

Electronic Supplementary Information

Additive Nanoscale Embedding of Functional Nanoparticles on Silicon Surface

Massimiliano Cavallini*^a, Felice C. Simeone^a, Francesco Borgatti^a, Cristiano Albonetti^a, Vittorio Morandi^b, Claudio Sangregorio^{cd}, Claudia Innocenti^d, Francesco Pineider^d, Emilia Annese^e, Giancarlo Panaccione^e, Luca Pasquali^f

a- CNR-ISMN Via P. Gobetti 101 I-40129 Bologna (I)

b- CNR-IMM Bologna Via P. Gobetti 101 I-4012 Bologna (I)

c- CNR-ISTM Milano Via C. Golgi 19 I-20133 Milano (I)

d- INSTM and Dep. of Chemistry “ U. Schiff” Università di Firenze, Via della Lastruccia 3-13, 50019 Sesto Fiorentino (FI) (I).

e- CNR-INFN-TASC S.S. 14-Km 163.5, AREA Science Park, I-34149 Basovizza (TS) (I)

f- Dep. of Materials and Environmental Engineering, University of Modena and Reggio Emilia, Via Vignolese 905 - 41100 Modena (I)

Methods

Substrate was Si(100)/SiO wafer with native oxide, that was cleaned by a standard protocol: sonication for two minutes in electronic-grade water (milli-pure quality), two minutes in acetone (chromatography quality) then two minutes in 2-propanol (spectroscopic grade quality). A metallized stamp obtained by replica molding via Polydimethylsiloxane curing of a written DVD were used for n-EM. Metallization is obtained by evaporation 100 nm of Au under UHV conditions. The NPs are deposited on the stamp or surface by spin coating or lithographically controlled wetting^{29,30}. Nanoembedding is obtained using the stamp as described in the text, applying +20V voltage for 10 seconds under a controlled relative humidity of 80%. All residual NPs and possible impurities, were removed by sonication in pure solvent (toluene) for 15min. In this way, all NP which are not embedded into the SiO_x stripes are removed.

M. Cavallini et al. *Nanoscale* 2010 (ESI)

NP synthesis

The synthesis of CoFe_2O_4 nanocrystals was carried out starting from stoichiometric amount of cobalt and iron acetyl acetonate. Briefly, a solution obtained dissolving 0.56 g (2.17 mmol) of $\text{Co}(\text{acac})_2$ (acac = acetylacetonate), 4 g (15.47 mmol) of 1,2-hexadecandiol, 3.3 g (12.34 mmol) of oleylamine and 3.4 g (12.04 mmol) of oleic acid in 15 mL of dibenzylether was heated to 150 °C and then 1.53 g (4.34 mmol) of $\text{Fe}(\text{acac})_3$ in 15 mL was added to the mixture. The solution was first kept 20 min. at 200°C, then 20 min. at 300°C. and finally cooled down at room temperature. The nanoparticles were precipitated from the solution and washed by addition of ethanol and centrifugation and redissolution in toluene. Because of the monodispersity of the nanoparticles, no further size selection procedure was needed. The final product consists of homogenous stoichiometric Cobalt Ferrite NPs with average size 6.0 nm \pm 1.3 nm (Fig. S1 containing ~1332 atoms on the surface).

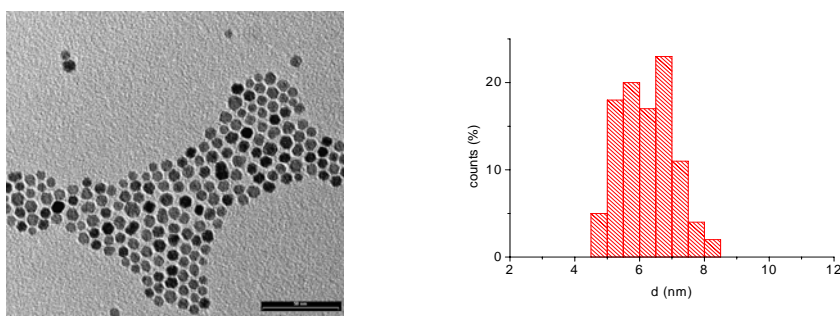


Figure S1. Transmission electron microscopy image of the as synthesized NPs (left) and corresponding particle size distribution (right) obtained by statistical analysis over ~150 particles. The image was obtained with a CM 12 Philips operating at 120 kV. The scale bar is 50 nm.

The number of surface metal ions was evaluated as :

$$(V_{\text{surf}}/V_{\text{np}}) * N_{\text{tot}} = 0.29 * 4594 = 1332$$

where V_{surf} is the volume occupied by surface ions and corresponds to the volume of a 3.2 Å thick layer, 3.2 being the average M-M distances in CoFe_2O_4 NPs [3], V_{np} is the total volume of a NP calculated from the average diameter obtained from TEM measurement, and N_{tot} is the total number of metal ion in a single NP calculated as $Z * V_{\text{np}} / V_{\text{cell}}$ where $Z=24$ and V_{cell} is the unit cell volume estimated from the lattice parameter obtained from XRD patterns.

Stamp preparation

A metalized stamp obtained by replica molding via Polydimethylsiloxane curing of a written DVD were used for N-EM. Metallization is obtained by evaporation 100 nm of Au under UHV conditions. Figure S2 shows the topography of used stamps:

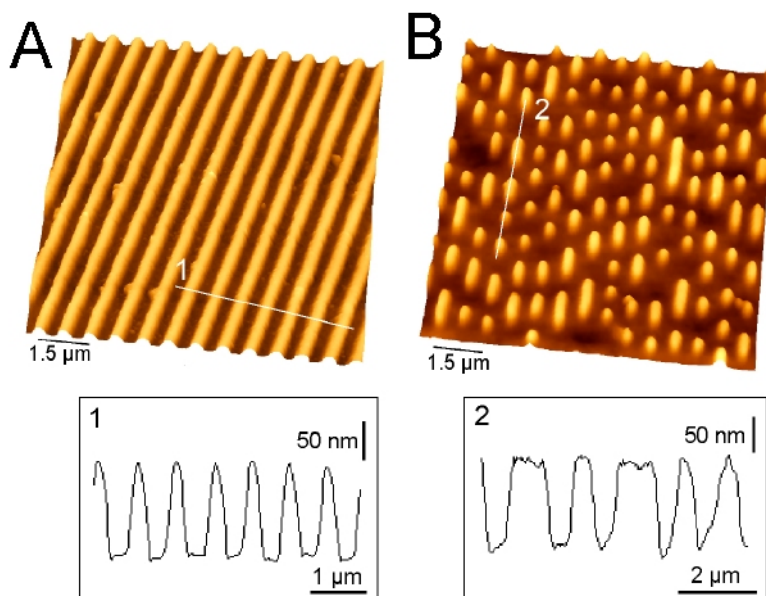


Figure S2. A) AFM topography of the stamp used for 1- and 2- step process of N-EM. B) AFM topography of the stamp used for printing of logic pattern.

XAS/XPS

The X-ray Absorption and Photoemission Spectroscopy measurements (XAS and XPS, respectively) were performed at the APE beamline located at the Elettra synchrotron radiation source in Trieste [3]. The samples (size 5x5 mm²) were prepared ex-situ with NPs embedded in stripes (single-step process) or grids (double-step process). Reference samples with non-processed thick films of NPs were prepared by drop casting on the metallic (molybdenum) sample holder. The samples were placed in UHV environment at a base pressure below 10⁻⁹ mbar and cooled down to 80 Kelvin, to reduce damaging effects induced by the incident x-ray photon beam.

The x-ray beam impinged on the surface with an angle of 45 degrees with respect to the surface normal. This geometry has been chosen to guarantee adequate surface and

M. Cavallini et al. *Nanoscale* 2010 (ESI)

subsurface sensitivity for both XAS and XPS. The XAS spectra at Fe (690 – 740 eV) and Co (765 – 800 eV) $L_{2,3}$ thresholds were recorded by collecting the total electron yield (TEY). The XAS signal was normalized to the incident flux by measuring the drain current of a gold-grid reference monitor. The incident x-ray beam size was about 50x500 mm (vertical x horizontal). The photon energy resolution for XAS spectra was 0.1 eV for both iron and cobalt $L_{2,3}$ edges. The electron analyzer for XPS measurements was oriented at 45 degrees with respect to the incident beam, hence collecting the photoelectrons emitted from the sample surface at normal emission geometry. The global energy resolution (beam and analyzer) was around 0.6 eV. The XPS spectra were collected with photon energy set at 1140 eV.

Figure S3 shows Si2p photoelectron spectra collected with photon energy 1140 eV over different positions of a sample surface with NPs embedded in grids (2-step process).

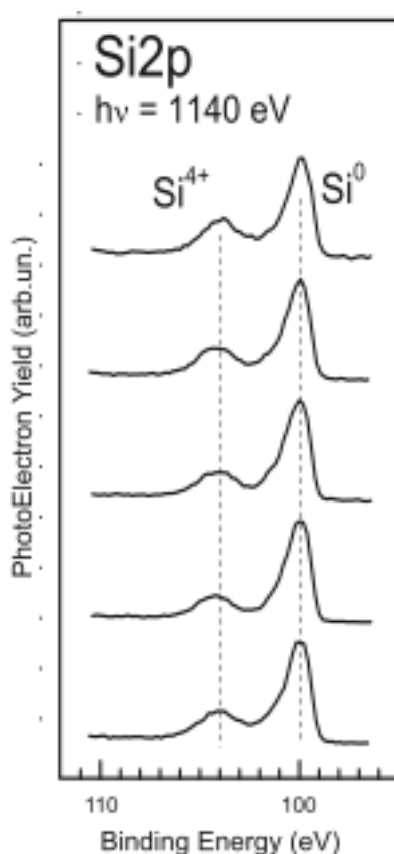


Figure S3. Si2p photoelectron spectra collected with photon energy 1140 eV over different positions of a sample surface with NPs embedded in grids (2-step process). The position of the peaks on the binding energy scale indicates the presence of bare Silicon (B.E. ~100 eV) and Silicon oxide (B.E. ~104 eV). The branching ratio of these two signals is basically constant over all surface regions.

M. Cavallini et al. *Nanoscale* 2010 (ESI)

SQUID Magnetic Measurements

The magnetic properties were studied with a Quantum Design Ltd. SQUID magnetometer operative in Reciprocating Sample Option (RSO) mode. The temperature dependence of ZFC-FC magnetizations were collected in a static field of 10mT after cooling the samples down to 2 K in a zero magnetic field (ZFC) or in the same probe field of 10mT (FC).

References ESI

- [1] M. Cavallini, F. Biscarini *Nano Letters* 2003, **3**, 1269.
- [2] D. Carta, et al., *J. Phys. Chem. C* **2009**, *113*, 8606–8615
- [3] G. Panaccione, et al., *Rev. Sci. Instrum.* 2009, **80**, 043105.