Electronic Supplementary Information

Gas Phase Condensation of Superparamagnetic Iron Oxide-Silica Nanoparticles – Control of the Intraparticle Phase Distribution

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S1 Infrared absorptions of the raw powders hematite and quartz

In order to compare the infrared absorption characteristics of the components of the raw powder mixtures, α-Fe₂O₃ and α-quartz, their Fourier transform infrared (FTIR) spectra (FTIR spectrometer Alpha-P with evaluation software Opus, Bruker, Rheinstetten, Germany) were measured (Fig. S1). The spectra reveal that the absorption of α-quartz at the wavelength (λ = 10.59 µm) of the CO₂ laser radiation exceeds the absorption of α-Fe₂O₃. Assuming the same laser vaporization conditions this causes a higher vaporization rate of α-quartz compared with α-Fe₂O₃.

Fig. S1 Comparison of the infrared absorption characteristics of α-Fe₂O₃ (red) and SiO₂ (black) at the wavelength (λ = 10.59 µm) of the CO₂ laser radiation.
TEM investigation of the spatial distribution of the $\gamma$-Fe$_2$O$_3$ inclusions

TEM micrographs of two composite NPs (sample CN50) with multiple $\gamma$-Fe$_2$O$_3$ segregations were recorded at incrementally (10° increments) altered tilt angles between 0° and 60° (Fig. S2). Segregations located within the volume of the NPs such as no. 6, 10, and 11 as well as segregations at the surface of the NPs such as no. 2, 3, and 13 are strongly displaced upon a tilt. Segregation no. 12 simply changes its position from below to above the projection plane, and segregation no. 9 changes its position only slightly. Given the composite nanoparticle is located within a Cartesian (x-y-z) coordinate system with the z-axis parallel to the incident electron beam, the x-axis as the tilt axis, and the x-y-plane as the projection plane the displacement $d$ for segregations adhering to the surface can be calculated as a function of the tilt angle $\beta$ (Eq. S1).

$$d = \sqrt{2r_s \sin \left(\frac{180 - \beta}{2} - \sin^{-1}\left(\frac{p}{r_s}\right)\right)} \sqrt{1 - \cos \beta}$$

(S1)

The parameter $r_s$ is the radius of the cross section perpendicular to the tilt axis at the x-position of the considered segregation and $p$ the distance of the segregation from the tilt axis before the tilting. The calculated displacements for segregations no. 3 and 10 are in good agreement with the measured displacement whereas for segregation no. 9 the actual displacement is far less than predicted. Therefore, segregations no. 3 and 10 must be located close to the composite nanoparticle’s surface whereas segregation no. 9 must be located close to the tilt axis.

Fig. S2 Complete series of TEM micrographs of two composite NPs (sample CN50) with multiple $\gamma$-Fe$_2$O$_3$ inclusions recorded at
incrementally (10° increments) altered tilt angles from 0° to 60° (a to g). The segregations are numbered for an easy tracking.

S3 Particle size distributions of the Fe$_2$O$_3$@SiO$_2$ nanopowder samples
**S4** ζ-potentials of aqueous dispersions of the composite nanopowders

![Fig. S4 ζ-potential of all nanocomposites in aqueous dispersion in the pH range of 2-11.](image)

**S6** Silanization of Fe$_2$O$_3$@SiO$_2$ composite nanopowders with [3-(2,3-epoxypropoxy)-propyl]-trimethoxysilane

Surfaces activated with epoxy groups are attractive systems for the covalent immobilization of biomolecules. Even at mild conditions epoxides are reactive to many nucleophiles (e.g. hydroxide, amine, or thiol groups) of proteins, and the resulting chemical bonds are very stable. Therefore, the silanization with an epoxysilane can provide a chemically reactive interface for the covalent protein immobilization.$^{51}$

Thus, in order to prove the reactivity of the particles’ silica surface, Fe$_2$O$_3$@SiO$_2$ composite NPs were silanized with [3-(2,3-epoxypropoxy)-propyl]-trimethoxysilane. In the presence of water the epoxysilane’s alkoxy groups are hydrolyzed. Condensation of the silanol groups of the hydrolyzed epoxysilane and silanol groups bonded to the silica surface results in the formation of covalent -Si-O-Si- bridges (Fig. S5). The resulting terminal epoxide group can then be used for further reactions, such as protein immobilization.$^{52}$

![Fig. S5 Schematic of the reaction of silanol groups on a silica surface with [3-(2,3-epoxypropoxy)-propyl]-trimethoxysilane.](image)

600 mg portions of the Fe$_2$O$_3$@SiO$_2$ powder samples CN40 and CN80 as well as of the pure SiO$_2$ and γ-Fe$_2$O$_3$ nanopowders were
weighed into centrifuge tubes. Each sample was dispersed in 0.5 ml [3-(2,3-epoxypropoxy)-propyl]-trimethoxysilane (GLYMO, Merck, Darmstadt, Germany) with 49.5 ml water-free toluene at room temperature. After 18 h the nanopowders were centrifuged and rinsed three times with toluene at 3000 rpm min\(^{-1}\) for 2.5 min. Subsequently the rinsed powders were dried at 70°C for 24 h in a drying oven. For comparison, pure \(\gamma\)-Fe\(_2\)O\(_3\) and SiO\(_2\) nanopowders were subjected to the same silanization procedure. Furthermore, blank tests were conducted. For this purpose, CN40 and CN80 nanopowders as well as the \(\gamma\)-Fe\(_2\)O\(_3\) nanopowder were subjected to the silanization procedure described above. However, the volume of epoxysilane was replaced by toluene.

The chemical bonding of the epoxysilane was qualitatively examined by Fourier transform infrared (FTIR) spectroscopy (FTIR spectrometer Alpha-P with evaluation software Opus, Bruker, Rheinstetten, Germany). The FTIR spectra were recorded (range: 375 cm\(^{-1}\) – 4000 cm\(^{-1}\), resolution: 2 cm\(^{-1}\), number of scans: 100) in attenuated total reflection (ATR) mode. The mass fractions of carbon and hydrogen in the silanized nanopowders were determined by elemental (CHN) analyses (CHN-932 equipped with autosampler and thermal conductivity detector, LECO Instrumente GmbH, Germany). From the carbon and hydrogen portions and the initial masses (2 mg – 3 mg) of the samples the mean molar concentrations \(c_{\text{epoxysilane}}\) of epoxysilane in the samples were calculated. Furthermore, the NPs’ loading densities \(\alpha\) with epoxysilane were determined using the molar concentrations \(c_{\text{epoxysilane}}\) and the measured specific surface areas \(S_{\text{BET}}\) (cf. Table 1) of the nanopowder samples CN40 and CN80.

In the FTIR spectra (Fig. S6) of the epoxy-silanized SiO\(_2\) and Fe\(_2\)O\(_3@\)SiO\(_2\) nanopowders the bonding of the epoxysilane to the silica surface of the NPs is indicated by the presence of C–H\(_2\) vibrations in the wave number region between 2800 cm\(^{-1}\) and 2900 cm\(^{-1}\) (Fig. S6, inset). In contrast, these vibrations are missing in the spectrum of the unmodified Fe\(_2\)O\(_3@\)SiO\(_2\) nanopowder.

![Fig. S6 FTIR spectra of the epoxy-silanized Fe\(_2\)O\(_3@\)SiO\(_2\) (CN80) and SiO\(_2\) nanopowders as well as of the unmodified Fe\(_2\)O\(_3@\)SiO\(_2\) nanopowder (CN80).](image)

The results of the CHN analysis of the silanized composite nanopowders CN40 and CN80 along with the calculated values of the epoxysilane concentrations in these samples and the NPs’ loading densities with epoxysilane are summarized in Table S1.

**Table S1** C and H mass fractions in the silanized nanopowders CN40 and CN80, calculated concentrations \(c_{\text{epoxysilane}}\) of epoxysilane in these nanopowders, and the NPs’ loading densities \(\alpha\) with epoxysilane.
FTIR spectroscopy (Fig. S6) and CHN analyses (Table S1) confirm the successful silanization of the composite nanopowders CN40 and CN80. In contrast, the CHN analyses of the silanized γ-Fe₂O₃ nanopowders as well as of the blank samples resulted epoxysilane concentrations and loading densities with epoxysilane of about \( c_{\text{epoxysilane}} \approx 0.6 \times 10^{-4} \text{ mol g}^{-1} \) and about \( \alpha \approx 1.2 \text{ nm}^{-2} \), respectively. These at least for the blank samples fictitious values apparently reveal the sensitivity limit of the analysis technique.

The silanization of the nanopowders was conducted in water-free epoxysilane/toluene reaction media. However, the reaction of epoxysilane with the NPs’ surfaces should not proceed in the absence of water.\(^3\) The nevertheless successful silanization of the Fe₂O₃@SiO₂ NPs is attributed to traces of water on their surfaces. These initiate the hydrolysis and condensation of the silane to the NPs’ silica surfaces.\(^4\) Hence, in water-free reaction media the coverage with epoxysilane cannot exceed a monolayer. This is supported by the NPs’ loading densities in samples CN40 and CN80 (cf. Table 1) which are below the corresponding loading density \( \alpha = 4 \text{ nm}^{-2} \) of a closed monolayer of epoxysilane.

### Table 1: Epoxysilane Concentrations and Loading Densities for CN40 and CN80 Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>C [mass%]</th>
<th>H [mass%]</th>
<th>( c_{\text{epoxysilane}} ) [mol g(^{-1})]</th>
<th>( \alpha ) [nm(^{-2})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN40</td>
<td>2.27</td>
<td>0.49</td>
<td>( 3.15 \times 10^{-4} )</td>
<td>2.70</td>
</tr>
<tr>
<td>CN80</td>
<td>1.71</td>
<td>0.32</td>
<td>( 2.37 \times 10^{-4} )</td>
<td>2.51</td>
</tr>
</tbody>
</table>

Multimedia file: Rotating Fe₂O₃@SiO₂ NP.AVI

**Title:** Animated tilting of γ-Fe₂O₃@SiO₂ nanoparticles with multiple iron oxide inclusions.

**Legend:** The animation illustrates the spatial distribution of γ-Fe₂O₃ inclusions within the composite nanoparticles of sample CN 50. It is composed of TEM micrographs of two particles recorded at incrementally altered tilt angles.

**Keywords:** nanocomposite, iron oxide, silica, morphology, spatial distribution, TEM, rotation