Supporting information

Non-uniform growth of composite Layer-by-Layer assembled coatings via three-dimensional expansion of hydrophobic magnetite nanoparticles

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S1. Investigation of appearance and size distribution of the initial primary magnetite NP in their original heptane suspension

		Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm): 26,89	Peak 1:	30,19	100,0	8,912
PdI: 0,099	Peak 2:	0,000	0,0	0,000
Intercept: 0,914	Peak 3:	0,000	0,0	0,000
Result quality : Good				

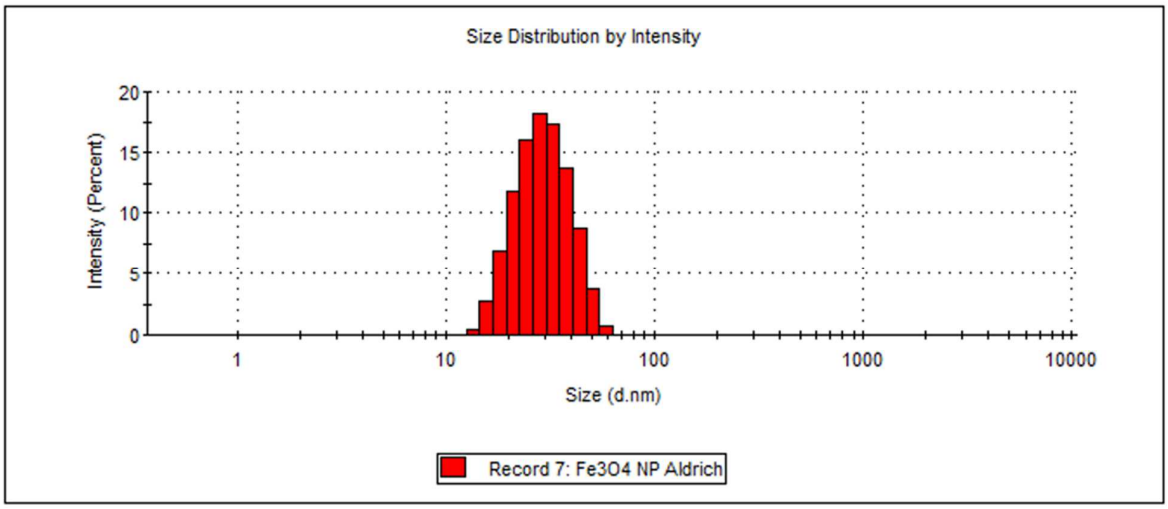

Figure S1a. Distribution of magnetite nanoparticles size measured by DLS.

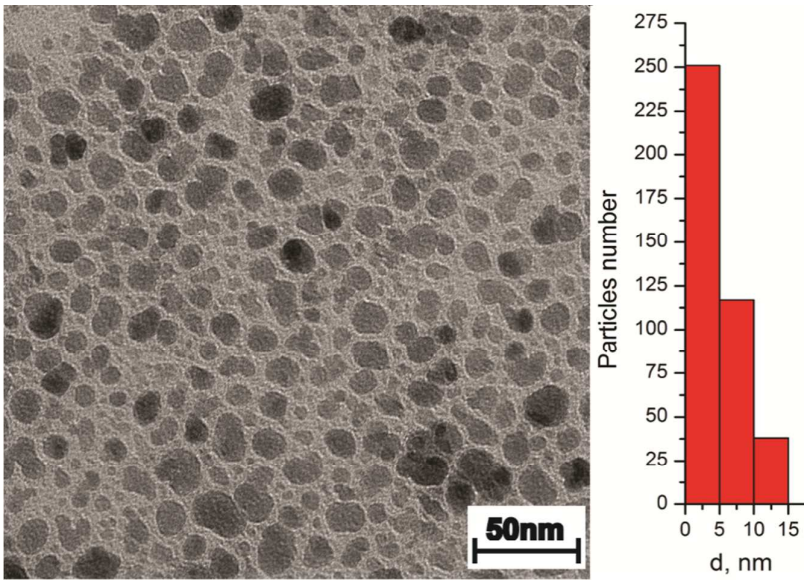

Figure S1b. Distribution of magnetite nanoparticles size measured by TEM.

S2. Determination of concentration of Fe_3O_4 NP in initial suspension

Concentration of magnetic nanoparticles was determined experimentally by weighing a dry residue of nanoparticles in the suspension. In particular, we took 1 ml of initial nanoparticles suspension and put it in a small glass Petrie dish of certain mass. Afterwards, the dish with nanoparticles suspension was heated up to 80°C and dried at this temperature for several hours in a drying chamber until the mass of the dish with a dry nanoparticles residue leveled off. Thus, by knowing the volume of

suspension and the mass of the nanoparticles we calculated their concentration. The drying was carried out for three times. As a result, we figured out the concentration of the nanoparticles to be 5.6±0.1 mg/ml.

S3. The structural formulas of substances involved in LbL assembly

We used poly(ethyleneimine) (PEI) aqueous solution for preparation of nanocomposite coatings by layer-by-layer assembly technique described in our manuscript. The name of PEI according to IUPAC nomenclature is poly(iminoethylene). The structural formula of PEI monomeric unit is shown in Figure S2a.

Another one important agent playing a significant role in a layer-by-layer process described in our manuscript is oleic acid. According to IUPAC nomenclature the name of oleic acid is (9*Z*)-Octadec-9-enoic acid. The structural formula of oleic acid is shown on Figure S2b.

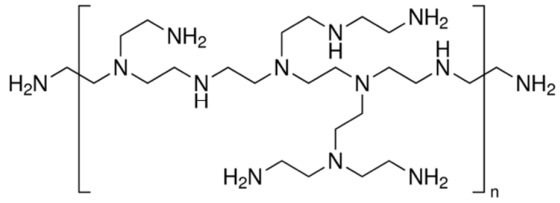

Figure S2a. Structural formula of poly(ethyleneimine) monomeric unit.

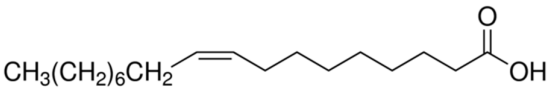

Figure S2b. Structural formula of oleic acid.

S4. Sketch of LbL deposition and detailed description of PEI/Fe_3O_4 NP multilayers preparation

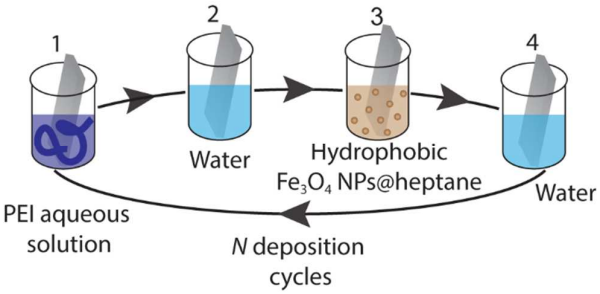

Figure S3. Sketch of the LbL deposition.

Figure S3 shows the sketch of LbL assembly procedure employed in our work. In general, this is a traditional LbL deposition as it was shown initially by Decher (Decher, G., *Science* **1997**, *277*, 1232-1237) and Schmitt et al. (Schmitt, J. et al. *Adv. Mater.* **1997**, *9*, 61-65) and does not require any additional equipment.

In more detail, after cleaning (see "Materials and methods" section in the manuscript) the substrates were immersed into PEI aqueous solution (2 mg/ml) for 30 seconds (first step on Figure S3). Afterwards, the substrates were washed for three times in deionized water (second step on Figure S3) and dried under an air stream. This lead to formation of PEI surface layer on the substrate. Then, the substrates were immersed into a hydrophobic nanoparticles suspension for 15 min (third step on Figure S3). The deposition was carried out in initial undiluted suspension without any additional stirring or shaking. Finally, after nanoparticles adsorption, the substrates were washed with deionized water (fourth step on Figure S3) and dried under an air stream as well. The particular mechanism of hydrophobic nanoparticles adsorption is given in the manuscript. Further, PEI and

magnetite nanoparticles deposition was iterated to achieve the desired number of PEI/Fe_3O_4 NP bilayers.

S5. Determination of free oleic acid concentration in Fe_3O_4 NP suspension by chromatographic analysis

Concentration of free oleic acid molecules in magnetite nanoparticles by chromatographic measurements was found as follows. First, we separate the nanoparticles from supernatant by centrifugation so that to exclude oleic acid coupled with the nanoparticles from quantification. The centrifugation was carried out at $15 \cdot 10^3$ rpm for 10 min for three times. Afterwards, the supernatant was diluted by a factor of 10 in chloroform. The resulted sample was tested on Trace GC-DSQ (Thermo Scientific) chromate-mass-spectrometer with following parameters:

- Helium gas (99.995%) was used as a mobile phase with the flow rate of 1 ml/min;
- Type of chromatographic column: TR-5MS with length of 30 meters, outer diameter of 0.32 mm, and film thickness of 0.25 μm;
- Analysis was carried out for 55 min;
- Heating profile: 80°C for 5 min, afterwards heating to 240°C with a rate of 4°C/min, and finally stabilization for 10 min.
- Analysis was carried out in a range from 45 to 300 atomic mass units (Full Scan Mode).
- The volume of tested samples was 1 μl.

In particular, analysis was performed in a few steps. First, reference sample of oleic acid dispersed in chloroform (229.5 ppm) was tested. This allowed to plot the calibration curve that was used to determine the concentration of oleic acid in tested sample. According to this procedure we found the concentration of free oleic acid molecules in supernatant to be 2.4 mg/ml.

S6. AFM images of the PEI/Fe_3O_4 NP nanocomposites formed with washing in heptane.

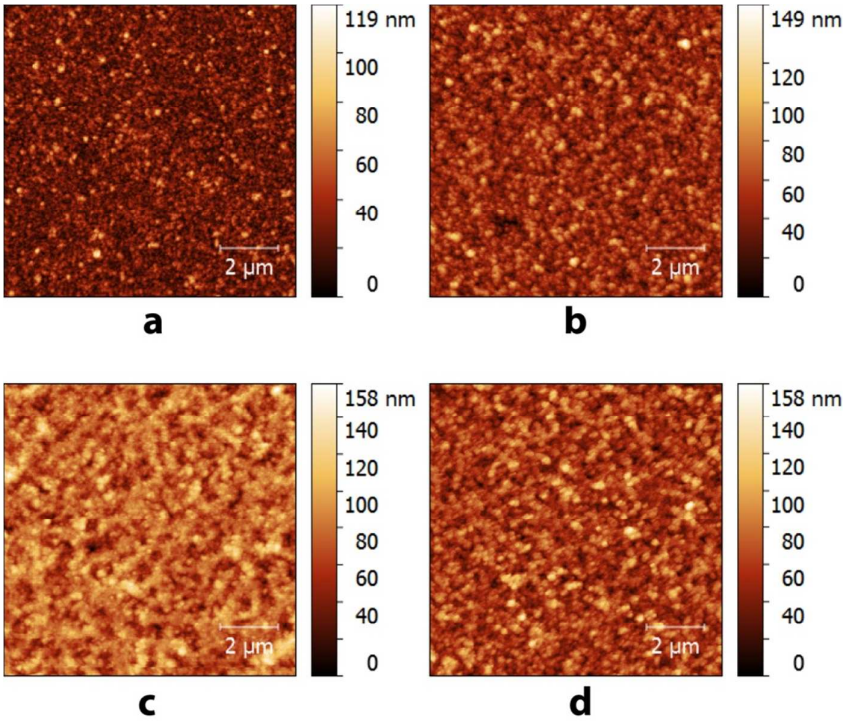

Figure S4. AFM images of the nanocomposites with 5 (a), 10 (b), 15 (c), and 20 (d) PEI/Fe_3O_4 NP bilayers formed with washing in heptane.