Facile synthesis of manganese oxide loaded hollow silica particles and their application for methylene blue degradation

Qingnan Meng, Siyuan Xiang, Wei Cheng, Qiaonan Chen, Pengfei Xue, Kai Zhang, Hongchen Sun, Bai Yang

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A B S T R A C T

A facile poly acrylic acid (PAA) soft templating method was developed to fabricate manganese oxide loaded hollow silica particles (MHSPs). The synthesis involves PAA-Mn aggregation to form spherical particles and silica coating layer formation on the outer surface of the particles. Subsequent calcination in air at 500 °C removes the polymer inside the particles, and hollow silica spheres with trapped metal oxide particles are thus formed. The PAA traps the Mn ions and forms aggregates which template the silica shell formation in this process. The Mn content and the structure of the MHSPs can be tuned by changing doses of the Mn salt initially added. Moreover, decomposition of PAA during calcination endows high surface areas of the MHSPs. Catalytic oxidation of methylene blue (MB) with H2O2 was tested on the MHSPs. The results show that the MHSPs with hollow structure and high surface areas enhance the catalytic activity compare to the corresponding manganese oxide solid particles (MSPs). This strategy can also be used to synthesize other metal oxides (such as MgO and NiO) loaded hollow silica particles.

1. Introduction

Manganese oxides are known to be active catalysts for numerous chemical processes such as organic synthesis [1–4], CO and NOx removal from waste gas [5,6], dye decomposition [7–12], and water oxidation [13]. The catalytic activity of manganese oxides has been attributed to the capability of Mn to change its valence states and to store and release oxygen selectively from its various oxide crystalline lattices [2]. Up to now, great efforts have been made to enhance the catalytic performance of manganese oxides by carefully controlling their morphology and porosity [6,10,14,15]. However, the unsupported catalysts always undergo sintering during the reactions especially at elevated temperature [16]. Immobilizing manganese oxides onto an inert support seems to have more practical significance because they can hinder the aggregating and sintering of neighboring particles and expose more active sites toward the reactants [17–19].

Recently, hollow silica particles are found to be promising catalyst supports due to their low toxicity, low density, and high chemical and mechanical stability [20]. The silica shell, which allows small molecules to diffuse in and out, serves as a shield for the embedded catalyst inside to be leached out during solution reactions and prevents their aggregation and sintering [21,22]. In addition, via controlling the porosity of the silica shell with an appropriate silane coupling agent, size-selectivity toward reactants can also be improved [3,23,24]. Two strategies are commonly used to incorporate catalyst into hollow silica particles [25–33]. In the first one, hollow silica particles are prepared first and then combined either directly with the preformed catalyst (such as metal particles and enzyme) [25,26] or metal ions via impregnation, followed by converting them into a desired form (e.g., metal or metal oxide) [27–30]. Unfortunately, this method often leads to locating the catalyst outside the silica shell [28]. Moreover, the impregnation needs to be repeated several times in order to achieve the desired precursor loadings, and the catalyst often blocks the pores on the silica shell, leading to reduction in the overall surface area [29,30]. In the second one, the catalyst (always nanoparticles) is prepared first, and then, silica shell is formed outward [23,31–33]. Although the structures of the catalyst particle can be well controlled, the preparation process seems to be very tedious [32]. Multi-steps are needed for coating the catalyst particles and selectively removing of the template layer between the catalyst core and the silica shell [23].

Our interest is to develop a facile synthesis method without the drawbacks mentioned above to fabricate manganese oxide loaded hollow silica particles with high surface areas for catalysis. We employed a poly acrylic acid (PAA) soft templating method, and the synthesis process is schematically illustrated in Scheme 1. It has been reported that PAA forms aggregate particles in an
ammonia–ethanol solution, which provides template for the synthesis of hollow silica particles [34,35]. In the present work, we found that PAA could chelate Mn ions and stabilize them in the ammonia solution. By dropping the solution into ethanol, we obtained PAA-Mn aggregate particles. We then coated the as-prepared particles with a layer of silica via in situ hydrolysis of TEOS. After collecting the PAA-Mn@SiO2 particles by centrifugation and calcining them at 500 °C in air, the polymer was removed, and the trapped manganese ions were transformed into manganese oxide inside the silica shell.

Our method has the following features: (1) the metal oxides are mainly located inside the hollow silica particles. This is because the metal ions are trapped by the PAA aggregate template; (2) the metal oxide particle and the hollow structure form simultaneously, so multi-steps as in the other methods [32] are no longer needed; (3) the Mn content as well as the morphology of MHSPs can be easily tuned by changing the initial dose of the Mn salt; and (4) more importantly, the released gas molecules such as H2O, CO2 and CO during the PAA decomposition facilitate the porous structure formation of the MHSPs. We tested the MHSPs as catalyst for catalytic oxidation of methylene blue (MB), an important reaction for wastewater treatment [8]. The MHSPs showed superior catalytic activity than the corresponding manganese oxide solid particles (MSPs) catalyst obtained without silica shell protection and a porous Mn3O4 nanorod catalyst reported in the literature [10].

2. Experiment

2.1. Chemicals

Tetraethoxysilane (TEOS, 27 wt%), ammonia solution (28%), absolute ethanol (99.5%), Mg(Cl)2·6H2O, NiCl2·6H2O, and H2O2 were all purchased from Beijing Chemical Factory. Methylene blue trihydrate (MB·3H2O) and Mn(CH3COO)2·4H2O were purchased from Sinopharm Chemical Reagent Co. Poly (acrylic acid) (PAA, M.W. = 1800) was obtained from Aldrich. Deionized water with an electrical resistance of 18 MΩ cm was made in the lab using Millipore and used in all experiments.

2.2. Preparation of MHSPs

In a typical synthesis, a certain amount (0.1, 0.2 and 0.3 mmol) of Mn(CH3COO)2 was first dissolved in 0.2 mL water and then injected into 2 mL ammonia solution containing 120 mg PAA under sonication. Next, the as-prepared solution was dropped into 90 ml absolute ethanol under vigorous magnetic stirring and then continued to stir for at least 15 min to form a stable colloidal dispersion. The silica coating was performed by adding 0.75 mL of TEOS into the colloidal dispersion. The reaction was promoted by ultrasound for 2 h (40 KHz, 150 W) while keeping the reaction temperature below 35 °C by changing water in the sonicator. The silica coated particles were collected by centrifugation (8500 rpm, 15 min), washed with absolute ethanol, and sequentially dried at 60 °C. Finally, MHSPs were obtained by calcination at 500 °C for 5 h. MHSPs-n was used to denote the manganese oxide loaded hollow silica particles prepared with different amount of manganese acetate added in the first step (n = 1, 2, 3 for 0.1, 0.2, and 0.3 mmol Mn(CH3COO)2 added).

By changing the Mn(CH3COO)2 solution with Mg(Cl)2 or NiCl2 solution (both containing 0.2 mmol metal salt), MgO and NiO loaded hollow silica particles (MgO@HSPs and NiO@HSPs) were synthesized via the same method.

2.3. Catalytic oxidation of methylene blue (MB) with H2O2

The catalytic oxidation of MB with H2O2 was chosen as a modal reaction to test the catalytic activity of the MHSPs. The catalytic reaction was carried out in a 250 mL glass flask that contains 50 mL MB aqueous solution (100 mg/L), 50 mL distilled water, and 10 mg MHSPs. After adding 20 mL 30 wt% H2O2 aqueous solution, the mixture was allowed to react at 80 °C with continuous stirring. For a given time interval (10, 20 or 30 min), 1 mL of the mixture solution was taken out and put into a volumetric flask and then quickly diluted with distilled water to 25 ml for the UV–Vis measurement. And the degradation of the MB was evaluated as the method described elsewhere [8,10].
2.4. Characterization

Transmission electron microscopy (TEM) images were obtained on a Hitachi H-800 electron microscope at an acceleration voltage of 200 kV with a CCD camera. UV–Vis spectra were recorded on a Perkin–Elmer Lambda 800 UV–Vis spectrophotometer. Fourier transform infrared (FTIR) spectra were obtained on a Bruker VERTEX 80 V using KBr pellets. The particle sizes of the PAA-Mn aggregate particles were collected on a Zetasizer NanoZS (Malvern Instruments). X-Ray diffraction (XRD) analysis was performed by X-ray diffraction (XRD) (Model Rigaku Ru-200b), using a nickel-filtered CuK\textalpha\ radiation. X-ray photoelectron spectroscopic (XPS) analysis was done on an ESCALAB 250 spectrometer. Thermogravimetric (TGA) curves were obtained on a TA Instruments Q-500 thermogravimetric analyzer. N\textsubscript{2} adsorption–desorption measurements were conducted on a Micromeritics ASAP 2010 instrument. Pore volume and the specific surface area were measured by using BJH and Brunauer–Emmett–Teller (BET) method.

3. Results and discussion

3.1. Fabrication of PAA-Mn aggregate particles and sequential coating of silica

Generally, when Mn salt (Mn(CH\textsubscript{3}COO)\textsubscript{2}) is added to an ammonia solution, Mn\textsuperscript{2+} ions react with OH\textsuperscript{−} and form Mn(OH)\textsubscript{2}. Then, the Mn(OH)\textsubscript{2} is partially oxidized to MnOOH in the ambient air which quickly precipitates out from the solution [36]. However, when PAA molecules are present in the ammonia solution, a clear brown solution is formed after adding Mn salt (see Fig. S1). Because of the strong interactions between the COO\textsuperscript{−} groups of the PAA chains in the ammonia solution by forming stable ion pair, the Mn ions can reduce the electrostatic repulsion between the COO\textsuperscript{−} groups of the PAA-Mn aggregate particles is stabilized by the electrostatic repulsion between the negative charged COO\textsuperscript{−} groups of the partially deprotonated PAA chains, which makes the solution stable for several days [34].

The average size and the size distribution of the aggregate particles formed with different doses of Mn salt were measured by DLS (Fig. 1). Without the Mn salt addition, the average size of the aggregate particles is 196.9 nm (Fig. 1a, and the values are obtained directly by the measurement equipment of Zetasizer NanoZS). The average size increases from 259.8 nm to 359.1 nm and 586.2 nm as the dose of Mn salt increases from 0.1 mmol to 0.3 mmol. The size distribution curves (Fig. 1b) show that without Mn salt added, the peak of the size distribution curve is maximized at 157.9 nm. When Mn salt was added together with the PAA, the peaks of the distribution curve shift to larger values. The corresponding polydispersity indexes (PDI) of the aggregate particles (Fig. 1a) also increase remarkably compared to that of the counterpart formed by PAA alone. This suggests that the aggregate particles become more polydisperse by adding the Mn salt into the PAA ammonia solution. From these results, we can conclude that the Mn ions can reduce the electrostatic repulsion between the PAA chains in the ammonia solution by forming stable ion pair with the COO\textsuperscript{−} group, which leads to the formation of larger aggregate particles.

A typical TEM image of the as-prepared PAA-Mn aggregate particles (with 0.2 mmol Mn) is shown in Fig. 2a. Most of the aggregate particles are spherical with a nice smooth surface. Thanks to the presence of ammonia in the colloid solution, the PAA-Mn aggregate particles can be directly coated with a silica layer by adding TEOS into the colloid solution. As we can see in Fig. 2b, after silica coating, the surfaces of the particles become rougher than those seen in Fig. 2a. From the corresponding EDX mapping images in Fig. 2c, we can conclude that a silica layer has been successfully coated onto of the PAA-Mn aggregate particles, while the Mn ions are trapped mostly inside. The driving force for the silica deposition on the PAA-Mn aggregate particles is the interaction of amminated carboxylic groups on the aggregate particle surface and the silanol groups on the partially hydrolyzed TEOS species [34]. The silica coated PAA-Mn aggregate particles (PAA-Mn@SiO\textsubscript{2}) were separated from the solution by centrifugation and washed with ethanol. Unlike the previous work [34,35], the crucial part of this synthesis is to wash the PAA-Mn@SiO\textsubscript{2} particles with ethanol rather than with water. The reason is that water dissolves PAA-Mn aggregates and the porous silica shell formed by the Stöber method allows the dissolved PAA-Mn complex to diffuse out and lost [34]. Removal of the dissolved PAA-Mn complex leads to an unstable silica shell.

3.2. Formation of MHSPs and their characterization

Calcination of the PAA-Mn@SiO\textsubscript{2} particles at 500 °C in air removes the organic components and oxidizes the Mn ions to Mn oxides, and MHSPs are formed. The removal of PAA is confirmed by FTIR spectroscopy (Fig. 3). In the spectrum of the PAA-Mn aggregate particles (line a), the strong peak at 1713 cm\textsuperscript{−1} is characteristic C=O stretching vibrations of the protonated carboxylate groups. The peaks at 1453 cm\textsuperscript{−1}, 1555 cm\textsuperscript{−1}, and 1406 cm\textsuperscript{−1} are

![Fig. 1](image-url) (a) The average diameter and PDI (polydispersity indexes) of PAA-Mn aggregate particles with different dose of Mn salt and (b) the corresponding size distribution curves.
due to CH₂ and carboxylate (COO⁻/COO⁻) groups, corresponding to the CH₂ bending, asymmetric and symmetric C—O stretching of the COO⁻/COO⁻ group, respectively [33]. For the PAA-Mn@SiO₂ particles (line b), new peaks around 1103 cm⁻¹, 799 cm⁻¹, and 466 cm⁻¹ arise, which belong to the Si—O—Si asymmetric stretching and symmetric modes and the bending of Si—O bond [36]. After calcination in air, nearly all the peaks belong to PAA disappear, while those belonging to SiO₂ still retain (line c). The formation of manganese oxides is confirmed by the stretching vibrations of Mn—O—Mn at 616 cm⁻¹ [38].

TGA measurements are carried out to further understand the calcination process in air (Fig. S2). At temperatures below 150 °C, only a small amount of weight loss (about 3%) was observed, corresponding to desorption of water and ammonia. The main weight loss occurred between 200 and 400 °C due to the decomposition of PAA and the generation of the manganese oxides. The actual Mn contents in the MHSPs were determined by ICP, which increases from 15.8% to 32.3% with increasing the Mn salt (Table 1).

TEM images of the MHSPs are shown in Fig. 4. For MHSPs-1 (Fig. 4a), hollow spheres are obtained. The hollow sphere size of this material is in the range of 50–200 nm with the shell thickness of 13–17 nm. High-magnification TEM image given in Fig. 4b clearly shows the existence of small manganese oxide particles inside the hollow silica spheres (the circles in Fig. 4b). For MHSPs-2 (Fig. 4c), most of the hollow particles are between 85 and 250 nm. The shells of the particles become coarser and the thickness slightly increased (20–25 nm). Solid cores can be seen inside most of the hollow spheres. The size of the core particle is smaller than the inner diameter of the shell, and there is void in between (see Fig. 4c). Selected-area electron diffraction (SAED) patterns confirm the crystal nature of the core particle corresponding to Mn₃O₄ [38]. With the Mn salt dose increasing, the overall size and the shell thickness of the MHSPs-3 are further increased to 200–400 nm and 30–45 nm, respectively (Fig. 4d). The rattle-type structure is kept, and the shape of the core becomes more irregular.

The structure transformation from hollow to rattle-type correlates with the Mn loading. It is understood from the TEM images (Fig. 4c) that the Mn ions initially are uniformly distributed in the PAA aggregates. During calcination, the manganese oxide crystals nucleate and grow on the silica shell. The morphology of

| Table 1  |
|----------|----------|----------|----------------|----------------|
| Product code | Particle size (nm) | Mn content (%) | Mn₃O₄ crystal size (nm) | BET Surface area (m² g⁻¹) | Pore volume (cm³ g⁻¹) |
| MHSPs-1 | 50–200 | 15.8 | 8.4 | 298.2 | 0.61 |
| MHSPs-2 | 85–250 | 27.4 | 11.9 | 217.4 | 0.53 |
| MHSPs-3 | 200–400 | 32.3 | 13.5 | 145.4 | 0.33 |

* The MHSPs-1, MHSPs-2 and MHSPs-3 is the product obtained by adding 0.1, 0.2 and 0.3 mmol Mn salt.

* Mn content is measured using ICP.

* Mn₃O₄ crystal size is calculated by the Scherrer equation based on the (211) patterns.

* Estimated from the single-point amount adsorbed at P/P₀ = 0.98.
the product still looks like pure hollow particles when the Mn precursor content is low (such as MHSPs-1). With increasing the Mn precursor content (MHSPs-2 and 3), more manganese oxide particles are formed and they agglomerate into small balls in the interior space of the hollow particles [39].

XRD patterns of the MHSPs are shown in Fig. 5. The diffraction pattern of the amorphous silica is characterized by a broad peak centered at 2\(\theta\) = 23.6\(^\circ\). In addition to the amorphous silica, weak peaks at 2\(\theta\) = 36.0\(^\circ\), 44.4\(^\circ\), and 59.9\(^\circ\) are observed in the sample of MHSPs-1, which can be assigned to the crystal planes (211), (220) and (224) of hausmannite Mn\(_3\)O\(_4\) (JCPDS 80-0382). As the Mn content is increased, the above peaks become sharper, and more peaks of hausmannite Mn\(_3\)O\(_4\) can be visualized. Based on the (211) XRD patterns, the crystal sizes are calculated by the Scherrer equation [38] (Table 1). The results show that the grain size increased from 8.4 to 13.5 nm as the Mn content increases.

The surface structure of the MHSPs can be obtained from XPS data. The Mn 2p\(_{3/2}\) binding energies of all three MHSPs are around 642.1–642.4 eV (Fig. 6), which shift to higher energies compared to the standard Mn 2p\(_{3/2}\) binding energies of Mn\(_3\)O\(_4\) [36]. This could be attributed to the presence of Mn\(^{4+}\) species in the MHSPs according to the literature (641.3–641.4 eV) [2]. However, the content of the Mn\(^{4+}\) contained phase (such as MnO\(_2\)) is low, and the phase could not be detected by XRD.

N\(_2\) adsorption-desorption isotherms of the MHSPs samples (Fig. 7) exhibit typical type-IV isotherms, indicating the presence of mesopores. H3-type hysteresis loops at the relative pressure (P/P\(_0\)) above 0.45 are present for each sample, suggesting adsorption of N\(_2\) molecules in the hollow voids [40]. The BET surface areas are measured to be 298.2, 217.4, and 145.4 m\(^2\) g\(^{-1}\) for MHSPs-1, MHSPs-2, and MHSPs-3, respectively (see Table 1). The surface areas are much larger than the reported values of the hollow silica particles based catalysts in which the core template is removed by dissolution [35]. The high surface areas of MHSPs are attributed to the additional pore generation due to the released gases during the PAA decomposition and the structure formation.

![Fig. 4. TEM images: (a) MHSPs-1, (b) An enlarged image of the silica shell of MHSPs-1 showing the manganese oxide particles inside the hollow silica particles, (c) MHSPs-2, insert is the SAED of the core area, and (d) MHSPs-3.](image)

![Fig. 5. XRD patterns of the MHSPs.](image)

![Fig. 6. XPS spectra for Mn 2p peaks of MHSPs.](image)
To further evaluate the protection of the silica shell on the inside manganese oxide particle, a control experiment was conducted by directly calcining the PAA-Mn aggregate particles (as shown Fig. 2a). As we can see from Fig. 8a, we obtained irregular manganese oxide solid particles (MSPs) without silica coating. This indicates that without the silica shell, PAA aggregate particles cannot survive sintering of the manganese oxide particles. As a consequence, the corresponding XRD pattern of the MSPs gives much sharper and more intense diffraction peaks which can be perfectly indexed to bixbyite α-Mn$_2$O$_3$ (JCPDS 41-1442) (Fig. 8b). The Mn 2p$_{3/2}$ binding energy of the MSPs is 641.4 eV (Fig. S3), indicating the absence of the Mn$^{4+}$ species on the surface [12]. The valence states of the manganese oxides are determined by the availability of O$_2$ during calcination, since the silica shell can reduce the availability of O$_2$ during the burning of PAA, which creates an oxygen-deficient inner environment [2] and leads to the formation of Mn$_3$O$_4$ phase. On the contrary, without the silica shells, O$_2$ molecules in air can diffuse freely and Mn$_3$O$_4$ phase is consequently formed. However, the reason for presence of Mn$^{4+}$ in MHSPs is not clear. They may result from the oxidation of the adsorbed Mn ions (Mn$^{2+}$ and Mn$^{3+}$) on the silica shells. Moreover, the BET surface area of the MSPs is only 18.3 m$^2$ g$^{-1}$, indicating that the silica shell is indispensable for the high surface areas of MHSPs.

3.3. Catalytic performance of MHSPs

The manganese oxides such as Mn$_3$O$_4$, Mn$_2$O$_3$, and MnO$_2$ have been reported to be good oxidation catalysts [7–12]. The as-prepared MHSPs may also be good oxidation catalysts. We chose MB oxidation with H$_2$O$_2$ as a model reaction to examine the catalytic performance of MHSPs. Fig. 9a is the typical UV–Vis absorption spectra of MB taken at different reaction time (t = 0, 10, 20, 30, 40, and 60 min) using MHSPs-2 as a catalyst and H$_2$O$_2$ as an oxidant. The spectrum at t = 0 was recorded for the MB solution before the reaction. To maintain the same total volume as in the case of reaction solution, we added the same volume of H$_2$O instead of H$_2$O$_2$. Similar to the literature [8,10], four characteristic absorption peaks of MB are observed at 245, 292, 614, and 712 nm.

Fig. 7. Nitrogen-adsorption/desorption isotherms of MHSPs.

Fig. 8. (a) TEM image of manganese oxide particles obtained without the silica shell protection (other parameter the same to MHSPs-2) and (b) its corresponding XRD pattern.

Fig. 9. (a) Typical UV–Vis absorption spectra of the MB solution recorded at different time during the catalytic oxidation experiment (MHSPs-2 was used as the catalyst.) and (b) Time profiles of MB degradation: MHSPs-1, 2, and 3 + MB (line a, b and c); H$_2$O$_2$ + MB (line d); MHSPs-1, 2, and 3 + H$_2$O$_2$ + MB (line e, f and g); MSPs (shown in Fig. 8a) + H$_2$O$_2$ + MB (line h).
664 nm in the spectrum. When MHSPs-2 and H$_2$O$_2$ were added, the reaction starts at 80 °C. The absorption peak of the MB at 664 nm decreases more than 50% after only 10 min at 80 °C and the peak position undergoes blueshift, indicating that catalytic degradation of MB has taken place. The other two peaks at 245 and 292 nm are masked by the strong absorption of H$_2$O$_2$ below 300 nm. As the reaction proceeding, the peak continuously declines, and finally, the solution becomes colorless and the 664 nm band disappears (Fig. 9a), suggesting a complete degradation of MB.

The degree of degradation of MB can be expressed as $(I_0 - I_t)/I_0 \times 100\%$, in which $I_0$ is the absorption intensity at 664 nm for $t = 0$ and $I_t$ is the absorption intensities at 664 nm for $t \neq 0$. As shown in Fig. 9b, in the absence of H$_2$O$_2$, all the MHSPs samples show negligible decolorization (line a, b and c). If only H$_2$O$_2$ is used without adding the catalyst, the MB degradation is only about 21.3% after 90 min (line d). In contrast, when both MHSPs and H$_2$O$_2$ are added, the MB degradation increases to above 88.5% after 40 min and further to 99.8% after 90 min (line e, f and g). For comparison, the MS sample show 24.2% MB degradation at 40 min and 84.4% at 90 min. The catalytic performances of MHSPs are also higher compared to that of porous Mn$_3$O$_4$ nanorods [10]. This can be attributed to the porous structures and the large surface area of the MHSPs which provides more accessible reactive sites and facilitate the material exchange. The lower activity of the sample MHSPs-1 which has a largest surface area compared to MHSPs-2 and MHSPs-3 is due to lower manganese oxides loading.

Other metal oxides such as MgO and NiO loaded hollow silica particles (MgO@HSPs and NiO@HSPs) can also be synthesized in the same way. The TEM images of the MgO@HSPs and NiO@HSPs are shown in Fig. S4a and b. The presences of MgO and NiO in the corresponding products are confirmed by XRD respectively (Fig. S4c and d). Similar to the MHSPs, the MgO are prone to form a large particle in the hollow silica shell when 0.2 mmol MgCl$_2$ was used. However, the rattle-type structure can hardly be observed in the case of NiO@HSPs (Fig. S4b). Instead, small NiO particles around 4–9 nm can be seen in the inner shell of the hollow silica particles. This may come from the fact that Ni$^{2+}$ forms soluble complex with ammonia, which limits the amount of Ni$^{2+}$ bonded to the PAA chains (see Fig. S5). Consequently, less Ni$^{2+}$ ions were trapped in the PAA aggregate particles and small NiO particles were formed inside the silica shell.

4. Conclusion

MHSPs were synthesized via a PAA soft templating method. The PAA interacts with metal ions forming aggregate particles, which then acts as a template for silica shell formation. The removal of the PAA and the formation of the manganese oxide in the silica shell were achieved simultaneously by calcination in air. The hollow structure of the silica endows the MHSPs high surface areas. The Mn content and the structure of the MHSPs can be tuned by varying the metal ions added in the solution. The MHSPs showed better catalytic performance for MB oxidation with H$_2$O$_2$ than the corresponding MSs prepared without the silica coating. The hollow structure and high surface area of MHSPs are critical for enhancing the catalyst activity. This synthesis method can be extended to synthesize other metal oxide-MHSPs as long as a suitable metal ion precursor can be found.

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Appendix A. Supplementary material

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