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## A facile and environmentally friendly route to multiferroic nanorods and their size-dependent magnetic properties†

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Multiferroic  $\text{ErMn}_2\text{O}_5$  nanorods have been synthesized via a surfactant-templated hydrothermal route. An environmentally friendly natural surfactant (Arabic gum) has been utilized as a template to prepare  $\text{ErMn}_2\text{O}_5$  nanorods with a controllable morphology and size (i.e., nanorods with various lengths and basically invariable diameter).  $\text{ErMn}_2\text{O}_5$  nanorods show strong size-dependent magnetic properties that correlate with: (a) a critical length for magnetization, and (b) recognizable divagation between FC and ZFC curves at low temperature. The former could be ascribed to the competition between surface strain and uncompensated spin at the surface, and the latter to Er antiferromagnetic ordering.

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### Introduction

The recent advances in utilizing multiferroic materials as the building blocks provide unique opportunities for the development of next generation transducers, ferromagnetic resonance devices, and magnetic memory storage elements, to name a few.<sup>1–3</sup> Among multiferroic materials, the unique orthorhombic  $\text{RMn}_2\text{O}_5$ , including  $\text{YMn}_2\text{O}_5$ ,<sup>4</sup>  $\text{TbMn}_2\text{O}_5$ ,<sup>5</sup>  $\text{DyMn}_2\text{O}_5$ ,<sup>6</sup>  $\text{GdMn}_2\text{O}_5$ ,<sup>7</sup> and  $\text{RMn}_2\text{O}_5$  ( $\text{R} = \text{Bi}, \text{Eu}$  and  $\text{Dy}$ ),<sup>8</sup> have garnered considerable attention as they undergo a paramagnetic to antiferromagnetic (AFM) transition at Néel temperature ( $T_N = 39\text{--}45\text{ K}$ ), whereas a ferroelectric transition occurs at or slightly below  $T_N$  for the Mn

spin sublattice.<sup>8</sup> Intriguingly, magnetic properties of multiferroic  $\text{YMn}_2\text{O}_5$ <sup>9</sup> and  $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ <sup>10</sup> particles display a weak ferromagnetism and profound size dependence. It is noteworthy that the synthesis of  $\text{RMn}_2\text{O}_5$  particles noted above requires a high temperature solid-state process, which leads to the aggregation of particles. In order to explore the correlation between the multiferroic properties and the size of materials, it is crucial to synthesize uniform multiferroic nanomaterials with narrow size distribution.

Hydrothermal synthesis stands out as an effective method among other various strategies to produce nanomaterials due to its advantageous simple and low-temperature processing characteristics. Several multiferroic materials have been prepared via the hydrothermal route, including  $\text{BiFeO}_3$  nanowires,<sup>11</sup>  $\text{YbMnO}_3$  and  $\text{LuMnO}_3$  platelets,<sup>12</sup>  $\text{BiMn}_2\text{O}_5$  crystals,<sup>13</sup>  $\text{BaMnO}_3$  nanoparticles,<sup>14</sup>  $\text{RMn}_2\text{O}_5$  ( $\text{R} = \text{La}, \text{Pr}, \text{Nd}, \text{Tb}, \text{Bi}$ ) and  $\text{LaMn}_2\text{O}_{5+d}$ .<sup>15</sup> Moreover,  $\text{TbMn}_2\text{O}_5$  nanorods,<sup>16</sup>  $\text{RMn}_2\text{O}_5$  ( $\text{R} = \text{Gd}$  and  $\text{Sm}$ ) nanorods and nanoplates,<sup>17</sup> and  $\text{YMn}_2\text{O}_5$ <sup>18</sup> nanorods have also been reported. However, the synthesis of one-dimensional (1D) multiferroic nanomaterials with uniform size remains a challenge. More importantly, the fundamental understanding of the structure–property relationship in  $\text{RMn}_2\text{O}_5$  is still critically lacking.

Among  $\text{RMn}_2\text{O}_5$ ,  $\text{ErMn}_2\text{O}_5$  multiferroics possess a non-centrosymmetric magnetic structure<sup>19</sup> and a large magnetic susceptibility.<sup>20</sup> To date, very few efforts have been made in synthesizing morphologically controlled 1D  $\text{ErMn}_2\text{O}_5$  nanostructures. Surprisingly, little is virtually known regarding the magnetic properties and ferroelectric properties of  $\text{ErMn}_2\text{O}_5$  due to its chemical and structural complexity.<sup>21,22</sup> In particular, it is of key importance to reveal the correlation between the controllable size and the magnetic properties of uniform  $\text{ErMn}_2\text{O}_5$  nanorods.

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† Electronic supplementary information (ESI) available: XRD profiles of products synthesized at various pH values at 250 °C for 64 h; FT-IR, Raman and UV-Vis spectra of as-prepared nanorods; TGA/DSC curves of  $\text{ErMn}_2\text{O}_5$  nanorods; representative XRD profiles of  $\text{ErMn}_2\text{O}_5$  nanorods prepared using  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  as the divalent manganese source with various amounts of Arabic gum at different pH values; typical TEM images of  $\text{ErMn}_2\text{O}_5$  nanorods synthesized at various amounts of Arabic gum; influence of the amount of Arabic gum on the length of nanorods; representative HRTEM images of  $\text{ErMn}_2\text{O}_5$  nanorods showing the core-shell nanostructures; TEM images of  $\text{ErMn}_2\text{O}_5$  nanorods produced at a high amount of Arabic gum; the surface to volume ratio of nanorods; Table S1: equivalent diameters of nanorods; and Table S2: magnetic properties at 10 K; temperature dependence of the magnetization for  $\text{ErMn}_2\text{O}_5$  nanorods with various sizes (large scale), showing zero field cooling (ZFC) and field cooling (FC) curves with an applied magnetic field at 500 Oe. Magnetic properties of  $\text{ErMn}_2\text{O}_5$  nanorods (with and without Arabic gum) at the length of 210 nm were measured at 10 K. See DOI: 10.1039/c4tc02828g

Herein, we report, for the first time, the synthesis of size-tunable uniform  $\text{ErMn}_2\text{O}_5$  nanorods *via* a surfactant-templated hydrothermal reaction and the exploration of their magnetic properties occurred uniquely at the nanoscale. A significant feature of our strategy to note is the facile and environmentally friendly hydrothermal synthesis of  $\text{ErMn}_2\text{O}_5$  multiferroics capitalizing on a naturally non-toxic surfactant (*i.e.* Arabic gum) as a template. Quite interestingly, the length of  $\text{ErMn}_2\text{O}_5$  nanorods can be readily tailored by the Arabic gum template. The  $\text{ErMn}_2\text{O}_5$  nanorods exhibited a strong correlation of magnetic property with the size of nanorods. It is surprising that the magnetization of  $\text{ErMn}_2\text{O}_5$  nanorods,  $M_s$ , increased with the length of nanorods up to a critical value ( $L = 175$  nm) and then decreased substantially by the superconducting quantum interference device (SQUID) measurements, due largely to the subtle competition between the surface strain of  $\text{ErMn}_2\text{O}_5$  nanorods and the incomplete magnetic compensation on the surfaces between sublattices.<sup>23</sup> Most importantly, recognizable divagation between zero field cooling (ZFC) and field cooling (FC) was observed due to the antiferromagnetic ordering of Er.

## Experimental section

Multiferroic  $\text{ErMn}_2\text{O}_5$  nanorods were synthesized *via* an Arabic gum-templated hydrothermal reaction. Precursors, including  $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{KMnO}_4$  and  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (AR, Aladdin, Shanghai, China), were of analytical grade and used as received. In a typical reaction, first, 2 mmol  $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  was dissolved in 60 ml of distilled water containing Arabic gum, and then 2.8 mmol of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  and 1.2 mmol of  $\text{KMnO}_4$  were simultaneously added into  $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  solution under constant magnetic stirring. The molar ratio of Er:Mn was controlled to be 1:2, based on the chemical composition. The molar ratio of  $\text{Mn}^{2+}:\text{Mn}^{7+}$  was designed to be 7:3 in order to achieve the desired average manganese oxidation state in the resultant products. The amount of Arabic gum was calculated according to the output of the final product. Second, after the solution was stirred using a magnetic bar for 30 min at room temperature, the NaOH solution ( $1 \text{ mol L}^{-1}$ ) was introduced dropwise into the above mixture to regulate the pH value ( $\text{pH} = 3-7$ ). Finally, the mixture was transferred to a Teflon-lined stainless steel autoclave with an inner volume of 80 ml. The autoclave was sealed and placed in a digital-type temperature-controlled oven at  $250^\circ\text{C}$  for 64 h. After the reaction was completed, the solution was cooled down to room temperature. The obtained products were filtered and washed with distilled water several times, and dried at  $60^\circ\text{C}$  overnight. For comparison, manganese acetate was also used to synthesize  $\text{ErMn}_2\text{O}_5$  nanocrystals (*i.e.*, 25 nm sized  $\text{ErMn}_2\text{O}_5$ ).

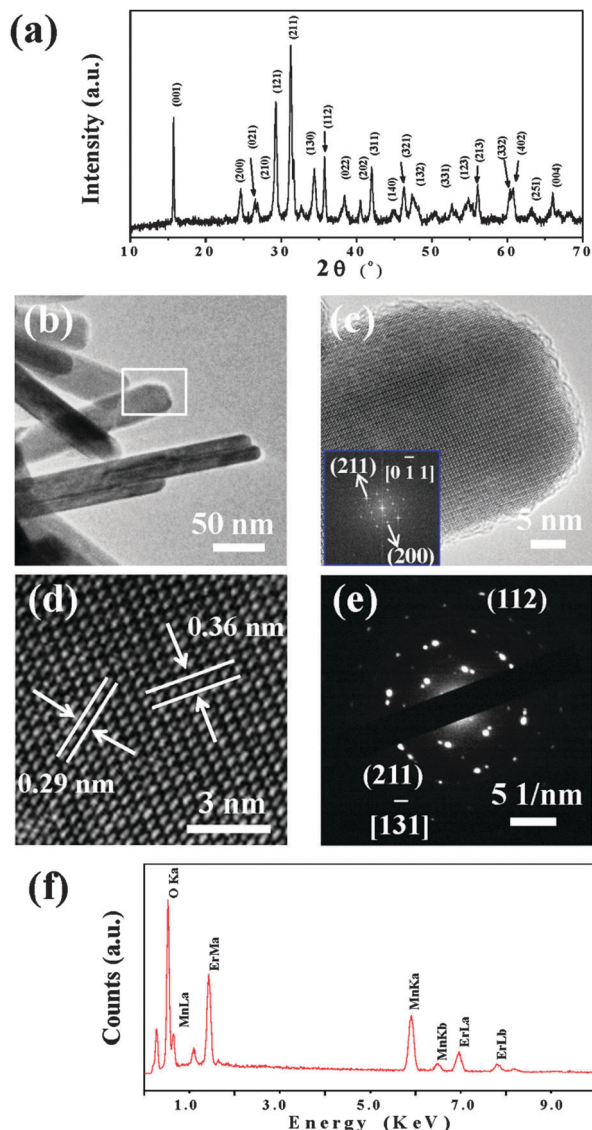
The crystalline phases of the samples were analyzed by X-ray diffraction (XRD) (D8 Advance, Bruker, Karlsruhe, Germany) with Cu K $\alpha$  radiation of  $2\theta$  from  $10$  to  $80^\circ$ . The transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and selective area electron diffraction (SAED) images were carried out to examine the size and morphology of nanorods using a JEM-2100HR electron microscope

(JEOL, Tokyo, Japan) with an accelerating voltage of 200 kV. An energy dispersive spectrometer (EDS) (EPMA1600, Shimadzu, Kyoto, Japan) was utilized to detect the elemental composition in the selected area of nanorods. Microstructural observation of nanorods was performed by scanning electron microscopy (SEM) (Zeiss, LEO 1530 VP, Germany). The composition and chemical states of surface elements of samples were investigated by XPS (Kratos Axis Ultra DLD, Japan), using Al K-alpha as the X-ray source. The spectra were calibrated with respect to the C 1s peak resulting from the adventitious hydrocarbon at the energy of 284.8 eV. FT-IR, Raman and UV-Vis spectra of  $\text{ErMn}_2\text{O}_5$  nanorods were recorded using a Fourier transform infrared spectrometer (Vector 33, Bruker, Germany), a Micro-Raman spectrometer (LabRAM Aramis, HJY, France) and a UV-Vis spectrophotometer (Unicam UV500, Thermo Electron Corporation, USA), respectively. The magnetic behavior was measured using a superconducting quantum interference device (SQUID; Quantum Design Inc. USA).

## Results and discussion

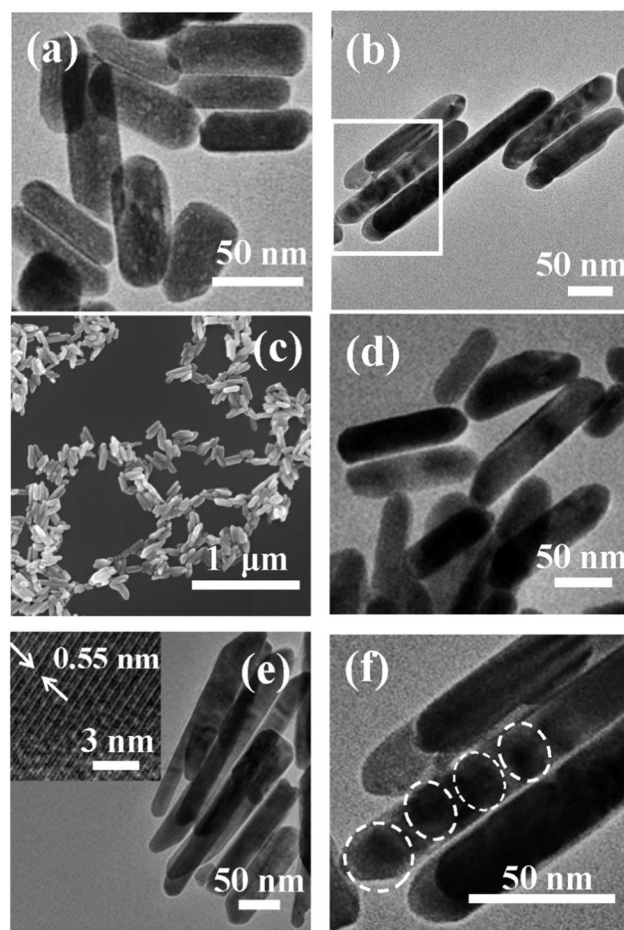
Fig. 1a shows a typical XRD profile of  $\text{ErMn}_2\text{O}_5$  nanorods hydrothermally synthesized at  $\text{pH} = 3$  at  $250^\circ\text{C}$  for 64 h (see Experimental; without the addition of Arabic gum as the template). All the peaks can be readily indexed to pure orthorhombic  $\text{ErMn}_2\text{O}_5$  (JCPDS No. 50-0296) (Fig. S1a, ESI $^\dagger$ ). We note that in this work orthorhombic  $\text{ErMn}_2\text{O}_5$  can be synthesized at  $\text{pH} = 3-7$ . The formation of  $\text{MnO}_2$  was inevitable at  $\text{pH} < 2$ . Conversely, the peaks which can be assigned to  $\text{ErMnO}_3$  (JCPDS No. 14-0689) were yielded at  $\text{pH} = 8$  (Fig. S1b, ESI $^\dagger$ ). In addition to XRD, the FT-IR (Fig. S2, ESI $^\dagger$ ), Raman (Fig. S3, ESI $^\dagger$ ), UV-Vis (Fig. S4, ESI $^\dagger$ ), and TGA and DSC (Fig. S5, ESI $^\dagger$ ) measurements were performed to further verify the success in producing  $\text{ErMn}_2\text{O}_5$  nanorods and gain insight into their structural features, which agreed well with the reported results on  $\text{ErMn}_2\text{O}_5$ .<sup>8,24-26</sup>

The TEM measurements revealed that  $\text{ErMn}_2\text{O}_5$  nanorods synthesized at  $\text{pH} = 3$  without using the Arabic gum template were approximately 600 nm long with an average diameter of 60 nm (Fig. 1b). A close-up marked with a white rectangle in Fig. 1b showed that the spacing between adjacent lattice fringes was 0.29 nm and 0.36 nm (Fig. 1c and d), corresponding to the (211) and (200) lattice planes of orthorhombic  $\text{ErMn}_2\text{O}_5$ , respectively. The selective area electron diffraction (SAED) pattern displayed the sharp diffraction spots (Fig. 1e), indicating the formation of single crystalline  $\text{ErMn}_2\text{O}_5$ . The Fast Fourier Transformation (FFT) pattern (inset in Fig. 1c) taken from a single nanorod can be indexed to an orthorhombic  $\text{ErMn}_2\text{O}_5$  single crystal recorded along the  $[0\bar{1}1]$  zone axis. Clearly, SAED and FFT unequivocally proved that each  $\text{ErMn}_2\text{O}_5$  nanocrystal was composed of a single crystalline domain. To confirm the chemical composition of  $\text{ErMn}_2\text{O}_5$  nanorods, energy dispersive X-ray spectroscopy (EDS) spectra (Fig. 1f) were obtained from several selected positions of the sample, clearly showing the existence of Er, Mn, and O.



**Fig. 1**  $\text{ErMn}_2\text{O}_5$  nanorods hydrothermally synthesized at pH = 3 at 250 °C for 64 h without the addition of Arabic gum. (a) XRD profile of  $\text{ErMn}_2\text{O}_5$  nanorods; and (b) TEM images of  $\text{ErMn}_2\text{O}_5$  nanorods. The close-up marked with a white rectangle in (b) is shown in (c); (c) and (d) represent HRTEM images of  $\text{ErMn}_2\text{O}_5$  nanorods. The inset in (c) shows the corresponding FFT pattern; (e) the corresponding SAED pattern; and (f) the EDS spectrum of the as-prepared nanorods.

Interestingly, the morphology of  $\text{ErMn}_2\text{O}_5$  nanorods can be controlled by altering the reaction conditions (*i.e.*, the addition of Arabic gum as the template and the types of precursors). In particular, the amount of Arabic gum had a crucial influence on the dimensions of  $\text{ErMn}_2\text{O}_5$  nanorods. Arabic gum, a naturally non-toxic surfactant, was employed as a template for hydrothermal synthesis of  $\text{ErMn}_2\text{O}_5$  nanorods. Arabic gum is an environmentally friendly natural polysaccharide, and has been utilized to prepare monodisperse micro-sized silver and copper particles in our previous work.<sup>27,28</sup> Arabic gum exhibits a delicate balance between hydrophobicity (ascribed to protein and rhamnose in Arabic gum) and hydrophilicity (due to the



**Fig. 2** Representative TEM images of  $\text{ErMn}_2\text{O}_5$  nanorods obtained using  $\text{MnCl}_4 \cdot 4\text{H}_2\text{O}$  as the divalent manganese source at pH = 3 with various amounts of Arabic gum as the template. (a) 6 wt%, (b) 7.5 wt%, (d) 8 wt%, and (e) 10 wt%, respectively. An HRTEM image is shown as an inset in (e). (f) The close-up of a white box in (b) shows the oriented attachment of  $\text{ErMn}_2\text{O}_5$  nanocrystals (marked with dashed circles). (c) A low magnification SEM image of the sample with 7.5 wt% Arabic gum.

presence of hydroxy (–OH) and carboxy (–COOH) groups in Arabic gum), and is an excellent O/W emulsifier,<sup>29</sup> as in many other hydrocolloids. Fig. 2 compares the different  $\text{ErMn}_2\text{O}_5$  nanostructures obtained using various amounts of Arabic gum as the template at 250 °C for 64 h (see Experimental). Some corresponding XRD profiles of  $\text{ErMn}_2\text{O}_5$  nanorods are shown in Fig. S6 (ESI†). Quite intriguingly, rather than the diameter, the length of nanorods depended sensitively on the amount of Arabic gum added in the hydrothermal reaction (Fig. 2). For example, the nanorods with a nearly uniform diameter,  $D = 28 \pm 3$  nm and an average length,  $L = 54 \pm 5$  nm were yielded at 2 wt% Arabic gum (*i.e.*, the weight percentage of Arabic gum to the resultant  $\text{ErMn}_2\text{O}_5$ ) (Fig. S7 and S8, ESI†), indicating that a small amount of Arabic gum could exert a surprising influence on the morphology of nanorods as compared with  $\text{ErMn}_2\text{O}_5$  nanorods produced without adding Arabic gum (*i.e.*, template-free; Fig. 1b).

The length of nanorods increased as the amount of Arabic gum was increased (Fig. 2a–e), and reached approximately



210 ± 30 nm at 10 wt% Arabic gum (Fig. 2e), while the diameter of nanorods remains roughly constant,  $D = 28 \pm 3$  nm. A further addition of Arabic gum led to the rupture of nanorods, as will be discussed in more detail later. The lattice spacing of 0.55 nm was determined by HRTEM (inset in Fig. 2e), corresponding to the (001) crystalline plane of orthorhombic  $\text{ErMn}_2\text{O}_5$ . The low magnification SEM image of the sample with 7.5 wt% Arabic gum is shown in Fig. 2c, where a large amount of  $\text{ErMn}_2\text{O}_5$  nanorods was seen. The length of nanorods as a function of the amount of Arabic gum is summarized in Fig. S8 (ESI†).

The composition and chemical states of  $\text{ErMn}_2\text{O}_5$  nanorods synthesized at 250 °C at pH = 3 with 5 wt% Arabic gum were measured by X-ray photoelectron spectroscopy (XPS). The survey spectrum of  $\text{ErMn}_2\text{O}_5$  nanorods shown in Fig. 3a indicated that the main peaks at 168 eV, 285 eV, 530 eV, and 642 eV can be assigned to the binding energies of Er 4d (Fig. 3b), C 1s, O 1s (inset in Fig. 3b), and Mn 2p, respectively. The C 1s peak can be ascribed to the adsorption of Arabic gum on the  $\text{ErMn}_2\text{O}_5$  surface. The XPS measurements suggested that the element ratio of Er:Mn is 1:2, and no other elements can be detected. Fig. 3c depicts the Mn 2p XPS spectrum of  $\text{ErMn}_2\text{O}_5$  nanorods. The spectrum was split by the spin-orbit interactions into the Mn 2p<sub>3/2</sub> and Mn 2p<sub>1/2</sub> peaks. The Mn 2p spectrum of  $\text{ErMn}_2\text{O}_5$  nanorods showed two main peaks at 642 eV and 654 eV, which are in good agreement with the previous results of  $\text{TbMn}_2\text{O}_5$ <sup>16</sup> and  $\text{BiMn}_2\text{O}_5$ <sup>13</sup> containing the mixed Mn<sup>3+</sup>/Mn<sup>4+</sup> valencies. Mn<sup>3+</sup> ion 2p<sub>3/2</sub> binding energy in a hexagonal manganite  $\text{YMnO}_3$ <sup>30</sup> is 641.6 eV and the binding energy of the Mn<sup>4+</sup> ion 2p<sub>3/2</sub> in a cobalt-doped  $\text{LiMnO}_2$ <sup>31</sup> is 643.2 eV. Therefore, the Mn 2p<sub>3/2</sub> spectrum clearly showed an overlap of Mn<sup>3+</sup> 2p<sub>3/2</sub> and Mn<sup>4+</sup> 2p<sub>3/2</sub> peaks, signifying a mixed Mn<sup>3+</sup>/Mn<sup>4+</sup> state in  $\text{ErMn}_2\text{O}_5$ .

The formation of nanorods *via* the surfactant-templated hydrothermal route may be rationalized as follows. At the high concentration of Arabic gum, worm-like micelles composed of Arabic gums are formed. These cylindrical micelles (the top central panel in Scheme 1), by which the  $\text{ErMn}_2\text{O}_5$  nanorods are templated, evolve into long worm-like micelles with a constant diameter under hydrothermal conditions (the top right panel in Scheme 1) as the concentration of Arabic gum increases.<sup>32,33</sup> Upon the addition of precursors,  $\text{ErMn}_2\text{O}_5$  nanorods are gradually grown (the bottom right panel in Scheme 1).  $\text{ErMn}_2\text{O}_5$  nanorods are then yielded *via* Ostwald ripening (the bottom left panel in Scheme 1).<sup>34</sup> Of particular interest is that a thin layer of Arabic gum with a 3–5 nm thickness was seen on the surface of the as-prepared  $\text{ErMn}_2\text{O}_5$  nanorods (Fig. S9, ESI†), corroborating the existence of the surfactant template. However, a further increase in the amount of Arabic gum (> 10 wt%) leads to the rupture of worm-like micelles, creating the fractured nanorods (Fig. S10, ESI†).<sup>35,36</sup>

The size-dependent magnetic properties of  $\text{ErMn}_2\text{O}_5$  nanorods were explored by the superconducting quantum interference device (SQUID) measurements. As noted above,  $\text{RMn}_2\text{O}_5$  exhibits a helical antiferromagnetic (AFM) ordering below the Néel temperature of  $T_N = 39$ –45 K and a ferroelectric (FE) ordering at  $T_N$  or somewhat lower temperature than  $T_N$ .<sup>25</sup> For  $\text{ErMn}_2\text{O}_5$ , it has zig-zag chains running along the *a*-axis,

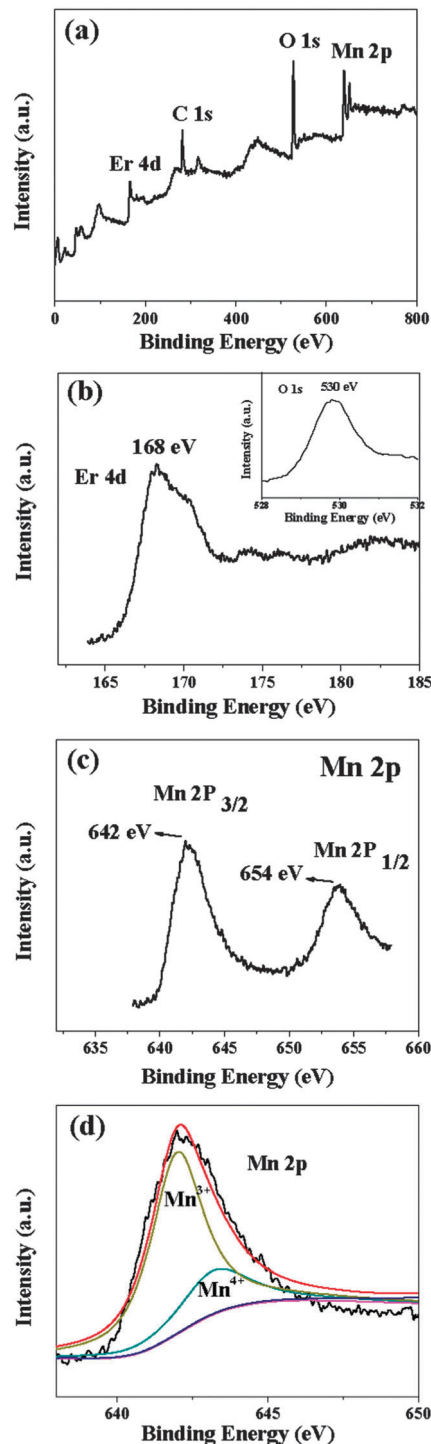
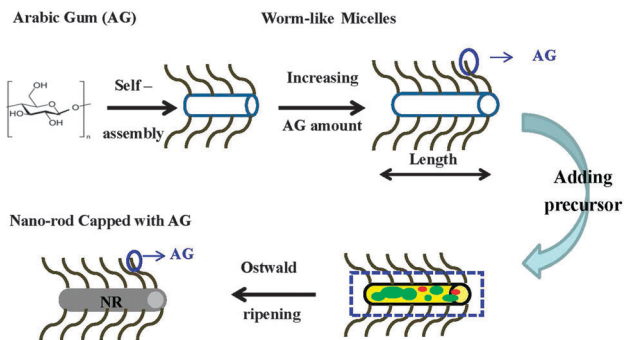


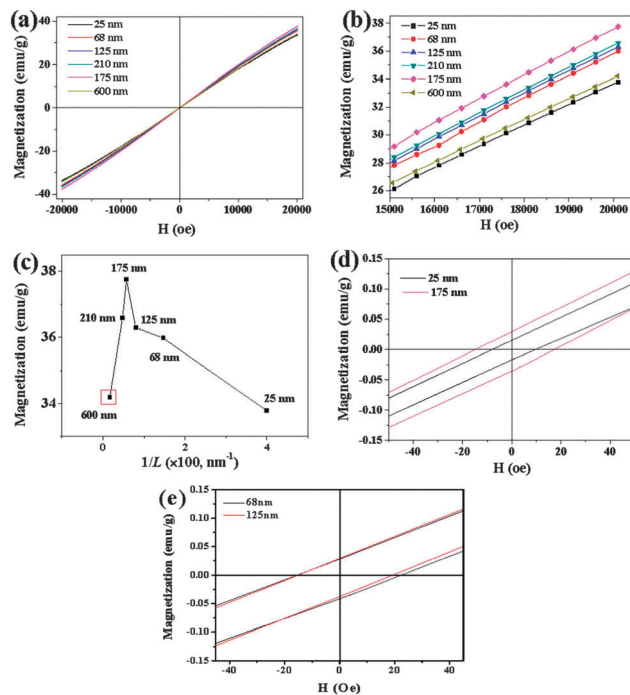
Fig. 3 (a) The XPS spectrum of  $\text{ErMn}_2\text{O}_5$ . (b) The XPS spectrum of Er 4d (inset: O 1s). (c) The XPS spectrum of Mn 2p. (d) Fine XPS spectra of Mn 2p<sub>3/2</sub>.

and thus a perfectly commensurate AFM structure.<sup>22</sup> An anti-ferromagnet comprises two spin sublattices (*i.e.*, ferromagnetic (FM) interactions within one sublattice, and AFM interactions between sublattices).<sup>23</sup> It is well known that the FM surface spins are vertical to the AFM axis of the core.<sup>23,37</sup> The spins in AFM nanoparticles were considered to form a multi-sublattice configuration, suggesting that the reduced coordination of surface



**Scheme 1** Schematic illustration of the formation of nanorods by capitalizing on worm-like micelles composed of Arabic gum as the template.

spins resulted in an important change in the magnetic ordering of the whole particle.<sup>38</sup>  $\text{BiFeO}_3$ <sup>39</sup> and  $\text{TbMn}_2\text{O}_5$ <sup>16</sup> synthesized by a hydrothermal approach showed a weak ferromagnetism, which was attributed to incomplete spin compensation between the two sublattices on the surface of particles. To reveal the size dependent hysteresis intrinsic to  $\text{ErMn}_2\text{O}_5$  nanorods, the magnetization behaviors of  $\text{ErMn}_2\text{O}_5$  nanorods with different lengths were measured at 10 K (Fig. 4a and b). The measurements showed that the magnetic response of  $\text{ErMn}_2\text{O}_5$  nanorods increased to a maximum magnetization of  $37.74 \text{ emu g}^{-1}$  at the length of the nanorod,  $L = 175 \text{ nm}$  as the  $L$  decreased (with a nearly constant diameter,  $D = 28 \pm 3 \text{ nm}$ ; Fig. 4a). With a further decrease of  $L$ , the magnetization reduced (Fig. 4b). The core (antiferromagnetic; AFM) and surface (with uncompensated spin) structure is crucial to account for the weak ferromagnetism of AFM materials.<sup>16,23,38,39</sup> Fig. 4c depicts the magnetic properties of synthesized  $\text{ErMn}_2\text{O}_5$  nanorods as a function of the length of nanorods. For single-domain AFM nanorods, the magnetization is expected to scale as  $\sim (1/L + 2/D)$  (i.e., the surface to volume ratio; eqn (S4) and (S5), and Table S1, ESI†), where  $L$  is the length and  $D$  is the diameter of nanorods ( $D = 28 \pm 3 \text{ nm}$ ), respectively.<sup>23,40</sup> It is obvious that the magnetic properties of  $\text{ErMn}_2\text{O}_5$  nanorods at  $L \geq 175 \text{ nm}$  correlated heavily with their length due to the finite size effect. The magnetization can be reasonably explained with the presence of the AFM core and the FM surface (uncompensated spin on the surface).<sup>23</sup> The long-range AFM ordering is often interrupted on the surface of very small particles, leading to the measurable incomplete spin compensation in AFM ordered materials.<sup>23,39</sup> Compared to the zero-dimensional  $\text{BiFeO}_3$  nanoparticles,<sup>23</sup> the 1D  $\text{ErMn}_2\text{O}_5$  nanorods exhibited a similar characteristic at the length above 175 nm. As the length of  $\text{ErMn}_2\text{O}_5$  nanorods was continuously reduced, the magnetization instead decreased (Fig. 4c). Clearly, the superposition of an AFM core and a FM surface can no longer be applicable here for smaller nanorods. This seemingly quite complicated size dependent magnetization may be interpreted by “surface strain”.<sup>41</sup> For small nanoparticles, the surface strain can cause the coordination distortion and lattice disorder that diffuses into the entire particle,<sup>23</sup> further producing the frustrated spin structures, thereby resulting in a decreased magnetization as the length of  $\text{ErMn}_2\text{O}_5$  nanorods decreased.



**Fig. 4** (a) Magnetic properties of  $\text{ErMn}_2\text{O}_5$  nanorods at different lengths,  $L$  (at a nearly constant diameter,  $D = 28 \pm 3 \text{ nm}$ ) measured at 10 K, showing the hysteresis loops. The nanorods were prepared by capitalizing on Arabic gum as the template. For comparison, the hysteresis loop of nanorods with a  $L$  of 600 nm and a  $D$  of 60 nm (i.e., the sample prepared without the use of Arabic gum as the template) was also measured. We note that nanorods with a  $L$  of  $125 \pm 20 \text{ nm}$  and a  $D$  of  $28 \pm 3 \text{ nm}$  were produced with 4 wt% Arabic gum at pH = 7. Moreover, 25 nm of  $\text{ErMn}_2\text{O}_5$  nanocrystals were produced using manganese acetate as the divalent manganese source with 0.5 wt% Arabic gum at pH = 3. The other nanorods shown in the plot were obtained with various contents of Arabic gum at pH = 3 using  $\text{MnCl}_4 \cdot 4\text{H}_2\text{O}$  as the divalent manganese source (Fig. 2 and Fig. S8, ESI†). (b) The close-up of (a) from  $H = 15000$  to  $20000 \text{ Oe}$ . (c) The magnetization of the as-prepared  $\text{ErMn}_2\text{O}_5$  nanorods at  $20000 \text{ Oe}$  as a function of  $1/L$ . The magnetizations of  $\text{ErMn}_2\text{O}_5$  nanorods with: (d) a  $L$  of 175 nm (magenta curve) and 25 nm (black curve), respectively, and (e) a  $L$  of 125 nm (red curve) and 68 nm (black curve), from  $H = -50$  to  $50 \text{ Oe}$ .

The presence of shifted hysteresis loops (Fig. 4d and e) supported the core-shell model of magnetization on  $\text{ErMn}_2\text{O}_5$  nanorods, where the exchange bias of magnetic hysteresis was a result of exchange coupling between the uncompensated spin on the surface and the AFM core. The exchange coupling present at the interface between the FM surface and the AFM core can induce a unidirectional anisotropy of the FM layer.<sup>42</sup> Table S2 (ESI†) summarizes the Curie-Weiss temperature,  $\theta_{\text{CW}}$ , the effective magnetic moments,  $\mu_{\text{eff}}$  (calculated from the inverse magnetic susceptibilities,  $1/\chi$  plot, as a typical sample shown in Fig. S11a, ESI†), the derived coercivities,  $H_{\text{c}}$ , and the remnant magnetization,  $M_{\text{r}}$ . These parameters reflected explicitly that the exchange coupling, dipolar interparticle interactions, and interfacial interactions were all attributed to the finite size effect (varied length of the nanorod with a nearly constant diameter).<sup>5</sup> It is interesting to note that the maximum effective paramagnetic moment of  $10.81 \mu_{\text{B}}$  occurred for the 175 nm long nanorods. More interestingly, the small  $M_{\text{r}}$  and

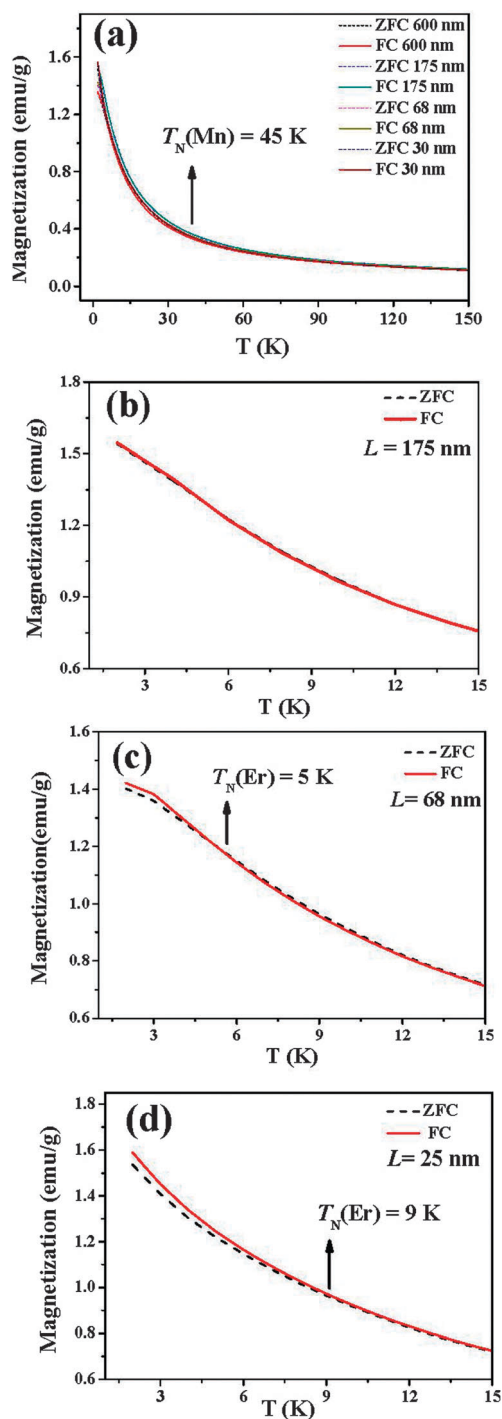


Fig. 5 (a) Temperature dependent magnetization of  $\text{ErMn}_2\text{O}_5$  nanorods at different lengths, showing zero field cooling (ZFC) and field cooling (FC) curves at magnetic field,  $H = 500$  Oe. (b)–(d) Expanded plots of ZFC and FC curves of  $\text{ErMn}_2\text{O}_5$  nanorods with an  $L$  of 175 nm, 68 nm, and 25 nm, respectively.

the absence of saturation suggested the strong interparticle interactions.<sup>23,43</sup>

Fig. 5 shows the temperature dependence of magnetization of  $\text{ErMn}_2\text{O}_5$  nanorods at a magnetic field strength of 500 Oe after the zero-field cooling (ZFC) and with the field cooling (FC). It has been demonstrated that below 50 K, the magnetic

susceptibility,  $\chi(T)$  of  $\text{TbMn}_2\text{O}_5$  nanorods increased dramatically owing to a weak ferromagnetism below the Neel temperature ( $T_N$  (Mn)).<sup>16</sup> The long-range incommensurate sinusoidal AFM ordering of the  $\text{Mn}^{3+}/\text{Mn}^{4+}$  spins ( $T_N$  (Mn)  $\approx 45$  K) was observed (Fig. 5a and Fig. S11b, ESI†) due to the commensurate AFM ordering that is almost co-linear.<sup>2,5</sup> No difference was observed between the ZFC and FC magnetization curves of templated  $\text{ErMn}_2\text{O}_5$  nanorods at  $L = 175$  nm (Fig. 5b), similar to the findings in  $\text{TbMn}_2\text{O}_5$  nanorods<sup>5,16</sup> and  $\text{ErMnO}_3$ .<sup>44</sup> Therefore, it is surprising that there existed a recognizable divagation between the FC and ZFC magnetization curves in  $\text{ErMn}_2\text{O}_5$  nanorods at the length below 175 nm (a nearly constant  $D = 28 \pm 3$  nm) at low temperatures ( $\sim 5$ –9 K). In particular, the temperature at the divagation point (*i.e.*  $T_N$  (Er)) increased to  $\sim 9$  K (Fig. 5d) from 5 K (Fig. 5c and Fig. S11c, ESI†) as the length of nanorods decreased to 25 nm. The divagation of ZFC and FC magnetizations at low temperatures is a typical characteristic of spin-glass behavior.<sup>5,39,45</sup> It is well known that various exchange interactions among the  $\text{R}^{3+}$ ,  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  spins and the lattice polarization induce a number of phase transitions in  $\text{RMn}_2\text{O}_5$ .<sup>5,21</sup> The moments of the  $\text{Mn}^{4+}$  ions are predominantly ferromagnetically coupled above  $T_N$  (RE), and the ordering of the rare-earth (RE) moments enhances this coupling.<sup>21</sup> Moreover, it has been reported that the high value of polarization of  $\text{DyMnO}_3$  above the ordering temperature of Dy ( $T_N$  (Dy) = 6.5 K) arises because of the increased amplitude of the Mn spin spiral.<sup>5</sup> Thus, in this work the possible reason for the divagation is the contribution of the magnetic ordering of Er. Notably, the significant magnetization decrease for shorter nanorods ( $L < 175$  nm length) at 10 K may suggest a slow onset of AFM ordering of Er at or slightly above  $T_N$  (Er) ( $\sim 5$ –9 K).

## Conclusions

In summary, we developed a viable template-assisted hydrothermal synthesis of 1D multiferroic  $\text{ErMn}_2\text{O}_5$  nanorods. The environmentally friendly natural polysaccharide, Arabic gum, was exploited as the template to readily regulate the length of  $\text{ErMn}_2\text{O}_5$  nanorods. The resultant  $\text{ErMn}_2\text{O}_5$  nanorods exhibited strong size dependent magnetic properties. The magnetization was first increased as the length of  $\text{ErMn}_2\text{O}_5$  nanorods decreased, followed by a decrease when the length of nanorods was continuously reduced. A critical length of 175 nm was found, at which the magnetization reached a maximum. The AFM ordering temperature ( $T_N$  (Er) = 5–10 K) of Er was identified in shorter nanorods. The magnetization transition can be reasonably ascribed to the AFM ordering of Er, and the competition between surface strain and uncompensated spin on the surface. These magnetic properties signified that the exchange coupling, interfacial interactions, and strong interparticle interactions resulted from the finite size effect.

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