

Supporting Information for

**Inorganic-organic chain assemblies as lamellar reactive nanoreactors for growing one-dimensional Cu(OH)<sub>2</sub> and CuO nanostructures**

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## 1. Experimental Details

Using two-dimensional (2-D) inorganic-organic chain assemblies as lamellar nanoreactors, we developed a facile synthetic strategy for growing one-dimensional (1-D) nanostructures in a general manner and applied the technique toward fabrication of Cu(OH)<sub>2</sub> and CuO nanostructures. In this work, we selected two typical inorganic-organic chain assemblies as lamellar nanoreactors: Cu<sub>2</sub>(C<sub>11</sub>H<sub>23</sub>CO<sub>2</sub>)<sub>4</sub>·2H<sub>2</sub>O (abbreviated Cu-lau) and Cu(C<sub>12</sub>H<sub>25</sub>SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O (abbreviated Cu-lau).

As shown in Figure 1, 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-step syntheses were conducted as follows:

- A) Synthesis of the lamellar nanoreactors, Cu-lau and Cu-DS
- B) Synthesis of Cu(OH)<sub>2</sub> and CuO nanostructures using the lamellar nanoreactors by NaOH treatments

### A. Synthesis of the lamellar nanoreactors, Cu-lau and Cu-DS

CuCl<sub>2</sub>·2H<sub>2</sub>O (99%, Aldrich), sodium laurate (97%, TCI), sodium dodecylsulfate (98.5%, Aldrich), and NaOH (97%, Aldrich) were used as received. Cu-lau and Cu-DS, were synthesized in aqueous media via self-assembly. The Cu-lau compound was

prepared by adding 0.04 mol CuCl<sub>2</sub>·2H<sub>2</sub>O to 500 mL of a 0.08 M sodium laurate aqueous solution at room temperature. Cu-DS was also prepared by adding 0.05 mol CuCl<sub>2</sub>·2H<sub>2</sub>O to 100 mL of a 0.5 M sodium dodecylsulfate aqueous solution at room temperature. In all cases, shortly after the solutions had been mixed, a blue precipitate formed. In the case of Cu-lau, deep blue aggregates separated from the aqueous solution and floated on the surface of the aqueous solution, indicating that the aggregates were hydrophobic. The precipitates were filtered, washed with deoxygenated water, and dried under vacuum at room temperature.

The chemical formulas of the inorganic-organic chain assemblies used as lamellar reactive-templates were verified by elemental analysis. [Analysis observed (calculated) for C<sub>48</sub>H<sub>96</sub>O<sub>10</sub>Cu<sub>2</sub> (Cu-lau): C, 59.45 (60.03%); H, 9.39 (10.07%); C<sub>24</sub>H<sub>58</sub>O<sub>12</sub>S<sub>2</sub>Cu (Cu-DS): C, 42.52 (43.26%); H, 8.65 (8.77%); S: 9.74 (9.62%).]

## B. Synthesis of the Cu(OH)<sub>2</sub> and CuO nanostructures using the lamellar nanoreactors by NaOH treatments

The nanoreactor, Cu-lau (or Cu-DS), was dispersed in 50 mL water to a concentration of 1 mmol, giving an immiscible shiny blue dispersion of hydrophobic particles at room temperature and 50°C, respectively. The mixture was vigorously stirred. After incubating in water, 50 mL of a 0.6 M NaOH solution was added to the beaker. After vigorous stirring, the immiscible dispersions became translucent and precipitated to form brown-colored and black-colored, respectively, corresponding to Cu(OH)<sub>2</sub> and CuO products. Similarly, we conducted on the above procedures all but different precursor, Cu-DS. The products were washed several times with water and ethanol, then dried under vacuum at

room temperature.

## 2. Characterization

The structures of the precursors (Cu-lau or Cu-DS), and the Cu(OH)<sub>2</sub> or CuO products were characterized by powder X-ray diffraction. Powder X-ray diffraction data were collected on a XRD diffractometer (XRD, PANalytical, X'pert-pro MPD) operated at 40 kV and 40 mA in the Bragg–Brentano  $\theta$ – $2\theta$  mode (Cu K $\alpha_1$ , 1.5424 Å), using naturally oriented samples on glass sample holders. The alkyl-chain headgroup and the organic chain structure of the precursors (Cu-lau or Cu-DS) and the as-prepared products are analyzed by FT-IR. The FT-IR spectra were obtained using a Perkin-Elmer Spectrum 100 FT-IR spectrometer in the attenuated total reflectance (ATR) mode over the range 650–4000 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup>.

The morphology of the products was observed by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4300). In addition, the crystallinity of Cu(OH)<sub>2</sub> nanowires was further examined by high-resolution transmission electron microscopy (HRTEM, JEOL JEM-3010).

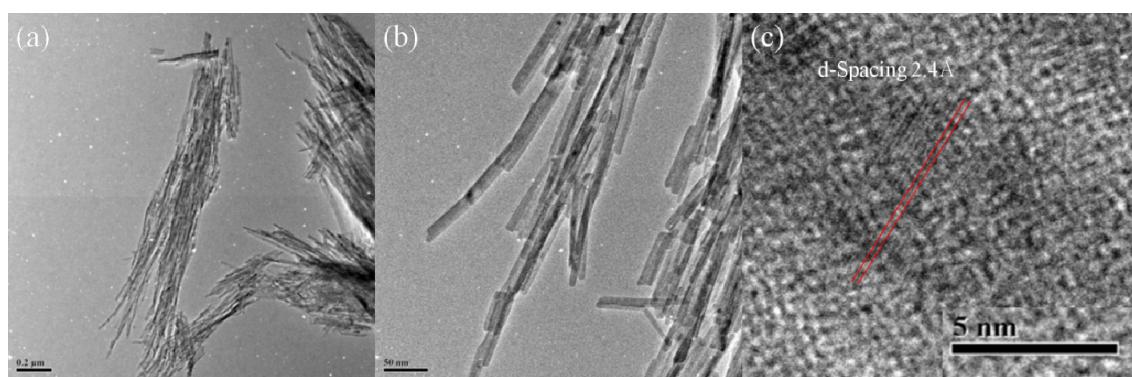
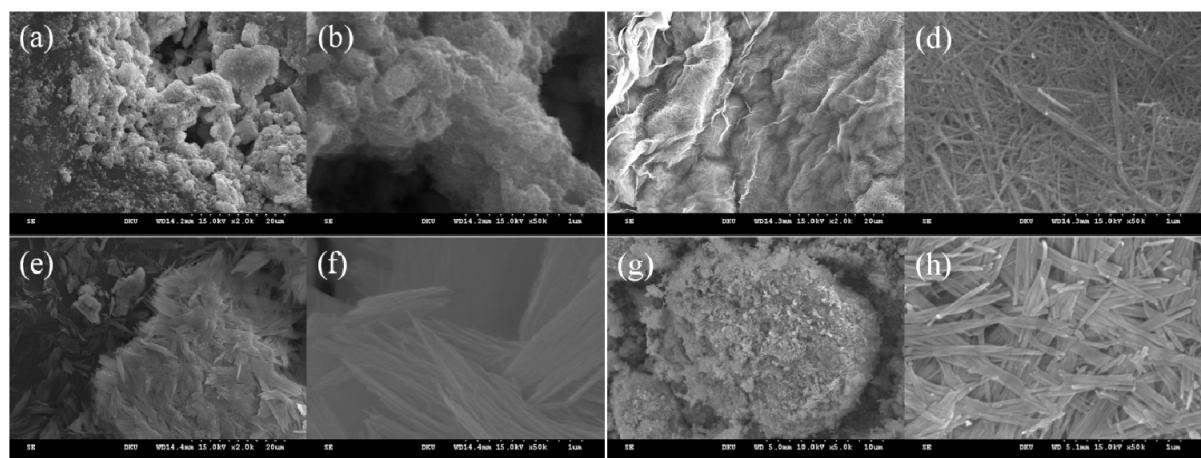


Figure S1. (a)–(c) The TEM and HRTEM images of Cu(OH)<sub>2</sub> obtained from Cu-lau reveals their nanowire with bundle type

### 3. On the role of lamellar nanoreactor: template effects on confined crystallization

In general, crystallization of another nanostructure within surfactant assemblies is a complex process. Therefore, we conducted on the control experiments without the lamellar nanoreactor to investigating the template effect, as followings (Figure S2).



*Figure S2.* SEM images of  $\text{Cu}(\text{OH})_2$  nanostructures obtained from different reaction conditions, (a)-(b),  $[\text{Cu}^{2+}]:[\text{OH}^-]=1:2$  without template, shows no morphologies; (c)-(d),  $[\text{Cu}^{2+}]:[\text{OH}^-]=1:30$  without template, shows the nanowire morphologies on the surfaces; (e)-(f),  $[\text{Cu}^{2+}]:[\text{OH}^-]=1:30$  with Cu-lau (hard-template); (g)-(h),  $[\text{Cu}^{2+}]:[\text{OH}^-]=1:30$  with Cu-DS (soft-template).

$\text{Cu}(\text{OH})_2$  products were synthesized from  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  without template at room temperature by NaOH treatment. In these cases, the concentration of NaOH was strongly influenced on the morphology of  $\text{Cu}(\text{OH})_2$  products. When the concentration ratio of  $\text{OH}^-$  to  $\text{Cu}^{2+}$  is 2.0, the  $\text{Cu}(\text{OH})_2$  products show no characteristic morphologies (Figure S2(a)-(b)). When the concentration ratio of  $\text{OH}^-$  to  $\text{Cu}^{2+}$  is 60.0, most of  $\text{Cu}(\text{OH})_2$  products show the plate-like morphology with some nanowires at the surface of the plates.

The amount of OH<sup>-</sup> ions play an important role for the formation of Cu(OH)<sub>2</sub> nanowires by forming the complex [Cu(OH)<sub>4</sub>]<sup>2-</sup> and by absorption on the surfaces of Cu(OH)<sub>2</sub> crystals during the crystal growth processes.<sup>1</sup> Therefore, the aspect ratios of Cu(OH)<sub>2</sub> nanowires were not controlled without template.

In this work, we present a template-directed synthetic strategy for one-dimensional nanostructure using inorganic-organic chain assemblies formed lamellar nanoreactor. In this work, we selected two typical inorganic-organic hybrids, Cu<sub>2</sub>(C<sub>11</sub>H<sub>23</sub>CO<sub>2</sub>)<sub>4</sub>·2H<sub>2</sub>O (*Cu-lau*) and Cu(C<sub>12</sub>H<sub>25</sub>SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O (*Cu-DS*). Although two systems exhibited lamellar structures with long-chain bilayered, the local structure of confined crystallization sites differed from each other. According to the strength of binding interactions between the interfaces, Cu-lau and Cu-DS are classified as hard- and soft-template, respectively. Therefore, our synthetic strategies are based on the “confined crystallization” within the hydrophilic regions of lamellar nanoreactors.

#### 4. References

1. (a) J. Sun, Y. Jia, Y. Jing, Y. Yao and W. Li, *J. Nanosci. Nanotechnol.*, 2007, **7**, 4562; (b) J. Sun, Y. Jia, Y. Jing, Y. Yao and W. Li, *Russ. J. Inorg. Chem.*, 2008, **53**, 36.