetic anisotropy, respectively. This helps us to reveal the role of $H_{\text{assist}}$ (or in other words,
the external synthetic conditions) in determining the magnetic properties of the nanoscale ferrites, and to find an optimized growth condition for obtaining favorable nanochains for the practical application of magnetic 1D nanodevices. The magnetic configuration of a selected single chain is imaged by the advanced technique of XMCD in photoemission electron microscopy (XMCD-PEEM), and the magnetic DWs are revealed to be created at the particle-boundaries after magnetization. Furthermore, two types of foreign dopants (Co and Zn) are incorporated in the nanochains, and the dopant-dependent cation distribution is also investigated by XMCD, which opens up a promising avenue to tailor the magnetic properties of ferrite nanochains fabricated by the magnetic-field-assisted approach.

2. Results and Discussion

2.1. \( H_{\text{assist}} \)-Dependent Magnetic Properties of Magnetite Nanochains

A stack of magnetite nanochains are achieved by utilizing the magnetic-field-assisted self-assembly growth strategy, with various \( H_{\text{assist}} \) ranging from 0 to 3500 Oe. The magnetic-field-assisted method, where an external magnetic field is imposed during synthesis, is a relatively simple and low-cost technique.\(^{[20-22]}\) It does not rely on any templates, with the movement of the particles and formation of the chain-like shape well controlled by the \( H_{\text{assist}} \)^{[12,23]} and thus overcomes the common drawbacks of other template-based low-yield approaches (such as anodic aluminum oxide hard template or Lecithin soft template\(^{[24-28]}\)).

**Figure 1a** shows a typical scanning electron microscopy (SEM) image of the longest magnetite nanochains prepared under the highest \( H_{\text{assist}} \) of 3500 Oe, giving an average chain length of about 5 µm and fairly homogeneous particle size of about 200 nm. This particle size is larger than those of other self-assembled single magnetic particles reported to date,\(^{[29]}\) overcoming the so-called superparamagnetic limit \(^{[30]}\) (where random flipping of the magnetic moment with time is induced by thermal fluctuations and the nanoparticles lose their stable
magnetic order and become superparamagnetic\(^{(31)}\) for magnetic applications. Figure 1b is a bright-field transmission electron microscopy (TEM) micrograph of one magnetite nanochain, and the contrast is quite the same within one particle. When the sample is tilted, the particle contrast changes at the same time within the whole individual particle, implying that each particle is a single crystal. Further confirmation is done using convergent beam electron diffraction (CBED), as shown in Figure 1c. A CBED pattern from one particle is observed when the electron beam is along the [111] zone axis of the particle, showing that the particle is indeed a single crystal. More information about the boundary between two adjacent particles is shown in Supporting Information Figure S2.

Figure 1d-f show the magnetic hysteresis loops of the chains, characterized by vibrating sample magnetometry (VSM). The solid and dashed lines represent the loops taken with the external magnetic field applied along and perpendicular to the chains, respectively. A uniaxial magnetic anisotropy is clearly observed, with the easy axis along the chain direction and hard axis normal to it. This particular aspect, as has been systematically studied in our previous work, originates from the chain-like shape.\(^{(12)}\)

Figure 1g-h summarize the crucial parameters of the hysteresis loops along the chain direction, including the coercivity \((H_C)\), squareness \((M_R/M_S)\), saturation magnetization \((M_S)\), and anisotropy of the demagnetizing field \((H_{S,\perp} - H_{S,\parallel})\). The first two parameters characterize the total magnetic anisotropy of the nanochains,\(^{(32)}\) both of which exhibit an overall increasing trend with \(H_{assist}\), as shown in Figure 1e. This implies that the total magnetic anisotropy is strengthened, probably due to the enhanced shape effect (or the uniaxial magnetic anisotropy) with increasing \(H_{assist}\), which is analyzed by calculating the anisotropy of the demagnetizing field as follows.

Assuming the internal saturation field is isotropic, the anisotropy of the demagnetizing factors \((N_x\) and \(N_z\) perpendicular to and \(N_y\) along the chain direction) may be evaluated by the
anisotropy of demagnetizing field, i.e., \((N_y - N_x)M_S = H_{S_\perp} - H_{S//}\), where \(H_{S_\perp}\) and \(H_{S//}\) represent the saturation fields along the normal and along the chain length, respectively. As shown in Figure 1f, the magnitude of \(H_{S_\perp} - H_{S//}\) shows a similar \(H_{\text{assist}}\)-dependence as that of the total magnetic anisotropy, suggesting that the shape effect plays an important role in the increasing trend of the latter. Specifically, the \(H_{\text{assist}}\) facilitates the growth of the chains, and the chain length increases when \(H_{\text{assist}}\) increases, while the particle size remains unchanged, leading to an increasing length-to-width aspect ratio with increasing \(H_{\text{assist}}\). This results in an enhanced uniaxial magnetic anisotropy, which could be the main source of the strengthened total magnetic anisotropy here.

Note that the sources of the magnetic anisotropy in the ferrite nanochains can be complicated, since a contribution of the cation distribution cannot be excluded. This will be discussed in Section 2.2, where a detailed investigation by XMCD is performed on the cation distribution, showing a non-monotonic trend with \(H_{\text{assist}}\).

2.2. \(H_{\text{assist}}\)-Dependent Cation Distribution of Magnetite Nanochains

Figure 2a shows the inverse spinel structure of magnetite containing two non-equivalent Fe sites, where the \(T_d\) sites are occupied by Fe\(^{3+}\) ions and the \(O_h\) sites by both Fe\(^{2+}\) and Fe\(^{3+}\) ions. This cationic arrangement leads to the formation of two sublattices, which are ferrimagnetically coupled, as indicated by the spin directions shown in the figure. Accordingly, any change in the cation distribution will result in a considerable variation of the magnetic properties of the chains. The following investigation aims to unravel the relation between the \(H_{\text{assist}}\)-dependent spectral structural details and the magnetic properties of the nanochains.

The XMCD measurement geometry is schematically illustrated in Figure 2b. The incidence angle of the X-ray beam is set to 60° relative to the sample surface normal, where the
nanochains are aligned in parallel on top of the silicon substrate (the same as shown in Figure 1a). The X-ray absorption (XA) spectra, corresponding to transitions from the 2p core levels to the unoccupied 3d states, are recorded in total-electron yield (TEY) mode at room temperature. The XMCD is obtained by reversing the helicity vector of the 90% circularly polarized X-rays, where the external magnetic field is applied along the direction of the aligned nanochains.

Figure 2c shows an example of the analysis of the spectra measured for the chains with $H_{\text{assist}} = 2500$ Oe. The sum over the Fe $L_{2,3}$ XA spectra, $\sigma^- + \sigma^+$, is similar to that of bulk Fe$_3$O$_4$. By taking the difference between the XA spectra recorded with parallel and antiparallel alignment of sample magnetization and helicity vector, the XMCD spectrum is obtained as $\sigma^- - \sigma^+$. The relative proportions of the three Fe components, Fe$^{2+}$, Fe$^{3+}$ $T_d$, and Fe$^{3+}$ $O_h$, primarily make up the intensities of the three main peaks (negative, positive, and negative, respectively) across the Fe $L_3$ edge (~708-714 eV). The cation distribution over the three Fe sites is then systematically and precisely monitored.

Using atomic multiplet calculations, the values for the relative site occupancies, i.e., the ratio of the individual cations [Fe$^{2+}$ $O_h$]:[Fe$^{3+}$ $T_d$]:[Fe$^{3+}$ $O_h$] are obtained from the best-fit to the measured XMCD spectrum, as shown in Figure 3a. The $H_{\text{assist}}$-dependence of the ratios is summerized in Figure 3b, and the saturation magnetization $M_s$ is also displayed for comparison, since the changes in the cation distribution will be directly reflected in $M_s$. For the magnetite particles (i.e., $H_{\text{assist}} = 0$), the [Fe$^{2+}$ $O_h$]:[Fe$^{3+}$ $T_d$]:[Fe$^{3+}$ $O_h$] is 0.98:0.73:1, resulting in a [Fe$^{2+}$]:[Fe$^{3+}$] ratio of 1.13:2, which is slightly higher than the 1:2 ratio expected for stoichiometric magnetite. When $H_{\text{assist}}$ increases, the [Fe$^{2+}$ $O_h$]:[Fe$^{3+}$ $O_h$] ratio first shows a marginal rise and then a steep decrease, whereas the [Fe$^{3+}$ $T_d$]:[Fe$^{3+}$ $O_h$] ratio first decreases followed by a slight increase. This strong $H_{\text{assist}}$ dependence of cation distribution suggests the nontrivial influence of the external synthetic conditions in the nanoscale ferrites, which is
more complicated than in the case of bulk ferrites. Clearly, the $H_{\text{assist}}$-dependence of the $[\text{Fe}^{2+}\text{O}_6]_m[\text{Fe}^{3+}\text{O}_4]$ ratio shows a high consistency with that of $M_S$. This seems to be in line with the fact that the $\text{Fe}^{2+}$ cation on the $O_6$ site gives the greatest contribution to $M_S$, suggesting a dominant role of the cation distribution, over the shape effect of the chain structure induced by $H_{\text{assist}}$ (such as the changes in the demagnetizing field and the magnetization non-uniformity within the chain), in modification of $M_S$.

In a given crystal lattice, the $\text{Fe}^{2+}$ ions in $O_h$ sites not only determine $M_S$ but also influence the magnetic anisotropy, since they contribute to a positive anisotropy constant, while the $\text{Fe}^{3+}$ ions do not contribute strongly to the magnetic anisotropy. As shown in Figure 3b, the $\text{Fe}^{2+}$ cation ratio shows a non-monotonic trend with $H_{\text{assist}}$, which is discrepant with the monotonous increasing trend of the magnetic anisotropy (shown in Figure 1f). This suggests that the $H_{\text{assist}}$-dependent cation distribution does not play a decisive role in the change of the magnetic anisotropy, and seems to confirm our previous explanation on the observed increase in the magnetic anisotropy, which is ascribed to an enhanced shape effect (or increasing demagnetizing factor along the direction of the chain) with $H_{\text{assist}}$.

From the above $H_{\text{assist}}$-dependences, we find that when $H_{\text{assist}} = 2500$ Oe, the magnetite nanochains maintain the high $M_S$ of nearly 90 emu/g as the magnetite particles do (approaching the bulk value), while for $H_{\text{assist}} = 3500$ Oe the $M_S$ has a clear drop to around 75 emu/g. On the other hand, the magnetic anisotropy shows a drastic enhancement when $H_{\text{assist}}$ increases from 0 to 2500 Oe, while the increase from 2500 Oe to 3500 Oe becomes much weaker. These features suggest that 2500 Oe would be relatively an ideal value for $H_{\text{assist}}$ to facilitate the chains’ growth for applications in magnetic 1D nanodevices. Correspondingly, we select single chains under this $H_{\text{assist}}$ value for XMCD-PEEM imaging, with the aim to monitor their magnetic configurations manipulated by external magnetic fields, which would be key for their practical applications.
2.3. Magnetic Configuration of Single Magnetite Nanochain

The magnetite chains, prepared with $H_{\text{assist}} = 2500$ Oe, are dispersed in stilled water with very low concentration and then transferred onto an $8 \times 8$ mm$^2$ undoped Si substrate by drop-casting. After drying in N$_2$ environment at room temperature, single chains are sparsely spread onto the substrate, and SEM picture of one such chain is shown in Figure 4a. The XMCD-PEEM on beamline 11.0.1 (PEEM3) at the Advanced Light Source with a spatial resolution of 30 nm is used to probe the domain configuration in a single magnetite nanochain. In contrast to other imaging techniques, such as magnetic force microscopy (MFM), which can influence and even switch the magnetic configuration$^{[38]}$ by the stray field from the detector, XMCD-PEEM is a nonintrusive technique, which allows for imaging of magnetic objects that do not provide stray fields.$^{[39]}$

Prior to taking the XMCD-PEEM images, we magnetize a selected chain by applying an external magnetic field ($H_{\text{ext}}$) along the direction of the X-ray polarization ($\rho$), as indicated by the purple arrow in Figure 4b. The PEEM image is captured at the remanent state, where the “white” and “black” contrasts represent the projection of the magnetization direction aligned parallel and antiparallel to the X-ray beam with right polarization, respectively.$^{[9,40]}$ In this remanant state, characteristic DWs are formed at the boundaries between the white and black magnetic domains, as indicated by the change in contrast.

To demonstrate that the white and black contrasts represent opposite directions of the magnetization, we also measure their XA spectra, as shown in the upper panel of Figure 4c. Specifically, they are generated by collecting a stack of images as a function of photon energy, selecting a region within these images, and computing the intensity as a function of the photon energy. XMCD spectra for the white and black regions are obtained, respectively, by reversing the circular polarization of the X-rays. As shown in the lower panel of Figure
4c, the reversed XMCD signal for the white and black regions confirms the opposite alignment of their magnetization, and their line shapes are consistent with that for the stack of magnetite chains in Figure 2c.

2.4. Tuning Magnetic Properties of Ferrite Nanochains by Foreign Dopants

1D nanochains of Co- and Zn-ferrite particles are also prepared utilizing the magnetic-field-assisted method, with $H_{\text{assist}} = 2500$ Oe. Their compositions are determined by energy dispersive X-ray (EDX) analysis as $\text{Co}_{0.5}\text{Fe}_{2.5}\text{O}_4$ and $\text{Zn}_{0.15}\text{Fe}_{2.85}\text{O}_4$. The doping concentrations of Co and Zn are selected based on two competing considerations: On the one hand, we attempt to dope with as much as possible transition metal atoms to maximize the effect of doping, which may practically ease the present study of crystal chemistry. On the other hand, precaution must be taken to ensure the concentration is not too high, so that the dopant atoms can be fully incorporated into the nanoparticles instead of forming clusters of, e.g., CoO or ZnO.[41]

Hysteresis loops of the Co- and Zn-ferrite nanochains are shown in Figure 5a and 5b, respectively. Compared to the magnetite nanochains, we notice that both $H_C$ and $M_R/M_S$ are enhanced in the Co-ferrite nanochains, while the Zn dopants tend to reduce these in general, as shown in Figure 5c. Within the scope of this work, the Co dopants considerably enhance the magnetic anisotropy, or in other words, make the Co-ferrite chains much “harder” than the magnetite chains. In contrast, the Zn dopant weakens the magnetic anisotropy, making the chains magnetically “softer” than those of magnetite. This opens up a promising avenue to tailor the magnetic properties of the nanochains fabricated by the magnetic-field-assisted approach, which is especially useful for DW devices, since it is well known that the magnetic anisotropy determines the DW width and stability in the magnetic 1D nanostructures[8].

Figure 6a shows sum of the XA spectra taken at the Fe $L_{2,3}$ edge, compared with that of the
magnetite nanochains prepared with $H_{\text{assist}} = 2500$ Oe. These spectra look similar to each other, suggesting that the Co or Zn addition does not dramatically affect the nanoparticle formation. Figure 6b shows that upon addition of Co, the intensity of the Fe$^{2+} O_h$ peak decreases rapidly, accompanied by a slight increase in the Fe$^{3+} T_d$ peak intensity. On the other hand, when the Zn dopant is incorporated, both peaks show a comparable drop in intensity, as shown in Figure 6c. Quantitatively, upon doping of Co and Zn, the $[\text{Fe}^{2+} O_h]:[\text{Fe}^{3+} T_d]:[\text{Fe}^{3+} O_h]$ ratio diminishes to 0.37:0.65:1 and 0.65:0.57:1, respectively. This indicates that in the Co-ferrite nanochains, the substitution is predominantly into the Fe$^{2+} O_h$ sites, with a small amount of Co residing on the Fe$^{3+} T_d$ site, which is similar to bulk Co-ferrites and most of the reported Co-ferrite nanoparticles (see also Supporting Information Figure S2 for XMCD spectra of Co and their fitting).\textsuperscript{[42,43]} In the Zn-ferrite nanochains (see Supporting Information Figure S3 for XA spectra of non-magnetic Zn), replacement of non-magnetic Zn substitutions in the Fe$^{3+} T_d$ sites is observed, accompanied by a comparable decrease in the Fe$^{2+} O_h$ site occupancy. The latter decrease could be attributed to that when Fe$^{3+} T_d$ is replaced by Zn$^{2+} T_d$, part of Fe$^{2+} O_h$ can be oxidized to Fe$^{3+} O_h$ in order to maintain an overall charge balance;\textsuperscript{[44]} and a simultaneous occupation of Zn in Fe$^{2+} O_h$ site cannot be excluded though.

The above analysis explains why the magnetic anisotropy of the ferrite chains changes upon different doping: Occupying the $O_h$ sites, the magnetic Co$^{2+}$ ions are responsible for the high magnetocrystalline anisotropy of the ferrites. Specifically, the crystal field interaction is not able to remove the orbital degeneracy of the Co$^{2+}$ ion at the $O_h$ site, so that the orbital magnetic moment is not quenched, which produces the magnetocrystalline anisotropy\textsuperscript{[45]} and thus enhances the magnetic anisotropy of the chains. For the Zn-ferrite nanochains, non-magnetic Zn$^{2+}$ ions cause comparable reductions in both the Fe$^{2+} O_h$ and Fe$^{2+} T_d$ intensities. On the one hand, the Zn$^{2+}$ electronic charge distribution, which occupy the $T_d$ site, is close to
spherical symmetric, so that these ions do not give a substantial contribution to the magnetic anisotropy. On the other hand, here only the Fe$^{2+}$ ions contribute to a positive anisotropy constant and thus play a leading role in the magnetic anisotropy.$^{[46]}$ Therefore, dilution of the Fe$^{2+}$ cations on the $O_h$ sites by non-magnetic Zn may reduce the total magnetic anisotropy.$^{[34]}$

3. Conclusions
Using the method of magnetic-field-assisted self-assembly, we have produced quasi-1D nanochains of spherical magnetite particles. Element-specific XMCD is performed to investigate the cation distribution of the chains, which is demonstrated to be strongly dependent on $H_{\text{assist}}$. This $H_{\text{assist}}$ dependence, which is highly consistent with that of the saturation magnetization, suggests that in the nanoscale ferrites the external synthetic conditions play a nontrivial role that is more complicated than in the case of bulk ferrites. Our study enables us to optimize the growth conditions for these magnetic-field-assisted self-assembled nanochains. We conclude that magnetite nanochains fabricated with $H_{\text{assist}} = 2500$ Oe serve as a good candidate for practical applications in magnetic 1D nano devices, mainly because of their high saturation magnetization of nearly 90 emu/g (approaching the bulk value) and relatively large magnetic anisotropy induced from the chain-like shape. Precise pinning of DWs, at the boundaries between black and white domains, in a single chain is monitored for the first time by XMCD-PEEM. Foreign dopants are introduced into the nanochains and the dopant-dependent cation distribution is also investigated by XMCD, demonstrating that the magnetic anisotropy in the ferrite chains can be modified in a controlled way by the type of dopant, which offers a practical guideline for accurate control and optimization of nanoscale magnetism in different kinds of ferrite chains for future applications serving diverse demands.$^{[47]}$
4. Experimental Section

**Materials**: Preparation of the chains is achieved by using a modified method of aging ferrous hydroxide gel with KNO$_3$[^48] under an applied magnetic field $H_{\text{assist}}$. Specifically, KOH (0.005 mol) and KNO$_3$ (0.2 mol) are first dissolved in a conical flask containing 60 mL mixed solution, which consists of double distilled deoxygenated water and ethylene alcohol of defined ratios. Then N$_2$ gas is passed through the solution for half an hour. After that, a 40 mL of additional solution is poured into the conical flask: For magnetite chains, this additional solution contains 0.00252 mol FeSO$_4$; For Co-ferrite (or Zn-ferrite) chains, CoSO$_4$ (or ZnSO$_4$) is also included, where the total amount of metal ions is kept constant as 0.00252 mol, while the molar ratio of [Co]:[Fe] or [Zn]:[Fe] is varied for different purposes. After thoroughly mixing and shaking the two solutions, the conical flask is immersed in a water bath at 90°C under an applied magnetic field $H_{\text{assist}}$ for reaction. During the reaction process, N$_2$ gas is kept passing through the solution to prevent oxidation of Fe$^{2+}$ in the system. After a few hours (4 hours for magnetite and Co-ferrite chains, and 2 hours for Zn-ferrite chains) the chains are finally formed with a yield of 1.6 g per 100 mL per day, which is comparable to, or greater than, yields obtained by other bacterial synthesis methods.

**Characterizations**: Synthesized chains are dispersed in distilled water by vigorous stirring and ultrasonic treatment, to form dilute suspensions with a concentration of 0.1 mg/mL. These suspensions are then drop-casted onto silicon substrates (4 × 4 mm$^2$) under an external magnetic field of 3000 Oe to align the chains along the field direction. After drying in N$_2$ environment at room temperature, thin layers of aligned chains are formed with a thickness of about 30 µm, which are ready for subsequent experimental characterization. For structural and morphological characterization, X-ray diffraction (XRD) is carried out over a 20 range of 10°-70° using a Rigaku Smartlab diffractometer with Cu $K\alpha$ radiation, and scanning electron microscopy (SEM) images are acquired using a FEI Siren system. TEM was performed on
FEI/Philips CM-20 TEM operated at 200kV with LaB₆ filament. Magnetic measurements are performed using a vibrating sample magnetometer (VSM, Lakeshore, Model 7300) equipped with a 1 T magnet. All measurements, including the XMCD and XMCD-PEEM, are carried out at room temperature.

**XMCD Measurements:** X-ray absorption (XA) spectra at the Fe, Co, and Zn L₂,₃ edges are acquired at room temperature on beamline I1011 at MAX-Lab in Lund, Sweden. After normalization to the incident beam intensity, the XMCD is obtained as the difference between the two XA spectra measured with opposite circular polarization. To obtain the cation distribution over the three Fe sites, the experimental XMCD is fitted by assuming an atomic multielectron model, in which the transitions $3d^n \rightarrow 2p^53d^{n+1}$ are calculated using multiplet theory, and the spin-orbit and electrostatic interactions are treated on an equal footing. The intra-atomic electrostatic interactions include the $2p$-$3d$ and $3d$-$3d$ Coulomb and exchange interactions. The wave functions of the initial- and final-state configurations are calculated in intermediate coupling using Cowan’s atomic Hartree-Fock code with relativistic corrections. For the Fe $O_h$ and $T_d$ sites the crystal-field parameters are taken as $10Dq = 1.2$ eV and $-0.6$ eV, respectively. The line spectra are convoluted by a Lorentzian of $\Gamma = 0.3$ (0.5) eV for the $L_3$ ($L_2$) edge to account for intrinsic core-hole lifetime broadening and a Gaussian of $\sigma = 0.2$ eV to account for instrumental broadening.

**XMCD-PEEM Imaging:** Images of the magnetic domain structure are captured using XMCD in photoemission electron microscopy (XMCD-PEEM) in zero field and at room temperature, utilizing the PEEM III end-station on beamline 11.0.1.1 at the Advanced Light Source, Berkeley. The ratio of the XA signals at the Fe $L_3$ and $L_2$ edges measured with left or right circularly polarized X-rays is used to obtain the XMCD-PEEM images. The magnetic contrast in the PEEM images is proportional to the projection of the magnetization direction along the X-ray helicity vector, so that domains aligned parallel and antiparallel to the helicity
vector show up in white and black, respectively.\textsuperscript{[9,40]} XA spectra are taken from a region that shows up as black or white, which can be generated from any part of the PEEM image ranging from 10×10 nm\(^2\) to 10×10 \(\mu\)m\(^2\) in size. Averaged “black” and “white” XA spectra are then divided by the background absorption signal, \(I_0\), which is taken from a region without nanoparticles. By reversing the X-ray helicity vector, the XMCD for each selected region is obtained as the differences between XA spectra with opposite helicities.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1. a) Scanning electron microscopy (SEM) image of magnetite nanochains prepared under a magnetic field $H_{\text{assist}} = 3500$ Oe and aligned on a silicon substrate by an external magnetic field. b) Bright-field transmission electron microscopy (TEM) micrograph of one magnetite nanochain. c) Convergent beam electron diffraction (CBED) pattern of one particle shown darker in b). d-f) Hysteresis loops of magnetite nanochains fabricated with different values of $H_{\text{assist}}$, i.e., 0, 2500, and 3500 Oe, respectively. During the measurement by vibrating sample magnetometer (VSM), the external magnetic field was applied parallel (solid lines) and perpendicular (dashed lines) to the chain direction. g,h) $H_{\text{assist}}$ dependences of the coercivity ($H_C$), squareness ($M_R/M_S$), anisotropy of the demagnetizing field ($H_{S_\perp} - H_{S//}$), and saturation magnetization ($M_S$), respectively, along the direction of the chains.
Figure 2. a) Representative part of the spinel structure for magnetite showing the different tetrahedral ($T_d$) and octahedral ($O_h$) cation sites. The arrows represent the different spin directions of the Fe$^{2+}$ $O_h$ (green), Fe$^{3+}$ $T_d$ (blue), and Fe$^{3+}$ $O_h$ (orange) cations, resulting in a ferrimagnetic ordering. b) Schematic diagram of the experimental geometry for X-ray magnetic circular dichroism (XMCD) measurements. c) Typical Fe $L_{2,3}$ XMCD spectrum of the magnetite nanochains prepared with $H_{\text{assim}} = 2500$ Oe, obtained by taking the difference of the X-ray absorption (XA) spectra recorded with opposite photon helicity vectors, $\sigma^- - \sigma^+$. 
Figure 3. a) Top: Experimental data (dots) with best-fit (solid line) of the Fe $L_{2,3}$ XMCD spectra for the magnetite chains prepared with $H_{\text{assist}} = 2500$ Oe. The best-fit spectra give the values for the relative site occupancies. Bottom: The decomposition of the best-fit spectrum into the spectra of the $\text{Fe}^{3+} T_d$, $\text{Fe}^{3+} O_h$, and $\text{Fe}^{2+} O_h$ components. The color-coded numbers indicate the proportions of the components, where the error bar for each site occupancy is ±0.02 cations. b) $H_{\text{assist}}$ dependences of the cation ratios $[\text{Fe}^{2+} O_h]:[\text{Fe}^{3+} O_h]$ and $[\text{Fe}^{3+} T_d]:[\text{Fe}^{3+} O_h]$ obtained from the calculated fits, compared with the trend of $M_S$. 
Figure 4. a) SEM image of a single magnetite nanochain, prepared with $H_{\text{assist}} = 2500$ Oe, showing an average particle size of about 200 nm. b) XMCD-PEEM image showing black and white contrasted magnetic domains along a chain, where the magnetic domain walls (DWs) are located at the boundaries between each domain. c) XA and XMCD spectra taken from selected black and white regions in PEEM images, respectively, indicating opposite directions of the magnetization between each other.
Figure 5. a,b) Hysteresis loops of the Co- and Zn-ferrite nanochains, respectively, prepared with $H_{\text{assist}} = 2500$ Oe. The loops are measured with the external field parallel (solid lines) and perpendicular (dashed lines) to the chains, respectively. c) Variation of the coercivity ($H_C$) and squareness ($M_R/M_S$), along the direction of the chains, upon Co and Zn doping.
**Figure 6.** a) Sum of Fe $L_{2,3}$ XA spectra for magnetite (grey), Co- and Zn-ferrite nanochains (black), respectively, prepared with $H_{\text{assist}} = 2500$ Oe. b,c) Top: Experimental data (dots) with best-fit (solid lines) of the Fe $L_{2,3}$ XMCD spectra for the Co- and Zn-ferrie nanochains, respectively. Bottom: Decomposition of the best-fit spectrum for each sample into the spectra for the Fe$^{3+} T_d$, Fe$^{3+} O_h$, and Fe$^{2+} O_h$ components.
Magnetic-field-assisted self-assembled one-dimensional nanochains of spherical ferrite particles are investigated by XMCD, revealing the important role of $H_{\text{assist}}$ in determining the magnetic properties of such nanoscale ferrites. $H_{\text{assist}} = 2500$ Oe offers a favorable fabrication condition to obtain suitable nanochains for applications in magnetic one-dimensional nanodevices, and the first observation on precise pinning of domain walls is achieved by XMCD-PEEM.

XMCD and XMCD-PEEM Studies on Magnetic-Field-Assisted Self-Assembled One-Dimensional Nanochains of Spherical Ferrite Particles