Reagent control over the size, uniformity, and composition of Co–Fe–O nanoparticles†

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Cobalt–iron–oxide (Co–Fe–O) nanoparticles have been prepared by the thermal decomposition in benzyl ether of Fe(acac)$_3$ and Co(acac)$_2$ in the presence of a mixture of oleic acid and oleylamine templating (surface capping) ligands, and 1,2-hexadecanediol (HDD) as an accelerating agent. The Co percentage may be tuned by adjusting the amount of Co(acac)$_2$ precursor without influencing the average particle size or particle size distribution. Counter to prior reports the presence of the HDD accelerating agent results in broader nanoparticle diameter distribution; however, for the smallest average sizes a small amount of HDD appears to be beneficial. The effects of changes in the templating ligand concentration and the relative amounts of oleic acid *versus* oleylamine have been investigated to optimize particle size distribution. Dilution of all the reagents is detrimental to particle size control. Our method for producing 5 nm Co–Fe–O nanoparticles with narrow distributions has reduced the amount of HDD while simultaneously reducing the reaction time.

Introduction

Recently there has been a dramatic increase in research towards the synthesis of nearly monodisperse metallic and metal oxide nanoparticles.[1] This has been driven in part by their potential applications as contrast agents,[2] magnetic recording media,[3] energetic materials,[4] and catalyst precursors for the growth of carbon nanotubes (CNTs).[5] In the majority of applications control over the size and size distribution are important considerations. Many synthetic approaches exist for the production of metallic and metal oxide nanoparticles with some demonstrating more control over particle diameter and size distribution than others.[1] Common approaches towards the preparation of narrowly disperse metallic and metal oxide nanoparticles include co-precipitation of metals salts,[6] polyol process,[7] thermal decomposition of organometallic precursors,[8] or hydrolysis of metal salts (*e.g.*, sol–gel).[9] Of these methods the thermal decomposition of organometallic precursors in non-coordinating, high boiling organic solvents in the presence of templating/surface capping ligands has proven to be a robust approach towards achieving both mono- and polymetallic nanoparticles with decent control over nanoparticle size and distributions.[10]

Nanoparticle synthesis in non-coordinating solvents was originally developed for the synthesis of semiconductor nanocrystals;[11] however, recently it has become an attractive method for producing metallic and metal oxide nanoparticles. For example, the one-pot synthesis has been achieved of nearly monodisperse magnetite (Fe$_3$O$_4$) and various bimetallic nanoparticles (*e.g.*, NiFe$_2$O$_4$, MnFe$_2$O$_4$, and CoFe$_2$O$_4$) from the thermal decomposition of metal acetylacetonate (acac) precursors in high boiling aliphatic and aromatic ethers.[10,12,13] By altering reaction conditions, such as the metal precursor-to-surfactant (templating ligand) ratio, solvent, and metal precursor concentration, it was possible to produce nanoparticles with tunable sizes from 4 to 15 nm with very narrow size distributions.

Although the driving force towards the preparation of most ferrite nanoparticles has been to exploit their magnetic properties, the ability to produce metallic nanoparticles with very narrow size distributions is very attractive for CNT growth.[14] Aside from the difficulties associated with the physical processing of CNTs the large scale incorporation of CNTs into electronic devices and applications for energy storage and transfer has been plagued by the inability to produce CNTs with specific diameters and defined (n,m) types. Mostly this has been attributed to poor control over the catalyst precursors used to grow CNTs. The use of nearly monodisperse discrete metal catalysts could allow for the ability to produce CNTs with very narrow diameter distributions thereby enriching specific tube chiralities.

We are concerned with understanding CNT growth from the point-of-view of the catalyst precursors and particles from which they are grown. Specifically we are interested in determining what characteristics, mainly particle size and elemental composition, are desirable to obtain high yield CNT growth with respect to the number of catalytic species present. Because we are specifically targeting the growth of single walled carbon nanotubes (SWNTs) we have aspired to limit the overall metallic composition of the catalytic species to less than *ca.* 2500 metal atoms (4–5 nm in oxide form) by using discrete metal oxide nanoparticles as the catalyst precursors. Based on results from our previous research that show the advantages of Co–Fe alloys

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for CNT growth,[15] we have chosen to focus our initial investigation on Co–Fe–O nanoparticles with varying atomic percentages of Co since this composition offers potential advantages over the constituent oxides for high yield CNT growth.

Though the synthesis of $CoFe_2O_4$ nanoparticles has been previously reported,[16] limited studies exist that observe the specific roles of the individual reactants. Typical reactions conditions for these particles include the use of acetylacetonate precursors dissolved in high boiling organic solvents. The addition of templating ligands to the reaction mixture promotes the decomposition of the metal precursors eventually leading to formation of a seed from which nanoparticle growth occurs. Additional reactants are often added to serve as activation agents resulting in lower reaction temperatures while simultaneously enhancing the overall rate of the reaction.

The mechanism for nanoparticle growth in non-coordinating solvents has been investigated in order to determine the effects of the various reactants on the overall size, shape, and distribution of the nanoparticles.[17] Our interest, however, lay in tailoring the elemental composition of discrete nanoparticles and the effect this has on the growth of SWNTs; therefore we have expanded upon these previous studies and performed a detailed study attempting to understand the effects of the individual reactants with respect to nanoparticles size and particle size distribution, as well as investigating the ability to generate tunable Co content.

Experimental

Fe(acac)₃, oleic acid [$CH_3(CH_2)_7CH=CH(CH_2)_7CO_2H$, 90%], oleylamine ([$CH_3(CH_2)_7CH=CH(CH_2)_8NH_2$, >70%], 1,2-

hexadecanediol [$CH_3(CH_2)_{13}CH(OH)CH_2OH$, HDD], and benzyl ether were all purchased from Aldrich. Co(acac)₂ was purchased from Alfa Aesar. All chemicals were used as received. Particle size was determined by small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) measurements. SAXS measurements were obtained on a Rigaku Smartlab Diffractometer with a Cu-Kα radiation source. Samples were prepared by sealing a concentrated nanoparticle solution in hexanes into a 1 mm glass No. 50 capillary (Hampton Research). TEM analysis was performed on a high resolution JEOL 2100 field emission gun transmission electron microscope. Samples were prepared by drop drying a dilute nanoparticle solution in hexanes onto a 400 mesh copper grid with an ultrathin carbon film (Ted Pella, Inc.). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) measurements were obtained on a Perkin Elmer Optima 4300DV. Samples were prepared by digesting a 0.50 mL of a concentrated nanoparticle solution into 10 mL of a HNO_3 : HCl (4 : 1) mixture. A 0.25 mL sample of the digested sample was then diluted to 10 mL with a 2% HNO_3 solution. ICP-standards were obtained from Aldrich and Inorganic Adventures.

Synthesis of Co–Fe–O nanoparticles

A 100 mL round bottom flask fitted with a condenser, thermometer, magnetic stir bar, and rubber septa served as the reaction vessel. A general synthesis for the formation of Co–Fe–O nanoparticles was performed by combining Fe(acac)₃ (0.176 g, 0.50 mmol), Co(acac)₂ (0.064 g, 0.25 mmol), 1,2-hexadecanediol (0.388 g, 1.5 mmol), oleic acid (1 mL, 3 mmol), and

Table 1 Reaction conditions for Co–Fe–O nanoparticle formation

Reaction	Fe(acac)₃/mmol	Co(acac)₂/mmol	HDD/mmol	Oleic acid/mmol	Oleylamine/mmol	Particle size/nm	Distribution (%)
1	0.50	0.25	0.00	3.00	3.00	6.8	9.7
2	0.50	0.25	1.50	3.00	3.00	5.2	12.7
3	0.50	0.25	3.00	3.00	3.00	6.0	15.3
4	0.50	0.25	5.00	3.00	3.00	7.1	21.1
5	0.50	0.25	1.50	0.00	0.00	9.4	28.1
6	0.50	0.25	1.50	0.25	0.25	8.5	25.4
7	0.50	0.25	1.50	0.50	0.50	8.4	23.8
8	0.50	0.25	1.50	1.00	1.00	7.9	20.5
9	0.50	0.25	1.50	2.00	2.00	5.8	15.4
10	0.50	0.25	1.50	3.00	3.00	4.7	15.2
11	0.50	0.25	1.50	4.00	4.00	4.5	14.9
12	0.50	0.25	1.50	0.00	6.00	5.9	22.1
13	0.50	0.25	1.50	1.50	4.50	6.1	20.8
14	0.50	0.25	1.50	3.00	3.00	5.2	12.7
15	0.50	0.25	1.50	4.50	1.50	8.1	24.7
16	0.50	0.25	1.50	6.00	0.00	^{a}	^{a}
17	0.125	0.063	0.375	0.750	0.75	7.7	16.5
18	0.188	0.094	0.563	1.125	1.125	7.3	24.3
19	0.250	0.125	0.750	1.50	1.50	5.5	18.3
20	0.313	0.156	0.938	1.875	1.875	5.9	16.2
21	0.375	0.188	1.125	2.25	2.25	5.5	14.0
22	0.500	0.250	1.50	3.00	3.00	5.3	13.9
23	0.625	0.313	1.875	3.75	3.75	5.4	15.1
24	0.713	0.038	1.50	3.00	3.00	5.2	13.3
25	0.638	0.113	1.50	3.00	3.00	4.9	13.3
26	0.563	0.188	1.50	3.00	3.00	5.2	15.8
27	0.500	0.250	1.50	3.00	3.00	5.3	13.9

^{a} Yield too low to allow suitable analysis.

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oleylamine (1 mL, 3 mmol) with benzyl ether (37.5 mL) in the reaction vessel. The reaction mixture was set to stir and the reaction vessel was externally heated under a blanket of nitrogen. The reaction mixture was heated to reflux (ca. 270–280 °C) at a heating rate of ca. 10 °C min^{-1}. Reflux was maintained for 15 min after which the heat was removed and the reaction mixture was allowed to cool to room temperature. Upon cooling the reaction mixture was poured into EtOH and centrifuged. The resulting decant was discarded and the nanoparticles were washed again in EtOH and centrifuged again. The resulting decant was again discarded and the nanoparticles were dried and suspended in hexanes.

Results and discussion

Our initial investigation focused on establishing the appropriate reaction conditions that produced the overall smallest nanoparticles with the narrowest size distributions. This was accomplished through a series of studies focusing on individual components of the reaction system such as the amount of accelerating (reducing) agent, templating ligand, and solvent volume. For this investigation we chose to use reaction conditions to that of Sun et al.[10,13] as the baseline. These include the use of Fe(acac)$_3$ and Co(acac)$_2$ as the metal precursors, oleic acid, and oleylamine as templating ligands, 1,2-hexadecanediol (HDD) as an accelerating agent, and benzyl ether (bp = 298 °C) as the solvent. In a typical reaction all reactants were heated to between 270 °C and 280 °C depending on the amounts of the templating ligands and HDD used for the specific reaction conditions. Nanoparticle formation was observed by a change in the reaction color from a deep red to a blackish-brown. Nanoparticle sizes and distributions were determined by small angle X-ray scattering (SAXS) from concentrated hexanes solutions providing for accurate particle size and distribution
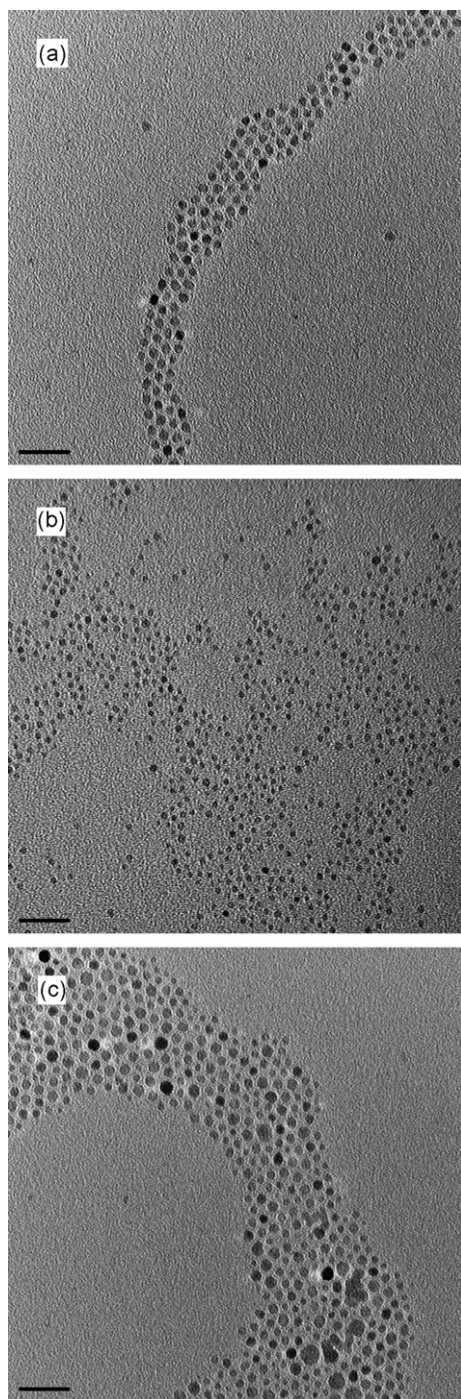

Fig. 1 Representative TEM images of Co–Fe–O nanoparticles formed in the presence of (a) 0 mmol (1), (b) 1.5 mmol (2), and (c) 5.0 mmol (4) of 1,2-hexadecanediol (HDD). Scale bars are 30 nm.
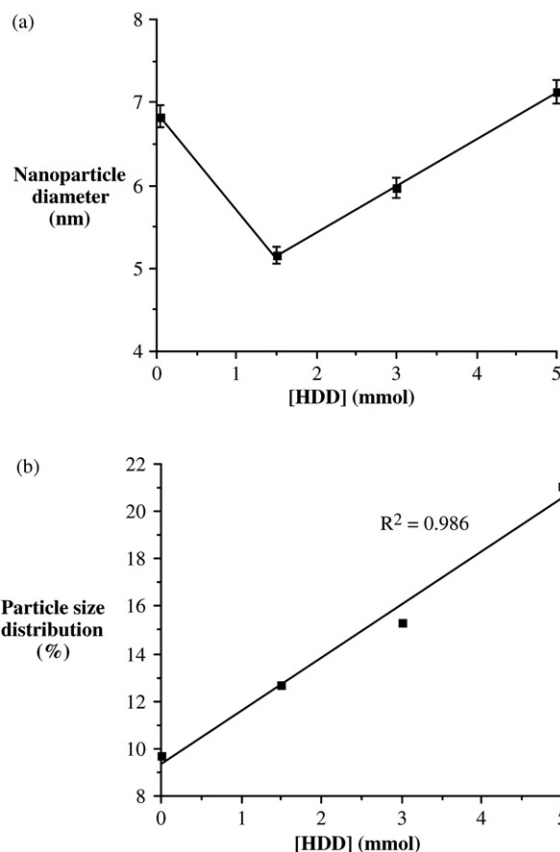

Fig. 2 Dependence of Co–Fe–O nanoparticle size (a) and particle size distribution (b) as a function of 1,2-hexadecanediol (HDD) concentration.

measurements from the bulk solution. Particle morphology (shape and distribution) was confirmed by transmission electron microcopy (TEM).

We note that this work was all performed with the use of a Variac™ and heating mantle. Possibly even finer control over the nanoparticle diameter distributions may be obtained by use of external oil baths and thermocouple control over the heating rates.

Dependence on 1,2-hexadecanediol concentration

The $CoFe_2O_4$ nanoparticles prepared by Sun et al.[10,13] required a five-fold excess of HDD and very high metal-to-solvent volume ratios. Our initial study was to determine the effect which the HDD had on the overall particle sizes and distributions to determine if the five-fold excess was necessary to achieve nanoparticle formation and uniform distributions. In addition, HDD is the most expensive reactant within the system, therefore if the amount of HDD can be reduced while still achieving similar results this would be beneficial to the overall cost of production. With this in mind we performed a series of four reactions with the HDD concentrations varied while maintaining constant concentrations for all additional reactants at a constant volume of benzyl ether, as shown in Table 1 along with a summary of the nanoparticle sizes and distributions as determined by SAXS measurements. TEM images of nanoparticle samples 1, 2, and 4 are shown in Fig. 1.
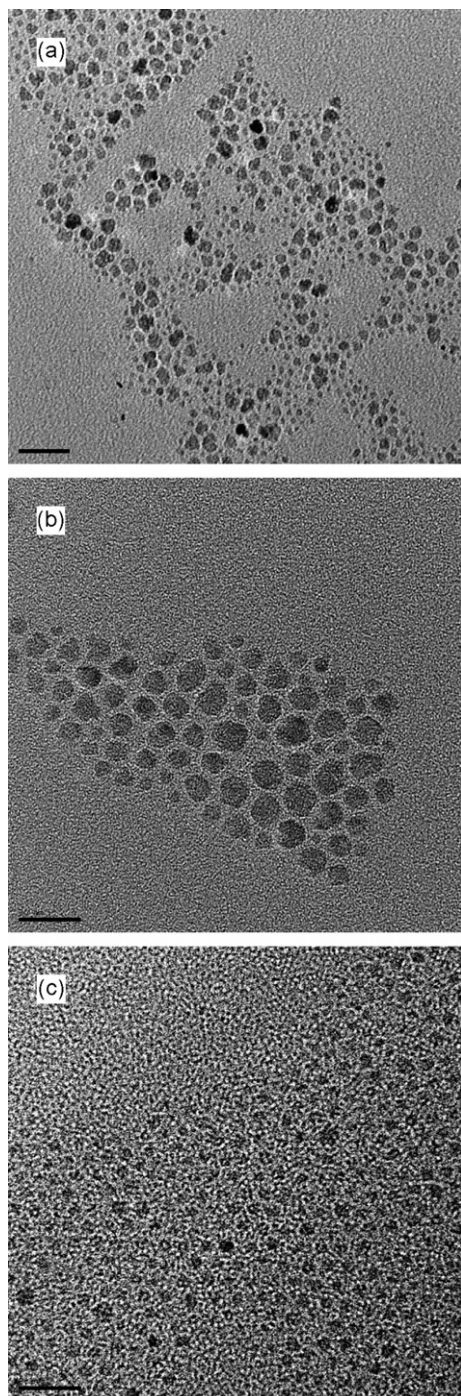

Fig. 3 Representative TEM images of Co–Fe–O nanoparticles formed (a) in the absence of ligand (5), and in the presence of (b) 0.5 mmol (6) and (c) 8.0 mmol (11) of ligand (oleic acid + oleylamine). [Oleic acid] = [oleylamine]. Scale bars are all 20 nm.
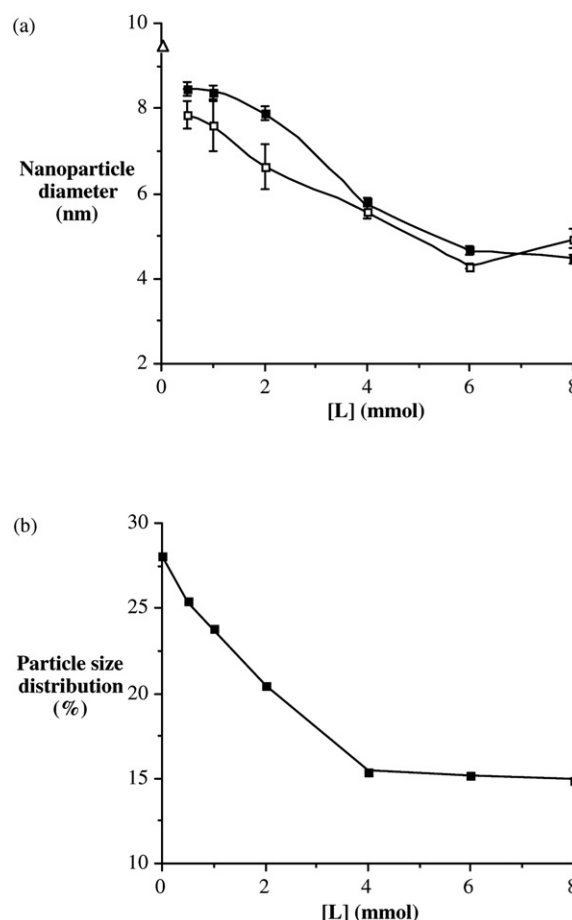

Fig. 4 Dependence of (a) Co–Fe–O nanoparticle size as measured by SAXS (■) and TEM (□), and particle size distribution (b) as a function of the concentration of templating ligand (oleic acid and oleylamine), where [oleic acid] = [oleylamine]. The particle size for sample 5 (no oleic acid and oleylamine) is shown for comparison (△).

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Performing the reaction in the absence of HDD (**1**) resulted in particles of comparable average size to those obtained using the literature conditions (**4**).[10,13] However, the presence of HDD did appear to have some affect on the ability to obtain small diameter nanoparticles since a decrease in the average nanoparticle diameter was observed as the amount of HDD was decreased (Fig. 1b and 2a).

Possibly more interesting than the effect on particle size is the linear dependence of the nanoparticle diameter distributions as a function of the HDD concentration (Fig. 2b). The absence of HDD resulted in nanoparticles with the narrowest distribution suggesting that the synthesis resulted in nearly monodisperse particles (Fig. 1a). As the HDD concentration was increased to 5 mmol, however, the particle size distribution doubled. There does not appear to be any significant effect of the morphology of the particles by the presence of HDD (Fig. 1).

Based upon the foregoing, the addition of HDD is detrimental to the uniformity of the nanoparticle size, but small amounts of HDD either promote nanoparticle nucleation or limit growth (hence a small average particle size). The use of HDD is a compromise between a small average particle size and a narrow distribution. Finally, given the high cost of HDD, these results suggest that (within the present reagent mixture) unless particles sizes <7 nm are needed it is not necessary to add HDD to the reaction mixture.

Dependence on ligand concentration

After determining the optimum concentration of HDD for the formation of nanoparticles with small diameters with respectable diameter distributions (*i.e.*, 1.5 mmol) the next series of reactions were performed to observe the effect of varying the total concentration of templating ligands. Since it is believed that oleic acid is responsible for the *in situ* formation of the metal oleate complexes prior to nanoparticle formation,[10,13] we expected to see dramatic changes in the average diameters and distributions as we progressed to lower concentrations of ligand. Conversely it was expected that smaller nanoparticle diameters would be achieved by increasing the concentration of ligand thereby providing more ligand to stabilize the increase in surface area that would accompany the decrease in size. The ratio between oleic acid and oleylamine was held constant in these experiments. TEM images for nanoparticles **6–11** are shown in Fig. 3 and a summary of reaction conditions and the nanoparticle diameters and distributions can be found in Table 1.

The overall trend observed for reactions **6–11** is similar to that expected, *i.e.*, as the total ligand concentration was decreased an increase in the average nanoparticle size (Fig. 4a), accompanied by a dramatic increase in the diameter distribution (Fig. 4b). Increasing the amount of templating ligand resulted in a decrease in the nanoparticle diameter; however, the decrease does appear
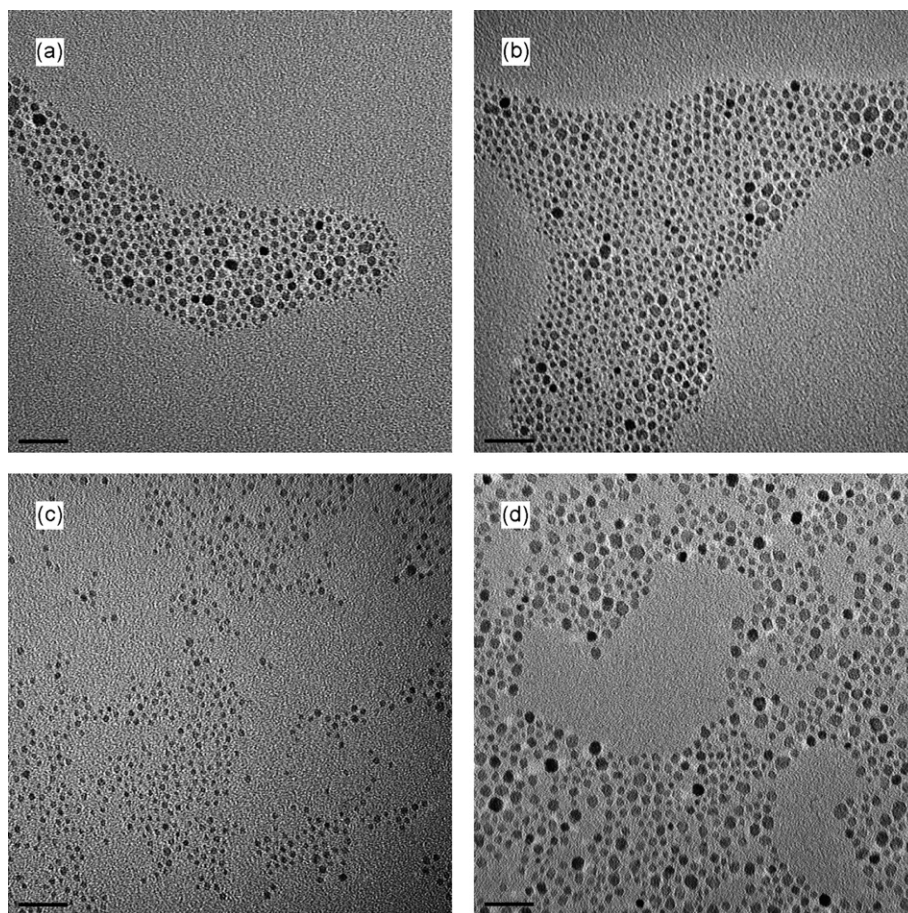

Fig. 5 TEM images of Co–Fe–O nanoparticle formed with varying oleic acid : oleylamine ratio. (a) 0 : 6.0 mmol (**12**), (b) 0.33 (**13**), (c) 1.0 (**14**), and (d) 3.0 (**15**). [oleic acid] + [oleylamine] = constant. Scale bars are all 20 nm.

to approach a limit of approximately 4.5 nm. A similar limit is observed with regard to particle size distribution (Fig. 4b). Although nanoparticle yields were not directly determined a visible decrease in yield was also observed as the ligand concentration was decreased.

Surprisingly nanoparticle formation was observed in the absence of any templating ligands (Fig. 4a). This is interesting considering that it is generally accepted that the formation of metal oleates precedes the formation of nanoparticles under the conditions studied,[10,13] however the absence of any oleic acid suggests that possibly the formation of metal alkoxides occurs in the presence of HDD and could provide a pathway for nanoparticle formation. The particles that were formed in the presence of HDD only (**5**) were soluble in hexanes indicating that the HDD was also serving as a templating ligand. The fact that the observed average particles diameters (9.4 nm) in the absence of oleic acid and oleylamine are larger than the trend shown in Fig. 4a suggest that HDD is not as efficient a ligand as oleic acid and oleylamine. However, the fact that nanoparticles are formed suggest that HDD may compete with the templating ligands when used in large excess possibly leading to an increase in the particle size distributions, which supports our previous observations (Fig. 2a).

Dependence on oleic acid : oleylamine ratio

The following series of experiments were performed to determine which of the templating ligands, oleic acid or oleylamine, was responsible for the production of small particle diameters and narrow distributions. Previously reactions have generally been performed under equal concentrations of oleic acid and oleylamine.[10,13] By adjusting the ratios of the two capping ligands, while holding all other reactions conditions constant, we hoped to determine the relative capping efficacy of the ligands (*i.e.*, carboxylic acid *versus* amine). A series of reactions were performed with varying oleic acid : oleylamine ratios ranging from oleic acid rich systems to oleylamine rich systems. A summary of the reaction conditions for the formation of nanoparticles **12–16**, along with the resulting diameters and size distributions is shown in Table 1. TEM images for nanoparticles **12–16** are shown in Fig. 5.

Noticeable changes in the nanoparticle diameter and distribution were observed resulting from the change in the templating agent ratios. The complete absence of oleylamine (**16**) resulted in extremely low yields and therefore particle size and distribution were not able to be determined. This suggests that oleic acid itself is not a sufficiently good ligand and/or the oleylamine provides an additional function. However, in general the oleic acid rich systems had larger nanoparticle diameters than the equivalent oleylamine rich samples (Fig. 6a) with a broad particle size distribution (Fig. 6b). As compared with the equimolar system (**14**) larger nanoparticle sizes were observed for the oleylamine rich systems along with a very broad nanoparticle distribution. The optimum conditions for small size and narrow distribution appear to be an equimolar mixture of oleic acid and oleylamine.

Based on the particle morphologies observed from TEM images (Fig. 5) it is clear that the oleylamine has a significant effect on maintaining the spherical shape of the nanoparticles. As the ratio was changed to an oleic acid rich system the
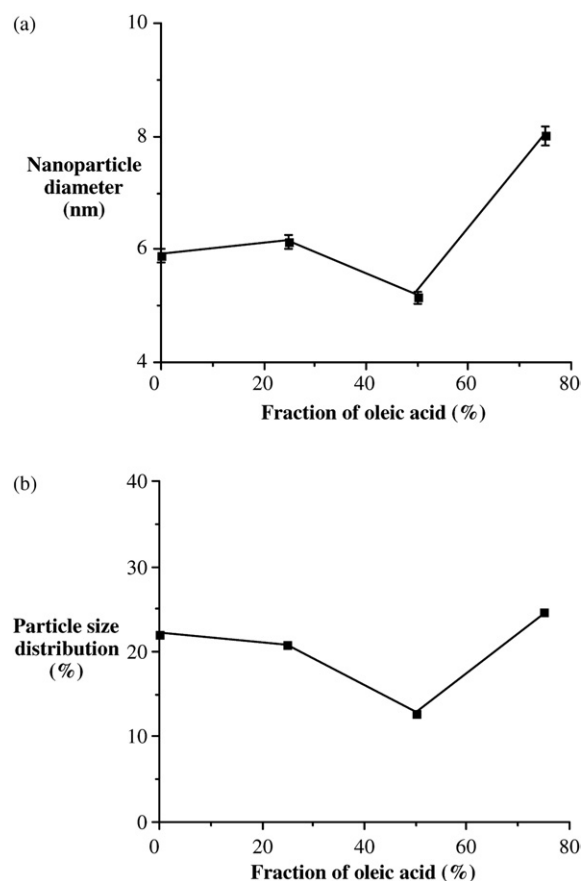

Fig. 6 Dependence of Co–Fe–O nanoparticle size (a) and particle size distribution (b) as a function of the oleic acid to oleylamine ratio.

nanoparticles formed were much more faceted and did not maintain their spherical character (Fig. 5d).

Dependence on metal precursor concentration

Irrespective of the chemistry that leads to decomposition of the metal precursors to form molecular fragments, nanoparticle formation does not occur until these "monomers" combine to form nuclei (seeds) from which nanoparticles eventually grow. Ideally nucleation and growth are separate events with growth not occurring until the solution has become saturated with nuclei. With this in mind we performed a series of experiments aimed at achieving the formation of very small nanoparticles through the dilution of the metal precursors. In theory this should favor the formation of nuclei over nanoparticle growth since the solution should be less saturated with nuclei at lower metal concentrations. To maintain similar reaction conditions for all metal concentrations the concentrations of HDD and the templating ligands were adjusted to be constant with respect to the concentration of metal precursors. A summary of these reaction conditions is presented in Table 1 and TEM images for the nanoparticles prepared in reactions **17–23** are shown in Fig. 7.

Under the reaction conditions investigated a decrease in nanoparticle size was not observed with a decrease in the total metal precursor concentration. Instead the opposite trend was
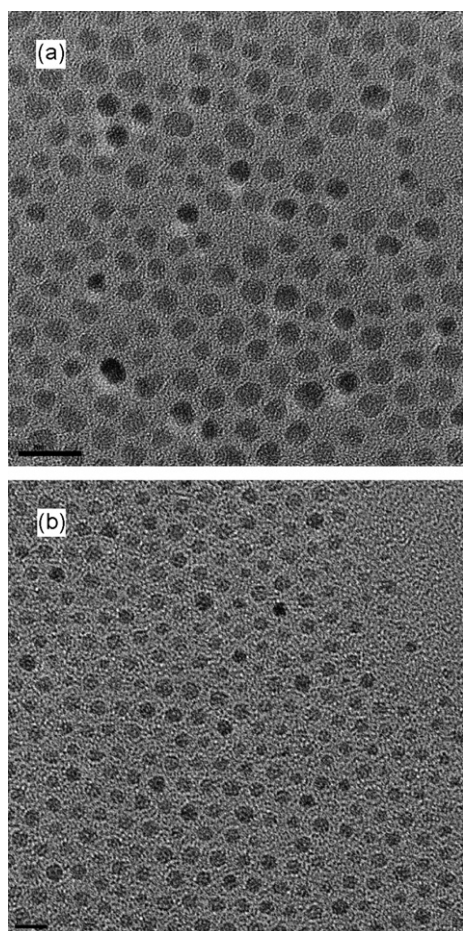
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Fig. 7 Representative TEM images for Co–Fe–O nanoparticles produced using (a) 5.0 mM (**17**) and 25.0 mM (**23**) total metal precursor concentrations. Scale bars are all 20 nm.

Fig. 8 Dependence of Co–Fe–O nanoparticle size (a) and particle size distribution (b) as a function of the metal precursor concentration.

observed (Fig. 8a). It is possible that at low concentrations surface effects may be important, however, it is also possible that as the metal concentration is decreased seeding is disfavored and hence where seeds are formed they grow to larger particles. Thus, the relative rate of the seed *versus* growth process would control the size of the particles. As the metal precursor concentration was decreased a slightly higher particle size distribution was observed, although this appears to reach a maximum before reducing again (Fig. 8b). Both measurements suggest an increase in metal precursor concentration results in both a smaller average size and a tighter distribution.

Controlling metal ratio

The majority of cobalt ferrites that have been reported in the literature are of the $CoFe_2O_4$ type. This specific ratio is important for magnetic studies, however much less important as a bimetallic catalyst for CNT growth. Towards this end we have performed a series of experiments to demonstrate the ability to produce Co–Fe–O nanoparticles with tunable atomic percentages for Co^{2+}. It is currently unknown what percentage is the most desirable for CNT growth but our previous studies with CoFe spin on catalysts have demonstrated that the incorporation of a small percentage of Co can drastically
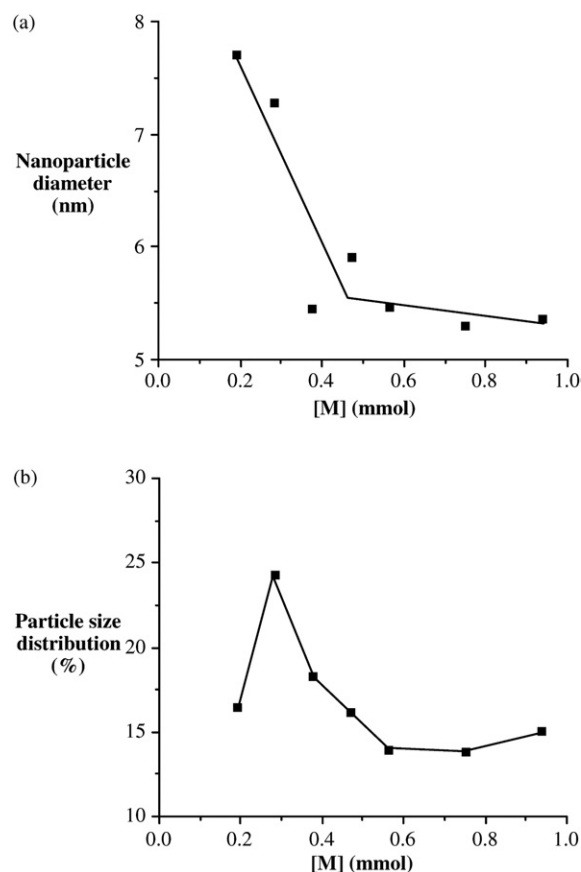
enhance the growth of CNTs over Fe alone.[15] If suitable CoFe catalysts are to be prepared it is important that the Co : Fe ratio be readily controlled, in particular by the reagent ratios. As such this will indicate whether the rate of precursor decomposition is comparable for each metal. To do this we performed a series of reactions (**24–27**) varying the $Co(acac)_2$ concentrations at 5–33% with respect to the total metal precursor concentration, *i.e.*, $Co(acac)_2 + Fe(acac)_3$. Since the total molar concentration of metal was constant throughout all four reactions the concentrations of HDD and templating ligands were also held constant. The nanoparticle diameters, distributions, and percentage Co for reactions **24–27** are shown in Table 1.

To determine the amount of Co that was effectively incorporated into the Co–Fe–O nanoparticles from the $Co(acac)_2$ precursors nanoparticle samples from each reaction were analyzed by ICP-AES. As may be seen from Fig. 9, not only did the Co concentration increase linearly with increasing $Co(acac)_2$ precursor concentration (Fig. 9, solid line) but also only a very small percentage of $Co(acac)_2$ was not directly incorporated into the nanoparticles (see difference between solid and dashed lines in Fig. 9). The nanoparticle diameters and distributions were also relatively constant (Table 1) which demonstrates the reproducibility of the reaction conditions and its insusceptibility to the metal composition within the range studied.
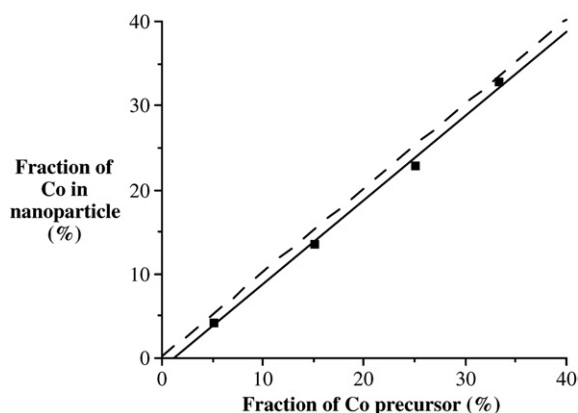
Fig. 9 Atomic percentage of cobalt incorporated into Co–Fe–O nano-particles *vs.* the amount Co(acac)$_2$ used in the reaction ($R^2 = 0.997$). Ideal ratio shown as dashed line.

Conclusions

We have reported the synthesis of Co–Fe–O nanoparticles with the ability to tune the Co concentration by adjusting the amount of Co(acac)$_2$ precursor. Importantly, the average particle size and particle size distribution are not affected significantly by the changes in the Co : Fe ratio within the range we desire for SWNT catalysts. However, we note that for Co rich compositions there are significant alterations in the particle size and shape. This method has been derived from several reports on the synthesis of CoFe$_2$O$_4$ nanoparticles that often incorporate a large excess of the reducing agent (accelerating agent), HDD. We have demonstrated that the presence of HDD results in broader nanoparticle diameter distributions, and it is therefore undesirable if the narrowest particle size distribution is sought. However, for the smallest average sizes a small amount of HDD appears to be beneficial. The optimum balance between small particle size and narrow distribution is obtained under our conditions with a molar HDD : M(acac)$_n$ ratio of 2 : 1. In a similar fashion we determined that a ligand : M(acac)$_n$ molar ratio of at least 8 : 1 provides the smallest and more uniform particles. Dilution of all the reagents is detrimental to particle size control, since presumably a critical concentration is necessary to ensure growth of each seed particle.

In summary, we have shown that 5 nm Co–Fe–O nanoparticles with narrow distributions can be synthesized with a reduced amount of HDD (the most expensive reagent), as compared to prior methods, while simultaneously reducing the reaction time from 2 h to only 40 min from start to finish. This is important when considering the issues of scale-up of nanomaterials.

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