

Facile Route to α -FeOOH and α -Fe₂O₃ Nanorods and Magnetic Property of α -Fe₂O₃ Nanorods

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α -FeOOH nanorods with diameters of 15–25 nm and lengths up to 170–300 nm were synthesized in high yield via a facile and template-free hydrothermal method at low temperature. After calcining the as-synthesized α -FeOOH at 250 °C for 2 h, we could obtain α -Fe₂O₃ nanorods. Interestingly, the as-obtained α -Fe₂O₃ nanorods exhibited weakly ferromagnetic characteristics at low temperature and superparamagnetic property at room temperature, which is different from the behavior of the corresponding bulk material.

Introduction

The physical and chemical properties of nanoparticles are essentially different from those of bulk materials and largely dependent on their size, shape, and surface chemistry.^{1–3} One-dimensional (1D) nanocrystals have become one of the most highly energized research fields, as it is generally accepted that one-dimensional nanostructures can be expected to exhibit superior electrical, optical, mechanical, and magnetic properties because of their anisotropic morphologies.^{4–6}

Iron oxyhydroxide and iron oxide are important materials with many industrial applications. Goethite (α -FeOOH) can be used as a pigment and is the most important precursor in the synthesis of iron oxides such as hematite (α -Fe₂O₃) and maghemite (γ -Fe₂O₃). Hematite (α -Fe₂O₃), the thermodynamically stable crystallographic phase of iron oxide with a band gap of 2.2 eV, is a very attractive material because of its wide applications in catalysis, gas sensors, magnetic recording materials, pigments, and paints.^{7–13} Its nontoxicity,

low cost, and relatively good stability are definitely very attractive features for these applications. There has been much interest in the development of synthetic methods to produce one-dimensional α -Fe₂O₃ nanostructures, such as vapor–solid growth techniques,^{14–15} templated synthesis methods,¹⁶ methods employing polycrystals or single crystals as growth substrates,¹⁷ and the sol–gel process.¹⁸ The vapor technique usually requires special equipment and high temperatures, whereas the methods employing templates or substrates often encounter difficulties with prefabrication and postremoval of the templates or substrates and usually result in impurities. The hydrothermal process appears to have some advantages, including mild synthetic conditions, simple manipulation, and good crystallization of the products. Recently, a surfactant-assisted hydrothermal process was adopted for the synthesis of β -FeOOH and α -Fe₂O₃ nano-

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rods.¹⁹ However, in that method, there was a small amount of residual CTAB in the products. Thus, the development of facile and template-free methods to create pure α -Fe₂O₃ one-dimensional nanostructures is of great significance.

In this paper, we propose a facile route for fabricating α -FeOOH nanorods via a low-temperature hydrothermal method. The α -FeOOH nanorods could be obtained with high yield (>90%) and good reproducibility. Through heating the as-obtained α -FeOOH nanorods at 250 °C for 2 h, we obtained single-crystalline α -Fe₂O₃ nanorods, preserving the same rodlike morphology. Magnetic measurements showed that the as-obtained α -Fe₂O₃ nanorods exhibited weakly ferromagnetic characteristics at low temperature and a superparamagnetic property at room temperature, which is different from the behavior of the corresponding bulk material.

Experimental Section

1. Experimental Procedure. All chemicals were analytical grade, purchased from the commercial market, and used without further purification before utilization. The α -FeOOH nanorods were synthesized via a solution chemical route involving two steps. (1) Room-temperature reaction: A mixture of FeSO₄·7H₂O (0.5 mmol) and anhydrous CH₃COONa (1 mmol) was added into a 100 mL beaker; 20 mL of distilled water was then put into the beaker, and the above solution was immediately stirred vigorously in air. A yellowish suspension appeared in the solution after several seconds, and the amount of suspension increased with continuous stirring. The above solution was stirred for about 20 min, and a yellow suspension was finally obtained. (2) Hydrothermal treatment: The yellow suspension obtained from step (1) was transferred into a 20 mL Teflon-lined autoclave up to 80% of the total volume. The autoclave was sealed and heated at 100 °C for 8 h. The autoclave was then cooled to room temperature naturally. The final yellow solid products were centrifuged and washed with distilled water and absolute ethanol several times, and then dried at 40 °C under a vacuum for 4 h. The α -Fe₂O₃ nanorods were obtained by heating the as-obtained α -FeOOH nanorods in air at 250 °C for 2 h.

2. Characterization of Samples. X-ray powder diffraction (XRD) patterns of the products were recorded on a Japan Rigaku D/max- γ A X-ray diffractometer at a scanning rate of 4° per minute with 2θ ranging from 20 to 80°, using Cu K α radiation ($\lambda = 1.54178$ Å). Transmission electron microscopy (TEM) images were collected on a Hitachi Model H-800 transmission electron microscope using an accelerating voltage of 200 kv. Selected-area electron diffraction patterns were performed on samples during TEM measurements. Thermal gravimetric analysis (TGA) of the as-synthesized α -FeOOH nanorods was carried out on a Mettler Toledo TGA/SDTA 851e thermal analyzer at a heating rate of 10 °C/min from room temperature to 500 °C under a N₂ atmosphere. The magnetic property of the as-synthesized α -Fe₂O₃ nanorods was investigated with a superconducting quantum interference device (SQUID) magnetometer (MPMS-7).

Results and Discussion

XRD Studies. As shown in Figure 1a, all the reflections of the XRD pattern can be indexed to pure orthorhombic α -FeOOH (space group *Pbnm* (No. 62)) with lattice constants

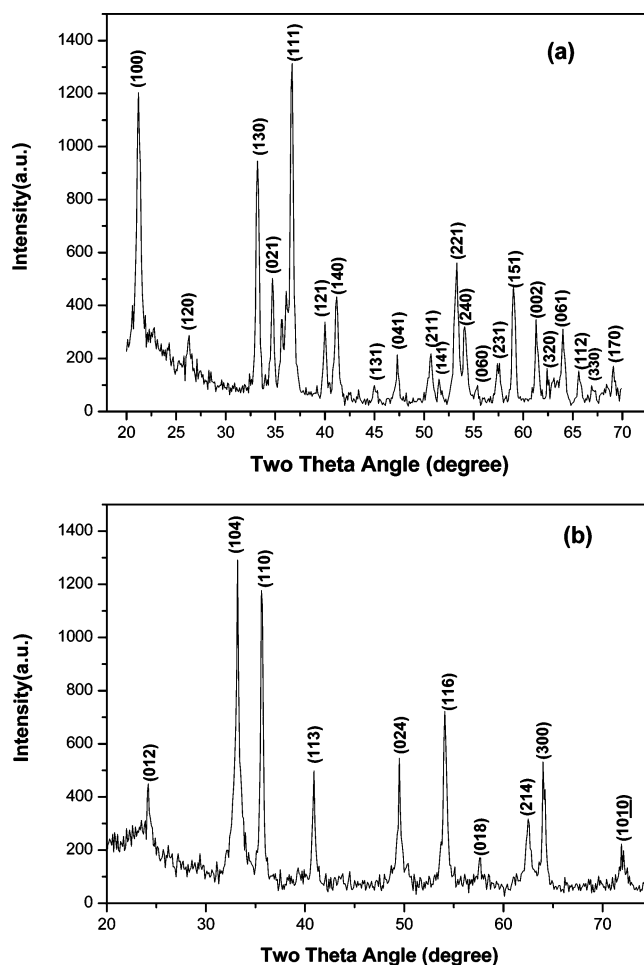


Figure 1. XRD pattern of (a) α -FeOOH and (b) α -Fe₂O₃ nanorods.

$a = 4.610$ Å, $b = 9.956$ Å, and $c = 3.024$ Å (JCPDS 29-713). No characteristic peaks of impurities are observed. After heating the as-obtained α -FeOOH nanorods at 250 °C for 2 h, we could obtain the pure hexagonal phase of α -Fe₂O₃ (JCPDS 33-664, $a = 5.035$ Å, $c = 13.749$ Å), as revealed by the XRD pattern in Figure 1b.

Morphologies of Samples. TEM analysis provides further insight into the morphology and particle size of the as-obtained products. As shown in panels a and b of Figure 2, more than 90% of the samples dispersed on the copper grids show a rodlike morphology. The α -FeOOH nanorods have diameters of 15–25 nm and lengths of 170–300 nm. The aspect ratio is greater than 10. It is worth mentioning that the morphology of nanorods can be preserved after heating the α -FeOOH to produce α -Fe₂O₃, as can be seen in Figure 2b. The insert images in panels a and b of Figure 2 are the selected-area electron diffraction (SAED) patterns taken from a single rod of the as-synthesized samples, which reveal the single-crystal nature of the as-obtained products. The high-resolution transmission electron microscopy (HRTEM) image of an individual α -Fe₂O₃ nanorod (Figure 2c) shows that the nanorod is structurally uniform with an interplanar spacing of about 2.58 Å, which corresponds to the (110) plane of hexagonal α -Fe₂O₃.

Thermal Gravimetric Analysis of the As-Prepared α -FeOOH Nanorods. The thermal gravimetric analysis

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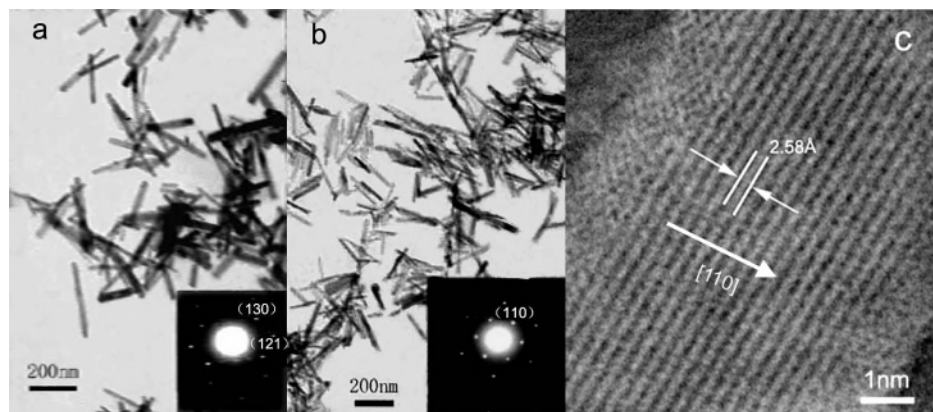


Figure 2. TEM images of (a) α -FeOOH and (b) α -Fe₂O₃ nanorods; insert is the SAED patterns of the corresponding sample. (c) HRTEM pattern of α -Fe₂O₃ nanorods.

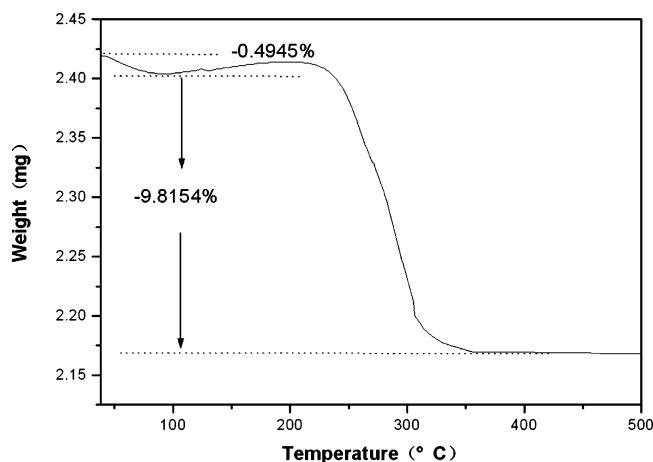
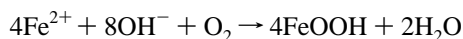
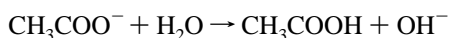


Figure 3. TGA curve of the as-prepared α -FeOOH nanorods.

(TGA) curve of the as-prepared α -FeOOH nanorods is shown in Figure 3. There are two weight loss steps in the temperature ranges 30–85 and 240–355 °C. The weight loss (0.4945%) at 30–85 °C may be attributed to the emission of physically adsorbed water, whereas that at 240–355 °C (9.8154%) may be ascribed to the decomposition of α -FeOOH. The weight loss ceased at 355 °C, even though heating continued to 500 °C. As a consequence, the stable residue can reasonably be ascribed to the thermodynamically crystallographic phase of iron oxide— α -Fe₂O₃. The XRD pattern (Figure 1b) of the products obtained by heating the as-synthesized α -FeOOH nanorods at a temperature of 250 °C for 2 h also confirms the presence of the pure hexagonal phase of α -Fe₂O₃.

Formation Mechanism of the α -FeOOH Nanorods.



As shown in the above equation, Fe²⁺ reacted with OH⁻ (produced by the hydrolysis of CH₃COO⁻) and O₂ at room temperature, producing a yellow FeOOH suspension. The hydrolysis of CH₃COO⁻ caused a uniform rise in the solution pH, which prevented the occurrence of high local supersaturation (as is the case with the addition of a strong base) and allowed nucleation to occur homogeneously throughout

the solution. As the reaction proceeded, the OH⁻ produced by the hydrolysis of CH₃COO⁻ increased. As a result, the yellow suspension increased. It is well-known that the growth mechanism is very important for exploring synthetic methods of one-dimensional nanostructures. Therefore, we performed several experiments that involved intercepting the intermediates at different hydrothermal reaction times to investigate the growth mechanism. Under a shorter reaction time, such as after 5 min of the hydrothermal reaction, a large amount of plate structures were obtained (Figure 4a). The thin flakes tended to curl under the elevated temperature and pressure, as shown in Figure 4b (after heating for 20 min). After heating for 30 min, some thin flakes broke into small nanoneedles (Figure 4c) via a rolling-broken-growth (RGB) process.²⁰ And finally, small nanoneedles would grow into nanorods after heating for 1 h (Figure 4d).

We studied the influence of the molar ratio of CH₃COONa to FeSO₄ on the morphology of the products in our synthetic system. The initial molar ratio of CH₃COONa to FeSO₄ was varied from 4 to 1, whereas the amounts of FeSO₄ and water were kept constant. After the room-temperature reaction and the subsequent hydrothermal process, nanoparticles were obtained when the CH₃COONa:FeSO₄ ratio was 1. With a further increase in the CH₃COONa content, i.e., CH₃COONa:FeSO₄ = 2, 3, or 4, nanorods were obtained. We also studied the influence of pH on the morphology of the products. When CH₃COONa:FeSO₄ was 2:1, under which condition nanorods were obtained, the pH of the yellow suspension before the hydrothermal reaction was 5.5. When the pH of the above yellow suspension was adjusted to 5.0 by H₂SO₄ solution or to 6.0 by NaOH solution, nanorods could also be obtained. When CH₃COONa:FeSO₄ was 1:1, under which condition nanoparticles were obtained, the pH of the yellow suspension before the hydrothermal reaction was 5.4. Even though the pH of the above suspension was adjusted to 5.5, the as-obtained products were still nanoparticles. So we think CH₃COONa played a more important role than OH⁻ in the formation of the nanorods. To learn more about the role of CH₃COO⁻ in the formation of the nanorods, we performed the experiments in a different way. After the room-temper-

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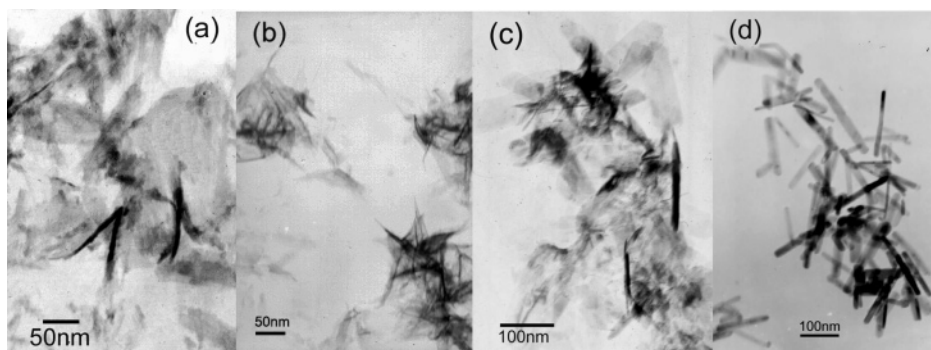


Figure 4. TEM image of the samples obtained at different hydrothermal reaction times: (a) 5 min, (b) 20 min, (c) 30 min, and (d) 1 h.

ature reaction, the as-obtained yellow suspension was washed with double-distilled water to remove the remnant ions and then hydrothermally treated. The as-obtained products were nanoneedles, which was the usual shape of α -FeOOH. In our synthetic system, replacing CH₃COONa with another carboxylate, such as CH₃CH₂COONa, NaOOCH₂CCH₂COONa, or C₆H₅COONa, led to similar one-dimensional α -FeOOH nanostructures being obtained. But if Na₂CO₃ was used in our synthetic system, only nanoparticles could be obtained. It was reported that the carboxyl group has a coordination that could favored the formation of one-dimensional nanostructures.²¹ Therefore, we believe that the coordination of the carboxylate has played a similar role in our synthetic system in the formation of α -FeOOH nanorods.

Magnetic Property of the As-Synthesized α -Fe₂O₃ Nanorods. Bulk α -Fe₂O₃, besides the Néel temperature ($T_N = 960$ K), has a first-order magnetic transition at $T_M = 263$ K, which is called the Morin transition. Below T_M , the antiferromagnetically (AF) ordered spins are oriented along the c axis, whereas above T_M , spins lie AF in the basal plane of the crystal with a ferromagnetism component.^{22,23} Because of nanoscale confinement, nanomaterials can exhibit unusual magnetic behaviors that are quite different from those of conventional bulk materials. For example, α -Fe₂O₃ particles smaller than 20 nm in diameter have shown a suppression of the Morin transition and stay in the weakly ferromagnetic state at least down to 5 K.^{24–26} It is commonly recognized that the methods of material preparation and their relations to the morphology, surface condition, and strains are important factors determining the material physical properties.²⁷ To the best of our knowledge, there has been no report on the magnetic property of α -Fe₂O₃ nanorods with an aspect ratio greater than 10. Herein, we investigated the magnetic property of the as-synthesized α -Fe₂O₃ nanorods with

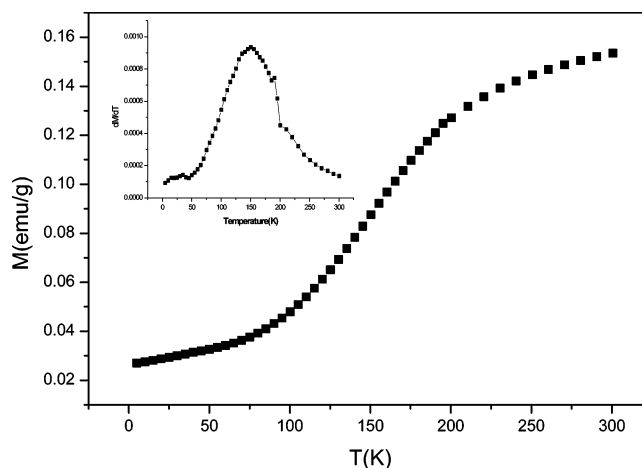


Figure 5. Magnetization vs temperature curve of the as-synthesized α -Fe₂O₃ nanorods at an applied field of 100 Gs.

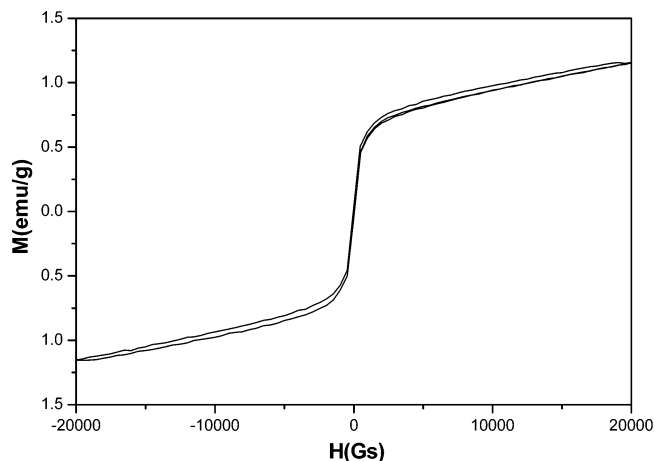


Figure 6. Magnetic hysteresis loop of the as-synthesized sample at 293 K.

diameters of 15–25 nm and lengths of 170–330 nm by a superconducting quantum interference device. Figure 5 shows the magnetization versus temperature curve of the α -Fe₂O₃ nanorods at an applied field of 100 Gs. The blocking temperature of the as-obtained α -Fe₂O₃ nanorods is about 150 K, which is determined by the sharp peak in the dM/dT curve.²⁷ The field-dependence curve of the as-obtained α -Fe₂O₃ nanorods measured at 293 K (Figure 6) shows almost no hysteresis; the coercive force and remnant magnetization are zero, which is characteristically similar to typical superparamagnetic materials.²⁸ The superparamagnetic property has also been observed for spherical

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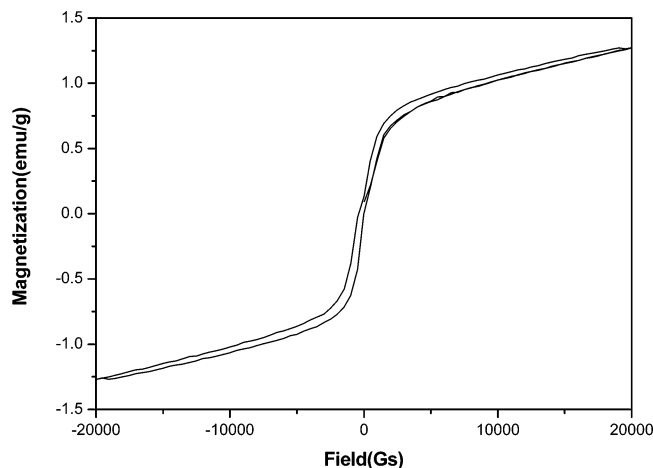


Figure 7. Magnetic hysteresis loop of the as-synthesized sample at 5 K.

α -Fe₂O₃ nanoparticles with diameters smaller than 20 nm.²⁶ The superparamagnetic phenomenon is due to the small size of the as-obtained product. According to the literature, when the size of the magnetic particles decreases, the particles change from multidomain to single domain.²⁹ If the single-domain particles become small enough, the magnetic moment in the domain fluctuates in direction because of thermal agitation, which leads to superparamagnetism. At low temperatures, such as 5 K, the M - H curve (Figure 7) displays a small hysteresis with coercive force of 187 Oe and remnant magnetization of 0.06 emu/g, indicating its weakly ferromagnetic property at low temperature. No saturation of the magnetization as a function of the field is observed up to the maximum applied magnetic field. In fact, bulk α -Fe₂O₃ is antiferromagnetic below the Morin transition temperature ($T_M = 263$ K), which does not show any hysteresis. α -Fe₂O₃ nanoparticles with an average diameter of 3 nm were found to show a coercive force of 50 Oe at 5 K.³⁰ Compared to spherical nanoparticles, one-dimensional nanostructures have increased anisotropies in both the shape

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anisotropy and magnetocrystalline anisotropy, which exert influence on their magnetic properties.^{31–34} Shape anisotropy can increase the coercivity.^{31,33–34} Enhanced anisotropy induces large magnetic coercivity, where the magnetic spins are preferentially aligned the long axis and their reversal to the opposite direction requires higher energies than that for spheres.³⁴

Conclusion

A low-temperature hydrothermal process was employed for the preparation of α -FeOOH nanorods. CH₃COO⁻ played an important role in the rod-morphology formation. The formation mechanism of the α -FeOOH nanorods followed the rolling-broken-growth model. Single-crystalline α -Fe₂O₃ was obtained after heat-treating the as-obtained α -FeOOH nanorods, which retain the same nanorod morphology, at 250 °C. The proposed method has great advantages in large-scale industrial manufacturing for a simple hydrothermal process, such as inexpensive raw materials, high purity, and a high morphology yield of the products. Magnetization measurements showed that the as-synthesized α -Fe₂O₃ nanorods showed a blocking temperature at 150 K. The M - H curve showed superparamagnetic behavior of the as-synthesized α -Fe₂O₃ nanorods at 293 K and weakly ferromagnetic property at 5 K, which is different from the magnetic property of bulk α -Fe₂O₃ (antiferromagnetic at low temperature and ferromagnetic above T_M).

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