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Relaxation times of colloidal iron platinum in polymer matrixes

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Supporting Information

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I) Synthesis of hydrophobic FePt nanoparticles
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I.1) Chemicals
Octyl ether (99%), 1,2 hexadecanediol (Tech 90%) and iron pentacarbonyl (99.99%), oleic acid (Tech90%), oleyl amine (Tech 70%) were purchased from Sigma, 1,2 hexadecanediol (>98.0%) was also purchased from TCI Europe, platinum acetylacetonate (98%) was purchased from ABCR chemicals. All solvents used for precipitation and re-dispersion of the particles (methanol, ethyl acetate, chloroform, toluene and hexane) were purchased as anhydrous solvents from Sigma.

I.2) FePt synthesis
For the synthesis of the iron platinum particles we followed the recipe previously reported by Sun [5]. In this synthesis method a combination of oleic acid and oleyl amine was used to stabilize the monodisperse FePt colloids and prevent oxidation. FePt particles were obtained by the reduction of $Pt(acac)_2$ (acac= acetylacetonate, $CH_3COCHCOCH_3$) by a diol and the decomposition of $Fe(CO)_5$ in high-temperature solutions. 1,2-hexadecanediol was used to reduce the $Pt(acac)_2$ to Pt metal. Briefly in a 50 ml three neck flask 10 ml of octyl ether, 95 mg of $Pt(acac)_2$ and 195 mg of 1,2 hexadecanediol were mixed under nitrogen atmosphere. The temperature was raised to 100°C until the solution turned into clear translucent yellow color. A mixture of oleic acid (0.08 ml), oleyl amine (0.08 ml), and iron pentacarbonyl (0.06 ml) was injected quickly under vigorous stirring into the $Pt(acac)_2$ solution. The mixture solution was heated to 280 °C at a heating rate of 12 °C/min. The solution was incubated at this temperature for 15 minutes. Finally the heating mantle was removed to stop the reaction. At room temperature particles were precipitated from the solution by addition of anhydrous methanol (15 ml) and a small quantity of ethyl acetate (2-3 ml) in order to prevent phase separation of the solvents. The supernatant was discarded, and the precipitate containing the hydrophobic FePt nanoparticles could be redispersed in chloroform, toluene or hexane. If the precipitation of these particles was performed at a moderate speed (800 rpm) the re-dispersed solution was stable for months

I.3) Comments to nanoparticle synthesis
During the synthesis $Pt(acac)_2$ and 1,2 hexadecanediol dissolve well in octyl ether at 100^0C giving a clear translucent yellow solution. Sometimes we observed that, under the same conditions, the above mentioned chemicals were not dissolving well in octyl ether. As final result it was not possible to get a clear translucent yellow solution at 100^0C. In particular the solution sometimes started making gel near 150^0C when it was cooled down after reaching 280^0C. To dissolve this gel we used small amounts of toluene and the particles were precipitated again (at room temperature) using methanol and finally redispersed in chloroform. Nevertheless after one day these particles started precipitating in chloroform indicating that they were no longer stable. We think that this problem is due to the 1,2hexadecandiol: we had used two packages of this chemical (chemical#1 Cat#21,374-8, Lot# S10101-462; chemical#2 Cat# 21,374-8 Lot# S42511-277) from Sigma. For chemical #1 the synthesis was working well and we did not observe any gel formation, also the particles were stable after precipitation in chloroform for months whereas for chemical #2 the synthesis process was less efficient (gel formation and particle precipitation were observed sometimes as described above). For the confirmation we purchased 1,2 hexadecandiol also from TCI Europe and

synthesized FePt particles with this chemical. In this case chemicals dissolved well at 100^0C giving a clear yellow solution. We also did not observe any gel formation when the sample was cooled down after synthesis and particles were stable in chloroform after the washing step with methanol and toluene. Moreover, in the latter case (chemical from TCI) the size distribution is roughly found to lie between 3 and 5nm. In summary 1,2 hexadecanediol is very critical for the FePt particle synthesis.
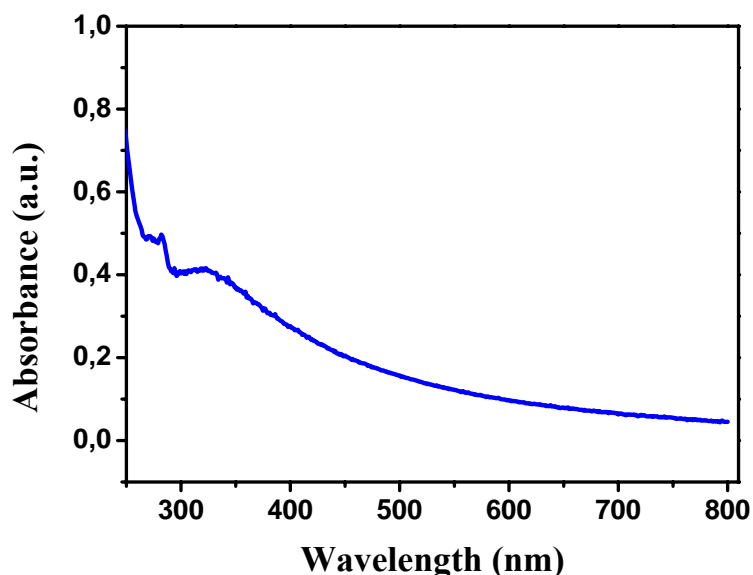
I.4) Absorption spectrum of FePt nanoparticles

Figure SI-I.2.1: UV/vis absorption spectrum of FePt particles dissolved in chloroform.

I.5) Size characterization with transmission electron microscopy (TEM)

TEM analysis was carried out to characterize the morphology and the size distribution of the FePt nanoparticles. Here the nanoparticles dissolved in chloroform (before the polymer coating) are described. The average diameter of one FePt nanoparticle (only the inorganic FePt part, without the organic surfactant shell) was determined to be 3.16 ± 0.44 (3.2 ± 0.4) nm.
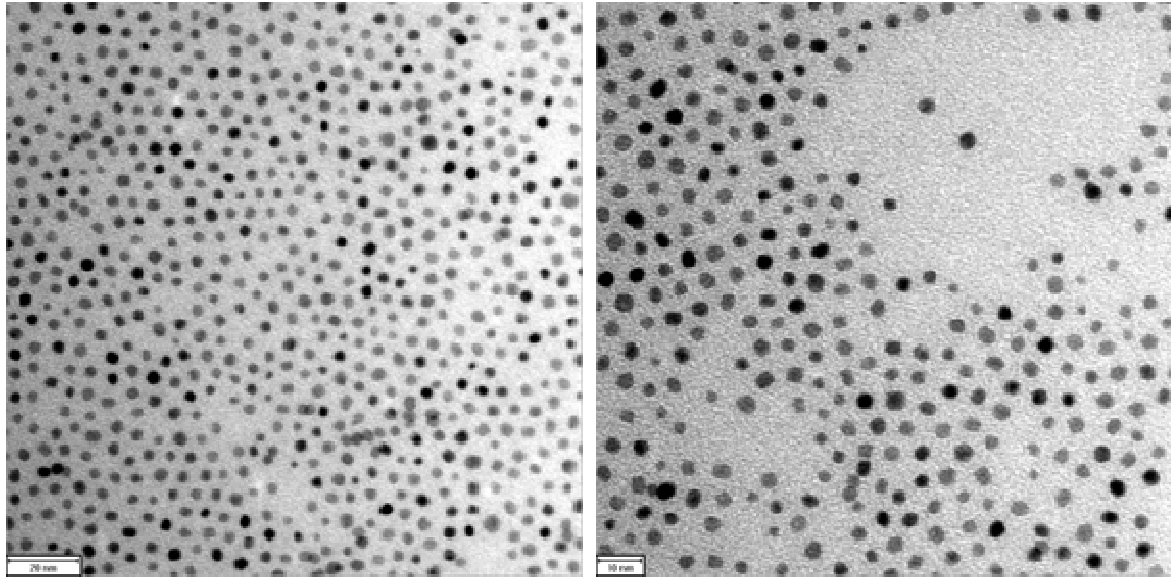
Figure SI-I.3.1: TEM images of FePt particles which had been dissolved in chloroform. The scale bars correspond to 20 and 10 nm.
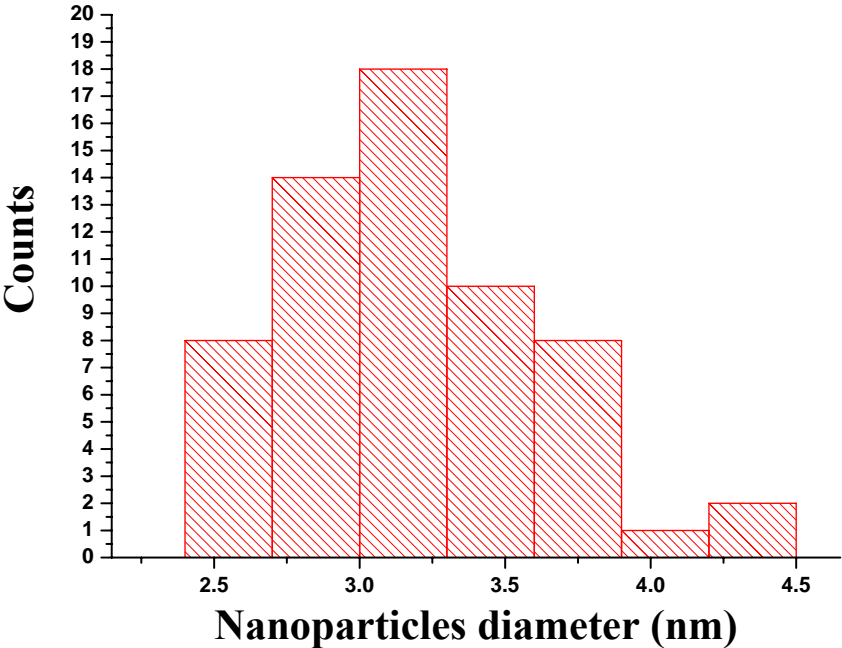

Figure SI-I.3.2: Histogram of the size distribution of the diameter of the FePt particles as obtained from the TEM images (3.2 ± 0.4 nm).

II) Embedding of hydrophilic FePt nanoparticles in polyelectrolyte capsules

Estimation of the number of hydrophilic (= polymer-coated) FePt particles per capsule

To estimate the number of FePt nanoparticles per capsule, we calculated the number of Fe atoms per FePt nanoparticle (i), then we calculated the number of FePt nanoparticles in the sample solution (ii) and finally we calculated the number of FePt nanoparticles per capsule (iii). Below the legend used during the calculations is given.

a: refers to atoms
p: refers to particles
m^a_{Fe}: refers to the mass of 1 Fe atom
m^a_{Pt}: refers to the mass of 1 Pt atom
ρ_{FePt} : refers to density of FePt
V^p_{FePt}: refers to the volume of 1 FePt nanoparticle (diameter 3.2 ± 0.4 nm)
m^p_{FePt}: refers to the mass of 1 FePt nanoparticle (diameter 3.2 ± 0.4 nm)
m^a_{FePt}: refers to the mass of 1Fe + 1Pt atom
N^a_{FePt}: refers to the number of Fe atoms + number of Pt atoms in one FePt nanoparticle
N^a_{Fe}: refers to the number of Fe atoms per FePt particle
N^p_{FePt}: refers to the number of FePt particles in the sample solution
N_{Fe} = number of detected Fe atoms within the sample solution
c_{Fe} = concentration of Fe atoms in sample solution
V = Volume of sample solution
N_{caps} = number of capsules in the sample solution

(i) Calculation of the number of Fe atoms per FePt nanoparticle:

To calculate the number of Fe atoms per FePt nanoparticle firstly we calculated the mass of one FePt nanoparticle of 3.2 nm (m^p_{FePt}) using the following formula $m^p_{FePt} = \rho_{FePt} \bullet V^p_{FePt}$, where ρ_{FePt} is the mass density of FePt which is **14 g/cm³** as reported by Wu et al. [37] and V^p_{FePt} is the volume of one FePt nanoparticle calculated using the formula $V^p_{FePt} = 4/3\ \pi\ r^3$, where **r** is the radius of one FePt nanoparticle. The calculated volume V^p_{FePt} is $1.72\bullet10^{-20}$ **cm³**. Using the above calculated ρ_{FePt} and V^p_{FePt} values, the mass of one FePt nanoparticle (m^p_{FePt}) was calculated to be $2.40\bullet10^{-19}$ **g**.

The total atomic mass of one Fe and one Pt atoms (m^a_{FePt}) was obtained by adding the atomic mass of these two elements (m^a_{FePt}: m^a_{Fe}+ m^a_{Pt}). Given $m^a_{Fe} = 9.27\bullet10^{-23}$ **g** and $m^a_{Pt} = 3.24\bullet10^{-22}$ **g**, m^a_{FePt} is $4.17\bullet10^{-22}$ **g**.

The number of Fe and Pt atoms in one 3.2 nm FePt nanoparticle was obtained by dividing the mass of one FePt nanoparticle (m^p_{FePt}) with the total atomic mass of one Fe and one Pt atom (m^a_{FePt}). We found 576 atoms of Fe and Pt in one FePt nanoparticle (N^a_{FePt}). Since we assumed that there are 50% of Fe atoms and 50% Pt atoms in one FePt nanoparticle of 3.2 nm, the total number of Fe atoms in one FePt nanoparticle is N^a_{Fe}= **288**.

The error is directly correlated to the error in determining the volume of one FePt nanoparticle. As the diameter has been determined to be 3.2 ± 0.4 nm the volume V^p_{FePt} is $17.2 \pm 6,0$ nm³. This corresponds to an error of 33%. In this way the accuracy in the number of Fe atoms in one FePt nanoparticle is N^a_{Fe}= **288 ± 91.**

(ii) Calculation of the number of FePt nanoparticles in the sample solution (N^p_{FePt}):

From the ICP measurements we measured the Fe-concentration c_{Fe} for the capsules samples containing low (S2), medium (S3) and high (S4) concentration of FePt nanoparticles (see the capsule synthesis section). Moreover, the concentration of Fe of the original nanoparticle solution was measured (Control without capsules).

From the Fe concentration c_{Fe} we got the total number of Fe atoms (N_{Fe}) within each sample by $N_{Fe} = c_{Fe} \bullet V \bullet N_A$ with the Avogadro number $N_A = 6.02 \bullet 10^{+23}$. The volume of the samples was $V = 2$ ml. Accuracy in the measurements is around 10%.

- Concentration of Fe atoms in S1 sample (Control: FePt particles without capsules)

  $c_{Fe} = 0.84 \bullet 10^{-3}$ mol / 2 ml

  From this concentration value we got the total number of Fe atoms (N_{Fe}) in this sample, which was $N_{Fe} = 5.06 \bullet 10^{+20}$. As we know, one FePt particle contains 288 ± 91 (N^a_{Fe}) Fe atoms, thus the number of FePt nanoparticle in the sample solution (N^p_{FePt}) was calculated simply by dividing N_{Fe} with 288 and the calculated value was $N^p_{FePt} = 1.76 \bullet 10^{+18}$.

- Concentration of Fe atoms in S2 sample (low capsule concentration)

  $c_{Fe} = 0.23 \bullet 10^{-3}$ mol / 2 ml

  From this concentration value we got the total number of Fe atoms (N_{Fe}) in this sample, which was $N_{Fe} = 1.39 \bullet 10^{+20}$. The number of FePt nanoparticles in the solution thus was $N^p_{FePt} = 4.81 \bullet 10^{+17}$.

- Concentration of Fe atoms in S3 sample (medium capsule concentration)

  $c_{Fe} = 0.44 \bullet 10^{-3}$ mol / 2 ml

  From this concentration value we got the total number of Fe atoms (N_{Fe}) in this sample, which was $N_{Fe} = 2.65 \bullet 10^{+20}$. The number of FePt nanoparticle in solution (N^p_{FePt}) was $9.2 \bullet 10^{+17}$.

- Concentration of Fe atoms in S4 sample (high capsule concentration)

  $c_{Fe} = 1.3 \bullet 10^{-3}$ mol / 2 ml

  From this concentration value we got the total number of Fe atoms (N_{Fe}) in this sample, which was $N_{Fe} = 7.83 \bullet 10^{+20}$. The number of FePt nanoparticles in the sample (N^p_{FePt}) was $2.72 \bullet 10^{+18}$.

Related to the accuracy in determining N^p_{FePt} the error of these values is around 30%.

(iii)   Calculation of the number of FePt nanoparticles per capsule (N^p_{FePt} / N_{caps})

The number of capsules N_{caps} in the samples S2, S3, S4, and S5 (capsules without FePt) (with sample volume $V = 2$ ml) was counted

sample S2 : $N_{caps} = 1.8 \bullet 10^{+9}$

sample S3: $N_{caps} = 2.8 \bullet 10^{+9}$
sample S4: $N_{caps} = 4.1 \bullet 10^{+9}$
sample S5: $N_{caps} = 2.8 \bullet 10^{+9}$

Finally, the number of FePt nanoparticles per capsule was obtained by dividing the calculated number of FePt nanoparticles (N^P_{FePt}) by the calculated number of capsules (N_{caps}) in the original samples. Theses values (N^P_{FePt}/N_{caps}) are reported in the Table 1 of capsule characterization section.

sample S2 : $N^P_{FePt}/N_{caps} = 4.81 \bullet 10^{+17} / 1.8 \bullet 10^{+9} = 2.6 \bullet 10^{+8}$
sample S3: $N^P_{FePt}/N_{caps} = 9.2 \bullet 10^{+17} / 2.8 \bullet 10^{+9} = 3.2 \bullet 10^{+8}$
sample S4: $N^P_{FePt}/N_{caps} = 2.72 \bullet 10^{+18} / 4.1 \bullet 10^{+9} = 6.6 \bullet 10^{+8}$

As described above the major source of error is the determination of the nanoparticle diameter due to the limited narrowness of the size distribution and in this way the amount of iron atoms per nanoparticle. Counting FePt nanoparticles therefore has an error of around 33%, whereas error in counting capsules is associated to an error of 10%. Therefore errors in determination of N^P_{FePt}/N_{caps} are around 33%:

sample S2 : $N^P_{FePt}/N_{caps} = (2.6 \pm 0.9) \bullet 10^{+8}$
sample S3: $N^P_{FePt}/N_{caps} = (3.2 \pm 1.1) \bullet 10^{+8}$
sample S4: $N^P_{FePt}/N_{caps} = (6.6 \pm 2.3) \bullet 10^{+8}$

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