

Magnetic nanoparticles and superparamagnetic resonance (2) “ Structure and electronic states of magnetic nanoparticles ”

Product used : Electron Spin Resonance spectrometer (ESR), Q-band (ES-SQ5)
 Transmission Electron Microscope (TEM)

Particle size and specific surface area

When we assume the particle as a sphere, a parameter S_s , which is the ratio of the surface area ($S = 4\pi r^2$) to its volume ($V = \frac{4}{3}\pi r^3$), is expressed as

$$S_s = \frac{S}{V} = \frac{3}{r} \quad (1)$$

Surface area is in inverse proportion to the particle radius. S_s is the specific surface area, and r is the radius of the particle. Figure 1 shows the relation between sphere's diameter and calculated specific surface area according to eq.(1). This plot lets us know that the surface area of the mesoscopic matter is to be very large.

This unique largeness of the specific surface area significantly affects the physical properties of nano-ordered particle materials. This is because the surface poses discontinuous interface, and can generate different electron states from uniform and periodic crystal in the inner region of the particle.

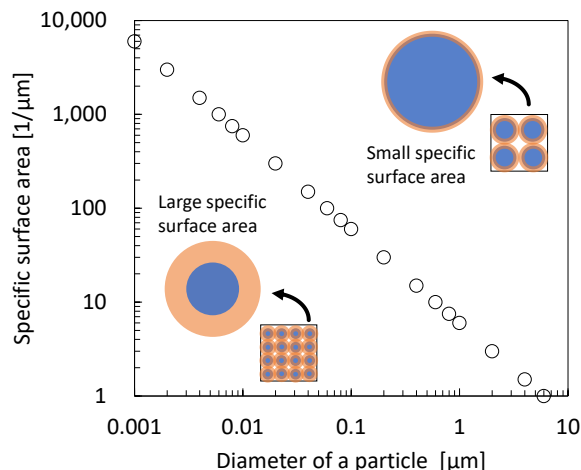


Fig. 1 Particle diameter and specific surface area.

Core-shell structure of magnetic nanoparticles

Magnetic nanoparticles (MNPs) is expected for medical and industrial materials. Therefore, the uniform size regulation of the particle is necessary to obtain the reproductivity or stability, because quantum size effects make the physical properties change drastically. Homogeneity as the materials strongly depends on the narrowness of the size distribution. Above all, evaluation that checks the shape and measures the size distribution using transmission electron microscope (TEM) is important on the process of MNPs synthesis. Moreover, it is advocated that the mesoscopic MNPs hold core-shell structure in the term of magnetic morphology as shown Fig. 2^[1-3]. Figure 3 shows superparamagnetic resonance (SPR) spectra and bright field images obtained using TEM and size distribution histograms of different sized MNPs (Fe_3O_4). These spectral patterns vary drastically with getting smaller a particle size, in spite of the same elemental composition. Furthermore, there seems that each spectrum consists of two components with different line widths (broad and narrow ones). The obtained data by TEM show that particles are sphere and have a uniform size distribution. The data of the TEM support that these spectral variations are strongly correlated to the particle diameters.

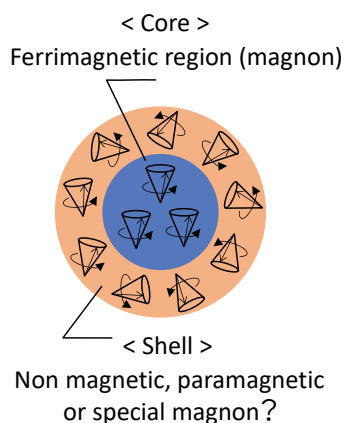


Fig. 2 Core-shell magnetic morphology.

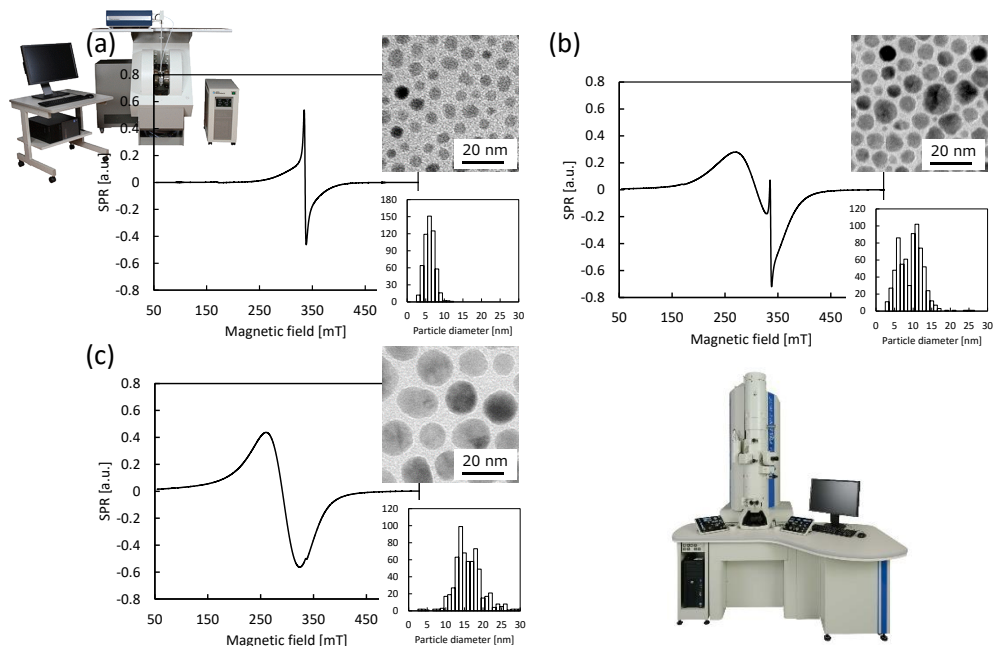


Fig. 3 SPR spectra of Fe_3O_4 magnetic nanoparticles dispersion in toluene (0.625 mg/mL), images obtained using TEM (JEM-2100Plus, The accelerating voltage is 200 kV) and size distribution of the particles, (a) with diameter of 5 nm, (b) 10 nm, and (c) 20 nm.

Core-shell structure inferred from saturation property of SPR spectra

Electron spins located in the different environments have different energy level spacing and intrinsic interaction. Therefore, each relaxation path or velocity by microwave excitation is not the same, the respective spin has a unique relaxation time (spin-lattice relaxation : T_1 , spin-spin relaxation : T_2). Since the spin relaxation time of the usual ferromagnets is very short, direct observation of relaxation time is very difficult. However, measurements of microwave power dependence (saturation property) make it possible to distinguish different spins.

Spectra shown in Fig. 4 are irradiated power variations of superparamagnetic resonance by MNPs (Fe_3O_4). It can be seen that every spectrum consists of two components, which are broad one and narrow ($g \sim 2$) one. As the diameters of the particles are getting smaller, the narrow components ratio is increasing. The narrow components are easy to saturate, but its g-value and line width are constant. On the contrary, the broad components do not saturate even over 160 mW, and its line widths increase with power levels. These spectral properties imply two distinct different spins in a particle, and it leads to support the core-shell structure model of the MNPs^[2].

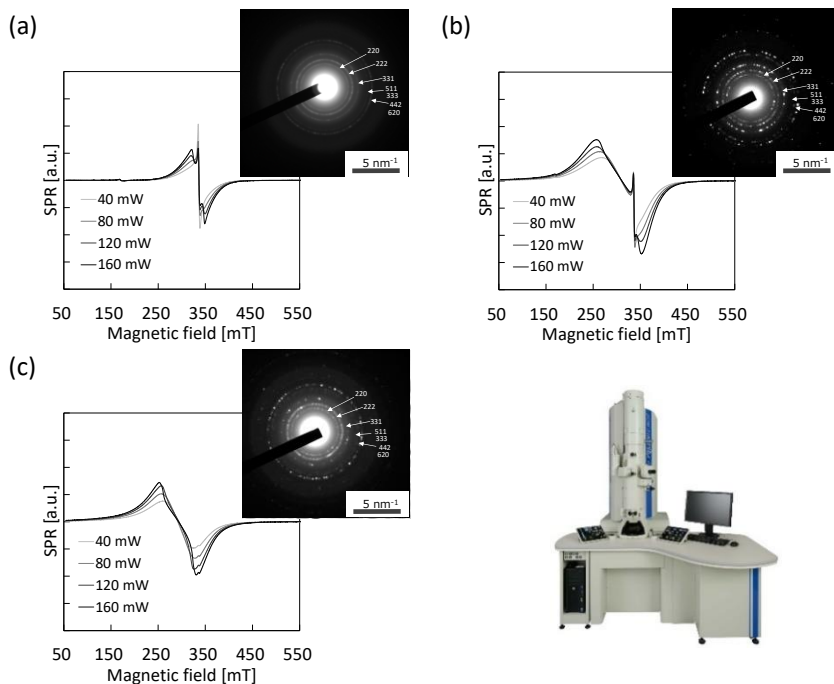


Fig. 4 Microwave power dependence of SPR spectra of Fe_3O_4 magnetic nanoparticles dispersion in toluene (0.625 mg/mL) and electron diffraction, with a diameter of (a) 5 nm, (b) 10 nm, and (c) 20 nm.

* Electron diffraction patterns were obtained using JEM-2100Plus (the accelerating voltage is 200 kV). Three diffraction patterns of the magnetic nanoparticles as shown in (a) – (c) were coincident with the known diffraction pattern of Fe_3O_4 .

Characterization magnetic nanoparticles by multi-frequency FMR/SPR spectra

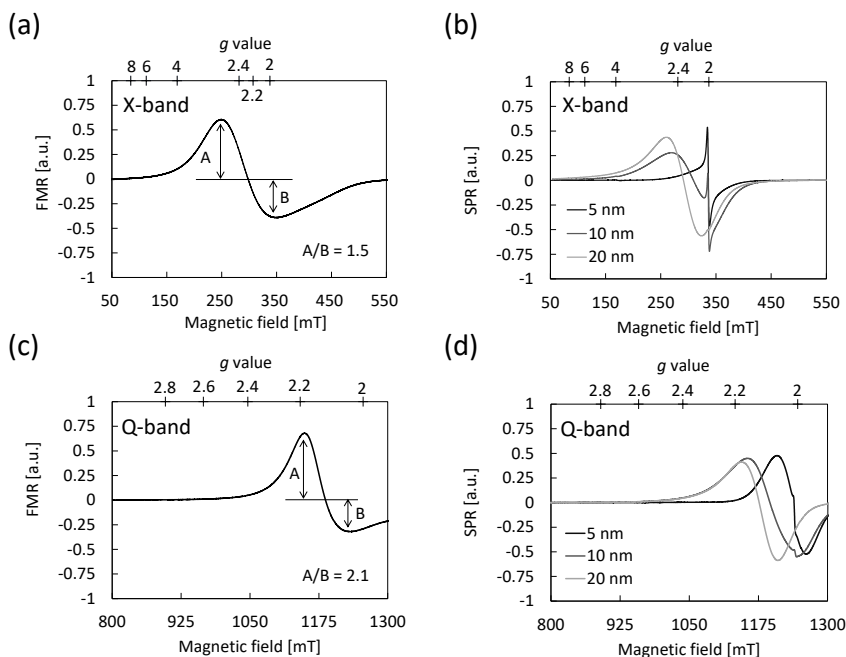


Fig. 5 ESR spectra of magnetite (Fe_3O_4) particles with different diameters using multi-frequency.

(a) X-band FMR spectrum of Fe_3O_4 powder with diameter of 50 – 100 nm. (b) X-band SPR spectra of Fe_3O_4 magnetic nanoparticles dispersion in toluene (0.625 mg/mL). (c) Q-band spectrum of (a). (d) Q-band spectra of (b). Q-band spectra were obtained using ES-SQ5 (as shown above picture).

Reference: [1] Y. Komorida, Doctor thesis "Studies of Magnetic and Structural Properties of Magnetic Nanoparticles under Hydrostatic Pressure" (2010).

[2] S. Tatum, *Concepts and Functions of Ferromagnetic Resonance* (NY research press, 2015).

[3] K. L. Krycka et al. *Phys. Rev. Lett.* **104**, 207203 (2010).

[4] F. Gazeau et al., *Journal of Magnetism and Magnetic Materials*, **202**(2-3), 535-546 (1999).

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