Communicating objects are demanded for product security and the concepts of a circular economy or the Internet of Nano Things. Smart additives in the form of particles can be the key to equip objects with the desired materials intelligence as their miniaturized size improves applicability and security. Beyond their proposed identification by optical signals, magnetic signals deriving from magnetic particles can hypothetically be used for identification but are to date only resolved roughly. Herein, a magnetic particle-based toolbox is reported, that provides more than 77 billion \((77 \times 10^9)\) different magnetic codes, adjustable in one single particle, that can be read out unambiguously, easily, and quickly. The key towards achieving the vast code variety is a hierarchical supraparticle design that is inspired by music: similarly to how the line-up variation of a musical ensemble yields distinguishable overtones, the variation of the supraparticle composition alters their magnetic overtones. By minimizing magnetic interactions, customizable signals are spectrally decoded by the simple method of magnetic particle spectroscopy. A large number of chemically adjustable magnetic codes and the possibility of their remote, contactless detection from within materials is a breakthrough for unexploited labeling applications and pave the way towards materials intelligence.

1. Introduction – A Miniaturized Magnetic Marker Technology

The Internet of Nano Things\cite{1} envisions that even the smallest subunits of materials are able to communicate. This could ultimately yield materials intelligence\cite{2}—a crucial step towards turning true and thorough industrial digitization, circular economy, and product security concepts into reality. On a macroscopic scale, radio-frequency identification (RFID) chips\cite{3} are a fascinating solution to provide the demanded intelligence for objects. Further miniaturization reduces the available spatial dimensions so that intelligence can be put into a micro- or even nanoscale particle. State-of-the-art developments using micron-sized particles provide mostly optically\cite{4-15} (UV–vis or Raman spectral) or graphically\cite{16} (i.e., on the lower micro- or nano-scale spatially designed segments) resolvable unique and adjustable signals. Other innovative approaches\cite{17,18} include, for instance, encoding via deoxyribonucleic acid (DNA) segments,\cite{19} but typically demand considerable effort to read out the stored information. In this context, it is surprising that magnetic particles are hardly reported to equip materials with a fingerprint and thus intelligence, albeit the potential of magnets to carry information is long known with the obvious example of magnetic hard disc data storage devices. However, the latter only works if magnetic moments are spatially distributed to provide a series of “magnetization up” and “magnetization down” events when scanned over the targeted area, representing “0” and “1”, that is, bits.

Although three different nanoparticle types were simultaneously quantified within a dispersion,\cite{20} storing information in a single magnetic particle in the form of a unique signature remains challenging. For almost a decade, only three qualitatively different magnetic fingerprints in a single magnetic were proposed.\cite{21,22} In 2019, an approach to achieve six distinguishable magnetic fingerprints, by utilizing one magnetic nanoparticle type, was reported by our group.\cite{23} Very recently, 29 different magnetic compositions were decoded by an automated decoding algorithm.\cite{24} We understand the fingerprint of magnetic materials as their intrinsic signature, while the deliberate adjustment thereof should be denoted as magnetic codes.

Utilizing magnetic fingerprints of different materials is in principle possible but requires advanced technological expertise to synthesize a large variety thereof. Preferably, an approach that merges different fingerprints within a single marker and thereby increases the number of available codes would significantly pave the way to materials intelligence using smart magnets.\cite{21,23} As magnetic signals can be transmitted through many materials that would not allow optical information to pass, such particles could be integrated within and not only on top of the surface of arbitrary objects, thus protecting...
the information against environmental harm but also against obvious detection and thus counterfeiting.\textsuperscript{[23,26]} If such a magnetic particle marker could be achieved, it would equip materials with intelligence in many fields: it could further reduce the number of counterfeit products, which yield global annual damages of almost 500 billion US\$ (2.5 \% of global imports),\textsuperscript{[27]} enable the identification and recycling of dark plastics,\textsuperscript{[23,28–30]} or permit the tracking—as well as monitoring—of goods and value chains, and finally could render quality control of materials and processes possible (Figure 1).\textsuperscript{[19]}

Although such a magnetic marker technology seems very promising, until now it is commonly accepted that too few magnetic codes are resolvable from magnetic markers, preventing research to achieve it.\textsuperscript{[17]}

Herein we report on a magnetic particle-based toolbox with the potential to provide more than 77 billion ($77 \times 10^9$) different magnetic codes, adjustable in one single particle, that can be read out unambiguously, easily, and quickly.

2. Results and Discussion

2.1. Hierarchical Supraparticle Design

In this work, we utilized a hierarchical particle design and adapted the principles of a musical ensemble to provide a universal toolbox for a large variety of adjustable magnetic codes.

Figure 1. An intelligent magnetic particle with a unique code turns arbitrary objects into communicating items. Magnetic materials are environmentally-friendly, inexpensive and, most importantly, their signal is unaffected by optical constraints so that read-out is possible even if the marker is hidden within objects. This grants access to a vast variety of unexploited marking applications.

Figure 2. Schematic illustration of the hierarchical design used to fabricate code supraparticles: after selection of the signal carrying a) superparamagnetic nanoparticles (SPION), nanocomposite particles are synthesized by encapsulation within b) polystyrene. After the assembly of these coding elements in different ratios, c) supraparticles are obtained. Their structure is freely adjustable by modification of the underlying steps. This yields a variation of their inherent magnetic code. Code variation includes but is not limited to the choice of magnetic nanoparticles, synthesis parameters, or most importantly, a change of assembled coding element ratios.
The hierarchical design is schematically illustrated in Figure 2. The bottom layer consists of magnetic nanoparticles. Exemplarily, three different types of superparamagnetic iron oxide nanoparticles (SPIONs) were synthesized in a co-precipitation reaction. Iron oxides are considered as an ideal material basis as they are inexpensive, environmentally friendly, and scientifically well-understood. By substituting an increasing amount of iron oxides with cobalt oxides during co-precipitation synthesis, variation between doping levels: no doping (Figure 2a blue particles, SPION1), low doping (green particles, SPION2), and high doping (red particles, SPION3), easily modifies their magnetic properties as the magnetocrystalline anisotropy is increased. Meanwhile, other properties such as morphology and size (hydrodynamic diameters of \( \approx 15\) nm) remain unchanged (see Figures S1–S4, Supporting Information). The modification during synthesis of the SPIONs is represented by different slopes of the harmonic spectra of the nanocomposite particles (Figure 3b).

Proceeding from the discussed “instruments”, now the “ensemble” was formed by an assembly of different ratios of these nanocomposite particles (Figure 3c–e).

Similar to the impressive human ear, which sensitively differentiates various ensemble line-ups by their harmonic spectra, MPS (see detailed description later) excellently identified different supraparticle compositions by their magnetic harmonic spectrum (Figure 3f).

Different ensembles, that is, supraparticles, which consist of solely one type of instrument, that is, nanocomposite particle, exhibit clearly different harmonic spectra (intense blue, green, and red solid lines with squares). These supraparticles have varying magnetic fingerprints as the employed SPIONs were modified during synthesis (and thus the nanocomposite particles that were assembled thereof). In order to enhance the code variety based on these fingerprints, a mixing of the respective nanocomposite particles yielded supraparticles with varying ratios ranging from 1:1 (dark squares) to 15:1:1 (blue hues), 1:15:1 (red hues), and 1:1:20 (green hues, in total 20 different ratios are shown in Figure S7, Supporting Information). As desired, the different compositions are magnetically represented by differing declines of the normalized magnetization amplitude and thereby provide a unique code for each composition. A scanning electron micrograph (Figure 3d) visualizes such a magnetic code supraparticle. Importantly, the structure appears identical for easily varied ratios of instruments (Figure 4a–c). High magnification overview images (Figure 4d) as well as cross-section analysis (Figure 4e) including EDX mapping (Figure 4f,g) exhibit a homogeneous hierarchical structure of the supraparticle. Light scattering size measurements (Figure 4h) reveal the achieved size of only a few micrometers for the presented magnetic code particles. To summarize this, the variation of the hierarchical supraparticle composition can be exploited to tailor unique magnetic codes (a detailed technical explanation and a confirmation by other magnetization measurements are provided in Table S8, Supporting Information).

Importantly, if different SPIONs are assembled directly, particle-particle interactions will arise and yield harmonic spectra that do not follow the expected trends (Figure 5 and Table S9, Supporting Information). This alternative approach is thus not feasible to accurately adjust a vast variety of code particles. This is, as upon agglomeration of magnetic nanoparticles, their close proximity strongly alters their magnetic properties in the utilized setup.\(^{37–39}\) Thus, the hierarchical approach prevents strong coupling of individual nanoparticles\(^{40}\) and is key to distinguishing different compositions by MPS. The different supraparticles can still be easily distinguished after several weeks of storage in ambient conditions, which is essential for a functional marker (see Figure S10, Supporting Information).

Clearly inferior, traditionally proposed\(^{37,72}\) single value parameters, such as saturation magnetization or coercivity, measured with conventional magnetometers only provide a very limited number of qualitatively different signals (see Figure S11, Supporting Information).\(^{32}\)
Figure 3. a) Analogously to instruments, unique in their character due to the art of musicianship, nanocomposite particles, consisting of different superparamagnetic iron oxide nanoparticles (SPION1, SPION2, and SPION3) and polystyrene are obtained with unique b) harmonic spectra. In a second step, these instruments form an ensemble that represents the c) instrumental composition. Similarly, nanocomposite particles are assembled into so-called supraparticles, as shown by d) SEM and schematically illustrated for a e) 5:1:1 ratio. The codes of such supraparticles are well-distinguishable by analyzing their normalized magnetization amplitude as f) function of harmonics (multiples of the excitation frequency $f_0$): supraparticles that consist of one type of nanocomposite particle (intense blue, green, and red curves with squares) exhibit clearly different magnetization amplitude decays as a function of their higher harmonics. Mixing of the nanocomposite particles/instruments in a 1:1:1 ratio (black curve) represents the desired decline within the range of the references. Increasing the relative amount of one nanocomposite particle within the supraparticle, the magnetization amplitude shifts towards the respective reference (blue hues: 5:1:1, 9:1:1, 15:1:1, red hues: 1:3:1, 1:7:1, 1:15:1, and green hues: 1:1:5, 1:1:10, 1:1:20). Error bars represent standard deviation of five averaged measurements.
2.3. Magnetic Particle Spectroscopy as Advanced Detection Technology

In order to understand the great relevance of the approach developed here in terms of code variety, but even more importantly, also towards its application as a magnetic marker technology, one has to at least roughly comprehend the principle of MPS (more thorough explanations are given in Figure S6, Supporting Information, in original[36,41] and previous[23,37,38] publications): the measured voltage, induced by a magnetic sample which is exposed to an AC magnetic field, is fast Fourier transformed (FFT) to obtain the harmonic spectrum. As

Figure 4. SEM images of supraparticles consisting of different mass ratios of nanocomposite particles made of SPION1:SPION2:SPION3: a) 1:1:3, b) 1:1:5, and c) 1:1:9. In terms of size, composition, and morphology, all supraparticles appear identically. Thus, a visual differentiation of their code-carrying properties is not possible, increasing the level of security against counterfeiting. d) A high magnification image of (c) is provided, which shows the nanocomposite particles that are present within the supraparticle. e) A cross-section with subsequent elemental mapping by f) EDX and its respective g) energy spectrum show a homogeneous distribution of iron and cobalt within the supraparticle. As cobalt was used for doping of the iron oxide nanoparticles during synthesis, its intensity is way lower compared to iron. Carbon, oxygen, aluminum, silicon, and platinum are present due to the incorporation of the supraparticles in lacquer and subsequent cutting during cross-section preparation. The decreased intensity of carbon, iron, and cobalt on the left side of the supraparticle is due to a smaller sample thickness and thus less counts of the respective elements. h) The cumulative size distribution of a representative supraparticle sample indicates a size distribution of diameters between 0.4 and 20 µm. More precisely, 10 % (d(v, 0.1)) of the sample volume is smaller than 1.2 µm and 90 % (d(v, 0.9)) is smaller than 10.8 µm.
Figure 5. MPS spectra of supraparticles synthesized by the direct assembly of nanoparticles without fabricating nanocomposite particles (i.e., “instruments”) first. Unexpectedly, supraparticles consisting of SPION1 (1:0:0, blue circles) or SPION2 (0:1:0, green circles) exhibit almost identical signal decays which are also similar to the 5:1:1 and 1:1:5 mixtures. Contradictory, the 1:5:1 mixture exhibits a signal similar to the supraparticle consisting of SPION1 rather than SPION2. It is concluded that the course of the MPS spectra is dominated by interparticle-interactions which yield unpredictable signal evolution in MPS. Thus, the direct assembly of nanoparticles into supraparticles is not suitable to tailor magnetic codes.

As MPS detects signal variations due to material composition, shape, or size of magnetic nanoparticles, many of the particles reported in the literature, will represent unique harmonic spectra\(^\text{[44]}\) (in our group alone we observed several tens of different signal decays within the last two years, see Figure S12, Supporting Information). Conservatively assuming that only 100 nanoparticle types are applicable, we calculated that more than 77 billion \((77 \times 10^9)\) unique magnetic codes can be synthesized with our approach. The encoding is achieved by variation of the utilized magnetic nanoparticles and their ratio within code-carrying supraparticles. A detailed derivation and explanation thereof can be found in the Supporting Information.

3. Conclusion

In summary, we presented an approach to quantitatively adjust the magnetic properties of micron-sized supraparticles. This is essential for a miniaturized magnetic marker technology based on particles. Freely adjustable codes were obtained by compositional variation of supraparticles. The key to this was mixing nanocomposite particles which in turn were synthesized from different SPIONs and polystyrene. The possibility to sensitively and quantitatively modify magnetic properties by structural modification can be adapted by the countless research groups working on magnetic materials towards new innovative applications. In this work, the signal is used as a magnetic code, which is sensitively deciphered in milliseconds by MPS, and is detected from particles embedded inside other materials as well. This facilitates an application of miniaturized markers into many disregarded objects, such as dark materials that struggle with optical constraints such as light absorption and are therefore challenging to identify. The presented utilization of inexpensive and environmentally-friendly magnetic materials will be highly demanded as the centerpiece of communicating objects.

4. Experimental Section

Synthesis of Different Iron Oxide Nanoparticles: SPIONs were obtained by a co-precipitation reaction. To synthesize SPION1, FeCl\(_3\) \(6\) H\(_2\)O (10.80 g, 40 mmol, Sigma Aldrich, >99%) and FeCl\(_2\) 4 H\(_2\)O (3.98 g, 20 mmol, Fluka, >99%) were dissolved in deionized water (225 mL) at room temperature and mixed with 30% aqueous ammonia solution NH\(_3\)(aq.) (25 mL). SPION2 and SPION3 were synthesized by partial

This representation is spectral, a quantitative description is obtained after normalizing the magnetization amplitude to the maximum intensity. Different signal declines then represent different samples and thereby different codes. This approach is advantageous because the decline is physically unaffected by marker concentration, external influences (such as readout sensitivity), or the presence of diamagnetic/paramagnetic material and thus ideally suited to identify unknown objects by their marker signal. Furthermore, measurements are easily performable in seconds by untrained personal at ambient conditions\(^\text{[42]}\) with a customizable and inexpensive physical setup, which does not require sophisticated cooling circuits. However, interfering magnetic materials, external magnetic fields\(^\text{[43]}\) or metallic shielding might alter the magnetic excitation and the particle’s response, which will have to be taken into account for industrial application. Only a few milligrams of the marker were required to sensitively resolve their structural modifications in this work. Thinking ahead towards the identification of macroscopic objects, sensors with customizable geometries will be demanded for the detection of the incorporated magnetic markers. Such handheld sensors, which are feasible with MPS, will have to be sufficiently cheap and will thus result in a worse signal-to-noise ratio (SNR) compared to the herein utilized laboratory device. This will lead to a less sensitive differentiation of different magnetic codes. However, by increasing the amount of magnetic marker material, this can be easily compensated.

Going further, the spectral representation provides the possibility to use multiple harmonics rather than only one value as a code identifier. Thereby, samples that might look very similar at lower harmonics (Figure 3d, green curves, 3rd–11th harmonic) are distinguishable at higher harmonics (19th); it should be noted that the y-axis is plotted with a logarithmic scale, that is, the “spacing” between the signal intensities is orders of magnitude. Thus, the hierarchical supraparticle synthesis presented here is suitable to generate a vast variety of unique magnetic codes by a combination of exchangeable nanoparticles. At the same time, it provides a scalable, uncomplicated, and versatile possibility to be adapted by other researchers to combine almost any kind of magnetic nanoparticles. MPS is sufficiently sensitive to mirror relatively small changes in magnetic properties, as demonstrated in this work, by simply adding a dopant to an established synthesis protocol. Thus, this approach is feasible for many groups even with limited expertise in magnetic nanoparticle synthesis.
substitution of FeCl₃ 6 H₂O with CoCl₂ 6 H₂O (Sigma Aldrich, >98%). For SPION2, 10.0 g FeCl₃ 6 H₂O (37 mmol) and 0.72 g CoCl₂ 6 H₂O (3 mmol) and for SPION3, 9.2 g FeCl₃ 6 H₂O (34 mmol) and 1.43 g CoCl₂ 6 H₂O (6 mmol) were used, while the amount of FeCl₃ 4 H₂O was unchanged. Subsequently, the black precipitate was magnetically separated after 60 s of stirring, washed three times with deionized water, and dispersed in deionized water (250 mL) for 2 min. To stabilize the nanoparticle solution, oleic acid (6.5 g, Sigma Aldrich, >85%) was added over 5 min while stirring for 45 min. To remove excess oleic acid, the dispersion was washed with ethanol (125 mL) 3 times and decanted. Afterwards, cyclohexane was added to form a stable ferrofluid.

Synthesis of Nanocomposite Particles (i.e., “Instruments”): To synthesize nanocomposite particles, the reaction-free solvent evaporation emulsion technique described in another publication was modified. First, polystyrene (0.25 g, Sigma Aldrich) was dissolved in an appropriate amount of cyclohexane while heating at 60 °C for approximately 90 min. Second, an appropriate amount of one of the three iron oxide dispersions was pre-heated and added to this solution to end up with 250 mg iron oxide and 20 g cyclohexane. Third, an emulsion was created after the addition of a 0.5 wt% aqueous solution of sodium dodecyl sulfate (20 mL, Acros Organics, 85% pure) by continuous ultrasonication with an ultrasonic horn (Branson sonifier 450) for 5 min. To evaporate cyclohexane and form nanocomposite particles, the emulsion was stirred at 60 °C overnight. This was done for SPION1, SPION2, and SPION3 similarly to obtain three types of nanocomposite particles (instruments).

Synthesis of Supraparticles (i.e., “Ensemble”): To synthesize supraparticles, the dispersions were mixed so that the nanocomposite particles’ mass represented the desired ratio within supraparticles. After mixing the dispersions accordingly, hierarchical supraparticles were synthesized in a spray-dryer (Büchi Labortechnik AG, B290 mini). During spray-drying, liquids were finely atomized into small droplets which were dried in a heated atmosphere. Upon evaporation of the solvent, the nanocomposite particles assembled and formed supraparticles. The composition was thus easily varied by variation of the amount of employed nanocomposite particles in the dispersion. Spray-drying was performed with 10 % pump speed, flow rate of 40 L min⁻¹, 100 % aspirator power, and the inlet-temperature was set to 130 °C which yielded an outlet temperature of 65 °C. The dried powder was collected and subsequently analyzed.

X-Ray Diffraction: Nanoparticle dispersions were dried under ambient conditions to perform X-ray diffraction analyses with a D5005 X-ray diffractometer (Siemens AG) from 5–80° in steps of 0.02° for 2 s per step.

Dynamic Light Scattering: Measurements were conducted with a Malvern Instruments (Worcestershire, UK) Zetasizer Nano ZEN 3600 in a quartz cuvette in appropriate dilution. Measurement data shows the volume-weighted intensity distribution averaged from 5 measurements while each measurement performed 20 individual runs.

Transmission Electron Microscopy: Nanoparticle dispersions were diluted and dropped onto a carbon-coated copper TEM grid. Images were acquired with a JEM-2010 (JEOL) with an acceleration voltage of 200 kV.

Fourier Transform Infrared Spectroscopy: Fourier transform infrared spectroscopy measurements were performed on nanoparticle dispersions dried from dispersion after incorporation into a KBr pellet with a MagnaIR 760 ( Nicolet) between 400–4000 cm⁻¹ in transmission 50 measurement mode.

Magnetic Particle Spectroscopy: MPS measurements were conducted on 50 μL SPION dispersions and approximately 10 mg supraparticle powder using an MPS unit from Pure Devices GmbH (Rimpar, Germany) in a sinusoidal alternating field of 20.1 kHz from –300 to +300 Oe. The spectrum of each sample was generated by averaging five MPS measurements, whereas the individual measurement time was 200 ms. A reference spectrum without a magnetic sample was performed before every measurement and subtracted automatically.

Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy: Scanning electron microscopy (SEM) was carried out on powder samples adhered to a sticky carbon pad with a SUPRA 25 SEM from Carl Zeiss AG (Oberkochen, Germany) at 5 kV using a secondary electron detector. Cross-sections were prepared by incorporation of powder samples into a lacquer, dried, and cut with a razor blade. Due to the necessary thermal drying of the lacquer at 120 °C, supraparticles containing polystyrene were slightly deformed. Cross-section images were acquired at 10 kV acceleration voltage to confirm homogeneous particle distribution within the supraparticles.

Energy-dispersive X-ray spectroscopy (EDX) measurements were performed with an EDAX detector at 15 kV at a working distance of 8.5 mm to confirm a homogeneous distribution of iron oxide and polystyrene within supraparticles.

Laser Light Scattering: In order to obtain the size distribution of supraparticles, laser light scattering measurements were conducted with a Malvern Instruments (Worcestershire, UK) Mastersizer 2000 with a wet dispersion unit Hydro 2000S while stirring with 2000 rpm without ultrasonication. Data analysis was performed with the Mastersizer 2000 software and the cumulative volume was plotted as a function of size distribution.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Author Contributions
Overarching research goals were developed by K.M., S.W., and S.M. Preceding experiments, knowledge acquisition, and identification of key problems was performed by S.M. Supervision of the whole project was done by S.W. and K.M. The used emulsion methodology was established in the group by J.R. and adapted to iron oxide nanoparticles by S.M., J.P., and J.R. Experiments were designed and planned by S.M. Support of Gyusang Yi (FAU) for syntheses of nano and supraparticles according to plans and supervision of S.M. is acknowledged. Characterization methods were performed by S.M., J.P., and J.R. Interpretation and conclusions were drawn by S.M. and scientifically discussed with S.W. and K.M. Original publication draft was written by S.M., reviewing and editing performed by S.W., K.M., and S.M. All authors proof-read and commented on the publication. All figures were created by S.M. except Figure 1 and Figure 2 which were created by S.M. and J.R.
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