

Ionic Self-Assembly in Solution: Synthesis, Morphology Control, and Mechanism of $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]_3[\text{Fe}^{\text{III}}(\text{CN})_6]_2$ Micro-Crystals

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Abstract

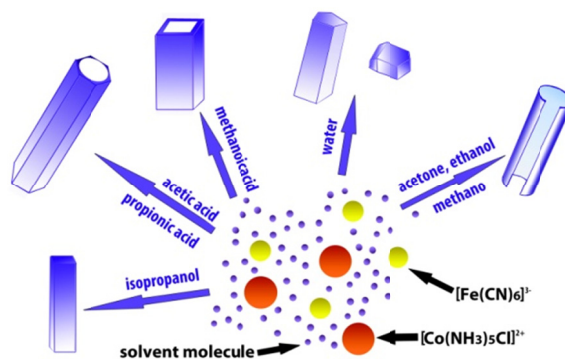
In this contribution, the preparation of the supramolecular nano-/microcrystals $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]_3[\text{Fe}^{\text{III}}(\text{CN})_6]_2$ via a simple and efficient solution ionic self-assembly approach was reported. The results demonstrated that the morphologies of these microcrystals could be changed arbitrary by tuning the solvent. Various shapes such as polyhedron, microrod, rectangular tube, tubular hexagonal prism, and tubular hexagonal prism were obtained in different solvents. The polarity and the acidity of solvent showed a significant effect on the shape of the products. The regrowth process and its possible mechanism of these microcrystals were also recounted in detail.

Keywords: self-assembly, solution, synthesis, morphology, micro-crystals

1. Introduction

In the past decades, the overwhelming majority of attention has been paid to the sculptural and architectural control of nano-/microcrystals with well-defined shapes and sizes, since the size, shape, morphology, dimensionality, and texture of the nano-/microcrystals and their assembly architectures have significant influences on varying their optical, electronic, catalytic, and magnetic properties (Alivisatos, 1996; Jin et al., 2001; Peng, Manna, Wickham, Scher, & Alivisatos, 2000; Roucoux, 2002; Shi, Qi, Ma, & Cheng, 2003; Xie, Huang, Li, Liu, & Qian, 2000). Self-assembly refers to the spontaneous organization of molecules, molecular clusters, and aggregate structures into various shapes by attractive forces or weak-bond formation. This provides an effective and versatile approach for constructing ordered systems at a molecular level (Fendler, 2001). Meanwhile, self-assembly in solution has also attracted an interest due to the possibility of integration of molecular systems into functional mesoscopic devices and macroscopic materials (Boal, Ilhan, & DeRouchey, 2000). What's more, it is seductive that ionic self-assembly of microscopic particle in solution is a facile synthetic method to prepare supramolecular materials (Faul & Antonietti, 2003; Fu & Yao, 2001; Sun, Du, Zhang, Dong, & Wang, 2007) and that's helping to develop simple and efficient route to prepare microparticles with well-defined shapes and sizes (Fu, Xiao, Yao, & Yang, 2003; Xiao et al., 2003).

Previous research of ionic self-assembly was mainly focused on the coordination compounds, because the coordination compounds offer great variety and flexibility in molecular design and further tunability in electronic and optical properties (Chen, Peng, & Li, 2008; Sun et al., 2007; Tian et al., 2004; Wurthner, 2004). The noncovalent intermolecular interactions of coordination compounds, such as the van der Waals force, π - π stacking, electrostatic interaction, and hydrogen bonding are the keys of ionic self-assembly. The van der Waals force, π - π stacking and hydrogen bonding in preparing in ionic self-assembly of metal-organic nanomaterials were well researched (eg. 8-hydroxyquinolate metal complexes, metalloporphyrins) (Balakrishnan et al., 2005; Chiu et al., 2003; Hu et al., 2007; Zhao et al., 2006). Much success has been achieved in the synthesis of inorganic or metal-organic nanocrystals; by contrast, the preparation and shape control over the nanostructures of inorganic coordination complexes has been met with limited success.



Scheme 1. The different shapes of $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]_3[\text{Fe}^{\text{III}}(\text{CN})_6]_2$ which were prepared in different solvents

Moreover, the electrostatic interaction in ionic self-assembly of inorganic coordination ionic was less studied (Sun, Luo, & Zhai, 2010).

In this work, we reported on the preparation of a series of supramolecular microparticles via a simple and efficient solution ionic self-assembly approach (Scheme 1). The formation of these microcrystals were occurred in a single process, which was carried out by mixing $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}$ and $\text{K}_3\text{Fe}(\text{CN})_6$ solution at room temperature. The polarity and the acidity of solvent showed a greater effect on the process of ionic self-assembly.

The detailed reaction and shape evolution process of these structures were studied, too. The regrowth process and its possible mechanism of the ionic self-assembly process were also recounted in detail.

2. Experiment

The supramolecular microcrystals (sample 1) were prepared as follows: In a typical experiment, 200 μL of 0.1 M $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}$ aqueous solution was diluted with deionized water into 10 mL first, followed by introducing 200 μL of 0.1 M $\text{K}_3\text{Fe}(\text{CN})_6$ aqueous solution. After the reaction solution has been stirred for 10 minutes, a large quantity of orange precipitates was observed. The other microcrystals were prepared in the similar method, except the 200 μL of 0.1 M $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}$ aqueous solution was diluted with different solvent into 10 mL. Product was collected by filtration, washed two times with distilled water and then dried in vacuum and dispersed in water for further characterization. Scanning electron microscopy (SEM) and the energy dispersed spectrum (EDS) were tested on a JSM-6510 (Rigaku, Japan) operated at an accelerating voltage of 20 kV.

3. Results and Discussion

Figure 1 showed typical SEM image of as-formed precipitates. It was obvious that these microcrystals, which were prepared in H_2O environment, were well-defined, and their length ranges from 4 to 6 μm , although several large microrods with shorter aspect ratio were found as well.

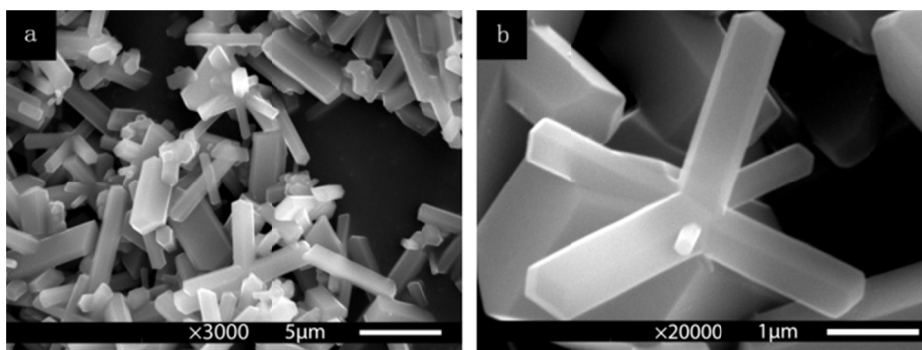


Figure 1. The SEM images of sample 1

To investigate the influence of solvent on the formation of particles, 18 kinds of solvents were examined. Figure 2 showed the SEM images of the obtained microcrystals prepared in the acid solvents (methanoic acid, acetic acid and propionic acid). It should be noted that the shape of the products changed significantly when the solvent

were organic acid. When the microcrystals were prepared in acid solvent, the longer aspect ratio products were obtained. Moreover, it was intriguing that the structures of the obtained products were hollow without exception.

The SEM image of the products which were prepared in methanoic acid is shown in Figure 2a. It reveals the hollow or tubular characteristics of these microcrystals which were 3–5 μm in length. Further close observation from a high-magnification image of the parallel tubes (Figure 2b) indicates that these tubes possess a rectangular cross section with dimensions in 400 nm and a relatively uniform wall thickness (30–50 nm).

When the solvent was acetic acid, the obtained products were tubular hexagonal prisms (Figures 2d and 2e). These hexagonal prisms were 40–50 μm in length. The tubes possess a regular hexagon cross section with dimensions 5 μm and a relatively uniform wall thickness (500 nm). The tubular hexagonal prisms turn into smaller when the solvent was propionic acid. The diameter of a single tube was about 3.5 μm , with the length about 15–20 μm . The thickness of the tube wall was about 20 nm. The tube wall of these products which were prepared in acid solution was all intact. Meanwhile, there were a handful of microcrystals which were of solid (about 5–10%).

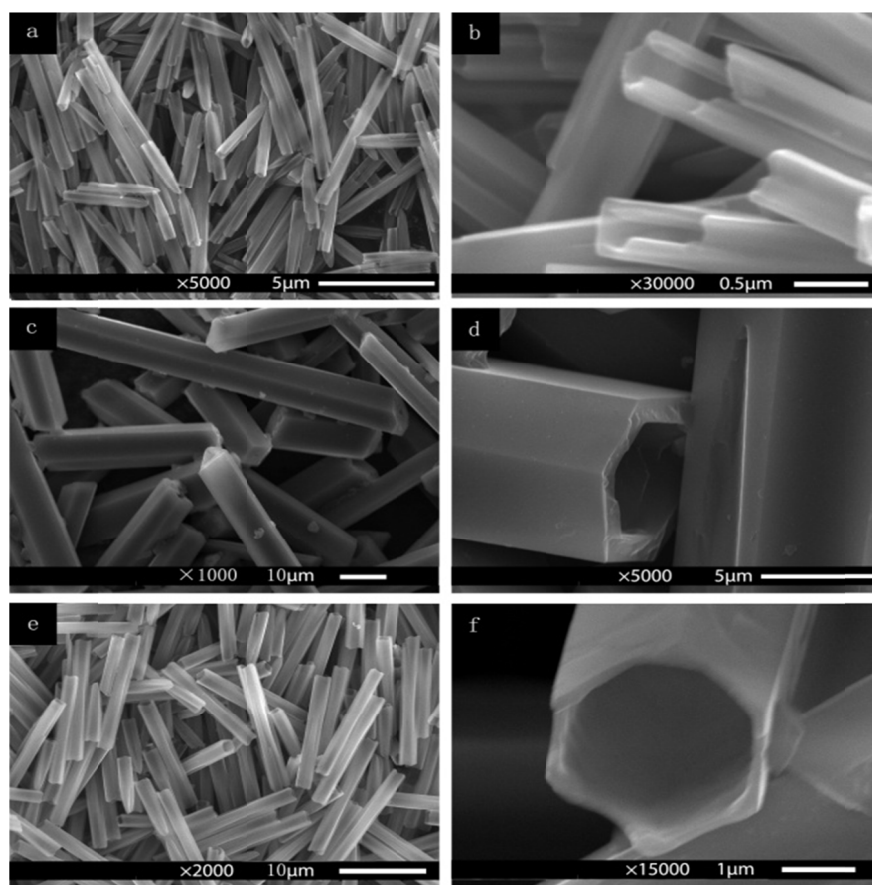


Figure 2. The SEM images of obtained products in different acid solution (a, b) methanoic acid (c, d) acetic acid (e, f) propionic acid

The neutral organic solvent was also explored to the formation and the assembly of the microcrystals. Figure 3 showed the SEM images of the products which were prepared in ethanol, acetone, as well as isopropanol.

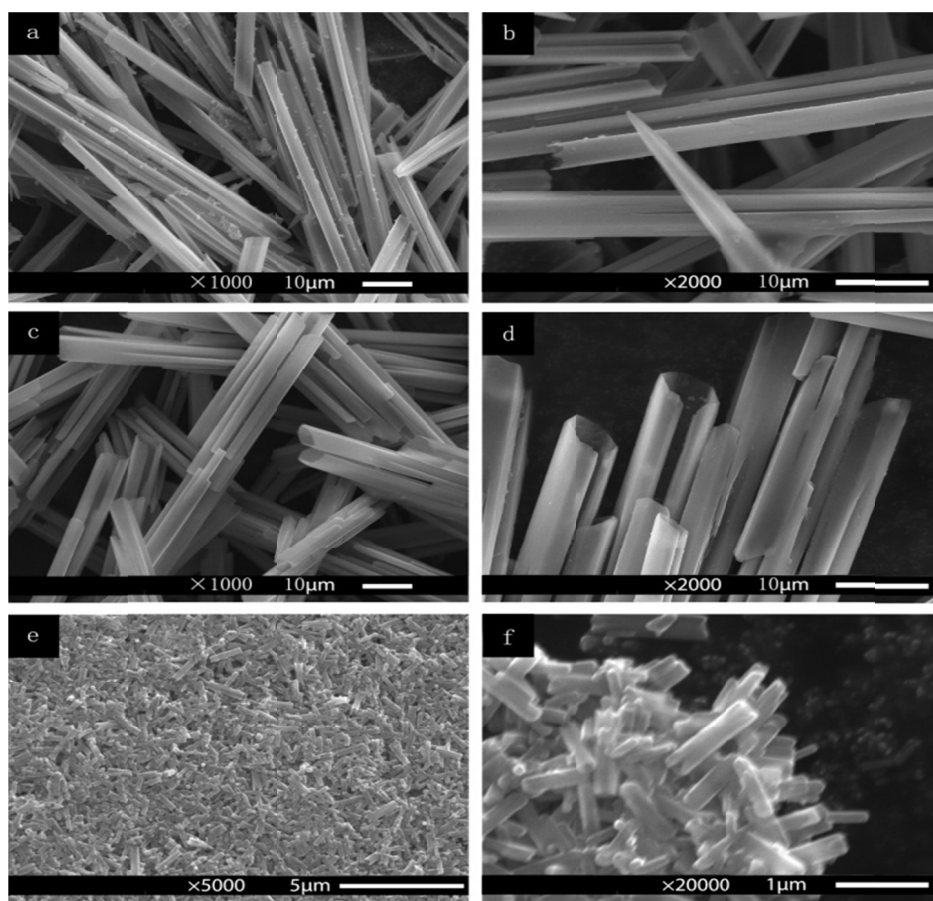


Figure 3. The SEM imagines of obtained products in different organic solution (a, b) ethanol, (c, d) acetone, and (e, f) isopropanol

When the solvent was ethanol or acetone the as-formed precipitates were half-belt and half-tube (Figures 3a and c). The cross section of the tube was horseshoe-like (Figures 3b and 3d). Unlike the products which prepared in acid solvent, the cross section of these microcrystals was approaches in the circular or elliptic, moreover, there were some sealed tubes and belt-like structures mingled with among the products. There were no obvious differences in size between these two kinds of products. It was found that the isopropanol could influence the morphology of the microcrystals. When the reaction was in isopropanol, the obtained crystals were nanotubes, the diameter of a single nanotube is about 100 nm, with the length about 1 μm .

The detailed results of the influence of solvent in reaction on the shape and sizes of the obtained microcrystals are listed in Table 1.

Based on the series of experimental results, a general trend of the morphology of $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}][\text{Fe}^{\text{III}}(\text{CN})_6]_2$ microcrystals in different solvent is clearly demonstrated. When the reaction took place in acid solvent, the obtained microcrystal was microtube, and the cross section was rectangle or hexagon. As the ratio of the water in the reaction increased, the bore diameter decreased of the micro-tubes being smaller, and the products which prepared in pure water would be microrods. However, the impact of the polarity of organic acid on the size of microcrystals was unclear. The microcrystals are half-belt and half-tube with a horseshoe-like cross section in neutral organic solvent. Similar with the situation in organic acid, the bore diameter reduces until out of sight when the ratio of water increases in neutral organic solvent. At the same time, the impact of the solvent on the size of microcrystals was easily trackable: the smaller impact of the solvent, the smaller of the size of microcrystals. The solvent with high impact (like DMF and DMSO) does not produce anything because the product ($[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}][\text{Fe}^{\text{III}}(\text{CN})_6]_2$) could be dissolved in DMF and DMSO.

Table 1. Influence of solvents on the final morphology and size of the obtained microcrystals

Medium	Length [μm]	Diameter [μm]	Hollow or not/ bore diameter	Final shape
H ₂ O	10	3	N/A	polyhedron, microrod
H ₂ O : methanoic acid =1:1	5	0.5	Y/0.2 μm	rectangular tube
Methanoic acid	7	0.5	Y/0.45 μm	rectangular tube
H ₂ O : acetic acid =1:1	20	5	Y/2 μm	tubular hexagonal prism
Acetic acid	40	5	Y/4 μm	tubular hexagonal prism
H ₂ O : Propionic acid =1:1	12	3	Y/1.5 μm	tubular hexagonal prism
Propionic acid	15	3.5	Y/3 μm	tubular hexagonal prism
H ₂ O : methanol =1:1	50	5	Y/ 1 μm	half-baked tube
Methanol	60	5	Y/4 μm	half-baked tube
H ₂ O : ethanol =1:1	60	5	Y/2 μm	half-baked tube
Ethanol	60	5	Y/4.5 μm	half-baked tube
H ₂ O : acetone =1:1	75	5	Y/1 μm	half-baked tube
Acetone	150	5	Y/4.5 μm	half-baked tube
H ₂ O : isopropanol =1:1	3	0.5	N/A	microrod
isopropanol	1	0.1	Y/80 nm	nanotube
DMF				No
DMSO				No
HCl (0.1 M)				No
HCl (1 M)				No

The chemical composition of the obtained microcrystals was determined by EDS analysis (Figure 4). Five peaks corresponding to C, N, Fe, Cl and Co elements were observed, revealing that these particles are products from $[\text{Co}^{\text{III}}(\text{NH}_3)_5]^{2+}$ and $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$. Considering the fact that $[\text{Co}^{\text{III}}(\text{NH}_3)_5]^{2+}$ and $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ is positively and negatively charged, respectively, we can suggest that electrostatic interactions between these two components cause them to assembly into the final microcrystals. What's more, the EDS spectrums of all the products were remained identical, implying that there was no great difference in structure between them in different solvents.

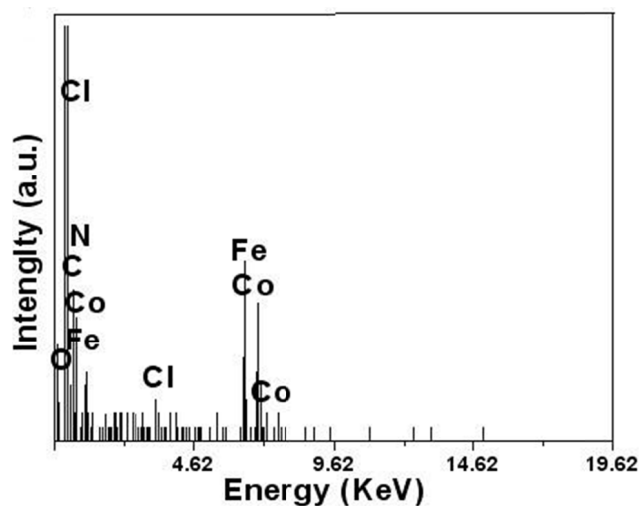
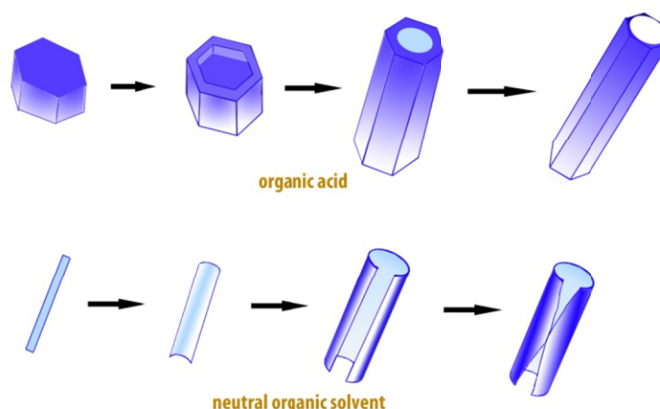


Figure 4. EDS analysis of the product

The possible model for the growth of the microtubes in acid solvent may be an eroding process (Scheme 2). The rectangular hexagonal or prism microcrystals were obtained at the early stage of the reaction. These short aspect ratio microcrystals served as starting templates for the nucleation of the microtubes. When the reaction continued, the aspect ratio of the microcrystal being longer, and the proton in the solvent begin to dissolve the center part of the prism at the same time. The foregoing solid part of the prism was finally dissolved and the bore diameter of the tubes being larger (Liang et al., 2004; Mayers & Xia, 2002). Figure 2 showed that there are some solid prisms in the products. This may be the proof of this process.



Scheme 2. The model for the growth of the tubular and half-belt structure

The model for the growth of the half-belt structure in neutral organic solvent may be another process (Schmuck & Wienand, 2003). At the early stage of the reaction, the $[\text{Co}^{\text{III}}(\text{NH}_3)_5]^{2+}$ and $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ self-assembled into belt-like structures, this nano-sized crystallites served as starting templates for the nucleation of $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]_3[\text{Fe}^{\text{III}}(\text{CN})_6]_2$ half-belt. When the reaction continued, the belt-like structures start to curl up at the corners. Figure 3a showed there are a small quantity of belt-like or curled up microbelt in the products. As the reaction proceeds, the rolling up of the nanobelt gradually extends along the whole axis until these two edges fuse together. The different polarity of the solvent impacts the reaction rates of coordination ions, this resulted in the change of aspect ratio.

4. Conclusions

The formation of supramolecular nano-/microcrystals through the ionic self-assembly in solution was observed detailedly. Various shapes of the nano-/microcrystals were obtained, the electrostatic attractive interactions between positively charged $[\text{Co}^{\text{III}}(\text{NH}_3)_5]^{2+}$ and negatively charged $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ were suggested to be a driving force of the process occurring in different medium. The acid medium leads the tube-like structures and the neutral organic solvent lead the half-belt structures. The regrowth process of the microcrystals prepared in acid or neutral solvent was starkly different. This work offered detailed information of the coordination ionic self-assembly in different solution. Our results can be beneficial to synthesize other functional particles, with unique shapes especially the micro-/nanotubes, and controlled sizes via more simple method.

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