One-Pot Synthesis of Hollow/Porous Mn-Based Nanoparticles via a Controlled Ion Transfer Process

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Supporting information:

Synthesis of HMnO, HMnP and PMnP NPs
In a typical synthesis of 10 nm HMnO NPs, 5 mL OAm was dissolved in toluene (12 mL) in a 25 ml Teflon-lined autoclave, then diluted water (0.2 mL), Mn(acac)₂ (1 mmol), and triethyl phosphate (0.4 mL) were added into the solution under stirring. The autoclave was sealed and placed in an oven at 180 °C. After 9 h reaction, the autoclave was cooled down to room temperature under a stream of tap water. The dispersion was precipitated with ethanol. The resultant precipitate was redispersed in hexane and let stand overnight to remove the sediments. The upper solution containing the product was collected. Similarly, 10 nm HMnP NPs were made by replacing 5 mL OAm with 1 mL oleic acid (OA) + 4 mL OAm and by heating the reaction mixture for 7.5 h. 20 nm porous Mn phosphate (PMnP) NPs of Mn₃(PO₄)₂ were obtained by changing the surfactant to 2 mL OA + 3 mL OAm and heating the reaction mixture for 9 h. The yields of the HMnO NPs, HMnP NPs and HMnP NPs in solid product, which contains NPs and sediments, are 85%, 52% and 67% respectively. Larger NPs, such as 20 nm HMnO, 20 nm HMnP and 45 nm PMnP, could be produced when extra 1 mL of OAm was introduced to the reaction system.

Synthesis of porous MnS nanoparticles:
For synthesis of the 40 nm porous MnS nanoparticles, 3 mL OAm and 2mL OA was dissolved in 12 mL toluene in a 25 ml Teflon-lined autoclave, then 1.5 mmol sulfur powder, 0.1mL diluted water, 1 mmol Mn(acac)₂, and 0.4mL triethyl phosphate were added into the solution in succession with stirring. After this, the autoclave was rapidly sealed and placed in oven which was already at 180 °C. 12 hours later, the autoclave was cooled down to room temperature under a stream of tap water. The dispersion was precipitated with ethanol. The resultant precipitate was redispersed in hexane and let stand overnight to remove the sediments. The upper solution containing the product was collected. The XRD pattern (JCPDS 40-1289) of the sample is shown in Fig.S 13c. EDS spectrum is shown in Figure S5d.

Synthesis of porous hydroxyapatite nanoparticles:
For synthesis of the porous hydroxyapatite nanoparticles, 5 mL OAm was dissolved in 12 mL toluene in a 25 ml Teflon-lined autoclave, then 0.2mL diluted water, 1 mmol Ca(acac)₂, and 0.2mL triethyl phosphate were added into the solution in succession with stirring. After this, the autoclave was rapidly sealed and placed in oven which was already at 190 °C. 12 hours later, the autoclave was cooled down to room temperature under a stream of tap water. The dispersion was precipitated with ethanol. The resultant precipitate was redispersed in hexane and let stand overnight to remove the sediments. The upper solution containing the product was collected. The XRD pattern (JCPDS 09-0432) of the sample is shown in Fig.S 13d.

Fig. S1 TEM images of the as-synthesized hollow NPs: (a) 20 nm HMnO, (b) single NP of 20 nm HMnO, (c) 20 nm HMnP, (d) 45 nm PMnP
Fig. S2 XRD patterns of evolution of HMnO: (a) 3h, (b) 6h, (c) 9h.

Fig. S3 XRD patterns of evolution of HMnP: (a) 3h, (b) 4h, (c) 5h, (d) 6h, (e) 7.5h, (f) annealed at 500℃ for 2 h.
**Fig. S4** XRD patterns of the PMnP samples: (a) 3h, (b) 6h, (c) 9h, (d) annealed at 500°C for 2 h.

**Fig. S5** EDS spectra of (a) HMnO, (b) HMnP, (c) PMnP, (d) porous MnS nanoparticles.
Fig. S6. TEM images and corresponding schemes of formation (insert) of the HMnO samples after reaction for a) 3h, b) 6h, c) 9h; the HMnP samples after reaction for d) 3h, e) 4h, f) 5h, g) 6h, h) 7.5h i) 9h; the PMnP samples after reaction for j) 3h, k) 6h, l) 9h.
Fig. S7. (a) Scanning electron microscopy (SEM) images, (b) TEM images, (c) XRD pattern of the precipitations.

Fig. S8 TEM images of the nanoparticles obtained according to the recipe of (a) HMnO, (b) HMnP, (c) PMnP without using triethyl phosphate.

Fig. S9 TEM images of the nanoparticles obtained according to the recipe of (a) HMnO, (b) HMnP, (c) PMnP without using water.
Fig. S10 TEM images of the nanoparticles obtained according to the recipe of (a) HMnO, (b) HMnP, (c) PMnP except the substitution of triethyl phosphate by trioctyl phosphate.

Preparation of water-dispersible HMnO:
Water-dispersible HMnO was prepared by replacing the hydrophobic surfactant of obtained HMnO to PEG-based surfactant. Protocatechuic acid is used as a binding group to link PEG chain and the surface of the nanoparticles (Reaction (S1) and Scheme S1). The resulting hollow nanoparticles could be well dispersed in water and showed no aggregation (Figure S11).

Relaxation properties Measurements:
$T_1$ relaxation times of the HMnO with varying concentrations were measured on a 3.0 T clinical MR system (Magnetom Trio, Siemens Medical Solutions, Erlangen, Germany). The specific relaxivities ($r_1$ and $r_2$) of water-disperse HMnO can be calculated from the plot of $1/T_1$ and $1/T_2$ vs concentration of manganese (Fig. S12).

BET data:
The specific surface areas of 10 nm HMnO, 10 nm HMnP and 25 nm PMnP are measured by the BET method to be 57.7, 56.8 and 52.3 m$^2$/g.

Relaxivity measurements
The relatively small surface area may be contributed to the closed shell or small pore sizes of the NPs. To test the performance of these NPs as MRI contrast agent, water soluble 20 nm HMnO was prepared by replacing OAm with protocatechuic acid-PEG based ligand,36 and the relaxation property of the NPs was examined (see the supporting information). The value of $r_1$ and $r_2$ for HMnO are 0.86 ms$^{-1}$s$^{-1}$ and 9.6 ms$^{-1}$s$^{-1}$ (Figure S12), which show that HMnO NPs are a potential MRI probe. Further experiments on using these NPs as contrast agents and for other biomedical applications are underway.
Scheme S1 Preparation of protocatechuic acid-PEG based ligand.

Fig. S12 a) TEM images of the water soluble HMnO NPs. b) Plots of $T_1$ versus Mn concentration and $T_1$-weighted images and c) plots of $T_2$ versus Mn concentration and $T_2$-weighted images for the water-dispersible HMnO NPs.

Fig. 13 TEM image of a) porous MnS NPs, b) porous hydroxylapatite and XRD patterns of c) porous MnS NPs, d) porous hydroxylapatite.