Supplementary Information for

Mechanochemical surface functionalisation of superparamagnetic microparticles with in-situ formed crystalline metal-complexes: a fast novel core-shell-particle formation method

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Experimental section

Materials and methods

Elemental analyses for C, H and N were carried out with Vario analyzers, models Microtube and EL (Fa. Elementar Analysesysteme GmbH).

Morphological investigations were determined on a field emission scanning electron microscope (FE-SEM) ULTRA plus (Fa. Zeiss) with a GEMINI electron beam column. Mapping was carried out using electron dispersive X-ray spectroscopy (EDX) with a silicon drift detector (SDD) X-Max 50 mm² (Oxford Instruments) with a voltage of 12 keV for the detection of the surface coverage of the microparticles with the Zn-complex. The instruments were calibrated using calibration files of Oxford Instruments prior to analysis.

Fraunhofer diffraction was done with a Microtrac BLUEWAVE. To obtain good dispersions in isopropyl alcohol, the samples were treated with ultrasound (40 W, 60 s) prior to analysis.

X-ray fluorescence spectroscopy (XRF-spectroscopy) was carried out on a PANalytical Axios Advanced. The samples were analysed as dry, loose powder under He-atmosphere.

Magnetic properties were recorded with a vibrating sample magnetometer (VSM, VersaLabTM 3T, Cryogen-free Vibrating Sample Magnetometer), cycling the applied field from -30 to +30 kOe for two times with a step rate of 100 Oe/s. Detailed analyses were carried out by cycling the applied field from -5 to +5 kOe at 5 Oe/s. The temperature was set to 293 K (20 °C, RT). What is obtained via the VSM technique is a magnetization curve for the sample that is measured as function of the applied field. At very high fields, the material reaches magnetic saturation. This value (M_s) can be read out (it is typically given in the cgs unit *emu*). As the magnetization strength is a function of the amount (mass) of magnetic material, the value has to be weighted by the measured sample mass and given as *emu/g*. For a magnetic particle sample where a non-magnetic surface coating is added, this adds to the mass, but not to the measured M_s , thus from the decline in emu/g, (from uncoated to coated particles), the weight fraction of the added (non-magnetic) surface coating can be determined. As only very small quantities (a few mg) of sample are measured, the error with respect to the correctly determined actual sample mass (a source of errors might be unavoidable moisture uptake during sample preparation which increases the sample mass) is non-negligible and may influence the final emu/g result for the saturation magnetisation by up to 10%.

The powder diffraction patterns were recorded with a θ/θ x ray powder diffractometer (D8 Discover Da Vinci, Bruker AXS) with parallel beam geometry (Goebel mirror, Cu K_{α} radiation, $\lambda = 154.1$ pm) in reflection mode.

Thermal investigations of the bulk substances were carried out with simultaneous DTA/TG measurements (NETZSCH STA-409). Samples of about 25-35 mg were heated in aluminium oxide crucibles from room temperature to 700°C with a constant heat rate of 10°C/min and a constant gas flow of an argon (Linde 5.0) / nitrogen (Linde 5.0) mixture (40 ml/min).

ZnCl₂ (99.99%) and 1,2,4-1H-triazole (98%) were purchased from abcr and Sigma Aldrich.

Synthesis/Modification

Synthesis of $[ZnCl_2(TzH)_2]$ @Fe₃O₄/SiO₂

Syntheses were carried out in a ball mill Lab Wizz LMLW 320/2 ball mill (Fa. Laarmann) in stainless steel vials (volume 2 ml, 5 steel milling balls, diameter 3 mm).

To exclude that any magnetic material from the steel ball mill contaminated any samples, which would yield wrong results for the magnetic measurements, the non-magnetic complex (synthesis: see below) alone was milled and measured via VSM. As no magnetic signal could be detected, it was concluded that no (magnetic) contamination originates from the milling vials.

Therefore, 15 mg of the microparticles, 6.8 mg (0.05 mmol) of $ZnCl_2$ and 10.4 mg (0.15 mmol) TzH were added to a ball mill vessel and ground for five minutes with a frequency of 15 Hz. The obtained brown-coloured solid was placed in a double chamber ampoule. To remove the excess of TzH, the ampoule was placed in a horizontal tube oven with a temperature gradient, ranging from 120°C to room temperature. Yield: 20.3 mg = 71%.

For the washing procedure, 20 mg of the particles were suspended in 20 ml hexane under inert gas conditions and treated with ultrasonic radiation for five minutes. The particles were separated with a permanent magnet from the solvent and dried at a temperature of 80 °C under reduced pressure for two days.

Yield: 13.4 mg = 67%.

Elemental Analysis

Based on the composite character of the core-shell particles, elemental analyses were carried out five times for the as-synthesised particles and five times for the washed particles, and the average values were determined for each case. It shows that washing and magnetic separation reduce the excess of organic components:

Calcd.: C: 8.75, H: 1.11, N: 15.32 %; found for as-synthesised particles: C 11.35, H: 1.55, N: 19.53; relative variance: C: 2.60, H: 0.44 N: 4.21 %; found for washed particles: C: 10.88, H: 1.62, N: 16.99, relative variance: C: 2.13, H: 0.55, N: 1.67%.

Comparison of different mechanochemical conditions and reactant to microparticle ratios

Different milling times and frequencies, as well as the variation of the reagents to microparticle ratio, lead in every tested case to the formation of the complex $[ZnCl_2(TzH)_2]$. Powder pattern a) exhibits the main reflections of the complex and the characteristic main reflection of the microparticles at 35.5° in 20 and indicates the formation of microparticles coated with [ZnCl₂(TzH)₂]. In contrast, diffraction patterns b) and c) (see Figure S1) only show the reflections of [ZnCl₂(TzH)₂]. There is reason to conclude that in all cases the formation of coated particles occur. However, the inner core, which contains the microparticles, cannot be detected via powder diffraction methods because of the substantially higher percentage of the complex compound used in reactions b) and c).

Characterisation

X-ray structure analysis



Figure S1: X-ray diffractograms of composite core/shell particles at different milling times and frequencies as well as different reagents to microparticle ratios. a) milling time: 5 min, frequency: 15 Hz, composite core-shell particles with a mass ratio of $[ZnCl_2(TzH)_2]$ to microparticles 1/1; b) milling time: 15 min, frequency: 20 Hz, composite core-shell particles with a mass ratio of $[ZnCl_2(TzH)_2]$ to microparticles 10/1; c) milling time: 15 min, frequency: 25 Hz, composite core-shell particles with a mass ratio of $[ZnCl_2(TzH)_2]$ to microparticles 0f 14/1; d) powder pattern simulated from single crystal X-ray data on $[ZnCl_2(TzH)_2]$; e) powder pattern of the Fe₃O₄/SiO₂ particles prior to coating.



Figure S2: Unit cell of the complex [ZnCl₂(TzH)₂] along the x-axis.

IR spectroscopy



Figure S3: Comparison of IR spectra of the coated Fe_3O_4/SiO_2 particles, $[ZnCl_2(TzH)_2]$ and the Fe_3O_4/SiO_2 particles prior to coating (from top to bottom). The IR spectrum of the complex-coated particles shows the typical N-H stretching modes of the triazole ligand in the range of 3100-3200 cm⁻¹, as well as the strong Si-O signal of the microparticle shell at 1100 cm⁻¹.

Thermal Analysis

Thermoanalytical investigations were conducted with a simultaneous DTA/TG measurement setup under an inert gas atmosphere (Ar/N₂ mixture). Thermal analysis of the pure Zn-complex (Figure S4 a)) and the composite particles (Figure S4 b) and c)) exhibit similar endothermic signals 1 and 5 with increasing microparticle ratio. For signals 2 - 5, the endothermic DTA signal is accompanied with a mass loss in the TG curve. The composite nature of the core-shell particles is shown by a decrease of signals 2 and 3 and a premature occurrence of an endothermic process, signal 4. In case c), signals 2 and 3 are hardly in the heat flow associated with two weak TG signals in accordance with the high Fe_3O_4/SiO_2 content. The presence of the complex species is thereby proven for all cases.



Figure S4: Simultaneous DTA/TG of a) pure $[ZnCl_2(TzH)_2]$, b) composite core-shell particles with a mass ratio of $[ZnCl_2(TzH)_2]$ to microparticles 14/1, c)) composite core-shell particles with a mass ratio of $[ZnCl_2(TzH)_2]$ to microparticles 1/1. Heating rate: 10 °C/min; gas flow: 40 ml/min of a 1/1 mixture of Ar and N₂.

X-ray fluorescence spectroscopy:

For elemental analysis of the solid particles in addition to the aerial resolved EDXinvestigations, XRF spectroscopy was conducted as a second method. Analysis of a dry, loose powder of the coated Fe_3O_4/SiO_2 particles yields characteristic fluorescence-peaks which can be qualitatively taken as a fingerprint. The method can detect elements with an atomic mass above the mass of Na. A quantitative ratio of the detected elements is provided by the instrument, which is based on relating signal intensities of the measured emission peaks to the amount of the elements, yielding the respective fingerprint signal. Table S1 lists the obtained results. It can be seen that all detectable elements can be found. However, the quantitative results cannot be taken as absolute (and therefore reliable values), as XRF suffers from sample-matrix effects, i.e., it is only a semi-quantitative method that allows to compare relative values between different samples. Nevertheless, it proofs that all expected elements are found (the 1,2,4-1H-triazole part of the shell-complex is not visible in the elemental fractions table as the elements H, C and N are too light).

Table S1: X-ray fluorescence (XRF) spectroscopy measurement under inert gas atmosphere (He) of the coated Fe_3O_4/SiO_2 particles indicating the presence of all participating elements (Si, Fe, Cl, Zn). For convenience, the fraction of the elements Si and Fe are transformed to the mass-fraction values of the respective oxide-compounds.

component name	percentage (wt%)	absolute error (%)
SiO ₂	46.8	0.2
Fe ₃ O ₄	39.7	0.1
Cl	8,4	0.08
Zn	5.1	0.07