Synthesis and Characterization of Magnetic Nanoalloys from Bimetallic Carbonyl Clusters

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Magnetic nanoparticles are potentially useful for biomedical research because of their unique chemical and physical properties. In particular, magnetic alloy nanoparticles are of interest because of their magnetic properties and chemical stability. However, controlling the composition of magnetic alloy nanoparticles can be difficult when they are produced from two or more precursors. This could be overcome by using a single precursor of bimetallic carbonyl cluster in a thermal decomposition process. We have used this novel synthesis method to produce $FeCo_3$, $FeNi_4$, $FePt$, and Fe_4Pt alloy magnetic nanoparticles, with average diameters of 7.0, 4.4, 2.6, and 3.2 nm. 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. Different 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.

Introduction

Magnetic nanoparticles (NPs) have many potential applications in biomedicine and engineering.[1-3] For biomedical applications, iron oxide NPs can be used because of their biocompatibility and biodegradability. However, iron oxide NPs have a relatively low saturation magnetization compared to transition metal magnetic NPs, which requires the use of NPs that are tens of nanometers in diameter.[4] The use of larger NPs can be a problem, especially if they aggregate, as they could potentially cause an embolism and damage to blood vessels.[5] It is therefore desirable to use smaller NPs that have enhanced magnetic properties, e.g., those made from zerovalent metals such as Co or Fe and alloys that contain these

metals such as Fe−Pt, Fe−Ni, or Fe−Co. However, Co or Fe NPs are difficult to obtain because of their sensitivity to oxidation in the atmosphere, which diminishes their magnetic properties.[6,7] This makes magnetic alloy NPs particularly interesting because of their high saturation magnetization[8] and resistance against oxidation.

Alloy nanoparticles form when two or more metals coaggregate to produce compositionally ordered structures, with properties that differ from those of bulk alloys or NPs of the individual components.[9-13] A variety of methods have been used to synthesize alloy NPs such as

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coreduction of mixed metal ions in aqueous solution[14−19] and polyol,[8,20,21] sequential reduction[22−25] of metal ions, electrochemical methods,[26−28] radiolysis,[29−31] microwave plasma decomposition,[32] reduction of double complexes,[33,34] and the thermal decomposition of two or more metal carbonyls.[7,35−37] A "true" alloy nanoparticle is formed when there is no preferential aggregation of metal atoms into monometallic areas of the nanoparticle, i.e., there is not any kinetically induced phase separation of the constituent metal atoms of the alloy nanoparticles.[36] This can prove difficult when producing alloy NPs from separate sources, such as the decomposition of two or more carbonyl compounds because of their different decomposition temperatures.[21] Other processes, such as polyol reduction, have produced alloy NPs such as Fe−Co and Fe−Ni; however, controlling the composition of the NPs remains a challenge.[21]

These problems may be overcome by employing bimetallic compounds as single-source molecular precursors, in order to have different metals always in intimate contact. Among these, bimetallic carbonyl clusters are quite attractive, because they can be prepared with different compositions and, moreover, they are decomposed under very mild conditions.[38,39] The use of a single bimetallic precursor can avoid the problems associated with the different reaction kinetics when using more than one precursor. This approach has been well-documented by the use of homo- and bimetallic metal carbonyl clusters for the preparation of supported metal nanoparticles to be used in heterogeneous catalysis.[40−45] Conversely, very little is known on the use of bimetallic carbonyl clusters as precursors of ligand stabilized bimetallic magnetic nanoparticles. An interesting exception is represented by the use of the neutral $Fe_3Pt_3(CO)_{15}$ for the preparation of FePt nanoparticles having high coercitivity.[46] A larger spectrum of metals and compositions may be reached by using anionic instead of neutral bimetallic carbonyl clusters, because of the richer chemistry of the former.

Thus, we herein report on the preparation of different types of bimetallic magnetic nanoparticles starting from molecular bimetallic carbonyl cluster anions, i.e., $[FeCo_3(CO)_{12}]^-$,[47,48] $[Fe_3Pt_3(CO)_{15}]^{2-}$,[49] $[FeNi_5(CO)_{13}]^{2-}$[50] and $[Fe_4Pt(CO)_{16}]^{2-}$.[49] In our experiments, the thermal decomposition of the anionic bimetallic carbonyl clusters systematically resulted in the formation of a series of alloy NPs, with a composition reflecting that of the precursor, i.e., $FeCo_3$, FePt, $FeNi_4$, and Fe_4Pt. Thus, this method seems to eliminate the problems of phase separation and composition control. From this series, the $FeCo_3$ NPs were chosen for further investigation because of their high saturation magnetization and relatively large size. The reaction conditions used to synthesize these NPs were investigated to determine the effect this would have upon the physical characteristics of the NPs.

Experimental Section

All chemicals and solvents were obtained from Sigma-Aldrich Ltd. (Gillingham, UK) and used without further purification. The cluster salts $[NEt_4][FeCo_3(CO)_{12}]$,[47,48] $[NMe_3CH_2Ph]_2$-$[Fe_3Pt_3(CO)_{15}]$,[49] $[NMe_4]_2[FeNi_5(CO)_{13}]$,[50] and $[NMe_3CH_2Ph]_2$-$[Fe_4Pt(CO)_{16}]$[49] were prepared according to methods in the literature. Their structures are shown in the Supporting Information, Figure S6−S9.

Using standard airless conditions, in a typical synthesis, oleic acid, OA, (22 mM) and trioctylphosphine oxide, TOPO, (8.8 mM) were dissolved in anhydrous 1,2-dichlorobenzene, DCB, (4 mL) and heated to 186 °C. A solution of the bimetallic

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Table 1. Composition of the Synthesized Alloy Nanoparticles as Determined by Elemental Analysis

precursor	Fe (% w/w)	Co (% w/w)	Ni (% w/w)	Pt (% w/w)	relative[a] molar amount Fe	relative molar amount Co	relative molar amount Ni	relative molar amount Pt	nanoparticle composition
$[FeCo_3(CO)_{12}]^-$	8.35	25.97			0.15	0.44			$FeCo_3$
$[FeNi_5(CO)_{13}]^{2-}$	10.94		44.83		0.20		0.76		$FeNi_4$
$[FePt(CO)_{15}]^{2-}$	11.58			37.47	0.21			0.19	$FePt$
$[Fe_4Pt(CO)_{16}]^{2-}$	16.02			14.6	0.29			0.07	Fe_4Pt

[a] Relative molar amounts for each element were calculated by dividing the percentage weight by the atomic mass of that element.

carbonyl cluster (52 mM) in DCB (1 mL) was rapidly injected into the ligand solution with vigorous stirring. The mixture was heated at this temperature for 10 min then cooled to room temperature. To investigate the effect of the nature of the ligand upon the size, shape, and composition of the NPs during synthesis, we replaced OA with either myristic acid (MA) or adamantane carboxylic acid (ADA) and TOPO was replaced with either hexadecyl amine (HDA) or oleyl amine (OLA) at the corresponding concentrations. All analysis and characterization was carried out on the as prepared NPs.

Transmission electron microscopy (TEM) samples were prepared by adding 20 μL of sample in DCB to a carbon-coated copper grid at room temperature and allowed to evaporate slowly in air. Images were obtained using an FEI Tecnai G2 120 kV TEM, operated at 100 kV and visualized using analySIS software. The diameter and standard deviation of the NPs was taken as the mean of a minimum of 200 NPs measured using Bersoft Image Measurement 5.2 software. Magnetic measurements, including the zero-field-cooled (ZFC), field-cooled (FC) magnetization, and hysteresis loops, were carried out in a Quantum Design MPMS SQUID magnetometer. Elemental analysis was carried out using a Spectro Ciros[CCD] ICP-AES. X-ray diffraction (XRD) patterns were obtained using a Rigaku RINT-2500 diffractometer (Cu Kα radiation line $\lambda = 1.5408$ Å; 40 kV/100 mA).

Results and Discussion

Different bimetallic alloy NPs (i.e., $FeCo_3$, $FePt$, $FeNi_4$ and Fe_4Pt) have been prepared by thermal decomposition of bimetallic carbonyl clusters (i.e., $[NEt_4][FeCo_3(CO)_{12}]$,[47,48] $[NMe_3CH_2Ph]_2[Fe_3Pt_3(CO)_{15}]$,[49] $[NMe_4]_2[FeNi_5(CO)_{13}]$,[50] and $[NMe_3CH_2Ph]_2[Fe_4Pt(CO)_{16}]$,[49]) in the presence of ligands (vide infra). Very importantly, the composition of the alloy NPs produced was controlled exclusively, in most cases, by the composition of the bimetallic carbonyl cluster precursor employed, independently from other experimental conditions (vide infra). For example, the Fe−Co NPs were produced from $[NEt_4][FeCo_3(CO)_{12}]$ retained the 1:3 composition of the precursor. The composition of the alloy NPs was calculated from the relative mass of each metal by elemental analysis (Table 1). This would indicate that the decomposition of the molecular cluster follows the classical LaMer model,[51] where supersaturating of solutes is followed by the formation of initial metal nuclei, then their agglomeration and growth.

All the NPs produced were spherical and the average diameter of the NPs varied depending on their metal composition. Figure 1a, for example, shows a TEM image of $FeCo_3$ NPs, synthesized from $[NEt_4][FeCo_3(CO)_{12}]$,

Table 2. Effect of Changing the Hydrocarbon Tail and/or the Head Group of the Stabilizing Ligand on the Size of $FeCo_3$ NPs

	Size of $FeCo_3$ NPs (nm)		
	hexadecyl amine	oleyl amine	TOPO
myristic acid	7.6 ± 1.4	6.8 ± 0.7	6.8 ± 1.0
oleic acid	8.1 ± 1.0	7.6 ± 1.8	6.8 ± 0.8
adamantane carboxylic acid	6.8 ± 0.8	7.1 ± 1.5	5.3 ± 0.7

with an average diameter of 6.8 ± 0.8 nm, whereas Figure 1b shows a TEM image of $FeNi_4$ NPs, produced under the same conditions (reactant concentrations, reaction temperature, and time), except using $[NMe_4]_2[FeNi_5(CO)_{13}]$ as a precursor, with an average diameter of approximately 4.1 ± 0.7 nm. Other compositions such as $FePt$ and Fe_4Pt, can also be obtained by simply changing the carbonyl cluster precursor (Figure 2).

The reaction conditions used in the synthesis of $FeCo_3$ NPs, such as the nature of the ligand, ligand concentration, and reaction temperature, were varied to investigate the effect it would have upon the size and shape of the synthesized NPs. Different sets of $FeCo_3$ NPs were synthesized in the presence of a combination of ligands with different hydrocarbon chain structures, i.e., "straight" (e.g., MA, HDA), "kinked" (e.g., OA, OLA) or "bulky" (e.g., TOPO, ADA). The size of the synthesized NPs are summarized in Table 2, and it was observed that varying the nature of the ligand resulted in a slight variation in nanoparticle size (from 5.3 to 8.1 nm), however, this was not statistically significant ($P = 0.02$, where P is the probability value). Previous research conducted by our group found that these ligands have been shown to affect both the size and shape of alloy NPs that were produced by the concurrent thermal decomposition/reduction of two or more precursors.[52] However, the present research, using $[NEt_4][FeCo_3(CO)_{12}]$ as a single precursor, found that changing the nature of the ligand while keeping all other reaction conditions constant (e.g., reactant concentration, temperature, reaction time) had no effect upon the shape or composition of the obtained $FeCo_3$ NPs. The TEM images and size distributions of NPs are shown in the Supporting Information, Figures S1−S3. Similar results were observed when $FeCo_3$ NPs were synthesized in OA at concentrations of 11 or 44 mM, while maintaining the TOPO concentration at 8.8 mM and all other reaction synthesis conditions.

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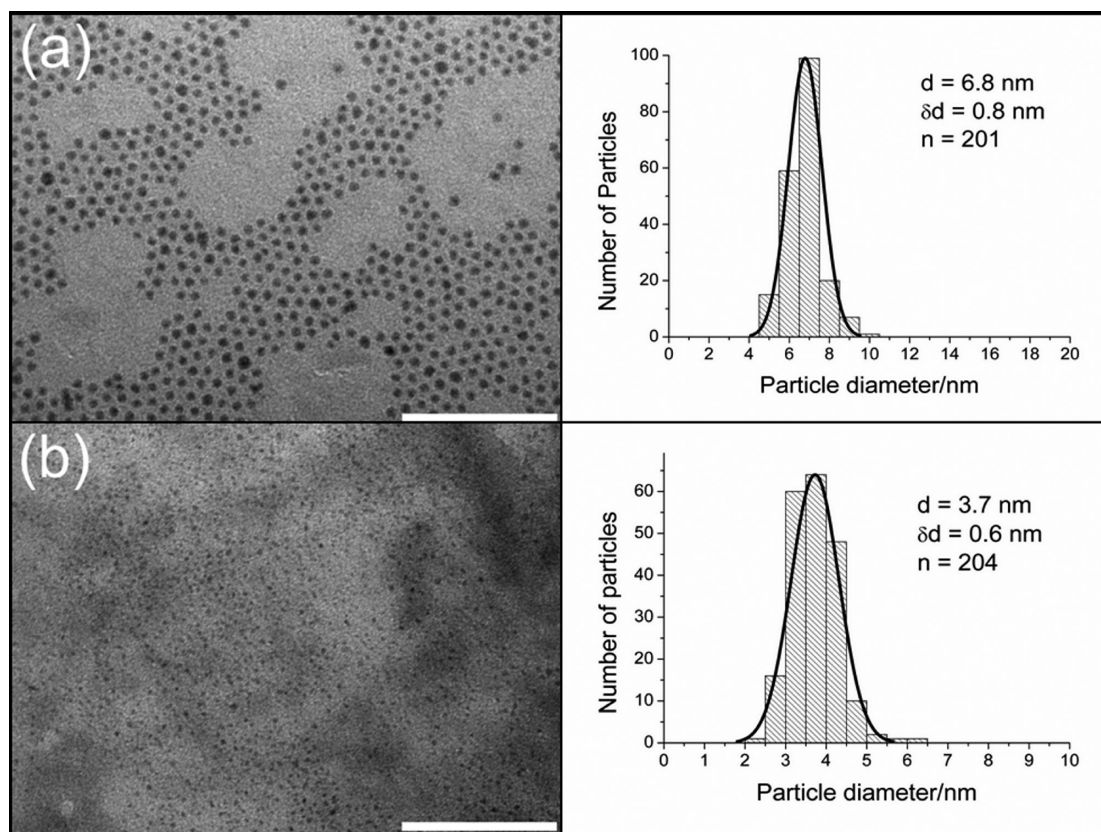
Figure 1. Typical TEM images and size distributions of (a) FeCo$_3$ and (b) FeNi$_4$ NPs synthesized by the thermal decomposition of [NEt$_4$][FeCo$_3$(CO)$_{12}$] and [NMe$_4$]$_2$[FeNi$_5$(CO)$_{13}$], respectively. Bar = 100 nm.
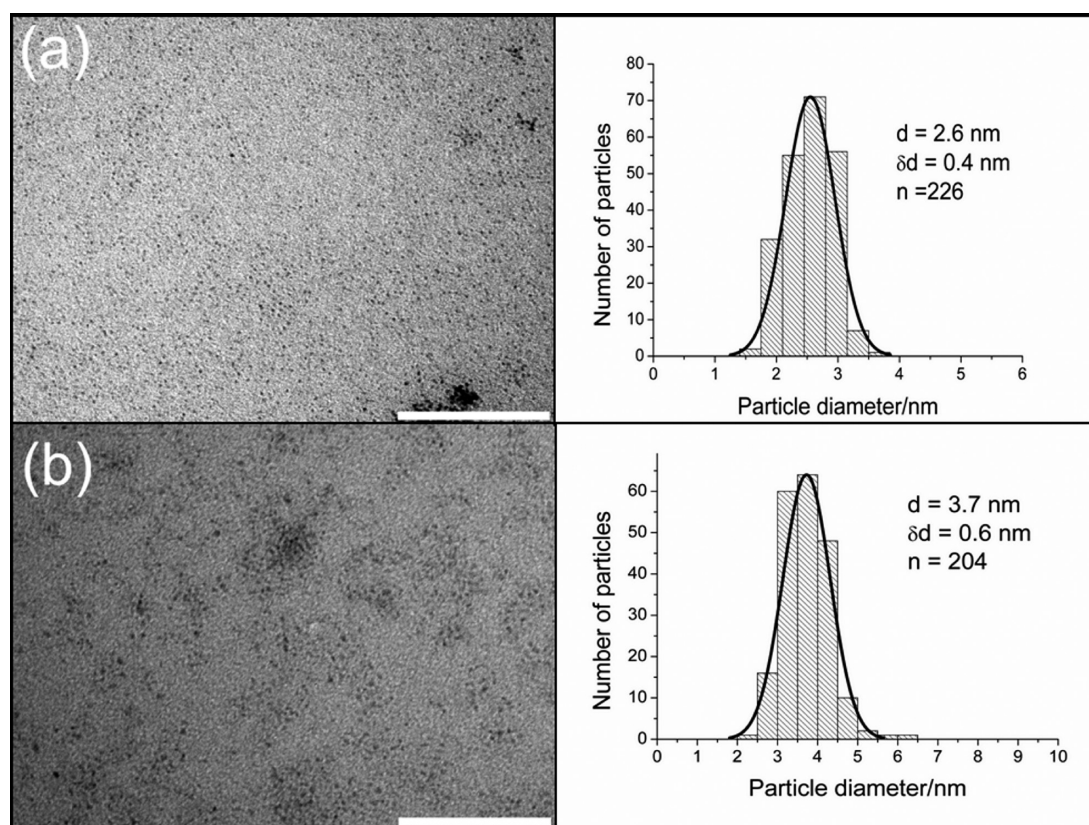

Figure 2. TEM images and size distributions of (a) FePt and (b) Fe$_4$Pt synthesized by the thermal decomposition of [NMe$_3$CH$_2$Ph]$_2$[Fe$_3$Pt$_3$(CO)$_{15}$] and [NMe$_3$CH$_2$Ph]$_2$[Fe$_4$Pt(CO)$_{16}$], respectively. Bar = 100 nm.
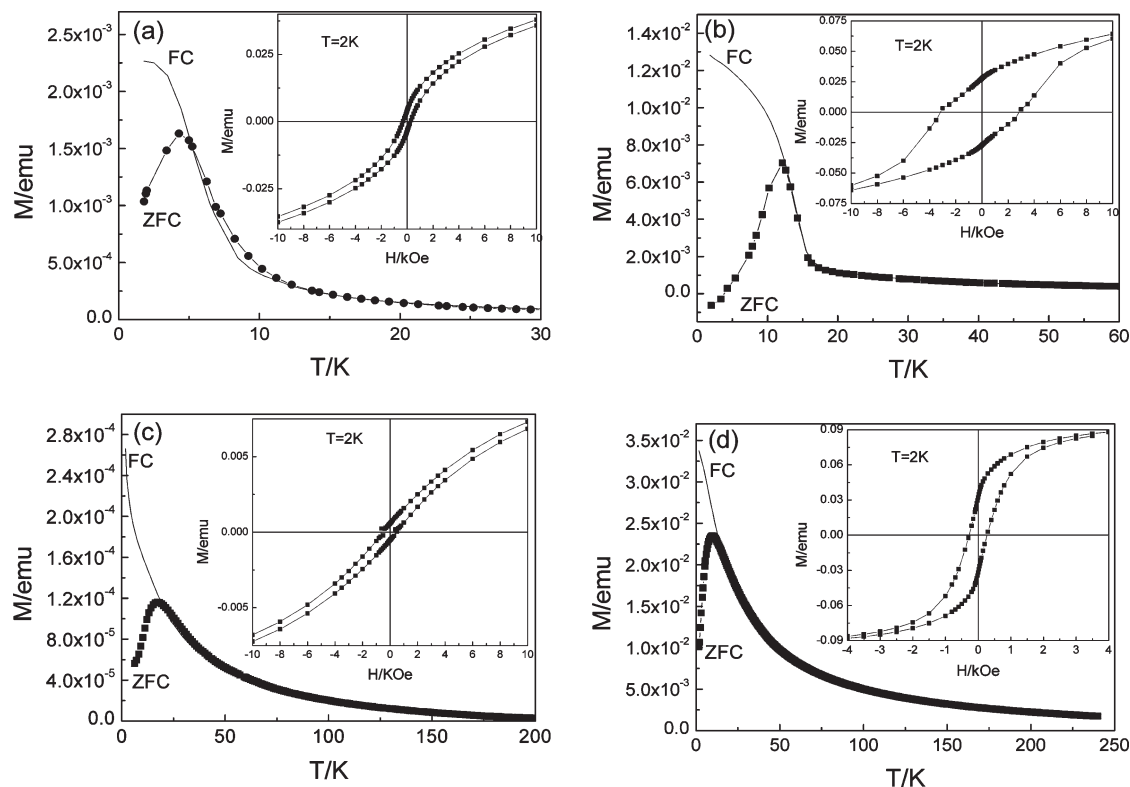
Figure 3. Zero-field-cooled and field-cooled magnetization curves of (a) $FeCo_3$, (b) $FeNi_4$, (c) FePt, and (d) Fe_4Pt alloy NPs synthesized by thermal decomposition of $[NEt_4][FeCo_3(CO)_{12}]$, $[NMe_4]_2[FeNi_5(CO)_{13}]$, $[NMe_3CH_2Ph]_2[Fe_3Pt_3(CO)_{15}]$, and $[NMe_3CH_2Ph]_2[Fe_4Pt(CO)_{16}]$. The insets show the hysteresis curves at 2 K for each sample.

Table 3. Summary of Some Physical Properties of the Alloy NPs Produced by Thermal Decomposition of Different Bimetallic Carbonyl Clusters

nanoparticle composition	diameter (nm)	T_b (K)	H_c at 2 K (Oe)	K (kJ/m^3)
$FeCo_3$	7.0	4	300	8
FePt	2.6	17	400	640
$FeNi_4$	4.4	12	3000	115
Fe_4Pt	3.2	10	250	130

TEM image and size distribution of the obtained NPs are shown in the Supporting Information, Figure S4. Syntheses at different reaction temperatures (e.g., 110, 186, or 286 °C) were carried out in the presence of OA (22 mM) and TOPO (8.8 mM), and no significant difference in the size, shape, or composition of the synthesized $FeCo_3$ NPs was observed (data not shown). This suggests that the dominating factor that controls the size, shape, and composition of the magnetic alloy NPs is the chemical composition of the bimetallic carbonyl precursor.

The zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves of magnetic alloy NPs are shown in Figure 3 and indicate that the NPs are superparamagnetic at room temperature. The sharp peaks in the ZFC curves and the splitting of the curves near to the blocking temperature indicate that the NPs have a narrow size distribution, which is consistent with the TEM images in Figures 1 and 2. Changing the ligand OA for MA and TOPO for HDA in the synthesis of the $FeCo_3$ NPs had no significant effect upon the magnetic properties of the synthesized NPs (see the Supporting Information, Figure S5). This suggests that the crystal structure of the NPs is not affected by the nature of the ligand used in their synthesis.
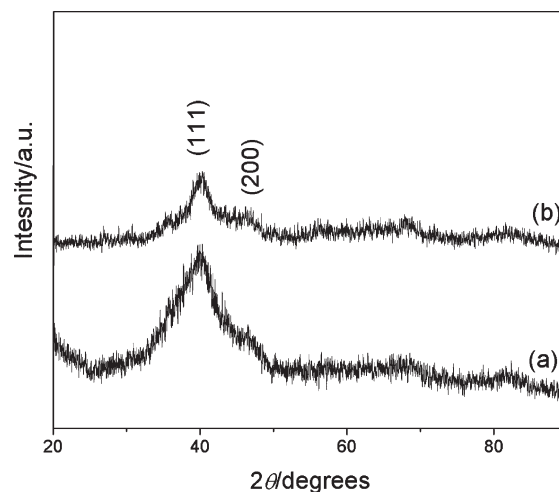

Figure 4. XRD patterns of (a) FePt and (b) Fe_4Pt alloy NPs synthesized by the thermal decomposition of $[NMe_3CH_2Ph]_2[Fe_3Pt_3(CO)_{15}]$ and $[NMe_3CH_2Ph]_2[Fe_4Pt(CO)_{16}]$, respectively.

Some physical properties of the magnetic alloy NPs are summarized in Table 3. An interesting point to note is the differences in the magnetic properties between the Fe−Pt alloy NPs. This type of material has many potential applications such as biomedicine,[53] catalysis[54] and data storage.[53,55] The XRD patterns in Figure 4 reveal that both FePt and Fe_4Pt NPs are fcc in structure (JCPDF

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00−002−1167). This would suggest that the differences in the magnetic properties of FePt and Fe_4Pt NPs are due to differences in their composition rather than differences in their crystal structure (e.g., fct Fe−Pt alloys have a typical anisotropy constant of 7000 kJ/m^3).[56] This indicates that subtle differences in the physical properties of the NPs can be achieved by use of the appropriate precursor.

Conclusion

A series of alloy NPs was synthesized by the thermal decomposition of bimetallic carbonyl clusters. The chemical and physical properties of the alloy NPs were only determined by the structure and composition of the cluster precursor. Changing the synthesis conditions, such as ligand concentration and ligand type had no significant effect upon the size, shape, or composition of the obtained NPs. This may be a result of the stability of the metal−metal bonds already present in the nucleus of the cluster that promote the development of new metal−metal bonds between the two elements in the forming NPs. The alloy NPs obtained are monodisperse and, more interestingly, they retain the composition of the molecular precursors, in the majority of cases. We have previously reported that water-soluble magnetic NPs can be produced in organic solvent with in the presence of an amphiphilic polymer;[57] we suggest that this approach could be used for the synthesis of magnetic alloy NPs. Alternatively, their hydrophobic surfaces can be replaced in a ligand exchange process[58]

with a hydrophilic ligand to render them water-soluble. This makes them potentially useful in biomedical applications such as MRI contrast agents, cell tracking and hyperthermia treatment of tumors. This work demonstrates that anionic bimetallic carbonyl clusters are ideal precursors for the preparation of alloy NPs with controlled composition and containing different metals (i.e., Fe−Co, Fe−Ni, Fe−Pt), which could be useful in applications such as catalysis and data storage. This is a versatile procedure and the scope of this work can be extended to several other nanoalloys (e.g., Fe−Rh, Fe−Pd, Fe−Ag, Fe−Au, Fe−Cd, Ni−Co, Ni−Rh, Ni−Pd, Ni−Pt, Ni−Cd, Ni−Au, Co−Pt; in different ratios), because of the fact that the chemistry of anionic bimetallic carbonyl clusters is well-established and rather rich.[59−61]

Supporting Information Available: TEM images and magnetic measurements of $FeCo_3$ NPs produced under different reaction conditions; XRD of $FeCo_3$ NPs molecular structures of precursors (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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