Organometallic based strategies for metal nanocrystal synthesis

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Organometallic strategies normally employed for the production of semiconductor quantum dots have been successfully applied to the synthesis of metal nanoparticles. By controlling parameters such as capping agents, reaction temperature and precursor chemistry, precise nanostructures can be obtained that exhibit highly desirable magnetic, optical and catalytic properties.

Introduction

Over the last decade, there has been immense interest in the preparation of nanostructured materials. A great deal of research has focused on quantum size effects in semiconductor nanocrystals, requiring high quality nanometre sized particles to clearly investigate the effects of charge carrier confinement. Until recently, traditional colloidal chemistry had been utilised for the preparation of nanoparticles, often giving materials with poor optical and physical properties. The majority of nanoparticle research focused on the preparation and photophysics of simple semiconductor particles, with a gradual improvement in synthesis, through aqueous chemistry, to reverse micelle based preparation, to organometallic based synthesis leading to robust, crystalline, passivated monodispersed nanocrystals.[1]

The preparation of metal nanoparticles however has not advanced as noticeably. Although gold colloids have been known for some time, notably reported by Faraday in 1857, little had been reported until the citrate reduction method in 1951 by Turkevich, which became the first popular method of preparation.[2] Brust developed a simple route to thiol passivated gold nanoparticles in the mid 1990's, which has been adopted as the current standard method of preparing noble metal nanoparticles.[3,4] There have been many advances using thiol passivated gold nanocrystals, including the demonstration of single electron transistors, molecular switches, and the controlled assembly of bimodal nanoparticles, all of which rely on the high quality of the nanoparticles used.[5–7] The Brust method, however, does not always lend itself to the preparation of a wide range of metal nanocrystals. Whilst the noble metals are easily prepared, some technologically important metals cannot be synthesised using this route. Magnetic nanoparticles such as iron, cobalt, nickel and some interesting free electron metals such as copper oxidise rapidly during synthesis. There are examples of the preparation of magnetic nanoparticles, such as the reverse micelle preparation of cobalt,[8] or the organometallic decomposition of metal carbonyls,[9] however, the degree of control over particle size, monodispersity or surface capping agent is often not as advanced as their semiconductor nanoparticle analogues. Even the 1 Gb/inch^2 CoPtCr nanomaterials developed by IBM displayed a wide distribution in size and shape.[10]

The importance of obtaining high quality, monodispersed metal nanoparticles of a specific size is evident when considering the case of magnetic materials. With semiconductor quantum dots, size quantization effects become manifest once the charge carriers are confined below a certain limit, the Bohr diameter of the exciton. The size of the particle then dictates the degree of confinement. With magnetic nanoparticles, there are two such limits. In a bulk magnetic material, there are numerous, small magnetic domains. If a particle is small enough (below *ca.* 70 nm in the case of cobalt, 14 nm for iron and 55 nm for nickel) it will consist of a single ferromagnetic domain.[11] If, however, the particle is too small, thermal effects will result in unstable magnetic orientations and the particle will become superparamagnetic and unusable in magnetic data storage devices. Hence the need for accurate control over particle size and morphology is greater in metal nanostructures than in semiconductor quantum dots.

In recent years, organometallic strategies applied to the preparation of semiconductor quantum dots have been utilised in the synthesis of metal particles, as these routes result in organic monolayer protected particles which are relatively air stable. The genesis of these so-called organometallic routes can be traced to the pioneering work of Bawendi and the use of tri-*n*-octylphosphine oxide (TOPO) as an effective capping agent.[12] The presence of the capping agent is essential in preparing nanosized particles as this inhibits agglomeration and increases processability, and in magnetic materials, inhibits the effects of dipole–dipole interactions. There are numerous relevant reviews of such nanoparticle chemistry;[13–15] particularly relevant is a recent review of magnetic particles by Hyeon.[16] Many studies have now been carried out in the area of capped metal nanoparticles and will be discussed.

Organometallic routes to metal nanoparticles can be traced back to the preparation of ferrofluids. An established method of preparing cobalt particles is the decomposition of

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$Co_2(CO)_8$, dicobaltoctacarbonyl, (DCOC) under an inert atmosphere, often in the presence of stabilising agents.[9,17,18] The thermal decomposition of DCOC is complex and proceeds through various unstable intermediates such as $Co_4(CO)_{12}$ and $Co_6(CO)_{16}$.[19,20] The rationale behind the use of a carbonyl complex is the clean decomposition pathway; at temperatures over 200 °C, the complex fully decomposes to cobalt and carbon monoxide in under one minute. The precursor has been used as the basis of the more up to date synthetic routes, which utilise complex capping agent chemistry to yield monodispersed particles of the required shape and size.

Cobalt is known to exist in two polymorphs, face centred cubic (fcc) and hexagonally close packed (hcp). The anisotropic high magnetic coercivity hcp phase is more useful for permanent magnetic applications, with fcc preferred for applications that require soft magnetism. Whilst both phases can exist at room temperatures, the fcc phase is favoured at elevated temperatures, and even at room temperature in small particles.[21,22] The thermal decomposition of DCOC in the presence of surfactants does not traditionally yield single crystal domain particles, rather multi-domained twinned crystals of the fcc phase with low energy stacking faults, referred to as mt-fcc by Murray *et al.*[23] Recent results have demonstrated that high quality single crystal materials can be obtained from the thermal decomposition of DCOC, by a judicious choice of capping agent and this will be discussed later.

Initial studies and epsilon cobalt

Initial investigations into organometallic routes to passivated, size controlled metal nanoparticles were undertaken by the Bawendi group, borrowing expertise from their previous studies on II–VI systems.[22] Thermolysis of DCOC in toluene with TOPO resulted in the preparation of capped, roughly spherical cobalt particles, 20 nm in diameter with a size distribution of *ca.* 15%. Increase in the growth temperature with the use of a higher boiling point solvent (butylbenzene) resulted in micrometer sized particles. The massive increase in growth with a slight increase in growth temperature and the ease of removal of the surfactant with washing indicated that the TOPO is only weakly bound. Elemental analysis suggested the particles were capped with one to two monolayers of metal oxide. The surfactant was easily removed and the particles then oxidised in air.[22,24]

The passivated particles, however, did not exhibit X-ray diffraction patterns consistent with any known phase of cobalt, cobalt oxide or phosphide (Fig. 1). Detailed analysis and modelling resulted in the assignment of a new phase of cobalt, designated ε-cobalt[22,24] (fcc and hcp cobalt have been previously referred to as α and β, whilst γ cobalt refers to the radioactive ^{60}Co isotope and δ-cobalt has already been assigned to an unexplained structure).[22] The polymorph epsilon cobalt exhibits the space group $P4_132$, a similar cubic phase to β-manganese, has a similar magnetic moment/cobalt atom as bulk fcc and hcp cobalt (1.70 μ_B compared to 1.75 and 1.72 μ_B respectively)[24] and is less dense than either the fcc or hcp phase (8.635 g cm^{-1} compared to 8.788 g cm^{-1} and 8.836 g cm^{-1} respectively.) The same reaction without TOPO yielded fcc cobalt nanoparticles. Gradually increasing the amount of TOPO in the reaction conditions increased the amount of ε-cobalt until no fcc phase was observed.[22]

Epsilon cobalt appeared metastable for months at room temperature and is irreversibly converted to the hcp phase upon annealing at 300 °C, and the fcc phase at 500 °C. To date, epsilon cobalt has not been observed in films prepared by other methods such as sputtering, evaporation, electrodeposition, *etc.*, and may only be accessible by solution routes. The same reaction with other ligands does not always give ε-cobalt, highlighting the important role specific ligands play in the preparation of novel magnetic materials.

General organometallic routes

Following the success of using DCOC and TOPO, other capping agents were investigated and found to have a pronounced effect on the crystal structure and size. Replacing TOPO with tri-*n*-octylphosphine (TOP) resulted in nanoparticulate cobalt with a mixed hcp–fcc structure. The size of the nanoparticles was increased by decreasing the amount of TOP or by lowering the reaction or injection temperature. Simple ligand exchange reactions with carboxylic acid salts were also found to be effective in varying the interdot spacing.[22]

Independent research at IBM also concentrated on organometallic solution routes to magnetic nanoparticulate materials.[25] The Murray group again used a TOPO based method to obtain cobalt nanoparticles in the size range from 2 to 11 nm. In this preparation cobalt chloride and oleic acid were dissolved in either dioctyl or diphenyl ether and heated. Trialkylphosphine was then added and the temperature increased to *ca.* 200 °C. The cobalt salt was then reduced by the addition of a dioctyl ether solution of superhydride. The particles, capped with oleic acid and the trialkylphosphine, were isolated by addition of a non-solvent after a growth period. Size fractionation narrowed the size distribution.

Here, the capping agents played a key role in dictating particle size. The use of sterically demanding phosphines such as TOP resulted in particles in the size range of 2–6 nm, whilst the smaller tributylphosphine (TBP) resulted in larger particles of up to 11 nm. The use of oleic acid (octadec-9-ene-1-carboxylic acid) can be traced back to earlier studies on iron colloids,[26] where the double bond is found to be an essential feature of the capping agent, giving added rigidity and stability to the surface passivation. The trialkylphosphine was found to be a labile capping agent and reversibly bound to the surface, slowing, but not stopping growth. Excessive washing of the nanoparticles easily removed the phosphine, and the nanoparticles were usually stored with a small amount of oleic acid to further protect the particles after isolation. Oleic acid is a strongly binding capping agent and on its own inhibits growth. A mixture of the two is therefore an excellent way of controlling particle growth. The ligand shell stabilised the colloid and offered a degree of protection against surface oxidation.

The nanoparticles prepared by this route were found to exhibit the epsilon cobalt structure, but could be converted to the more useful hcp phase when annealed under an inert atmosphere at 300 °C. During annealing, the passivating ligands were removed and nanoparticles quickly oxidised when

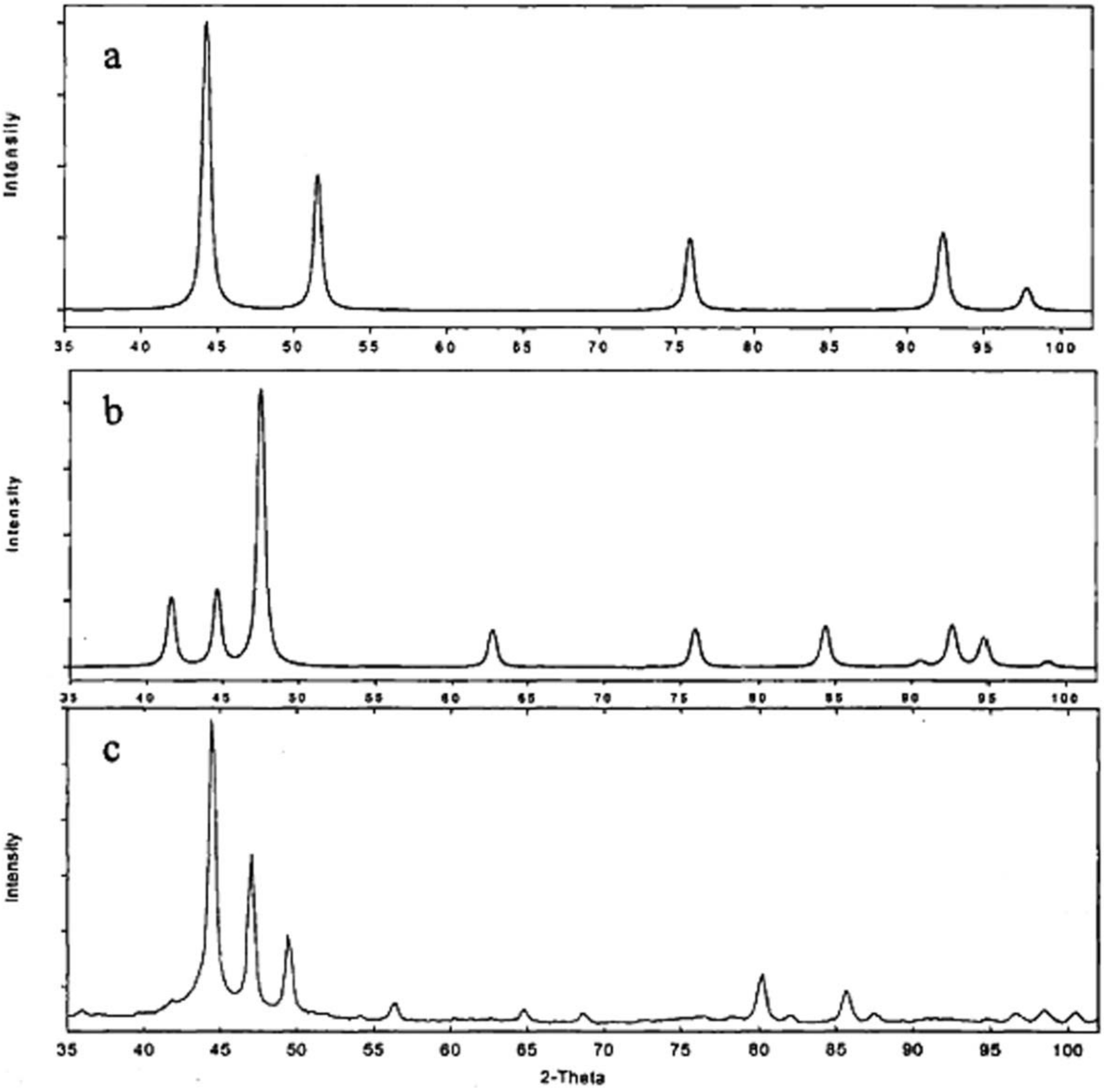

Fig. 1 X-ray diffraction patterns from a) fcc cobalt (simulated); b) hcp cobalt (simulated); c) ε-cobalt (experimental) (taken from ref. 22).

exposed to air. Washing the annealed samples in acetone caused a slight oxidation of the surface, hindering further oxidation. Thin films and superlattices of these nanoparticles could be prepared, and will be discussed later. Annealing films of 9 nm cobalt particles showed a change in coercivity from 500 Oe (ε-cobalt) to1450 Oe (hcp cobalt) when annealed at 300 °C, followed by a decrease in coercivity to 800 Oe at 500 °C (fcc cobalt). The as prepared particles in this study were found to be superparamagnetic at room temperature, and underwent the transition to ferromagnetic at approx. 165 K.

Capping agents are not the only parameter that can alter the particle internal crystal structure: hcp cobalt particles in the size range of 2–20 nm were prepared by reducing the cobalt salt with a polyalcohol rather than superhydride (often referred to as a polyol route, usually utilising ethylene glycol or glycerol.[23] However it has been found that longer chain alcohols such as 1,2-dodecanediol allow for solution homogeneity and cleaner reactions). Again the particle size could be controlled by altering the capping agents.

The IBM group also investigated the thermolysis of DCOC in ethereal solution of oleic acid and TBP, giving 8–10 nm multi-twinned fcc crystals.[23] It is interesting to note that similar work by the Bawendi group gave pure ε-cobalt with TOPO as a capping ligand, and fcc crystals with TOP as a capping ligand. The Alivisatos group were, however, able to prepare ε-cobalt nanoparticles in the size range 3–17 nm by the thermolysis of DCOC under an inert atmosphere using mixtures of oleic acid, lauric acid, pure and technical grade TOP and TOPO, using the high boiling point solvent *o*-dichlorobenzene[27] (Fig. 2). Initial experiments into particle morphology suggested rod like structures could be obtained,[28] with specifically oleic acid and TOPO as capping agents, although these were later actually found to be discs orientated on their edges.[20]

Shape control, growth mechanisms and superlattices

Discs of Co with an hcp structure could be reproducibly prepared by the thermolysis of DCOC in oleic acid and TOPO,

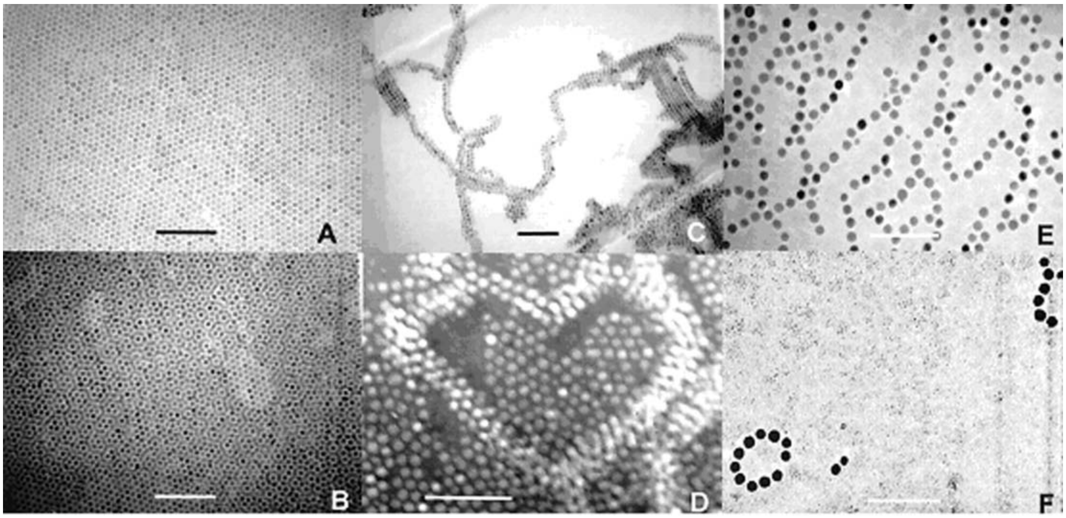

Fig. 2 A selection of Co nanoparticles prepared by the thermolysis of dicobaltoctacarbonyl under different conditions.[28] A) 10 nm epsilon cobalt nanoparticles; B) Bi-layer assembly of 10 nm epsilon cobalt nanoparticles; C and D) 12 nm epsilon cobalt nanoparticles; E and F) 16 nm epsilon cobalt nanoparticles.

and large yields could be obtained if the reaction was quenched seconds after precursor injection.[20] If the reaction was allowed to proceed, the discs re-dissolved and formed spherical particles. It was found that the formation of discs was easier if TOPO was replaced with long chain linear amines, although the discs eventually converted to ε-cobalt spheres if left for long enough at elevated temperatures. By controlling surfactant parameters and injection conditions, up to an 85% yield of hcp discs could be obtained, although physical separation was required to obtain a pure sample. The morphology of the discs could again be controlled by altering the precursor to solvent ratio and the reaction time. TEM studies showed long assemblies of discs lying on their edge, often in a parallel alignment, suggesting the discs were coupled. It was observed that the larger discs were often in the centre of the alignment, suggesting these so called 'ribbons' nucleate with the largest discs first followed by progressively smaller discs.

From these results, it was concluded that the TOPO acts as a selective absorber, altering the growth rates of different crystal facets, and that alkyl amines also strongly inhibit growth, specifically along the (001) face. This is interesting as earlier studies on TOPO and long chain amine passivated gold nanoparticles showed that the long chain amine was required for controlled spherical particle growth.[29] In the oleic acid and TOPO system, the diameter of the discs was found to be directly proportional to the concentration of TOPO. The role of TOPO is found to be essential as an atom exchange agent, required for size focusing. TOPO was also found to bind strongly to the (101) plane as determined by TEM and X-ray diffraction (XRD) studies.[20,28] These findings also lend weight to the Kossel–Stranski theory of selective growth on a particular crystal face rather than the suggested soft templating mechanisms. The Alivisatos group also found the choice of solvent was important, with less polar solvents preferred, and that the actual *position* of injection (halfway between the flask wall and the vortex) also had an effect on the particle size distribution.[20]

The growth of cobalt nanoparticles in TOP is different to that of CdSe quantum dots in TOPO. Once the cobalt nanoparticles have formed, they cannot re-dissolve back into solution and hence cannot grow onto the larger particles (Ostwald ripening), and the particle growth stops once the precursor is depleted. This suggests that the TOP binds relatively strongly to the particle surface during growth. The binding strength of TOPO appears different, and allows for Ostwald ripening in a similar manner to that of CdSe.[22]

Reproducible control over the morphology of nanoparticles is of great interest, as many optical, magnetic, catalytic and electronic properties of nanomaterials also depend on particle shape. In magnetic material, the need for elongated structures (shape anisotropy) is paramount. Even small deviations from spherical shapes can significantly alter the coercivity. For example, a change in aspect ratio in iron particles from 1.1 to 1.5 quadruples the coercivity.[11] The Alivisatos group have been extremely successful in preparing specifically shaped semiconductor quantum dots, using the theory that surfactant molecules bind more strongly to certain crystal faces than others. Dinega has been successful in preparing fcc single crystal triangular and rod shaped particles of cobalt by controlling the reaction temperature and by using a mixed solvent system of carboxylic acid salts and TOP.[22] The length and thickness of the rods can be controlled by altering the amount of capping agent. The cubic nature of the rods is also in contrast to the hcp discs reported by Alivisatos, further highlighting the complexity of the system. An important feature of the nanorods prepared by the thermolysis of DCOC in trialkylphosphines and carboxylic acid salts is their ferromagnetic character as opposed to the superparamagnetic properties observed in the analogous spherical particles, a property of shape anisotropy.[22]

It was proposed that the growth of both rods and triangles originates from small triangular seeds, and that rods form only with rapid growth or when there is insufficient surfactant to bind to one particular face.[22] Slow controlled growth allows for equal growth on all three sides. Again, triangular particles of gold have been observed in a pure TOPO system, whilst spherical particles required the stabilising amine.[29]

The Chaudret group also synthesised hcp Co nanoparticles by the thermolysis of $[Co(\eta^3\text{-}C_8H_{13})(\eta^4\text{-}C_8H_{12})]$.[30] Investigations were undertaken into the effects of the amine/oleic acid capping groups and the reaction atmosphere. By controlling these parameters, small superparamagnetic spherical particles could be controllably transformed to ferromagnetic rods, then wires.

For data storage applications, ordered arrays of particles are required, and to this end, superlattices of cobalt nanoparticles have been prepared using a methodology adopted from Murray *et al.*[31] Controlled slow evaporation of a solution of nanoparticles in a high boiling point solvent of a selected polarity with a small amount of non solvent resulted in ordered 2D and 3D supercrystals.[25,22] An interesting feature of the superlattices is the difference in close packing of the nanocrystals prepared by different methods. Cobalt particles (8 nm) prepared in TOP by the decomposition of DCOC resulted in spherical particles which assembled in the conventional hcp structure. Initial reports from the Murray group also reported the expected packing, with variation in interparticle spacing easily obtained by using nanoparticles with different length capping agents, and using different substrates to induce either 2D or 3D structures.[23,25] Firing the superlattice at *ca.* 300 °C resulted in the crosslinking of the organic capping agent, giving an amorphous carbon matrix in which the nanoparticles were held. Investigations into the carrier transport through a superlattice displayed spin dependent electron transport.[32]

However, cobalt nanoparticles capped with TOP and oleic acid (IBM method) reported by Wang were found to be faceted polyhedra of three distinct shapes, giving rise to three different types of self assembly due to face to face stacking of the anisotropic nanoparticles.[33] The presence of stacking faults and partial dislocations in the supercrystal disturbed the long range order.

Self-assembly into high quality 2D and 3D arrays was also performed in the presence of external magnetic fields, where the growth of a 2D superlattice was found to be dependent on the direction of the magnetic field.[34] Increasing the magnetic field induced the formation of a 3D crystal.

There have been numerous investigations into various physical and magnetic properties of passivated cobalt nanoparticles, including the presence of magneto-optical signals in larger particles which allowed assignment of the size of the effective magnetic core in a 10 nm particle.[35] The cross over from a blocked to superparamagnetic state with an increase in temperature has also been investigated as have the effect of particle size, morphology and magnetic core size on the cross over.[36]

Other notable studies include the relaxation and interaction effects by RF transverse susceptibility,[37] general magnetic properties of interacting cobalt arrays,[38] superparamagnetism in films of nanoparticles,[39] ferromagnetic resonance studies[40,41] and annealing effects.[42] A major stumbling block to practical applications is the superparamagnetism in nanoparticulate cobalt prepared in these size ranges. However, recent reports show that exchange interface coupling between ferromagnetic cobalt particles and an antiferromagnetic matrix can lead to ferromagnetic stability at high temperatures, possibly leading to workable devices in the nanoparticulate size range.[43]

An interesting application not initially envisaged is the use of cobalt nanoparticles as catalysts. The Chung group have used capped cobalt nanoparticles as a novel Pauson–Khand catalyst and as a catalyst for a one pot preparation of fenestranes.[44,45]

Magnetic metals and alloys

The IBM group have also reported the preparation of nickel nanoparticles in the size range of 8–10 nm by replacing the cobalt salt with a nickel salt in the polyol route, and using long chain amines instead of trialkylphosphines.[23] Alloys of the two metals could be prepared by mixing the precursors prior to the reaction. Green and O'Brien also reported the preparation of nickel nanowires by the reduction of a nickel salt in the presence of trialkylphosphine/trialkylphosphine oxide. The formation of small (*ca.* 5 nm) chromium nanoparticles was also reported in the same paper.[46] Chaudret *et al.* also reported a similar route to nickel nanoparticles by using a similar precursor in either hexadecylamine or TOPO, with shape control possible by altering the capping ligand. Investigations into the effects of the capping agent on the magnetism were also carried out.[47]

The IBM group also demonstrated the synthesis of iron nanoparticles by replacing DCOC with iron pentacarbonyl, $Fe(CO)_5$, giving particles which displayed evidence of disorder and a thick (2 nm) oxide shell.[23]

One of the earliest controlled organometallic routes to magnetic nanomaterials is the report by Hyeon on the sonochemical decomposition of iron pentacarbonyl in the presence of surface capping agents, such as oleic acid or polyvinylpyrrolidone (PVP).[26] The particles were relatively monodispersed, and this process opened the way to some of the above processes. Researchers from the same group improved the synthesis by using TOPO as a stabiliser, giving 2 nm particles which could then be used as seeds for rods up to 11 nm in length.[48] Hyeon then extended this work to produce highly monodispersed maghemite (Fe_2O_3) in the size range of 4 to 16 nm, by first preparing iron nanoparticles (reduction of iron carbonyl in the presence of oleic/lauric acid in dioctyl ether) followed by mild oxidation using trimethylamine oxide (Fig. 3). The procedure required no size selective precipitation and represents one of the first non-hydrolytic methods of oxidising metal particles.[49]

In similar work, iron bis(2-ethylhexyl) sulfosuccinate was reduced by sodium borohydride in the presence of TOPO under an inert atmosphere to give 3 nm iron particles.[50] Despite the fact the reducing agent was added in a water/pyridine mixture, the metal nanoparticles did not appear to oxidise, however, prolonged atmospheric exposure resulted in oxidation. The particles showed surface enhanced Raman scattering (SERS) and investigations were made into their use in the electrocatalytic reduction of hydrogen peroxide.

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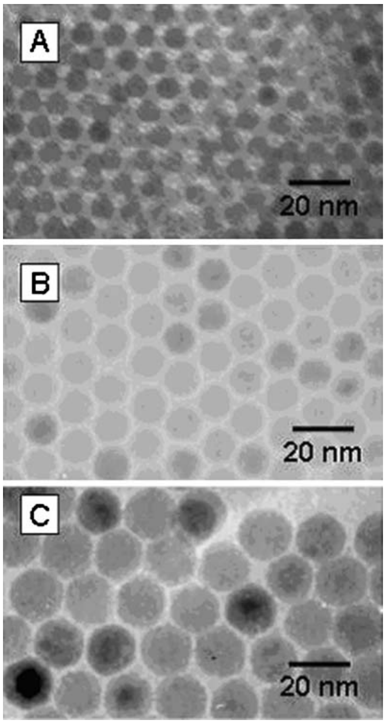

Fig. 3 Examples of iron nanoparticles.[16] A) 7 nm nanoparticles; B) 11 nm nanoparticles; C) 18 nm particles.

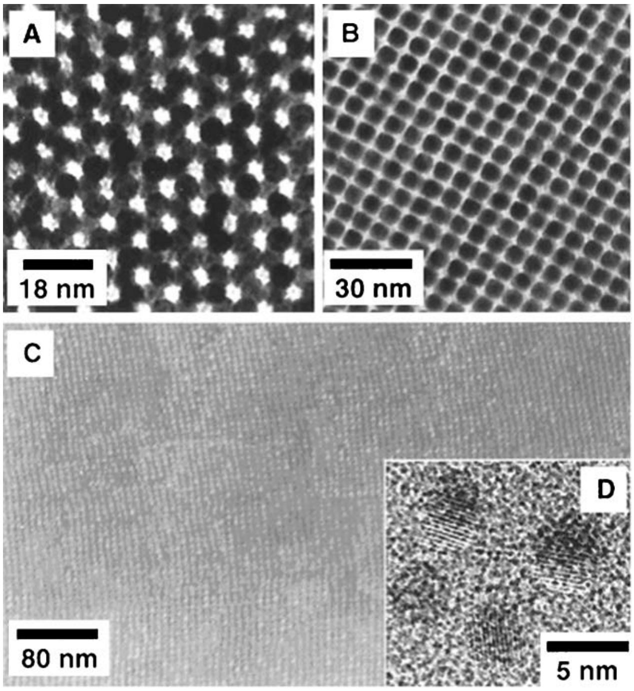

Fig. 4 Self assembled FePt nanoparticles.[51] A) 6 nm particles multilayer assembly; B) 6 nm FePt particles capped with hexanoic acid and hexylamine assembled in a square lattice; C) 4 nm FePt particles assembly (180 nm thick) after annealing; D) HRTEM image of annealed 4 nm FePt particles.

Investigations into the preparation of iron nanoparticles have led to the synthesis of the technically important magnetic alloy, FePt, as reported by the IBM group.[51,52] The group has developed the chemistry from the preparation of cobalt nanoparticles and extended it to the preparation of monodispersed FePt particles in the size range from 3 to 10 nm. To obtain high quality alloyed particles, both iron and platinum nuclei must be generated simultaneously, presenting a substantial challenge. In this case, platinum acetylacetonate (Pt(acac)$_2$) was reduced by a long chain dialcohol (polyol type process) whilst iron pentacarbonyl was decomposed thermolytically, both in the presence of oleic acid and a long chain amine. It is interesting to note that attempts to prepare alloys of cobalt and platinum (CoPt) using the above procedures usually resulted in sub-standard materials.[52] Altering the chemical composition of the alloy (from $Fe_{30}Pt_{70}$ to $Fe_{80}Pt_{20}$) was roughly achieved by altering the ratio of precursors, and an increase in the particle size was achieved by addition of extra precursor solution.

The monodispersed product could then assemble into 2D or 3D superlattices by controlled evaporation, with inter-particle spacing controlled by changing the capping agent.[51] For example, a superlattice with a cubic structure could be obtained by using hexanoic acid/amine, instead of the normal hexagonal superlattice using oleic acid/oleylamine (Fig. 4). Nanoring structures could also be prepared by evaporation of a dilute solution of FePt nanoparticles on a TEM grid.[53] Thermal annealing of a superlattice at 560 °C resulted in a change in the crystal structure from the superparamagnetic fcc (referred to as the A1 phase) to face centred tetragonal (fct, referred to as the L1$_0$ phase), making the assemblies ferromagnetic. Inclusion of oxygen in the annealing step resulted in the oxidation of the Fe constituents in the particles, giving Fe_3O_4 and Fe_2O_3, and induced the formation of both the L1$_2$ phase, FePt$_3$, and fcc platinum. This presents an obvious problem in processing, and dictates an inert atmosphere with less than 1 ppm of oxygen is required to prepare the FePt L1$_0$ phase.[54] The nanoparticles were again immobilised in a carbon matrix when annealed, similar to that observed in cobalt nanoparticles. The assemblies could support reversible magnetization transitions at room temperature, hinting at possible terabit/inch data storage capabilities in the near future. Assemblies of a controlled thickness could be obtained by using a blend of polymer and FePt, in which the polymer, such as polyethylenimine (PEI) or polyvinylpyrrolidone (PVP), replaces the oleic acid/amine.[55] Annealing of the assembly again gave the ferromagnetic fct phase. Whang at Georgia Tech has investigated the structure of FePt particles, finding a faceted truncated octahedron shape dominates the as-prepared nanocrystals. Also observed were the usual shapes such as the Marks truncated decahedron and twinned icosahedra. After annealing, a cuboctahedron becomes the dominant shape in the L1$_0$ phase.[56,57]

The synthesis route was then improved by replacing iron pentacarbonyl with iron(II) chloride, followed by high temperature reduction using superhydride.[58] This new route gave greater control over the final ratio of Fe : Pt in the nanoparticles whilst avoiding the toxic carbonyl species. It was also reported that assemblies of a controlled thickness could be obtained by adsorbing a layer of polyethylenimine and the FePt particles on an OH terminated surface, and again ferromagnetic fct phases could be obtained through annealing. Another way of preparing ordered arrays of FePt nanoparticles has been described by the Weller group, where a three-layer solution technique was employed. The nanoparticles were dissolved in toluene and placed in a tube, on top of which was added a buffer layer of propanol, followed by a layer of non solvent such as methanol. Slow diffusion of the non solvent through the buffer layer destabilised the solution and induced the growth of hexagonally packed micrometer sized supercrystals.[59]

The IBM group also used FePt nanocrystals in conjunction with Fe_3O_4 nanoparticles to prepare FePt–Fe_3Pt nanocomposites. Such exchange–spring magnets composed of hard (FePt) and soft (Fe_3Pt) magnetic materials have a large energy product relative to single phase materials.[60] An application not initially envisaged with FePt nanoparticles is the detection of bacteria at low concentrations, using nanoparticles conjugated to vancomycin to detect *E. coli.*[61]

One drawback in the preparation of nanoparticulate magnetic materials is the preparation of a ferromagnetic array. As described above, high temperature (560 °C) annealing of FePt particles transforms the material from the superparamagnetic A1 phase to the ferromagnetic $L1_0$ phase. This high temperature step can, however, lead to particle coalescence and the loss of positional order. The Nikles group have substantially reduced the annealing temperature, by adding silver acetylacetonate to the reaction, giving $[Fe_{49}Pt_{51}]_{88}Ag_{12}$ nanoparticles with a phase transition temperature of only 400 °C.[62,63] The annealed nanoparticles reportedly have more order and less coalescence then the high temperature analogues. In related work, Nikles has prepared superparamagnetic $Fe_xCo_yPt_{100-x-y}$ nanoparticles of approximately 3.5 nm diameter, using cobalt acetylacetonate, platinum acetylacetonate and iron pentacarbonyl in a dioctyl ether ether solution of oleic acid and amine.[64] The ratios of Fe : Pt : Co could be controlled by altering the ratio of precursors, and the resulting material could be converted to the tetragonal $L1_0$ phase at temperatures between 550 °C and 700 °C. The same group also prepared FePtCu nanoparticles with a similar size and magnetic properties by a similar method, using copper bis(2,2,6,6-tetramethyl-3,5-heptanedionate) instead of the cobalt precursors.[65] In both cases, the inclusion of either the copper or cobalt did not reduce the phase transformation temperature to the $L1_0$ phase, unlike the inclusion of silver.

Many investigations into the physical properties of FePt nanoparticles and FePt/polymer nanocomposites have been undertaken, including thermal stability studies of FePt arrays,[66] general magnetic and electronic studies,[67] near edge X-ray absorption fine structure (NEXAFS) studies, X-ray diffraction (XRD) and modelling studies.[68–72]

The synthetic route employed in the preparation of FePt nanocrystals allowed a number of similar metal alloy nanomaterials to be prepared. Cheon employed a similar method to prepare CoPt nanoparticles and Co/Pt core shell materials.[73] In this case, DCOC and platinum hexafluoroacetylacetonate (hfac) were used as precursors and the reaction proceeded *via* transmetalation, using toluene and either oleic acid or amine as stabiliser, with no diol present. Nikles also reported the preparation of 7 nm CoPt nanoparticles using cobalt tricarbonyl nitrosyl and $Pt(acac)_2$ as precursors.[74] Films of $Co_{48}Pt_{52}$ required 3 hours annealing at 700 °C to transform to the $L1_0$ phase. In the same paper, 11 nm FePd nanoparticles were also reported, prepared from acetylacetonate precursors, using oleic acid/amine as capping agents and 1,2-hexanediol as a reducing agent. The Weller group have prepared $CoPt_3$ nanoparticles in the size range 1.5–7.2 nm diameter, using standard precursors.[75] The group however found that oleic acid was too strong a binding agent for the preparation of $CoPt_3$, and differing capping agents such as 1-adamantanecarboxylic acid, *n*-tetradecylphosphonic acid and hexadecylamine were employed instead. The Fang group also prepared CoPt nanoparticles which could be dispersed in a poly(methylmethacrylate) matrix.[76] The precursors used were cobalt chloride and $Pt(acac)_2$, which were reduced by superhydride in the presence of oleic acid and oleylamine. Despite high temperature annealing, it was hard to ascertain whether the particles underwent a phase change from the fct to the fcc polymorph by XRD alone, however the increase in coercivity clearly indicated the transformation.

Polyol reduction was again used in the preparation of MnPt nanoparticles, where $Pt(acac)_2$ and $Mn_2(CO)_{10}$ were reduced/thermolysed in a dioctyl ether solution of 1,2-tetradecanediol and oleic acid/amine.[77] The Chaudret group have also prepared NiFe nanoparticles using iron pentacarbonyl and $Ni(C_8H_{12})_2$, although detailed experimental procedures were not provided.[78] SmCo nanoparticles have been prepared using DCOC and $Sm(acac)_3$ in dioctyl ether with oleic acid, however, no diol was used in the reaction.[79] In similar work, $SmCo_5$ particles were prepared using a diol and oleic acid/amine.[80] The ratio of the final product was controlled by altering the ratio of precursors, and $SmCo_2$ was also observed.

FeMo nanoparticles up to 14 nm in diameter were grown from the metal carbonyl complexes (ratio Fe : Mo carbonyls 5 : 1) in the presence of bis-2-hexylamine and octanoic acid. The particles were considered as iron particles doped with *ca.* 4% molybdenum, and were used as catalysts for carbon nanotubes grown by chemical vapour deposition (CVD).[81]

Not all systems form alloys. The reaction between silver perchlorate and DCOC in the presence of oleic acid and tridodecylamine produced 12 nm crystals with an Ag/Co core/shell structure instead of an alloy.[82] This is attributed to the fact that Ag seeds grow before the formation of Co in the preparation. Core/shell particles of Pt/Fe_2O_3 were grown by the reduction of $Pt(acac)_2$ by 1,2-hexadecanediol in the presence of oleic acid/amine, followed by particle growth and the addition of iron pentacarbonyl. It was assumed the iron oxidised during the washing or high temperature reaction process.[83] In similar experiments, highly monodispersed Pt/Co core/shell particles up to 7.6 nm in diameter have been prepared and the magnetic properties investigated, uncovering a high blocking temperature. The material was prepared in a two step process, initially using a polyol process to prepare 2.6 nm Pt cores from $Pt(acac)_2$, capped with oleylamine and oleic acid, followed by the decomposition of DCOC at a low temperature (*ca.* 140 °C). Varying the amount of cobalt precursor employed could vary the thickness of the shell.[84]

Other metals

The success of these new synthetic routes has prompted research into the preparation of non-magnetic metals for various reasons. Some metals are air sensitive and require strict surface protection by the organic monolayer, not easily achieved in previous methods. The control over shape and size has again initiated research into traditional inert metals such as gold and silver, where new organometallic routes allow the particle size to be tightly tuned, giving highly monodispersed materials.

One of the free-electron metals which should show a surface plasmon in the absorption spectrum is copper, however this is extremely hard to prepare using traditional colloidal chemistry. The Fischer group have prepared surface protected copper particles, which can be size fractionated, by solution thermolysis of a CVD precursor, $[Cu(OCH(Me)CH_2NMe_2)_2]$ in either trialkylphosphines or long chain amines.[85] The presence of the surface passivating agent protects the particles against oxidation, and by altering the capping agent, the particle size can be tuned from *ca.* 7 nm to just under 4 μm. Using a high concentration of precursor stock solution resulted in the formation of rod like particles up to 110 nm along the long axis.

The Chaudret group have prepared hexadecylamine capped indium nanowires using UV light and a cyclopentadienyl complex of indium (In(Cp)).[86] Surprisingly, the reaction without the long chain amine resulted in small (11 nm) particles with a slightly high aspect ratio due to the preferred axis of growth. Altering the precursor/capping agent ratio led to wires up to 200 μm in length. This methodology was extended to indium/tin (In_3Sn) particles and wires from the thermolysis of the cyclopentadienyl complex of indium and $Sn(NMe_2)_2$.[87] Irradiation of $Sn(NMe_2)_2$ alone in the presence of hexadecylamine led to square tin nanoparticles with a tetragonal internal structure. Using the HCl adduct of hexadecylamine resulted in the formation of regular superstructures, the composition of which could be altered by altering the concentration of the capping agent. The spontaneous thermolysis of the In(Cp) in the presence of a polymer stabiliser or in a toluene solution of TOPO has also been reported and resulted in small (*ca.* 4–6 nm) particles of indium.[88] The monodispersed particles could easily form a 2D superlattice, but oxidised over a matter of days to In_2O_3 particles. Indium nanoparticles have also been prepared by the reduction of indium salts by sodium borohydride in TOPO. The indium particles were then used as precursors for *in situ* preparation of indium pnictide nanorods.[89]

Another important material is bismuth, which has possible thermoelectric applications. Bismuth can also undergo a transition from semimetal to semiconductor with decreasing particle size. Semimetal bismuth (Bi) nanoparticles up to 100 nm in diameter have been prepared by reduction of bismuth 2-ethylhexanoate in the presence of oleic acid and TOP.[90] Size fractionation led to a monodispersed product which could self assemble to give 2D superstructures with short range hexagonal order. Another highly air sensitive material is lead (Pb), which has been prepared by the thermolysis of tetraethyllead with octanoic acid and TOP giving crystalline particles of *ca.* 20 nm diameter.[91] Altering interparticle spacing by using differing carboxylic acids gave a material that changed from a Mott insulator, through to a strongly localised superfluid, to a superfluid as the spacing decreased. The material was highly air sensitive even when capped, and fully oxidised over a matter of hours in air.

Highly monodispersed twinned fcc gold nanoparticles, approximately 9 nm in diameter, have been prepared by the reduction of tetrachloroauric acid ($HAuCl_4$) in TOPO and octadecylamine (Fig. 5).[29] The particles spontaneously assembled on a substrate without the need for size fractionation and produced large colloidal crystals up to 200 μm in size. The presence of octadecylamine appeared essential to prepare the monodispersed particles, as growth in TOPO alone gave particles up to 100 in size and of a variety of shapes, such as triangles and squares. The growth mechanism is assumed to be similar to that of capped cobalt nanoparticles described earlier, where TOPO is weakly bound, and in this case, the amine is strongly bound. Growth in TOPO alone is therefore uncontrolled and results in the various shapes and sizes. The presence of TOPO allowed for larger and more monodispersed particles to be prepared relative to simple amine capped gold particles.[92] The resulting amine/TOPO capped particles therefore had a slightly longer mean free path for the electrons, allowing for a strong surface plasmon resonance to be observed. The particles have been used to prepare Langmuir–Blodgett films that were utilised in the demonstration of a simple flash memory structure[93] and as an 'ink' in dip pen nanolithography.[94]

A similar methodology was used to prepare silver nanoparticles with a bimodal size distribution, capped with a variety of trialkylphosphine oxides and amines.[95] The results confirmed the strong binding mode of the amines and the weak, but essential, binding of the sterically demanding phosphine oxides. Highly monodispersed palladium nanoparticles, capped with either TOP or TOP and oleylamine, were also prepared by the thermolysis of a Pd–TOP complex, with the size controllable from 3.5 to 7 nm in diameter by altering the surfactants.[96] In a further development, mesityl complexes of copper, silver and gold have been used as

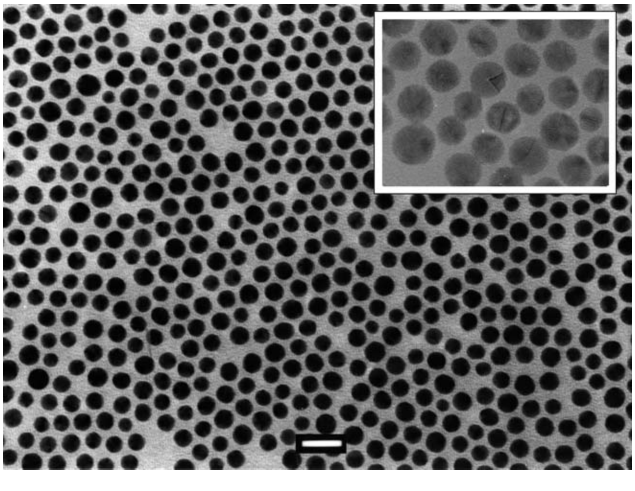

Fig. 5 9 nm gold particles capped with TOPO and octadecylamine, self assembled on a copper grid (bar = 20 nm).[29] Inset, high resolution image showing twinning planes and facets.

precursors to monodispersed nanoparticles capped with amines, or in the case of copper and silver, a mixture of amines and TOPO.[97]

In conclusion, a wide range of metal nanoparticles can be prepared using organometallic-based strategies. The size and shape can be controlled by altering experimental conditions (often based on capping agents) and designer materials can be produced, exhibiting novel magnetic, catalytic or optical properties. The kinetics of metals systems are largely unexplored, although Peng and Alivisatos have made notable advances in describing the ligand–metal interactions and growth conditions in the synthesis of analogous semiconducting nanoparticles.[98–100] Dushkin *et al.* have also reported an in-depth study on the kinetics of semiconducting particles, which give a valuable insight into organometallic routes to nanomaterials, despite the obvious differences in chemistry.[101] It should also be stressed that metal nanoparticles are not simple solid-state materials, and often exhibit unusual ripening processes that have not been explored in depth.[102] This branch of nanochemistry is very much in its infancy, and numerous advances and applications are expected in the very near future.

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