

The Magnetic Shielding Effect of Polymer Coated Nano-sized Iron Oxide

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Introduction

Superparamagnetic iron oxide nanoparticles (IONPs) are widely used as magnetic resonance (MR) relaxation agent with their strong T2 shortening effect [1]. The superparamagnetic property is an indispensable condition to MR contrast agent because MR signal intensity strongly depends on the magnetic property of MR agent. For clinical application, surface modification of iron oxide nanoparticles with biocompatible polymer would be required to prevent the toxicity of iron oxide and the aggregation of particles. In this study, we aim to investigate the magnetic shielding effect of the coating polymer on the iron oxide core when IONPs were coated by biocompatible polymer.

Material and Methods

Synthesis of nanoparticles : Ferric and ferrous chlorides (molar ratio 2:1) were dissolved in water at a concentration of 0.09M iron ions. Chemical precipitation was achieved at room temperature under stirring by adding 40% NH₄OH. The black precipitates were washed several times with pure water and separated by magnetic decantation. For the coating of polycaprolactone (PCL), 215ml of 0.46% (w/w) polyvinylpyrrolidone aqueous solution and 15ml of 5.57% (w/w) PCL acetone solution were added to IONPs and the reaction mixture was vigorously stirred for 1hr. After solvent evaporation, the resulting PCL coated IONP (PCLNP) was centrifuged to separate into different size and remove excessive polymer.

Characterization : The size and structure of the particles were evaluated with transmission electron microscope (TEM, H-7600, Japan, HITACHI) and X-ray diffraction (XRD, Philips, X-PERT). The average diameters of IONP and PCLNP were measured by dynamic light scattering (DLS, Particle Size Analyzer, UPA-150, microtrac, U.S.A) and the magnetic properties were estimated with a SQUID magnetometer (Quantum Design, MPMS 7.0).

Results and Discussion

Fig. 1 shows TEM images of (a) IONP and (b) PCLNP. The diameter of IONPs was ranged from 6 to 10nm. After coating with PCL, the PCLNPs were quite polydispersed with a diameter range from 20 to 30nm. The particle size distributions of IONP and PCLNP were measured by DLS (Fig. 2). The average diameters of IONP and PCLNP were 7nm and 24.7nm respectively. Fig. 3 shows XRD of PCLNP. The peaks for (220), (311), (400), (422), (511), and (440) were identified the core of PCLNP as Fe₃O₄. It is therefore confirmed that the coating process did not cause a phase change for the Fe₃O₄. Fig. 4 shows the magnetization curves for IONPs, PCLNP and PCL. At the same concentration of iron content, IONP and PCLNP showed superparamagnetic behavior but the saturation magnetization (M_s) of PCLNP was smaller than that of the IONPs. Our data demonstrate the influence of diamagnetism of PCL on PCLNP and suggest diamagnetic shielding effect. Fig. 5(a) shows the change of magnetic susceptibility for several different concentrations of PCLNP. As the concentration of PCLNP increased, the magnetic susceptibility of PCLNP increased. Also, the slope of decline at higher field is reduced as the concentration increased. Therefore, the diamagnetic shielding effect became less with increased concentration and it can be explained in a way that the superparamagnetism of iron core of PCLNP overcomes the diamagnetism of polymer as more PCLNP were assembled themselves. The temperature dependence of the observed diamagnetic shielding effect was shown in Fig 5(b). At the concentration of 454.1ppm, the magnetization value of PCLNP decreased as the temperature increased. However, there was no change in the slope of decline at higher field. The observed reduction in PCLNP magnetization can be explained by temperature behaviors of paramagnetism and diamagnetism. It has been known that the magnetic susceptibility of paramagnetic material decreases with temperature whereas the magnetic susceptibility of diamagnetic material does not depend on the temperature. Therefore, the observed reduction in PCLNP magnetization is solely dependent on temperature behavior of iron core of PCLNP. In conclusion, PCLNP was synthesized by forming monodisperse ferrofluid. The result of SQUID indicated that the coating polymer, PCL, caused magnetic shielding effect to the total magnetism of PCLNP due to diamagnetic property of PCL. The dependence of the diamagnetic shielding effect of PCLNP on the concentration showed that the shielding effect reduced as concentration increased. Finally, our measured data showed that the observed reduction in PCLNP magnetization with temperature is solely dependent on temperature behavior of iron core of PCLNP.

[1] Berry CC, Curtis ASG, J. Phys D: Appl. Phys. 36 (2003) R198-R206

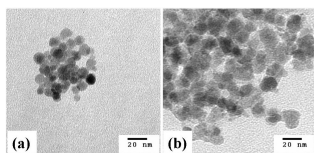


Fig. 1. TEM of (a) IONPs and (b) PCLNP

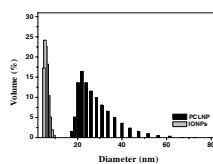


Fig. 2. DLS of IONPs and PCLNP

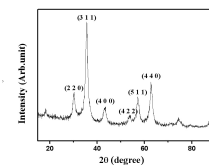


Fig. 3. XRD of PCLNP

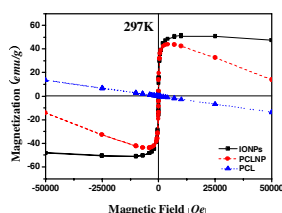


Fig. 4. Magnetization curves for IONPs, PCLNP and PCL

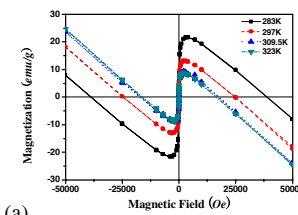
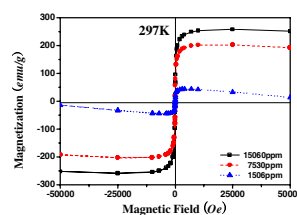


Fig. 5. The change of magnetism for different (a) PCLNP concentration at 297K and (b) temperature at 454.1ppm IONPs concentration