

Cross-Corresponding Preparation of Organometallic Acetylferrocene Micro-Nanostructures in Bidirection Using Top-Down and Bottom-Up Approaches

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The larch-fruit-like acetylferrocene micro-nanomaterials and beltlike acetylferrocene micro-nanomaterials have been cross-correspondingly prepared in bidirection by the top-down and bottom-up approach, respectively, and characterized by scanning electron microscope, transmission electron microscope and X-ray diffractometer. UV-Vis absorption spectra show that the redshift was found in the acetylferrocene micro-nanomaterials compared to that in solution. The formation mechanism of the acetylferrocene micro-nanomaterials is also proposed. This work provides a new strategy for the material synthesis and preparation and may realize the reuse of organometallic materials.

Key Words: Acetylferrocene micro-nanomaterials, Bidirectional preparation, Bottom-up, Top-down

Introduction

Nanostructured materials have been under intense multi-disciplinary study owing to their fascinating physical and chemical properties. So far, various techniques or methods have been exploited to synthesize the nanostructured materials, of which a great deal of research has focused on the potential applications. In fact, according to the elementary processes of size changes, the preparation approaches can be basically categorized into two classes: bottom-up and top-down approaches.¹⁻⁵ The bottom-up approach, for example, molecule self-assembly, is an approach by putting atoms or molecules in a desired pattern. In contrast, the top-down approach, for example, laser etching, is an approach by breaking down a bulk material to finer and finer particles.⁶ Until now, the two approaches have already been, respectively, used to prepare nano-materials, but their corresponding interrelation was less-considered.

Over the past several decades, inorganic semiconductor and metal nanomaterials prepared by the two approaches have been the focus of many researchers' work owing to their unique optical, electronic, magnetic and mechanical properties,^{7,8} and their potential applications have been extensively investigated.^{9,10} In recent years, since organic nanomaterials demonstrate novel functions in electronic and optical properties which are fundamentally different from those of inorganic nanomaterials, because of the presence of weak van der Waals intermolecular interaction,¹¹ there has been a tendency to extend the research of nanomaterials from metal and semiconductor nanomaterials into general organic compounds due to the diversity of organic molecules, and some organic nanomaterials have been prepared.¹²⁻¹⁵ Contrary to the research of inorganic and organic nanomaterials, little attention has been paid to the preparation of organometallic nanomaterials, to say nothing of that of metallocene nanomaterials. We have developed a convenient preparation method to organometallic ferrocene nanocrystals and investigated their electrochemical properties.¹⁶

Ferrocene and its derivatives have aroused considerable experimental and theoretical attention to their exceptional properties^{17,18} since its accidental discovery.¹⁹ Up to now, considerable efforts have been devoted to the synthesis of various ferrocene derivatives and their properties. Thereinto, acetylferrocene (AFc) has been identified as important intermediate and starting materials for the synthesis of other ferrocene derivatives, and it also has potential applications as important materials in the environment, and catalytic and optical fields.^{20,21} However, to the best of our knowledge, the preparation of AFc micro-nanomaterials has not been published in the scientific literature. Herein, we first report the preparation of AFc micro-nanomaterials, especially the cross-corresponding preparation in bidirection (top-down and bottom-up), by using the top-down and bottom-up approach, respectively, and investigate the corresponding combination of top-down and bottom-up approaches. In this paper, we can reach the same goal by using the top-down or bottom-up approach, as the old saying always states that all roads lead to Rome. This work represents a strategy for the preparation of nanostructured organometallic compounds.

Experimental Section

Materials and Apparatus. AFc was donated by Shanghai Huanxi chemical Co. Ltd and used directly without further purification. All other reagents were of analytical grade. Pure water, obtained by means of a water-purification system, was used in the experiments. All experiments were carried out at room temperature.

XRD patterns of samples were measured on a Bruker D8-advance X-ray diffractometer with Cu K α radiation ($\lambda = 0.154056$ nm). SEM and TEM images were acquired on a Philips XL-30E scanning electron microscope (SEM) by dropping products' suspension on a glass sheet and a Hitachi model 800 transmission electron microscope (TEM), respectively. IR spectra were measured on a Nexus FT-IR spectrophotometer using KBr pellets.

UV-visible absorption and fluorescence emission spectra were recorded on an Agilent 8453 spectrophotometer and a Shimadzu RF-5301 spectrophotometer, respectively.

Preparation of AFc Micro-Nanomaterials: Top-down Approach. The absolute ethanol (5 mL) was added to the AFc bulk materials (0.1 g) drop by drop with the aid of ultrasonication. To the mixture was added dropwise water (40 mL) at the rate of 5 mL/min under ultrasonic irradiation, and the resulting system was further treated with ultrasonication for 20 min, then centrifuged for 20 min. The precipitate was dried under vacuum at room temperature and the larch-fruit-like AFc micro-nanomaterials were obtained and designated as Sample 1.

Bottom-up Approach. In addition, a 3.3 mL solution of AFc in ethanol (0.13 M) was slowly injected into 10 mL of water under ultrasonic irradiation. The resulting suspension was further treated with ultrasonication for 20 min. The products were separated by centrifugation and then dried under vacuum at room temperature. The beltlike AFc micro-nanomaterials were obtained and designated as Sample 2.

Results and Discussion

The larch-fruit-like AFc micro-nanomaterials (Sample 1) and beltlike AFc micro-nanomaterials (Sample 2) have been prepared by the top-down and bottom-up approach, respectively (see Experimental Section). As shown in Figure 1, it is found interestingly that the products obtained at different stages in preparing the Sample 1 are similar to that of the Sample 2, such as a to h, b to g, c to f, and d to e in Figure 1. The preparation processes of the Sample 1 and Sample 2 are schematically showed in Figure 2. It is revealed that the Sample 1 was prepared using the AFc bulk materials as precursor by the top-down approach while the Sample 2 was prepared using the AFc molecules in solution as precursor by the bottom-up approach. The results show that the preparation processes of the Sample 1 and Sample 2 are reversible and the similar products can be obtained by either top-down or bottom-up approach. So, by using the top-down and bottom-up approaches, the Sample 1 and Sample 2 can be cross-correspondingly prepared in bidirection. The size of the Sample 1 is about 250 nm and the thickness of nano-sheets in the larch-fruit-like structure is about 25 nm (Figure 1a), while the length of the Sample 2 (Figure 1e) adds up to about 75 μm and the thickness 92 nm, and the long/wide ratio is about 25. Furthermore, the results can be confirmed by TEM images as shown in Figure 3, which indicate that the morphology of the Sample 1 is similar to that of the initial intermediate products of the Sample 2. This provides further evidence to the cross-corresponding preparation processes of the Sample 1 and Sample 2 in bidirection. The above results show that the cross-corresponding preparation strategy in bidirection is a simple and facile synthesis route to preparing the AFc micro/nano-materials from two directions. This preparation strategy may open an avenue to preparing different kinds of organometallic micro-nano-materials.

The internal structure of the products was determined by XRD in Figure 4 (XRD patterns of the intermediate products are showed in the Supporting Information). Also IR spectra of the intermediate products and samples are showed in the Supporting

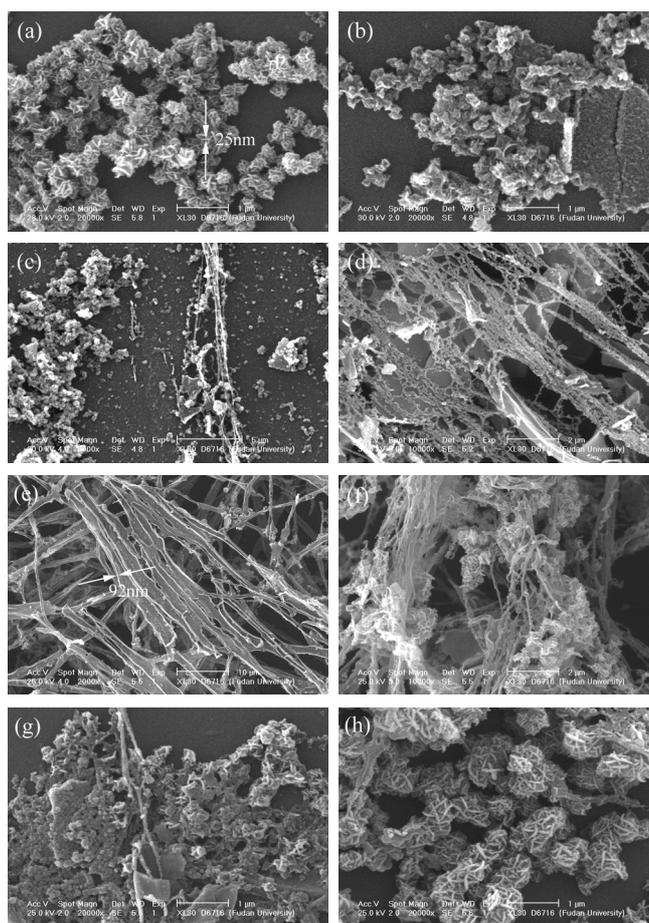


Figure 1. SEM images (1) top-down approach: (a) Sample 1, (b) the intermediate products of the Sample 1 when adding dropwise 7 mL of water and (c) adding dropwise 5 mL of water, and (d) AFc bulk materials added dropwise 1 mL of ethanol; (2) bottom-up approach: (e) Sample 2, the products when (f) 2.5 mL, (g) 1.2 mL, and (h) 0.7 mL solution of AFc in ethanol was slowly injected into 10 mL of water, respectively.

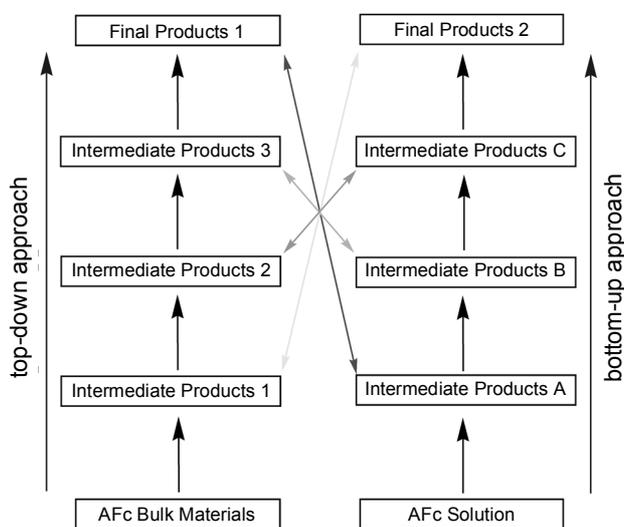


Figure 2. Preparation processes of the Sample 1 and Sample 2.

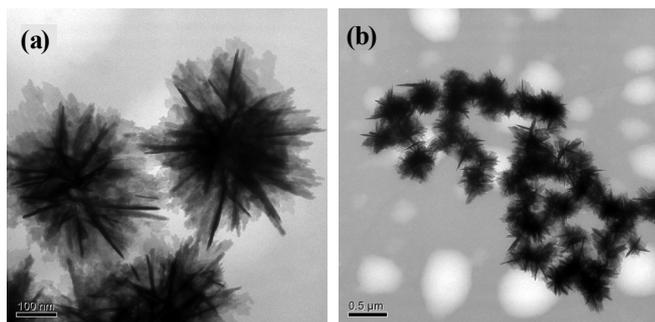


Figure 3. TEM images of (a) Sample 1 and (b) the intermediate products of the Sample 2 shown in Figure 1 h.

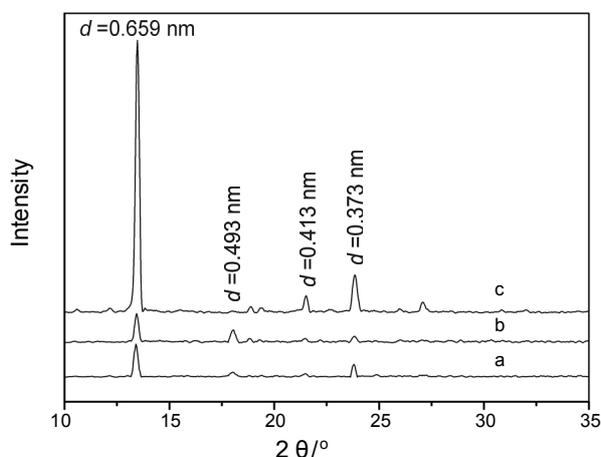


Figure 4. XRD patterns of (a) AFc bulk materials, (b) Sample 1, and (c) Sample 2.

Information), which indicate that the structure of the products and AFc bulk materials is identical and AFc was not decomposed in the preparation processes. The peaks at 2θ values of 13.42° , 18.01° , 21.50° and 23.82° in Figure 4 correspond to the d -spacing of 0.659 nm, 0.493 nm, 0.413 nm and 0.373 nm, respectively, which are consistent with the reported results,²² and the AFc crystals are in the monoclinic space group $P2_1/c$ at room temperature.²³ From Figure 4, it can be seen that the Sample 2 has higher crystallinity.

Figure 5 displays the UV-Vis absorption spectra of the AFc solution in ethanol, and the Sample 1 and Sample 2 dispersed in water. In Figure 5a, there are two resolved peaks at 337 and 457 nm, which correspond to $\pi-\pi^*$ and $n-\pi^*$ transitions, respectively. The two peaks were observed to shift to the longer wavelength region at 344 and 461 nm for the Sample 1 and 344 and 464 nm for the Sample 2 (Figure 5b), respectively. To explain the optical size-dependent property of organic nanoparticles, two reasons were considered.²⁴ One is the change of lattice state due to the increase in surface area. It is likely that the increase in surface area causes lattice softening, and therefore, the coulombic interaction energies between molecules are smaller, leading to wider band gaps. The other reason may be the electric field effect of surrounding media through the surface of the nanoparticles. In our experiments, the redshift

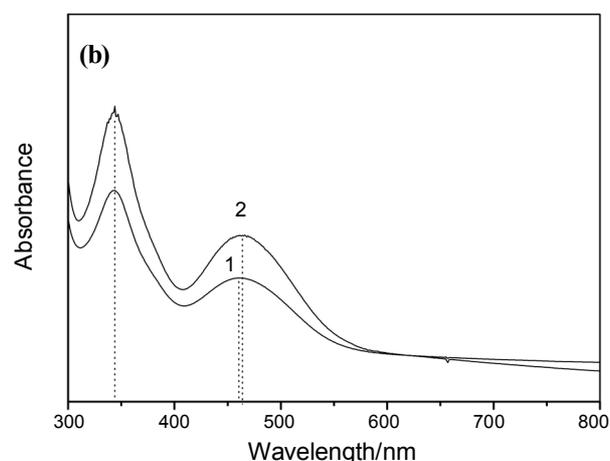
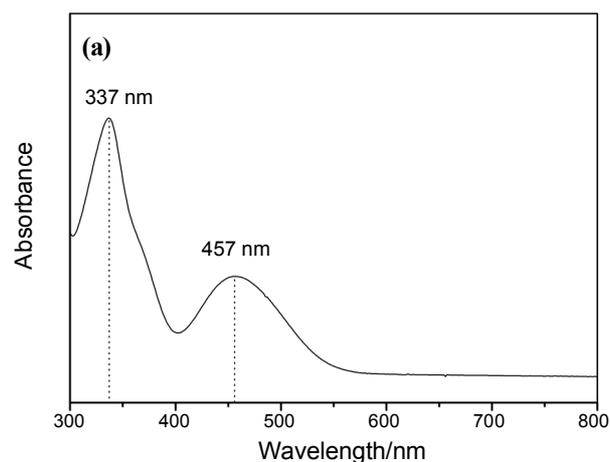


Figure 5. UV-Vis absorption spectra of (a) AFc solution in ethanol and (b): (1) Sample 1 and (2) Sample 2 dispersed in water.

may due to the polarizable environment of the surrounding AFc, which lowers the energy of the transition.²⁵

In order to investigate the effect of experimental condition on the formation of the AFc micro-nanomaterials a series of experiments were carried out. It was found that the mechanical power played a critical role in the formation of the AFc micro-nanomaterials. As shown in Figure 6, the AFc nanoparticles were prepared via the top-down approach with stirring while other conditions were kept unchanged. Furthermore, when an 1 mL solution of AFc in ethanol (0.13 M) was slowly injected into 10 mL of water with stirring using the bottom-up approach, the AFc nanoparticles were also obtained (Figure 7). Based on the results stated above, it can be seen that the two products prepared with stirring using the top-down and bottom-up approach, respectively, are similar and corresponding. Also it is shown that the sizes and morphologies of the products prepared with stirring are different from that prepared under ultrasonic irradiation. The changes in the sizes and morphologies of the products may result from the effect of ultrasonic and minimum interfacial energy. Moreover, it was reported that the adsorptive property of the AFc materials depends on the grain sizes of these materials.²⁶ Thus, the as-prepared AFc micro-nanomaterials with different sizes and morphologies may have some interesting properties and may have potential applications

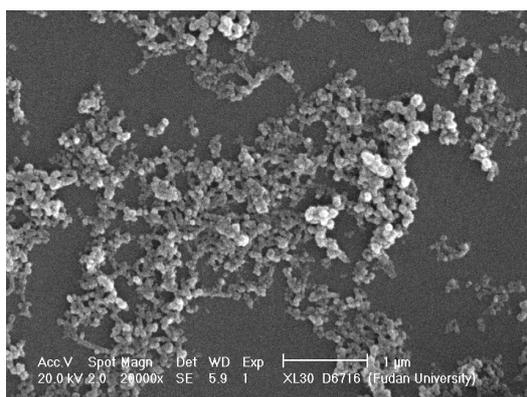


Figure 6. SEM image of AFc nanoparticles prepared *via* the top-down approach with stirring.

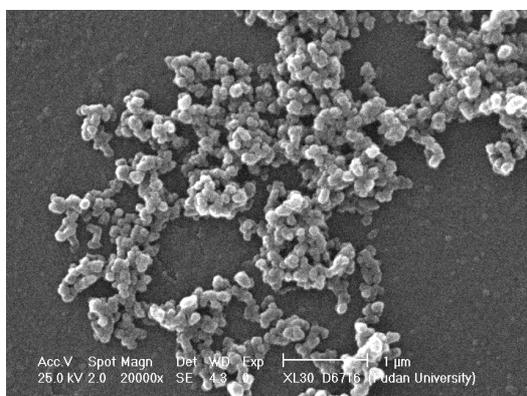


Figure 7. SEM image of AFc nanoparticles prepared *via* the bottom-up approach with stirring.

in many fields, and further work on the products is still under way.

A possible formation mechanism of the Sample 1 may be as follows. In our experiments, AFc is completely soluble in ethanol but poorly soluble in water. As is known, ethanol and water can dissolve one another. When water is gradually added to the AFc solution, the ethanol is gradually dissolved into water and the ethanol-rich environment of the AFc molecules is progressively replaced by the bulk water, then the concentration of AFc molecules in mixing solution reaches its solubility limit. In this case, the AFc molecules exposed in the poor solvent tends to aggregate together immediately. This process leads to the formation of amorphous particles, having a range of sizes.¹³ Aggregation is energetically favorable, while the introduction of an interface is unfavorable, so there is a balance between the two processes.²⁷ Moreover, ultrasound has been a very effective processing method in the preparation of nano-materials.^{28,29} These are the mechanical effects of ultrasonic cavitation. Cavitation, that is, the formation, growth and implosive collapse of bubbles in a liquid, can be used to influence chemical reactions by the cavitation energy.²⁹ In the experiment, the ultrasonic cavitation can accelerate the formation of crystal nuclei and prevent bulk growth. In addition, AFc nanoparticles (Figure 6 and 7) can be prepared in the absence of ultrasonic irradiation in order to maintain minimum inter-

facial energy. Therefore, we suppose that the ultrasonic cavitation may be responsible for the formation of the Sample 1. In the case of the Sample 2, those results (Figure 1h, 1g, 1f, 1e) suggest that the growth process of the Sample 2 is from particles to the beltlike structure. Besides, Li *et al.* suggested that once sizes of nanoparticles exceed about 50 nm, the growth rates in different directions are no longer equal.¹³ So, we speculate that the formation of the Sample 2 may result from single-direction aggregate growth of AFc particles.

Conclusion

In summary, the larch-fruit-like AFc micro-nanomaterials and beltlike AFc micro-nanomaterials have been cross-correspondingly prepared in bidirection by the top-down and bottom-up approach, respectively. It was found that the mechanical power played a critical role in the formation of the AFc micro-nanomaterials. The redshift was found in the AFc micro-nanomaterials compared to that in solution in UV-Vis absorption spectra. The size of larch-fruit-like AFc micro-nanomaterials is about 250 nm, while the length of beltlike AFc micro-nanomaterials adds up to about 75 μm and their long/wide ratio is about 25. It is hoped that other experiments will be carried out to find out their potential applications in nanotechnology and the cross-corresponding preparation strategy in bidirection may realize the reuse of organometallic materials. Our works provide a new idea for the cross-corresponding preparation of organometallic micro-nanomaterials in bidirection and the synthesis strategy may open the way to prepare other organometallic micro-nanomaterials.

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