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New insights into size-controlled reproducible synthesis of anisotropic Fe$_3$O$_4$ nanoparticles: The importance of reaction environment

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Synthesis of size-controlled anisotropic magnetite (Fe$_3$O$_4$) nanoparticles allows designing next-generation magnetic nanosystems with predetermined magnetic properties suited for particular applications in biomedical, information, and environment. In this work, we report a reproducible and economical approach for fabricating anisotropic Fe$_3$O$_4$ nanoparticles via the thermal decomposition method. Controlling the reaction environment, i.e. degassing pressure is essential to obtain the reproducible synthesis of anisotropic Fe$_3$O$_4$ nanoparticles along with monodispersity in the size and shape. At low degassing pressure, Fe$_3$O$_4$ nanocubes are formed and the increase in degassing pressure leads to the formation of Fe$_3$O$_4$ octahedra nanoparticles. To achieve good reproducibility (with respect to size and shape) between different batches, our finding reveals the importance of maintaining the same degassing pressure. The size of anisotropic Fe$_3$O$_4$ nanoparticles can be varied by changing the heating rate and the solvent amount. The amount of solvent has also influence on the shape of nanoparticles, and Fe$_3$O$_4$ nanoparticles of flower morphology are obtained at the high solvent amount. The work also provides new conceptual fundamental insights into understanding the growth mechanism of anisotropic Fe$_3$O$_4$ nanoparticles and thus, advancing the field of materials chemistry for rationally designing anisotropic nanoparticles with tunable magnetic properties.

The reproducible and economical synthesis of anisotropic magnetite (Fe$_3$O$_4$) nanoparticles (NPs) with narrow size distribution continues to be a topic of considerable interest owing to their unique magnetic properties$^1$ and numerous potential applications related to biomedical,$^2$ catalysis,$^4$ environment,$^6$ light emitting devices,$^7$ and sensing.$^8$ Anisotropic Fe$_3$O$_4$ NPs offers two main advantages. First, the magnetic properties of Fe$_3$O$_4$ NPs depend on the shape as well as their size and size distribution.$^9$-11 This allows the design of advanced magnetic NPs with predetermined properties suited for specific applications. Recent studies demonstrated that anisotropic Fe$_3$O$_4$ NPs offer higher magnetic hyperthermia efficiency,$^{12,13}$ enhanced contrast in magnetic resonance imaging,$^{11,14,15}$ better targeting efficiency due to a large surface to volume ratio,$^{16}$ and longer blood circulation time compared to spherical Fe$_3$O$_4$ NPs.$^{17}$ Second, the self-assembly of anisotropic Fe$_3$O$_4$ NPs depends on the shape, thus resulting in the rich variety of self-assembled superstructures of distinct morphologies.$^{18,19}$ Such magnetic superstructures exhibit collective magnetic and magnetically enhanced mechanical properties which can be tailored by the shape of NPs as well as morphology of self-assembled superstructures.$^{20}$

In last two decades, various approaches based on microemulsion,$^{21}$ co-precipitation,$^{22}$ hydrothermal,$^{23}$ and thermal decomposition$^{10,24-27}$ have been researched for the synthesis of anisotropic Fe$_3$O$_4$ NPs. Among these, thermal decomposition of iron oleate in the presence of oleic acid and/or sodium oleate and octadecene has been used to synthesize Fe$_3$O$_4$ NPs in different shapes (cubic, octapod, octahedra, plate, rods)$^{11,14,15}$ resulting in good control over shape and size (3-25 nm). However, this approach does not lead to fabrication of anisotropic Fe$_3$O$_4$ NPs with phase purity, which can negatively influence crystallinity/structure of NPs and, thus, their magnetic properties. An alternative approach is based on the thermal decomposition of iron (III) acetylacetonate (Fe(acac)$_3$) in the presence of oleic acid (OA) as a surfactant and dibenzyl ether (BE) as a solvent.$^{29}$ This reaction yields considerably larger anisotropic Fe$_3$O$_4$ NPs (size >70 nm) because of the faster reaction compared to one based on iron oleate. The rate of reaction can be slowed down by using either other ligands such as decanoic acid and 4-biphenylcarboxylic acid instead of oleic acid or a mixture of solvents (BE+ squalene or BE + octadecene + tetradecane).$^{30,16,29}$ The purpose for the use of solvent mixture is that BE decomposes to benzyl benzoate and benzaldehyde at high temperature, causing a temperature fluctuation of the reaction, which results into poor reproducibility between different batches. Despite the synthesis of Fe$_3$O$_4$ nanocube in size range of 15-100 nm, these...
synthetic approaches offer less flexibility in the shape control and require the use of additional expensive solvents and ligands. It is known that the rate of reaction kinetics depends on the several factors, including the activity of precursor, ligand type, the interaction between the ligand and precursor, temperature, time, heating rate and reaction environment.\textsuperscript{24, 30} However, the role of reaction environment (i.e. degassing pressure) and heating rate on the controlling the reaction kinetics and reproducibility in size-and shape-controlled synthesis of anisotropic Fe\textsubscript{3}O\textsubscript{4} NPs have not been investigated.

Here, we demonstrate a reproducible one-pot synthesis of pure anisotropic Fe\textsubscript{3}O\textsubscript{4} NPs with control over size and size distribution. The approach involves the decomposition of Fe(acac)\textsubscript{3} only in the presence of BE solvent and OA. Our results show that controlling the heating rate of the reaction and residual oxygen content in the reaction is crucial to regulate the reduction kinetics, and thus, to reproducibly obtain anisotropic Fe\textsubscript{3}O\textsubscript{4} NPs in different sizes with narrow size distribution despite the temperature fluctuation (±5°C) during the reaction. We also further elucidate the understanding of the reaction mechanism by controlled experiments. The proposed approach is very robust (i.e. high reproducibility between different batches) and economical because it does not rely on the use of a combination of expensive solvents (octadecene, squalene, tetradecane, sodium oleate) and additional ligands. Overall, this is the first study reporting the variation in the shape and size of Fe\textsubscript{3}O\textsubscript{4} NPs without any need for adding another solvent and ligands. The present work contributes to the fundamental mechanistic understanding of colloidal synthesis that will facilitate the design of magnetite NPs with predetermined magnetic properties tailored to specific applications.

In a typical synthesis, Fe(acac)\textsubscript{3} (0.706 g, 2 mmol) was added to a reaction mixture of 20 mL BE and 1.26 mL OA. The resultant solution was degassed (residual pressure~0.19 mbar) at room temperature for 90 min and then heated to 290°C at a rate 8°C/min under argon (Ar) atmosphere and vigorous magnetic stirring. After maintaining the reaction at this temperature for 30 min, the solution was cooled down to room temperature. The reaction product was precipitated with a mixture of toluene and isopropanol and magnetically separated. Bright field (BF) scanning transmission electron microscopy (STEM) images reveal the cubic morphology of Fe\textsubscript{3}O\textsubscript{4} NPs, and the average size of nanocubes is determined to be ~43 nm with standard deviation (SD) of ~5% (Fig. 1a and Fig. 1b). Note that due to the degassing of the reaction mixture, we observed lower fluctuation in the reaction temperature (290±15°C) during the reaction, which is significantly lower to previously reported literature.\textsuperscript{16} It should further be noted that similar size Fe\textsubscript{3}O\textsubscript{4} NPs of cubic morphology can be reproducibly synthesized between different batches at fix degassing pressure.

High resolution transmission electron microscopy (HRTEM) image reveal the single crystalline nature of cubic NP with rounded corner (Fig. 1c). The FFT pattern of single crystalline NP is indexed with the help of CrystBox software\textsuperscript{31} and the diffraction spots (220) and (400) correspond to the interplanar spacing values 2.95 Å and 2.09 Å respectively (Fig. 1d). The interplanar lattice spacing was also determined from the image produced from the inverse FFT by choosing (220) and (400) reflections and found to be approximately closed to theoretical values (2.95 Å and 2.09 Å) for Fe\textsubscript{3}O\textsubscript{4} system (see Fig. S1 ESI\textsuperscript{†}). These results suggest that nanocubes are formed because of the rapid growth along the <111> direction, and the surface of the final product is formed from six Fe\textsubscript{3}O\textsubscript{4} (100) facets with eight rounded corner Fe\textsubscript{3}O\textsubscript{4} (111) facets. The crystal structure of these NPs can be assigned to FCC (face centered cubic) Fe\textsubscript{3}O\textsubscript{4} structure based on the interplanar spacings and ratio between different planes, including angles between the planes. To confirm the crystal structure of Fe\textsubscript{3}O\textsubscript{4} NPs, we used X-ray diffraction. XRD pattern shows the presence of pure Fe\textsubscript{3}O\textsubscript{4} phase in the as-synthesized NPs, which are in agreement with JCPDS card no. 019-0629 (see Fig. S2 ESI\textsuperscript{†}).
To understand the growth mechanism of cubic shape $\text{Fe}_3\text{O}_4$ NPs, we collected intermediate reaction products from the reaction mixture at different time intervals and analyzed by TEM. At low heating rates (i.e. 5°C/min), we noticed the cubic morphology of NPs after the reaction time (t) of 2 min at 290°C (Fig. 3a and see Fig. S6a ESI†). As the reaction progresses further (4 min to 30 min), the size of NPs increased from ~13 nm to ~58 nm while maintaining the cubic morphology (Fig. 3a and see Fig. S6b-f ESI†). In the case of rapid heating rate (i.e. 10°C/min), we observe a rather different behavior compared to the reaction that occurred at low heating rate. Here, we observed the emergence of small octahedra NPs after t=2 min (Fig. 3b, left most panel and see Fig. S7 ESI†). These octahedra NPs transformed into truncated octahedra after t=4 min and 6 min (Fig. 3b and see Fig. S8 ESI†). At t=10 min, these truncated octahedra NPs changed to a mixture of truncated octahedra and cuboctahedra shape (see Fig. S9a, b ESI†). Finally, these NPs gradually changed to NPs with cubic morphology after 20 min of the reaction time (see Fig. S9c ESI†) and did not observe any further change in the morphology of NP (see Fig. S9d ESI†). Therefore, the shape evolution of NPs occurs in the first 20 min of the reaction, and at the same time, the size of NPs increases from ~9 nm to ~30 nm with an increase in the reaction time from 2 min to 30 min. These experimental results indicate that the heating rate influences the evolution of the cubic morphology of $\text{Fe}_3\text{O}_4$ NPs via two different pathways. This can be explained based on the availability of monomers, and the balance between the chemical potential of monomers ($\mu_m$) and the chemical potential of different crystallographic planes.\textsuperscript{33} The chemical potential of different crystallographic planes of $\text{Fe}_3\text{O}_4$ can be ranked as $\mu_{[100]} > \mu_{[110]} > \mu_{[111]}$ because the (100) planes are the least densely packed and the (111) planes have the highest packing density. When the heating rate is low, the precursor decomposes slowly over the time period, resulting in a sluggish rate of nucleation (low concentration of nuclei in the nucleation stage). As the reaction enters the growth stage, the growth rate of preformed nuclei is very slow due to a low concentration of available monomer (i.e. lower conversion rate of precursor to monomer). In this case, the chemical potential of monomers falls below the chemical potential of the (100) and (110) ($\mu_{[100]} > \mu_{[110]} > \mu_{[111]}$). The continuous deposition of monomers along the (111) planes, thus, leads to the formation of cubic shaped $\text{Fe}_3\text{O}_4$ NPs, and subsequently to growth of cubic NPs as the reaction progressed further (Fig. 3c).

At faster heating rates, the high rate of precursor decomposition leads to faster nucleation rate (i.e. the large number of nuclei) as well as provides a high concentration of monomer available to growth of the NPs. In this case, the chemical potential of monomers is initially higher than that of the crystallographic planes (i.e. $\mu_m > \mu_{[100]} > \mu_{[110]} > \mu_{[111]}$), so the growth occurs simultaneously along all the planes. The chemical potential of monomers drops due to consumption of monomers in the reaction as the reaction advances ($\mu_{[100]} > \mu_m > \mu_{[110]} > \mu_{[111]}$). As a result, this leads to the growth of octahedra and truncated octahedra NPs. In the later stage of growth, the chemical potential of monomers falls to the point where $\mu_{[110]} > \mu_{[111]}$. 

\begin{figure}[h]
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\caption{BF STEM images show the synthesis of different sized $\text{Fe}_3\text{O}_4$ nanocubes at varied heating rate. a) 3°C/min, 85 nm (SD~5%), b) 5°C/min, 58 nm (SD~5%), c) 7°C/min, 45 nm (SD~9%), d) 10°C/min, 35 nm (SD~7%), e) 15°C/min, 30 nm (SD~8%), and f) 20°C/min, 26 nm (SD~9%).}
\end{figure}
µ_m > µ_{[111]}. Therefore, NPs grow more rapidly along the (111) planes and the shape of NPs gradually changes from truncated octahedra (larger proportion of (111) facets than (100) facets) to cuboctahedra (a larger proportion of (100) facets than (111) facets), and finally to cubic shape NPs (Fig. 3d).

We performed several synthesis reactions at different heating rates and reaction times. The relationship between the time and size of Fe₃O₄ NPs at different heating rates is shown in Fig. 4. A small or no change in the size of NPs can be noticed with time at low heating rates (1°C/min and 2°C/min). However, NP size continuously increases in the first 60 min of the reaction at high heating rates (1°C/min and 2°C/min). After 60 min, a small increase in the size can be seen. These results suggest that the nucleation occurs at a lower temperature than 290°C in the case of low heating rate. The nuclei formed at low temperature consume monomers and quickly evolve into larger NPs, preventing further nucleation events at high temperature. A high heating rate promotes nucleation at high temperature, (290°C), and produces a large number of nuclei. The monomer concentration decreases due to their consumption by growing nuclei at the initial stage of the growth process, thus preventing nucleation events at the later stage of the reaction. In the later stage, the growth of NPs most likely occurs by an Ostwald ripening process, whereby either monomer from high surface energy facets or smaller NPs of high surface energy dissolve into the solution and redeposits on low surface energy facets or NPs. As a result, NPs of smaller sizes are produced at high heating rate because of the low monomer concentration in the later stage of the reaction.
We also investigated the influence of a commonly neglected reaction parameter, the residual oxygen content in the reaction environment, on the shape of Fe$_3$O$_4$ NPs. The content of residual oxygen was controlled by degassing the reaction solution at different pressures. On increasing the degassing pressure from 0.19 mbar to 0.40 mbar and 0.71 mbar while under similar reaction conditions (5°C/min and 290°C), truncated cubic (58 nm, SD~9%) and truncated octahedra (~57 nm, SD~4%) shaped Fe$_3$O$_4$ NPs formed (Fig. 5a and b). When the reaction was performed at a higher heating rate (10°C/min) at degassing pressure of 0.40 mbar and 0.71 mbar at similar reaction conditions, truncated octahedra NPs of size ~38 nm and ~37 nm (SD~8%) were obtained (Fig. 5c and d). Inset SEM images shown in Fig. 5c and d confirm the truncated octahedra morphology of NPs. Moreover, the size of truncated octahedra Fe$_3$O$_4$ NPs depends on the heating rate at similar reaction conditions (degassing pressure~0.71 mbar, 290°C), i.e. low heating rate resulted into large size of octahedra NPs (~57 nm) than to size obtained at faster heating rate (~37 nm). These results suggest that the synthesis of Fe$_3$O$_4$ NPs is very sensitive to the change in the content of residual oxygen in the reaction environment.

According to first-principle calculations, the Wulf shape of oxide material in thermodynamic equilibrium at low pressure and high temperature is a cube with [100] edges. In the case of Fe$_3$O$_4$ crystals, the cationic charge density of the (111) plane is higher than the other planes (110) and (100). On increasing the pressure, oxygen species present in reaction environment strongly adsorb onto the plane of high charge density, i.e. (111), thus, modifying the surface energy of facets, i.e. \( \gamma(111) > \gamma(100) > \gamma(110) \). As a result, the growth of NPs is suppressed in the <111> direction, and truncated octahedra shape possessing both (100) and (111) facets formed under thermodynamic equilibrium with oxygen species at reaction temperature. Therefore, the shape of NPs can be tailored by controlling the amount of residual oxygen (i.e. degassing pressure).

The amount of solvent can have influence on the shape and size of Fe$_3$O$_4$ NPs. To examine this, we varied the amount of BE solvent (10 mL, 20 mL, and 50 mL) and different reactions were performed at the heating rate of 10°C/min (T=290°C, t=30 min, degassing pressure=0.19 mbar). BF STEM images show the formation of cubic shaped Fe$_3$O$_4$ NPs of different sizes, i.e. 86 nm and 35 nm corresponding to 10 mL and 20 mL volume of the solvent (see Fig. S10a ESI† and Fig. 2d). When the amount of solvent was increased to 50 mL, we observed a flower morphology of Fe$_3$O$_4$ NPs of size~ 31 nm (see Fig. S10b ESI†). These flower shaped NPs are formed by joining of two, three, or more than three small individual NPs. Therefore, these NPs can also be termed as single twinned or multiply twinned. The observed decrease in size with the increase in solvent volume can be explained by a reduction in the concentration of available monomers in the reaction. In the case of a low solvent volume (10 mL), the probability of finding monomers to the close vicinity of growing NPs is high, which facilitates a higher mass transfer and, subsequently, a high growth rate. When the solvent volume is increased to 50 mL, the concentration of precursor and thus, the concentration of monomers in the solution is reduced. As a result, small sized NPs are formed because of a sluggish growth rate. Since small NPs possess high surface energy, therefore, smaller NPs join to form flower morphology, including single and multiple twinned Fe$_3$O$_4$ NPs to minimize the overall surface energy.

In conclusion, we have demonstrated shape-and size-controlled synthesis of Fe$_3$O$_4$ NPs via thermal decomposition of Fe(acac)$_3$ in the presence of OA and BE without any additional need for using a combination of solvents and ligands. When the reaction mixture was degassed at low pressure, Fe$_3$O$_4$ nanocubes formed, and their sizes can be varied by changing the heating rate. Our results showed two different nanocube formation mechanisms depending on the heating rate, as the heating rate influences the production of available monomers in the solution. The shape of Fe$_3$O$_4$ NPs changes from nanocube to octahedra when degassing pressure of the reaction mixture was increased. This transformation can be attributed to a modification in the surface energy of different crystalline facets in the presence of oxygen species. Our results suggest that the residual oxygen content in the reaction environment (or degassing pressure) is an essential experimental parameter that enables control over the shape as well as reproducibility in size from the different batches. The shape and size of Fe$_3$O$_4$ NPs can also be controlled by changing the volume of the solvent. The size of nanocube increases with the increase in the volume of the solvent, and at high amount of solvent, Fe$_3$O$_4$ NPs of flower morphology resulted. The difference in sizes and shapes can be understood based on the concentration of
monomers in the reaction mixture and mass transfer of monomers. Overall, these findings provide new conceptual insights and design rules for synthesizing Fe₃O₄ NPs with predetermined magnetic properties suited for specific applications such as magnetic hypothermia, contrast agent, photocatalysis, sensing, and energy storage.

Conflicts of interest

There are no conflicts to declare.

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Table of content (TOC): The reproducible synthesis of size-controlled anisotropic magnetite (Fe3O4) nanoparticles are demonstrated by thermal decomposition approach. The shape and size of nanoparticles are controlled via the reaction environment through degassing, heating rate and solvent volume.