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Facile Fabrication of Water-Soluble Magnetic Nanoparticles and Their Spherical Aggregates

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In this paper, we report a facile synthetic approach for preparing water-soluble Fe_3O_4 nanoparticles with a surface-surrounded layer by the use of polyethylene glycol(5) nonylphenyl ether (NP5) and cyclodextrin (CD) in aqueous medium and also for building nanostructured spherical aggregates from individual magnetic nanoparticles, which were dependent on the concentration of CD and NP5, respectively. The morphology of Fe_3O_4 nanoparticles was studied by transmission electron microscopy. The mesoporous, spherical aggregates of Fe_3O_4 particles possessed a BET surface area of ca. 141.1 $m^2\ g^{-1}$ without compromising that of the separated Fe_3O_4 nanoparticles with coating (164.6 $m^2\ g^{-1}$) and still possessed magnetic properties. This method is very meaningful because it directly produces water-soluble magnetic nanoparticles, which is very important for applications of magnetic nanoparticles in biomedical fields and nanostructured spherical aggregates as magnetic carriers.

Introduction

Magnetic nanoparticles of iron oxides have been explored for biological applications as tags in sensing and imaging and as activity agents in hyperthermia therapy.[1–5] Different synthetic techniques such as coprecipitation and microemulsion methods,[6,7] ultrasound irradiation,[8] and laser pyrolysis techniques[9] have been developed for producing particles smaller than 20 nm. These nonaqueous methods can control the particle size and shape with close to atomic layer precision—two important parameters that affect the chemical and physical properties of nanoparticles. However, the nanoparticles previously mentioned are organic-soluble, which will limit their use in the biomedical fields, especially for in vivo applications.[10] Therefore, it is desirable to synthesize water-soluble magnetic nanoparticles in aqueous solution, which will realize their potential in biological applications.

Furthermore, the uniqueness of magnetic carrier technology (MCT) has been reported by several research groups recently.[11–13] An attractive property of MCT is that the carriers can be separated easily from a complex multiphase system by an external magnetic device. However, the magnetic forces exerted on these tiny magnetic particles are extremely weak for any substantial migration of the particles to a desired location. Thus, it is desirable to synthesize clusters of the nanoparticles that can be operated by an external magnetic device without compromising the surface area determining adsorptive capacity. Self-assembly through noncovalent interactions (hydrogen bonding,[14,15] van der Waals forces,[16,17] and electrostatic forces[18,19]) with no external intervention provides a powerful method for employing preprogrammed materials with the potential for multidimensional ordering for the creation of a well-defined structure at the molecular level. For example, Rotello et al.[20] reported that polymeric layer protected gold particles self-assembled into spherical aggregates through hydrogen-bonding interactions. In their strategy, the polymers acted as the mortar to hold the colloidal particles together to form spherical aggregates.

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Nanoparticle dispersions can be stabilized by the use of a suitable surface coating, typically a surfactant or polymer. Polymer coatings that have been examined for magnetic nanoparticles vary from simple homopolymers to copolymers.[21] Herein, we report that individual polymeric layer-coated magnetic nanoparticles can be prepared and self-assembled into spherical aggregates by further reaction under controlled conditions. The layer used was polyethylene glycol(5) nonylphenyl ether (NP5), which is used to stabilize magnetic nanoparticles by the formation of surface coating and is a low molecular-weight polymer at the same time and yields aggregates of large size,[21] and cyclodextrin (CD), which is used to improve their miscibility with water by the formation of the second layer.[22] NP5 and CD can undergo self-assembly by holding together individual molecules (elemental bricks) in an orderly manner through noncovalent interactions to build up materials.[23,24] Depending on the reaction conditions, the aggregates of controlled size and shape can be synthesized easily.

Experimental Procedures

Chemicals. NP5, CD, iron (II) chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), and anhydrous iron (III) chloride ($FeCl_3$) were purchased from Sigma (Singapore) and used without further treatment.

Synthesis of Iron Oxide Nanoparticles with Surfactant Layer Coating. $FeCl_2 \cdot 4H_2O$ (0.158 g) and $FeCl_3$ (0.268 g) were dissolved in 45 mL of aqueous solution (including 0.244 g of 10% NP5 solution, w/w) with vigorous stirring and under N_2. After 30 min of mechanic stirring, 1.2 mL of ammonia aqueous solution (28%, w/w) in 30 mL of CD solution (5 mM) was added. The reaction was allowed to proceed for 1.5 h with constant and vigorous stirring to produce a water-based suspension. Finally, the suspension was filtered by filter paper, and the filtrate was stored for further use. Spherical aggregates of Fe_3O_4 particles can be prepared by controlling the concentration of NP5 at a fixed CD concentration (5 mM).

Characterization. The morphology of the products was examined by transmission electron microscopy (TEM, JEM-2010F). X-ray diffraction (XRD) patterns of the samples were recorded on a Siemens D5005 diffractometer equipped with a Cu Kα (1.5405 Å) X-ray source. Magnetic data were obtained on a SQUID magnetometer (Quantum MPMS-5S).The surface area of the product was measured by nitrogen adsorption−desorption isotherms using the Brunauer−Emmett−Teller (BET) method (Micromeritics Flowsorb 2300). The sample was degassed under vacuum at room temperature before measurement.

Results and Discussion

The formation of spherical aggregates is divided into two stages. The first stage is the formation of individual coated Fe_3O_4 nanoparticles, which is a typical chemical coprecipitation of Fe^{2+} and Fe^{3+} salts in ammonium hydroxide solution. In the second stage: (a) the individual nanoparticles will further be surrounded by polymeric surfactant to form a thicker layer if the concentration of CD is controlled, whereas they coagulate into aggregates (b) through intermolecular interactions if the concentration of NP5 is controlled.

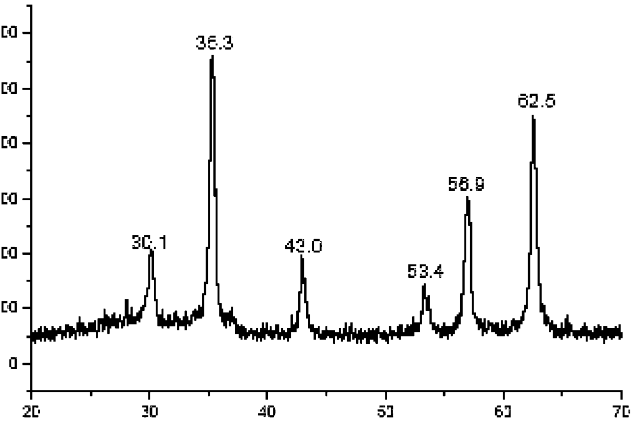

Figure 1. X-ray diffraction pattern of Fe_3O_4 nanoparticles on glass substrate.

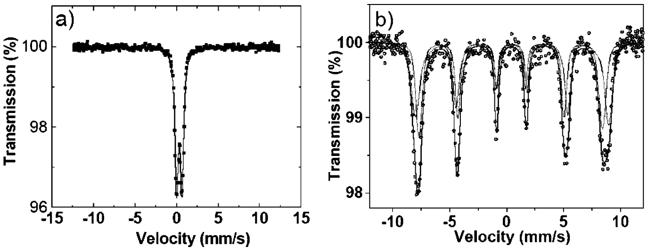

Figure 2. Mössbauer spectra of Fe_3O_4 nanoparticles at (a) room temperature and (b) 4.2 K.

The formation of Fe_3O_4 nanoparticles was identified from the X-ray diffraction pattern (Figure 1). The pattern obtained confirms that the nanoparticles prepared in this study are the Fe_3O_4 nanoparticles.[24] The Fe_3O_4 nanoparticles display several relatively strong reflection peaks in the 2θ region of 20−70°, which is quite similar to those of Fe_3O_4 nanoparticles reported by other groups, confirming that the nanoparticles prepared are Fe_3O_4. These strong Bragg reflections of Fe_3O_4 are at the 2θ angles of 30.1° ($d = 2.967$ Å), 35.4° ($d = 2.532$ Å), 43.0° ($d = 2.101$ Å), 53.4° ($d = 1.714$ Å), 56.9° ($d = 1.616$ Å), and 62.5° ($d = 1.484$ Å). The Bragg reflection peaks are all relatively broad because of the extremely small dimensions of the Fe_3O_4 nanoparticles.

In the XRD spectrum (as shown in Figure 1), we cannot exclude the possibility of the γ-Fe_2O_3 phase in the nanoparticles for the line broadening of the spectrum. Mössbauer spectroscopy is one of the most effective ways to distinguish the two phases.[25] The Mössbauer spectra of the spherical aggregates of the nanoparticles are shown in Figure 2 in the absence of an external magnetic field. The as-fitted parameters are listed in Table 1. At room temperature, only a doublet is observed, which clearly indicates the superparamagnetic behavior of the particles (Figure 2a). The as-fitted parameters are consistent with those reported for nanosized magnetite.[26] At a temperature of 4.2 K (blow the blocking

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Table 1. Mossbauer Parameters of Fe_3O_4 at Both Room Temperature and 4.2 K[a]

	paramagnetic Fe^{3+}			ferrimagnetic Fe^{3+}: A site				ferrimagnetic Fe^{3+}: B site			
T (K)	*δ (mm/s)*	*Δ (mm/s)*	*P (%)*	*δ (mm/s)*	*Δ (mm/s)*	*H (T)*	*P (%)*	*δ (mm/s)*	*Δ (mm/s)*	*H (T)*	*P (%)*
296	0.33	0.65	100								
4.2				0.32	−0.023	51.25	78.82	0.61	−0.18	48.70	21.18

[a] δ: Isomer shift; Δ: *quadrupole* splitting; *H*: hyperfine field; and *p*: area percentage.

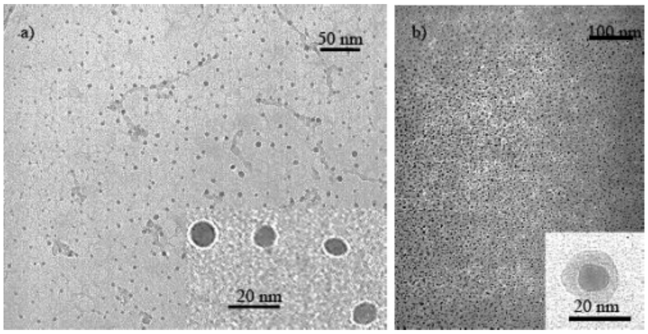
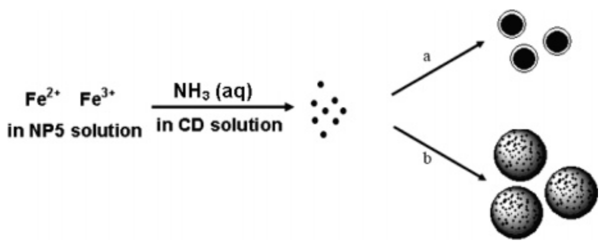


Figure 3. TEM images of Fe_3O_4 coated with a polymeric layer at different CD concentrations: (a) 5 mM and (b) 7.5 mM ([NP5] = 0.032 wt %, $[Fe^{2+}]$ = 0.01 M, and $[Fe^{3+}]$ = 0.02 M).

Scheme 1. Proposed Self-Assembly Process of Individual Nanoparticles to Form (a) Core−Shell Nanoparticles and (b) Their Spherical Aggregates



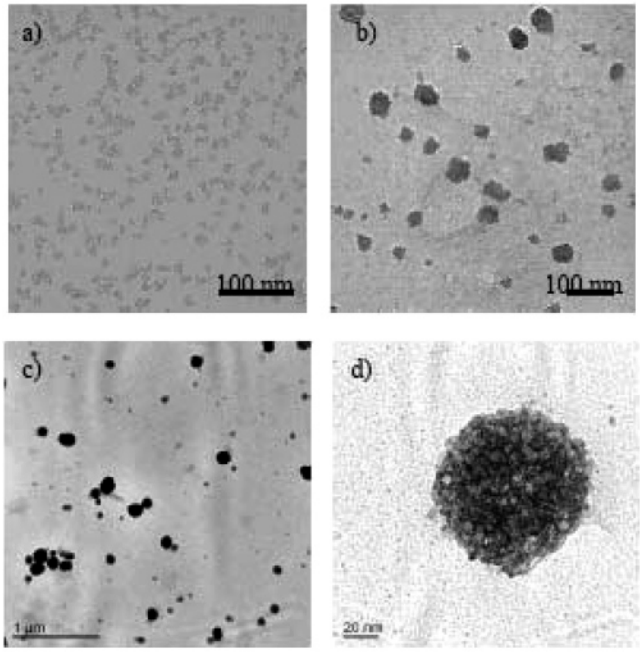


Figure 4. TEM images of Fe_3O_4 aggregates at different NP5 concentrations: (a) 0.065 wt %, (b) 0.13 wt %, and (c) 0.26 wt %. (d) Enlargement of panel c: ([CD] = 5 mM, $[Fe^{2+}]$ = 0.01 M, and $[Fe^{3+}]$ = 0.02 M).

temperature), the sample exhibited a general sextet shape demonstrating ferromagnetic behavior (Figure 2b). According to the fitting parameters shown in Table 1, the iron oxide should be in the magnetite (Fe_3O_4) phase.[25] The existence of Fe^{2+} was also verified by a large isomer shift value of 0.61 mm/s. It should be noted that the dispersed Fe_3O_4 particles showed similar spectra to those shown in Figure 2 when the Mössbauer spectra were taken at room temperature and 4.2 K, respectively.

The effect of CD concentration (represented by [CD]) on the morphology of coated Fe_3O_4 nanoparticles is shown in Figure 3. The thickness of the surfactant layer of Fe_3O_4 nanoparticles can be effectively tuned by controlling the CD concentration in our system. In Figure 3a, when [CD] is at 5 mM, the TEM image shows that uniform Fe_3O_4 nanoparticles with an inner diameter of about 10 nm are obtained. These nanoparticles are well-separated due to the coating on their surface, reducing their tendency to agglomerate. This result is also consistent with recent reports[21] suggesting that the coated Fe_3O_4 nanoparticles do not aggregate in the presence of a low concentration of NP5 polymer. Because of the low contrast of the polymers relative to that of the carbon substrate and thickness of the shell, only the cores of Fe_3O_4 nanoparticles can be seen in the micrograph. We have reported the preparation of Y-junction polyaniline nanostructures by this kind of nanoparticle as soft templates in aqueous solution.[27] The TEM image (Figure 3b) shows the Fe_3O_4 nanoparticles (inner diameter of about 10 nm) with a clear surfactant layer of about 3 nm when [CD] is increased to 7.5 mM. When a higher [CD] of 10 mM is used, irregularly coated Fe_3O_4 nanoparticles are obtained (see Supporting Information), with a surfactant layer thickness of about 5 nm. In particular, some Fe_3O_4 nanoparticles are only partially coated. This is also a major problem in the preparation of an outer shell of constant thickness on the cores.[28] The polymers (NP5 and CD in our system) want to minimize their interface.[28] As a result, the outer polymer shell tends to concentrate on one side of the core-Fe_3O_4 nanoparticles. In our system (Supporting Information, Scheme 1a), CD is used for the formation of the second ligand layer, whereby the hydrophobic cavity of cyclodextrin is penetrated by the hydrophobic tail of the first layer (NP5). Interdigitated bilayers have been formed finally.[22,29] Since the inner diameters of coated Fe_3O_4 nanoparticles at different reaction conditions are nearly the same, it is apparent that the CD concentration plays a key role in controlling the thickness of the surfactant layer, which would improve its miscibility with water.[22] In addition, the size of the nanoparticles is

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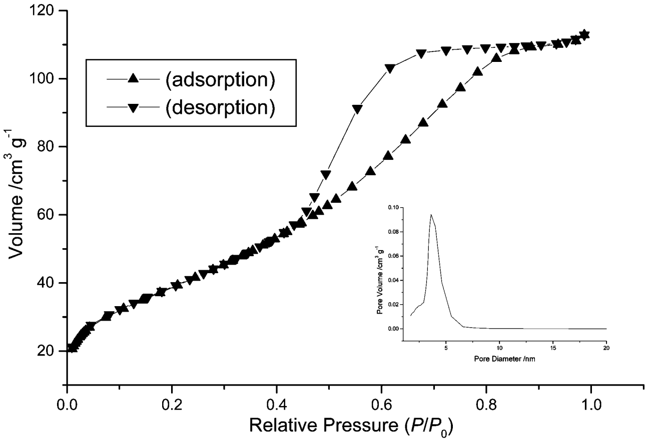

Figure 5. Nitrogen adsorption−desorption isotherm of the sample in Figure 3c measured at 77 K; inset shows pore diameter distribution of the sample.

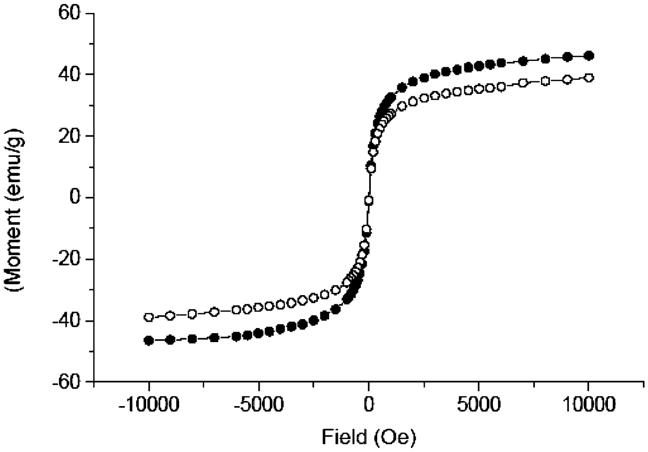

Figure 6. Room-temperature magnetization curves of obtained Fe_3O_4 nanoparticles. Solid circles: dispersed Fe_3O_4 nanoparticles and open circles: spherical aggregates of Fe_3O_4 nanoparticles.

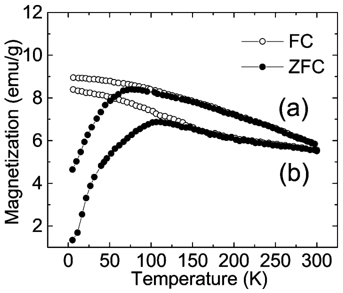

Figure 7. ZFC and FC curves of (a) dispersed Fe_3O_4 nanoparticles and (b) spherical aggregates of Fe_3O_4 nanoparticles (the applied magnetic filed of 100 Oe).

limited to about 10 nm, which is in agreement with the results obtained by other researchers who used the same coprecipitation method.[30,31]

The effect of the NP5 concentration on the morphology of coated Fe_3O_4 nanoparticles is shown in Figure 4. The TEM image (Figure 4a) shows that small aggregates of Fe_3O_4 nanoparticles with an average diameter of 25 nm are obtained when [NP5] is at 0.065 wt % under other fixed reaction conditions. The size and morphology change significantly as [NP5] is increased. Larger Fe_3O_4 nanoparticle aggregates are observed when [NP5] is 0.13 wt % (Figure 4b). These aggregates are nearly spherical and have a diameter of 40−75 nm. When [NP5] is at a high value of 0.26 wt %, distinct spherical Fe_3O_4 nanoparticle aggregates are formed with a diameter of 80−120 nm (Figure 4c). Figure 4d shows that the single spherical aggregate is made up of about 500−2000 small Fe_3O_4 nanoparticles with a diameter of about 10 nm. These results were also consistent with the reported work[21] that the size of the clusters is large when the polymer molecular weight is small (molecular weight of NP5 is about 448) and in sufficient concentration.

From the previously described results, the use of CD and NP5 is the key in preparing a sphere-like assembly, although the driving force has not been fully understood. After the formation of an inclusion complex with the hydrophobic groups of NP5, the hydroxyl groups of the CD rims can interact with the hydrophilic moiety of NP5 as well.[32] The increase of the NP5 concentration may lead to a linkage or bridging of the surface coating on the nanoparticles and cause singular nanoparticles to aggregate together instead of remaining as dispersed nanoparticles. A possible mechanism for the formation of the assembly of Fe_3O_4 nanoparticles is shown in Scheme 1b (Supporting Information).

In addition, these spherical aggregates are mesoporous. These mesoporous magnetic aggregates of sufficiently high specific surface area[33] can be used in the separation of target molecules from a multiphase complex system by external magnetic devices and would have a high load capacity of target molecules. The isothermal N_2 sorption data of the sample at 77 K are shown in Figure 5 and Table 2. Quantitative calculation shows that the spherical aggregates of Fe_3O_4 nanoparticles possesses a BET surface area of ca. 141.1 m^2 g^{-1} and a narrow distribution of pore diameters centered at 3.7 nm (Figure 5 inset). The as-synthesized spherical aggregates of the nanoparticles do not compromise the surface area determining adsorptive capacity as separated Fe_3O_4 nanoparticles with a coating have a BET surface area of ca. 164.6 m^2 g^{-1}.

The magnetic properties of the coated Fe_3O_4 nanoparticles were investigated with a superconducting quantum interference device (SQUID). Figure 6 shows the room-temperature magnetization (300 K) of as-prepared Fe_3O_4 nanoparticles (Figures 3a and 4c). The curves obtained at 300 K are perfectly superimposable as the field is cycled between −10 and 10 kOe. The curves are consistent with superparamagnetic behavior (also see Mössbauer spectrum in Figure 2a) and the nanoscale dimensions of the particles.[24,34,35] Their saturation magnetizations are 46.2 and 39.0 emu/g, respectively. The close value in the saturation magnetization of our samples mainly should be attributed to the same particle size. In addition, saturation magnetizations of our samples

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Table 2. Characterization of Bare Fe_3O_4 Nanoparticles, Single Fe_3O_4 Nanoparticles with Coating, and Mesoporous Aggregates of Fe_3O_4 Nanoparticles with Coating

samples	BET surface area ($m^2\ g^{-1}$)	M_s (emu g^{-1})
bare magnetite (Fe_3O_4)[a]	0.07	85
single nanoparticles with coating (Fe_3O_4)	164.6	46.2
mesoporous aggregates of nanoparticles (Fe_3O_4)	141.1	39.0

[a] As from ref 33.

are lower than those of similarly sized nanoparticles prepared by other methods,[36] which might be caused by the surface spin canting effects and the surfactant coating reducing the total magnetic moment of the nanoparticles and give rise to the decrease in the magnetization of the coating nanoparticles.[35]

A commonly used technique for the investigation of superparamagnetic relaxation is the field-cooled (FC) and zero-field-cooled (ZFC) magnetization, that is, the magnetization in a weak applied field as a function of increasing temperature after the sample has been cooled, respectively, in the presence and absence of a weak magnetic field. The ZFC and FC curves of dispersed Fe_3O_4 and spherical aggregates of Fe_3O_4 nanoparticles are shown in Figure 7. At high temperatures, the two sets of data (in Figure 7a,b, respectively) exhibit the same trend; that is, the magnetization decreases with increasing temperature. At low temperatures, however, the data significantly diverge. From the curves, one can see that the blocking temperature T_b of dispersed nanoparticles is approximately 71 K (Figure 7a) and for spherical aggregates of nanoparticles, T_b is 105 K (Figure 7b). The increase of T_b in the aggregates of Fe_3O_4 nanoparticles indicates an increase of dipole−dipole interactions of the nanoparticles due to the aggregates.[37]

Conclusion

In summary, we report a facile synthetic approach for preparing water-soluble Fe_3O_4 nanoparticles with a surface-surrounded layer by use of NP5 and CD in aqueous medium and also for building nanostructured spherical aggregates from individual magnetic nanoparticles, which were dependent on the concentration of CD and NP5, respectively. The mesoporous, spherical aggregates of the Fe_3O_4 nanoparticles possessed a BET surface area of ca. 141.1 $m^2\ g^{-1}$ without coating the separated Fe_3O_4 nanoparticles (164.6 $m^2\ g^{-1}$) and performed superparamagnetic behavior at room temperature. These mesoporous aggregates of Fe_3O_4 nanoparticles can be used in magnetic carrier technology. This method is also very meaningful because it directly produces water-soluble magnetic nanoparticles, which is very important for applications of magnetic nanoparticles in biomedical fields and nanostructured spherical aggregates as magnetic carriers.

The spherical aggregates of Fe_3O_4 nanoparticles can be used further as templates to form polyaniline microspheres. These polymeric hollow microspheres may have applications in drug delivery, cell transplantation, and removal of waste. Further studies are in progress.

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Supporting Information Available: Scheme of the proposed self-assembly process of individual nanoparticles; additional TEM images; and pore diameter distribution of the sample in Figure 3c. This material is available free of charge via the Internet at http://pubs.acs.org.

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