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ScienceDirect
Journal of Magnetism and Magnetic Materials 311 (2007) 78–83
Journal of magnetism and magnetic materials
www.elsevier.com/locate/jmmm

Design and synthesis of plasmonic magnetic nanoparticles

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Abstract

Core–shell nanoparticles containing both iron oxide and gold are proposed for bioseparation applications. The surface plasmon resonance of gold makes it possible to track the positions of individual particles, even when they are smaller than the optical diffraction limit. The synthesis of water-dispersible iron oxide-gold nanoparticles is described. Absorption spectra show the plasmon peaks for Au shells on silica particles, suggesting that thin shells may be sufficient to impart a strong surface plasmon resonance to iron oxide-gold nanoparticles. Dark field optical microscopy illustrates the feasibility of single-particle detection. Calculations of magnetophoretic and drag forces for particles of different sizes reveal design requirements for effective separation of these small particles.

Keywords: Magnetic nanoparticle; Plasmon; Dark-field microscopy; Magnetophoresis; Biosensing

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1. Introduction

Applications involving the controlled motion of magnetic micro- or nano-particles in microfluidic systems are diverse and growing rapidly. Some of the most interesting developments are in the fields of microbiology and biomedicine where magnetic particles are used to target, label, manipulate and separate biomaterials such as cells, enzymes, antigens and DNA [1–3]. Current clinical cell/biomolecule sorting devices are based on immunoaffinity columns or on high-gradient magnetic separation (HGMS) columns utilizing either micrometer-sized polymeric beads doped with magnetite, or nanometer-size iron dextran colloids, conjugated to targeting antibodies [4,5]. For HGMS, the two most important design parameters are (a) the magnetic moment of a magnetic label, and (b) the generation of a high magnetic field gradient [6]. Different strategies have been proposed to generate high gradient magnetic fields using magnetic dipole [7] or quadrupole sorting [8]. However, magnetophoretic microfluidic systems are also promising [9,10], and may be better suited for bioseparation involving extremely small amounts of material that could later be amplified, such as DNA purification or the separation of cell subpopulations with different degrees of surface antigen expression.

Here we describe a new type of magnetic nanoparticle (Fig. 1) that combines the advantages of magnetite for magnetic separation with the surface plasmon resonance of gold, which enables single particles to be tracked optically, even though they are smaller than the diffraction limit. The gold shells exhibit strong plasmonic bands in their UV–visible absorption spectra, providing a way to detect and quantitatively characterize the separation effectiveness in situ.

Conventional cytometric analysis requires fluorescent probe labelling, and hence extra effort is needed to conjugate fluorophore molecules onto the cell/magnetic particle complex. An additional advantage of the proposed gold shells is their extremely large molar extinction coefficient, greater than $10^5\,M^{-1}\,cm^{-1}$ at wavelengths in the ~500–600 nm range [11]. Resonant Rayleigh scattering efficiencies equivalent to ~10^6 fluorescent dye molecules [12] have been reported for gold nanoparticles. In addition, this plasmonic response is not vulnerable to the photobleaching effects that arise during prolonged and/or high intensity illumination of fluorescent tags.

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doi:10.1016/j.jmmm.2006.10.1169

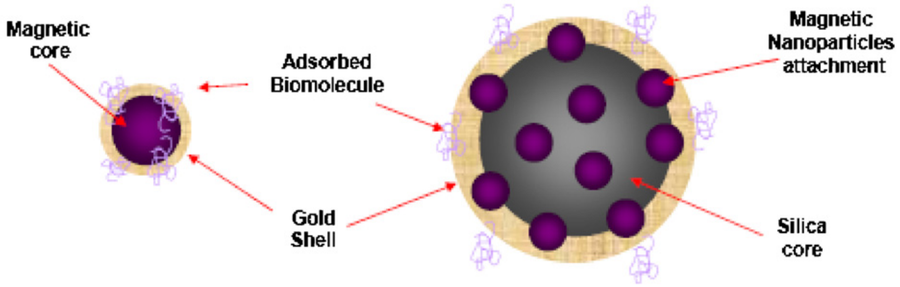

Fig. 1. Left: a nanoshell particle with magnetite core and gold shell. Right: a composite nanoparticle with silica core, decorated by magnetite nanoparticles and coated with a gold shell.

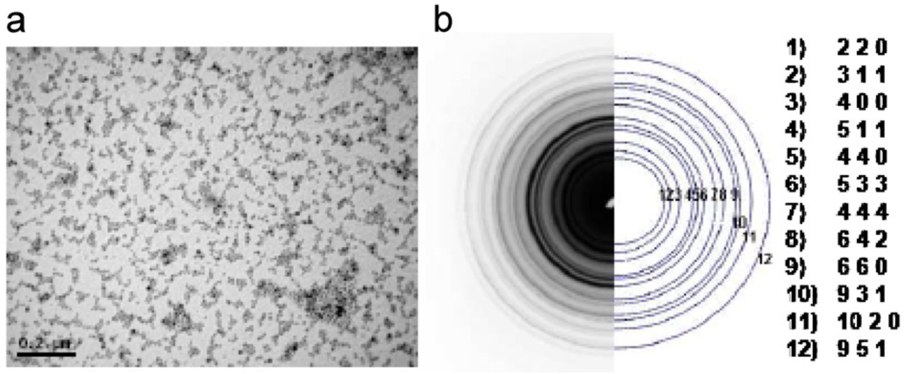

Fig. 2. (a) TEM micrograph and (b) characteristic electron diffraction rings of magnetite particles in toluene.

2. Particle synthesis

Synthesis of nanoshell and/or composite nanoparticles proceeds first by the synthesis of individual magnetite, Au, and silica nanoparticles. These are then assembled and subjected to further growth to create the gold shell, either with a magnetite core and a gold shell or a with a silica core, and then shells of magnetite and gold nanoparticles. The size of the constituent particles can have a dramatic effect on the magnetic properties (iron oxide particles) and plasmonic behavior (gold particles) and so synthetic control is very important to obtain a high degree of uniformity. A high-temperature polyol process developed by Sun et al. [13] was used to make magnetite nanoparticles in organic solvent. Oleic acid (OA) and oleylamine (OY) were used as capping agents that sterically stabilize the particles in toluene/hexane.

After the first step, 8 nm iron oxide nanoparticles with high crystallinity are obtained. Based on the lattice spacing corresponding to five strongest electron diffraction intensity rings (Fig. 2), the nanoparticles are identified as either magnetite or maghemite but the observed black color suggests that they are predominantly magnetite. These nanoparticles then serve as seeds for further growth. After two reaction stages, the average diameter of the magnetite nanoparticles was 11.05 ± 1.7 nm (shown in Fig. 2), with the size distribution shown in Fig. 3.

A modified Stöber process [14] was used to make silica spheres with a diameter of 50 nm. This involves the slow base hydrolysis of tetraethyl orthosilicate in ethanol. High monodispersity and spherical shape is ensured by slow diffusional growth over 24 h. Controlling the volume ratio of ammonium hydroxide to tetraethyl orthosilicate allows the particle size to be altered between 50 and 500 nm. Ultrafine gold nanoparticles with an average size of ~2 nm

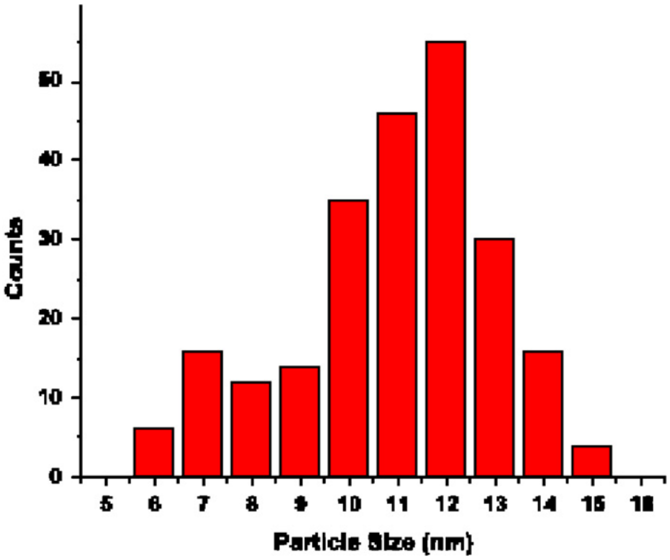

Fig. 3. Iron oxide particles size distribution. Scion Image Beta 4.03 for Windows 95 to XP was used to identify individual particles and ImageJ 1.36 was used to determine the average particle diameters.