

Synthesis of shape-anisotropic magnetic Fe-Pt nanoparticles for biomedical applications

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While the effects of size are relatively well known and studied for nanosized materials, shape is a less well-studied factor despite the potential benefits of shape anisotropic nanoparticles (NPs) over spherical NPs. Shape-anisotropic NPs have already found application in biomedicine, for example as MRI contrast agents superior to conventional ferrofluid contrast agents¹ and they have great potential for future applications including membrane protein mapping² and hyperthermia therapy. However, the controlled synthesis of monodisperse shape-anisotropic NPs is still an elusive target in most cases, especially when the NPs are intended for biomedical applications.

Here, we present a systematic study of the effects of surfactant concentration and structure on the morphology and composition of the resultant NPs. The Fe-Pt alloy NPs studied here were prepared by chemical synthesis^{3,4} starting from solutions of $\text{Fe}(\text{CO})_5$ and $\text{Pt}(\text{acac})_2$ in the presence of carboxylic acid and alkylamine surfactants. Figure 1 shows TEM images of Fe-Pt NPs with a selection of morphologies obtained in the presence of different surfactants.

Transfer of these hydrophobic NPs to water by ligand exchange using PEG ligands is demonstrated, as this will be the first step towards making the NPs suitable for biomedicine.

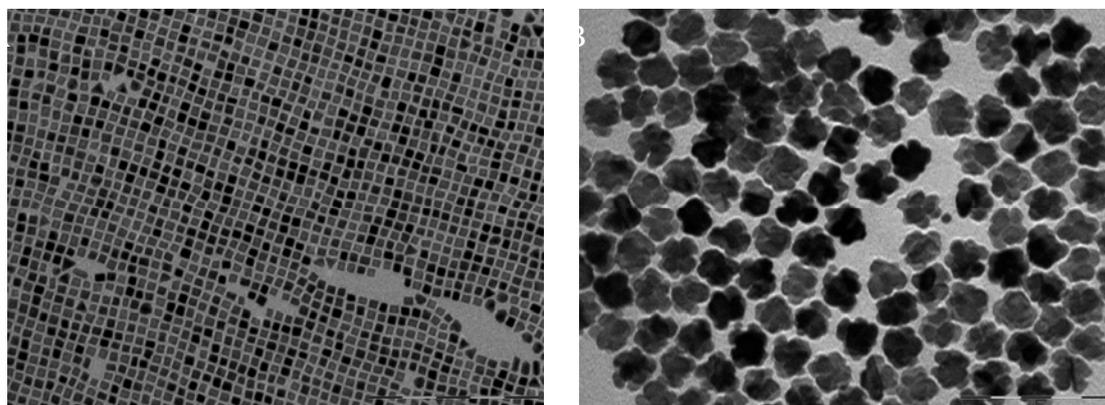


Figure 1: TEM images of Fe-Pt alloy NPs prepared from $\text{Fe}(\text{CO})_5$ and $\text{Pt}(\text{acac})_2$ by thermochemical synthesis in the presence of A) oleic acid and oleylamine B) 1-adamantane carboxylic acid and hexadecylamine.

Reference:

- [1] An, K. S. G. Kwon, M. Park, H. B. Na, S.-I. Baik, J. H. Yu, D. Kim, J. S. Son, Y. W. Kim, I. C. Song, W. K. Moon, H. M. Park and T. Hyeon, (2008) Synthesis of Uniform Hollow Oxide Nanoparticles through Nanoscale Acid Etching, *Nano Lett.*, 8 (12), 4252-4258
- [2] Slot, J. and H. Geuze, (1981) Sizing of Protein A-Colloidal Gold Probes for Immunoelectron Microscopy *J. Cell Biol.* 90, 533-536
- [3] Sun, S., C. B. Murray, D. Weller, L. Folks and A. Moser, (2000) Monodisperse FePt Nanoparticles and Ferromagnetic FePt Nanocrystal Superlattices, *Science*, 287, 1989-1992
- [4] Ung, D., L. D. Tung, G. Caruntuc, D. Delaportas, I. Alexandrou, I. A. Prior and N. T. K. Thanh, (2009) Variant shape growth of nanoparticles of metallic Fe-Pt, Fe-Pd and Fe-Pt-Pd alloys *CrystEngComm*, 11, 1309-1316

Relaxivity of cobalt nanoparticles, a novel MR contrast agent

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Magnetic nanoparticles offer a unique opportunity for cell tracking *in vivo*. By incorporating magnetic nanoparticles inside cells, their position within the body can be tracked with MRI. Magnetic nanoparticles composed of iron oxides are currently used as contrast agents in magnetic resonance imaging.^{1, 2} However iron oxides have a relatively low saturation magnetisation, requiring the use of larger particles. Transition metal nanoparticles, e.g. those made from cobalt, have a much higher saturation magnetisation value, allowing the use of smaller particles (< 5 nm), without compromising sensitivity.

This work describes the relaxation properties of cobalt nanoparticles, a novel MR contrast agent. We report T_1 , T_2 and T_2^* relaxivity values at different temperatures at both 1.5 T and 3 T. The particles of 3.8 nm were dispersed in tubes of 2% agarose gel at a range of concentrations. The tubes were placed in a water bath at 40°C and the temperature was monitored. T_1 , T_2 and T_2^* mapping was performed on Siemens 1.5T and 3T systems.

The figure shows that there was no detectable effect of temperature on any of the relaxivities. Field strength however had a significant effect with 1.5 T giving approximately double the T_1 relaxivity compared to 3 T but reducing the T_2 relaxivity. The opposite effect of field strength on T_1 and T_2 relaxivities is supported by empirical evidence from a study of USPIOs.³ The values for T_2 and T_1 relaxivity of 100 and 8 $\text{mM}^{-1}\text{s}^{-1}$ respectively at 1.5T are similar to those reported for USPIOs of larger size⁴ and the T_1 relaxivity is greater than that of Gd-DTPA (3.3 $\text{mM}^{-1}\text{s}^{-1}$ at 1.5T).⁴

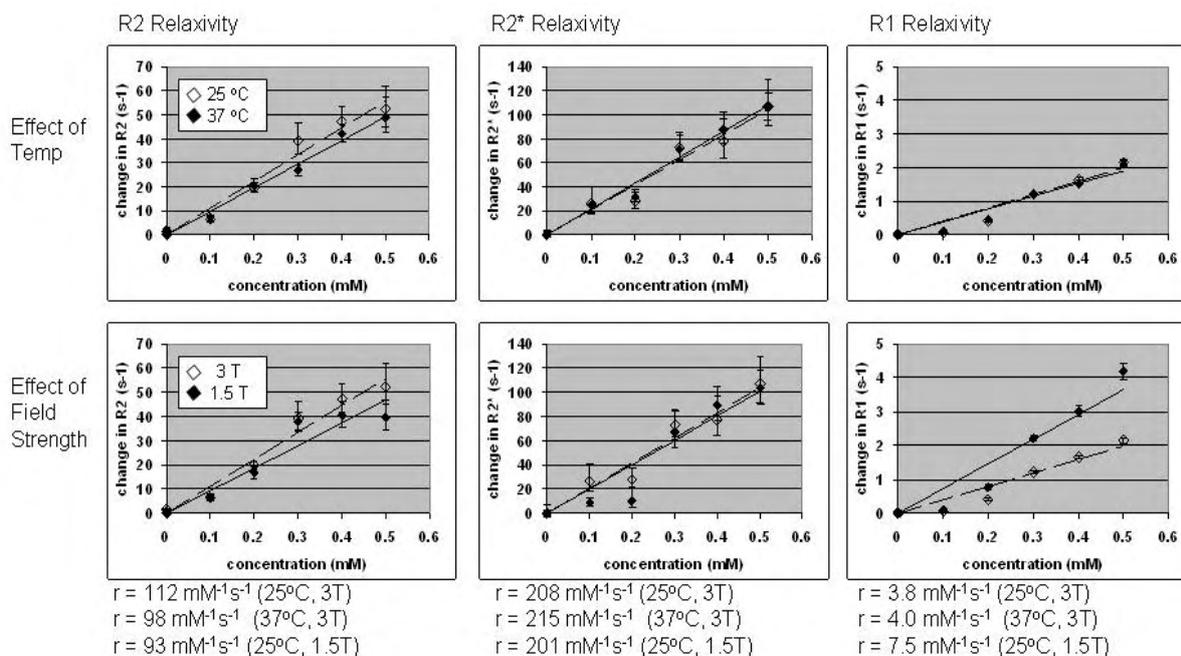


Figure 1: The relations between relaxivities of T_1 , T_2 and T_2^* and field strength, temperature and nanoparticles concentration.

Reference:

[1] Pankhurst, Q.A., et al., *Journal of Physics D-Applied Physics*, 2003. [2] Kim, D.K., et al., *Scripta Materialia*, 2001. [3] Simon et al, *European Radiology* 2006. [4] Roher et al, *Invest. Radiol.* 2005.

Synthesis of magnetic Co nanoparticles by pulsed laser irradiation of cobalt carbonyl in organic solution

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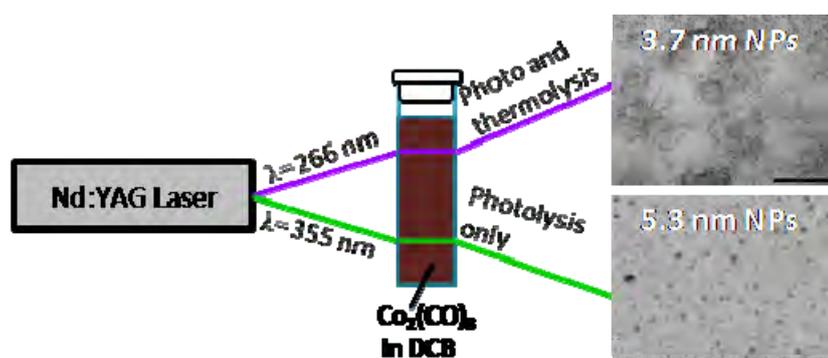
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Interest in producing magnetic nanoparticles (NPs) with controllable sizes has led to the development of new synthesis methods. For example, cobalt NPs have been produced by using a laser to induce the decomposition of vaporised $\text{Co}_2(\text{CO})_8$.¹ This laser evaporation method has been used to produce a variety of nanosized materials such as an FeCo alloy and silica coated iron oxide NPs.²⁻⁴ Ultraviolet irradiation of a cobalt(II) acetate solution has also been used to synthesize Co NPs which have certain morphologies depending upon the experimental parameters.⁵ Here, we report the synthesis of sub 4 nm cobalt nanoparticles by using pulsed laser irradiation to decompose cobalt carbonyl in a solution of stabilising ligands. The physical characteristics of the synthesized nanoparticles were determined by transmission electron microscopy, powder X-ray diffractometry and SQUID magnometry. It was possible to control the size of the synthesized nanoparticles by varying the reaction conditions such as the ligand concentration and wavelength of light used. The formation mechanism of the nanoparticles was investigated by changing these conditions. It is possible that this technique could be applied to the synthesis of a variety of nanomaterials with potential applications such as biomedicine, catalysis and water purification.



Reference:

- [1] Zhao, X. Q.; Veintemillas-Verdaguer, S.; Bomati-Miguel, O.; Morales, M. P.; Xu, H. B. *Phys. Rev. B: Condens. Matter Mater. Phys.* 2005, 71, 024106 1.
- [2] Moras, K.; Schaarschuch, R.; Riehemann, W.; Zinoveva, S.; Modrow, H.; Eberbeck, D. *J. Magn. Magn. Mater.* 2005, 293, 119.
- [3] Bomati-Miguel, O.; Leconte, Y.; Morales, M. P.; Herlin-Boime, N.; Veintemillas-Verdaguer, S. *J. Magn. Magn. Mater.* 2005, 290, 272.
- [4] Kurland, H. D.; Grabow, J.; Staupendahl, G.; Andra, W.; Dutz, S.; Bellemann, M. E. *J. Magn. Magn. Mater.* 2007, 311, 73.
- [5] Wang, C. Y.; Fang, J. Y.; He, J. B.; O'Connor, C. J. *J. Colloid Interface Sci.* 2003, 259, 411.

Fabrication of water-soluble magnetic nanoparticles by ligand-exchange with thermo-responsive polymers

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Magnetic nanoparticles have many potential biomedical applications¹ and each application requires nanoparticles with a tailored size and shape.² Thermal decomposition of organometallic complexes is a simple method for controlling the size, shape and composition of the synthesized nanoparticles. However, this method usually renders the nanoparticles insoluble in aqueous solutions. There are a number of methods of *in situ* synthesis to make water-soluble MNPs^{3,4}; however, various conditions need to be investigated for each of the required systems (e.g. size, shape, composition).

In this work, water-stable Co and γ -Fe₂O₃ nanoparticles were synthesised using a two-step method involving the thermal decomposition of the organometallic complexes in the presence of oleic acid followed by a ligand-exchange process with thermo-responsive polymers. Among the different thermo-responsive polymers investigated, it was found that the polymer based on poly(N-isopropylacrylamide) with either a co-monomer component of acrylic acid or acrylamide were best suited to stabilise Co and γ -Fe₂O₃ nanoparticles, respectively. The nanoparticles are found to be water-soluble at temperatures below coil-to-globule phase transition of the coating polymer and stable in alkali solution up to pH 5.5-12. The polymer coated Co and γ -Fe₂O₃ nanoparticles were water-soluble, stable up to 0.2 M and 0.5 M NaCl in phosphate buffer, respectively.

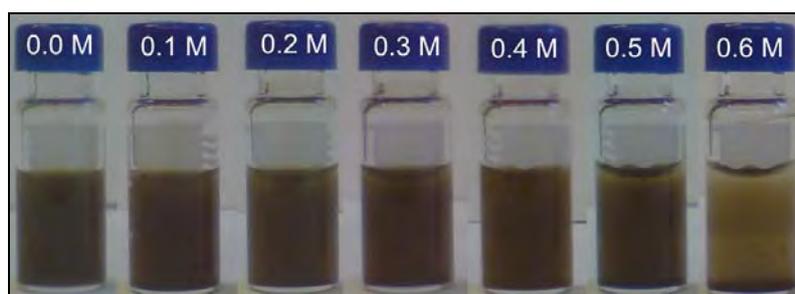


Figure 1. γ -Fe₂O₃ nanoparticles coated with polymer are stable up to 0.5 M NaCl in phosphate buffer.

Reference:

- [1] Q. A. Pankhurst, J. Connolly, S. K. Jones and J. Dobson, *J. Phys. D: Appl. Phys.*, 2003, 36, R167-R181.
- [2] A. K. Gupta and M. Gupta, *Biomaterials*, 2005, 26, 3995-4021.
- [3] I. Robinson, C. Alexander, L. T. Lu, L. D. Tung, D. G. Fernig and N. T. K. Thanh, *Chem. Commun.*, 2007, 44, 4602 - 4604.
- [4] L. T. Lu, L. D. Tung, I. Robinson, D. Ung, B. Tan, J. Long, A. I. Cooper, D. G. Fernig and N. T. K. Thanh, *J. Mater. Chem.*, 2008, 18, 2453 - 2458.

Synthesis and characterization of magnetic nanoalloys from bimetallic carbonyl clusters

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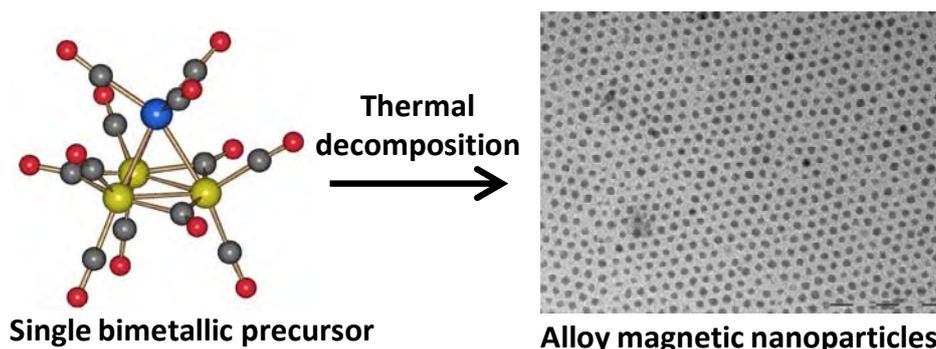
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Magnetic nanoparticles are an interesting subject of research because their unique chemical and physical properties make them potentially useful for biomedical applications. In particular, magnetic alloy nanoparticles are of interest due to their enhanced magnetic properties and chemical stability². However, controlling the composition of magnetic alloy nanoparticles can be difficult, when they are produced from two or more precursors³. This may be overcome by the use of a single bimetallic precursor. Here we report the synthesis of FeCo₃, FeNi₄, Fe₃Pt₃ and Fe₄Pt alloy magnetic nanoparticles with average diameters of 7.0 nm, 4.4 nm, 2.6 nm and 3.2 nm, respectively, by the thermal decomposition of bimetallic carbonyl clusters. The chemical and physical properties of the synthesized nanoparticles were examined by elemental analysis, transmission electron microscopy, powder X-ray diffractometry and SQUID magnetometry. The chemical composition of the synthesized nanoparticles reflected that of the bimetallic carbonyl cluster used for their synthesis. Changing the reaction conditions, such as ligand concentration, ligand type and reaction temperature had very little effect upon the chemical and physical properties of the synthesized nanoparticles. This work represents a versatile method for the synthesis of magnetic alloy nanoparticles and can be applied to a variety of other elements.



Reference:

[1] Pankhurst, Q. A.; Connolly, J.; Jones, S. K.; Dobson, J., *J. Phys. D:Appl. Phys.* 2003, 36, R167-R181.

[2] Thanh, N. T. K.; Robinson, I.; Tung, L. D., *Dekker Encyclopedia Nanoscience Nanotechnology* 2007, 1, 1 - 10

[3] Chaubey, G. S.; Barcena, C.; Poudyal, N.; Rong, C. B.; Gao, J. M.; Sun, S. H.; Liu, J. P., *J. Am. Chem. Soc.* 2007, 129, 7214-7215.

[4] Jeyadevan, B.; Shinoda, K.; Justin, R. J.; Matsumot, T.; Sato, K.; Takahashi, H.; Sato, Y.; Tohji, K., *IEEE Trans. Magn.* 2006, 42, 3030-3035.

Hydrophilic polymers as stabilizing agent for uniform porous silica nanospheres

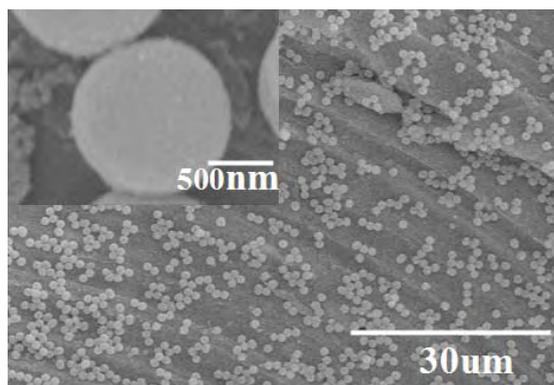
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The modified Stöber method has been employed to produce uniform mesoporous silica nanospheres. The porosity was introduced by the self-assembly of cationic surfactant cetyltrimethylammonium bromide (CTAB)[1-4]. Mesoporous silica particles were intensively investigated due to their broad applications in areas such as catalysis, controlled release, and separation science.

In this study, hydrophilic polymers were used to directly control the uniformity and spherical morphology of silica particles and CTAB as a porogen. The presence of poly(vinyl alcohol) (PVA) led to the formation of uniform well-dispersed porous silica nanospheres and microspheres. The silica mesostructure characterized by x-ray diffractin showed the diffraction peaks shifted to smaller angles (from 2.52° to 2.34°) and an increasing in d-spacings (from 3.27nm-3.78nm) with increasing PVA concentration. The size of silica particles was depended on the molecular weight and concentration of PVA, which demonstrated that PVA could effectively stabilize the nuclei growth of silica particles [5]. However, the addition of hydrophilic polymers polyvinylpyrrolidone (PVP) and poly (ethylene glycol) (PEO) produced particles with wider particles size distribution. PEG and high Mw. PVP polymers also resulted in more aggregated and fused silica particles. The nitrogen adsorption analysis showed mesopores (around 3.45nm) were produced. A bimodal pore size distribution was observed with the replacement of CTAB with another cationic surfactant dihexadecyldimethylammonium (DiCTAB). Surprisingly, with the addition of PVA, the surface area was reduced significantly and the pore volume was also decreased more than half. Mesopores were further expanded using a hydrothermal method with the addition of two types of swelling agents, which increased both pore size and pore volume up to 6.5nm and $1.11\text{cm}^3/\text{g}$ respectively.



Reference:

- [1] K. Schumacher, M. Grün, K.K. Unger, *Micropor. Mesopor. Mat.*, 27,1999, 201-206.
- [2] K.K. Unger, D. Kumar, M. Grün, G. Büchel, S. Lüdtkke, T. Adam, K. Schumacher, S. Renker, *J. Chromatography A*, 892, 2000, 47-55.
- [3] S.M. Chang, M. Lee, W.S. Kim, *J. Colloid Interface Sci.*, 286, 2005, 536-542.
- [4] Q. Li, S.E. Brown, L.J. Broadbelt, J.G. Zheng, N.Q. Wu, *Micropor. Mesopor. Mat.*, 59, 2003, 105.
- [5] W. Wang, J. Wang, P. Sun, Z. Yuan, D. Ding, T. Chen, *Mater. Lett.*, 62, 2008, 711–714

Observation of increased phase solubility in ceria bismuth solid solutions using continuous hydrothermal flow synthesis

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A continuous hydrothermal flow synthesis (CHFS) reactor has been used as a rapid and efficient synthetic route to produce a library of crystalline bismuth substituted ceria solid solutions of the formula $Ce_{1-x}Bi_xO_{2-x/2}$. The influence of the dopant in the crystal structure of the host lattice and on the materials' chemical properties was studied. All the materials were analysed using: Raman spectroscopy, XRD and EDX. Phase pure ceria cubic fluorite phases were prepared in the CHFS system for dopant levels of $x = 0 - 0.65$, far greater than previous levels of 0.55.¹ Particle sizes were calculated to be ca. 5 nm when $x = 0 - 0.65$ by using the Scherrer equation and the full width half maximum of the (111) Bragg peak. The greater solubility is attributed to metastable phases forming as a result of the fast reaction times and fast nucleation rates using continuous hydrothermal flow synthesis. The use of the CHFS system in this context facilitated rapid production (few seconds) of a series crystalline metal oxide solid solution nano-materials with particle properties (crystallinity, size) that are generally unobtainable via any other known single step processes.

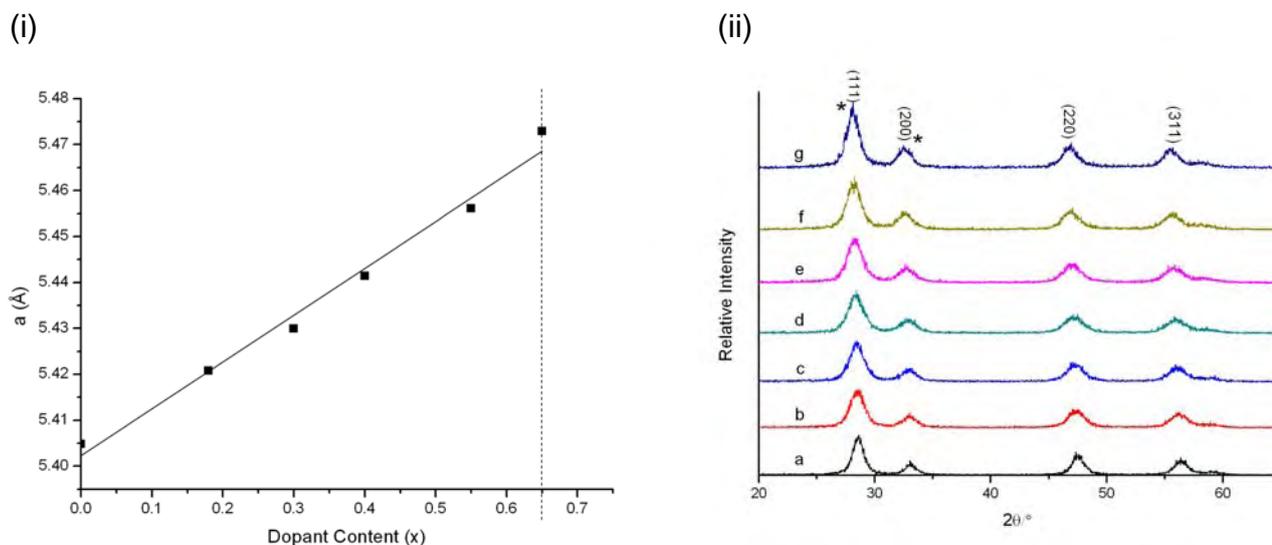


Figure 1. (i) Cubic lattice parameters, and (ii) XRD patterns of $Ce_{1-x}Bi_xO_{2-x/2}$, ($x = 0 - 0.7$), after heat-treatment at 500 °C for 12 h. * denotes possible appearance of secondary phase of $\alpha-Bi_2O_3$. (a) CeO_2 , (b) $Ce_{0.82}Bi_{0.18}O_{1.91}$, (c) $Ce_{0.7}Bi_{0.3}O_{1.85}$, (d) $Ce_{0.6}Bi_{0.4}O_{1.8}$, (e) $Ce_{0.45}Bi_{0.55}O_{1.73}$, (f) $Ce_{0.35}Bi_{0.65}O_{1.68}$, (g) $Ce_{0.3}Bi_{0.7}O_{1.65} + \alpha-Bi_2O_3$

Reference List

[1] Li, G. S.; Mao, Y. C.; Li, L. P.; Feng, S. H.; Wang, M. Q.; Yao, X. Solid solubility and transport properties of nanocrystalline $(CeO_2)_{1-x}(BiO_{1.5})_x$ by hydrothermal conditions. *Chemistry of Materials* **1999**, *11* (5), 1259-1266.

Continuous hydrothermal synthesis of lanthanum titanate phases for photocatalytic hydrogen generation from water

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Heterometallic titanates have gained interest as potential alternatives to TiO_2 as photocatalytic semiconductor materials for water splitting at higher efficiencies¹. Lanthanum titanate has been reported to show high quantum yields for hydrogen generation in particular². Continuous hydrothermal flow synthesis (CHFS) has been shown to be a rapid and efficient synthetic route to highly crystalline nanoparticulate metal ion doped TiO_2 materials³. In this presentation we describe the use of CHFS as a rapid synthesis route to the perovskite phases LaTiO_3 and $\text{La}_2\text{Ti}_2\text{O}_7$, and the atypically coordinated La_2TiO_5 phase.

A range of pure and mixed phase lanthanum titanates were achieved through variation of reaction pH and post-reaction heat treatment temperatures. Photocatalytic activity was enhanced by co-doping with NiO particles. Purity and morphology were characterised using powder XRD, Raman spectroscopy, SEM and BET. Photocatalytic activities were assessed by detection of H_2 generated from an alkaline sacrificial solution under UV irradiation.

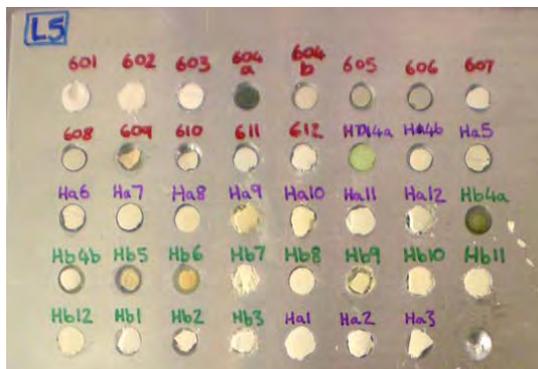


Figure (1) Lanthanum titanate printed dot sample library Red: untreated samples, Purple: treated at 850°C , Green: treated at 1150°C .

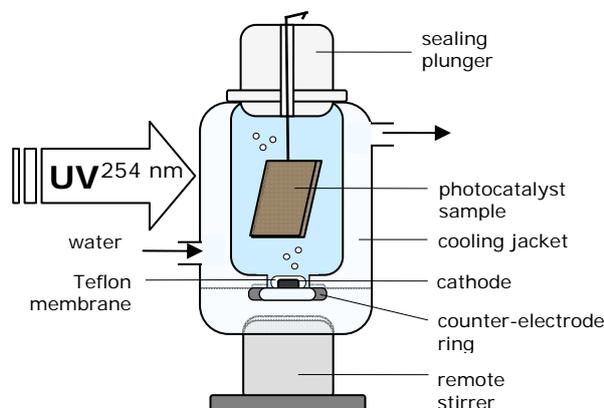


Figure (2) Gas sensing electrode for photocatalytic testing of materials.

Reference:

- [1] Osterloh, F. E. Inorganic materials as catalysts for photochemical splitting of water. *Chem. Mater.*, 2008, 20 (1), 35-54.
- [2] Kim, J.; Hwang, D. W.; Kim, H. G.; *et al.* Highly efficient overall water splitting through optimization of preparation and operation conditions of layered perovskite photocatalysts. *Topics in Catalysis*, 2005, 35, 295-303.
- [3] Goodall, J.; Kellici, A.; Chaudry, A.; *et al.* High throughput synthesis and photocatalytic assessment of doped titania nanopowders. *In press*.

Rapid hydrothermal single step synthesis of multiple bismuth molybdate phases

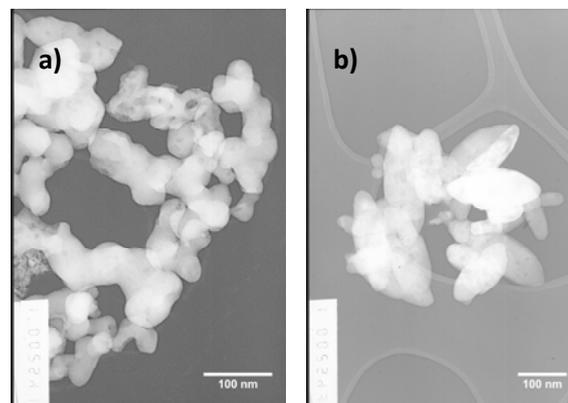
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Continuous hydrothermal syntheses have recently gained interest as a fast and controllable method for producing inorganic nanomaterials starting from a wide variety of soluble metal precursors and redox modifiers^{1,2}. The capacity of this technique to rapidly synthesise nano-materials that normally require energy intensive and time consuming methodologies, suggests this technique has a great deal of potential in metal oxide catalyst development, optimisation and evaluation³. Thus, we postulated that the rapidly supersaturating and crystallising environments within hydrothermal flow reactors may facilitate the formation of a variety of higher order crystalline metal oxide systems on a much smaller time scale than required by conventional methods⁴. The processing parameters of a rapid hydrothermal synthesis system (synthesis temperature (200-330 °C), starting solution stoichiometry and reaction pH (2-6)) were varied in order to target the three dominant phases of bismuth molybdate (Bi_2MoO_6 , $\text{Bi}_2\text{Mo}_2\text{O}_9$ and $\text{Bi}_2\text{Mo}_3\text{O}_{12}$), reacting soluble bismuth and molybdenum precursors, bismuth nitrate and molybdic acid respectively. Bismuth molybdates have been shown to have numerous catalytic applications ranging from photocatalytic water splitting⁵ to industrial oxidation and ammoxidation reactions utilising many substrates⁶⁻⁸. The phase purity and morphology of the material produced under varied reaction conditions were characterised using powder XRD, Raman spectroscopy, BET, photocatalytic testing and TEM. The synthesis of phase pure Bi_2MoO_6 and $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ were identified by both X-ray diffraction and Raman spectroscopy under certain reaction conditions. Mixed phase systems were also identified under certain reaction conditions, which are of interest to catalyst optimisation and development but were not further evaluated in this work. The photocatalytic activity of these materials was assessed to compare these rapidly synthesised materials with previously reported activities⁶. The morphology and size distribution of the materials produced were assessed using TEM.

Figures. Transmission electron microscope images of a) $\alpha\text{-Bi}_2\text{Mo}_3\text{O}_{12}$ b) $\gamma\text{-Bi}_2\text{MoO}_6$ nano-powder synthesised at pH 4 using superheated water in the hydrothermal flow system; magnification 140000 and 100000 x, respectively (bar = 100 nm).



Reference:

- [1] A. Cabanas, J. A. Darr, E. Lester, and M. Poliakoff, *Chemical Communications*, 2000901.
- [2] X. L. Weng, P. Boldrin, I. Abrahams, S. J. Skinner, S. Kellici, and J. A. Darr, *Journal of Solid State Chemistry*, 2008, 181, 1123.
- [3] A. Aimable, H. Muhr, C. Gentric, F. Bernard, F. Le Cras, and D. Aymes, *Powder Technology*, 2009, 190, 99.
- [4] A. M. Beale and G. Sankar, *Chemistry of Materials*, 2003, 15, 146.
- [5] H. H. Li, C. Y. Liu, K. W. Li, and H. Wang, *Journal of Materials Science*, 2008, 43, 7026.
- [6] J. Q. Yu and A. Kudo, *Chemistry Letters*, 2005, 34, 1528.
- [7] R. K. Grasselli, *Abstracts of Papers of the American Chemical Society*, 1984, 187, 8.
- [8] T. A. Hanna, *Coordination Chemistry Reviews*, 2004, 248, 429.

Increasing iron ratio in iron-platinum magnetic nanoparticles prepared in amphiphilic systems

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We present a detailed investigation of low temperature solution synthesis targeting homogenous composition of iron platinum nanocolloids (NCs). The high magnetic anisotropy of FePt (10^7 J/m³) makes FePt an ideal candidate for technological applications ranging from ultra high density recording media to bio-medical applications.^[1] In contrast to more usual thermal decomposition protocol, room temperature syntheses offer an attractive pathway that could dramatically simplify NC fabrication. However, a major hurdle is the inhomogeneous composition of the products.

We have investigated the role of amphiphilic molecules, precursor ions and reducing agents in NC synthesis. Parameters that prevent the formation of chemically homogeneous NCs were identified by ICP-OES, XRD, TEM, nanometric EDX, and SQUID magnetometry. These limiting parameters were then tuned to successfully increase the insertion of the iron in the Fe_xPt_{1-x} NCs. The limiting parameters and strategy we highlight here should be applicable to other alloys fabricated by co-reduction protocol.^[2]

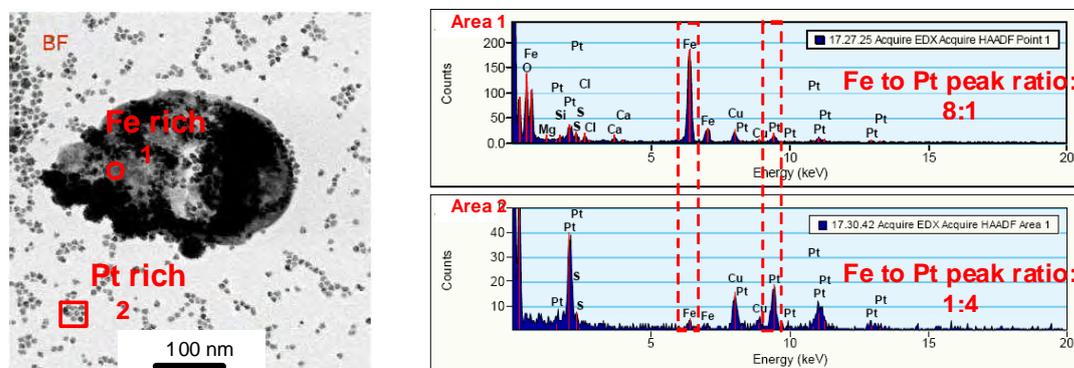


Figure 1. TEM images of FePt NCs dispersed in carbon film TEM grid and associated composition measured by nanometric EDX.

Reference:

[1] S.H. Sun, *Adv. Mater.* **2006**, 18 (4), 393-403.

[2] S. Chen, D. Maclaren, R. Baker, J. Chapman, D.J. Cole-Hamilton, S. Lee, P. André, *In preparation*.

FePt magnetic nanoparticles: syntheses, functionalization, cell toxicity studies & application as MRI contrast agent

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FePt magnetic nanoparticles offer great interests for biomedical applications such as magnetic separation, drug delivery, hyperthermia and MRI, because its high magnetic anisotropy is one of the highest of any known material. A natural question arises regarding the potential toxicity and biomedical applications of *fcc*-FePt.

In this context, we describe recent promising progresses in the syntheses of low polydispersity 1:1 ratio FePt NPs and their use as negative MRI contrast agents. ~ 5 nm *fcc* FePt NPs were synthesized by a modified thermal decomposition method & made to be water soluble by coating with NPs surface with cysteamine. Cytotoxicity studies of FePt NPs were carried out on A375M cell, while cell uptake of NPs through endocytosis was confirmed by TEM study. Longitudinal and transverse relaxations of cysteamine coated FePts was measured, with results suggest that *fcc*-FePt NPs already display superior properties when compared to commercial existing negative contrast agents.

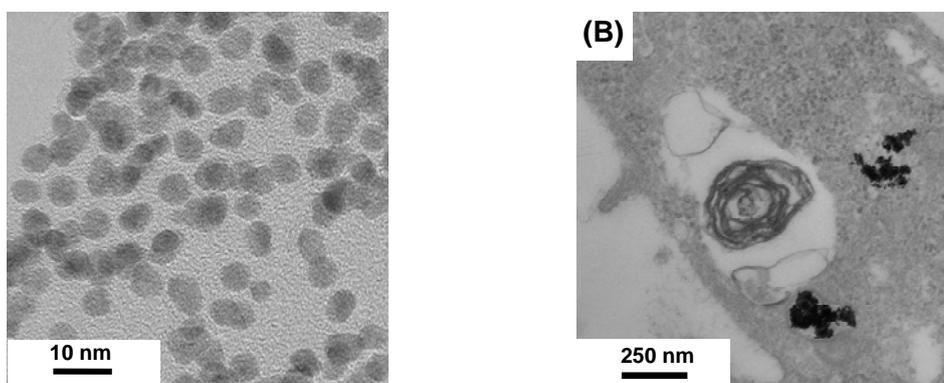


Figure 1. (A) TEM images of FePt NCs dispersed in carbon film TEM grid. (B) TEM image of cell up-taking FePt NCs.

New solvent: advantages for FePt NPs syntheses

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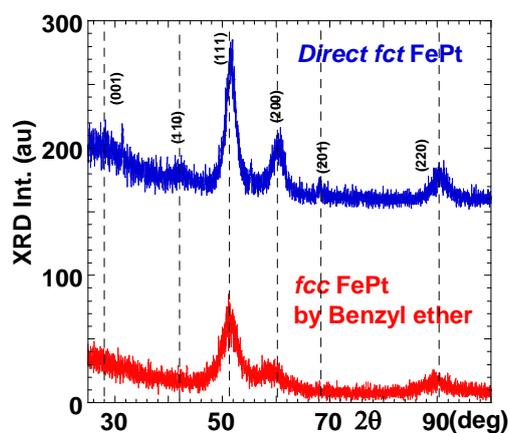
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Face-centred-tetragonal (*fct*) FePt NP is a promising candidate for future ultra-high density magnetic recording media of > 1 T bit/inch, because its magnetic anisotropy can reach 107 J/m³.^[1] For FePt NPs synthesis, most of methods reported so far require an indispensable post-annealing step above 550 °C to achieve *fcc* to *fct* crystalline phase transfer. Such high temperature often leads to undesirable aggregation and sintering. For this reason, it is highly desirable to design methods that enable the direct synthesis of *fct* FePt NPs at lower temperature.

In this context, we will describe our recent progress in obtaining *fct* FePt NPs which has not been reported to date. The products were characterised by XRD, HRTEM, and SQUID magnetometer. Investigations have been carried out to understand the factors affecting *fct* FePt NPs formation such as the nature of the solvent, the presence of surfactants, reaction temperature and time.^[2]



Reference:

[1] S.H. Sun, *Adv. Mater.* 2006, 18 (4), 393-403.

[2] S. Chen, M. J. Muldoon, K. Anderson, P. André, *In preparation.*

In/InN core/shell nanotubes solution based preparation

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The colloidal synthetic conditions to grow Indium Nitride (InN) nanotubes via the thermal co-decomposition of three different indium and nitrogen precursors have been investigated to produce core shell structures consisting of a metal indium core surrounded by a polycrystalline InN shell. Transition of the InN nanostructures from nanoparticles to nanotubes could be achieved by carefully tuning the reaction conditions.

XRD and TEM have been extensively used to both gain insight and understand the colloidal syntheses of InN nanostructures synthesized via a Solution-Liquid-Solid growth mechanism. This is a promising strategy to better control the fabrication of hollow- as well as hetero-nanostructures suitable for opto-electronic and energy related applications.

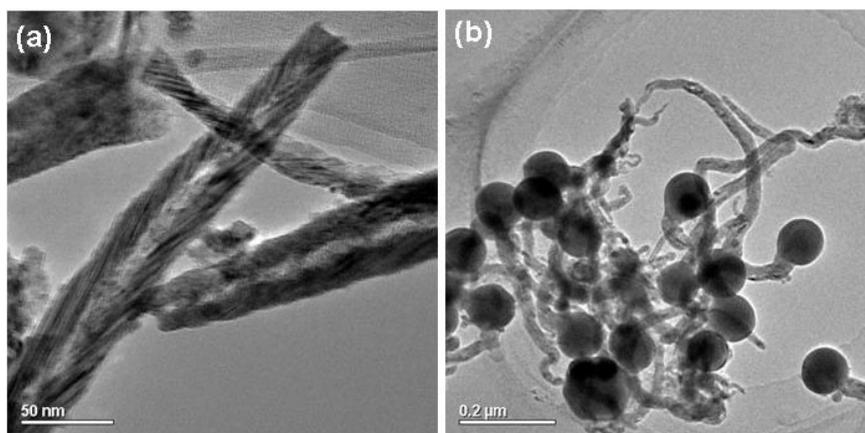


Figure 1. (a) InN nanotubes formed by co-decomposition of In and N precursors at 250 °C for 20 h, followed by a washing step. (b) Without the washing step, the same experimental conditions run for 10 h lead to drops of Indium metal with InN tails providing insight about the nanostructure growth.

Designing alternative paths towards *fcc*-FePt magnetic nanoparticles: Doped syntheses and ion-beam bombardment post-treatments

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We describe recent progress towards the controlled chemical syntheses of monodisperse FePt nanoparticles and the development of soft post-treatments to preventing the formation of aggregates of fused nanoparticles.

Iron Platinum (FePt) belongs to an important class of magnetic materials because, when its crystalline phase is face-centred-tetragonal (*fcc*), its magnetic anisotropy is one of the highest of any known material. This makes *fcc*-FePt an ideal candidate for a variety of technological applications, ranging from ultra high density recording media to bio-medical applications. However, colloidal syntheses most often lead to materials with a disordered face-centred-cubic (*fcc*) phase for which the magnetic properties are much weaker and which then require a post-treatment to be completed.

fcc-FePt nanoparticles were synthesised by a modified thermal decomposition protocol that allows accurate insertion of dopant elements and subsequent silica coating with a microemulsion method. The crystalline *fcc-fcc* phase transition was carried out by annealing the product under inert atmosphere in a furnace while the effects of ion-bombardment doses and conditions on the crystalline structure were investigated.

The nanoparticle properties were characterized by a combination of electron microscopy (TEM & SEM), X-Ray diffraction, atomic force microscopy, and SQUID magnetometer.

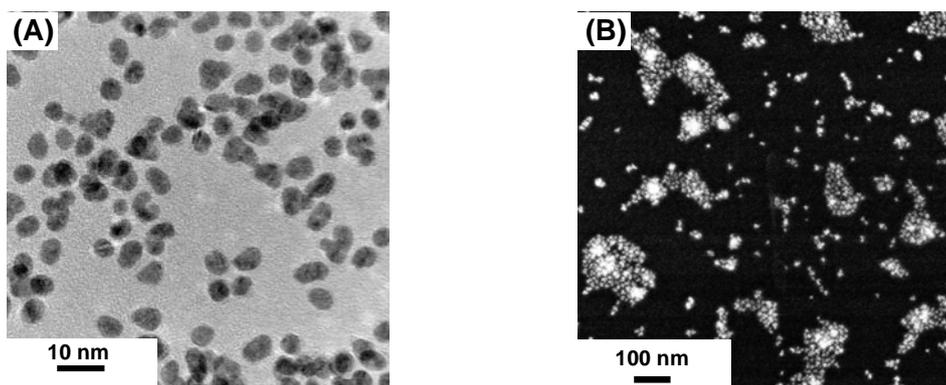


Fig.1. (A) TEM images of FePt NCs dispersed in carbon film TEM grid. (B) SEM image of FePt NCs on silicon substrate.