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Facile Fabrication and Magnetic Properties of Macroporous Spinel Microspheres from Layered Double Hydroxide Microsphere Precursor

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Macroporous $CoFe_2O_4$ spinel microspheres have been fabricated by a simple process involving calcination of layered double hydroxide microsphere precursor, which was originally prepared by spray drying with polystyrene as template.

Layered double hydroxides (LDHs) are a class of anionic clays whose structure is based on brucite ($Mg(OH)_2$)-like layers in which some of the divalent cations have been replaced by trivalent cations giving positively charged sheets.[1] This charge is balanced by intercalation of anions in the hydrated interlayer regions. LDHs can be represented by the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}(A^{n-})_{x/n}\cdot yH_2O$. The identities of the divalent and trivalent cations (M^{II} and M^{III}, respectively) and the interlayer anions (A^{n-}) together with the value of the stoichiometric coefficient (x) may be varied over a wide range, giving rise to a large class of isostructrual materials.[2] LDHs have a wide variety of applications including as additives in polymers, as precursors to magnetic materials, in biology and medicine, in catalysis, and environmental remediation.[3] Calcination of LDH is well known to give rise to mixed metal oxide materials, which are composed of $M^{II}O$ and $M^{II}M^{III}{}_2O_4$ phases. Previous work by Li et al. has shown that pure MFe_2O_4 (M = Mg, Co, and Ni) spinel ferrites can be obtained by calcination of LDHs at 900 °C, in which the molar ratio of $M^{II}/(Fe^{II} + Fe^{III})$ is adjusted to the same value as that in single spinel ferrite itself.[4] The saturation magnetization of the materials produced by calcination of LDH is higher than those of the spinel ferrites produced by the conventional ceramic and wet chemical routes, although the compositions of the materials are similar.

In recent years, magnetic naonoparticles with tubular[5] and spherical[6] structures have been of great interest for their potential applications including microwave adsorbing, catalysis, magnetically guided drug delivery, and medicine. Although such magnetic materials do have specific morphology, the procedures employed in their preparation have several limitations such as requiring many tedious and time-consuming steps, which are often difficult to carry out. There is a need for a simple, easily controlled synthetic strategy for the preparation of solid spherical magnetic particles, which is amenable to scale up.

Here, we report a simple approach to prepare macroporous pure $CoFe_2O_4$ spinel microspheres by a simple process involving calcination of CoFeFe–LDH microsphere precursor, which was originally prepared by spray drying using sulfonated polystyrene (PS) microspheres as template for constructing macropores. Spray drying has been considered an indispensable and convenient industrial technique, which has been widely used in food, pharmaceutical, ceramic, polymer, chemical, and various other industries to obtain dry particles from solution phase.[7] Recently, our group has successfully prepared microspherical MgAl–, NiAl–, ZnAl–, and CuZnAl–LDHs by this process.[8] Sulfonated PS microspheres with a diametere of 1 µm were used as template to tune the macroporous domain.[9] The morphology and texture as well as the magnetic properties of the resulting macroporous $CoFe_2O_4$ spinel microspheres are evaluated.

Uniform nanosized CoFeFe–LDH particles were prepared by a process developed in our laboratory involving separate nucleation and aging steps (SNAS).[10] The precursor slurry containing 3.0 wt % CoFeFe–LDH with or without 0.3 wt % sulfonated PS microspheres was fed into an atomizer, and an aerosol dispersion generated within the tubular reactor of a spray drying apparatus (model LPG-5, manufactured by Jiangyin Dry Apparatus Co., Ltd.). The prepared CoFeFe–LDH microspheres were calcined in air at 700 °C for 4 h at a heating rate of 0.5 °C min^{-1}, and then the resulting products were slowly cooled to room temperature. The experimental details can be found in ESI.[12]

CoFeFe–LDH nanoparticles with a $Co^{II}:(Fe^{II} + Fe^{III})$ ratio of 0.5 were synthesized successfully by the SNAS method,[10] and microspheres formed by spray drying of the resulting suspension. The powder XRD patterns for the LDH nanoparticles and the crushed microspheres are shown in Figures 1a and 1b. The diffraction peaks in the 2θ range 5–70° correspond to the characteristic reflections of LDH materials, with a series of (00*l*) peaks appearing as narrow symmetric lines at low angle, arising from the basal reflection and higher order reflections, and the

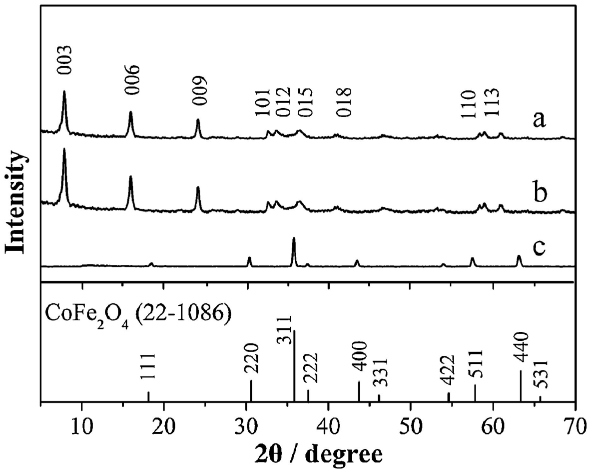

Figure 1. XRD pattern of (a) CoFeFe–LDH particles, (b) CoFeFe–LDH microspheres precursor prepared by spray drying using sulfonated PS microspheres as template, and (c) $CoFe_2O_4$ spinel microspheres prepared by calcination of (b). Patterns of $CoFe_2O_4$ spinel (JCPDF) is included for comparison.

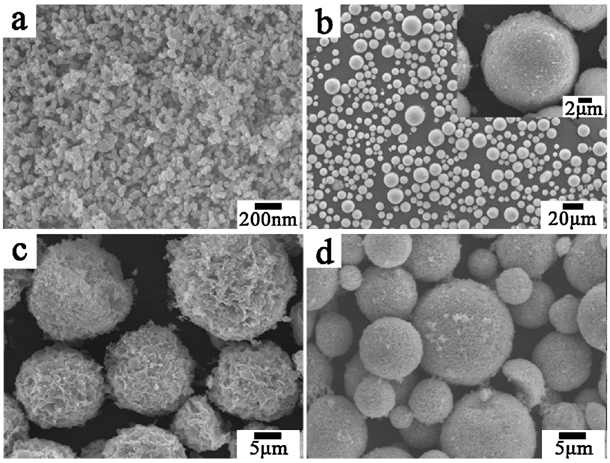

Figure 2. SEM image of (a) CoFeFe–LDH particles, (b) CoFeFe–LDH microspheres precursor prepared by spray drying using sulfonated PS microspheres as template. (c) and (d) are the $CoFe_2O_4$ spinel microspheres prepared by calcination of LDH microsphere precursor with and without sulfonated PS template prepared by spray drying, respectively.

characteristic pair of (110) and (113) reflections near 59°.[4] The elemental analysis of the LDH gives the following formula for $[Co_{0.34}Fe^{2+}{}_{0.32}Fe^{3+}{}_{0.36}(OH)_2](SO_4)_{0.20}\cdot 0.39H_2O$. The particle size of the CoFeFe–LDH is in the range of 20–200 nm with the modal value of the particle size distribution centered around 60 nm, as can be seen from the SEM micrograph in Figure 2a. Figure 2b shows a representative SEM image of the LDH microsphere product, which is composed of spherical particles with diameter ranging from 5 to 50 μm. Nanosized LDH building blocks can be clearly observed on the surface shown in the inset of Figure 2a, suggesting that the nanoparticle size of the LDH was retained when they were aggregated into spheres. After calcination of LDH microspheres at 700 °C for 4 h, the original reflections of the LDH have been lost and replaced by the expected peaks characteristic of a strongly crystalline $CoFe_2O_4$ spinel phase (Figure 1c). It was found that the spherical morphology was retained (Figure 2c) after calcination, though the roughness of the surface was increased compared with that of the LDH microspheres, which may be a result of the evolution of steam during decomposition. For comparison, $CoFe_2O_4$ spinel microspheres prepared by calcination of LDH microsphere precursor without sulfonated PS template were obtained, and the SEM image was shown in Figure 2d.

The particle size distribution of the as-formed CoFeFe–LDH with and without sulfonated PS template and the corresponding calcination production, without any sieving pre-treatment, was determined by low-angle laser light scattering. The results for the particle size distribution by volume are shown in Supporting Information (Figure S1). The particle diameter distribution for the two LDH microsphere precursors is in the range 5–80 μm, and the modal value of the particle diameter distribution is centered around 23 μm (Figures S1a and S1b), which is consistent with the results given by SEM. While for the two calcination production, the modal value of the particle diameter distribution is centered around 21 μm (Figures S1c and S1d), which is smaller than that of the LDH microsphere precursor.

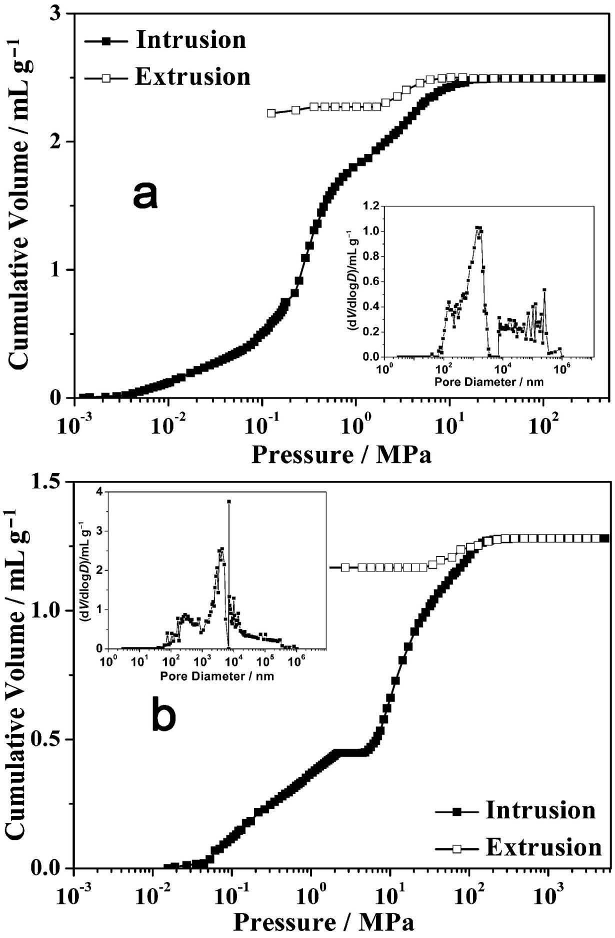

Figure 3. Mercury intrusion porosometry curve for $CoFe_2O_4$ spinel microspheres prepared by calcination of LDH microsphere precursor with (a) and without (b) sulfonated PS template. The inset shows the pore access diameter distribution.

The textural properties of the two $CoFe_2O_4$ spinel microspheres prepared by calcination of CoFeFe–LDH microsphere precursor with and without sulfonated PS template were determined using Mercury Intrusion Porosimetry, and the results are shown in Figure 3. The measured surface area and total pore volume of the $CoFe_2O_4$ spinel microspheres from the LDH microsphere precursor with sulfonated PS template were 12 $m^2\,g^{-1}$ and 2.49 $cm^3\,g^{-1}$, respectively, while those of the $CoFe_2O_4$ spinel microspheres from LDH microsphere precursor without sulfonated PS template were 7.4 $m^2\,g^{-1}$ and 1.28 $cm^3\,g^{-1}$, respectively. Analysis of the raw data using the conventional Washburn equation[11] gives a pore access diameter rather than the more common "pore size" owing to the deviations from the usual assumption of pore shape in mercury porosimetry. The results, shown in the inset of Figure 3a and Figure 3b, show a multiple-modal pore access diameter distribution in the mesoporous and macroporous ranges for the two $CoFe_2O_4$ spinel microsphere samples. In particular, a bigger macroporous domain for the $CoFe_2O_4$ spinel microspheres from LDH microsphere precursor with sulfonated PS template is revealed by the occupancy of a large amount of pore with diameter larger than 10000 nm. Besides, it can be seen from

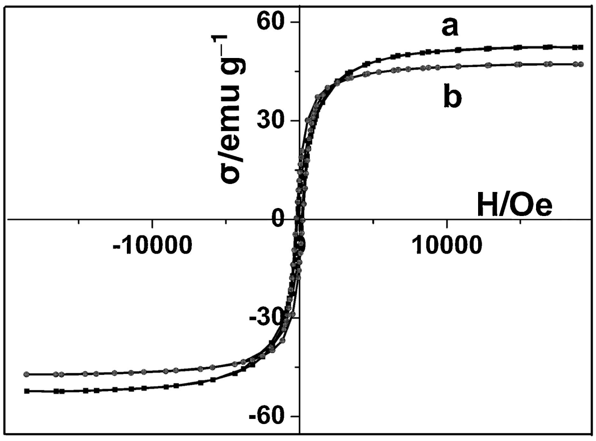

Figure 4. Hysteresis curve of $CoFe_2O_4$ spinel microspheres prepared by calcination of LDH microsphere precursor with (a) and without (b) sulfonated PS template.

SEM of the two broken spinel microspheres prepared by calcination of LDH microsphere precursor with and without sulfonated PS template (Figure S2), the macropores domains are left behind by the burning of the PS template, while the particle piled pores are found for the spinel microsphere from LDH microsphere precursor without sulfonated PS template.

The field dependence of the magnetization of the two synthesized spinel ferrites was measured using a VSM at room temperature. The hysteresis loops of samples produced are shown in Figure 4. The values of the saturation magnetization are evaluated by extrapolation of the magnetization vs. $1/H$ to $1/H = 0$. The saturation magnetization values are 51.2 and 47.2 emu g^{-1} for the $CoFe_2O_4$ spinel microspheres from LDH microsphere precursor with and without sulfonated PS template, respectively, and the coercive force values 205 and 215 Oe for the two samples. According to Li et al.,[4] the saturation magnetization values of spinel ferrites produced from LDHs precursor have higher values than those of MFe_2O_4 produced by conventional ceramic and wet chemical methods at a higher calcination temperature and a longer time. Seen from ref 4 (Table 3), the saturation magnetization is 86.1 emu g^{-1} for the $CoFe_2O_4$ spinel by calcination LDH precursor at 900 °C for 2 h. While the values of the saturation magnetization 73.4 and 73.1 emu g^{-1} are obtained for the $CoFe_2O_4$ spinels produced by the conventional ceramic and wet chemical routes at 1100 °C for 10 h, respectively. The major advantage of the new method is that it affords uniform distribution of all metals starting from the LDH and requires a much lower temperature and shorter time, leading to a lower chance of side-reactions occurring at room temperature. The hysteresis loops of samples produced are shown in Figure 4.

In summary, macroporous $CoFe_2O_4$ spinel microspheres have been fabricated by a simple process involving calcination of CoFeFe–LDH microspheres precursor, originally prepared by spray drying using sulfonated PS microspheres as template for constructing macropores. The resulting $CoFe_2O_4$ spinel microspheres maintain the original spherical morphology of the precursor LDH microspheres during the thermal decomposition process. The macroporous domain of the $CoFe_2O_4$ spinel microspheres, with surface area of 12 m^2 g^{-1} and total pore volume of 2.49 cm^3 g^{-1}, was created by burning away the sulfonated PS template. The saturation magnetization and coercive force are 52.8 emu g^{-1} and 205 Oe, respectively.

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12 Supporting Information is available. Experimental details, instrumentation, and particle size distribution. These materials are available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.