Supporting Information

Multifunctional Core@Satellite Magnetic Particles for Magnetoresistive Biosensors

Raffaele Campanile¹, Adriano Acunzo¹, Emanuela Scardapane¹, Antonio Minopoli¹, Veronica C. Martins², Rocco Di Girolamo³, Susana Cardoso²,⁴, Raffaele Velotta¹, Bartolomeo Della Ventura¹ and Vincenzo Iannotti¹,⁵,*

¹Department of Physics “E. Pancini”, University of Naples Federico II, Via Cintia 26, 80126 Naples, Italy
²INESC - Microsistemas e Nanotecnologias, Lisboa, Rua Alves Redol 9, 1000-049 Lisbon, Portugal
³Department of Chemistry, University of Naples Federico II, Via Cintia 26, 80126 Naples, Italy
⁴Instituto Superior Tecnico (IST), Universidade de Lisboa, Av. Rovisco Pais, 1649-004 Lisboa, Portugal
⁵CNR – SPIN (Institute for Superconductors, Oxides and other Innovative Materials and Devices), P.le Tecchio 80, 80125 Naples, Italy

*Corresponding authors: viannotti@unina.it

Table of contents

Figure S1. Color of the MNP cluster solution before and after the gold coating.

Figure S2. X-rays diffraction spectrum of CSMPs.

Section S3 (Figure S3). Numerical simulations (FDTD).

Figure S4. Magnetoresistive biochip.

Figure S5. Functionalization procedure.

Figure S6. Biochip detection platform.

Figure S7. Graphic User Interface.

Figure S8. Experimental setup.

Figure S9. Transfer curve of a spin valve (SV) sensor.
Figure S1. Suspension of MNP clusters as from the stock (a), and after the gold coating process (b). The concentration was $5\times10^9$ particles$\cdot$mL$^{-1}$ in both cases.
Figure S2. XRD pattern of core@satellite magnetic particles (Miller indices of both Au and Fe3O4 crystalline phases are indicated). Au diffraction peaks are observed at 38.2° (111), 44.4° (200), 64.9° (220), and 77.6° (311); moreover, Fe3O4 characteristic Bragg reflections are shown by their indices (220), (311), (511) and (440) at 30.3°, 35.7°, 57.3° and 62.9°, respectively.
Section S3

The optical response of MNP clusters and CSMPs was theoretically investigated by the finite-difference time-domain (FDTD) method implemented in Lumerical “FDTD solutions” tool. Figure S3a depicts the scheme of the simulation workspace, that included a Mie scattering setup with a scatterer placed at the center of a total-field scattered-field (TFSF) volume (1200 nm × 1200 nm ×1200 nm) whose bottom side acted as a linearly polarized plane wave source (bandwidth: 400-800 nm). The boundaries of a TFSF volume act as filters for the scattered fields in such a way that scattered radiation is the only one allowed to flow outward the TFSF volume region. Therefore, a power field monitor box (spectral resolution: 1 nm) placed around the scatterer collected the absorbed power, whereas a similar monitor box around the TFSF region collected the scattered power flows. Such a setup was placed inside a FDTD solver region (3200 nm ×3200 nm ×3200 nm) with background RI 1.333 (i.e., filled by water) and perfect matched layer (PML) boundary conditions (BCs) optimized for steep-angle radiation. Furthermore, a 2 nm step mesh override region was applied to the scatterer to retrieve accurate results within a reasonable simulation time.

It is worth noticing that the adoption of the power field monitor boxes allowed us to retrieve the theoretical absorption and scattering cross sections straightforwardly, i.e., by dividing the powers (collected by the monitor boxes) by the TFSF source intensity. Finally, we calculated the theoretical extinction cross section $\sigma_{\text{ext}}$ of the scatterer by adding them together.

In order to make a straightforward comparison between experimental and simulated spectra, we preliminarily estimated the experimental extinction cross sections $\sigma_{\text{ext}}$ of MNP clusters and CSMPs from the measured extinctions $E$. Since $E = \varepsilon l c_M$, where $\varepsilon \equiv \frac{N_A}{\ln(10)} \sigma_{\text{ext}}$ is the molar attenuation coefficient, $l$ the optical path and $c_M$ the sample molarity, it is easily seen that $\sigma_{\text{ext}} = \ln(10) \frac{E}{l c_V}$, in which $c_V$ is the number density of the scatterers in the sample solution ($5 \times 10^9$ particles/mL$^{-1}$, see Section 2.1).

We chose and set the Fe$_3$O$_4$ material dataset from Querry$^1$ for all the simulations involving MNP clusters and CSMPs. DLS measurements suggested a hydrodynamic diameter of $\approx$250 nm, but a sphere with such a value would yield a spectrum (red, in Figure S3b) $\approx$3–4 times larger than the experimental one (dashed black, in Figure S3b). On the contrary, the experimental spectrum was well reproduced by a sphere with diameter $\approx$150 nm, a value significantly different from that measured by DLS. Moreover, spheres with such a diameter (or larger) yielded spectra with modulations not found
in the real samples. The occurrence of such modulations, – which we can safely ascribe to interband electron transitions that come into play when bulk features become increasingly important – eventually suggested that the spherical shape was unsuitable to simulate clusters.

Thus, we modelled the MNP clusters as a Fe$_3$O$_4$ spheroid with a 250 nm major axis and 130 nm (equal) minor axes, the latter value being the output of an optimization procedure. Since in a real

Figure S3. (a) Scheme of the simulation workspace in Lumerical’s environment. Linearly polarized plane waves propagating along $z$ direction were used to theoretically investigate the optical response of an isolated CSMP. (b) Comparison between the experimental spectrum of Fe$_3$O$_4$ MNP clusters (dashed black) and the simulated spectra of Fe$_3$O$_4$ nanospheres with diameters ranging from 100 nm to 250 nm (solid lines). The experimental spectrum was well reproduced by a sphere with diameter approximately 150 nm, a value incompatible with DLS measurements. (c) Comparison between the experimental spectrum of Fe$_3$O$_4$ MNP clusters (dashed black) and the simulated spectra of single Fe$_3$O$_4$ spheroids with 250 nm major axis at varying minor axes (solid lines). The 250 nm × 130 nm × 130 nm spheroid (solid black) was taken as model for the actual MNP cluster geometry. (d) Comparison between the experimental spectrum of CSMPs (solid black) and the simulated spectra of single 250 nm × 130 nm × 130 nm spheroids at increasing degrees of covering by 15 nm AuNPs. The best agreement was found by a ≈85% covering (dotted magenta).
colloidal sample the particles are randomly oriented, the optical response of a spheroidal particle has to be averaged over its spatial orientations as well as over the light polarizations. For a given particle orientation, the optical response under unpolarized light was obtained by running two simulations with source polarization rotated 90 degrees with respect to each other, and then averaging the results.

As for the spheroid orientations, the cylindrical symmetry of the entire system around $k$ implies that the dependence on the solid angle reduces to $\sin(\theta)$, with $\theta$ the angle between $k$ and the major spheroid axis:

$$
\sigma_{\text{ext}}(\lambda) = \frac{\int_{0}^{\pi} \sigma_{\text{ext}}(\lambda, \theta) \sin(\theta) \, d\theta}{\int_{0}^{\pi} \sin(\theta) \, d\theta} \rightarrow \frac{\sum_{\theta_i=0}^{\pi/2} \sigma_{\text{ext}}(\lambda, \theta_i) \sin(\theta_i)}{\sum_{\theta_i=0}^{\pi/2} \sin(\theta_i)}.
$$

In equation (1), $\sigma_{\text{ext}}(\lambda, \theta_i)$ are the cross-section after the average over polarizations, whereas $\theta_i = 0, \pi/6, \pi/3, \pi/2$. Thus, each spectrum was achieved as the average of six spectra (three angles $\times$ 2 polarizations; the spectrum corresponding to $\theta = 0$ is null). Figure S3c shows $\sigma_{\text{ext}}(\lambda)$ spectra calculated according to (1), with minor axis of 120 nm (red), 130 nm (black), and 140 nm (blue) from which we deduce that $250 \text{ nm} \times 130 \text{ nm} \times 130 \text{ nm}$ spheroid satisfactorily reproduces the experimental data.

Eventually, a CSMP was modelled by 15 nm diameter spherical AuNPs$^2$ randomly distributed onto the $250 \text{ nm} \times 130 \text{ nm} \times 130 \text{ nm}$ spheroid in such a way that their center-to-center distances were at least 15 nm. Figure S3d shows $\sigma_{\text{ext}}$ spectra at various grades of covering of the spheroid surface: the best agreement was found with 260 AuNPs that corresponds to $\approx 85\%$ covering.

(1) Querry, M. R. Optical Constants, Report No. AD-A158 623. Crdc 1985, CR-85034, 1–413.

(2) Johnson, P. B.; Christy, R. W. Optical Constants of the Noble Metals. Phys. Rev. B 1972, 6 (12), 4370–4379. https://doi.org/10.1103/PhysRevB.6.4370.
Figure S4. a) Image of the PCB carrier containing the chip. The gold stripes in upper part are connected to the chip in center, the contacts are covered with silicon gel to prevent electrolysis during measurement. b) Microscope image (5x magnification) showing the 6 sensing regions. c) Microscope image (20x magnification) of one sensing region. d) Microscope image (50 x magnification) highlighting the sensors details, the gold squared frame (300 x 300 µm²) contains the 5 U-shaped SV sensors (80 × 2.6 µm²) covered by a gold pad (35 × 13 µm²).
Figure S5. (a) 1 mL of Ab solution at 25 µg·mL$^{-1}$ was pipetted in a standard quartz cuvette. (b) The cuvette was placed into the lamp and (c) irradiated for 30 s. (d) The solution with the irradiated Abs was spiked into the colloidal solution (e) magnetically stirred. The number of spikes was 10 and the volume of each spike was 1:20 v/v.
Figure S6. Detail of the biochip platform internals: 1) chip insertion site, 2) coil for magnetic drive, 3) battery, 4) box enclosing detection electronic, 5) USB port.
Figure S7. Screenshot of the graphic user interface (GUI) through which the platform is operated.
Figure S8. Experimental setup: on the left a syringe pump; on the right the biochip detection platform connected to a PC through a USB connector for data acquisition.
Figure S9. Transfer curve of a single U-shaped spin valve (SV) sensor (80 × 2.6 µm²)