



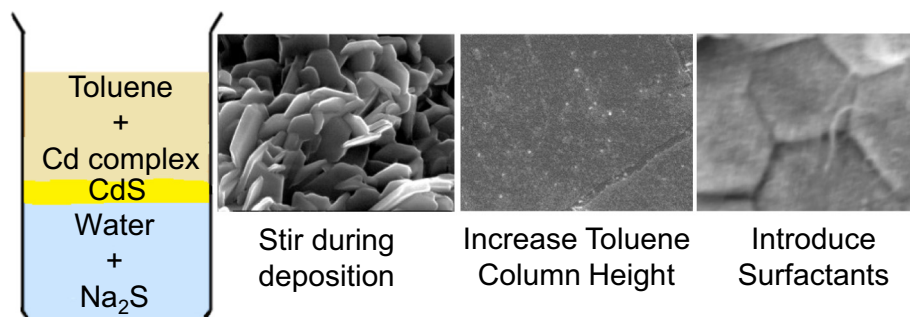
Characteristics of nanocrystalline thin films of cadmium sulphide deposited at the water-oil interface



^a School Chemistry and School of Materials, Oxford Road, The University of Manchester, Manchester M139PL, UK

^b School of Chemistry, Bangor University, Bangor LL57 2UW, UK

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 12 January 2017

Revised 17 February 2017

Accepted 17 February 2017

Available online 22 February 2017

Keywords:

CdS

Nanocrystals

Interfacial deposition

Thin films

Nanoparticles

ABSTRACT

Thin films of nanocrystalline CdS were obtained at the water-toluene interface by reacting cadmium diethyldithiocarbamate in toluene with aq. Na₂S. Three parameters unique to the topical deposition scheme: the effect of column heights, stirring and the action of molecular surfactants are systematically investigated. The obtained nanocrystalline aggregates are characterized by scanning- and transmission electron microscopy, X-ray diffraction and profilometric measurements. Conditions for obtaining smooth device quality thin films have been identified during these experiments.

© 2017 Elsevier Inc. All rights reserved.

1. Introduction

The area surrounding the interface between water and oil is emerging as an exciting medium for the growth and deposition of nanocrystalline thin films [1–5]. Starting with molecular precursors, nanostructured forms of topical materials such as: Au, Ag, CdS, PbS, ZnS, Fe₂O₃ and CeO₂ as well as graphene composites

[6,7] have been obtained using this technique. Detailed studies have been carried out in an attempt to uncover the growth mechanism, particularly in the case of Au using X-ray scattering, photoelectron spectroscopy and electron microscopy [3,5,8,9]. The interfacial deposition scheme is low cost, soft, scalable and is potentially capable of depositing films over large areas. In a typical reaction, a metal precursor dissolved in toluene is layered atop an aqueous column containing a precipitation agent such as Na₂S. If suitable precursors are chosen, the reaction proceeds at the region of contact between the two liquids and yields a film adhered to the water-oil interface. The deposit can then be transferred to a substrate of choice.

* Corresponding author.

E-mail address: john.thomas@bangor.ac.uk (P.J. Thomas).

¹ Present address: Department of Chemistry, University of Benghazi, Faculty of Education, 3188 Benghazi, Libya.



Despite the apparent simplicity of the scheme, processes underpinning interfacial precipitation are complex. Current understanding of surface potentials, diffusion and heat transport mechanisms across water-oil interface are insufficient to advance the area. Even the very nature of the interface between liquids such as water and toluene is subject to much debate [1]. Modelling or predicting the course or the outcome of an interfacial reaction is therefore fraught with difficulty. At present progress in this area is largely driven by experiments. It has been shown empirically that nature of deposits can be altered by conditions such as time, temperature and reagent concentrations [1,3]. However, parameters unique to the technique such as the role of column heights and effect of molecular surfactants are virtually unexplored [3,10]. The former can significantly alter interfacial pressure leading to deposits with new and interesting forms [1]. We considered it important to systematically explore the influence of such factors in dictating the macroscopic structure and properties of the interfacial deposits. We have chosen to study nanocrystalline thin films of CdS, a II-VI semiconductor with a band gap of 2.42 eV, an established photo-conductor with several current and many potential uses [11–14].

2. Methods and materials

The cadmium diethyldithiocarbamate precursor for the deposition of interfacial films was prepared following previous reports. Briefly, 15 mmol diethylamine and 15 mmol of carbon disulphide were added to a stirred 40 ml methanol containing 20 mmol sodium hydroxide. The addition was marked by the solution turning pale yellow. The mixture was then cooled to 4 °C using an ice bath and a 40 ml methanol solution containing 7 mmol cadmium chloride was added dropwise resulting in formation of a pale yellow precipitate. The solid was isolated and purified by re-crystallizing from toluene. Elemental analysis: found (%) (calculated): C 29.56 (30.00); H 4.57 (4.80); N 6.82 (6.80); S 30.67 (31.00); Cd 27.32 (27.40).

2.1. Deposition of CdS thin film at the water-toluene interface

CdS thin film was prepared by layering 30 ml of toluene containing 0.12 mmol cadmium diethyldithiocarbamate over a 30 ml aqueous column containing 0.25 mmol Na₂S in a beaker. The reaction vessel was introduced into an oven preheated to the desired temperature for different times. Following heating, the entire area of contact between the two liquids tuned to yellow signalling the formation of CdS thin film. The liquid phases stayed colourless. The thin film at the interface was transferred to different supports by dipping the substrates at an incline across the interface and moving them gradually upward.

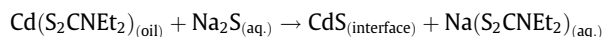
2.2. Characterization

X-ray diffraction was carried out with a Philips Xpert diffractometer utilizing monochromatic CuK α radiation. Samples for diffraction consisted of precipitates deposited on glass substrates. Scanning electron microscopy (SEM) was carried out with Philips Excel microscope equipped with a 30 kV field emission gun or Delong Instruments LVEM5, low-voltage electron microscope. Film thickness were measured with Dektak 8 surface profile measuring system.

3. Results and discussion

Standard conditions for CdS deposition consisted of reactions carried out at 40 °C for two hours with 30 ml aqueous layer and a 30 ml toluene layer measuring 2 cm in height. Following this

scheme, continuous thin film CdS deposits strongly adhered to the interface are obtained and were subsequently transferred to glass substrates. The following reactions take place in the vessel:



Scanning electron microscopy revealed growths that were dominated by microscopic platelets with rounded edges. High resolution imaging revealed coarse grained surfaces on the deposits hinting at a possible nanostructure (see Fig. 1a). Transmission electron microscopy carried out on interfacial growths treated with ultrasound to separate flocculates revealed that the films consists of hexagonal particles with rounded edges with overall dimension of around 7.0 nm (Fig. 1b). The X-ray diffraction pattern consists of broader than usual peaks characteristic of fine particulates of hexagonal CdS (see Fig. 2a). Profilometric measurements on flat glass substrates yielded average thickness of 90 nm. The optical bandgap was estimated to be 2.52 eV. The measured grain sizes, thickness and band gap are inline with a previous report of interfacial CdS obtained under similar conditions [15]. The effect of different variables on the standard scheme are presented below.

3.1. Effect of surfactants

Three surfactants with proven ability to bind to CdS: octylamine, tri-*n*-octylphosphine oxide(TOPO) and tetraoctylammonium bromide(TOAB) were introduced in different quantities at the start of the reaction to evaluate their effects on the growth and deposition of thin films. The affinity of octylamine and TOPO to CdS is well established and routes to alkylamine or TOPO/TOP capped CdS nanocrystals around [16,17]. TOAB is less well-known, but has been shown to quench luminescence by binding to the surface of CdS quantum dots [18]. We find that the intro-

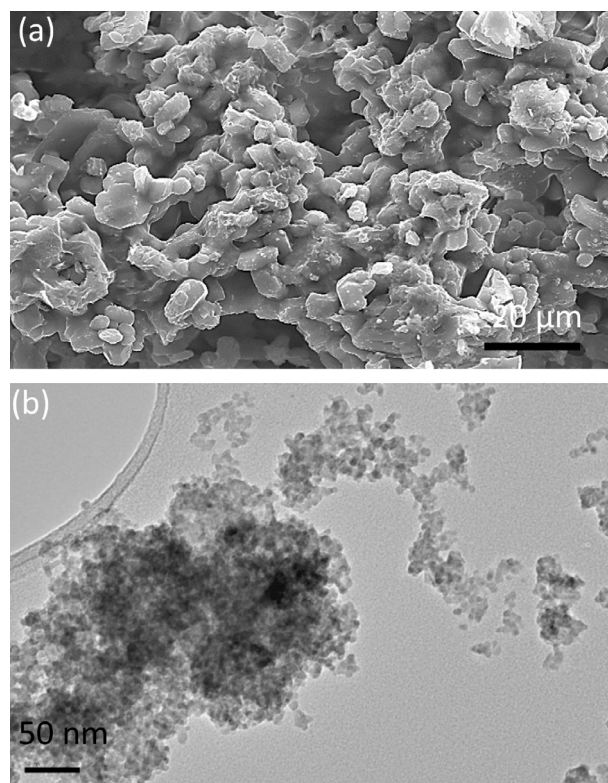


Fig. 1. Electron microscopic images of CdS nanocrystalline films. The films were obtained by reacting 30 ml of 33.3 mM aqueous Na₂S and 30 ml of 0.5 M toluene solution of Cd(S₂CNET₂)₂ at 40 °C after 2 h.

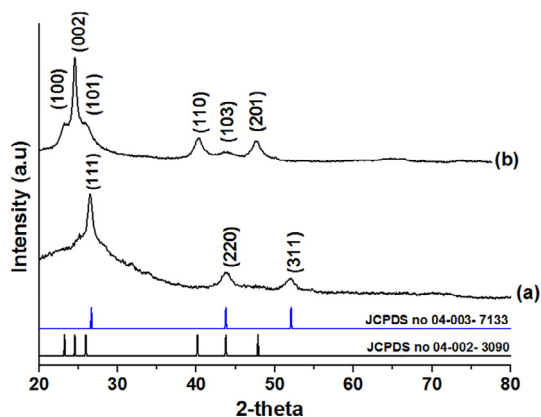


Fig. 2. X-ray diffraction patterns of CdS thin films grown (a) with octylamine and (b) without octylamine. The standard reference patterns for cubic and hexagonal forms are indicated below.

duction of the surfactants noticeably slows down interfacial deposition. In order to achieve films thickness of 90 nm, the deposition time had to be doubled to four hours. X-ray diffraction patterns (see Fig. 2) are consistent with cubic CdS. Here, the deposits appeared to consist of cubic rather than hexagonal nanocrystallites of CdS. Such a phase change is significant as routes to cubic thin films of CdS are rare [19–21]. However, the broader than usual

peak widths caused in part by the fine grained nature of the deposits makes unambiguous assignment difficult.

The surface of CdS deposits can be adorned by thiocarbamate liberated from the precursor and either TOPO, TOABr or octylamine. Evidence from Infrared spectra and microanalysis is ambiguous. Specifically, microanalysis for deposits produced with and without additional surfactants yielded C weight percentages of around ~5%. This is far lower than what is expected for fully capped colloidal nanocrystals [22,23]. However, these findings are inline with other detailed studies which indicate that such films deposited at the interface are particularly bare [24,25]. We are carrying out further studies of surface properties of these crystallites.

In addition to influencing the crystal structure, the surfactants have a profound effect on the microstructure and morphology of the interfacial deposits. We find broadly similar effects in the case of each of the surfactants, with concentration relative to metal precursor being the key parameter. At low concentration ratios (1:0.01, metal:surfactant), smooth films with vein like deposits are seen in the scanning electron micrographs (see Fig. 3). This is in contrast to the structures in Fig. 1a. Intermediate quantities in the range of 1:0.05–1:0.1, yield interfacial deposits with well defined hexagonal cells with longest dimension around 1.3–1.8 μm with around 100 nm separation between the cells. Such mesostructured assemblies are novel particularly following the interfacial deposition scheme. The assembly process is fragile and is critically dependent on the metal ion:surfactant ratio. Higher concentrations of surfactants lead to collapse of assembly leading

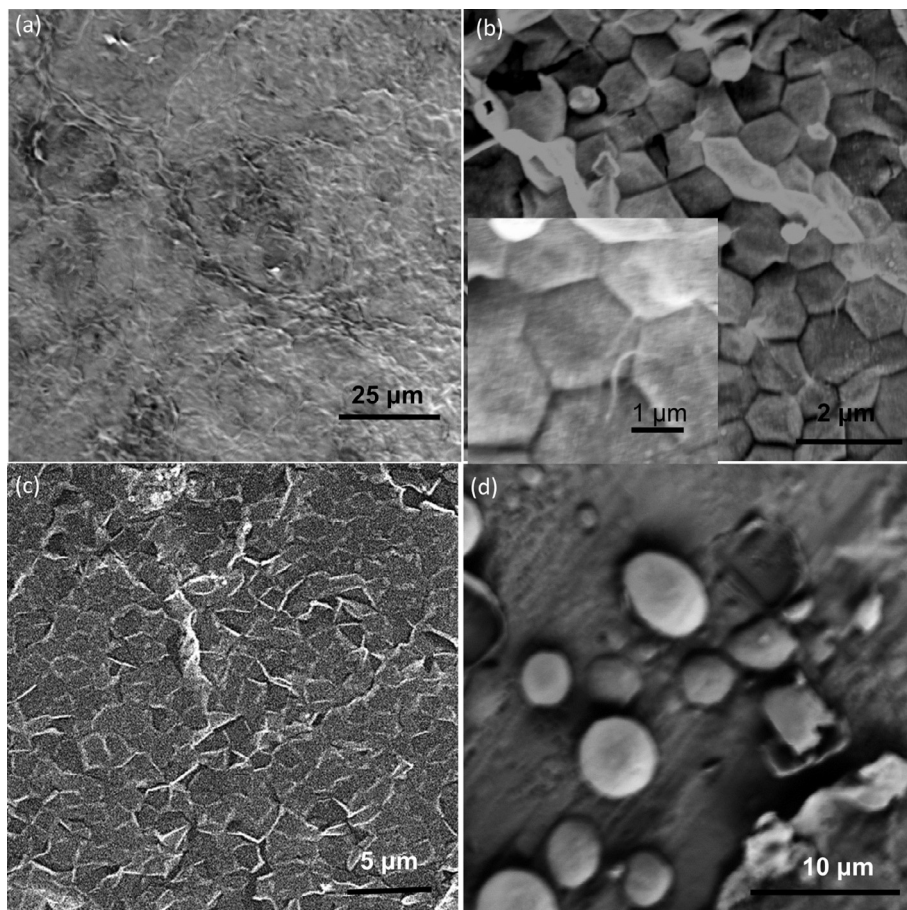


Fig. 3. Scanning electron micrographs of CdS films grown in the presence of different quantities of octylamine. The deposits were obtained with 30 ml of 33.3 mM aqueous Na_2S and 30 ml of 0.5 M toluene solution of $\text{Cd}(\text{S}_2\text{CNET}_2)_2$ containing (a) 0.15 mmol octylamine; (b) 1.5 mmol octylamine; (c) 1.5 mmol tetraoctylammonium bromide and (d) 3 mmol octylamine.

to precipitates that consist of spheroidal overlayers on a smooth deposit (Fig. 3d). Similar results were obtained with TOAB and TOPO. The cell structure following deposition with TOAB is shown in Fig. 3c. Previously, Au and Ag nanocrystals grown at the interface have been shown to adapt fractal and dendritic aggregates under the influence of surfactants [3,10]. Such structures have also been seen in the case of nanocrystals that are obtained by self-assembly at the interface [26]. These aggregates are believed to be driven by specific particle-surfactant interaction. In our case, the ubiquity of the cell structures suggests that the assembly process is generic and is perhaps independent of specific particle-surfactant interaction effects. We are as yet unable to ascertain the underlying cause of this process. We speculate that these large mesoscale patterns are a result of pattern forming convection currents at the interface of two-fluids such as Bernard-Marangoni cells [27–29].

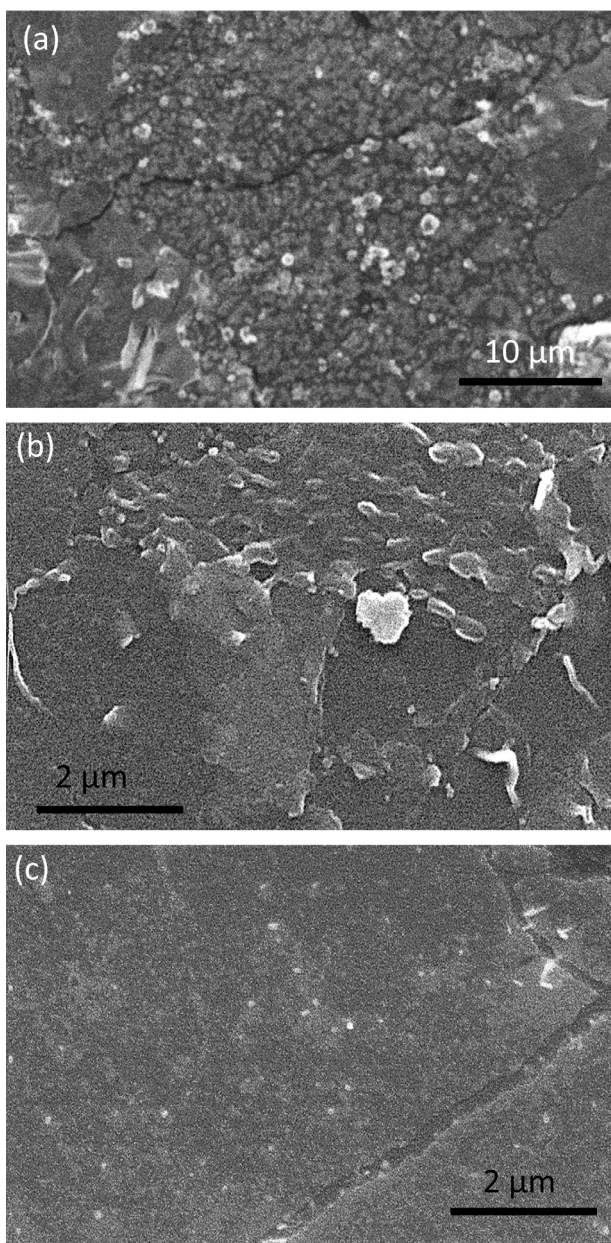


Fig. 4. Scanning electron micrographs of CdS deposits obtained with toluene column heights of: (a) 4 cm; (b) 6 cm and (c) 8 cm.

3.2. Effect of height

A series of experiments with different column heights of toluene were carried out in custom made tall form beakers. In these set of experiments, different volumes of the same stock solution of toluene was used and the concentration of the aq. layer increased to compensate for the increase quantity of the metal precursor. The column height was increased from the standard 2 cm to 8 cm. This change in height corresponds to an increase in pressure on an individual 7.0 nm grain of CdS from $8.57 \times 10^{-11} \text{ mN nm}^{-2}$ to $3.43 \times 10^{-10} \text{ mN nm}^{-2}$. For comparison, the pressure change herein is an order of magnitude higher than those accessible in a typical Langmuir-Blodgett deposition scheme [1]. The greatest height yielded very smooth films (compare Fig. 4c and 1a). There were no tangible change in other characteristics of the film including grain size, thickness and crystal structure. It is possible to make reliable contacts to carry out charge transport measurements on films of such quality. The sheet resistance of the thin film grown using a column height of 8 cm was $2 \times 10^5 \Omega \text{ cm}^{-2}$ and two orders of magnitude lower than those deposited at the shortest level of 2 cm. The fall is possibly due to better contact being established with the smoother surface of the former. The resistance values of the smooth layers herein are comparable to those of high quality films obtained using high temperature schemes such as vapour deposition [30].

3.3. Effect of stirring

Unlike in a traditional bath deposition, stirring has a different role in the interfacial scheme. Agitation of the contents of the beaker using a high speed orbital mixer during the deposition process is expected to lead to a greater area of contact between the two liq-

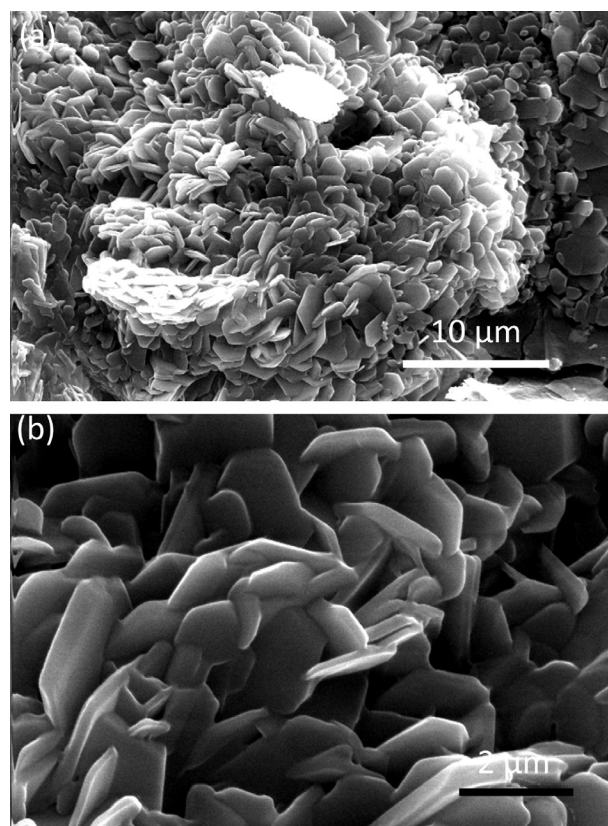


Fig. 5. Scanning electron micrographs of CdS deposits obtained while the two liquids are stirred with high speed orbital mixer.

uids as the original liquid interface is broken into smaller fragments. Heat flow, particularly across the water-oil interface is likely to be enhanced to some extent [31,32]. Agitation can lead to better diffusion and transport of ions to the interface. Combined with increased area of contact, greater interchange of ions between fluids is feasible [33,34]. We find that introduction of stirring leads to significant changes to the microstructure of the films. The deposits produced by stirring contain clear hexagonal platelets that form a macroscopic aggregate (see Fig. 5). Each of these platelets are about a micron wide and around 90 nm thick. We believe that the individual platelets adorn the droplets formed during the stirring process and come together to form loose interfacial aggregates at the end of mixing prior to transfer to substrate. The assembly into platelets lead to little change to the diffraction pattern and absorption spectra.

4. Conclusion

In summary, change of height, introduction of stirring and the use of surfactants produce tangible changes to the micro- and mesostructure of the films and extend as far as to influence the crystal structure of the obtained nanocrystalline CdS film. Smooth, device quality films can be produced by increasing the height of the toluene column to 8 cm. Apparently cubic CdS can be obtained by introducing surfactants during the deposition. For the first time, interfacial deposits were found to adopt mesoscale structures when under the influence of stirring or the introduction of surfactants during growth. The cause of such an assembly is currently uncertain and could be a topic of future studies. The dithiocarbamate family of metal precursors have proven useful in the interfacial growth of nanocrystalline forms of ZnS [15], PbS [35], Bi₂S₃ [36] and Cd(OH)₂ [37]. We envisage that the conclusions of this study can be applied to the broad range of materials following the route indicated.

References

- [1] P.J. Thomas, E. Mbufu, P. O'Brien, Thin films of metals, metal chalcogenides and oxides deposited at the water-oil interface using molecular precursors, *Chem. Commun.* 49 (2013) 118–127.
- [2] R.A.W. Dryfe, Modifying the liquid/liquid interface: pores, particles and deposition, *Phys. Chem. Chem. Phys.* 8 (2006) 1869.
- [3] C.N.R. Rao, K.P. Kalyanikutty, The liquid-liquid interface as a medium to generate nanocrystalline films of inorganic materials, *Acc. Chem. Res.* 41 (4) (2008) 489–499.
- [4] S.G. Booth, R.A.W. Dryfe, Assembly of nanoscale objects at the liquid/liquid interface, *J. Phys. Chem. C* 119 (2015) 23295.
- [5] R.A.W. Dryfe, A. Uehara, S.G. Booth, Metal deposition at the liquid-liquid interface, *Chem. Rec.* 14 (2014) 1013.
- [6] K. Bramhaiah, N.S. John, Hybrid films of reduced graphene oxide with noble metal nanoparticles generated at a liquid/liquid interface for applications in catalysis, *RSC Adv.* 3 (2013) 7765–7773.
- [7] K. Bramhaiah, V.N. Singh, N.S. John, Hybrid materials of ZnO nanostructures with reduced graphene oxide and gold nanoparticles: enhanced photodegradation rates in relation to their composition and morphology, *Phys. Chem. Chem. Phys.* 18 (2016) 1478–1486.
- [8] S.G. Booth, A. Uehara, S.Y. Chang, J.F.W. Mosselmans, S.L.M. Schroeder, R.A.W. Dryfe, Gold deposition at a free-standing liquid/liquid interface: evidence for the formation of Au(I) by microfocus X-ray spectroscopy (mu XRF and mu XAFS) and cyclic voltammetry, *J. Phys. Chem. C* 119 (2015) 16785.
- [9] A. Uehara, T. Hashimoto, R.A.W. Dryfe, Au electrodeposition at the liquid-liquid interface: mechanistic aspects, *Electrochem. Acta* 118 (2014) 26.
- [10] V.V. Agrawal, G. Kulkarni, C. Rao, Surfactant-promoted formation of fractal and dendritic nanostructures of gold and silver at the organicaqueous interface, *J. Coll. Interf. Sci.* 318 (2) (2008) 501–506.
- [11] P.R. Herczfeld, Low frequency oscillations in CdS photo-conductors induced by optical quenching, *Physica* 39 (1968) 439.
- [12] J. He, W. Ji, G.H. Ma, S.H. Tang, E.S.W. Kong, S.Y. Chow, X.H. Zhang, Z.L. Hua, J.L. Shi, Ultrafast and large third-order nonlinear optical properties of CdS nanocrystals in polymeric film, *J. Phys. Chem. B* (2005) 4373.
- [13] K.L. Chorpura, P.D. Paulson, V. Dutta, Thin-film solar cells: an overview, *Prog. Photovoltaics: Res. Appl.* 12 (2004) 69.
- [14] H.J. Kim, C.-W. Kim, D.Y. Jung, C. Jeong, Effect of reaction temperature of CdS buffer layers by chemical bath deposition method, *J. Nanosci. Nanotechnol.* 16 (2016) 5114.
- [15] D. Fan, P.J. Thomas, P. O'Brien, Deposition of CdS and ZnS thin films at the water/toluene interface, *J. Mater. Chem.* 17 (2007) 1381.
- [16] C.N.R. Rao, P.J. Thomas, G.U. Kulkarni, *Nanocrystals: Synthesis, Properties and Applications*, Springer, 2007.
- [17] V. Rotello (Ed.), *Nanoparticles: Building Blocks for Nanotechnology*, Springer, 2012.
- [18] T. Hiratani, K. Konishi, Surface-cap-mediated host-guest chemistry of semiconductor CdS: intercalative cation accumulation around a phenyl-capped CdS cluster and its notable effects on the cluster photoluminescence, *Angew. Chem. Intl. Ed.* 116 (44) (2004) 6069–6072.
- [19] I.-H. Choi, P.Y. Yu, Structural and optical properties of cubic-CdS and hexagonal-CdS thin films grown by MOCVD on GaAs substrates using a single-source precursor C₁₄H₃₀CdN₂S₄, *Phys. Stat. Sol. (b)* 242 (2005) 1610.
- [20] R. Lozada-Morales, O. Zelaya-Angel, G. Torres-Delgado, Photoluminescence in cubic and hexagonal CdS films, *App. Surf. Sci.* 175–176 (2001) (10th International Conference on Solid Films and Surfaces).
- [21] O. Zelaya-Angel, L. Hernandez, O. de Melo, J. Alvarado-Gil, R. Lozada-Morales, C. Falcony, H. Vargas, R. Ramirez-Bon, Band-gap shift in CdS: phase transition from cubic to hexagonal on thermal annealing, *Vacuum* 46 (8) (1995) 1083–1085.
- [22] S.J.O. Hardman, D.M. Graham, S.K. Stubbs, B.F. Spencer, E.A. Seddon, H.-T. Fung, S. Gardonio, F. Sirotti, M.G. Silly, J. Akhtar, P. O'Brien, D.J. Binks, W.R. Flavell, Electronic and surface properties of PbS nanoparticles exhibiting efficient multiple exciton generation, *Phys. Chem. Chem. Phys.* 13 (2011) 20275–20283.
- [23] J. Tang, L. Brzozowski, D.A.R. Barkhouse, X. Wang, R. Debnath, R. Wolowiec, E. Palmiano, L. Levina, A.G. Pattantyus-Abraham, D. Jamakosmanovic, E.H. Sargent, Quantum dot photovoltaics in the extreme quantum confinement regime: the surface-chemical origins of exceptional air- and light-stability, *ACS Nano* 4 (2) (2010) 869–878.
- [24] P.J. Thomas, G.L. Stansfield, N. Komba, D.J.H. Cant, K. Ramasamy, E. Albrasi, H. Al-Chaghouri, K.L. Syres, P. O'Brien, W.R. Flavell, E. Mubofu, F. Bondino, E. Magnano, Growth of nanocrystalline thin films of metal sulfides [CdS, ZnS, CuS and PbS] at the water-oil interface, *RSC Adv.* 5 (2015) 62291–62299.
- [25] D.J.H. Cant, K.L. Syres, P.J.B. Lunt, H. Radtke, J. Treacy, P.J. Thomas, E.A. Lewis, S. J. Haigh, P. O'Brien, K. Schulte, F. Bondino, E. Magnano, W.R. Flavell, Surface properties of nanocrystalline PbS films deposited at the water-oil interface: a study of atmospheric aging, *Langmuir* 31 (4) (2015) 1445–1453.
- [26] P.J. Thomas, E. Albrasi, S.N. Mlondo, P. O'Brien, The assembly of metal nanocrystals into films mediated by amines at the wateroil interface, *J. Phys. Chem. C* 115 (30) (2011) 14668–14672.
- [27] M.C. Cross, P.C. Hohenberg, Pattern formation outside of equilibrium, *Rev. Mod. Phys.* 65 (1993) 851–1112.
- [28] A. Golovin, A. Nepomnyashchy, L. Pismen, Pattern formation in large-scale Marangoni convection with deformable interface, *Phys. D: Nonlinear Phenom.* 81 (1995) 117–147.
- [29] L. Shtilman, G. Sivashinsky, Hexagonal structure of large-scale Marangoni convection, *Phys. D: Nonlinear Phenom.* 52 (1991) 477–488.
- [30] C. Kumar, N. Hoa, S.-G. Yoon, E.-T. Kim, J.-H. Lee, G.-H. Kim, Highly photoconductive CdS thin films synthesized by using chemical bath deposition, *J. Korean Phys. Soc.* 55 (2009) 284.
- [31] J.T. Davies, E. Rideal, *Interfacial Phenomena*, second ed., Academic Press, New York, 1963.
- [32] A.G. Volkov, D.W. Deamer, D.L. Tanelian, *Liquid Interfaces in Chemistry and Biology*, Wiley, Weinheim, 1998.
- [33] I. Benjamin, Static and dynamic electronic spectroscopy at liquid interfaces, *Chem. Rev.* 106 (2006) 1212.
- [34] Y. Lin, H. Skaff, T. Emrick, A.D. Dinsmore, T.P. Russell, Nanoparticle assembly and transport at liquid-liquid interfaces, *Science* 299 (5604) (2003) 226–229.
- [35] D. Fan, P.J. Thomas, P. O'Brien, Pyramidal lead sulfide crystallites with high energy {113} facets, *J. Am. Chem. Soc.* 130 (2008) 10892.
- [36] D. Fan, P.J. Thomas, P. O'Brien, Synthesis and assembly of Bi₂S₃ nanoparticles at the water-toluene interface, *Chem. Phys. Lett.* 465 (2008) 110.
- [37] S.N. Mlondo, E.M. Andrews, P.J. Thomas, P. O'Brien, Deposition of hierarchical Cd(OH)₂ anisotropic nanostructures at the water-toluene interface and their use as sacrificial templates for CdO or CdS nanostructures, *Chem. Commun.* (2008) 2768.

