Basic cadmium salts as phase-directing agent for the phase and morphology control of metal hydroxychlorides

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Basic cadmium salts (CdOHCl and $Cd(OH)NO_3{\cdot}H_2O$) were used as phase-directing agents to guide the phase development of various metal hydroxychlorides including $Cu_2(OH)_3Cl$, $Co_2(OH)_3Cl$, $Zn_5(OH)_8Cl_2(H_2O)$, $Sn_3O(OH)_2Cl_3$ and PbOHCl. The simple synthesis procedure includes only one step: solid basic cadmium salt was suspended in aqueous or ethanolic solution of metal salt for 6 h in ambient environment. The separated products from the solution had various morphologies such as sphere, bundle, sheet, hollow sphere and cube. The phase direction behaviour of basic cadmium salts can be attributed to their high reactivity, and most importantly to the structure similarity between basic cadmium salts and metal hydroxychlorides.

1. Introduction: Basic metal salt is an intermediate between metal salt and hydroxide or oxide, which includes oxyacetate, oxy-/hydroxyl-halide and hydroxyl-oxysalt. It is an important category of compounds, which can be used as functional materials in various applications [1–5] or as templates [6–11] for building diversified nanostructures. For example, fullerene-like nanocrystal of nickel hydroxychloride presented unusual magnetic phase transition behaviour at low temperature [5]. In this case, it was considered to be a new platform for investigating exotic magnetic phenomena at nanoscale. In another example, it was found that copper hydroxychloride with morphology of hollow nanosphere showed strong antibacterial effect on staphylococcus aureus [3]. At the same time, basic metal salts ($Y(OH)CO_3{:}Eu^{3+}$, $Zn_5(CO_3)_2(OH)_6$, $Cu_2Cl(OH)_3$, CdOHCl, etc.) [6–8, 10, 11] have been used as templates to prepare different nanostructures. For example, CdOHCl is a frequently used sacrificial template for the construction of various hollow structures [6, 8]. In an interesting work, ZnO having a complex nanostructure, ring-like nanosheets standing on spindle-like rods, was produced by nucleation in alkaline solution using $Zn_5(OH)_8Cl_2{\cdot}H_2O$ as precursor [9].

As basic metal salt, metal hydroxyl-halide has a structure consisting of c.p. layers with composition of X(OH) or $X(OH)_3$ (X = F, Cl or Br). Between these layers, metal atoms occupy, respectively, one-half or one-quarter of the octahedral interstices [12]. In general, metal basic salts including hydroxyl-halides can be prepared in various ways involving direct or indirect hydrolysis of metal salt. The hydrolysis was carried out at controlled conditions (temperature, acidity, metal-ion concentration, etc.), or indirectly by heating a hydrated salt [1, 2, 6–9, 13]. Other strategies such as hydrothermal, solvothermal or eletrochemistry routes were also used, although they were rarely applied for the preparation of basic metal salts [5, 14, 15].

Usually, the structure of inorganic compounds depends on the nature of reactants. It can be tuned by the reaction conditions (temperature, pressure, solvent, atmosphere, etc.) during synthesis, and its development can also be directed by the alien species (namely so-called structure-directing agent). Structure-directing agents (SDAs) include solvents, inorganic or organic compounds, functioning through their interaction with the ions of reactant or the generated intermediate [16–19]. The properties of functional group or active centre in SDA molecule could determine the structure of target product without structure similarity between them. In this Letter, a new strategy was proposed to direct the phase formation and control the morphology of various metal hydroxychlorides, using basic cadmium salts (CdOHCl and $Cd(OH)NO_3{\cdot}H_2O$) as phase-directing agents. This strategy utilised the structure similarity between phase-directing agent and hydroxychlorides. The produced hydroxychlorides owned different morphologies including sphere, bundle, sheet, hollow sphere and cube.

2. Experimental: Cadmium chloride hemi(pentahydrate) ($CdCl_2{\cdot}2.5H_2O$, ≥98%), cadmium nitrate tetrahydrate ($Cd(NO_3)_2{\cdot}4H_2O$), cobalt chloride hexahydrate ($CoCl_2{\cdot}6H_2O$, ≥99.0%), copper chloride dihydrate ($Cu(NO_3)_2{\cdot}2H_2O$ ≥99%), lead nitrate ($Pb(NO_3)_2$, ≥99%), zinc chloride ($ZnCl_2$, ≥98%), stannous chloride dihydrate ($SnCl_2{\cdot}2H_2O$, ≥98%), propylene oxide (C_3H_6O, ≥99.5%), thioacetamide (C_2H_5NS, ≥99%), absolute ethanol and acetone were obtained from Aladdin and used as received.

Synthesis of phase-directing agents: water and ethanol were used, respectively, as solvent for the preparation of CdOHCl and $Cd(OH)NO_3{\cdot}H_2O$. Propylene oxide was added to a 0.6 mol l^{-1} $CdCl_2{\cdot}2.5H_2O$ or $Cd(NO_3)_2{\cdot}4H_2O$ solution with molar ratio of propylene oxide to metal ions = 10. White precipitation was produced within 1 h under magnetic stirring. After reaction for 24 h, wet resultant (CdOHCl or $Cd(OH)NO_3{\cdot}H_2O$) was separated from the suspension by filtration and then washed by water (CdOHCl) or acetone ($Cd(OH)NO_3{\cdot}H_2O$).

Synthesis of metal hydroxychlorides and CdS: all products (metal hydroxychlorides and CdS) were prepared at same reaction conditions. The raw materials and solvents used for the preparation of target products were listed in Table 1. In a typical synthesis, phase-directing agent (CdOHCl or $Cd(OH)NO_3{\cdot}H_2O$) was suspended in an aqueous or ethanolic solution of metal salt under stirring for 6 h (the molar ratio of metal salt to basic cadmium salt was kept at 1.1). The final product was obtained by sequent steps including filtration, thorough water or acetone-washing and drying at 80°C.

Characterisation: XRD patterns of samples were measured in Shimadzu LabX XRD-6100 diffractometer using CuKa radiation. The morphology of samples was observed by JEOL 1400 transmission electron microscope.

3. Results and discussion: The XRD patterns of as-prepared phase-directing agents are shown in Fig. 1*a*. The diffraction lines of the sample prepared using $CoCl_2{\cdot}6H_2O$ as raw material are well indexed to CdOHCl, while the sample synthesised from $Cd(NO_3)_2{\cdot}4H_2O$ is identified as $Cd(OH)NO_3{\cdot}H_2O$. It is known that propylene oxide as precipitation agent would undergo protonation

Table 1 Phase and morphology of basic cadmium salts derived metal hydroxychlorides and CdS

Phase controlling agent	Raw materials	Solvent	Product	Morphology
CdOHCl	$Cu(NO_3)_2 \cdot 2H_2O$	Water	$Cu_2(OH)_3Cl$	Irregular shape
	$Pb(NO_3)_2$	Water/ethanol	PbOHCl	Sphere/bundle
	$ZnCl_2$	Water	$Zn_5(OH)_8Cl_2(H_2O)$	Sheet
	$SnCl_2 \cdot 2H_2O$	Water	$Sn_3O(OH)_2Cl_3$	Hollow sphere
	$CoCl_2 \cdot 6H_2O$	Water	$Co_2(OH)_3Cl$	Cube
	thioacetamide	Water	CdS	Fiber
$Cd(OH)NO_3 \cdot H_2O$	$Cu(NO_3)_2 \cdot 2H_2O$	Water	$Cu_2(OH)_3Cl$	Cube
	$ZnCl_2$	Water	$Zn_5(OH)_8Cl_2(H_2O)$	Sheet
	$SnCl_2 \cdot 2H_2O$	Water	$Sn_3O(OH)_2Cl_3$	Hollow sphere
	$CoCl_2 \cdot 6H_2O$	Water	$Co_2(OH)_3Cl$	Cube
	thioacetamide	Water	CdS	Sphere

of its oxygen and subsequent ring opening with linkage of nucleophilic anionic conjugate base (Cl^- or NO_3^- ions) to form substituted alcohol compound. It consumes the protons in the aquo complexes of cadmium ions and water, which promotes the hydrolysis of $[Cd(H_2O)_n]^{2+}$. Just like the cases occurring in previous works [20, 21], $[Cd(H_2O)_n]^{2+}$ ions cannot be fully hydrolysed and thus Cl^- or NO_3- ions occupy the lattice of crystallised species to form CdOHCl or $Cd(OH)NO_3 \cdot H_2O$ instead of hydroxide. This could be attributed the low acidity of aquo complexes of divalent metal ions in the solution (the related mechanism was described in literatures [20–23]). As shown in TEM images (Figs. 1*b* and *c*), both samples of CdOHCl and Cd(OH)$NO_3 \cdot H_2O$ present rod-like morphology between a few hundred nanometre and microns.

The obtained basic cadmium salts (CdOHCl and Cd(OH)$NO_3 \cdot H_2O$) were used as phase-directing agents to synthesise metal hydroxychlorides through a simple preparation procedure. The suspension of basic cadmium salts in metal salt solution for 6 h would produce the target metal hydroxychlorides. As shown in Table 1, various pure phase hydroxychlorides ($Cu_2(OH)_3Cl$, $Zn_5(OH)_8Cl_2(H_2O)$, $Sn_3O(OH)_2Cl_3$ and $Co_2(OH)_3Cl$) can be prepared using both CdOHCl and $Cd(OH)NO_3 \cdot H_2O$ as phase-directing agents. However, pure phase PbOHCl can be obtained only from

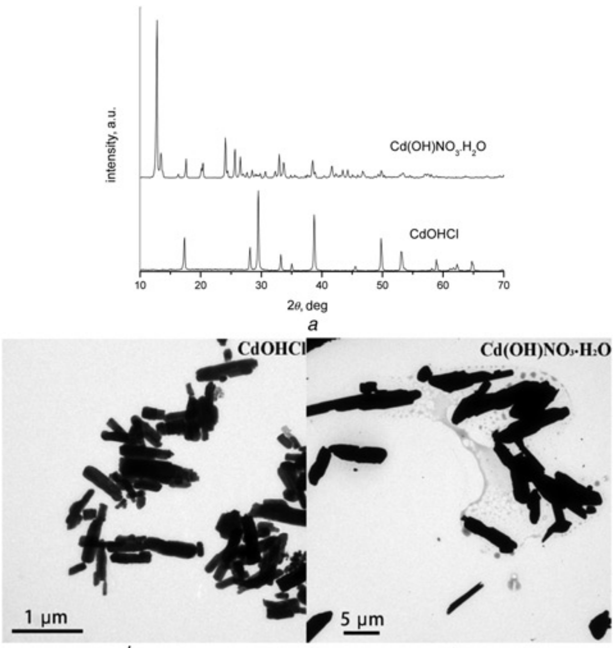

Fig. 1 *XRD patterns (a) of CdOHCl and $Cd(OH)NO_3 \cdot H_2O$ and their TEM images (b and c)*

$Co_2(OH)_3Cl$, and impurity can be found in the sample prepared from $Cd(OH)NO_3 \cdot H_2O$ at any reaction condition.

The metal hydroxychlorides prepared from CdOHCl present completely different morphology (Fig. 2) from CdOHCl (Fig. 1*b*). As shown in Fig. 2*a*, the 15–25 nm $Cu_2(OH)_3Cl$ particles have irregular shape. The $Co_2(OH)_3Cl$ particles with narrow size distribution centred at ∼7 nm have cubic shape (Fig. 2*b*). Sheet-like $Zn_5(OH)_8Cl_2(H_2O)$ with lateral size between 0.1 and 1 μm can be observed (Fig. 2*c*). It is quite interesting to notice that $Sn_3O(OH)_2Cl_3$ particles have morphology of hollow sphere with diameter between a few hundred nanometre and microns (Fig. 2*d*). At higher magnification (inset in Fig. 2*d*), it can be observed that the shell of hollow sphere is composed of much

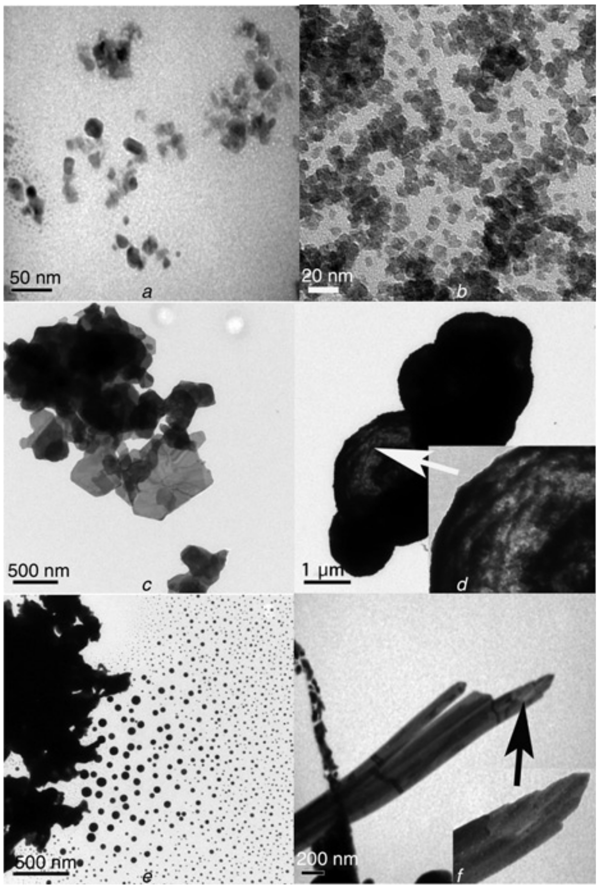

Fig. 2 *TEM images of metal hydroxychlorides synthesised using CdOHCl as precursor: $Cu_2(OH)_3Cl$ (a), $Co_2(OH)_3Cl$ (b), $Zn_5(OH)_8Cl_2(H_2O)$ (c) and $Sn_3O(OH)_2Cl_3$ (d) were produced in water; PbOHCl was prepared in water (e) and ethanol (f)*

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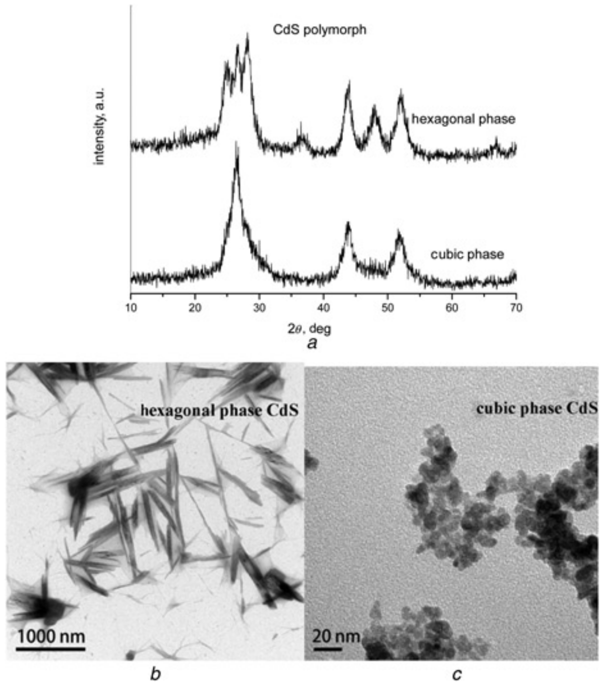

Fig. 3 *XRD patterns of the two CdS polymorph (a) and their TEM images (b and c). Hexagonal and cubic phase CdS were prepared respectively from CdOHCl and Cd(OH)NO_3·H_2O*

smaller particles of ∼20 nm. In the case of PbOHCl, the TEM images demonstrate the effect of solvent on the morphology development of PbOHCl (Figs. 2*e* and *f*). In Fig. 2*e*, the PbOHCl sample prepared in aqueous solution presents well-dispersed spherical nanoparticles with diameter of 10–90 nm. In the left of this image, it is observed that some nanoparticles are agglomerated together forming larger particles with irregular morphology. In Fig. 2*f*, the PbOHCl sample prepared in ethanolic solution has nanowire-like morphology with length of 1–5 μm. As observed in the inset, the PbOHCl nanowires are actually composed of stacked nanowires with diameter of ∼30 nm in parallel (namely nanobundle). Using Cd(OH)NO_3·H_2O as precursor, pure phase metal hydroxychlorides ($Cu_2(OH)_3Cl$, $Zn_5(OH)_8Cl_2(H_2O)$, $Sn_3O(OH)_2Cl_3$ and $Co_2(OH)_3Cl$) can be prepared at the same reaction conditions as CdOHCl. $Zn_5(OH)_8Cl_2(H_2O)$, $Sn_3O(OH)_2Cl_3$ and $Co_2(OH)_3Cl$ have the almost same morphologies and size as those prepared from CdOHCl. Only exception is $Cu_2(OH)_3Cl$, which shows much definite cubic shape.

To further prove the ability of basic cadmium salts for the control of phase and morphology, thioacetamide was added, respectively, to the aqueous suspension of CdOHCl and Cd(OH)NO_3·H_2O. As shown in the XRD patterns (Fig. 3*a*), hexagonal and cubic phase of CdS can be obtained, respectively, using CdOHCl or Cd(OH)NO_3·H_2O as phase-directing agent. In the TEM images, the hexagonal phase CdS presents fibriform morphology (Fig. 3*b*) and the cubic phase CdS has spherical shape (Fig. 3*c*).

Lots of metal hydroxides and basic metal salts, including the basic cadmium salts and metal hydroxychlorides prepared in this Letter, have CdI_2-type-layered structure. Partial replacement of the OH groups in a CdI_2-type $M(OH)_x$ layer will produce the layer of $M_x(OH)_yX_z$. For hydrated hydroxychlorides, its charge is balanced by the halogen ions between layers with water molecules occupying the remaining interlayer space. For the CdI_2-type basic salts containing groups such as NO_3^- SO_4^{2-} and CO_3^{2-}, one O atom in the group is insert to the $M(OH)_x$ layer and the group's plane is perpendicular to the $M(OH)_x$ layer. The other O atoms in the group are hydrogen-bonded to OH^- ions of the adjacent layer [12]. Based on this knowledge, we can propose that the phase-directing effect of basic cadmium salts results from its structure similarity with the target hydroxychlorides, and also from their high reactivity at mild reaction conditions. As observed in TEM images, the morphology of basic cadmium salts is completely different from that of produced hydroxychlorides. Thus, the reaction should start with the gradual dissolution of basic cadmium salt, continue with the formation of target hydroxychlorides and end up with the complete consumption of basic cadmium salt. Using PbOHCl as a typical example, the formation process of metal hydroxychlorides can be described in the following equations.

$$CdOHCl \rightarrow Cd^{2+} + OH^- + Cl \quad (1)$$

$$Cd^{2+} + OH^- + Cl^- + Pb^{2+} \rightarrow PbOHCl\downarrow + Cd^{2+} \quad (2)$$

4. Conclusion: In summary, it is proposed that basic cadmium salts (CdOHCl and Cd(OH)NO_3·H_2O) work as phase-directing agents, which are able to guide the phase formation of metal hydroxychlorides and control their morphology. CdOHCl and Cd (OH)NO_3·H_2O were prepared through an epoxide precipitation route. They were then suspended in metal salt solution for a few hours to produce various metal hydroxychlorides including $Cu_2(OH)_3Cl$, $Co_2(OH)_3Cl$, $Zn_5(OH)_8Cl_2(H_2O)$, $Sn_3O(OH)_2Cl_3$ and PbOHCl, which had different morphologies. It was also found that the morphology of PbOHCl could be controlled by solvents: the using of water and ethanol, respectively, resulted in sphere and bundle-like nanostructure.

The investigation shows that phase-directing effect of basic cadmium salts results from its structure similarity with the target hydroxychlorides, and also from their high reactivity under mild reaction conditions. To the best of our knowledge, this is the first discovery for the phase-directing phenomenon which occurs in the nano-synthesis area. We found that this discovery worked for transitional metal elements although pure phase hydroxychlorides for some elements could not be obtained yet. Further work is being carried out to study the extension of this phenomenon to other categories of metal elements such as rare earth, and also the building of nanostructures. This strategy will initiate a new general avenue for the phase and morphology control of nanostructures.

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