ELECTRON MICROSCOPY OF SELF-ASSEMBLED SUPERPARAMAGNETIC PLASMON RESONANT COLLOIDAL NANOSTRUCTURES

R.N. Taylor, J.L. Hutchison and P.J. Dobson*

Dept. of Materials, Univ. of Oxford, Parks Road, Oxford, OX1 3PH, UK
*Dept. of Engineering Science, Univ. of Oxford, Parks Road, Oxford, OX1 3PJ, UK

The development of techniques to form identical nanostructures in solution is of great importance to many applications. In recent years there has been a departure from the most simple of requirements – to produce identical pure nanoparticles. It is clear that such pure particles, whilst often displaying interesting and potentially useful properties have other drawbacks such as chemical and colloidal instability or undesirable surface properties. It is therefore becoming increasingly common to engineer such pure particles into identical nanostuctures, which retain or enhance the favourable properties whilst passivating against the unfavourable. As the toolkit of possible particle engineering strategies becomes more elaborate, it is clear that multi-functional structures also become possible. This means the combination of properties which would traditionally be mutually exclusive in pure materials or composites using traditional formation techniques, e.g. ceramic processing.

This work aims to combine two classes of quite strongly functional nanoparticulate materials, namely those with magnetic and plasmon resonant properties. It is well known that below a certain size particles of ferro- or ferrimagnetic material can only support a single magnetic domain and that for very small particles thermally-activated rotation of the magnetisation gives rise to superparamagnetic behaviour at ambient conditions. A simple method for the formation of such small particles comprising of iron oxide (magnetite or maghemite) has been known for some time[1]. A controlled agglomeration of these nanoparticles onto larger monodisperse cores would retain the superparamagnetic behaviour whilst increasing the effective dipole per particle. Gold sols have long been known for their deep colours which are due to a collective optical frequency oscillation of conduction electrons. Furthermore, it has recently been confirmed that the formation of a thin gold shell around a dielectric core results in a similar resonance but with a far greater tunability, namely in the core diameter to shell thickness ratio[2]. The formation of nanostructures combining these components would allow for the magnetic modulation of optical properties and also provide individual building blocks for subsequent magnetic directed self-assembly of nanochains. These nanochains are expected to behave like tiny transmission lines, with particles connected through the near-field of their shell plasmon resonances.

We have made use of a JEOL 4000EX transmission electron microscope to evaluate the various stages of nanostructure fabrication. The growth of superparamagnetic plasmon resonant nanostructures followed the general scheme shown in Figure 1(a):

(i) Monodisperse 250nm silica spheres were produced by the well-known Stoeber process.[3]

(ii) Iron oxide (maghemite) nanocrystals with an approximate size of 8nm were attached to the cores by the layer-by-layer (LbL) process.[4]

(iii) A barrier layer of silica was then grown by a modified Stoeber process.
(iv) A gold shell was finally grown around the structures using a successive gold colloid attachment gold reduction process.

This manufacturing process therefore is an example of how three distinct strategies (LbL, sol-gel and seeded growth) can be utilised on the same nanoscale workpiece. Figure 1(b) shows the result of magnetic directed assembly of the particles in Fig.1(a)(iv).

Electron microscopy was essential to the optimisation of the silica barrier layer and to monitor attachment of the seed gold colloid. In the former case, a thin or broken silica layer would adversely effect the attachment of seed colloid whereas a thick layer would effectively shield the interparticle magnetic interaction which could ultimately be useful when performing magnetic directed assembly. Microscopy was also utilised to estimate the decrease in surface roughness as the silica thickness.

In this contribution we will present recent work on the self-assembly of multi-functional colloidal nanostructures, making note particularly of the microscopical features of our analysis.

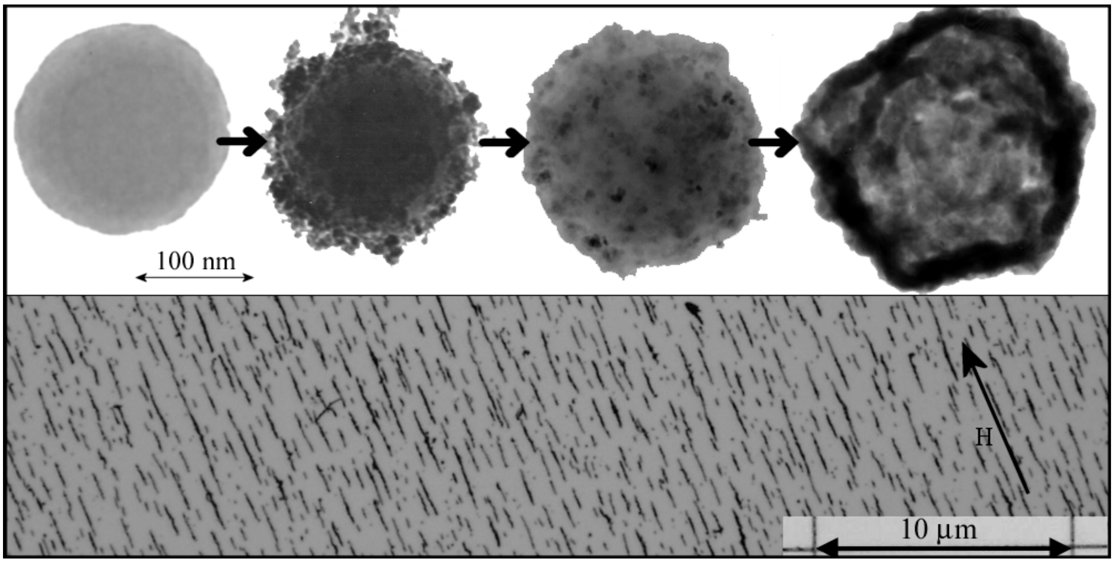

Figure 1: (a) Composite electron micrograph showing the key stages in the construction of superparamagnetic plasmon resonant nanostructures (see text for details of individual stages) (b) Optical micrograph of the magnetic-field directed assembly of nanochains of particles shown in (a)(iv)

References

1. Massart, R. (1981) IEEE Trans. Magn. (1981) 17, 1247.
2. Oldenburg S.J. et al. (1998) Chem. Phys. Lett. 288, 243.
3. Stober, W., Fink, A., Bohn, E. (1968) J. Colloid Interface Sci., 26, 62.
4. Caruso F. et al. (1999) Adv. Mater. 11(11), 950.
email: robin.taylor@materials.ox.ac.uk