Electronic supplementary information (ESI)

Poly(vinyl alcohol)/sodium alginate/magnetite composites: Magnetic force microscopy for tracking the magnetic domains

Alex Carvalho Alavarse[1*], Jean Bezerra Silva[2], Henning Ulrich[2], Denise Freitas Siqueira Petri[1]

1: Fundamental Chemistry Department, Institute of Chemistry, University of São Paulo, Av. Prof. Lineu Prestes 748, São Paulo, 05508-000, Brazil

2: Department of Biochemistry, Institute of Chemistry, University of São Paulo, Av. Prof. Lineu Prestes 748, São Paulo,05508-000, Brazil

*Corresponding author. Email: a.alavarse@usp.br

MFM theory background

The principles of MFM can be found in excellent literature reports[1–4]. Briefly, the interaction force (F_{ts}) between the tip and the surface causes small displacements (z) with respect to the rest position (z_0) of the cantilever. F_{ts} can be described after a Taylor expansion[5]

$$F_{ts} \approx \frac{dF_{ts}}{dz}\Big|_{z = z0}\, z(t) \quad (1)$$

The long-range force interactions between the magnetic probe and the magnetic sample can be correlated with the shift in frequency ($\Delta\omega$), amplitude (ΔA), or phase ($\Delta\ \Phi$) from the initial parameters of the oscillating cantilever. For the detection of the magnetic force, the tip is lifted (> 10 nm) to avoid the contribution of van der Waals forces. The phase signal (Φ) of the oscillating cantilever shifts when F_{ts} occurs. The phase signal (Φ) during the F_{ts} becomes[5]

$$\Phi(\omega) = tan^{-1}\left(\frac{m\omega\omega_0}{Q(k + \frac{dF_{ts}(z)}{dz} - m\omega^2}\right) \quad (2)$$

where m is the mass of oscillating probe, ω is the excitation frequency, ω_0 is the initial resonant angular frequency, Q is a quality factor, and k is the spring constant of the cantilever. Without any external acting force, k is equal to $m\omega_0^2$ and if $\frac{dF_{ts}(z)}{dz} << k$, the phase can be described as a function of $\frac{dF_{ts}}{dz}$ [5]

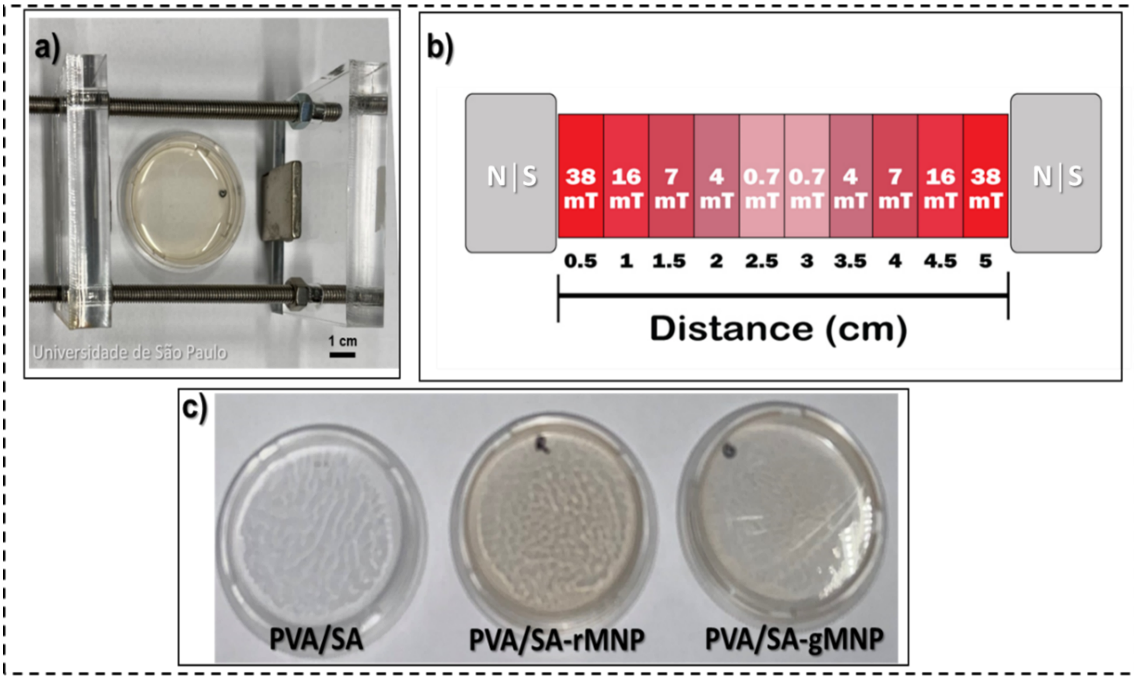
$$\Phi(\omega_0) = tan^{-1}\left(\frac{k}{Q\frac{dF_{ts}}{dz}}\right) \quad (3)$$

After some mathematical approximations, the relation between the phase shift ($\Delta\Phi$) and F_{ts} can be given by[5]

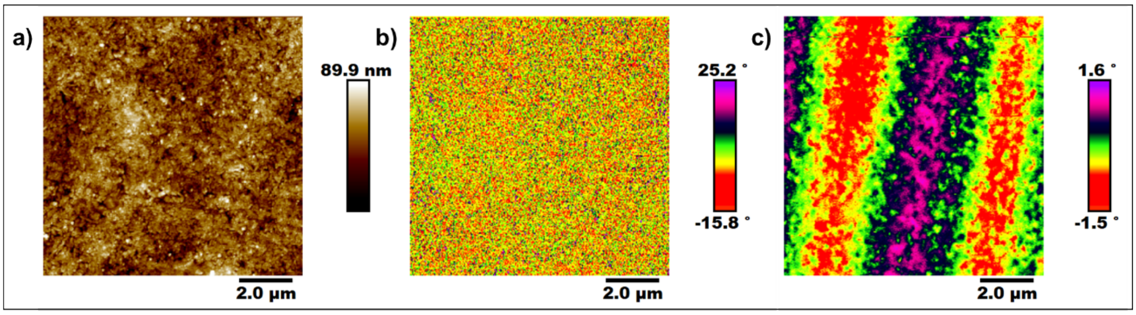
$$\Delta\Phi(\omega_0) = \frac{\pi}{2} - tan^{-1}\left(\frac{k}{Q\frac{dF_{ts}}{dz}}\right) \approx \frac{Q}{k}\frac{dF_{ts}}{dz} \quad (4)$$

The stronger the magnetic interaction between the magnetic probe and the magnetic surface, the larger is the phase shift [6]. Even avoiding short-range interactions, $\Delta\Phi$ can be affected by adverse signals such as electrostatic interactions, acoustic and vibrational noise, for example. Then, the investigation of magnetic domains by MFM shall be performed carefully.

Figure Support Information (FSI)



FSI 1. Setup formed by two parallel NdFeB magnets. The aqueous PVA/SA/MNPs dispersion was positioned between the magnets and dried in an oven at 40 °C overnight. (**b**) Magnetic field as a function of the distance (**c**) Hydrogels (dry state) samples after 16 h of drying. **PVA/SA** (without MNPs), **PVA/SA-rMNP** (with MNPs dispersed randomly) and **PVA/SA-gMNP** (with MNPs oriented by the external magnetic field).



FSI 2. (**a**) AFM topography, (**b**) normal phase (amplitude setpoint = 310 mV and drive amplitude = 171 mV) and (**c**) MFM phase (lift height = 30 nm) of a floppy disk sample.

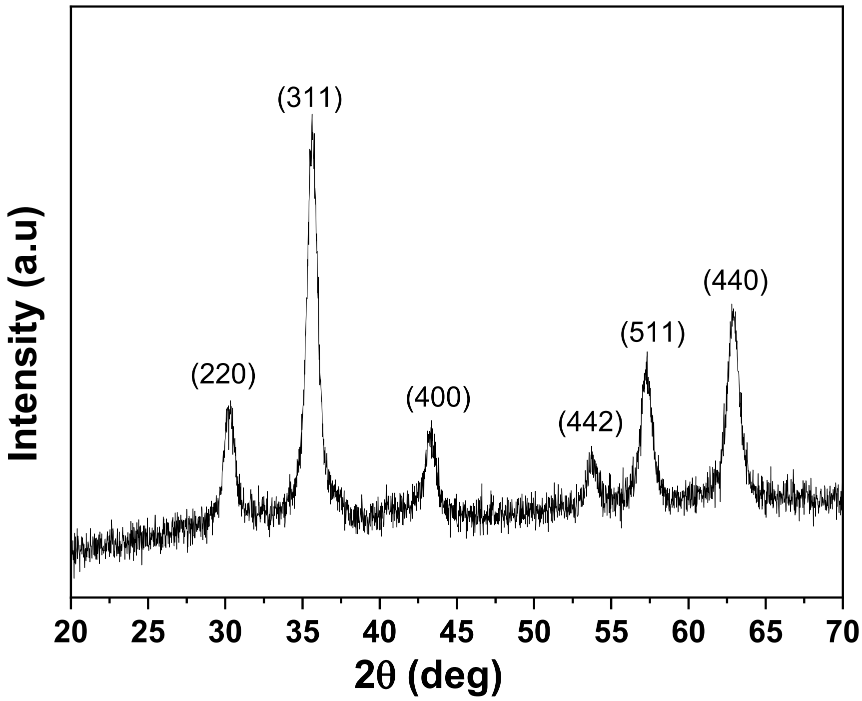
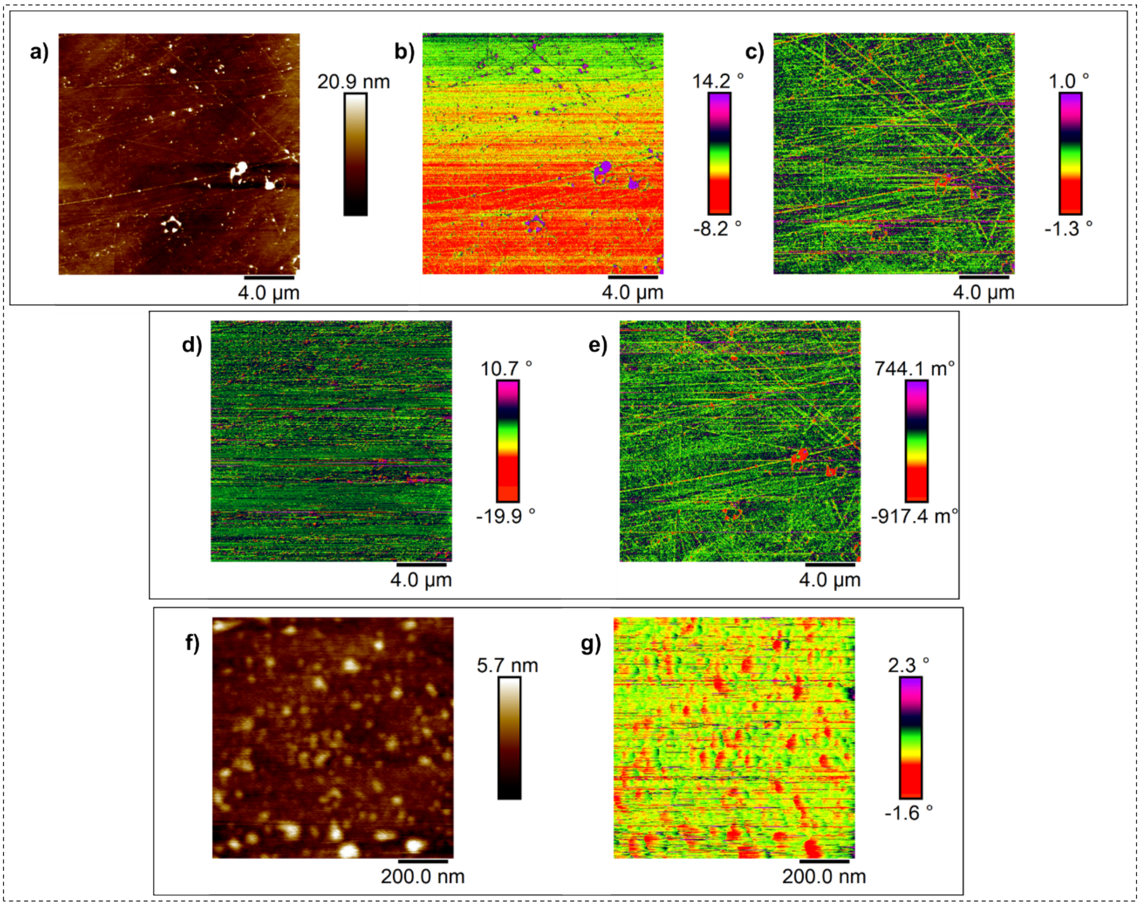
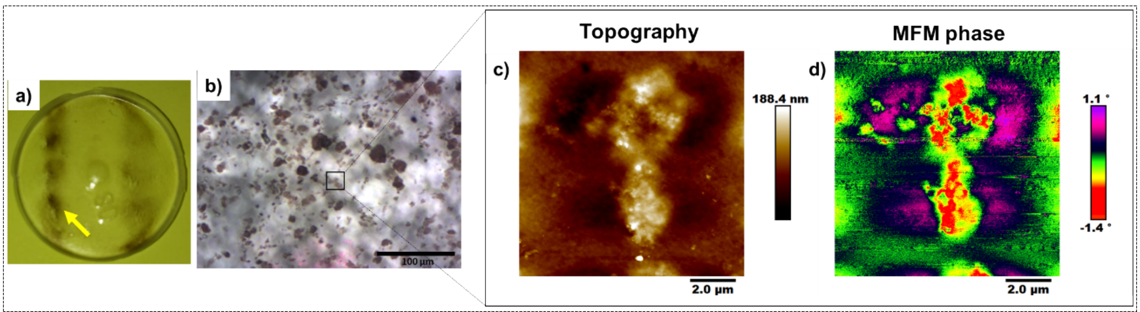


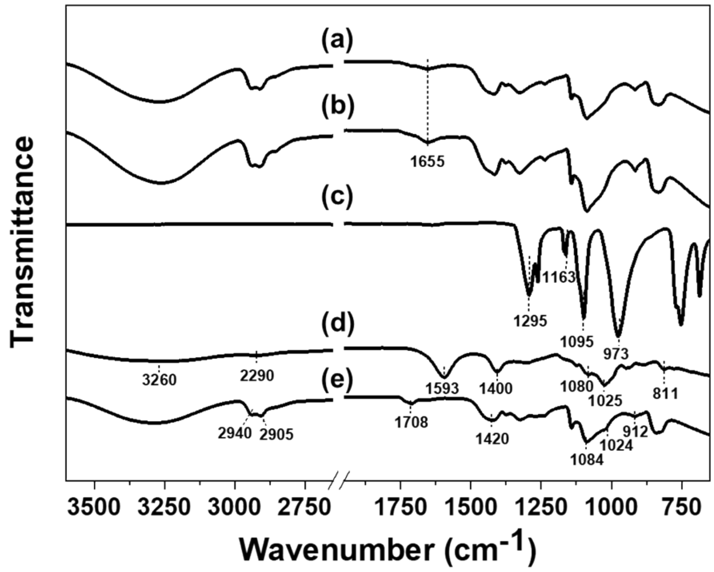
Figure FSI 3. X-ray diffractogram of synthetized MNPs (powder).



FSI 4. (**a**) AFM topography, (**b**) normal (amplitude setpoint = 250 mV and drive amplitude = 1309 mV) and (**c**) MFM images of MNPs coated with CTAB. (**d**) The MFM scanning ranging the lift mode = 10 nm to (e) 50 nm shows that the magnetic domains (red dots) were enhanced after coating the MNPs. The magnetic domains are possible to observe in single domains as shown in topographic (**f**) and MFM phase (lift height = 50 nm) (**g**) images.



FSI 5. (**a**) Photomicrograph, (**b**) optical micrography, (**c**) AFM topography (amplitude setpoint = 290 mV and drive amplitude = 1012 mV) and (**d**) MFM phase (lift height = 30 nm) of PVA/SA-MNP previous dried on magnetic strips. The yellow arrow in (**a**) indicates the magnetic clusters formed by the presence of two pieces of magnetic stripes.



FSI 6. FTIR-ATR spectra of (**a**) PVA/SA-rMNP (**b**) PVA/SA hydrogel, (**c**) STMP, (**d**) SA and (**e**) PVA precursors.

Table Support Information (FSI)

TSI 1: FTIR Bands of main precursors used for PVA/SA hydrogel synthesis

STMP		Sodium alginate		PVA	
Wavenumber (cm^{-1})	Band assignment	Wavenumber (cm^{-1})	Band assignment	Wavenumber (cm^{-1})	Band assignment
1293	P=O stretching [7]	3400-3200	OH stretching [8]	330-3200	OH stretching [9]
1163	P=O stretching [10]	2290	CH stretching [8]	2940/2905	CH/CH_2 stretching [9]
1095	P-O bending (Liu et al. 2018)	1593	COOH stretching (asymmetric) [8]	1734/1708	C=O stretching [9]
973	O-P-O stretching (Liu et al. 2018)	1400	COOH stretching (symmetric) [8]	1420	CH_2 bending [9]
		1080	C-O-C stretching	1084	C-O stretching [11]
		947/881	Mannuronic/Guluronic acids stretching [12]	1024	C-C stretching [9]
		811	Na-O stretching [13]	912	C-C stretching [11]

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