Mn-Doped Maghemite (γ-Fe₂O₃) from Metal–Organic Framework Accompanying Redox Reaction in a Bimetallic System: The Structural Phase Transitions and Catalytic Activity toward NOx Removal

Junhyung Lee†‡ and Seung-Yeop Kwak*†§

1Department of Materials Science and Engineering and 2Research Institute of Advanced Materials (RIAM), Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 08826, Korea
3Korea Transformer Co., Ltd., 415, Siheung Dae-ro, Geumcheon-gu, Seoul 08523, Korea

ABSTRACT: Mn-doped maghemite (γ-Fe₂O₃) particles were generated from a binary metal (Fe,Mn)-based metal–organic framework (MOF) via thermal decomposition under air. The X-ray photoelectron spectroscopy analysis revealed that the synthesis of Fe/Mn-MOF accompanied the reduction of the metal ions. The existence of Mn ions in this synthetic process leads to thermally stable maghemite particles under air. A temperature-induced structural phase transition from γ-Fe₂O₃ to α-Fe₂O₃ was observed through a mixed phase with another structure. Mn-doped γ-Fe₂O₃ and α-Fe₂O₃ exhibit superparamagnetic behavior. The sample annealed at 600 °C showed a mixed magnetic hysteresis loop indicating the existence of an intermediate structural phase between γ-Fe₂O₃ and α-Fe₂O₃ during the phase conversion from FeMn-MOF. The constructed Mn-doped iron oxides are active toward reducing nitric oxide with NH₃. The NO conversion is 97% over Mn-doped γ-Fe₂O₃ calcined at 320 °C.

1. INTRODUCTION

Maghemite (γ-Fe₂O₃) is an Fe₂O₃ polymorph that consists of one-third of the tetrahedral sites and two-thirds of the octahedral sites bearing Fe³⁺ cation.¹ Nanosized γ-Fe₂O₃ is considered a promising material for many applications, such as sensing, magnetic separation, in vivo medical imaging, drug delivery, and hyperthermia due to its nontoxicity, biocompatibility, chemical stability, and good magnetic property.²–⁷ In addition, γ-Fe₂O₃ is a vanadium-free catalyst candidate for selective catalytic reduction (SCR) to remove harmful nitric oxide gases.⁵,⁶ Thus, a variety of synthetic processes for the preparation of γ-Fe₂O₃ have been reported. However, most of the synthetic methods required complicated procedures, many additives, and an inert atmosphere.⁷–⁹ Moreover, this material has always suffered from innate thermal unstability.⁴ Thus, developing a novel and facile method to synthesize thermally stable γ-Fe₂O₃ as an effective material should be designed and is required. Metal oxide generation derived from metal–organic frameworks (MOFs) (also called coordination polymer) is a prominent method for a variety of applications owing to the easy preparation, tuning functionalities, and morphology modulation of MOFs.¹⁰–¹³ Thermal conversion from MOFs as precursors is influenced by the metal species, physical properties of the MOF scaffolds, temperature, atmospheric state, and physical environment.¹⁴–¹⁹ Despite the progress achieved to date, an understanding of the mechanisms or factors in forming the required crystal structure by thermal decomposition from MOFs is in the early stages of development. To obtain the desired nanomaterials, understanding the thermal transformation mechanism derived from MOFs precursors is necessary.

Even though several methods have been reported for the γ-Fe₂O₃ preparation via thermal decomposition from MOFs, they required oxygen-free atmosphere or reduction processes.²⁰,²¹ It is previously reported that doping Mn(III) into the γ-Fe₂O₃ structure suppresses the thermal conversion from the γ-Fe₂O₃ to the α-Fe₂O₃ phase.²² With this knowledge, we expected that γ-Fe₂O₃ can be prepared from bimetallic MOFs bearing iron and manganese under suitable synthetic conditions. In this study, we successfully prepared Mn-doped γ-Fe₂O₃ particles via thermal decomposition under air from an MOF containing Fe and Mn species. Interestingly, the reduction of the metal elements is observed from bimetallic MOF but cannot be monitored from MOFs with a single metal species. A thermal phase transformation from maghemite was also investigated. The structural and magnetic properties of the generated iron oxides were analyzed. In addition, the SCR catalytic activity of Mn-doped iron oxides was tested and linked to their structural transformation.

2. RESULTS AND DISCUSSION

The overall process for the preparation of Mn-doped γ-Fe₂O₃ and their phase transition are displayed in Scheme 1. First,
bimetallic FeMn-MOF particles (MOF) were synthesized using FeCl₃·6H₂O, MnCl₂·4H₂O, and sodium fumarate as precursors. Prepared FeMn-MOF was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), IR spectroscopy, energy-dispersive X-ray spectroscopy (EDS) element analysis, and thermogravimetric analysis (TGA).

The IR spectrum of the bimetallic FeMn-MOF shows a shift in the CO stretching frequency from 1548 to 1568 cm⁻¹ for the free carboxylate of organic ligand to 1592 and 1698 cm⁻¹, indicating the coordination of ligand to iron and manganese ions (Figure S1). The IR patterns of the FeMn-MOF were entirely similar to those of the synthesized Fe-MIL-88A particles.

As shown in the SEM and TEM images of the prepared bimetallic MOF, the particles exhibit a diamond shape with a length of approximately 200 nm (Figure 1). An EDS analysis was conducted to confirm the existence of both Fe and Mn elements in the synthesized particles (Figure 1). Thermogravimetric analysis (TGA) was conducted for the FeMn-MOF under air. The removal of the water below 100 °C and the complete thermal decomposition of organic building blocks above 440 °C via a two-step process were observed from the TGA curve for FeMn-MOF (Figure S2).

Manganese-doped maghemite (γ-Fe₂O₃) particles were produced through the calcination under air at 320 °C for 1 h using a furnace. The conversion of FeMn-MOF to Mn-doped γ-Fe₂O₃ particles during this process was confirmed by powder X-ray diffraction (XRD) pattern, SEM, high-resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM), EDS mapping, and X-ray photoelectron spectroscopy (XPS) analyses. The XRD patterns of these aged FeMn-MOF under air at 320 and 400 °C for 1 h contain the (220) and (311) peaks, which synchronized well with the structure of the γ-Fe₂O₃ crystals (International Centre for Diffraction Data, ICDD No. 00-025-1402) (Figure 2).

To investigate the thermal stability and phase transition of Mn-doped γ-Fe₂O₃, FeMn bimetallic MOFs were calcined at increased temperatures. The calcination of FeMn-MOF was conducted at 600 and 800 °C for 1 h. The XRD patterns show sharp diffraction peaks for (104) and (110) at 2θ = 33.18 and 35.3°, which agree with the rhombohedral structured α-Fe₂O₃. It is known that γ-Fe₂O₃ is a thermally unstable structure among iron oxide polymorphs. These results show that the Mn-doped γ-Fe₂O₃ system is quite thermally durable because Mn(III) suppresses the transition from the γ-phase to the α-phase, which requires higher energy. When FeMn-MOF was thermally treated at 400 and 600 °C, FeMn-400 displays the peak at 2θ = 32.8° and FeMn-600 shows the peak at 2θ = 55.1°, which are considered as a ε-Fe₂O₃ structure (ICDD No. 00-016-0653). Additionally, the shoulder near the peak (104) in FeMn-600 was observed, which disappeared in FeMn-800. It is postulated that a thermally induced phase transition from FeMn-320 (γ-Fe₂O₃) to FeMn-800 (α-Fe₂O₃) was formed via an intermediate phase.

Figure 1. (a) SEM and (b) TEM images of FeMn-MOF particles. (c) The scanning transmission electron microscopy (STEM)-EDS maps displaying the distribution of Fe, Mn, and O of FeMn-MOF.
Figure S3 displays the HRTEM images of the samples aged at different temperatures. It is obvious that the increased calcination temperature induced the morphological changes. The morphology of the $\gamma$-Fe$_2$O$_3$ particles from FeMn-MOF shows an irregular shape. From the TEM images of prepared iron oxides via calcination, the aggregation of particles was observed, the length of irregularly shaped particles was increased, and they became interconnected, as the calcination temperature increased under air. This process contains thermal oxidation of the organic blocks and the agglomeration of metal oxide particles. An EDS mapping analysis using STEM was conducted to identify the presence of both Fe and Mn elements in the prepared Mn-doped iron oxides samples (Figure S4). The Mn mapping is detected throughout all of the particles, and the Fe mapping is consistently overlapped in

Figure 2. Powder X-ray diffraction patterns of Mn-doped iron oxides annealed at 320, 400, 600, and 800 °C.

Figure 3. XPS spectra of (a) Mn 2p for the Mn-MOF and FeMn-MOF; (b) Mn 2p for the FeMn-320, 400, 600, and 800; (c) Fe 2p for the Fe-MIL-88A and FeMn-MOF; and (d) Fe 2p for the calcined FeMn-MOF at 320, 400, 600, and 800 °C.
all of the iron oxide particles generated at different temperatures. The EDS mapping images prove that manganese is well dispersed in the iron oxide particles retaining the maghemite or hematite structure.

Using Scherrer’s equation from the (311) peaks at $2\theta = 35.6^\circ$, the average crystalline size of the FeMn-320 and -400 are 10.38 and 10.9 nm, respectively. The average crystalline size of FeMn-600 and -800 calculated with the Scherrer’s equation are 39 and 57 nm. The particle size of FeMn-600 and -800 are larger than the calculated crystalline size because the particles may consist of several different crystals.

The surface area of the newly prepared Mn-doped iron oxides particles was measured by the Brunauer–Emmet–Teller (BET). The generated Mn-doped ($\gamma$-Fe$_2$O$_3$) shows surface area of 62.0993 m$^2$/g, whereas increasing the calcination temperature reduced the surface area to 45.1486, 15.8991, and 4.0526 m$^2$/g. The N$_2$ adsorption/desorption curve pattern of all of the samples is similar (Figure S5). The low surface area can be explained by

![Figure 4. Magnetic hysteresis loops of (a) Mn-doped Fe$_2$O$_3$ structures prepared by thermal conversion at (b) 320 °C, (c) 400 °C, (d) 600 °C, and (e) 800 °C from FeMn-MOF.](image-url)
the increasing calcination temperature inducing the agglomeration of Mn-doped iron oxide particles. To identify the chemical state and binding energy of iron and manganese of the prepared MnFe-MOF and aged Mn-doped iron oxides, the XPS analysis was carried out. Figure 3 displays that the peaks for FeMn-MOF for Fe 2p1/2 are observed with the binding energy at approximately 709.01 and 710.7 eV. The binding energy at 709.01 eV designate to Fe(II) cation and the peak at 710.7 eV is the fingerprint of Fe(III) species (Table S1).23 The XPS spectra of Fe 2p1/2 for the Fe-MIL-88A containing only iron show that Fe(III) species at 710.98 and the satellite peak at 717.04 eV were dominant rather than the peak at 709.64 eV of Fe(II). In addition, the XPS analysis was conducted after the calcination of FeMn-MOF at 320, 400, 600, and 800 °C. The XPS spectra for all of the samples show similar patterns. The appearance of Fe 2p1/2 peaks at 709.69 and 710.83 eV of FeMn-320 represents the coexistence of Fe(II) and Fe(III) cation. The intensity of Fe(III) peak increased and the binding energy of Fe 2p1/2 shifted to be higher as the heating temperature was increased.

As shown in Figure 3, the Mn 2p spectra of FeMn-MOF are displayed. The Mn 2p1/2 and 2p3/2 peaks are shown at a binding energy ranging from 630 to 660 eV. The asymmetric Mn 2p peaks indicate the existence of mixed-valence manganese. The peak at 640.47 eV is assigned to Mn(II) species and the peak at 642.13 eV is characteristic of the Mn(III) cation, respectively. The broad peak at 637.76 eV was also monitored, indicating the generation of more reduced Mn species. The intensity of Mn(II) is found to be slightly higher than that of Mn(III). The XPS analysis of the Mn MOF is shown in Figure 3. The peak at 640.67 eV is a feature of Mn(II), whereas the peak at 641.85 eV is characteristic of the Mn(III) species. After the pyrolysis of FeMn-MOF at 320 °C, the XPS spectra for the binding energy of relevant Mn species were generated. The Mn(II) of FeMn-320 can be found in the peak at 640.76 and the peak at 641.84 eV is characterized as the Mn(III) cation. There is also a small broad peak at 639.80 eV. As the calcination temperature increased, the binding energies of Mn 2p3/2 peaks shifted to the higher energies and the intensity of Mn(III) species became higher than Mn(II) species. These results indicate that oxidation has occurred during the calcination process. It is observed from the XPS quantitative analysis that the atomic ratio of Fe/Mn as 6.8:3.2 (FeMn-320), 6.1:3.9 (FeMn-400), 6.6:3.4 (FeMn-600), and 5.8:4.2 (FeMn-800).

In addition, these results suggest that a redox reaction occurred in this bimetallic synthetic system. It is known that the γ-Fe2O3 structure is not only generated starting from magnetite (Fe3O4) spinel formation, which consisted of Fe2+ and Fe3+, but is also in a thermally unstable crystal phase.10,11 It is also reported that the calcination of iron-containing MOFs under air generated the hematite structure (α-Fe2O3) even under 400 °C.12 Thus, the mechanism for the γ-Fe2O3 structure formation via thermal decomposition from bimetallic MOFs is related to the existence of manganese in this synthetic system, and Mn3+ ions provide thermal stability to the γ-Fe2O3 structure.

The magnetic properties of the prepared manganese-doped iron oxides were investigated using vibrating sample magnetometer (VSM) at room temperature. Figures 4 and 5 depict the plots of the magnetization versus the applied magnetic field for the Mn-doped Fe2O3 derived from FeMn-MOF via thermal treatment. The FeMn-320 exhibited superparamagnetic behavior showing the magnetization value of 36.24 emu/g. It is a similar magnetization value compared with manganese-doped γ-Fe2O3.22 The magnetization of FeMn-400 was 57.143 emu/g. Although the mixed crystal structures were observed by XRD analysis, the magnetization of FeMn-400 increased above the magnetization of FeMn-320 exhibiting a superparamagnetic pattern. The magnetization of FeMn-320 and -400 are much less than that of the bulk γ-Fe2O3 materials (73–74 emu/g).24 The M−H curve after calcination of FeMn-MOF at 600 °C illustrates that the sample exhibits a ferromagnetic and paramagnetic mixed hysteresis loop, with a coercivity of $H_c = 284.88$ Oe. The magnetization value is 1.22 to −0.95 emu/g. The decreased magnetization of FeMn-600 can be explained by the thermal phase transformation from γ-Fe2O3 to α-Fe2O3. The magnetization curve of FeMn-800 displays a very weak ferromagnetic behavior, showing a coercivity of 88.84 Oe. The magnetization value is approximately 3.152 emu/g, which is approximately three times higher than that of bulk α-Fe2O3 (0.3 emu/g).

Although the bulk α-Fe2O3 is antiferromagnetic, it is reported that manganese doping enhances the magnetization value of the α-Fe2O3.25 It is suggested from the magnetic properties that FeMn-600 is the intermediate state, whereas the γ-Fe2O3 phase is transformed into the α-Fe2O3 phase.

Because maghemite is a promising candidate as an SCR catalyst, the catalytic activity of the Mn-doped iron oxides having γ-Fe2O3 (FeMn-320, 400) or α-Fe2O3 (FeMn-600, 800) structures in the SCR of NO with NH3 was studied. The NOx conversion over FeMn-320 increased as the reaction temperature increased, and 97% NOx removal was achieved at 250 °C. The NOx conversion in a temperature range from 150 to 300 °C was observed to be over 80%. The maximum NOx conversion of FeMn-400 was 93% at 250 °C. The entire conversion efficiency of NOx sharply declined. The maximum NOx conversion of FeMn-600 and FeMn-800 was 93 and 86%, respectively, at 250 °C. The drastic decrease of catalytic activity after pyrolysis above 600 °C can be attributed to the phase transition from γ-Fe2O3 to α-Fe2O3. It is reported that the γ-phase of iron oxide exhibited a higher SCR catalytic activity than the α-phase.6 Furthermore, the surface area of the Mn-doped iron oxide samples diminished with increased calcination temperature, causing a lower catalytic activity of NO removal.
3. CONCLUSIONS
To sum up, we have developed a facile method to generate Mn-doped γ-Fe₂O₃, and the thermal phase transformation to α-Fe₂O₃ was observed via thermal decomposition from bimetallic FeMn-MOF. It is postulated that introducing Mn(II) ions induces the redox reactions during the synthesis of FeMn-MOF, which are not observed with single metal species, and are responsible for the formation of γ-Fe₂O₃ via thermal conversion from FeMn-MOF. Even though γ-Fe₂O₃ is a thermodynamically unstable structure, the conversion from Mn-doped γ-Fe₂O₃ to Mn-doped α-Fe₂O₃ requires a high activation energy because Mn ions suppress the transition. FeMn-320 and -400 display superparamagnetic behavior at room temperature, which is an inherent characteristic of the Mn-doped γ-Fe₂O₃ structure. FeMn-800 shows a very weak ferromagnetic behavior with a drastically decreased magnetization value indicating that a thermal phase transition to Mn-doped α-Fe₂O₃ occurred. Interestingly, the mixed ferromagnetic and paramagnetic behavior was observed from FeMn-600 despite the transformation to the α-Fe₂O₃ structure, suggesting the existence of an electronic phase intermediate. The SCR catalytic activity of NO with NH₃ of all Mn-doped Fe₂O₃ was measured. When the γ-Fe₂O₃ structure was formed, a good catalytic activity with a 97% NO conversion rate at 250 °C at GHSV 30 000 h⁻¹ was presented. The thermal crystalline structure transformation to α-Fe₂O₃ resulted in a decreased catalytic activity.

4. EXPERIMENTAL SECTION
4.1. Materials and Instrument. All of the chemicals obtained from commercial resources were used without further purification. Fe-MIL-88A particles were synthesized with modification according to a method previously reported.¹ The morphology of the synthesized materials was investigated using a field-emission scanning electron microscope (Carl Zeiss SUPRA 55VP) operated at an accelerating voltage of 3.0 kV and equipped with energy-dispersive spectroscopy (EDS) capabilities. All of the scanning and high-resolution transmission electron microscopy (STEM and HRTEM, respectively) images and electron diffraction patterns were obtained using JEOL JEM-2000EXII and JEM-ARM200F instruments operated at 200 kV. The X-ray diffraction studies of the crystal structure were conducted using an XRD equipped with a Cu Kα radiation source (50 kV, 100 mA, λ = 1.541 Å) at room temperature. Thermogravimetric analysis (TGA) was carried out on a TA Instruments Q500 at up to 800 °C, with a heating rate of 10 °C under air. The field-dependent magnetization of each sample was measured ranging from −15 to 15 kOe using a Lake Shore 7410 vibrating sample magnetometer (VSM). The X-ray photoelectron spectroscopy (XPS) measurements were acquired on a KRATOS AXIS with Mg Kα X-rays as the excitation source (1253.6 eV). The N₂ adsorption−desorption isotherms were recorded at 77 K on a micrometrics 3flex surface characterization analyzer apparatus. The specific surface area of the samples was calculated using the multipoint Brunauer−Emmett−Teller (BET) method.

4.2. Preparation of Iron–Manganese Bimetallic Metal–Organic Framework (FeMn-MOF), Fe-MIL-88A, and Mn MOF. FeCl₃·6H₂O (27 g, 100 mmol) and MnCl₂·4H₂O (19.7 g, 100 mmol) were dissolved in 400 mL of deionized water at 60 °C. Then, 100 mL of sodium fumarate aqueous solution (32 g, 200 mmol) was added to the mixed solution and, subsequently, precipitate was generated. The mixture was stirred at 60 °C overnight and cooled to room temperature. The final brown products were isolated by centrifugation and then washed with deionized water and acetone twice. In addition, Fe-MIL-88A and Mn-MOF were prepared via identical procedures using only one metal species (200 mmol).

4.3. Phase Transition of Manganese-Doped Iron Oxides. Bimetallic MOF was moved into a ceramic boat and placed into a furnace. The calcination process was performed at 320, 400, 600, and 800 °C for 1 h under air condition with a heating rate of 5 °C/min and then quenched. Hereafter, the samples prepared by this method are called FeMn-X, where X indicates the calcination temperature.

4.4. Catalytic Performance Test. The catalytic activities of the prepared iron oxides for the selected catalytic reduction of NO with NH₃ were carried out in a fixed-bed reactor with an inner diameter of 10 mm. The reaction gas composed of 400 ppm NO, 400 ppm NH₃, and 3% O₂ with N₂ as the balance gas. The total flow rate was 1000 mL/min and the gas hourly space velocity (GHSV) was 30 000 h⁻¹. The flow rate of all of the gases were controlled by mass flow regulators. The outlet concentrations of NO and NO₂ gas were monitored using a Testo 350k analyzer.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01865.

Additional IRα analysis, TEM images, TGA curve, N₂ adsorption−desorption isotherm, and EDS mapping images; Figures S1–S5, Table S1 (PDF)

AUTHOR INFORMATION
Corresponding Author
*E-mail: sykwak@snmu.ac.kr.

ORCID
Junhyung Lee:0000-0002-7763-8227
Seung-Yeop Kwak:0000-0002-8903-4287

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This research was supported by the Ministry of Environment of Korea as part of the “Dissemination of R&D Results and Commercialization” Program.

REFERENCES
(1) MacHala, L.; Tuček, J.; Zbořil, R. Polymorphous transformations of nanometric iron(III) oxide: A review. Chem. Mater. 2011, 23, 3255−3272.
(2) Singh, K.; Ohlan, A.; Kotnala, R. K.; Bakhshi, A. K.; Dhawan, S. K. Dielectric and magnetic properties of conducting ferromagnetic composite of polyaniline with gamma-Fe₂O₃ nanoparticles. Mater. Chem. Phys. 2008, 112, 651−658.
(3) Hu, J.-S.; Zhong, L. S.; Song, W. G.; Wan, L. J. Synthesis of hierarchically structured metal oxides and their application in heavy metal ion removal. Adv. Mater. 2008, 20, 2977−2982.
(4) Yoo, D.; Lee, J.-H.; Shin, T.-H.; Cheon, J. Theranostic magnetic nanoparticles. Acc. Chem. Res. 2011, 44, 863−874.
(5) Mou, X.; Zhang, B.; Li, Y.; Yao, L.; Wei, X.; Su, D. S.; Shen, W. Rod-shaped Fe₃O₄ as an efficient catalyst for the selective reduction of nitrogen oxide by ammonia. Angew. Chem., Int. Ed. 2012, 51, 2989−2993.
(6) Qu, W.; Chen, Y.; Huang, Z.; Gao, J.; Zhou, M.; Chen, J.; Li, C.; Ma, Z.; Chen, J.; Tang, X. Active tetrahedral iron sites of γ-Fe₂O₃.
catalyzing NO reduction by NH3. *Environ. Sci. Technol. Lett.* 2017, 4, 246–250.

(7) Wei, X.; Zhou, Y.; Li, Y.; Shen, W. Polymorphous transformation of rod-shaped iron oxides and their catalytic properties in selective reduction of NO by NH3. *RSC Adv.* 2015, 5, 66141–66146.

(8) Capone, S.; Manera, M. G.; Taurino, A.; Siciliano, P.; Rella, R.; Lubi, S.; Benkovicova, M.; Siffalovic, P.; Majkova, E. Fe2O3/γ-Fe2O3 Nanoparticle Multilayers Deposited by the Langmuir-Blodgett Technique for Gas Sensors Application. *Langmuir* 2014, 30, 1190–1197.

(9) Delahaye, E.; Escax, V.; El Hassan, N.; Davidson, A.; Aquino, R.; Dupuis, V.; Perzynski, R.; Raikher, Y. L. "Nanocasting": Using SBA-15 Silicas as Hard Templates to Obtain Ultrasmall Monodispersed γ-Fe2O3 Nanoparticles. *J. Phys. Chem. B* 2006, 110, 26001–26011.

(10) Song, Y.; Li, X.; Sun, L.; Wang, L. W. Metal/metal oxide nanostructures derived from metal–organic frameworks. *RSC Adv.* 2015, 5, 7267–7279.

(11) Xia, W.; Mahmood, A.; Zou, R.; Xu, Q. Metal–organic frameworks and their derived nanostructures for electrochemical energy storage and conversion. *Energy Environ. Sci.* 2015, 8, 1837–1866.

(12) Xu, X.; Cao, R.; Jeong, S.; Cho, J. Spindle-like mesoporous α-Fe2O3 anode material prepared from MOF template for high-rate lithium batteries. *Nano Lett.* 2012, 12, 4988–4991.

(13) Salunkhe, R. R.; Kaneti, Y. V.; Yamauchi, Y. Metal–Organic Framework-Derived Nanoporous Metal Oxides toward Supercapacitor Applications: Progress and Prospects. *ACS Nano* 2017, 11, 5293–5308.

(14) Das, R.; Pachfule, P.; Banerjee, R.; Poddar, P. Metal and metal oxide nanoparticle synthesis from metal organic frameworks (MOFs); finding the border of metal and metal oxides. *Nanoscale* 2012, 4, 591–599.

(15) Cho, W.; Park, S.; Oh, M. Coordination polymer nanorods of FeMIL-88B and their utilization for selective preparation of hematite and magnetite nanorods. *Chem. Commun.* 2011, 47, 4138–4140.

(16) Lee, J.; Kwak, S.-Y. Tubular Superstructures Composed of α-Fe2O3 Nanoparticles from Pyrolysis of Metal-Organic Frameworks in a Confined Space: Effect on Morphology, Particle Size, and Magnetic Properties. *Cryst. Growth Des.* 2017, 17, 4496–4500.

(17) Salunkhe, R. R.; Kamachi, Y.; Torad, N. L.; Hwang, S. M.; Sun, Z.; Dou, S. X.; Kim, J. H.; Yamauchi, Y. Fabrication of symmetric supercapacitors based on MOF-derived nanoporous carbons. *J. Mater. Chem. A.* 2014, 2, 19848–19854.

(18) Torad, N. L.; Hu, M.; Ishihara, S.; Sukegawa, H.; Belik, A. A.; Imura, M.; Ariga, K.; Sakka, Y.; Yamauchi, Y. Direct synthesis of MOF-derived nanoporous carbon with magnetic Co nanoparticles toward efficient water treatment. *Small* 2014, 10, 2096–2107.

(19) Kaneti, Y. V.; Tank, J.; Salunkhe, R. R.; Jiang, X.; Yu, A.; Wu, K.C.-W.; Yamauchi, Y. Nanoarchitectured design of porous materials and nanocomposites from metal-organic frameworks (MOFs). *Adv. Mater.* 2017, 29, No. 1604989.

(20) Kim, E.; Yoon, M. Facile synthesis of γ-Fe2O3@porous carbon materials using an Fe-based metal–organic framework: structure and porosity study. *J. Porous Mater.* 2015, 22, 1495–1502.

(21) Lee, H. J.; Cho, W.; Lim, E.; Oh, M. One-pot synthesis of magnetic particle-embedded porous carbon composites from metal–organic frameworks and their sorption properties. *Chem. Commun.* 2014, 50, 5476–5479.

(22) Lai, J.; Shaft, K. V. P. M.; Loos, K.; Ulman, A.; Lee, Y.; Vogt, T.; Estourne, C. Doping γ-Fe2O3 Nanoparticles with Mn(III) Suppresses the Transition to the α-Fe2O3 Structure. *J. Am. Chem. Soc.* 2003, 125, 11470–11471.

(23) Yamashita, T.; Hayes, P. Analysis of XPS spectra of Fe2+ and Fe3+ ions in oxide materials. *Appl. Surf. Sci.* 2008, 254, 2441–2449.

(24) Bate, G. Particulate Recording Materials. *Proc. IEEE* 1986, 74, 1513–1525.

(25) Cui, H.-J.; Cai, J.-K.; Shi, J.-W.; Yuan, B.; Ai, C.-L.; Fu, M.-L. Fabrication of 3D porous Mn doped α-Fe2O3 nanostructures for the removal of heavy metals from wastewater. *RSC Adv.* 2014, 4, 10176–10179.