Size & Shape control, Co

Evolution of crystal structure, size, and shape with time after the injection of a solution of 0.6 g of Co$_2$(CO)$_8$ in 3 ml of o-dichlorobenzene into 0.1 ml of oleic acid and 0.2 g of TOPO in 12 ml of o-dichlorobenzene at 182°C. (A) XRD pattern at 15 s corresponding to a hcp-Co crystal structure. (B) TEM micrograph of the solution at 15 s; (C) 100 s; (D) 300 s; and (E) 1800 s. (F) XRD pattern at 1800 s corresponding to a [epsilon] -Co crystal structure. Bar, 100 nm

Self-Assembly: Reduction-4

Size & Shape control, Co

Single surfactant
- sphere

Surfactant mixture
- anisotropic

Separate nucleation & growth

Core-shell structures

Cationic Surfactant (CTAB)

- Water in oil nano-emulsion
- Nano-crystal size determined by enclosed water-pool size
- Metal salts can be dissolved into the water pool: Fe(II) → Fe(0)

Lithography


Fe core is metallic
Jagged Au shell surface may compromise oxidation resistance

Self-Assembly: Reduction-6

Figure 1 TEM images showing binary nanoparticle assemblies. a, Fe₃O₄ (8 nm):Fe₅₀Pt₂₀ (4 nm) assembly; b, Fe₃O₄ (8 nm):Fe₅₀Pt₂₀ (4 nm) assembly; and c, Fe₃O₄ (12 nm):Fe₅₀Pt₄₀ (4 nm) assembly. The assembly contained Fe₃O₄ and Fe₅₀Pt₂₀ binary nanoparticle assemblies with a mass ratio of Fe₃O₄:Fe₅₀Pt₂₀ = 1:10 and was formed by solvent evaporation of the mixed nanoparticle dispersions on amorphous carbon-coated TEM grids. All images were acquired using a Philips CM12 microscope at 120kV.

Figure 4 Typical hysteresis loops of two FePt-based nanocomposites. The composites were made from the annealed Fe₃O₄:Fe₅₀Pt₂₀ assemblies with particle mass ratio being kept constantly at Fe₃O₄:Fe₅₀Pt₂₀ = 1:10. a, Fe₅₀Pt₁₀:Fe₅₀Pt₅₀ (4 nm):Fe₅₀Pt₄₀ (4 nm) assembly. The loop shows single-phase-like behaviour, indicating effective exchange coupling between Fe₅₀Pt₁₀ and Fe₅₀Pt₅₀. b, A nanocomposite from Fe₃O₄ (12 nm):Fe₅₀Pt₄₀ (4 nm) assembly. Owing to the phase separation in the 12 nm:4 nm assembly as illustrated in Fig. 1c, the annealed sample contained large body centred cubic (b.c.c.) Fe grains as confirmed by HRTEM and EDS, rendering a nanocomposite with the hysteresis showing two-phase behaviour. The kink at low field is related to the magnetization reversal of the soft Fe.


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Self-Assembly: Reduction-7


FIG. 1. TEM images of (a) FePt/Fe$_3$O$_4$ and (b) FePt/CoFe$_2$O$_4$ core/shell structured nanoparticle assembly with shell thickness of 2 nm.

FIG. 3. (a) A typical magnetic hysteresis loop of an FePt/Fe$_3$O$_4$ nanoparticle assembly with shell thickness of 1 nm; (b) normalized coercivity $H_c$ of FePt/Fe$_3$O$_4$ nanoparticles as a function of Fe$_3$O$_4$ volume fraction [the curve is calculated from Eq. (2), and dots are data points]; and (c) hysteresis loop of FePt/CoFe$_2$O$_4$ nanoparticles with CoFe$_2$O$_4$ shell thickness of 2 nm.
II-J. Nanotemplates: Copolymer-1

TEM micrographs: (A) A spherical microdomain monolayer film before RIE. The lighter regions are the PB domains that were degraded and removed by ozonation, and the darker background is the PS matrix. (B) Hexagonally ordered arrays of holes in silicon nitride after RIE. The lighter regions are ~15-nm-deep holes that were etched out. (C) A cylindrical microdomain monolayer film before RIE. The darker lines are osmium-stained PB cylinders that lie parallel to the surface. (D) Fingerprint-like lines in silicon nitride after RIE. The darker regions are ~15-nm-thick ridges in the silicon nitride, which were protected from RIE.

Nanotemplates: Copolymer-2

Realized over 1cm², 100 billion holes

Nanotemplates: Copolymer-3


Lithography 64
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Nanotemplates: Copolymer-4

Adding a dimension: Use electric field to align the cylinders

Nanotemplates: Copolymer-5

Generating high spatial frequency arrays from low spatial frequency templates

**Nanotemplates: Copolymer-6**

**FIG. 1.** 0.5 Tbit/in² ($L_o=38$ nm) BPM array consisting of MLs deposited onto Si pillar substrates fabricated via e-beam directed assembly of block copolymer films. SEM micrographs of (a) the block copolymer film after selective removal of the PMMA cylinder cores, (b) Si pillars after Cr lift-off using the template in (a) and subsequent reactive ion etching, and (c) magnetic BPM after depositing a Co/Pd ML thin film onto the pillar structures (left: top view, right: section view at 85° angle). (d) Bright field TEM cross-sectional image through two consecutive rows of bits (into the image plane) that are 180° phase shifted with respect to each other.

**FIG. 3.** Normalized SFD vs density for BPM fabricated by e-beam alone (solid circles) and by directed assembly (open circles).
Nanotemplates: Sphere Nanolithography

Fig. 1. Schematic diagrams of single-layer (SL) and double-layer (DL) nanosphere masks and the corresponding periodic particle array (PPA) surfaces. (A) (111) SL mask, dotted line = unit cell, a = first layer nanosphere; (B) SL PPA, 2 particles per unit cell; (C) 1.7×1.7 μm constant height AFM image of a SL PPA with M=Ag, S=mica, D=264 nm, d_m=22 nm, r_d=0.2 nm s⁻¹. (D) (111) (1×1)-b DL mask, dotted line = unit cell, b = second layer nanosphere; (E) DL PPA, 1 particle per unit cell; (F) 2.0×2.0 μm constant height AFM image of a DL PPA with M=Ag, S=mica, D=264 nm, d_m=22 nm, r_d=0.2 nm s⁻¹.

Nanotemplates: Sphere Nanolithography

FIG. 1. Schematic diagram of the fabrication process. Top view (upper) and cross-sectional view (lower). (a) Arrangement of latex beads. (b) Thinning of latex array by reactive ion etching (RIE) with oxygen. (c) Sputter evaporation of Pt–Pd. (d) Removal of thinned latex beads. (e) Formation of hole array with CF$_4$ RIE.

FIG. 2. SEM images of the sample at each fabrication process step. The original latex diameter is 200 nm. (a) Arrangement of latex beads. (b) Thinned latex array with O$_2$ RIE for 90 s. (c) Removal of the thinned latex beads with acetone soaked cotton bud. (d) Completed 83 nm 6 hole array after CF$_4$ RIE for 300 s. (e) Cross-section of the cleaved sample of (d). The scale bars at the bottom right of (a)–(d) all show 500 nm.

Nanotemplates: Sphere Nanolithography

Figure 1. Schematic of the fabricating process for arrays of nanorings shown from a side view (left column) and a top view (right column): a) a monolayer of polystyrene (PS) nanospheres is deposited onto the substrate; b) a thin film of Co is sputter-deposited over the surface and PS nanospheres; c) an Ar+ ion beam is used, in normal incidence, to etch away the sputtered Co film and thus leaving only the nanorings protected under the PS nanospheres; d) a capping layer of Au or Cu is deposited over the entire surface to prevent oxidation. e) Schematic of the tapered cross-section of a nanoring.

Figure 3. a) Tilted-view micrograph of the Co rings after annealing in oxygen. b) Close-up of the bare Co rings. c) A collection of Co rings freed from the substrate.