Growth of nanocrystals and thin films at the water–oil interface

BY G. L. STANSFIELD¹, P. V. VANITHA¹, H. M. JOHNSTON¹, D. FAN¹, H. ALQAHTANI², L. HAGUE², M. GRELL² AND P. JOHN THOMAS¹,*

¹School of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, UK
²Department of Physics and Astronomy, University of Sheffield, Hicks Building, Hounsfield Road, Sheffield S3 7RH, UK

The use of the water–oil interface provides significant advantages in the synthesis of inorganic nanostructures. Employing the water–toluene interface, luminescent CdS nanocrystals have been obtained at a relatively modest temperature of 35°C. The diameters of the particulates can be varied between 1.0 and 5.0 nm. In addition, we have devised a new method for transferring thin films at the water–toluene interface onto solid substrates. Using this method, thin films consisting of Au and Ag nanocrystals spread over very large areas (square centimetres) are obtained in a single step. These films are directly usable as ingredients of functional devices. We show this by constructing a working amine sensor based on films of Au nanocrystals. The materials obtained have been characterized by X-ray diffraction, scanning and transmission electron microscopy, absorption and emission spectroscopy and charge transport measurements.

Keywords: Au thin films; CdS nanocrystals; oil–water interface

1. Introduction

The natural world artfully harnesses the interface between immiscible liquids to carry out vital processes such as growing bones and contracting muscles (Volkov et al. 1998). In contrast, synthetic chemists generally regard such an interface as an intractable barrier to be circumvented by the use of phase transfer reagents. A small number of studies have explored the use of the water–oil interface to synthesize inorganic nanostructures, materials that have assumed great significance in recent times (Faraday 1857; Brust et al. 1994; Rao et al. 2005; Fan et al. 2007a,b; Rao & Kalyanikutty 2008). In these studies, the use of the interface leads to remarkably simple and straightforward routes to complex solids. Inspired by the above, we seek to develop the water–oil interface as a full-fledged, generic, benign soft-chemical medium for the growth and deposition of thin films and nanoscopic material. In this paper, we present two recent results from our laboratory that aptly illustrate the synthetic potential of the water–oil interface.

*Author for correspondence (john.thomas@manchester.ac.uk).

One contribution of 14 to a Theme Issue ‘Nanoparticles’.
The first study identifies a simple route to luminescent CdS nanocrystals and the second is concerned with generating uniform thin films of metal nanocrystals extending to very large areas (several square centimetres).

Careful consideration of current understanding of the structure and properties of the water–oil interface suggests the interface and its immediate environs possess features well suited for synthesis of solids with reduced dimensions. The interface introduces steep gradients in ionic concentration with critical lengths of the order of nanometres, owing to limited mixing of the liquids around the original interface (Birdi 1997). With appropriate precursors, these gradients can create a spatially confined region of supersaturation for the growth of low-dimensional crystallites. These crystallites can then be quickly extracted from the interface to yield a dispersion of nanocrystals (Faraday 1857). This method, originally due to Faraday, has been very successfully adapted by Schiffrin as well as others for the synthesis of metal nanocrystals such as Au (Brust et al. 1994), Ag (Kang & Kim 1998), Pt (Horswell et al. 1999) and Pd (Chen et al. 2000). However, this technique has remained largely unexplored for the synthesis of semiconductor nanocrystals. Recently, CdS and CdSe nanocrystals have been obtained by employing cadmium myristate in toluene and aqueous thio- or selenourea, in an autoclave (Pan et al. 2004, 2005). Core-shell nanocrystals such as CdS/CdSe have been obtained by alternating the two reactions (Pan et al. 2008).

Crucially, the semiconductor nanocrystals exhibited band-edge, size-tunable emission, which is characteristic of crystallites with low defects (Murray et al. 1993; Lazell & O’Brien 1999; Malik et al. 2001; Peng & Peng 2001; Battaglia & Peng 2002; Nair et al. 2002; Yu & Peng 2002; Li et al. 2003; Pradhan et al. 2003; Park et al. 2004; Mohamed et al. 2005). Such band-edge emission is critical for applications and was hitherto only achieved using non-facile methods that usually involve high temperatures (Murray et al. 1993; Lazell & O’Brien 1999; Malik et al. 2001; Peng & Peng 2001; Nair et al. 2002; Park et al. 2004). Thus, interfacial schemes hold out the promise of producing high-quality crystallites under mild conditions (Pan et al. 2004, 2008). We therefore considered that a new route to semiconductor nanocrystals, reliant on the barrier provided by the water–oil interface, to be a worthy addition to the arsenal of available techniques.

Recent investigations by Rao and co-workers and groups in Manchester have led to interfacial schemes that directly yield thin films of inorganic nanostructures adherent to the water–oil interface (Dryfe 2006; Thomas et al. 2007; Rao & Kalyanikutty 2008). As in the case for solution growth of nanocrystals, this reaction is initiated by a seeding step, following which the natural tendency of the interface to adsorb and confine nano- and microscopic particulates is allowed to proceed unfettered (Binks 2002; Aveyard et al. 2003). As the reaction progresses, the adsorbed seed particulates either grow into larger forms or become a part of a network of similar species, yielding granular thin films (Gautam et al. 2004; Fan et al. 2008a,b; Mlondo et al. 2008, 2009). Adopting this method, Rao and co-workers have obtained nanometre-thick single-crystalline scrolls of CuS that extend to several micrometres (Gautam et al. 2004). Crystalline nanoceria, a material with established catalytic uses, has been obtained in a single step, in the form of conformal thin films, by the use of the water–oil interface (Mlondo et al. 2009). Single crystalline PbS deposits were found to grow in the form of pyramids exposing high index {331} facets

Phil. Trans. R. Soc. A (2010)
Growth of nanocrystals and thin films

(Fan et al. 2008a,b). By employing the water–oil interface, hierarchical anisotropic Cd(OH)$_2$ structures leading to CdO and CdS nanowires have been obtained (Mlondo et al. 2008).

The structural regularity inherent to the water–oil interface ensures the uniformity of deposits over large areas. However, such regularity is routinely lost when the deposits are transferred to solid support owing to crude transfer protocols. Herein, we report the results of our studies on a potent transfer process for films of metal nanocrystals produced at the water–toluene interface. We find that, by adopting this method, uniform films of metal nanocrystals extending to several square centimetres can be produced. We show that such films are ideally suited for use in sophisticated electronic devices by fabricating a sensor using simple lithographic techniques.

2. Experimental

(a) Synthesis of cadmium diethyldithiocarbamate

The dithiocarbamate was prepared using methods reported previously (O’Brien & Nomura 1995). Briefly, Cd(S$_2$CNEt$_2$)$_2$ was prepared by adding 1.13 ml of diethylamine and 0.65 ml of carbon disulphide to a stirred 40 ml methanol solution of 0.27 M sodium hydroxide. The solution was then cooled to 4°C using an ice bath and a 40 ml methanol solution of 0.14 M cadmium chloride was added dropwise, resulting in precipitation of the thiocarbamate as a yellow solid. The crude product was purified by re-crystallizing from hot toluene. Elemental analysis (%) found: C, 29.48; H, 4.96; N, 6.75; S, 31.42; Cd, 27.86. Calcd: C, 29.40; H, 4.90; N, 6.86; S, 31.37; Cd, 28.45.

(b) Synthesis of chlorotris(triphenylphosphine)silver(I)

The complex was prepared using a method previously reported (Sanghani et al. 1982). To a stirred dispersion of AgCl (1.43 g, 10 mmol) in dichloromethane (150 ml), a solution of triphenylphosphine (TPP) (10.97 g, 40 mmol), also in dichloromethane, was added dropwise and the stirring continued for an hour. The clear liquid obtained was filtered and, to the filtrate, pentane was added to precipitate a white crystalline solid. Elemental analysis (%) found: C, 69.45; H, 4.84; Cl, 4.23; P, 9.69; Ag, 11.02. Calcd: C, 69.71; H, 4.84; Cl, 3.82; P, 10.00; Ag, 11.62.

(c) Synthesis of CdS nanocrystals

In a typical reaction, a 30 ml toluene solution containing 0.05 mmol Cd(S$_2$CNEt$_2$)$_2$ and 26 mmol octylamine was heated to 35°C and layered atop a heated and stirred aqueous solution (30 ml) containing 1.00 mmol thioacetamide in a jacketed reaction vessel. The reaction temperature was held constant by circulation of water. In a few minutes, the toluene layer acquired an orange–yellow colour and turned progressively yellow during the course of the reaction. The progress of the reaction was monitored by drawing aliquots from the toluene layer at different reaction times. The effects of reaction time and reagent concentrations were systematically investigated. At the end of the reaction, the aqueous layer was discarded and the nanocrystals dispersed in toluene.
were precipitated with methanol and redispersed in toluene. This dispersion was used for further characterization. The particulates were characterized by X-ray diffraction, transmission electron microscopy (TEM), UV-visible and fluorescence spectroscopy. TEM analysis was carried out using a Technai CM 200 microscope.

(d) Interfacial deposition of Au and Ag films

Interfacial deposition was accomplished using a method reported previously (Agrawal et al. 2005). Briefly, a 10 ml 1.5 mM toluene solution of chlorotriphenylphosphinylgold(I) (Au(PPh\textsubscript{3})Cl) was layered atop 16 ml of 6.25 mM aqueous sodium hydroxide in a 100 ml beaker (diameter 4.8 cm). To initiate the reaction, 330 μl of 50 mM aqueous tetrakis(hydroxymethyl)phosphonium chloride (THPC) was injected into the lower layer. The beaker was immediately transferred to an oven set at the desired temperature. At the end of the reaction, a film with metallic yellow lustre was seen at the interface between toluene and water.

Interfacial Ag films were obtained using the above procedure and by replacing the Au precursor with chlorotris(triphenylphosphine)silver(I). In this case, the film at the interface possessed a lustrous grey sheen.

Scanning electron microscopy (SEM) was carried out using an XL30 FEG SEM.

(e) Charge transport measurements

Charge transport measurements were carried out using a home-built system composed of a closed-cycle He cryostat, Keithley 2400 Series Source-Measure unit and a Lakeshore 325 Temperature Controller. Au contacts were thermally evaporated onto the glass substrates containing the Au films. The samples were mounted onto the cold finger of the closed-cycle cryostat. Contacts to the electrodes were made using copper wires and conductive silver paint. The sample was held in a vacuum of 10\textsuperscript{−6} mbar and cooled down to 15 K, while DC resistance measurements were carried out.

(f) Fabrication of the amine sensor

A sensor was constructed using a square wave generator circuit as shown in figure 1. Here, \(V_{\text{out}}\) is the square wave, read using an oscilloscope. We used an Op Amp type AD822 with ±1.5 V supply voltage (note: the rated capability of this Op Amp is from ±1.5 to ±18 V) and capacitance \(C = 3.3\ \text{nF}\). For \(R_1/R_2\), we used a 100 kOhm potentiostat. The sample was used as resistor \(R\). The frequency \(f\) of the resulting square wave depends on \(C, R_1, R_2\) and \(R\). The response to the amine vapour is thus measured as a frequency that is inversely proportional to resistance. This measurement is carried out using an AC voltage, and field stress that could result from a DC bias is avoided.

Octylamine was cooled to 0°C in an ice bath and the saturated vapours from this vessel were mixed with the desired quantity of N\textsubscript{2} gas using mass flow controllers and allowed to flow over the film sensor. The concentration of the amine was determined from estimated saturated vapour pressure. There are no reports of vapour pressure of octylamine at 0°C. However, Steele et al. (1996) reported saturated vapour pressures at higher temperatures. These data were
extrapolated to 0°C using the Clausius–Clapeyron equation. The reference scale exposure fraction (ranging from 0.0 to 1.0) was arrived at by designating the extrapolated saturated vapour pressure at 0°C, 282 ppm as 1.0.

3. Results and discussion

A typical TEM micrograph of CdS nanocrystals synthesized using 30 ml of 33.3 mM aqueous thioacetamide and 30 ml of 0.5 M toluene solution of Cd(S₂CNEt₂)₂ containing 2.1 ml octylamine at 35°C after 15 h is shown in figure 2. Nearly spherical particles with diameters of 4.9 ± 0.5 are seen throughout the image. The X-ray diffraction pattern reveals broad peaks characteristic of the wurtzite form of CdS.

Figure 3a shows the absorption spectra of various batches of CdS nanocrystals obtained at times between 3 and 15 h. The absorption consists of a sharp threshold that gradually shifts to lower energies (from 2.81 to 2.49 eV) with the progress of the reaction. A similar trend is seen in the case of the primary peak whose position decreases from 3.31 to 2.68 eV with time. The changes in the optical spectra are due to quantum confinement effects that cause diameter-dependent shifts to the optical band gap (Rao et al. 2007). We follow the method due to Sarma and co-workers, which has been shown to provide accurate estimates of mean diameter and diameter distribution from the absorption spectra (Viswanatha & Sarma 2006).

We find that the diameters and diameter distribution obtained from the absorption spectra are comparable to those obtained from TEM. The diameter of the particulates increases from 2.5 ± 0.2 to 5.1 ± 0.5 nm as the reaction progresses (figure 3b). In all cases, the distribution in diameter was less than 10 per cent about the mean, indicating that the present soft-chemical method yields fairly monodispersed nanocrystals. The peaks obtained at times between 5 and 15 h
Figure 2. TEM images of CdS nanocrystals synthesized using 30 ml of 33.3 mM aqueous thiocacetamide and 30 ml of 0.5 M toluene solution of Cd(S$_2$CNEt$_2$)$_2$ containing 4.2 ml octylamine at 35°C for 15 h. Scale bar, 10 nm.

are slightly asymmetrical, possibly owing to a bimodal distribution of particle diameters. We are carrying out a detailed TEM analysis to ascertain if this is indeed the case.

Emission from the various batches of CdS nanocrystals consists of an intense band close to the absorption edge and a broad defect band at lower energies (figure 4). The dominance of the band-edge luminescence (or excitonic luminescence) in the emission spectra indicates that the as-synthesized nanocrystals have low defect densities. This is in stark contrast to other low-temperature methods that only succeed in producing nanocrystals with weak excitonic emission bands (Spanhel & Anderson 1990; Pradhan & Efrima 2003; Tong & Zhu 2006; Rogach 2008). Considering that previous interfacial methods (carried out at 100°C) have also been successful in observing excitonic emission, this ability to produce nanocrystals with low defect densities could be due to features unique to the biphasic system. We note that, with the singular exception of the emission band from the nanocrystals obtained at 3 h, the excitonic band can be fitted to a single Gaussian peak with widths of approximately 45 nm. This is comparable to widths of emission bands of CdS nanocrystals produced by the best high-temperature methods (typically around 30 nm) (Murray et al. 1993; Lazell & O’Brien 1999; Malik et al. 2001; Peng & Peng 2001; Nair et al. 2002; Park et al. 2004; Rogach 2008). Emission from nanocrystals grown at times between 5 and 15 h consists of a small shoulder at the high-energy side of the primary peak. This corresponds to the observed asymmetry in the absorption spectrum (figure 3a) and a dip in the growth curve of the particulates (figure 3b), indicating that the distribution in diameters is possibly bimodal.
Figure 3. (a) Absorption spectra of aliquots drawn at different times from CdS nanocrystals grown at 35°C, employing 30 ml of 33.3 mM aqueous thioacetamide and 30 ml of 0.5 M toluene solution of Cd(S$_2$CNEt$_2$)$_2$ containing 4.2 ml octylamine. The various times are (a) 3 h; (b) 5 h; (c) 6 h; (d) 10 h; (e) 15 h. (b) Estimates of the diameters of CdS nanocrystals obtained at different times from the absorption spectrum. The error bars in the plot indicate the distribution in diameters of the particulates.

Thus, the quality of the crystallites obtained herein, judged in terms of monodispersity and emission widths, is similar to those obtained by thermolysis of organometallic precursors. The gradual growth observed herein is in line with slow dynamics associated with interfacial transport processes (Birdi 1997; Binks 2002) and have been observed previously in semiconductor nanocrystals grown at the interface (Pan et al. 2004, 2005, 2008, 2009). Significantly, throughout this long period of growth, the nanocrystals retain their monodisperse nature. The diameter distribution is always less than 10 per cent of the mean.

Phil. Trans. R. Soc. A (2010)
We find that octylamine plays a significant role in controlling the diameters of the nanocrystals. Halving the volume of octylamine more than doubles the distribution in diameters of the particulates. When the quantity of octylamine is doubled to 8.4 ml, only tiny seed particulates are obtained. As previously reported by us and others, in the absence of octylamine, films of CdS nanocrystals adhered to the interface are produced (Wu et al. 2002; Gautam et al. 2003; Fan et al. 2007a,b). A completely different mechanism (self-limiting growth with continuous production of nuclei) was observed in these studies. In the present reaction, when the concentration of Cd$^{2+}$ and S$^{2-}$ sources was doubled, the particulates obtained possessed a wider distribution of diameters. An increase in the relative concentration of the thiocarbamate reduced the intensity of emission, possibly owing to adsorption of Cd$^{2+}$ ions at the surface of the nanocrystals. When octylamine was replaced with tri-$n$-octylphosphine oxide, no formation of particulates was observed. As thioacetamide only decomposes partially at neutral pH, a large excess of thioacetamide was essential to initiate the reaction (Hodes 2002).

As alluded to earlier, CdS and CdSe nanocrystals have been synthesized in autoclaves at modest temperatures using Cd salts of a long-chain carboxylic acid and aqueous thio- or seleno urea (Pan et al. 2004, 2005, 2008, 2009). In the present report, open vessels and air-stable precursors in common use have been employed for synthesizing high-quality CdS nanocrystals at a temperature a few degrees above the ambient. Dithiocarbamates belong to a family of compounds whose chemistry is well known and analogues are readily available, making the present benign method potentially generic (Hogarth 2005). We are currently carrying out detailed investigation of the growth mechanism as well as seeking ways to synthesize other metal sulphide nanocrystals.
4. Nanocrystalline films of gold

We have adapted a method reported by Rao and co-workers for obtaining Au nanocrystals at the water–toluene interface (Agrawal et al. 2005). The growth and properties of such films have been extensively investigated.

Transfer of the films from the interfacial region onto solid supports was accomplished using the following procedure. A glass substrate held in a vertical orientation (relative to the interface) by attachment to a mechanical dipper is made to pierce the film and become completely immersed in the aqueous layer, where it is left for a minute. Transfer of the film to the substrate takes place when the slide is slowly withdrawn across the interface. The rate of transfer can be adjusted by adapting different speeds of substrate withdrawal. However, we found that different rates of transfer ranging from 0.25 to 5 cm s\(^{-1}\) have no discernible effects on the properties of the films produced. The dipping cycle can be repeated several times. We notice that the film is not transferred to the substrate during the first dip from the toluene layer. As the glass substrate passes through the toluene column, a thin layer of toluene moves along, preventing the adhesion of the films to the substrate. Indeed, when the substrates are rendered hydrophobic, no transfer takes place. Making the surface hydrophilic aids the successful transfer of films. We believe that, as the glass substrate is left to ‘rest’ for a minute in the aqueous layer, the glass loses its toluene coating and becomes more amenable to transfer.

We have systematically investigated the effect of temperature, precursor concentrations and reaction time on the nature and properties of the films of Au nanocrystals.

Photographs showing uniform films spread over areas of several square centimetres are shown in figure 5.

SEM images reveal that the film produced at 50°C and for a time period of 180 min is uniform and continuous, spanning many millimetres (figure 6a,b). Folds (figure 6a) and cracks (figure 6b) are seen in the film, possibly as a result of the transfer from the interface to the substrate. High-resolution images reveal irregular clusters with diameters of 70 nm. AFM images reveal another layer of hierarchy in the morphology. The clusters can be resolved into spherical particulates with diameters of about 10 nm.

In fact, TEM images (figure 7) obtained by dispersing the films (by sonication) reveal spherical crystallites with diameters of approximately 10 nm. The tendency to aggregate is apparent in the image. Thus, the films deposited at the interface consist of large microscopic spheroidal aggregates of Au nanocrystals. Similar mesoscalar structures with hierarchy have been observed in films of Bi\(_2\)S\(_3\) (Fan et al. 2008a,b), Cd(OH)\(_2\) and Pd (Zheng & Li 2005) grown at the water–toluene interface. At present, there is insufficient understanding of the factors that cause such assembly.

X-ray diffraction from (figure 8) the interfacial film reveals a pattern typical of Au, albeit with slightly broader peaks characteristic of nanocrystals. A degree of orientation along (111) is apparent from the pronounced intensity of the peak at 38.1° relative to the others.

The surface structure of the Au particulates is important in determining the electronic properties of the film. Previous studies suggest that THPC, the reducing agent employed, is also capable of acting as a surface ligand.
Figure 5. The film on the left is a nanocrystalline film of silver obtained using Ag(PPh₃)Cl in toluene (1.5 mM) atop aqueous sodium hydroxide (6.25 mM). THPC (50 mM) was used as a reaction initiator via injection into the aqueous layer. The nanocrystalline film of gold on the right is obtained using Au(PPh₃)Cl in toluene (1.5 mM) layered atop aqueous sodium hydroxide (6.25 mM). Again, THPC was used to initiate the reaction. The Au and Ag films formed have been transferred onto glass substrates.

\[
P(CH₂OH)₄^+ + OH^- \rightarrow P(CH₂OH)₃ + HCHO + H₂O
\]

Scheme 1.

(Duff et al. 1993). These and other studies suggest that, in the presence of NaOH, THPC is hydrolysed to generate formaldehyde (scheme 1), which reduces the precursor producing Au(0) and TPP (Hoffman 1921, 1930; Reeves & Guthrie 1956). Other products include tris(hydroxymethyl)phosphine (THP) and possibly a small quantity of the corresponding oxide, THPO.

THP, TPP and even THPO are all capable of binding and stabilizing Au nanocrystals (Schmid et al. 1988; Duff et al. 1993). We have carried out preliminary experiments that indicate the presence of phosphorus-containing ligands. X-ray photoelectron spectroscopy reveals the presence of P and an Au : P ratio of 17 : 1. IR spectra consist of bands characteristic of THP and TPP.

Clear differences were discernible in charge transport measurements carried on Au films obtained at different deposition temperatures (figure 9). Films obtained using a deposition temperature of 50°C had a resistance of 4.42 MΩ at room temperature, and it rose to 4.78 MΩ at 40 K. The negative correlation with temperature is characteristic of a semiconductor.

At a lower deposition temperature, the resistance is significantly higher. However, the behaviour with respect to temperature is similar. We presume the change in resistance is due to a fall in particle diameter accompanying a reduction in the deposition temperature.

An amine-sensing device fabricated as indicated before exhibited a specific response to amine vapours (figure 10). At an exposure fraction of 0.5 (141 ppm octylamine) for 500 s, a frequency change of 0.11 kHz was seen. A similar change
Figure 6. SEM images show uniform and continuous nanocrystalline films of gold which span many millimetres. Au(PPh₃)Cl in toluene (1.5 mM) was layered on top of aqueous sodium hydroxide (6.25 mM) and 330 µl (50 mM) THPC was injected into the bottom layer to initiate the reaction. The Au film obtained at the interface was transferred onto glass substrates. (a) Folds and (b) cracks can be observed as a result of the transfer process. The films can be said to comprise irregular aggregates of individual Au nanocrystals, and this is observed in the AFM images (c,d). (c) Resolution is 1 µm × 1 µm and (d) resolution is 250 nm × 250 nm. Scale bars, (a) 2 µm and (b) 500 nm.

was obtained when the concentration was doubled and the exposure time halved. With an exposure of 99 ppm of octylamine for 250 s, a frequency change of 0.04 kHz was observed. Thus, the response of the device is directly proportional to the concentration of the amine. We believe the response to be due to adsorption of amine molecules to the surface of the nanocrystals that make up the sensor.

5. Nanocrystalline films of silver

Ag films were obtained using Ag(PPh₃)₃Cl in toluene (10 ml, 1.5 mM), layered on top of aqueous sodium hydroxide (16 ml, 6.25 mM) and then injecting 330 µl (50 mM) THPC into the bottom layer to initiate the reaction. The Ag film formed at the interface was transferred onto a glass substrate and analysed.
Figure 7. TEM image showing aggregation of spherical Au nanocrystals to form clusters. A film of Au nanocrystals was obtained using Au(PPh₃)Cl as a precursor in toluene (1.5 mM) and aqueous sodium hydroxide (6.25 mM). THPC (50 mM) was injected into the aqueous layer to initiate the reaction. The Au film formed at the interface was transferred onto a glass substrate, which was added to toluene and sonicated for 5 min to disperse the nanocrystals. One drop of this was applied to a holey TEM grid and analysed. Scale bar, 20 nm.

Figure 8. Powder X-ray diffraction pattern for a nanocrystalline film of gold prepared at 50°C over 180 min. A film of Au nanocrystals was obtained using Au(PPh₃)Cl in toluene (1.5 mM) and aqueous sodium hydroxide (6.25 mM) and by then injecting (50 mM) THPC into the aqueous layer. The Au film formed at the interface was transferred onto a glass substrate for analysis by X-ray diffraction. Broad peaks can be observed, which are characteristic of nanocrystals. The Au 111 peak at 38.1° is very intense, owing to orientation in the Au film.
Figure 9. Plot showing the variation of resistance with temperature for interfacial films of Au nanocrystals prepared at temperatures indicated in the graph. To prepare the films, an Au(PPh₃)Cl precursor in toluene (1.5 mM) was layered on top of aqueous sodium hydroxide (6.25 mM). To initiate the reaction, 330 μL (50 mM) THPC was injected into the bottom layer. The Au film formed at the interface was transferred onto glass substrates for analysis.

Figure 10. Response of the amine sensor to amine vapours of different concentrations. The change in resistance is converted to a response in the frequency domain, as outlined in the experimental section. The value 1.0 on the exposure fraction corresponds to a concentration of 282 ppm of octylamine. Black line, frequency versus time; grey line, concentration versus time.
Figure 11. SEM images of nanocrystalline films of silver obtained at 50°C over 180 min. A film of Ag nanocrystals was obtained using Ag(PPh₃)₃Cl in toluene (1.5 mM) atop aqueous sodium hydroxide (6.25 mM). Injection of (50 mM) THPC into the aqueous layer gave rise to an Ag thin film at the interface of the two liquids after 180 min. For analysis by scanning electron microscopy, the Ag films were transferred onto glass substrates. Folds can be seen in (a); however, the films are continuous and uniform, spanning many square millimetres (b). Scale bars, (a) 2 μm and (b) 20 μm.

Figure 12. Powder X-ray diffraction pattern for a nanocrystalline film of silver showing broad peaks, which are characteristic of nanocrystals. The film was prepared at 50°C over a time period of 180 min. Ag(PPh₃)₃Cl in toluene (10 ml, 1.5 mM) was layered on top of aqueous sodium hydroxide (16 ml, 6.25 mM) and injecting 330 μl (50 mM) THPC into the bottom layer to initiate the reaction. The Ag film formed at the interface was transferred onto a glass substrate and analysed.

SEM images (figure 11a,b) reveal uniform and continuous deposits spanning large areas. Nanometric Ag particles can be seen throughout the deposits in images obtained at higher magnification (figure 11a). Small sections of the deposit consist of creases and cracks. In contrast to films of Au nanocrystals, Ag nanocrystals do not form hierarchical structures.
Figure 13. The graph shows the variation in resistance of the nanocrystalline Ag film with temperature. The films were made at 50°C for 180 min. A 1.5 mM solution of Ag(PPh₃)₃Cl in toluene (10 ml) was layered atop 16 ml 6.25 mM aqueous sodium hydroxide. The Ag film was observed at the interface and transferred onto a glass substrate to be analysed in a closed cycle with an He cryostat. Contacts were made to the film using copper wires and conductive silver paint.

X-ray diffraction (figure 12) from the interfacial film reveals a pattern typical of Ag albeit with slightly broader peaks characteristic of nanocrystals. These films exhibit strikingly different transport characteristics. The room temperature resistance is very low (approx. 50 Ω). Further, with a change in temperature, the resistance falls, suggesting the film is metallic (figure 13).

6. Conclusion

In summary, we have uncovered a new facile scheme for high-quality CdS nanocrystals. Adopting this method, luminescent CdS nanocrystals with sharp excitonic emission can be obtained at a low temperature of 35°C. The diameters of the nanocrystals as well as the emission maximum could be readily tuned by varying the reaction time.

Uniform films of Au and Ag nanocrystals spread over areas of several square centimetres can be obtained at the water–toluene interface and can be faithfully transferred to glass and other substrates using a mechanical dipping procedure discovered herein. The Au films make good sensors of amine vapours.

The authors wish to thank the Royal Society, RCUK and the University of Manchester for funds.

References


Growth of nanocrystals and thin films


*Phil. Trans. R. Soc. A* (2010)


