Deposition of hierarchical $Cd(OH)_2$ anisotropic nanostructures at the water–toluene interface and their use as sacrificial templates for CdO or CdS nanostructures†

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Hierarchical anisotropic structures ranging from triangular 'platelets' to nanofibres of $Cd(OH)_2$ are synthesized at a water–toluene interface; the nanowires are used as sacrificial templates to produce CdO wires and CdS nanostructures, preserving many structural aspects.

The areas surrounding the interface between two fluids possess unique properties distinct from the familiar bulk due to the domineering roles of viscosity and surface tension.[1] Studies in this area find inspiration in nature's reliance on the interfacial area to carry out diverse functions such as muscular contraction and bone growth.[2] Control over interfacial properties is now recognized as important for many areas of applications such as in the food processing, metallurgy and petrochemical industries.[3] Herein, we report a novel use for fluid interfaces by demonstrating their ability to grow nanowires of the semiconductor $Cd(OH)_2$. The process is exceedingly simple and is potentially generic. Further, the $Cd(OH)_2$ nanowires can be converted to CdS or CdO nanostructures by thermal and/or chemical treatment.

Cadmium hydroxide is a transparent, wide band-gap semiconductor with a brucite type layered structure. It has a number of possible applications including use in solar cells. Previously, long $Cd(OH)_2$ nanowires have been prepared using a hydrothermal method,[4] and anisotropic nanostructures grown on silicon substrates through the hydrothermal crystallization of pre-deposited colloidal precursors.[5] Monoclinic $Cd(OH)_2$ nanowires have been obtained on glass substrates by chemical bath deposition.[6] Nanowires of $Cd(OH)_2$ have been found to be useful sacrificial templates in the synthesis of CdS, CdSe, CdO or silica nanostructures.[4,7]

Hierarchical $Cd(OH)_2$ nanostructures are obtained as deposits at the interface between water and toluene. In a typical synthesis, a toluene solution containing cadmium cupferronate and octylamine is stood in contact with an aqueous solution containing NaOH. $Cd(OH)_2$ structures are obtained in the form of white deposits spread across the interfacial region from reaction vessels held at 70 °C for 19 h.‡ The deposits completely covered the interfacial region and were transferred to glass substrates. The solutions in both layers remained clear throughout. SEM images (see Fig. 1) show that the deposits consist of uniform wires pointing upwards. The diameters of the wires are about 188 nm, while their lengths are microscopic. The lengths could not be accurately measured due to the manner in which the nanowires grow.

The wires grow out in bunched groups from seeds rather than being uniformly distributed on the surface of the interface. This is clearly visible in Fig. 1a, where two different regions are indicated. The seeds nucleating the growth seem to adorn some specific underlying layer. We have isolated the underlying structure by growing films under different conditions. Films grown for 2 h at 50 °C consisted of large triangular 'plate-like' structures with microscopic edge lengths (see Fig. 1b). Small, short stumps terminating in a hexagon-like feature extend from the centre of each triangular platelet. The wires primarily adorn the edges of these hexagonal features. Upon saturation of the edge locations, the wires begin to grow off the other edges of the triangular platelets forming hierarchical 'hedgehog' structures. The deposits grown for 10 h at 60 °C consist of platelets adorned with shorter wires (see Fig. 1c and 2). At short deposition times, interfacial deposits consist of small tightly-packed spherical granules. The triangular structures grow on top of this

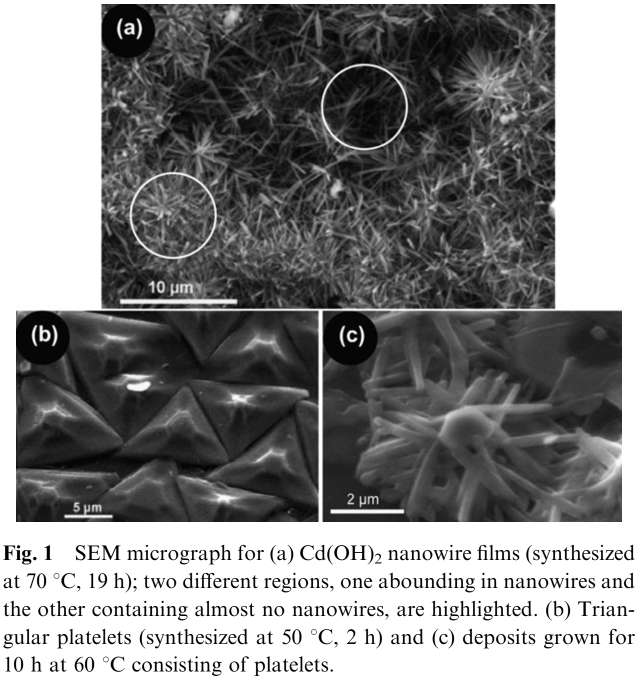

Fig. 1 SEM micrograph for (a) $Cd(OH)_2$ nanowire films (synthesized at 70 °C, 19 h); two different regions, one abounding in nanowires and the other containing almost no nanowires, are highlighted. (b) Triangular platelets (synthesized at 50 °C, 2 h) and (c) deposits grown for 10 h at 60 °C consisting of platelets.

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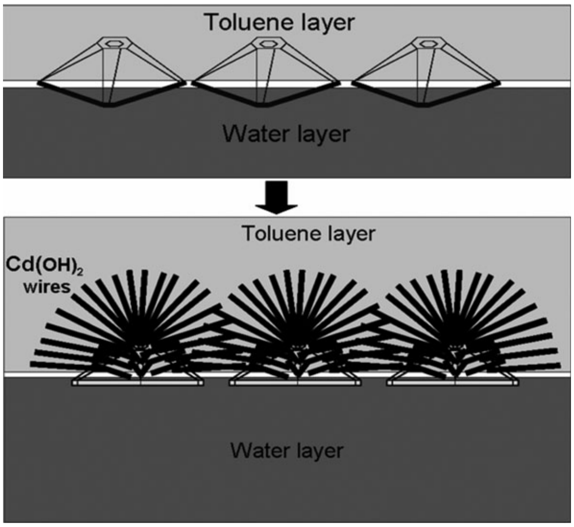

Fig. 2 Schematic diagram illustrating the growth of Cd(OH)$_2$ nanowires from the interfacial triangular platelets to the 'hedgehog' structures. When cadmuim cupferronate in toluene is reacted with aqueous NaOH in a beaker between 50 and 70 °C, the platelets form initially (~2 h) and transform into hedgehog structures after 19 h.

granular layer. X-Ray diffraction patterns of the wires and those of triangular platelets were characteristic of hexagonal β-Cd(OH)$_2$ crystallites (brucite structure, JCPDS no. 31–0228) oriented along the (001) direction (see Fig. 3). The degree of orientation is substantially increased following the growth of wires. The wires present uniform contrast along their entire length in the transmission electron microscope (TEM) (see Fig. 4). However, the wires were prone to beam damage. Hence, the high resolution images consisted of grains with dimensions between 4–10 nm with lattice spacing corresponding to separation between the 100 planes of β-Cd(OH)$_2$.

The origin of anisotropic growth at the water–toluene interface can be traced to factors associated with formation of the interface between the immiscible liquids and colloidal adsorption at fluid interfaces. Layering of liquids such as water and toluene on top of each other leads to a number of changes in the properties of the liquids in immediate vicinity of interface.[3] The mechanisms of ion and heat transfer are altered. Additionally, limited mixing of the two solvents takes places around the interfacial region. The mixed layers lead to the formation of the initially obtained spherical granules. These granules posses high interfacial energy (around $10^4\ k_BT$ per particle at room temperature) and are adsorbed at the fluid interface forming Pickering emulsions.[3] The emulsion formation lowers the interfacial tension, permitting limited diffusion of hydroxide ions across the water–toluene interface. The hydroxide ions liberate the bound Cd^{2+} species forming the platelets under near equilibrium growth conditions. The platelets are low-dimensional adaptations of the equilibrium form and have been previously observed as additional products in the synthesis of monoclinic Cd(OH)$_2$ nanowires.[6] The interfacial adsorption of the larger platelets leads to a greater fall in interfacial tension. The elevated temperatures and much lowered interfacial tension results in more effective hydroxyl ion diffusion, prompting the growth of nanowires under kinetic control in metal-ion depleted conditions. The 001 direction is presumably the preferred growth direction. We find that a high relative concentration of hydroxide ions is essential to obtain wire growth. Under conditions of low hydroxide ion concentration or temperatures, only the triangular platelet structures are obtained.

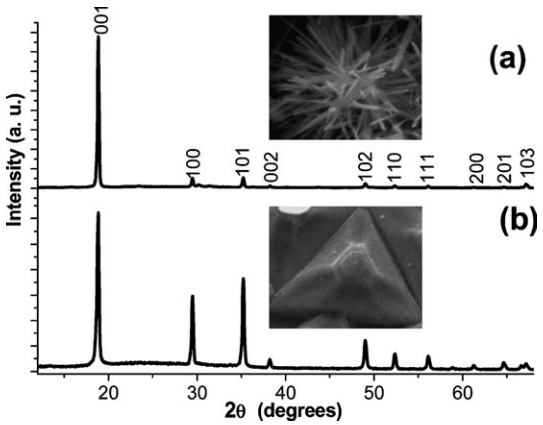

Fig. 3 XRD patterns of the (a) wires (synthesized at 70 °C, 19 h) and of the (b) triangular platelets (synthesized at 50 °C, 2 h) of hexagonal β-Cd(OH)$_2$ crystallites (brucite structure, JCPDS no. 31–0228).

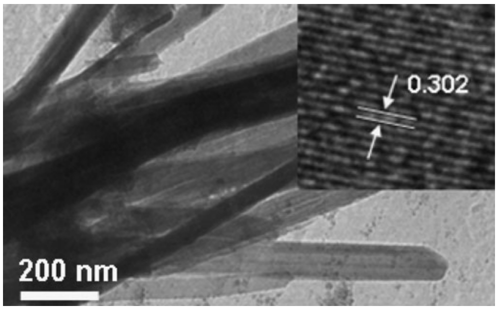

Fig. 4 TEM of Cd(OH)$_2$ wires and the HRTEM image showing the lattice planes (inset).

The hierarchical Cd(OH)$_2$ structures can be converted to CdO by calcination at 250 °C for 8 h. The XRD patterns revealed the presence of cubic CdO with the rock salt structure (JCPDS no. 75–1529, Fig. 5a) slightly oriented along the 111 plane. SEM images reveal that calcination has largely preserved the anisotropic morphology (see Fig. 6a). However, the underlying triangular platelet structures have been lost. The SEM and TEM images show that the diameters of the CdO wires are about 162 nm (see Fig. 6a; TEM images are provided in the ESI†). The Cd(OH)$_2$ structures can be converted to CdS nanostructures by heating the films at 180 °C for 2 h in an atmosphere of H_2S (see Fig. 5b and 6b). The CdS structures consist of string-like features made up of flocculated nanoparticles with diameters in the range of 15–30 nm (see TEM images provided in the ESI†).

Recently, liquid–liquid interfaces have been used to grow films of nanocrystals,[8] as well as to assemble particles from well-dispersed colloids.[9] This report significantly extends the scope of synthetic schemes involving fluid interfaces by demonstrating their ability to generate one-dimensional nanostructures. We envisage this method to be a significant addition to the arsenal of techniques used to obtain anisotropic nanostructures.

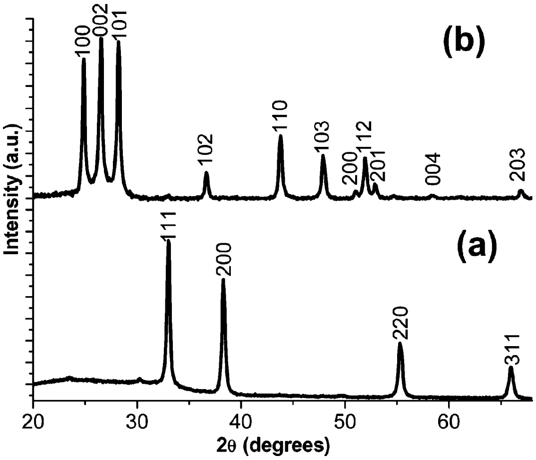

Fig. 5 XRD patterns for (a) CdO wires and (b) CdS particles.

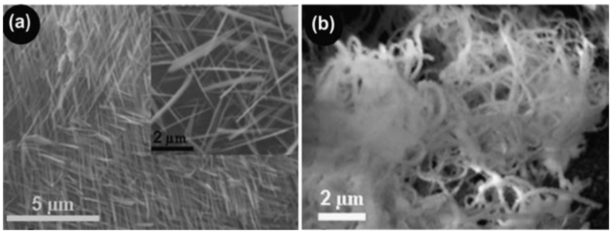

Fig. 6 SEM images for (a) CdO wires and (b) CdS particles.

In conclusion, $Cd(OH)_2$ wires of uniform morphology have been grown at a liquid–liquid interface without the use of any templates. These $Cd(OH)_2$ wires proved to be good sacrificial templates for the growth of one-dimensional CdO or CdS nanostructures. The factors promoting interfacial growth are largely extrinsic, suggesting that this is a potentially useful generic method to synthesize one-dimensional nanostructures. This study could also prove useful to theoreticians as there has been a significant interest in the computer simulation[10] of the growth and stability of simple anisotropic structures, such as rods at interfaces. The work offers the possibility of extending these studies to more complex hierarchical structures.

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Notes and references

‡ Synthesis of $Cd(OH)_2$ nanowires: a 20 ml toluene solution containing 20 mg of cadmium cupferronate (2.59 mmol l^{-1}) and 1 ml of octylamine is stood in contact with a 20 ml aqueous solution containing 41.44 mg of NaOH (0.05 mol l^{-1}) in a beaker (100 ml, 5.3 cm diameter, 8 cm high). The reaction vessel was covered and transferred to an incubator at 70 °C and allowed to stand for 19 h. $Cd(OH)_2$ structures were obtained in the form of white deposits spread across the interfacial region. The deposits covered the whole of the interfacial region and were transferred to a glass substrate previously introduced at the bottom of the reaction vessel by removing the solutions with a syringe, moving the film to the bottom of the vessel. The solutions in both layers remained clear throughout.
Synthesis of CdO wires and CdS nanostructures: $Cd(OH)_2$ nanowires were converted to CdO by calcination at 250 °C for 8 h, and to CdS nanostructures by heating the films at 180 °C for 2 h in an atmosphere of H_2S.

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