

The synthesis of mesoporous silicates containing bimetallic nanoparticles and magnetic properties of PtCo nanoparticles in silica†

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Using a one-pot approach employing true liquid crystal templating on neutral surfactants and simple metal salt precursors, mesostructured, mesoporous silicates have been prepared in which bimetallic nanoparticles are deposited; magnetic properties of PtCo systems so prepared are evaluated.

The incorporation of mixed metal nanoparticles into the pore structure of MCM-41 type materials is currently of great interest due to the wide variety of catalytic applications associated with metal alloys and clusters. The incorporation of mixed metal clusters has been studied extensively by Johnson, Thomas and co-workers¹ through the thermolytic decarbonylation of carbonyl clusters within the pores of silica. Other post-synthesis approaches to bimetallic particles within mesoporous silica, such as incipient wetness impregnation, have also been investigated although often, upon thermolysis, separation of the metals was observed. For example, Panpranot *et al.*² observed the formation of discrete particles of Co₃O₄ and RuO₂ rather than the formation of alloyed particles.

Previously we have described the 'one-pot' synthesis of mesoporous silicates containing nanoparticles of noble metals or first-row transition metals.³ These were prepared using a true liquid crystal templating approach⁴ in which the hexagonal H₁ mesophase of C₁₂EO₈ was prepared using an aqueous solution containing a metal present as a simple anionic complex – a chlorometallate anion for the noble metals and as an EDTA complex for the first-row metals.³ The resulting materials have thick pore walls and contain metal nanoparticles that are either one or two pore widths in diameter.

The simplicity of this approach is very appealing and we wished to see exactly how flexible the method could prove. To this end, we undertook the synthesis of a series of mesoporous silicates using this method, in which we used a mesophase prepared from an aqueous solution containing two, different anionic complexes to attempt the preparation of mixed metal nanoparticles. Four

combinations of metals were chosen, using the metal sources indicated, namely PdAu (K₂[PdCl₄] and K[AuCl₄]), PtCo (K₂[PtCl₄] and Na₂[Co{EDTA}]) and PdRu (K₂[PdCl₄] and Na₃[Ru{EDTA}] – [RuCl₆]³⁻ proved insufficiently soluble). In common with previous preparations, C₁₂EO₈ was employed as the surfactant, TMOS as the source of silicon, and the whole condensation was carried out at pH = 2 (HCl) under gentle, dynamic vacuum. The gel so formed retained the optical texture of an H₁ hexagonal phase. For calcination, the sample was heated in air at 3 K min⁻¹ to the desired temperature (400 or 600 °C) and then held at that temperature for 5 h prior to cooling. Both the as-synthesised and calcined materials were analysed by low-angle X-ray scattering (example as Fig. S1†), while the calcined material was characterised by BET-N₂ sorption analysis, transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX).

The structural data for the silicates are collected in Table 1. With the exception of the PtCo material calcined at 600 °C, the BET surface areas are all rather similar at around 800 m² g⁻¹. There is a degree of variation in the pore diameters (23.5 to 28.1 Å) and, combined with the lattice parameter from X-ray (42.7 to 45.3 Å) gives pore walls in the range 16 to 21 Å.

TEM and EDX analysis was used to characterise the metal nanoparticles within the porous silicate. Fig. 1(a) shows the particles to be confined within the pore structure but not confined within single pores, rather the particles appear to expand such that they fill two pores on the projection. This behaviour is similar to that observed previously for monometallic Co.³ Even when the particles fill in single pores, it is not necessary to have their particle sizes smaller than the pore size. Fig. 1(b) shows a TEM image from the specimen containing PdRu. Particles in single pores can be seen and the silicate wall of the mesopores around these particles is often distorted for accommodating larger particles. EDX results from either multiparticles or single particles show bimetallic nature for each specimen, although the ratio of the two metals is often variable. Some typical EDX spectra are shown in Fig. S2.†

HRTEM images from each sample revealed the detailed structures of the bimetallic nanoparticles (Fig. 2). Most particles have sizes either about 10 nm or about 5 nm, and have a single domain structure as shown in Fig. 2(b and c). However, many particles have a multi-domain structure as shown in Fig. 2(a). In both cases, the morphologies of the particles are the same (spherical). The principal *d*-spacing measured from Fig. 2(a) is 0.183 nm, which can be indexed onto the (210) of the cubic unit cell of Au with *a* = 0.408 nm. The other metal component, Pd, has a slightly smaller unit cell with *a* = 0.389 nm. Both Pt and Co have

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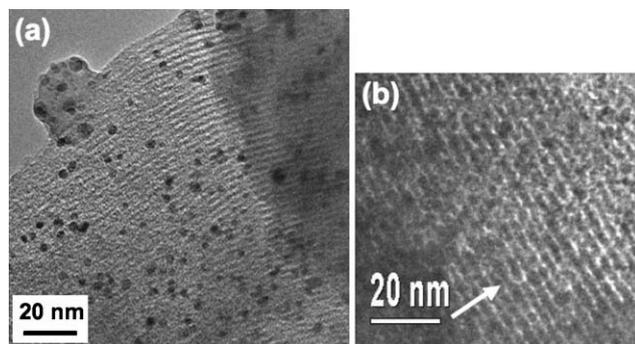
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† Electronic supplementary information (ESI) available: X-Ray diffraction pattern; EDX spectra. See DOI: 10.1039/b607471e

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Table 1 Characteristics of bimetallic silicates containing Pt and Co

Material	Calcination temperature/°C	wt% metal in silicate ^a	Atomic% metal in particles ^a	Surface area/m ² g ⁻¹	Pore diameter/Å	<i>d</i> -spacing/Å	Lattice parameter/Å	Pore wall thickness/Å
PtCo	400	Pt – 5.7 Co – 1.8	Pt – 49 Co – 51	734	26.5	37.0	42.7	16.2
PtCo	600	Pt – 5.7 Co – 1.8	Pt – 49 Co – 51	581	26.4	37.1	42.9	16.5
PdAu	400	Pd – 0.56 Au – 0.62	Pd – 48 Au – 52	849	28.1	39.2	45.3	17.2
PdRu	400	Pd – 3.9 Ru – 2.9	Pd – 56 Ru – 44	823	23.5	38.7	44.7	21.2

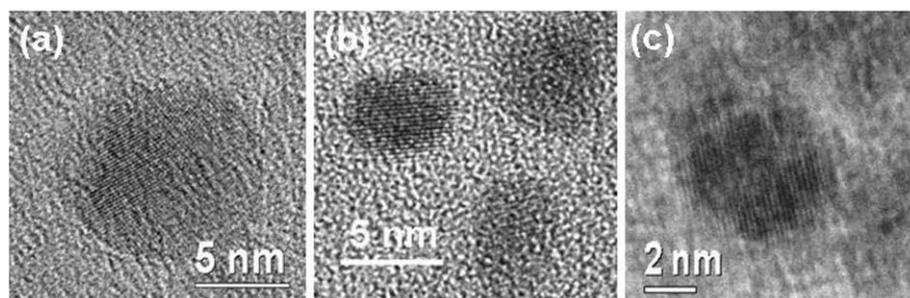
^a Calculated.**Fig. 1** TEM images of mesostructured silica containing (a) PtCo, calcined at 400 °C and (b) PdRu. The arrow indicates wall distortion.

cubic unit cells with $a = 0.392$ and 0.36 nm, respectively. The d -spacing observed from Fig. 2(b) is 0.22 nm, which can be indexed to the (111) planes of Pt. The d -spacing measured from Fig. 2(c) is about 0.21 nm, which can be indexed either to the (002) of the hexagonal unit cell of Ru with $a = 0.270$ and $c = 0.428$ nm, or to the (111) of cubic unit cell of Pd with $a = 0.389$ nm.

Using the data in Table 1, particle volumes of PtCo are estimated to be of the order of 80 nm³. For the purpose of ultra-high density magnetic recording an ideal media should consist of a mono-dispersion of non-interacting, single-domain nanoparticles in an inert, non-magnetic host. To ensure a low noise media the particle size must be small relative to the volume occupied by one recorded bit yet its anisotropy energy volume product must be large in comparison with the thermal energy of the environment to ensure the long-term stability of recorded data. When particle sizes are of necessity reduced below about 10 nm, the above constraints demand the use of high anisotropy alloys such as PtCo or PtFe and from this year, the recording industries switch from

longitudinal to perpendicular mode recording, which determines that the magnetic anisotropy should be directed perpendicular to the recording plane. Many routes are being explored to realise this type of media including those based on chemical,⁵ lithographic,⁶ biological⁷ and sputtering⁸ processes. Current continuous thin-film recording media are produced predominantly by sputtering, and Cary *et al.*,⁹ amongst others, have shown that it is possible to extend this technology also to produce advanced, including high anisotropy nano-particulate, media although further refinement of the techniques are required to attain the true mono-dispersion of the particle sizes desired. Better control of this parameter is currently obtained by chemical synthesis using some form of template or self-assembly process as first demonstrated by Sun *et al.*⁵ for PtFe nano-particulate recording media. It was therefore anticipated that the TLCT technique might be exploited in a similar manner with the hexagonally structured network of pores achievable with this technique also offering better control of particle volume and separation, whilst the homogeneous mixing of the metal complexes prior to mesophase formation would lead to truly bimetallic particles and allow for facile variation of the ratio of the two metals. Having previous sputtering experience with alloys of PtCo we chose, in the first instance, to continue with this alloy.

EDX analysis was used to probe the composition of the PtCo particles and, when averaged over an area of sample, an atomic ratio of $45 : 55$ (Co : Pt) was found, which is close to the calculated value given in Table 1. However, examination of three particles in that area showed Co : Pt ratios that varied from $44 : 56$ to $97 : 3$ – at present, we have no explanation for this variation. In order to characterise our samples magnetically, they were ground to a fine powder and pressed into a disk 15 mm in diameter and approximately 1.5 mm thick. The in-plane or longitudinal magnetic properties of the two PtCo samples were then observed

**Fig. 2** HRTEM images of the bimetallic nanoparticles encapsulated in mesoporous silicates: (a) PdAu, (b) PtCo and (c) PdRu.

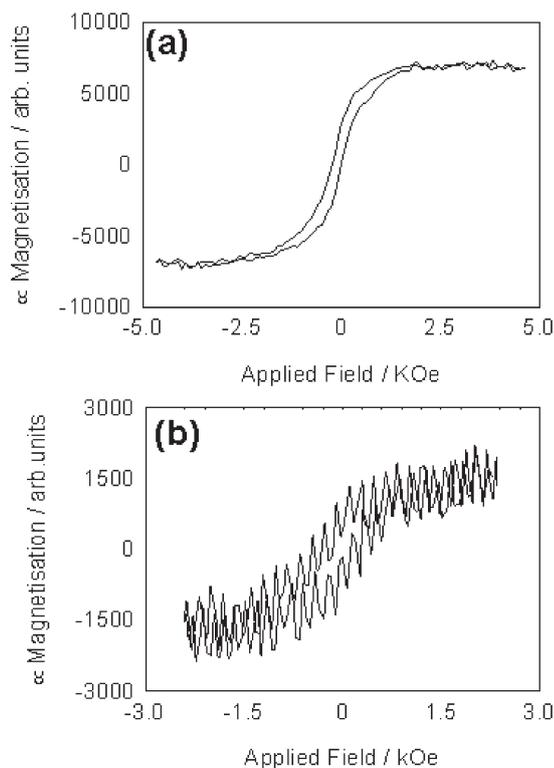


Fig. 3 Graph of magnetisation vs. applied field for (a) sample calcined at 400 °C and (b) sample calcined at 600 °C.

using a vibrating sample magnetometer (VSM), which produced a magnetisation loop showing sample magnetisation as a function of applied magnetic field. Fig. 3a shows the loop obtained from the sample annealed (calcined) at 400 °C. This is a ferromagnetic loop displaying coercivity. If, as indicated above, the particle volume in this sample is of the order of 80 nm³ then the form of this loop demonstrates the formation of at least one phase of PtCo with an anisotropy energy significantly greater than that of pure Co. Dispersions of cobalt particles (or Co and Pt in an unalloyed form) having volumes less than about 230 nm³ are not ferromagnetically

stable at room temperature and would exhibit only a hysteresis-free, superparamagnetic magnetisation curve. To achieve PtCo particles crystallised in the yet higher anisotropy L10 phase often associated with the anisotropy axis being orientated normal to the surface of the media requires annealing at temperatures ≈ 650 °C.¹⁰ Fig. 3b shows the sample calcined at 600 °C. Its in-plane magnetisation is clearly reduced greatly which from previous experience with sputtered films we take as evidence that that the desired L10 phase is now dominant with the anisotropy axis directed out of plane. Unfortunately, because of the nature of these samples we are not able to confirm this by our usual technique of polar Kerr magnetometry. We conclude that materials prepared in this way show promising magnetic properties and behave as would be expected for a PtCo bimetallic material despite being composed of particles of a range of compositions.

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