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# Inorganic–organic chain assemblies as lamellar nanoreactors for growing one-dimensional $Cu(OH)_2$ and CuO nanostructures†

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**One-dimensional $Cu(OH)_2$ or CuO nanostructures were fabricated using inorganic–organic chain assemblies, $Cu(C_nH_{2n+1}X)_2{\cdot}nH_2O$ (X = $CO_2$, $SO_4$) as a lamellar nanoreactor, along with NaOH treatment. The shapes and aspect ratios of the $Cu(OH)_2$ or CuO nanostructures could be varied by adjusting the hydrophobicity of the lamellar nanoreactors.**

In general, the properties of an inorganic material depend greatly on morphology, size, and crystallographic form.[1] A challenge in material science is to develop synthetic strategies for the controlled synthesis of nanostructured materials at the mesoscopic level. Solution-phase synthetic approaches have several advantages over conventional gas-phase synthetic approaches in terms of cost, energy consumption, and large-scale production capabilities.[2] Various types of molecular nanoreactors, including micelles, vesicles, microemulsion, polyelectrolyte capsules, and liquid crystals, have been applied toward exploring molecular templates as nanoreactors for the preparation of nanostructures.[3] However, harsh conditions or complicated procedures are generally required to remove hard templates, and soft templates are limited in their templating capabilities. An alternative approach is provided by sacrificial or reactive template methods,[4] which provide both a template and a reactive precursor that takes advantage of the highly anisotropic crystal structures of solids.

Over the past several decades, numerous works have investigated the morphology of $Cu(OH)_2$ materials and other basic copper salts.[5] These materials possess a well-characterized layered structure that provides precursor materials to exploit the unusual morphologies of CuO.[6] $Cu(OH)_2$ nanowires may be synthesized by three routes: precipitation of cupric salts, such as $CuX_2$ (X = $NO_3$, Cl), by mixing ammonia and NaOH in solution,[7] oxidation of copper foil in a basic ammonia solution,[8] and chemical transformation of basic copper(II) salts ($Cu_2(OH)_3X$) as precursors by NaOH treatment *via* anion exchange.[9] There remains a considerable need to develop facile and mild methods for generating $Cu(OH)_2$ and CuO nanowires/nanorods. Therefore, it is necessary to explore molecular templating systems controlled *at the molecular level* for the generation of inorganic 1-D nanostructures.

Lipid-like inorganic–organic hybrids with long alkyl-chain derivatives, such as metal soaps, sulfonates and sulfates,[10] have not been used as templates for the synthesis of nanomaterials, although they form well-characterized self-organized assemblies. Due to their amphiphilic nature and the self-organization of the alkyl chain assemblies, these hybrids form bilayer headgroup structures. Their two-dimensional (2-D) structures provide promising candidate lamellar nanoreactors by presenting distinct chemical interface environments to polar guest species. Herein, we report a template-directed synthetic strategy for preparing uniform $Cu(OH)_2$ and CuO nanowires/nanorods using lamellar inorganic–organic nanoreactors formed by $Cu(C_nH_{2n+1}X)_2{\cdot}nH_2O$ upon introduction of a bridging $OH^-$ ligand *via* NaOH treatment. Our synthetic strategies are based on the confined crystallization within the hydrophilic regions of lamellar nanoreactors.

In this work, we selected two typical inorganic–organic hybrids as lamellar nanoreactors: $Cu_2(C_{11}H_{23}CO_2)_4{\cdot}2H_2O$ (for short, Cu-lau)[11] and $Cu(C_{12}H_{25}SO_4)_2{\cdot}4H_2O$ (for short, Cu-DS).[12] Although the two typical chain assemblies displayed lamellar structures with long-chain bilayer structures the local copper(II) structures within the hydrophilic regions differed dramatically (Fig. 1). The Cu-lau consisted of discrete paddle-wheel Cu(II) dimers capped by four carboxylate chains and two waters, whereas the Cu-DS exhibited discrete Cu(II) monomers

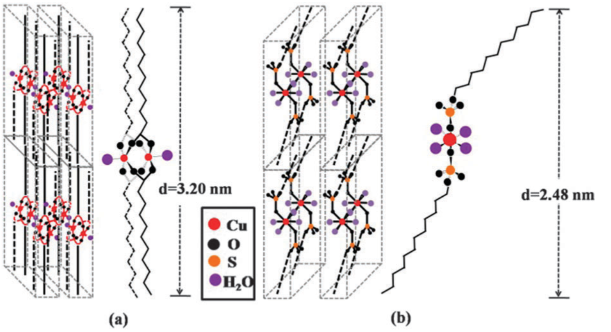

**Fig. 1** Schematic illustration of the crystal and molecular structures of two compounds that behave as lamellar nanoreactors: (a) Cu-lau, displayed paddle-wheel binuclear Cu(II) complexes capped by carboxylate and dehydrate ligands; (b) Cu-DS, exhibited mononuclear Cu(II) complexes with coordinated sulfate and tetrahydrate ligands.

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coordinated by two sulfate alkyl-chains and tetrahydrates. The crystal structure revealed that the Cu(II) ions were more tightly bound to the headgroups in Cu-lau than in Cu-DS, which favored alignment of the alkyl chains normal to the basal plane. According to the strength of binding interactions between the interfaces, Cu-lau and Cu-DS are conveniently classified as hard- and soft-template, respectively.

The two nanoreactors Cu-lau and Cu-DS were synthesized in an aqueous solution, as described previously.[10c] The compositions, crystal structures, and alkyl chain structures of the nanoreactors Cu-lau and Cu-DS were analyzed by elemental analysis, powder XRD, and FT-IR, respectively.† The two nanoreactors, Cu-lau (and Cu-DS), were dispersed in water at room temperature, giving immiscible shiny blue-colored dispersions as a result of the particle hydrophobicity. After incubating in the aqueous solutions, addition of NaOH produced translucent solutions that formed brown-colored precipitates, corresponding to $Cu(OH)_2$. And two precursors were dispersed in water at 50 °C, and addition of NaOH to dispersions yielded black-colored precipitates, corresponding to CuO. The crystal structures and morphologies of the as-prepared products obtained by NaOH treatment were analyzed by powder XRD, FT-IR, and FE-SEM.†

Fig. 2(a) shows the powder XRD patterns and FT-IR spectrum of the Cu-lau precursor. The higher order peaks (00*l*) of the XRD patterns of Cu-lau indicated the presence of a lamellar structure with an interlayer spacing of $d = 3.20$ nm.[13] Fig. 2(b) and (c) show the XRD patterns and FT-IR spectra of the $Cu(OH)_2$ and CuO products. The diffraction peaks of the two products corresponded to those of bulk orthorhombic $Cu(OH)_2$ (JCPDS 80-0656)[14] or monoclinic CuO (JCPDS 72-0629).[15] Inspection of the XRD patterns of $Cu(OH)_2$ and CuO revealed that reflections of the parent Cu-lau at low $2\theta$ range disappeared, and peaks corresponding to the surfactant were not observed. This result indicated that the starting material, which acted as a template, had been expelled from the as-prepared nanostructure after complete reaction. The transformation from Cu-lau into $Cu(OH)_2$ and CuO was also observed in the FT-IR spectra (Fig. 2, right). The FT-IR spectra of Cu-lau exhibited features over the regions 3000–2800 $cm^{-1}$ and 1600–1300 $cm^{-1}$, which corresponded to the stretching vibrations of $–CH_2–$ (or $–CH_3$) and the stretching vibrations of $–CO_2$, respectively.[16] In the case of $Cu(OH)_2$ and CuO, the vibrations characteristic of Cu-lau or other amorphous functionalized carboxylate surfactants were not observed. The XRD and FT-IR spectra demonstrated that NaOH treatment provided an effective method for removing the hydrophobic alkyl-chains after finishing the reaction.

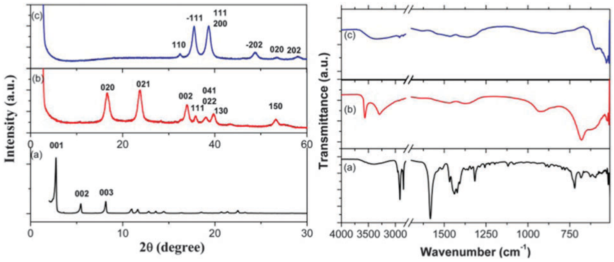


**Fig. 2** XRD patterns (left) and FT-IR spectra (right) of (a) Cu-lau (nanoreactor), (b) $Cu(OH)_2$ nanowires, and (c) CuO nanorods.

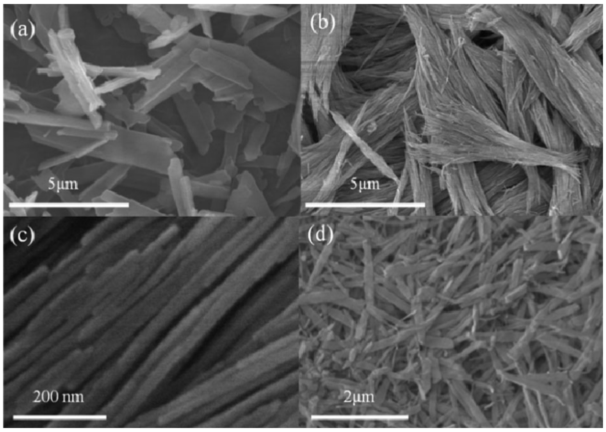


**Fig. 3** FE-SEM images of (a) Cu-lau (hard-template) showing the thin plate morphologies, (b) $Cu(OH)_2$ nanowires, (c) high-magnification view of the $Cu(OH)_2$ nanowires, and (d) CuO nanorods.

Fig. 3(a) shows that Cu-lau assumed a thin plate-like morphology, as expected, indicative of a layered structure. FE-SEM images (Fig. 3(b) and (c)) revealed that the $Cu(OH)_2$ products consisted of uniform nanowire arrays 20 nm in diameter and several microns in length. In addition, the crystallinity of $Cu(OH)_2$ nanowires was further examined by HRTEM (Fig. S1, ESI†). The CuO products (Fig. 3(d)) also revealed nanorod arrays on relatively short length scales.

Similar experiments were conducted using the nanoreactor Cu-DS to investigate the effects of the binding strength of the inorganic–organic nanoreactor. Fig. 4(a) shows the XRD patterns of Cu-DS, $Cu(OH)_2$, and CuO, demonstrating a complete transformation from Cu-DS to $Cu(OH)_2$ and CuO nanostructures. All XRD peaks of Cu-DS were consistent with those reported previously. The interlayer spacing was found to be $d = 2.48$ nm,[12] which was smaller than that of Cu-lau. FE-SEM images of Fig. 4(b)–(d) show that Cu-DS, $Cu(OH)_2$, and CuO exhibited microplates, nanorods, and nanoparticles, respectively. In general, the XRD and FE-SEM results revealed a close resemblance to Cu-lau, but their aspect-ratios of the 1-D nanostructures obtained are shortened.

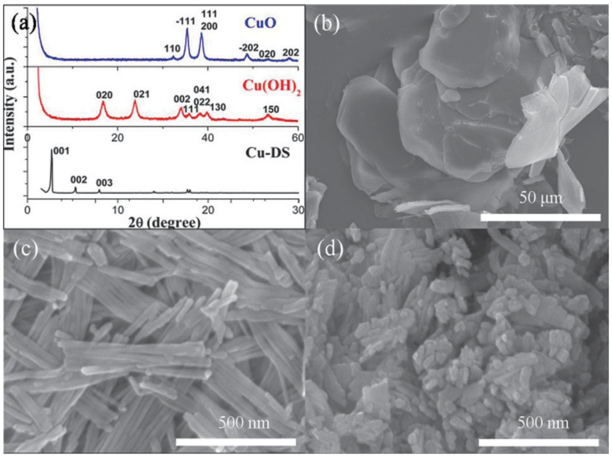
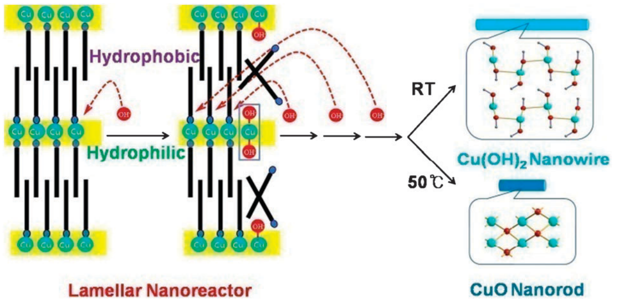


**Fig. 4** (a) XRD patterns of the Cu-DS (soft-template), $Cu(OH)_2$, and CuO. FE-SEM images of (b) Cu-DS, (c) $Cu(OH)_2$ nanorods, and (d) CuO nanoparticles.



**Scheme 1** Schematic diagram of the synthetic strategy for preparing 1-D nanostructured materials using a lamellar nanoreactor, which acts as both a metal ion supplier and a structural template. The selective penetration of $OH^-$ ions into the hydrophilic sheets yielded the $Cu(OH)_2$ and CuO nanostructures.

An important feature of the $Cu(OH)_2$ or CuO products is that the nanowires were uniformly aligned in a particular orientation as bundles, irrespective of lamellar nanoreactors. The uniform nanowire-like morphologies of $Cu(OH)_2$ could be understood by considering the role of the lamellar nanoreactor, consisting hydrophilic metal region and hydrophobic alkyl-chain regions alternately (Fig. 1). The synthetic strategies are represented in Scheme 1. Upon NaOH treatment, $OH^-$ selectively penetrated the hydrophilic sheets of the amphiphilic bilayers and simply reacted with Cu(II) ions arranged in an orderly fashion within the sheets to yield the directional growth of the $Cu(OH)_2$ nanowires. Formation of the $Cu(OH)_2$ products disrupted the interactions between the Cu(II) ions and the headgroups in amphiphiles, which led to electrostatic repulsion between surfactants to produce bundle $Cu(OH)_2$ nanowires due to hydrogen bonding interactions between the $Cu(OH)_2$ nanowires. At higher reaction temperatures, CuO nanorods with small aspect ratios were obtained, ascribed to the reduced template effect and dehydration of $Cu(OH)_2$.[17] As the reaction temperature was increased, lamellar structures became unstable due to breaking of the interchain interactions, including the hydrogen-bonding and hydrophobic interactions. The bridging $OH^-$ ligands penetrated the copper ions in the hydrophilic sheets, yielding intermediate $Cu(OH)_2$ nanowires that did not grow completely. By controlled experiments without template, the template effects *via* confined crystallization of a lamellar nanoreactor are confirmed in Fig. S2, ESI.†

It is worth noting that the shapes and aspect ratios of the $Cu(OH)_2$ or CuO nanostructures were varied by choosing Cu-lau or Cu-DS as nanoreactors. Although the alkyl chains were similar in size, the interlayer *d*-spacings of the chain assemblies of Cu-lau and Cu-DS were different, 3.20 nm and 2.48 nm, respectively. The differences in the *d*-spacings and the organic chain structures could be understood by considering the packing of the Cu(II) coordination sphere as shown in Fig. 1. The binding affinity of the lamellar nanoreactor at inorganic–organic interfaces thereby increased with the tight packing of the Cu(II) coordination and the highly aligned alkyl chains normal to the basal plane. Penetration of the $OH^-$ ions into the lamellar nanoreactors, which could be controlled *via* the hydrophobicity, played an important role in the selectivity of the lamellar nanoreactors.

In summary, we successfully fabricated uniform, 1-D $Cu(OH)_2$ and CuO nanostructures from self-assembled inorganic–organic chain assemblies *via* NaOH treatment. The morphologies of the $Cu(OH)_2$ and CuO nanostructures obtained from Cu-lau and Cu-DS were almost identical, that is, independent of the nanoreactor, but the aspect ratios of the nanostructures depended on the hydrophobic strength of the inorganic–organic chain assembly precursors.

In this work, we demonstrated that inorganic–organic chain assemblies acted as lamellar nanoreactors for the formation of 1-D nanostructures. This synthetic strategy using lamellar nanoreactors provides a general method for tuning the shape and aspect ratio of 1-D nanostructures by controlling the alkyl chain length and the binding affinity of the hydrophilic groups.

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