# *Communications*

## Synthesis of Magnetite Nanoparticles in Mesoporous Copolymer Template: A Model System for Mass-Loading Control

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In recent years the design and synthesis of nanometer-scale particles has been the focus of intense fundamental and applied research, with special emphasis on their size-dependent properties.[1,2] Among others, magnetic metal-oxide nanoparticles have been conveniently synthesized using chemical condensation reactions in an alkaline medium.[3,4] However, the tendency of isolated nanostructures to aggregate themselves into bigger clusters during the synthesis had represented a critical obstacle for size control.[5] Alternatively, mesoporous-based polymer templates have been efficiently used to host chemical reactions, not only avoiding nanoparticle clustering but also providing stable frameworks against chemical degradation.[6-9] Though different metal-oxide-based nanoparticles have been synthesized using a wide variety of polymeric frameworks, little has been done to understand and to quantitatively describe the mechanism that controls the amount of material synthesized in the template.[10] In particular, the role played by the metal-ion concentration ($C$) used to load the polymeric matrix as well as the number ($N$) of chemical cycles the template is submitted to. In this study, the synthesis of magnetite nanoparticles in mesoporous styrene–divinylbenzene (Sty–DVB) template has been used as a model system to investigate the effect of both parameters $C$ and $N$ upon the amount of magnetic material incorporated in the polymeric matrix.

The Sty–DVB copolymer used in this study was synthesized by suspension polymerization in the presence of inert diluents.[11] Apparent density (0.44 g/cm$^3$), surface area (140 m$^2$/g), average pore diameter (13 nm), toluene regain (1.52 cm$^3$/g), heptane regain (1.24 cm$^3$/g), percentage of volume swelling in toluene (100%), and percentage of volume swelling in heptane (58%) were parameters used to characterize the spherical, micrometer-sized polymeric template. Sulfonation of the Sty–DVB spheres were performed using concentrated sul-

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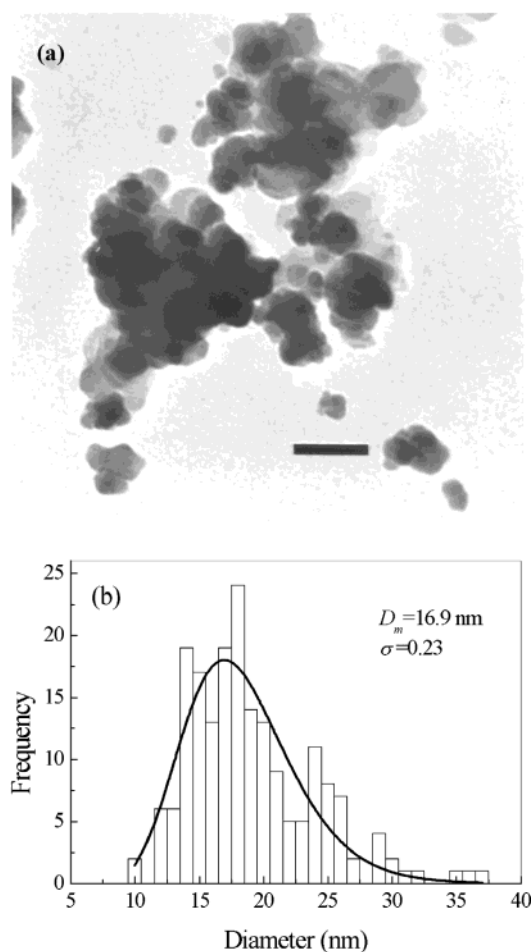(8) Underhill, R. S.; Liu, G. *Chem. Mater.* **2000**, *12*, 2082.

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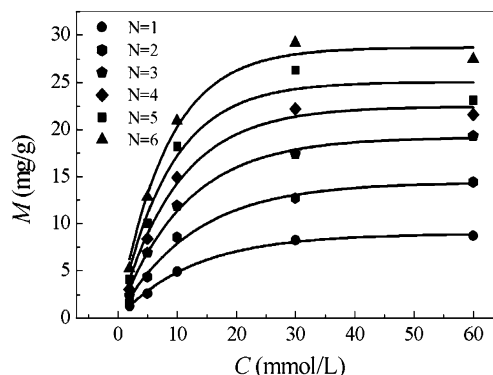(10) Qi, L.; Cölfen, H.; Antonietti, M. *Chem. Mater.* **2000**, *12*, 2392.

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furic acid (2 g of polymer/30 mL of sulfuric acid). The reaction was carried out in the presence of dichloroethane (40% in volume with respect to sulfuric acid). The Sty−DVB spheres were first suspended in dichloroethane for a few minutes. Then, sulfuric acid was added slowly while the temperature was maintained at 70 °C for 4 h. The Sty−DVB polymer particles (200-$\mu$m average diameter) were separated by filtration, washed thoroughly with deionized water, and dried at 60 °C for 24 h. The ion-exchange capacity (4.8 mmol of H$^+$/g) was determined as described in the literature.[12] This means that the maximum retention of bounded ferrous ion is 2.4 mmol/g of template (1 ferrous ion:2 sulfonate groups).

Several composite samples were prepared using 0.5 g of the sulfonated resin dispersed in 50 mL of FeSO$_4$ aqueous solution (bath solution). The ferrous-ion concentration (*C*) spanned from 2 to 60 mmol/L whereas 1−6 chemical cycles (*N*) were performed. The composite preparation followed a three-step procedure (one full chemical cycle). First, the sulfonated polymeric spheres were mixed with the bath solution and stirred for 1 h, at room temperature. Second, the polymer particles were separated by filtration and washed thoroughly with water until no iron was detected in the eluent. Third, the alkaline oxidation of the ferrous ion was performed by treating the ferrous-loaded resin with 50 mL of aqueous solution containing potassium hydroxide (0.018 mol) and sodium nitrate (1.3 × 10$^{-3}$ mol), at 70 °C for 15 min, under stirring. This particular chemical route of synthesizing magnetite, via partial oxidation of aqueous ferrous ion, has been described by Couling and Mann.[13] The composite was washed with water until the pH of the eluent was neutral and dried in an oven at 60 °C for 2 h. A representative number of samples were characterized by Mössbauer spectroscopy, X-ray diffraction, and transmission electron microscopy (TEM). For instance, the room-temperature Mössbauer spectra (data not shown) of the composite samples (*C* = 30 mmol/L, *N* = 2, 4, and 6) were resolved for two sextets. The fitted internal magnetic field was 489 ± 1 kOe (Fe$^{3+}$ tetrahedral A-site) and 452 ± 1 kOe (Fe$^{2+}$/Fe$^{3+}$ octahedral B-site). These values are reasonably close to the reported values for bulk magnetite,[14] ideal composition, Fe$^{3+}$[Fe$^{2+}$Fe$^{3+}$]O$_4$. In support of the Mössbauer data, the X-ray diffraction data (not shown) of the composite samples (*N* = 4 and *C* = 5, 10, 30, and 60 mmol/L) indicate magnetite as the main iron oxide phase. The average peak position (relative intensity) of the (220), (311), and (400) lines of the samples investigated were 30.296 ± 0.019° (27 ± 2), 35.665 ± 0.016° (100 ± 2), and 43.319 ± 0.018° (22 ± 2), whereas the magnetite ASTM data are 30.122° (30), 35.455° (100), and 43.099° (20), respectively. The TEM image of a representative sample (*C* = 30 mmol/L, *N* = 6) and the corresponding size histogram are shown in parts (a) and (b), respectively, of Figure 1. The size histogram in Figure 1b was curve-fitted using the log-normal *P*(*D*) = [exp(−2$\sigma^2$)/(2$\pi$)$^{1/2}$$\sigma D_m$]{exp[−ln$^2$(*D*/*D*$_m$)/2$\sigma^2$]} function,

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**Figure 1.** (a) TEM image of the composite sample *C* = 30 mmol/L and *N* = 6 (note the horizontal 40-nm bar size). (b) Particle size histogram obtained from the TEM data.



**Figure 2.** Total iron incorporation in the polymeric template (*M*) versus ferrous ion concentration (*C*) in the bath solution after *N* chemical cycles.

where *D*, *D*$_m$, and $\sigma$ are the particle diameter, the average particle diameter, and standard deviation, respectively.

A Perkin-Elmer 5000 atomic absorption system was used to obtain the iron content of the composite samples. Symbols in Figure 2 represent the total iron incorporation, in units of milligram of iron per unit gram of template, as a function of *C*, for different *N* values. The data shown in Figure 2 were analyzed in terms of a simple ion-incorporation model. The model describes ferrous ion incorporation as a result of the first two steps of the composite preparation process. The first step

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represents the copolymer ferrous charge whereas the second step accounts for the partial ferrous discharge. After ion diffusion into the template and the steady-state concentration is achieved, ferrous ion will be found in three different environments, namely, the left ferrous ion in the bath solution, ferrous ion inside the template nanocavity but bounded to a sulfonic-related site, and unbounded ferrous ion inside the polymer nanocavity. The increment in ferrous ion incorporation ($\Delta M$), driven either by the increment in ferrous ion concentration ($\Delta C$) or number of cycles ($\Delta N$), can be described by

$$\Delta M = (\partial M/\partial C)\Delta C + (\partial M/\partial N)\Delta N \qquad (1)$$

As long as ferrous ion is available at the sulfonic-related site and the site concentration is higher than the sulfonic-bounded ferrous ion concentration, the rate at which iron is incorporated in the polymeric template (driven either by $C$ or $N$), $\partial M/\partial C$ and $\partial M/\partial N$ are given by $\alpha(M_{\alpha N} - M)$ and $\beta(M_{\beta C} - M)$, respectively. Note that $\alpha$ and $\beta$ represent characteristic parameters describing the adsorption degree of ferrous ion by the polymeric template, whereas $M_{\alpha N}$ and $M_{\beta C}$ represent the maximum ferrous ion incorporation associated to a particular $N$ and $C$ value, respectively. After taking into account the appropriated boundary conditions, solution of eq 1 leads to $M(C,N) = A[1 - \exp(-\alpha C)][1 - \exp(-\beta N)]$, with $A = M_{\alpha 1}/[1 - \exp(-\beta)]$. However, before alkaline oxidation is performed (third step) partial ferrous ion desorption occurs due to the washing procedure (second step). It is assumed that the washing step takes out from the template mainly the excess of unbounded ferrous ion.

Therefore, at the end of the second step $M_{\alpha 1}$ is reduced to $M_0 = \lambda M_{\alpha 1}$, where $\lambda < 1$ represents the degree of ferrous ion desorption. Solid lines in Figure 2 represent the best curve fitting using $M(C,N) = \{M_0/[1 - \exp(-\beta)]\}[1 - \exp(-\alpha C)][1 - \exp(-\beta N)]$, with $M_0 = 6.6$ mg/g, $\alpha = 0.1$ (mmol/L)$^{-1}$, and $\beta = 0.04$. The $\alpha$ value means that, for a single chemical cycle ($N = 1$), 50% of maximum iron loading is obtained using $C = 7$ mmol/L. Furthermore, the $\beta$ value means that 50% of maximum iron loading ($C \gg 1$ mmol/L) is obtained after performing $N = 17$ chemical cycles.

In summary, stable magnetite nanoparticles have been synthesized in mesoporous styrene−divinylbenzene copolymer template. In addition, the Sty−DVB system was used to quantitatively investigate the effects of both ferrous ion concentration ($C$) and number of cycles ($N$) upon the amount of magnetic material ($M$) incorporated in the template. In the range of our investigation, it was observed that a very simple mathematical model could be used to explain the amount of magnetic material incorporated in the template. Though it is reasonable to expect that the model discussed in this study could be used to fit similar data, it should be stressed that the fitted parameters ($M_0$, $\alpha$, and $\beta$) are expected to change according to the physical (e.g., average pore diameter) and chemical (e.g., ion exchange capacity) characteristics of the polymeric template.