

# Foam-based synthesis of cobalt nanoparticles and their subsequent conversion to Co<sub>core</sub>Ag<sub>shell</sub> nanoparticles by a simple transmetallation reaction

Tanushree Bala, Sujatha K. Arumugam, Renu Pasricha, B. L. V. Prasad\* and Murali Sastry\*

Materials Chemistry Division, National Chemical Laboratory, Pune – 411 008, INDIA.  
E-mail: sastry@ems.ncl.res.in; E-mail: blyprasad@dalton.ncl.res.in

Received 19th November 2003, Accepted 21st January 2004  
First published as an Advance Article on the web 18th February 2004

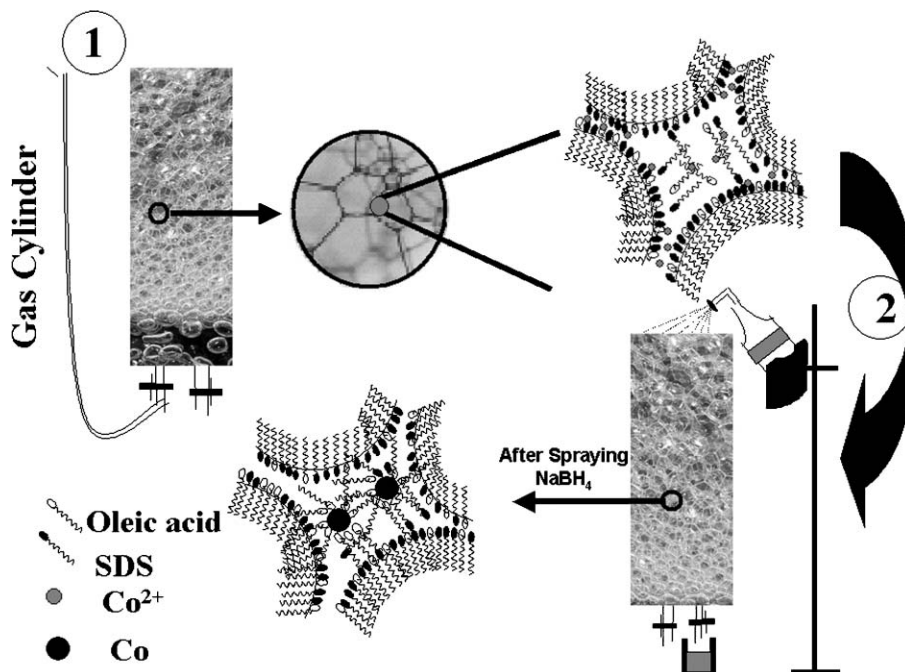
Cobalt nanoparticles have been synthesized *via* a novel, foam-based protocol. The foam is formed from an aqueous mixture of Co<sup>2+</sup> ions, an anionic surfactant and oleic acid where the cobalt ions are electrostatically entrapped by the surfactant at the thin borders between the foam bubbles and their junctions. The entrapped cobalt ions may be reduced *in-situ* by a moderately strong reducing agent resulting in the formation of nanoparticles with the foam playing the role of a template. The nanoparticles are immediately capped and stabilized against oxidation by oleic acid present in the foam matrix. The oleic acid-capped Co nanoparticles can be redispersed either in an aqueous or organic medium making this procedure very attractive. The cobalt nanoparticles are readily converted to Co<sub>core</sub>Ag<sub>shell</sub> nanoparticles by simple addition of a silver salt to the Co nanoparticle solution, the cobalt atoms on the nanoparticle surface acting as localized reducing agents for the silver ions.

## 1 Introduction

Transition metal nanoparticles, especially those of Fe, Co and Ni are considered to be very important for many technological<sup>1</sup> and catalytic<sup>2</sup> applications. When synthesized in an aqueous medium, these nanoparticles are favored for various biological applications.<sup>3</sup> However, one of the drawbacks of the synthesis of Fe, Co and Ni nanoparticles in an aqueous medium is that they are highly unstable and undergo oxidation necessitating their use immediately after preparation.<sup>4</sup> To overcome the problem of oxidation, attempts have been made to synthesize these nanoparticles in an organic environment with suitable protective agents.<sup>5</sup> In this paper we restrict our discussion to cobalt nanoparticles although the general chemistry involved in the nanoparticle synthesis of other two metals, namely Fe and Ni, is rather similar. The general synthetic procedure adopted for the synthesis of cobalt nanoparticles generally proceeds along two pathways: (i) a reverse micelle-based method, and (ii) purely organic solution-based methods. Reverse micelles are water droplets in oil stabilized by a monolayer of surfactant. Preparation of cobalt nanoparticles by this method involves multiple steps with the preparation of Co(AOT)<sub>2</sub> [AOT = bis(2-ethylhexyl) sulfosuccinate] being the first step.<sup>6a</sup> Subsequently, micellar solutions of Co(AOT)<sub>2</sub> with Na(AOT) and sodium borohydride in water with Na(AOT) are mixed to carry out the reduction of Co<sup>2+</sup> ions. They are then extracted under anaerobic conditions, covered with trioctylphosphine and redispersed in pyridine.<sup>6a</sup> Purely organic-based methods also involve complex synthetic procedures and high temperatures where [Co<sub>2</sub>(CO)<sub>8</sub>] is reduced with the hot trioctylphosphane-oxide (TOPO) reagent.<sup>6b</sup> The resulting Co nanoparticles are stabilized by the TOPO itself or in several cases by organic carboxylic acids like oleic acid and lauric acid, *etc.*, which are taken together with TOPO. High temperature polyol processes in which a high boiling point alcohol is used both as solvent and as reductant have also been successful in synthesizing cobalt nanoparticles.<sup>7</sup> Here, the typical synthetic procedure involves the addition of 1,2-dodecanediol to hydrated cobalt

acetate in diphenyl ether, in presence of oleic acid and trioctylphosphine at 250 °C, where particle size control is achieved by changing the relative concentrations of cobalt acetate and oleic acid. The above procedures have been quite successful in obtaining good quality Co nanoparticles in organic solvents and generally result in the formation of ordered arrays of superlattices upon drying on suitable substrates.<sup>5–7</sup> However, the complexity involved in the above synthetic procedures is quite evident, requiring many steps (reverse micelle method) and the use of non-regular chemicals (purely organic-based methods). It is also clear that scaling up of these synthetic procedures will be rather cumbersome. As mentioned above, for biological applications as well as scaling up purposes the synthesis of these nanoparticles in an aqueous medium is preferred. For these reasons we have been looking for alternative avenues for the synthesis of Fe, Co and Ni nanoparticles in water using simple salts routinely available in the laboratory as metal sources with an option for scaling up the yield relatively easily.

Herein we report the synthesis of cobalt nanoparticles using liquid foams as a template. Liquid foams have been restricted to the domain of physicists so far, where the majority of studies have been carried out to understand the physics of foams with respect to their formation and stability.<sup>8</sup> Davey and co-workers have used foams as templates for the nucleation of calcium carbonate crystals<sup>9</sup> but the possibility of carrying out chemical reactions in foams as a means of synthesis of materials with an in-built, scale-up option is still in its infancy. We have recently embarked on a program aimed at understanding the use of liquid foams in the synthesis of nanomaterials. Our strategy involves the formation of foams with aqueous solutions of metal ions and a suitable anionic or cationic surfactant (depending on the charge of the metal ion) as the first step as shown in Scheme 1. Subsequently, the desired chemical reaction such as reduction (for preparation of metal nanoparticles) or complexation (for the preparation of minerals) is carried out resulting in the formation of the required nanomaterials *within the foam*. The first studies on the formation of gold



**Scheme 1** Drawing showing the different steps involved in the foam-based synthesis of stable cobalt nanoparticles. Steps 1 and 2 are described in the text in detail.

nanoparticles in foams have yielded interesting results with some indication of morphology variation in the gold nanoparticles that reflects the complex structure of the foam.<sup>10</sup> In this paper, we extend this process for the synthesis of cobalt nanoparticles. Initial studies on the formation of Co nanoparticles by complexing  $\text{Co}^{2+}$  ions with pure sodium dodecyl sulfate (SDS) as the foaming surfactant did not yield stable nanoparticles in water. We then revised our strategy and oleic acid was taken along with SDS to form the foam. The resulting Co nanoparticles from this revised strategy were quite stable in both aqueous as well as organic media.

We have also devised a simple strategy to prepare core-shell structures of cobalt and silver, respectively. Preparation of core-shell nanomaterials assumes significance for two reasons: (i) improved stability of the nanoparticles, and (ii) flexibility in surface modification. It is recognized that it is quite easy to modify the surfaces of noble metal nanoparticles like gold and silver using simple thiol or amine chemistry.<sup>11</sup> We envisaged that if we can prepare core-shell structures of Co (core) and Ag (shell), it would not only render the cobalt nanoparticles more robust chemically but also provide us with the manipulative ability to modify the surface properties of the Co nanoparticles. To make the  $\text{Co}_{\text{core}}\text{Ag}_{\text{shell}}$  nanostructures, we have employed a simple transmetallation<sup>12</sup> reaction wherein the cobalt atoms residing on the surface of cobalt nanoparticles were effectively used as reductants for aqueous silver ions. Thus, the use of surface cobalt atoms as a reducing agent would yield core-shell structures thereby obviating the need to employ an external reducing agent for Ag ions. The Co and  $\text{Co}_{\text{core}}\text{Ag}_{\text{shell}}$  nanomaterials were characterized by transmission electron microscopy (TEM), selected area electron diffraction (SAED), Fourier Transform Infrared (FTIR) spectroscopy, UV-visible spectroscopy and powder X-ray diffraction methods. Presented below are details of the investigation.

## 2 Experimental details

### 2.1 Chemicals

Cobalt chloride hexahydrate ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ), SDS (sodium dodecyl sulfate), silver sulfate ( $\text{Ag}_2\text{SO}_4$ ), oleic acid (*cis*-9-octadecenoic acid,

$\text{C}_{17}\text{H}_{33}\text{COOH}$ ) and sodium borohydride ( $\text{NaBH}_4$ ) were obtained from Aldrich Chemicals and used as-received.

### 2.2 Preparation of cobalt-silver nanocrystals in aqueous SDS/oleic acid foam

In a typical experiment, a rectangular column of 50 cm height and a square base of  $10 \times 10 \text{ cm}^2$  with sintered ceramic discs embedded in it were used for generation of the foam. An aqueous mixture of 50 ml of  $1 \times 10^{-3} \text{ M}$  cobalt chloride solution, 10 ml of  $1 \times 10^{-3}$  oleic acid in methanol and 40 ml of  $1 \times 10^{-1} \text{ M}$  SDS was taken in the rectangular column and the foam built up by injecting nitrogen at a pressure of 1–5 psi through the porous ceramic disc fixed to the bottom of the foam column. Stable foams of up to 50 cm height could be routinely obtained. After carefully draining out the excess aqueous SDS/oleic acid and  $\text{CoCl}_2$  solution in the foam, the cobalt ions in the foam were subjected to reduction by spraying sodium borohydride solution into the foam. As the cobalt ions were reduced and nanoparticle formation progressed, the foam changed to a gray color and gradually collapsed. The collapsed foam solution containing the cobalt nanoparticles was collected through an outlet provided at the bottom of the column. This solution was then subjected to centrifugation at 5000 rpm for 30 min following which the pellet and supernatant were separated. The pellet was washed several times with ethanol before further characterizations were carried out. This pellet could be easily redispersed either in water or organic solvents like toluene. In a control experiment the foam was formed without prior addition of oleic acid and the reduction carried out. Although the experiment progressed exactly the same way as in the presence of oleic acid, the final cobalt nanoparticle solution was extremely unstable and, except with TEM, no further characterization could be carried out.

For the preparation of core-shell particles, the pellet of oleic acid-stabilized Co nanoparticles (5 ml) after centrifugation was collected, washed several times with ethanol, and to this 1 ml of  $5 \times 10^{-5} \text{ M}$   $\text{Ag}_2\text{SO}_4$  solution was added. The color of the solution immediately changed to brownish yellow indicating formation of the Ag shell.

### 2.3 UV-vis spectroscopic studies

The optical properties of the cobalt and  $\text{Co}_{\text{core}}\text{Ag}_{\text{shell}}$  nanoparticle solutions were monitored using a Jasco UV-vis spectrophotometer (V570 UV-VIS-NIR) operated at a resolution of 2 nm.

### 2.4 Fourier transform infrared (FTIR) spectroscopy measurements

FTIR spectra were recorded from drop-coated films of the samples deposited on a Si (111) substrate on a Perkin Elmer, Spectrum-One Spectrometer operated in the diffuse reflectance mode at a resolution of  $4\text{ cm}^{-1}$ . The spectrum of pure oleic acid was also recorded for comparison.

### 2.5 X-Ray diffraction (XRD) measurements

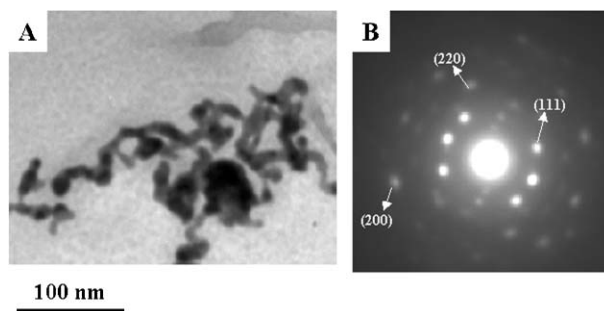
XRD measurements on the  $\text{Co}_{\text{core}}$  and  $\text{Co}_{\text{core}}\text{Ag}_{\text{shell}}$  nanoparticles were performed by casting the respective nanoparticle solutions in the form of films on glass substrates by simple solvent evaporation. The diffraction measurements were carried out on a Philips PW 1830 instrument operating at 40 kV and a current of 30 mA with  $\text{Cu K}\alpha$  radiation

### 2.6 Transmission electron microscopy (TEM) measurements

TEM measurements were performed on a JEOL model 1200EX instrument operated at an accelerating voltage of 120 kV. Samples for TEM studies were prepared by placing a drop of the solutions on carbon-coated copper grids. The films on the TEM grids were allowed to dry for 2 min following which the extra solution was removed using a blotting paper.

## 3 Results

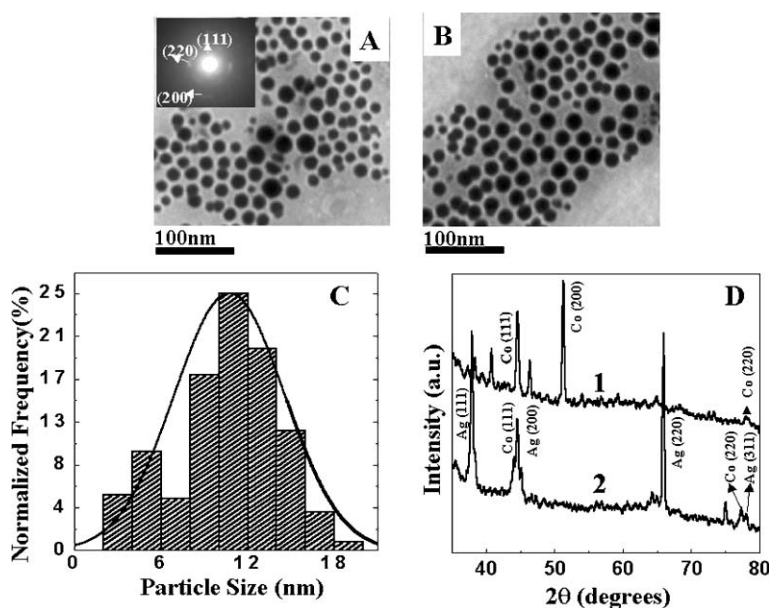
Fig. 1A shows the TEM image of cobalt nanoparticles prepared with just SDS and cobalt ions as the foam constituents. Particles with typically tape-like morphology are observed along with a smaller percentage of spherical particles. The SAED from these particles is shown in Fig. 1B, which clearly supports the formation of crystalline cobalt nanoparticles. It is important to note here that this particular sample was imaged immediately (within minutes) after the sample preparation. The



**Fig. 1** (A) TEM pictures of cobalt nanoparticles. These were obtained when the foam was formed from the aqueous mixture of  $\text{Co}^{2+}$  ions and SDS. (B) Selected area electron diffraction from the same particles. The diffraction could be indexed to the fcc phase of cobalt.

cobalt nanoparticle solution prepared with only SDS as the foaming agent was generally grayish-black immediately after preparation. However, within minutes this solution was observed to turn green. Powder X-ray diffraction analysis (results not included here) of a film prepared from this green solution revealed the formation of cobalt oxide. Hence this procedure was abandoned and we have used an alternative strategy for obtaining stable cobalt nanoparticles in aqueous/organic solutions.

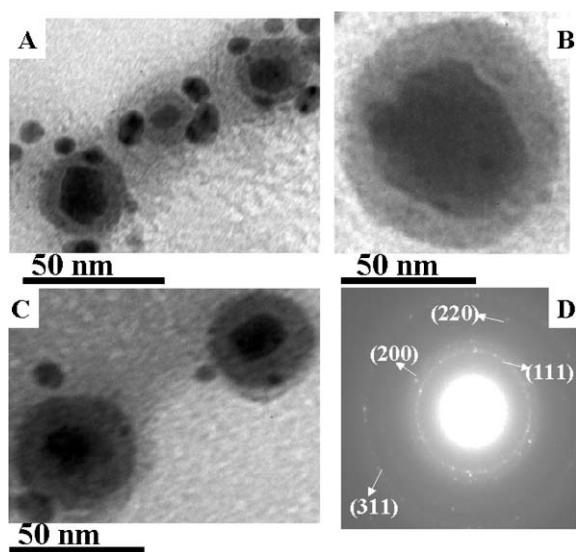
The TEM micrographs of the nanoparticles obtained by the alternative strategy where oleic acid was added to the surfactant/cobalt ion solution prior to the formation of foams are displayed in Fig. 2A and B. A perceptible change in the morphology and arrangement of the nanoparticles is clearly visible. This suggests an important change in the environment around the cobalt ions when the reduction is taking place inside the foam. The particles are predominantly spherical and of uniform size. Analysis of the particle size histogram obtained from measurement of the diameters of over 250 particles revealed the average size to be  $11 \pm 3\text{ nm}$  (Fig. 2C). These particles are also highly crystalline as can be clearly seen from the electron diffraction which can be well indexed to fcc phase cobalt (inset Fig. 2A).<sup>6a</sup> Further evidence for the existence of the fcc phase is given in the XRD pattern of solution-cast films of oleic acid-stabilized Co nanoparticles (curve 1, Fig. 2D).



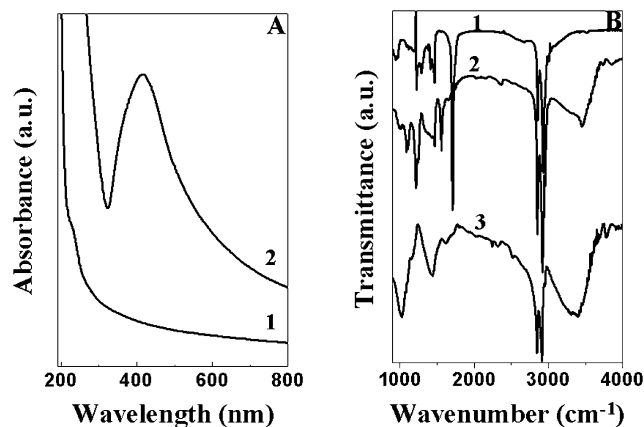
**Fig. 2** (A), (B) TEM pictures, from different areas on the grid, of cobalt nanoparticles obtained when oleic acid was added to the  $\text{Co}^{2+}$  and SDS aqueous mixture prior to the formation of foam. The SAED pattern indexed to fcc cobalt is included as the inset in (A). (C) A particle size histogram of Co nanoparticles. (D) XRD patterns recorded from films of  $\text{Co}_{\text{core}}$  (curve 1) and  $\text{Co}_{\text{core}}\text{Ag}_{\text{shell}}$  nanoparticles (curve 2) solution-cast onto glass substrates.

This is in agreement with earlier reports wherein it was observed that while bulk cobalt assumes an hcp phase, smaller particles, especially in the nanoscale regime, crystallize in the fcc phase.<sup>13</sup> These Co nanoparticle solutions were highly stable in aqueous medium against oxidation and sedimentation and could be stored as solutions for long periods of time. An aqueous/organic dispersion of these nanoparticles could be readily obtained by separating the nanoparticles from water by centrifugation and redispersing the resulting paste-like pellet in water/organic solvents such as toluene. Efrima and co-workers obtained similar results where oleic acid-capped silver nanoparticles were found to be dispersible in both aqueous as well as organic media.<sup>14</sup> Thus, this simple foam-based synthetic procedure yields stable dispersions of cobalt nanoparticles in aqueous as well as organic media.

As mentioned in the introduction, preparation of cobalt core and noble metal shell nanoparticles improves their stability as well as providing one with the additional manipulative ability associated with noble metal shells. For the preparation of  $\text{Co}_{\text{core}}\text{Ag}_{\text{shell}}$  nanoparticles, we have used a simple transmetallation<sup>12</sup> reaction taking advantage of their respective redox potentials (*vide infra*). The striking difference in the contrast of the TEM pictures recorded from the Co nanoparticle solution after addition of silver salt (Figs. 3A–C) clearly reveals the darker Co core and lighter Ag shell. The electron diffraction from the core–shell structures (Fig. 3D) could be indexed based on the fcc structure of silver. The SAED pattern did not show any reflections that could be associated with the core cobalt nanoparticles. While this is not fully understood at this stage, a possible explanation could be that the presence of a thick Ag shell (*ca.* 5–10 nm thick) prevents efficient electron scattering from the cobalt core. Such penetration depth issues would not be important in XRD analysis of the core–shell structures. The XRD pattern recorded from a solution-cast film of the  $\text{Co}_{\text{core}}\text{Ag}_{\text{shell}}$  nanoparticles is shown as curve 2 in Fig. 2D. In addition to the  $\text{Co}_{\text{core}}$  Bragg reflections, the crystalline  $\text{Ag}_{\text{shell}}$  contributes to the signal. The silver Bragg reflections could be indexed on the basis of the fcc structure as shown in the figure. The optical properties of the oleic acid-stabilized Co nanoparticle and the  $\text{Co}_{\text{core}}\text{Ag}_{\text{shell}}$  solutions were probed by UV-vis spectroscopy (Fig. 4A, curves 1 and 2, respectively). Cobalt nanoparticles do not have any noticeable absorption in the UV-visible region (curve 1) and the spectrum obtained matches well with reported UV-vis spectra of cobalt nanoparticles.<sup>15</sup> After reaction of the Co nanoparticle solution with  $\text{Ag}_2\text{SO}_4$ , a



**Fig. 3** (A), (B) and (C) TEM pictures of  $\text{Co}_{\text{core}}\text{Ag}_{\text{shell}}$  nanoparticles from different areas of the TEM grid. (D) Selected area electron diffraction from these particles.



**Fig. 4** (A) UV-vis spectra of the cobalt nanoparticle (curve 1) solution and that of the  $\text{Co}_{\text{core}}\text{Ag}_{\text{shell}}$  nanoparticle solution (curve 2). (B) FTIR spectra of pure oleic acid (trace 1), Co nanoparticles capped with oleic acid (trace 2), and  $\text{Co}_{\text{core}}\text{Ag}_{\text{shell}}$  nanoparticles capped with oleic acid (trace 3).

clear peak around 410 nm is observed and is attributed to the formation of metallic silver in the nanoscale regime. This absorption band arises due to excitation of surface plasmon vibrations in the Ag shell. The FTIR spectra obtained from pure oleic acid, Co nanoparticles covered with oleic acid and  $\text{Co}_{\text{core}}\text{Ag}_{\text{shell}}$  nanoparticles are displayed in Fig. 4B (spectra 1, 2 and 3, respectively). The carboxylic acid band around  $1707\text{ cm}^{-1}$  in pure oleic acid is shifted to  $1553\text{ cm}^{-1}$  in the presence of Co nanoparticles and to  $1611\text{ cm}^{-1}$  after the Ag shell is formed. These shifts clearly indicate that the chemical environment in which the carboxylic acid is present is different in each step of our synthesis: in the first step it is on the surface of the Co nanoparticles and then in the  $\text{Co}_{\text{core}}\text{Ag}_{\text{shell}}$  case it is bound to the Ag surface. Although it is difficult to unequivocally ascertain the formation of core–shell structures from UV-vis and FTIR studies alone, these results in conjunction with the TEM pictures and X-ray diffraction results, and the fact that the reduction of  $\text{Ag}^+$  ions can take place only on the surface of cobalt nanoparticles, clearly provide evidence for the formation  $\text{Co}_{\text{core}}\text{Ag}_{\text{shell}}$  structures.

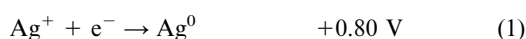
## 4 Discussion

After the excess liquid has been drained out of the foam, there are essentially two spatially distinct locations in the foam where metal nanoparticle nucleation and growth could occur. One is the extremely thin region between two air bubbles. Here, the ‘liquid lamellae’ are very similar to two Langmuir monolayers juxtaposed one on top of the other with the thickness corresponding to a few nanometers. The second location is the junction of four air bubbles (Scheme 1). This contains a slightly larger liquid pool generally of micron dimensions. In both these locations,  $\text{Co}^{2+}$  ions are expected to be present through electrostatic complexation with the anionic surfactant, SDS. The presence of two types of locations for cobalt ions may enforce a shape variation in the resulting nanoparticles. For example, the entrapment of cobalt ions in the liquid lamellae and their subsequent reduction might result in flat nanoparticles. However, we would like to caution that a number of other factors, such as preferential binding of surfactant molecules with specific crystallographic faces, *etc.*, may lead to anisotropic crystal growth. Further work is required to conclusively establish the role of spatially distinct regions in the foam in directing morphology variation and this is currently in progress. Formation of such anisotropic nanoparticles has been reported earlier where the metal ions immobilized at the air–water interface were subjected to reduction.<sup>16</sup> On the other hand, the junction between four bubbles is

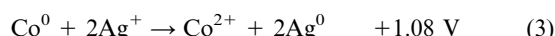
much more isotropic in extent and no such shape anisotropy would occur for cobalt nanoparticles nucleated and grown at these sites. We observe both flat particles as well as spherical particles in the case of cobalt nanoparticles obtained with just SDS present in the foam column along with cobalt ions. Similar results were also obtained for Au nanoparticles with the foam-based synthesis.<sup>10</sup> However, the cobalt nanoparticles obtained with these experimental conditions were extremely unstable and cobalt oxide is formed within minutes, preventing us from carrying out any further analysis of this sample. This suggests that SDS is not a good capping agent for the cobalt nanoparticles and cannot protect them against oxidation.

The presence of oleic acid in the foam column changes the scenario drastically. Not only did we obtain very stable cobalt nanoparticles, the shape of the nanoparticles observed is different as well in that now more spherical particles are obtained. Both SDS and oleic acid are anionic surfactants and, hence, owing to purely entropic considerations we expect both these molecules to be present in the foam lamellae. However, it is not clear at this stage what percentage of the oleic acid molecules present in solution are transported to the surface of the bubbles. It is likely that a large fraction of oleic acid (and indeed SDS) is present in the water channels of the foam. During *in-situ* nucleation and growth of the Co nanoparticles, the stability of the Co nanoparticles formed in the foam containing oleic acid suggests that oleic acid binds more strongly to the surface of the Co nanoparticles than SDS. This may be rationalized in terms of electrostatic complexation of carboxylic acid groups in oleic acid with unreduced Co ions bound to the surface of the Co nanoparticles. This is supported by the shifts observed for the carboxylate bands in FTIR spectra from 1707 cm<sup>-1</sup> in pure oleic acid to 1553 cm<sup>-1</sup> in the presence of Co nanoparticles (Fig. 4B). This strong binding of oleic acid to the nascent Co nanoparticles could also be responsible for inhibiting anisotropic growth of the Co nanoparticles.

We have utilized the redox potentials of Ag and Co to our advantage to prepare the Co<sub>core</sub>Ag<sub>shell</sub> nanocomposites. From the reported redox potentials, the reduction of silver ions by cobalt metal can easily proceed and this forms the basis of core-shell structure formation in our scheme:



Therefore,



is an energetically favorable reaction. There are reports of using a similar methodology for the formation of Co-Pt core-shell structures in the literature.<sup>12</sup> However, those reactions are carried out at elevated temperatures and with slightly complex reaction conditions.

In conclusion, an extremely simple and hitherto unexplored foam-based synthesis of cobalt nanoparticles has been reported. The instability of cobalt nanoparticles in aqueous medium is overcome by using oleic acid as one of the constituents of the foam. The oleic acid-stabilized Co nanoparticles are extremely stable against oxidation and may be readily redispersed in both water and non-polar organic solvents such as toluene. Utilizing the redox potential matching of Co and Ag<sup>+</sup> ions, Co<sub>core</sub>Ag<sub>shell</sub>

nanocomposites were easily synthesized by simple reaction of oleic acid-stabilized Co nanoparticles with Ag<sup>+</sup> ions. This methodology is general and may be extended to the formation of other nanoparticle core-shell systems.

## Acknowledgements

B. L. V. P. thanks the National Chemical Laboratory for a start-up grant. T. B. thanks the Council for Scientific and Industrial Research (CSIR), Govt. of India, for a research fellowship.

## References

- D. D. Awschalom and D. P. DiVincenzo, *Phys. Today.*, 1995, **48**, 43–48; J. Shi, S. Gider, K. Babcock and D. D. Awschalom, *Science.*, 1996, **271**, 937–941; C. M. Sorensen, in *Nanoscale Materials in Chemistry*, K. J. Klabunde, ed., Wiley, New York, 2002, pp. 169–222.
- M. Moreno-Manas and R. Pleixats, *Acc. Chem. Res.*, 2003, **36**, 638–643; V. Kesavan, P. S. Sivanand, S. Chandrasekharan, Y. Kolytipin and A. Gedankan, *Angew. Chem., Int. Ed.*, 1999, **38**, 3521–3523; V. Kesavan, D. Dhar, Y. Kolytipin, N. Perkas, O. Palchik, A. Gedankan and S. Chandrasekharan, *Pure Appl. Chem.*, 2001, **73**, 85–89.
- P. Tartaj, M. del Puerto Morales, S. Veintemillas-Verdaguer, T. González-Carreño and C. J. Serna, *J. Phys. D: Appl. Phys.*, 2003, **36**, R182–R197.
- G. N. Glavee, K. J. Klabunde, C. M. Sorensen and G. C. Hadjipanayis, *Langmuir*, 1992, **8**, 771–773; G. N. Glavee, K. J. Klabunde, C. M. Sorensen and G. C. Hadjipanayis, *Inorg. Chem.*, 1993, **32**, 474–477; S. U. Son, S. I. Lee, Y. K. Chung, S. W. Kim and T. Hyeon, *Org. Lett.*, 2002, **4**, 277–279.
- For a general review of synthesis of magnetic nanoparticles, see: T. Hyeon, *Chem. Commun.*, 2003, 927–934.
- (a) C. Petit, A. Taleb and M. P. Pileni, *J. Phys. Chem. B*, 1999, **103**, 1805–1810; (b) S. Sun and C. B. Murray, *J. Appl. Phys.*, 1999, **85**, 4325–4330; (c) D. P. Dinega and M. G. Bawendi, *Angew. Chem., Int. Ed.*, 1999, **38**, 1788–1791; (d) V. F. Puentes, K. M. Krishnan and A. P. Alivisatos, *Science*, 2001, **291**, 2115–2117.
- C. B. Murray, S. Sun, W. Gaschler, H. Doyle, T. A. Betley and C. R. Kagan, *IBM J. Res. Dev.*, 2001, **45**, 47–56; C. B. Murray, S. Sun, H. Doyle and T. A. Betley, *MRS Bull.*, 2001, 985–991.
- D. Weaire and S. Hutzler, *The Physics of Foams*, Oxford University Press, Oxford, 1999; A. Bhattacharyya, F. Monroy, D. Langevin and J.-F. Argillier, *Langmuir*, 2000, **16**, 8727–8732.
- B.-D. Chen, J. J. Cilliers, R. J. Davey, J. Garside and E. T. Woodburn, *J. Am. Chem. Soc.*, 1998, **120**, 1625–1626.
- S. Mandal, S. K. Arumugam, S. D. Adyanthaya and M. Sastry, *J. Mater. Chem.*, 2004, **14**, 43–47.
- A. Kumar, S. Mandal, P. R. Selvakannan, R. Pasricha, A. B. Mandale and M. Sastry, *Langmuir*, 2003, **19**, 6277–6282; S. Mandal, P. R. Selvakannan, S. Phadtare, R. Pasricha and M. Sastry, *Proc. Indian Acad. Sci., Chem. Sci.*, 2002, **114**, 513–520; P. R. Selvakannan, S. Mandal, S. Phadtare, R. Pasricha and M. Sastry, *Langmuir*, 2003, **19**, 3545–3549; B. L. V. Prasad, S. I. Stoeva, C. M. Sorensen and K. J. Klabunde, *Chem. Mater.*, 2003, **15**, 935–942.
- J.-I. Park and J. W. Cheon, *J. Am. Chem. Soc.*, 2001, **123**, 5743–5746.
- O. Kitakami, H. Sato, Y. Shimada, F. Sato and M. Tanaka, *Phys. Rev. B*, 1997, **56**, 13 849–13 854.
- W. Wang, S. Efrima and O. Regev, *Langmuir*, 1998, **14**, 602–610.
- J. A. Creighton and D. G. Eadon, *J. Chem. Soc., Faraday Trans. 1*, 1991, **87**, 3881; B. G. Ershov, N. L. Sukhov and E. Janata, *J. Phys. Chem. B*, 2000, **104**, 6138–6142.
- A. Swami, A. Kumar, P. R. Selvakannan, S. Mandal, R. Pasricha and M. Sastry, *Chem. Mater.*, 2003, **15**, 17–19.