Controlled Synthesis of Manganese Oxide Nanoparticles Encaged in Hollow Mesoporous Silica Nanoreactors and Their Enhanced Dye Degradation Activity

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ABSTRACT: In this study, controlled synthesis of hollow mesoporous silica nanoreactors with small manganese oxide nanoparticles in their cavities (MnₓOᵧ@HMSNs) is reported, and the dye degradation performance in the presence of hydrogen peroxide over MnₓOᵧ@HMSNs is investigated. Specifically, triple ligands (a compound with three dipicolinic acid groups) were used to coordinate manganese ions to form negatively charged coordination complex networks, which further combine with positively charged copolymers to obtain metal ion-containing polymer micelles. Following silica deposition onto micellar coronas and calcinations simultaneously result in hollow mesoporous silica nanoreactors and manganese oxide nanoparticles in their cavities. In this work, the influences of synthetic parameters on the structures are studied in detail. The obtained MnₓOᵧ@HMSNs show greatly enhanced activity and stability for a series of dye degradations. The performance enhancement is ascribed to their unique nanostructures, where mesoporous silica walls provide protection to the inner MnₓOᵧ nanoparticles and the small size of the manganese oxide nanoparticles greatly enhances the dye degradation activity.

1. INTRODUCTION

Hollow porous silica nanoreactors are well recognized as potential materials for drug delivery and energy storage because of their good thermal stability and environmental friendliness. Especially, hollow mesoporous silica nanoreactors (HMSNs) with small metal or metal oxide nanoparticles (NPs) inside their hollow cavities (M@HMSNs or MₓOᵧ@HMSNs) are considered as catalytic nanoreactors for various heterogeneous reactions, where mesoporous silica walls provide protection to the inner NPs with fast mass transportation, and the residence of small NPs inside hollow cavities prevent the inner NPs from leaching into the solution.

Besides the template-free synthetic methods for hollow nanospheres, the traditional templated methods to prepare M@HMSNs or MₓOᵧ@HMSNs either start with the metal or metal oxide NPs in microemulsion droplets onto which silica is deposited, or load functional NPs into presynthesized hollow silica nanoreactors. Although these two methods have achieved great progress, synthesis of HMSNs with small NPs (<2 nm) inside their cavities is still challenging in which the small size of functional NPs is crucial to obtain high catalytic efficiency by the maximum usage of active atoms.

Herein, we report a new synthetic method to simultaneously obtain hollow mesoporous silica nanoreactors and small MnₓOᵧ NPs (~1.6 nm) in their hollow cavities (MnₓOᵧ@HMSNs). The influences of synthetic parameters on their structures and reaction conditions on dye degradations are also studied in this work. In the synthesis, triple ligands instead of our previous reported double ligands are used to coordinate Mn ions to form negatively charged coordination complex networks, and the resulting negatively charged complex networks further combine with positively charged quaternized poly(2-vinylpyridine)-b-poly(ethylene oxide) (P2MVP₁₂₈-b-PEO₄₇₇) copolymers to form metal ion bound polymer micelles. After silica deposition onto micellar coronas and subsequent calcination, HMSNs (~30 nm) with ~1.6 nm MnₓOᵧ NPs inside their cavities (~15 nm) are obtained. Scheme 1 shows the representative synthetic procedure for
2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization of Mn$_x$O$_y$@HMSNs. To synthesize HMSNs with Mn$_x$O$_y$ NPs inside their cavities, the key process is to form Mn ion bound polymer micelles. By mixing their corresponding Mn$^{2+}$, L$_3$ ligand, and positively charged copolymer aqueous solutions, Mn ion-containing micelles are obtained. As shown in Scheme 1, one Mn$^{2+}$ ion will coordinate with four carboxylate groups, resulting in two net negative charges for each coordination center. Since one L$_3$ molecule, a compound with three dipicolinic acid groups grafted on a benzene ring, has six carboxylate groups, the molar ratio of Mn/L$_3$ is set to 1.5/1.0. Each quaternized P2MVP$_{128}$-b-PEO$_{477}$ molecule (level of quaternization is $\sim$90%) will roughly have $\sim$115 positive charges. To keep charge balance, the ratio of polymer/L$_3$/Mn should be set to 1/38.3/57.5 to obtain stable micelles. Following silica deposition through the hydrolysis of tetramethyl orthosilicate (TMOS) and calcination will give Mn$_x$O$_y$@HMSNs. During the synthesis, other synthetic parameters such as pH values, TMOS/Mn ratios, and calcination temperatures are also required to be controlled to obtain small Mn$_x$O$_y$ NP integrated hollow mesoporous silica nanoreactors.

Figure 1 demonstrates transmission electron microscopy (TEM) images, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images, X-ray diffraction (XRD), and energy-dispersive spectrometry (EDS) studies of Mn$_x$O$_y$@HMSNs synthesized at a pH value of 3.0, 4.5, 8.0, and 8.5. The EDS measurement in Figure 1d confirms the presence of Mn elements in HMSNs, suggesting the formation of amorphous Mn$_x$O$_y$ due to high dispersion. It is concluded that Mn$_x$O$_y$@HMSNs have the nanostructures of hollow silica nanospheres with small Mn$_x$O$_y$ NPs inside their cavities.

Figure 1a demonstrates the TEM image of Mn$_x$O$_y$@HMSNs synthesized at a pH value of 4.5, TMOS/Mn ratio of 180/1, and 400 °C calcination. Figure 1b shows the HAADF-STEM image, Figure 1c displays the XRD patterns, and Figure 1d presents the EDS measurement. Scale bars are 50 nm.

Figure S1 reveals that the Mn$_x$O$_y$@HMSNs have a whole size of ~29.2 nm with ~15.4 nm hollow cavities, and the size of inner NPs is ~1.6 nm. Although the XRD patterns of Mn$_x$O$_y$@HMSNs in Figure 1c only show SiO$_2$ diffractions (around 22.0 2θ°), the EDS measurement in Figure 1d confirms the presence of Mn elements in HMSNs, suggesting the formation of amorphous Mn$_x$O$_y$ due to high dispersion. It is concluded that Mn$_x$O$_y$@HMSNs have the nanostructures of hollow silica nanospheres with small Mn$_x$O$_y$ NPs inside their cavities.

TEM images of Mn$_x$O$_y$@HMSNs synthesized at different pH values are presented in Figure 2. The materials synthesized at a pH value of 3.0 (Figure 2a) do not exhibit hollow nanostructures, indicating the nonexistence of Mn ion bound polymer micelles. At such a low pH value, L$_3$ molecules will be protonated as the carboxylic acid, which decreases their coordination with Mn$^{2+}$ ions. As shown in Figure 2b–e, hollow nanospheres with small Mn$_x$O$_y$ NPs inside cavities can be obtained at a suitable pH range from 4.0 to 8.0. When the pH value reaches 8.5 (Figure 2f), hollow nanospheres are no longer observed. Although L$_3$ molecules are fully deprotonated at such a high pH value of 8.5, most Mn ions precipitate as metal hydroxides, prohibiting the formation of Mn ion bound micelles. The suitable pH range for the formation of metal ion-containing polymer micelles by triple ligands is wider than that by double ligands because triple ligands can form...
coordination complex networks, which further increases the coordination stability between L₃ and metal ions, resulting in a wider pH range for micelles formation.

Figure 3 shows Fourier transform infrared (FT-IR) spectra of Mn₃O₇@HMPSNs calcined at different temperatures, while peaks disappear in the red pattern in Figure 3, indicating the complete removal of ligands and polymers to obtain smooth and dense appearance in Figure 4 f, suggesting the collapse of pores in the silica walls. When the calcination temperature increases to 1000 °C, solid silica with a smooth and dense appearance is observed in Figure 4 f, certainly due to the collapse of hollow cavities.

To control the silica wall thickness, molar ratios of TMOS/Mn in the synthesis were investigated. Figure 5 and Table 1 present TEM images and the real Si/Mn ratios of Mn₃O₇@HMPSNs synthesized at different TMOS/Mn ratios, respectively.

Table 1. Real Mn Loadings and Size Analysis of Mn₃O₇@HMPSNs Synthesized with Different TMOS/Mn Ratios

| TMOS/Mn  | Mn loadings (wt %) | Si/Mn | whole size (nm) | wall thickness (nm) |
|----------|--------------------|-------|----------------|---------------------|
| 90/1     | 1.90               | 24.2  | 4.5            |
| 120/1    | 1.40               | 28.3  | 6.4            |
| 180/1    | 1.00               | 29.2  | 6.9            |
| 240/1    | 0.85               | 31.6  | 7.0            |
| 270/1    | 0.60               | 31.8  | 7.5            |
| 300/1    | 0.46               | 33.7  | 8.5            |

The starting ratios in the synthesis. Obtained by inductively coupled plasma-optical emission spectrometry (ICP-OES). Obtained by the statistics histograms of TEM images in Figure 5. All materials were synthesized at a pH value of 4.5 and a calcination temperature of 400 °C.
tively, while their corresponding size distributions are shown in Figure S3. As confirmed by Figure S, all materials have similar hollow nanostructures. Table 1 reveals that with TMOS/Mn ratios increasing from 90/1 (Figure S5a) to 300/1 (Figure S5f), the whole size increases from 24.2 to 33.7 nm, accompanied by a wall thickness from 4.8 to 8.5 nm. When TMOS/Mn ratios increase from 90/1 to 300/1, the real Si/Mn ratios increase from 47/1 to 19/1. Overall, the real ratios of Si/Mn are approximately half of the starting TMOS/Mn ratios. TMOS hydrolysis at a pH value of 4.5 is slow and requires 4 days to collect solids for calcination. Silica containing metal ion bound micelles will precipitate due to their high densities while those partially hydrolyzed and not fully polymerized remain in the solution and will be separated from the metal-containing solids by centrifugation, resulting in smaller real Si/Mn ratios in HMSNs.

N₂ adsorption–desorption isotherms and pore size distributions of various Mn₃O₄@HMSNs synthesized at different conditions are presented in Figure 6. As demonstrated in Figure 6a, type IV isotherms with distinct hysteresis loops are observed for all tested Mn₃O₄@HMSNs, confirming their mesoporous nanostructures. Moreover, the hysteresis loop of Mn₃O₄@HMSNs calcined at 90 °C is significantly smaller than those of materials calcined at 400 °C, confirming the collapse of mesopores in silica walls during high-temperature calcination. Those aggregation voids between nanospheres result in adsorption uptakes at T/Pₒ ~ 0.90, while inflections around T/Pₒ ~ 0.46 in the desorption branches are originated from the delay of N₂ evaporation from hollow voids blocked by the surrounding mesoporous walls.37–39 Figure 6b presents their pore size distributions. For those materials calcined at 400 °C, a large percentage of pore volume is ascribed to mesopores around 9–15 nm. The pores above 20 nm in Figure 6b are indexed to the aggregation voids between nanospheres. The literature revealed that the sizes of hollow cavities cannot be directly obtained from pore size distributions because the N₂ evaporation from hollow voids is blocked by the surrounding mesoporous pores in the silica walls.39 Therefore, the sizes of hollow voids of such materials can only be obtained from the size analysis of TEM images (Figures S1 and S3).

Table 2 presents textural properties of various Mn₃O₄@HMSNs. Brunauer–Emmett–Teller (BET) specific surface areas and pore volumes of these materials are around 93–382 m²/g and 0.38–0.88 cm³/g, respectively. The average pore diameters are around 9.6–25.2 nm. Due to the increased calcination temperature, the specific surface areas of Mn₃O₄@HMSNs decrease from 382 m²/g with calcination at 400 °C to 93 m²/g with calcination at 900 °C, and a similar trend is also observed for pore volumes. The significant decrease of BET specific surface area at 900 °C is certainly due to the collapse of pores at such a high calcination temperature. However, Mn₃O₄@HMSNs calcined at such a high temperature of 900 °C still have hollow nanostructures (Figure 4e) and their specific surface areas remain 93 m²/g, indicating their high thermal stability.

### 2.2. Dye Degradations over Mn₃O₄@HMSNs

As an illustration, degradations of a series of dyes with H₂O₂ are used to demonstrate the unique catalytic properties of Mn₃O₄@HMSNs. Methylene blue (MB), orange II, and orange G are the main groups of dyes in wastewater.40–44 and their removal in the presence of H₂O₂ over transition metal ions (Fenton process)45–49 is recognized as an efficient way to treat wastewater. However, the classical Fenton process is typically carried out in a narrow pH range (<4),47,49,50 and the redox metal ions require strict regulation due to their toxicity, limiting the wide use of Fenton process in wastewater treatment.51,52 Therefore, supported transition metal oxide catalysts are highly desired to decrease the release of metal ions to water.53,54 Among various transition metal oxides, manganese oxides are good candidates, especially due to their low toxicity.54 It has been reported in the literature that bicarbonate not only assists degradations of dyes with H₂O₂ but also maintains basic conditions needed to decrease the release of metal ions.52 In this study, a series of dye degradations with H₂O₂ with bicarbonate were studied.

MB degradations over Mn₃O₄@HMSNs with different ratios of Si/Mn are shown in Figure 7 and their corresponding UV–visible spectra are shown in Figure S4. The initial MB degradation rates decrease with the increasing TMOS/Mn ratios. As shown in Table 1, with keeping the same amount of catalysts in each experiment, the Mn loadings decrease with...
As shown in Figure 8, the highest efficiency for MB removal is achieved with MnO₃@HMSNs calcined at 400 °C. With the calcination temperatures increasing, the degradation efficiency over MnO₃@HMSNs decreases. As shown in Table 2, the higher the calcination temperatures, the smaller the BET specific surface areas and pore volumes. The increased BET surface areas and pore volumes are probably due to the increased wall thickness of MnO₃@HMSNs, which is consistent with previous reports.7,8,58 The increased BET surface areas and pore volumes might enhance the mass transfer rate of MB molecules and facilitate the reaction of MB with the active sites of MnO₃@HMSNs. The decreased BET surface areas and pore volumes are probably due to the decreased wall thickness of MnO₃@HMSNs, which is consistent with previous reports.7,8,58 The decreased BET surface areas and pore volumes might decrease the adsorption capacity of MnO₃@HMSNs for MB molecules and facilitate the reaction of MB with the active sites of MnO₃@HMSNs. Therefore, control experiments using Mn(CH₃COO)₂ are necessary.54

Figure 8 shows the XRD patterns of MnO₃@HMSNs calcined at different temperatures. Due to their high dispersions and low metal loadings, XRD patterns of MnO₃@HMSNs calcined at <900 °C show SiO₂ diffractions, and distinct diffractions of MnO₂ are only observed when the calcination temperature reaches 900 °C. Therefore, control experiments using Mn(CH₃COO)₂ are investigated. Figure S7 presents XRD patterns of various MnO₃@HMSNs calcined at different temperatures. Obviously, MnO₃@HMSNs calcined at 400 °C consists of Mn₃O₄ and Mn₂O₃, while those calcined at >400 °C only show Mn₂O₃ diffractions. Therefore, besides the influences of BET surface areas and pore volumes at different calcination temperatures, the different oxidation states of Mn element could also influence their dye degradation efficiency when the calcination temperatures of MnO₃@HMSNs are different.54

Figure 9 presents MB degradations under different reaction conditions: solution volume, 24 mL; 50 mg/L MB; and 25 °C. If present, MnO₃@HMSNs 0.0100 g, 60 mM H₂O₂, and 25 mM NaHCO₃. MnO₃@HMSNs were prepared with a pH value of 4.5, and calcination temperature of 400 °C.

UV–visible spectra are shown in Figure S8. Here, MnO₃@HMSNs with a TMOS/Mn ratio of 90/1, pH value of 4.5, and calcination temperature of 400 °C are selected due to their high efficiency (Figure 7). As shown in Figure 9, the MB decolorization over MnO₃@HMSNs without H₂O₂ and NaHCO₃ (square curve) is negligible. Without MnO₃@HMSNs, MB decolorization with NaHCO₃ and H₂O₂ (pentagonal curve) is <5% and is consistent with an earlier study,55 where a low concentration of NaHCO₃ could not activate H₂O₂ without redox metal ions. Moreover, the result of (NaHCO₃ + H₂O₂) suggests that either H₂O₂ or percarbonate (HCO₃⁻) does not directly degrade MB, where percarbonate is produced through the equilibrium of H₂O₂ and bicarbonate.52,56

As shown in the triangle curve of Figure 9, the MB degradation with H₂O₂ over MnO₃@HMSNs is roughly 10%, while it is greatly enhanced with the addition of 25 mM NaHCO₃ (pentagram curve). According to the previous reports,7,8,58 the bicarbonate will react with hydroxyl radicals to produce relatively stable carbonate radicals that are more available than hydroxyl radicals for MB dye degradations with
enhanced efficiency. Further studies on the effect of NaHCO₃ concentrations on the MB degradation are shown in Figure S9, and their original UV–visible spectra are illustrated in Figure S10, where the MB degradation can reach >99% in the initial 10 min with the presence of 100 mM NaHCO₃. Figures S11 and S12 present the effect of catalyst weights on MB degradations over Mn₃O₄@HMSNs and their original UV–visible spectra, respectively. Figures S13 and S14 show the effect of H₂O₂ concentrations on MB degradations over Mn₃O₄@HMSNs and their original UV–visible spectra, respectively. Obviously, the MB degradation efficiency increases with increasing catalyst weight or H₂O₂ concentration.

**Figure 10** presents effects of radical scavengers on MB degradations over Mn₃O₄@HMSNs, and their original UV–visible spectra are shown in Figure S15. The radicals have been well accepted as the key reactive species during heterogeneous Fenton-like MB degradations with H₂O₂.⁵²,⁵⁹ and ascorbic acid is well known as a popular radical scavenger.⁶⁰ As shown in Figure 10 (the top curve), the addition of t-butanol radicals will significantly inhibit the MB degradation, confirming the presence of radicals during MB degradation over Mn₃O₄@HMSNs.

The effect of the addition of t-butanol on MB degradation is shown in Figure 10 (the blue curve). Although t-butanol is well known as a powerful scavenger for hydroxyl radicals (·OH),⁶¹ t-butanol does not show any inhibition effect at the concentration of 60 mM and will promote MB degradation at a higher concentration (Figures S16 and S17), suggesting that hydroxyl radical does not directly degrade MB. It is speculated that the promoting effect of t-butanol at high concentrations is due to the relatively longer lifetime of t-butanol radicals, which makes the t-butanol radicals more available for MB degradation than hydroxyl radicals, resulting in a promoting effect. In contrast, the addition of p-benzoquinone will significantly decrease the MB degradation rate (the purple curve), indicating an important role of superoxide radicals (O₂⁻).⁶² However, benzoquinone does not completely inhibit the MB degradation, suggesting that there are other reactive species responsible for MB degradation. As shown in Figures S9 and S10, bicarbonate greatly promotes MB degradations with H₂O₂, indicating the important role of carbonate radical (CO₃²⁻) on MB degradations.⁵² It is concluded that carbonate radicals and superoxide radicals play important roles in MB degradation over Mn₃O₄@HMSNs, where carbonate radicals are produced by the reaction of hydroxyl radicals with HCO₃⁻ anions, and the superoxide radicals are generated by further reaction of carbonate radicals with H₂O₂.⁵²

**Figure 11** presents degradations of orange II, orange G, rhodamine 6G, methyl orange, new coccine, and MB over Mn₃O₄@HMSNs. As shown in Figure 11a and their original UV–visible spectra in Figure S18, in the presence of 25 mM NaHCO₃, decolorizations of MB, orange II, orange G, and rhodamine 6G reach 94.7% at 60 min, 94.8% at 45 min, 92.4% at 120 min, and 92.5% at 300 min, respectively. In contrast, the decolorizations of new coccine and methyl orange only approach 76.3% at 300 min and 79.9% at 300 min, respectively. However, as shown in Figure 11b and their original UV–visible spectra of Figure S19, obvious improvements of degradations of new coccine and methyl range can be observed in the double concentration of 50 mM NaHCO₃. Decolorization (76.3%) of new coccine can be achieved within 90 min while an 85.1% of decolorization of methyl orange is observed at 30 min. Here, MB and rhodamine 6G represent cationic dyes, while orange G, new coccine, orange II, and methyl orange are examples of anionic dyes, showing wide adaptability of Mn₃O₄@HMSNs for degradations of various dyes, and this unique property is originated from hollow mesoporous nanostructures with active NPs inside cavities.

The control Mn₃O₄/SiO₂ with a similar Mn loading of 1.8 wt % was prepared for comparison. The synthetic procedure of Mn₃O₄/SiO₂ is described in the Supporting Information, and the comparison of a series of dye degradations over Mn₃O₄@HMSNs and Mn₃O₄/SiO₂ is summarized in Table S1. As
3. CONCLUSIONS

In this work, MnOx@HMSNs were synthesized by the deposition of silica onto manganese ion bound polymer micelles and subsequent calcinations, and the effects of synthetic parameters on the structures are studied in detail. Relevant characterizations confirm that these nanoreactors consist of hollow mesoporous silica nanospheres with small manganese oxide nanoparticles inside their cavities. The MnOx@HMSNs can be synthesized in a wide pH range from 4.0 to 8.0, and hollow nanostructures can be maintained in the calcination temperature range from 400 to 900 °C. Moreover, the thickness of silica walls and the Mn loadings can be adjusted through adjusting the starting TMOS/Mn ratios. The MnOx@HMSNs synthesized with a TMOS/Mn ratio of 90/1, pH value of 4.5, and calcination temperature of 400 °C display greatly enhanced degradations for a series of cationic and anionic dyes with H2O2 which is ascribed to their unique hollow mesoporous nanostructures with small MnOx NPs in hollow cavities. We believe that the synthetic methodology can be extended to synthesize other materials and such a type of material will find more applications in wastewater treatment.

4. EXPERIMENTAL SECTION

4.1. Chemicals. tert-Butanol (≥99%), alcohol (EtOH, 99.7%), manganese(II) nitrate (50 wt % aqueous solution), and nitric acid (HNO3, 65–68%) were purchased from the Shanghai Chemical Reagent Company. Tetramethyl orthosilicate (TMOS, 99.0%), methylene blue trihydrate (MB, 82%), and hydrogen peroxide (H2O2, 30%) were purchased from Adamsa Reagent. Methanol (CH3OH, 99.5%) was purchased from Sinopharm Chemical Reagent Co., Ltd. New coccine (75.0%) was purchased from Sigma-Aldrich. Manganese acetate (Mn(CH3COO)2, 98%), rhodamine 6G (95%), and methyl orange (96%) were purchased from Aladdin. Orange II sodium salt (>85%), p-benzoquinone (99.0%), and silicon dioxide (99.5%) were purchased from Macklin. Orange G (96%) was purchased from Merery. 1-Acetic acid was purchased from TCI (Shanghai) Development Co., Ltd. Synthesis of quaternized poly(2-vinylpyridine)-b-poly(ethylene oxide) (positively charged P2MVP128-b-PEO177, Mw/Mn = 1.1, Mw = 34.5 kg mol−1 level of quaternization is ∼90%) is described in the previous work.29,30,63 The 1,3,5-tris(2,6-dicarboxypyridin-4-yl)methyl]benzene ligands (L3) were synthesized according to the literature.31

4.2. Synthesis of MnOx@HMSNs. In a typical synthesis, 360 μL of 0.087 mM positively charged P2MVP128-b-PEO177 aqueous solution, 360 μL of 5.0 mM Mn(NO3)2 aqueous solution, and 240 μL of 5.0 mM L3 aqueous solution were mixed with 9.04 g of deionized water at room temperature in a 20 mL flask with magnetic stirring at 200 rpm, where the molar ratio of polymer/L3/Mn = 1 is equal to 1/38.3/57.5. The pH value of the above solution was adjusted to 4.5 (the studied pH range was from 3.0 to 8.5) using diluted nitric acid and sodium hydroxide aqueous solution. The obtained solution was further stirred for no less than 2 h to achieve the formation of uniform micelles. After that, 0.2845 g of 416 mM TMOS methanol solution (the molar ratio of TMOS/Mn = 90/1, the studied ratio range was from 90/1 to 300/1) was added into the flask. The resulting mixture was stirred for 2 days at 200 rpm. During the process, white solid precipitates can be observed around 24–48 h. The mixture was left untouched for another 4 days to complete silica polymerization. The white solids were collected.
by centrifugation and washing with water/ethanol several times. Finally, the solids were dried in an oven at 55 °C and further calcined at 400 °C (the studied range was from 400 to 1000 °C) in a muffle furnace for 3 h to obtain Mn\textsubscript{4}O\textsubscript{y}@HMSNs.

4.3. Characterizations. High-resolution transmission electron microscopy (HRTEM) images of various samples were obtained using a JEOl 2100 transmission electron microscope operated at 200 kV with an energy-dispersive spectrometer (EDS). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were obtained using a Talos F200X microscope operated at 200 kV in the STEM model. The thermal property of the samples was measured using a PerkinElmer Pyris Diamond thermogravimetric analyzer (TG/DTA) in the temperature range from 40 to 1200 °C at a heating rate of 10 °C/min with a gas flow rate of 100 mL/min in an air atmosphere. The Fourier transform infrared (FT-IR) spectra of the samples were recorded at a Nicolet Nexus 670 spectrophotometer. The metal loadings of samples were determined by an Agilent 725 inductively coupled plasma optical emission spectrometer (ICP-OES). Brunauer–Emmett–Teller (BET) specific surface areas, pore size distributions, and the adsorption–desorption isotherms of various materials were measured by N\textsubscript{2} adsorption at 77 K using an IQ automatic specific surface area and porous physical adsorption analyzer. UV–visible measurements were carried out using a UV-1800 spectrophotometer and pure water as the background.

4.4. Dye Degradations over Mn\textsubscript{4}O\textsubscript{y}@HMSNs. 4.4.1. Dye Degradations over Mn\textsubscript{4}O\textsubscript{y}@HMSNs. In a typical experiment, 4.00 mL of 300 mg/L MB aqueous solution, 50.4 mg of NaHCO\textsubscript{3} 144.0 μL of 30.0 wt % H\textsubscript{2}O\textsubscript{2}, and 19.86 g of deionized water were charged into a 30 mL flask with magnetic stirring at 650 rpm under room temperature. A portion of 0.0100 g of Mn\textsubscript{4}O\textsubscript{y}@HMSNs synthesized at different synthetic parameters was added into the above solution. During the reaction process, 1.0 mL of reaction mixtures were sampled at different time intervals and diluted 20 times by deionized water for UV–visible measurement.

The procedures of degradations of new coccine, methylene orange, orange II, orange G, and rhodamine 6G are the same as those of methylene blue degradations except that Mn\textsubscript{4}O\textsubscript{y}@HMSNs, XRD patterns, original UV–visible spectra and the effect of reaction conditions on MB degradations over Mn\textsubscript{4}O\textsubscript{y}@HMSNs (PDF)

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00171.

More synthesis of Mn\textsubscript{4}O\textsubscript{y}/SiO\textsubscript{2}, size histograms of various Mn\textsubscript{4}O\textsubscript{y}@HMSNs, XRD patterns, original UV–visible spectra and the effect of reaction conditions on MB degradations over Mn\textsubscript{4}O\textsubscript{y}@HMSNs (PDF)

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Notes

The authors declare no competing financial interest.

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