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Tailoring magnetic supraparticles for object identification by magnetic particle spectroscopy

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Abstract

Marking and identification of materials is becoming increasingly important due to complex global resource and supply chains. In this work, a miniaturized magnetic marking technology based on so-called supraparticles is presented. The hierarchical buildup of these microparticles, which are assembled from nanoparticles, allows to precisely tailor their structure. Superparamagnetic iron oxide nanoparticles as building blocks are used in this work. By surface modification and mixing them with silica nanoparticles, respectively, the supraparticle structure is varied. It is demonstrated that these structural modifications are readily detected by magnetic particle spectroscopy (MPS). Thereby, various distinguishable magnetic signals are feasible, which are even detected after incorporation into dark plastic. The presented magnetic marking technology thus proves its potential as an alternative marking technology to optical labels.

I Introduction

Marking and identifying arbitrary objects is of great importance in countless fields including quality control, anti counterfeiting or recycling. Well established marking technologies such as barcodes or radio frequency identification chips (RFID) need further improvements regarding their size or security against counterfeiting. Thus, the use of particles as markers for object identification is a feasible approach to overcome the drawbacks of RFID and barcode labels [1, 2].

We suggest using miniaturized magnetic objects to tag and identify objects. The so called supraparticles i.e., micrometer sized particles that are assembled from individual nanoparticles, are synthesized via spray-drying (Fig. 1).

Thereby, different nanoparticle building blocks can be assembled accurately in a toolbox-like approach. Thus, the structure of the supraparticle, which acts as a marker object, is modified similar to the variation of black and white lines in a barcode (Fig. 2). While the barcode is resolved optically, the supraparticle signal is decoded by magnetic particle spectroscopy (MPS). Its relatively easy setup, fast measurement speed and high sensitivity enable a magnetic marking technology.

In this work, we show that these supraparticles can act as magnetic marker objects. It is analyzed how their structural modification alters the resulting MPS signal

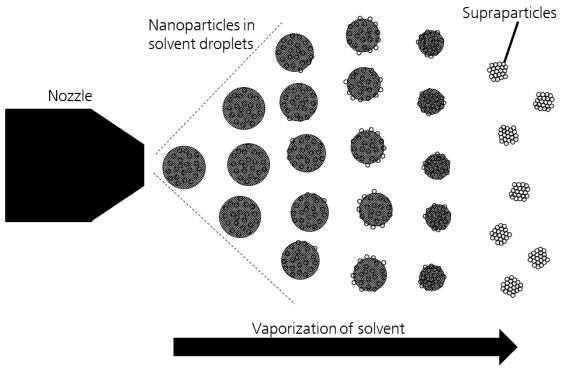

Figure 1: Schematic illustration of the supraparticle formation via a spray-drying process. The nanoparticle dispersion is sprayed in fine droplets by a nozzle. Due to vaporization of the solvent, the employed nanoparticles are forced into supraparticles.

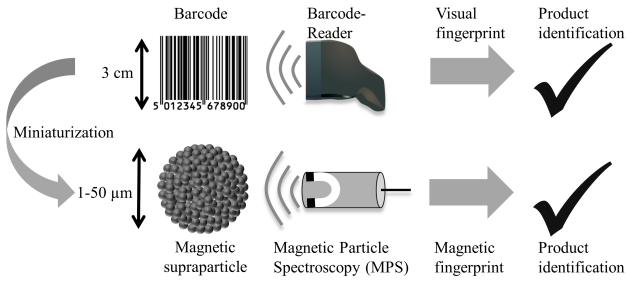

Figure 2: Similar to the variation of black and white lines in a barcode, the supraparticle structure is modified, representing a miniaturized marker object. Different structures yield various magnetic fingerprints, readily detected via MPS and thus enables product identification.

curves. Thereby, supraparticles with defined and unique magnetic fingerprints can be tailored and employed as marker objects [2].

II Material and methods

II.I Synthesis and modification of SPIONs

Superparamagnetic iron oxide nanoparticles (SPIONs) were obtained in a continuous precipitation process of iron salts in water and ammonia and subsequently stabilized with nitric acid to obtain a stable ferrofluid. Surface functionalization was achieved by hydrolysis and condensation reaction of triethoxy(octyl)silane (OCTEO) on the SPIONs as reported elsewhere [3].

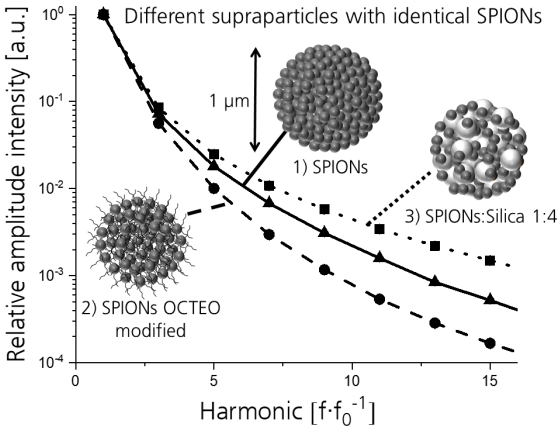

Figure 3: Normalized relative amplitude intensity of supraparticles consisting of identical superparamagnetic iron oxide nanoparticles (SPIONs) measured via MPS. If SPIONs are OCTEO modified before assembly into supraparticles (dashed line), the signal decays faster compared to SPIONs as prepared (solid line) or SPIONs mixed with silica nanoparticles (dotted line). Adapted with permission from Müssig, S.; Fidler, F.;Haddad, D.; Hiller, K.-H.; Wintzheimer, S.; Mandel, K.. Supraparticles with a Magnetic Fingerprint Readable by Magnetic Particle Spectroscopy: An Alternative beyond Optical Tracers. *Adv. Mater. Technol.* ***2019****, 291,* 1900300. *Copyright 2019 WILEY-VCH Verlag GmbH & Co. KGaA.*

II.II Synthesis of supraparticles

For composite supraparticles, the respective amount of ferrofluid was mixed with a SiO_2 nanoparticle dispersion (Köstrosol K2040, Chemiewerke Bad Köstritz, Germany) to obtain a weight ratio of iron oxide: silica of 1:4. and diluted with deionized water. The pure ferrofluid, the dispersion of mixed nanoparticles and the OCTEO modified SPIONs were subsequently spray-dried in a B-191 mini spray dryer from Büchi Labortechnik GmbH, Essen, Germany.

II.III Characterization

MPS measurements were conducted on magnetic samples which had masses between 3 mg (pure iron oxide) and 10 mg (1:4 mixture) using a magnetic particle spectrometer MPS unit, Pure Devices GmbH, Rimpar, Germany, in a sinusoidal alternating field of 20.1 kHz from 300 Oe to 300 Oe. The amplitude intensity of the higher harmonic spectrum was normalized to the corresponding fundamental intensity.

III Results and discussion

In order to understand how their structure alters MPS signals, three different types of supraparticles were manufactured: 1) Solely SPIONs assembled into supraparticles, 2) surface functionalized SPIONs with a silane (OCTEO)

and 3) SPIONs mixed with silica nanoparticles (Fig. 3). Although identical SPIONs were used in all cases, the normalized relative amplitude intensity varies for the different supraparticles (Fig. 3). This indicates that it is not only the intrinsic properties of the nanoparticles but also the magnetic interaction within the supraparticles, which plays a crucial role regarding their MPS signals [2, 4, 5]. It is thus possible to vary the magnetic response of supraparticles by structural and/or compositional modification, although identical nanoparticles are used.

Consequently, different signals could also be obtained for anisotropic [4] or hollow [5] supraparticles or by mixing nanoparticles with different MPS signals into one supraparticle. This finding facilitates to synthesize various magnetic supraparticles and enables them to act as markers to distinguish objects or serve as an anti counterfeiting label. In a proof of concept experiment, it was shown that the magnetic signal is detectable from inside a bulk material revealing great potential for future marking applications [2].

IV Conclusions

To summarize, magnetic supraparticles were synthesized from nanoparticle building blocks and characterized regarding their applicability as magnetic marker objects. It was shown that structural differences within the supraparticles are readily detected by magnetic particle spectroscopy. The combination of adjustable magnetic signals with the application related read out technique of MPS devices enables a magnetic marking technology.

Author's Statement

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