Exceeding natural resonance frequency limit of monodisperse Fe$_3$O$_4$ nanoparticles via superparamagnetic relaxation

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Magnetic nanoparticles have attracted much research interest in the past decades due to their potential applications in microwave devices. Here, we adopted a novel technique to tune cut-off frequency exceeding the natural resonance frequency limit of monodisperse Fe$_3$O$_4$ nanoparticles via superparamagnetic relaxation. We observed that the cut-off frequency can be enhanced from 5.3 GHz for Fe$_3$O$_4$ to 6.9 GHz for Fe$_3$O$_4$@SiO$_2$ core-shell structure superparamagnetic nanoparticles, which are much higher than the natural resonance frequency of 1.3 GHz for Fe$_3$O$_4$ bulk material. This finding not only provides us a new approach to enhance the resonance frequency beyond the Snoek’s limit, but also extend the application for superparamagnetic nanoparticles to microwave devices.

The frequency response of magnetic moment to an alternating magnetic field plays a vital role in designing the microwave, and even terahertz devices. The miniaturization and rapid increase in frequencies of electric devices require that magnetic materials possess high resonance frequency, large permeability, and low magnetic loss. The natural resonance frequency, $f_r$, originated from the magnetocrystalline anisotropy field, $H_K$, is generally regarded as the upper limit frequency, i.e. cut-off frequency, of magnetic materials. For traditional spinel ferrites, their natural resonance frequencies typically fall near or below 1 GHz. Although the resonance frequency can be enhanced by introducing additional magnetic anisotropies, including shape anisotropy, strain-induced anisotropy, as well as exchange anisotropy, it is a great challenge to increase both resonance frequency and permeability simultaneously due to the Snoek’s limit, i.e. the product of the susceptibility and the resonance frequency is proportional to the saturation magnetization.

Magnetic nanoparticles have attracted much research interest in the past decades due to their potential applications in ultrahigh density magnetic storage, biomagnetism, and microwave absorption. When the nanoparticle volume, $V_p$, is reduced to a certain extent that magnetic anisotropy energy, $K V_p$, is comparable to the thermal energy, $k_B T$, there exists a finite probability that the magnetization vector will reverse its direction by thermal fluctuation at certain temperature $T$. Both theoretical and experimental data indicated that the frequency dependence of the susceptibility for a single domain particle depended on the ratio of the magnetic anisotropy energy to the thermal energy ($\chi \propto K V_p / k_B T$). In the case of $\chi \ll 1$, the real part of the complex susceptibility $\chi'$ decreases monotonically with increasing $f$, whilst the imaginary component, $\chi''(f)$, has a maximum at a frequency $f_0 = 1/\tau$. $\tau$ is relaxation time is introduced to describe how rapidly this superparamagnetic/ferromagnetic relaxation takes place.

$$\tau = \tau_0 e^{K V_p / k_B T}$$

where $\tau_0$ is determined by the intrinsic precession rate of the spin moment in the equivalent field for magnetic anisotropy.

The frequency, $f_0 = 1/\tau = f_0 e^{-K V_p / k_B T}$, which superparamagnetic state transits to ferromagnetic one in frequency domain, will increase with decreasing the nanoparticle volume. Therefore, the superparamagnetic dynamics in...
GHz range, which is governed by both natural resonance frequency ($f_n$) and superparamagnetic/ferromagnetic relaxation rate ($f_r$), should be attractive and challenging issue. The great challenge is whether $f_n$ can be tuned to surpass $f_r$ or not.

In contrast to conventional bulk microwave ferrites, the magnetic properties of superparamagnetic nanoparticles can be easily tuned by controlling the volume, shape, anisotropy, dipolar interaction between particles, and by applying exchange bias and electric field\(^{18 – 21}\). However, the effect of superparamagnetism on high frequency properties is not well understood. Here, we adopted a novel technique to tune the cut-off frequency exceeding the natural resonance frequency limit of monodisperse Fe\(_3\)O\(_4\) nanoparticles via superparamagnetic/ferromagnetic relaxation. We observed that the cut-off frequency can be enhanced from 5.3 GHz for Fe\(_3\)O\(_4\) to 6.9 GHz for Fe\(_3\)O\(_4\)@SiO\(_2\) core-shell structure superparamagnetic nanoparticles, which are much higher than the natural resonance frequency of 1.3 GHz for Fe\(_3\)O\(_4\) bulk material. In addition to the enhancement of cut-off frequency, the magnetic loss is significantly reduced via SiO\(_2\) coating. This finding in superparamagnetic nanoparticles not only provides us a new approach to enhance the resonance frequency beyond the Snoek’s limit, but also opens a new avenue for exploring superparamagnetic nanoparticles in microwave devices.

**Results**

Figures 1(a) and 1(b) illustrate the Transmission electron microscopy (TEM) micrographs and X-ray diffraction (XRD) patterns for as-prepared Fe\(_3\)O\(_4\) nanoparticles and Fe\(_3\)O\(_4\)@SiO\(_2\) core-shell composites, respectively. Fe\(_3\)O\(_4\) nanoparticles have a regularly spherical morphology and an average size of 9.0 ± 0.5 nm with a narrow size distribution of (σ = 5%). Every Fe\(_3\)O\(_4\) particle was coated by the SiO\(_2\) shell after the magnetic collection process. For SiO\(_2\) thickness of 8.0 nm, nearly every Fe\(_3\)O\(_4\) core was located at the center of the core-shell structures, and the Fe\(_3\)O\(_4\)/SiO\(_2\) core-shell nanoparticles became well-dispersed in ethanol, which provide an indirect evidence of the decrease of interparticle interaction. Although the particle size of Fe\(_3\)O\(_4\) does not change obviously, the interspacing of nanoparticles increases via SiO\(_2\)-shell coating. XRD patterns of the samples indicate that all the highly crystalline peaks match well with the standard crystal phase of magnetite (JCPDS No. 894319, 19-0629). The broad peak around 15° to 35° presents the existence of amorphous-SiO\(_2\).

In order to determine the effect of interparticle spacing on the collective magnetic behavior of the Fe\(_3\)O\(_4\) nanoparticles, the temperature-dependent zero-field-cooled (ZFC) magnetization of the as-prepared Fe\(_3\)O\(_4\) and Fe\(_3\)O\(_4\)@SiO\(_2\) core-shell structure nanoparticles is measured at a low magnetic field of 100 Oe and shown in Fig. 2. The maxima of the ZFC curves related to the blocking temperatures, $T_B$, of superparamagnetic behavior shift from 86 K for as-prepared Fe\(_3\)O\(_4\) nanoparticles to 37 K for Fe\(_3\)O\(_4\)@SiO\(_2\). A similar trend was previously observed in dilute dispersed magnetic nanoparticles and by Monte Carlo simulations\(^{21 – 22}\). The dipole-dipole interaction results in an additional energy barrier for the thermal fluctuations, and consequently increases the blocking temperature.

Since the value of the blocking temperature for a given particle is dependent upon the observation time, which is determined by the instrument used, it will be useful to collect information using various techniques with observation times different over a large range. Figures 3(a) and 3(b) illustrate the \(^{57}\)Fe Mössbauer spectra collected at room temperature for as-prepared Fe\(_3\)O\(_4\) nanoparticles and Fe\(_3\)O\(_4\)@SiO\(_2\) core-shell nanoparticles, respectively. Although DC magnetization measurement indicates that a superparamagnetic behavior, the Mössbauer spectrum of as-prepared Fe\(_3\)O\(_4\) nanoparticles shows clearly two strong sextets and a weak doublet (5%) at room temperature, suggesting that a ferromagnetic behavior is dominated in this sample. The concentration of ferromagnetic phase decreases to 54% for Fe\(_3\)O\(_4\) coated with SiO\(_2\) shell (Fig. 3(b)). The two sextets with hyperfine fields ($H_{hf}$), and center shift ($\Delta$S) of one (487.55 kOe and 0.66 mm/s) and the other (456.5 kOe and 0.32 mm/s) suggest the Fe\(^{3+}\) ions on the octahedral sites and Fe\(^{2+}\) ions on the tetrahedral sites, respectively. The results are consistent with the room-temperature results observed for magnetic nanoparticles\(^{23}\). The hyperfine fields are lower than those of the bulk material and the resonance lines are broadened. The change in the Mössbauer spectra is due to the finite size effect, which can cause a higher percentage of surface atoms, additional stresses between atoms, and superparamagnetic behavior\(^{24}\). The stoichiometry of nanoparticles is

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**Figure 1** | (a) TEM micrographs; and (b) XRD patterns for as-prepared Fe\(_3\)O\(_4\) nanoparticles and Fe\(_3\)O\(_4\)@SiO\(_2\) core-shell composites.

**Figure 2** | Temperature-dependent zero-field-cooled (ZFC) magnetization of the as-prepared Fe\(_3\)O\(_4\) and Fe\(_3\)O\(_4\)@SiO\(_2\) nanoparticles.
extracted by comparing the relative areas of the \(^{57}\text{Fe}^2+\) and the \(^{57}\text{Fe}^3+\) using the following equation \(x = \text{Fe}^2+/\text{Fe}^3+ = (1/2^{\text{OctFe}^2+} + \text{Fe}^3+)\). According to the ratio of \(\text{Fe}^2+\) and \(\text{Fe}^3+\) of about 46.7%, one can deduce that the stoichiometry of nanoparticles is \(\text{Fe}^{1+}2 + 0.066\text{Fe}^{2+}1.066\text{O}4\). The possible reason for the slightly shift of \(\text{Fe}^2+\): \(\text{Fe}^3+ = 2:1\) is partly oxidation of \(\text{Fe}^2+\) ions on the surface layer or slight presence of vacancies in tetrahedral sites.

The different results obtained from Mössbauer spectra with those from DC magnetization measurements can be explained by the relationship between relaxation time \(\tau\) and the experimental observation time, \(t_{\text{obs}}\). It is well known that the magnetic behavior of a particle is dependent on the experimental observation time, \(t_{\text{obs}}\). For \(t_{\text{obs}} < \tau\), the particle shows ferromagnetic behavior, while for \(t_{\text{obs}} \gg \tau\), the particle is superparamagnetic behavior. Since the experimental observation time for Mössbauer measurements \((t_{\text{obs}} \sim 10 \text{ ns})\) is significantly shorter than that for DC magnetization measurements \((t_{\text{obs}} \sim 10 \text{ ns})\), a superparamagnetic behavior obtained by DC magnetization measurements can behave as ferromagnetism in shorter observation time scale, such as Mössbauer measurements. In other word, we can expect the superparamagnetic behavior can transit to ferromagnetic one in higher frequency regime.

In order to confirm our expectation, the frequency dependence of relative complex permeability, \(\mu_r = \mu' - j\mu''\), is measured in the frequency range of 0.1–10.0 GHz. It reveals that the real part, \(\mu'\), exhibit a relaxation behavior and decreases with increasing from 0.1 GHz to 2.0 GHz, and keeps a constant with further increasing frequency (Fig. 4(a)). An abrupt decrease to less than 1.0 was observed at 5.3 GHz and 6.9 GHz for the as-prepared \(\text{Fe}_3\text{O}_4\) nanoparticles and \(\text{Fe}_3\text{O}_4/\text{SiO}_2\) core-shell particles. The negative excursion in the real part of the susceptibility \((\chi' = \mu' - 1)\) implies a resonant behavior. The resonant behavior was more evident by the two peaks in the curves of the frequency dependence of imaginary part, \(\mu''\) (Fig. 4(b)).

According to the Kittel equation, the natural resonance frequency of a sphere-shaped magnetic particle is

\[
f_0 = \frac{\gamma H_K}{2\pi}
\]

where \(\gamma\) is the gyromagnetic ratio. For cubic symmetric system, the magnetocrystalline anisotropy field, \(H_K = \frac{4|K|}{3\mu_0M_s}\). Using the magnetocrystalline anisotropy constant \(K = -1.2 \times 10^6 \text{ J/m}^3\) and saturation magnetization \(M_s = 4.6 \times 10^5 \text{ A/m}\) for single crystal \(\text{Fe}_3\text{O}_4\), the theoretical calculation of the natural resonance frequency should be 1.5 GHz. Therefore, the first peak around at 1.3 GHz was assigned to the natural resonance frequency. The lower resonance frequency is related to the slightly smaller magnetocrystalline anisotropy for nonstoichiometric magnetite nanoparticles.

The second peak at 5.3 GHz and 6.9 GHz for the samples is attributed to the superparamagnetism/ferromagnetic transition relaxation rate, \(f_b\), respectively. In addition to the relaxation behavior, a resonance behavior was also predicted and observed at a frequency in the range of 30–60 MHz in a number of ferrofluids. In the case of a single particle, the results calculated by Raikher and Shliomus demonstrated that the transition between the region of the relaxation and resonance behaviors was depended on the ratio of the magnetic anisotropy energy to the thermal energy \((\alpha = KV/\kappa T)\) and occurred for \(\alpha \approx 0.73\). By using the magnetic anisotropy constant and the grain size of \(\text{Fe}_3\text{O}_4\) nanoparticles, \(\alpha \approx 0.85\) can be derived. Therefore, the dispersion of \(\mu'\) for our samples has both relaxation and resonance characteristics.

The calculated magnetic phase diagram against frequency for nanoparticle assembly by Haegesawa et al. demonstrates that the transition from superparamagnetic state to no response state is strongly dependent upon the ratio of the effective thermal field of \(H_t = k_BT/V\mu_0M_s\) to effectively magnetic anisotropy field \(H_K\). In the case of \(H_t < H_K\), with increasing frequency, nanoparticle assembly undergoes from superparamagnetic state into no response state through ferromagnetic state. In this case, \(f_0\) can be written as

\[f_0 = \frac{\gamma H_K}{2\pi}
\]
In our previous work\textsuperscript{20,21}, we found the blocking temperature increases with the strength of paramagnetism and ferromagnetism. Moreover, the SiO\textsubscript{2} coating provide us a new approach to enhance the resonance frequency beyond the Snoek’s limit, but also opens a new application field for superparamagnetic/ferromagnetism transition. In addition, the magnetic loss is significantly reduced via SiO\textsubscript{2} coating. The finding of non-gyromagnetic resonance mechanism in superparamagnetic nanoparticles not only provides us a new approach to enhance the resonance frequency beyond the Snoek’s limit, but also opens a new application field for superparamagnetic nanoparticles.

**Methods**

Monodisperse Fe\textsubscript{3}O\textsubscript{4} nanoparticles with 9.0 ± 0.5 nm diameter were synthesized in octadecene, instead of the diocyl ether used in a synthesis procedure reported in Refs. 30 and 31. SiO\textsubscript{2} coating onto the Fe\textsubscript{3}O\textsubscript{4} nanoparticles was carried out in reverse micelles by the hydrolysis of tetraethyl orthosilicate\textsuperscript{19,29}. Transmission electron microscopy (TEM) was performed on HITACHI H8100 at 120 kV to determine particle shape and size distribution. X-ray diffraction (XRD) patterns were used to characterize the crystal structure of the samples using a step-scanning with 0.02° step and 5 s integration time. Fe Mössbauer spectra at room temperature were recorded with a \textsuperscript{57}Co (Rh) source. The values of $C_S$ given here are relative to the room temperature value of α-Fe. DC magnetization measurements were performed on a Superconducting Quantum Design (SQUID) magnetometer (MPMS-XL). Zero-field-cooled (ZFC) DC magnetization measurements were carried from room temperature to 10 K at a field of 100 Oe. For magnetic and dielectrical spectra measurements, the Fe\textsubscript{3}O\textsubscript{4}/paraffin wax mixtures were prepared by homogenously mixing Fe\textsubscript{3}O\textsubscript{4} and Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2} nanoparticles with paraffin wax with a mass ratio of 7:3 and then pressed into the toroidal-shaped samples of 7.00 mm outer diameter and 3.04 mm inner diameter. The scattering parameters ($S_11$ and $S_21$) were measured by a vector network analyzer (Agilent N5224A) using a coaxial transmission–reflection method in the frequency range of 0.1–10 GHz. The complex permeability, $\mu_r$, and permittivity, $\varepsilon_r$, were determined from the scattering parameters using the Nicolson models\textsuperscript{16}. 

**Discussion**

According to the transmission line theory, for a single layer absorber with a backed metal plate, the reflection loss (RL) curves were simulated from the electromagnetic parameters at various sample thicknesses by means of the following expressions\textsuperscript{26}:

$$RL = 20\log_{10}\left(\frac{Z_{in} - Z_0}{Z_{in} + Z_0}\right)$$

where $f$ is the frequency of the electromagnetic wave, $d$ is the thickness of the sample, $c$ is the velocity of light, $Z_0$ is the impedance of air, and $Z_{in}$ is the input impedance of the sample.

Figure 6 illustrates the frequency dependence of RL for these two samples with thickness of 6.0 mm. It was observed the magnitude of absolute value of reflection loss of $|RL|$ decrease from 20.3 dB for as-prepared Fe\textsubscript{3}O\textsubscript{4} to 7.5 dB for Fe\textsubscript{3}O\textsubscript{4} coated with SiO\textsubscript{2} shell. In addition, a considerable reduction of RL can be obtained by SiO\textsubscript{2}-coating in whole frequency range of 0.1–10.0 GHz. The higher resonance frequency and lower magnetic loss make the Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2} core-shell nanoparticles suitable for high frequency application.

In conclusion, we have demonstrated that the high frequency properties of core-shell Fe\textsubscript{3}O\textsubscript{4}/SiO\textsubscript{2} superparamagnetic nanoparticles can be tuned via dipolar interaction. The cut-off frequency can exceed the natural resonance frequency by superparamagnetic/ferromagnetism transition. In addition, the magnetic loss is significantly reduced via SiO\textsubscript{2} coating. The finding of non-gyromagnetic resonance mechanism in superparamagnetic nanoparticles not only provides us a new approach to enhance the resonance frequency beyond the Snoek’s limit, but also opens a new application field for superparamagnetic nanoparticles.
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Author contributions
Z.H.C and H.T.Y. planned the experiments. N.N.S prepared the samples and carried out the microwave experiments. H.L.L performed Monte Carlo calculations; R.X., H.F.D. and X.Z.Q. contributed to the analysis and discussion for the results. Z.H.C wrote the paper and all authors comment on it.

Additional information
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