Supporting Information

Magnetic Nanoparticle Assembly Arrays Prepared by Hierarchical Self-Assembly on Patterned Surface

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Methods:

Nanoparticle synthesis: Cobalt ferrite nanoparticles were prepared by modifying the method in reference 1. 0.129 g cobalt (II) acetylacetonate ($Co(acac)_2$) and 0.353 g $Fe(acac)_3$, 1.29 g 1,2-hexadecandiol, 0.847 g oleic acid, 0.802 g oleylamine and 10 mL benzyl ether were mixed in a 100 mL three neck flask. The flask was degassed by a Schlenk line for 15 minutes and then filled with argon gas, which was repeated for 3 times. The flask was slightly heated during degassing. After that, the mixture was heated up to 200^{o}C and kept at this temperature for 2 hours, which was then heated to reflux for 1 hour. Finally, the mixture was cooled to room temperature and washed by ethanol for 3 times to remove excess chemicals. Precipitated cobalt ferrites nanoparticles was then dried and redispersed in 10 mL toluene. 10 μL oleic acid was added to stabilize the nanoparticles. The concentration of nanoparticles is ~1.5×10^{15} /mL.

Fabrication of IPHAs: A chromium mask with square patterned hole array and feature size ~ 3 μm was used for photolithography to make hole arrays in photoresist on a (100) silicon substrate, whose surface has an oxide layer of ~ 60 nm. The pattern was then transferred into the silicon oxide layer by hydrofluoric acid etch, followed by removal of photoresist with acetone. Anisotropic etch of silicon substrate was performed by immersing the substrate into a potassium hydroxide solution at 80^{o}C with agitation for 10 minutes. Finally, the substrate was then washed and sonicated in deionized water.

Fabrication of MNCAs: To perform self-assembly of nanoparticles on IPHA, 20 μL cobalt ferrite nanoparticle solution was put on top of the IPHA by a glass micro-

syringe over the patterned area (1 cm×1 cm) in a petri-dish. The solution was then covered by a fluorinated polyether plate. To reduce the evaporation rate, the petri-dish was covered by a glass slides with a small opening. After the solution was completely evaporated, the fluorinated polyether plate was removed, and the substrate was then polished to remove the excess nanoparticles on silicon walls.

Characterizations: Cobalt ferrite nanoparticles were deposited on a carbon film supported by copper grid for TEM imaging with Zeiss Libra 200FE operating at 200 kV. IPHAs and MNCAs were directly characterized without treatment by SEM (JOEL JSM-6490LV) and HRSEM (Zeiss Ultra 55). Magnetic hysteresis loops were measured at room temperature by a vibrating sample magnetometer (VSM, Model: BHV-525, Riken Denshi Co., Ltd.).

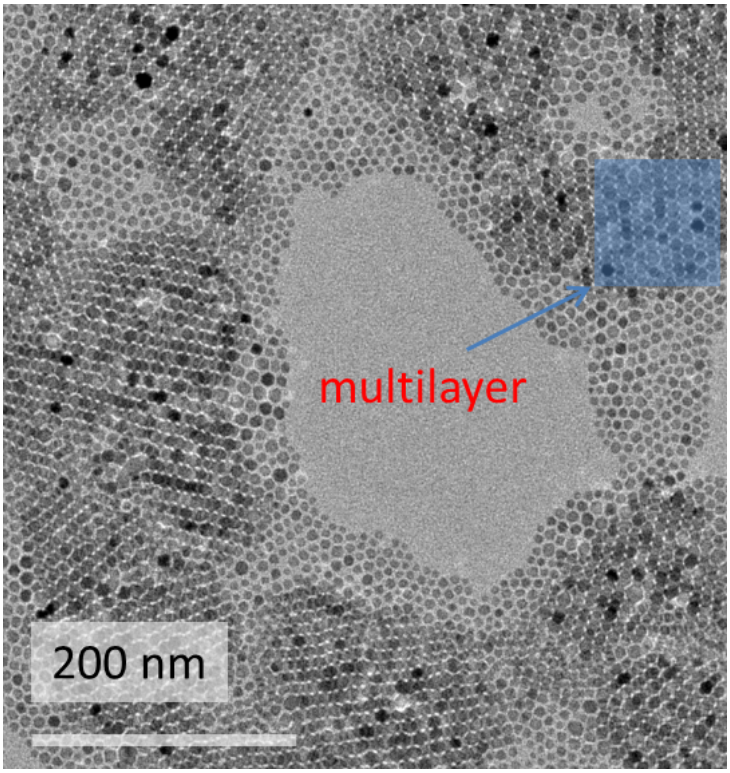

Figure 1S. A TEM image of cobalt ferrite nanoparticles that are used as the building blocks to fill the IPHAs.

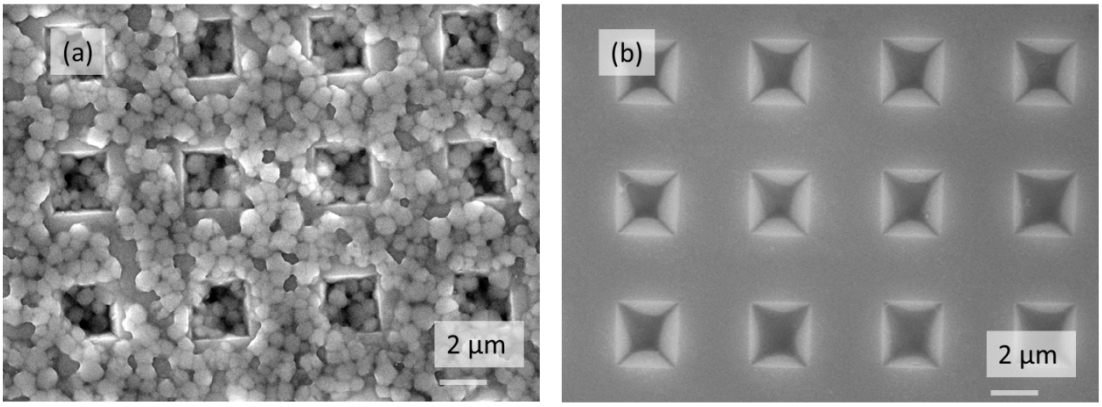

Figure 2S. SEM images of cobalt ferrite nanoparticles crystals formed by (a) naturally evaporating a droplet of nanoparticles solutions on an IPHA, and (b) by pulling an IPHA on silicon substrate out from the nanoparticle solution by a dip coater.

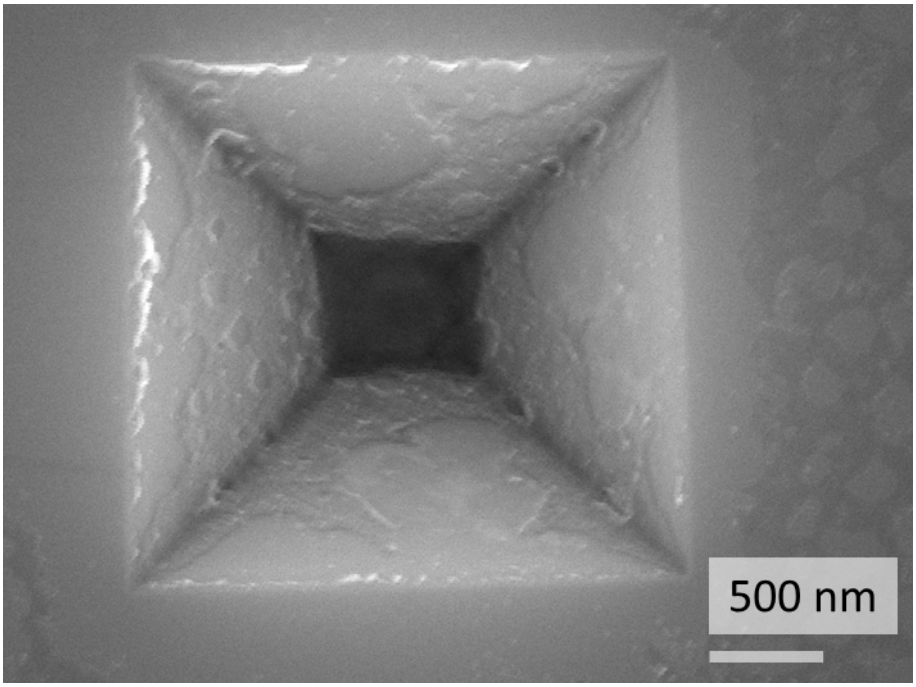

Figure 3S. A SEM image of a partially filled inverted pyramid hole. Nanoparticles diffused along the edge and sides.

Reference

1. S. H. Sun, H. Zeng, D. B. Robinson, S. Raoux, P. M. Rice, S. X. Wang and G. X. Li, *J Am Chem Soc*, 2004, **126**, 273-279.