



A novel waist-regulable dumbbell-like nanosuperstructure of (3-carboxy-1-acyl-propyl)-ferrocene

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ABSTRACT

Dumbbell-like nanosuperstructures of (3-carboxy-1-acyl-propyl)-ferrocene were successfully prepared by ultrasonic-pHcontrolling-precipitation method. The scanning electron microscope shows that as-obtained products were composed of nanorods. The length of the products is about 6–12 μm , the diameter of the two polar coronas and the middle part (waist) are respectively about 2–8 μm and 0.5–2 μm . The diameter of the nanorods that are the basic unit of the superstructures, is about 0.3 μm . X-ray diffraction analysis of the products indicated that the superstructures keep original crystal structure. The optical properties of the products were characterized by FT-IR spectrometer and UV spectrometer, and they display quantum size effect. This paper provides a novel method that has potential application in preparing other organometallic compounds superstructures, and more importantly, the as-obtained superstructures have widely applications. The possible mechanism was also proposed.

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1. Introduction

Ferrocene and its derivatives have drawn many attentions of scientists because of their good applications in electrochemistry [1–4], catalysts [5–8], life science and medicine [9–11]. With sandwich structure, ferrocene consists of a pair of cyclopentadiene with an iron atom squeezed between them. Because of the Π conjugated bond, electrons transfer easily in inner molecule. Therefore, ferrocene and its derivatives are widely used as catalysts for asymmetric synthesis [12–14], biosensors [15–20], etc.

A larger amount of efforts have been devoted to prepare nano-size/structural materials due to their marvelous characteristics that are different from those of bulk materials in the past decades. However, because of the low thermal stability and weak mechanical properties of organic metals, the fabrication process for inorganic nanomaterials such as hydrothermal method [21,22], soft template [23], even electric deposit [24] can not be applied to organometallic compounds. On the other side, the fabrication methods [25–28] about organic/polymer nanomaterials are not suitable for organometallic compounds either due to their partial inorganic properties. Based on above status, the organometallic nanomaterials have been rarely investigated. Therefore, it is significant to explore some novel methods to prepare organometallic nano/superstructure materials.

In this paper a new method of ultrasonic-pHcontrolling-precipitation is developed, which is used to prepare a novel dumbbell-like (3-carboxy-1-acyl-propyl)-ferrocene (Fig. 1) nanosuperstructure. We not only obtain an organometallic compound superstructure, but also present a novel preparation strategy of organometallic compound nanosuperstructure, which provide a method to prepare similar organometallic compound nano/superstructure material.

2. Experimental

2.1. Reagents and equipment

(3-carboxy-1-acyl-propyl)-ferrocene (98%) was donated by Shanghai Huanxi Chemical Co. Ltd. Polyvinylpyrrolidone (PVP) (99.5%) was used as received from China national Medicines corporation Ltd., without further purification. Pure water, obtained by means of a water-purification system, was used in the experiments.

Powder X-ray diffraction (XRD) pattern of sample was measured on 1710 X-ray diffraction with Cu $K\alpha$ radiation ($\lambda = 0.54184 \text{ nm}$) (Netherlands). Scanning electron microscopy (SEM, Philips XL30, Holland) measurements were performed with a field emission environmental scanning electron microscope. The optical properties of the products were characterized using IR spectroscopy (resolution 2 cm^{-1}) (Nicolet SX-170) and Agilent UV/Vis spectroscopy (Agilent 8453). Selected samples were subjected to ultrasonic irradiation by Ultra-sonication (KunShan Instrument Co. Ltd).

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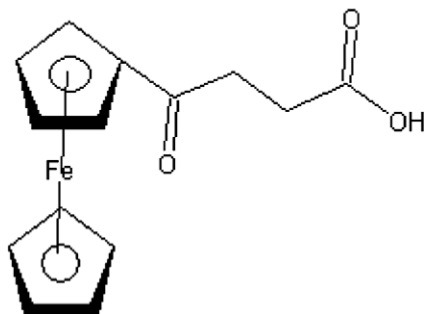


Fig. 1. Molecular structure of (3-carboxy-1-acyl-propyl)-ferrocene.

2.2. Preparation of (3-carboxy-1-acyl-propyl)-ferrocene superstructures

A typical procedure for the synthesis of (3-carboxy-1-acyl-propyl)-ferrocene superstructure was as following: 0.1 g (3-carboxy-1-acyl-propyl)-ferrocene bulk materials were added to 20 ml PVP solution (5–25 mg/ml). Then dilute NaOH (0.005 mol/L) was added dropwise into the above system under sonication. The solution would become transparent when pH value was equal to 8–9. Finally, dilute HCl solution was dropped to the mixed solution under sonication. The speed was controlled at one drop per second. After 30 min later, yellow precipitates appeared when pH value was down to 5.0. The dropping was stopped when pH value was equal to 3 while ultrasonic still lasted for 10 min. The products would be separated by centrifuge, then the precipitate was washed by pure water for 5 times, and dried under vacuum. The yellow powder was obtained.

3. Results and discussion

3.1. Morphologies and structures

The morphologies and sizes of as-obtained products were investigated with SEM, as shown in Fig. 2. The length of the products is about 6–12 μm , the diameter of the two polar corona and the middle part (waist) are about 2–8 μm and 0.5–2 μm , respectively. The diameter of the nanorods which are the basic unit of the superstructures, is about 0.3 μm . The dumbbell-like superstructures' waist becomes longer and the corona becomes smaller with the acidity decreasing, which clearly shows that the acidity influences the amounts of nucleus and the nucleating speed. The X-ray diffraction (XRD) pattern of the as-obtained products comparing with that of bulk materials is shown in Fig. 3, and result indicates that the superstructures keep original crystal structure.

3.2. Optical properties of the products

The IR spectra of as-obtained products and bulk materials of the (3-carboxy-1-acyl-propyl)-ferrocene have been observed in Fig. 4. The absorption peaks at 3550 cm^{-1} , 3000 cm^{-1} and 2700 cm^{-1} in spectrum b, corresponding to peaks at 3500 cm^{-1} , 3000 cm^{-1} and 2700 cm^{-1} in spectrum a, are attributed to the stretching vibration of O–H. These peaks in spectrum b become wider than those in spectrum a. The peak at 1665 cm^{-1} and 1486 cm^{-1} in spectrum b, corresponding to peaks at 1658 cm^{-1} and 1476 cm^{-1} in spectrum a, are assigned to the stretching modes of carboxyl (C=O) and acyl (C=O), respectively. It is obvious that, comparing with IR spectrum of the bulk materials (spectrum a), IR spectrum peaks of as-products (spectrum b) exhibit blue shift to some extent. The above two optical properties should be ascribed to the quantum size effect of nanomaterials. The characteristic absorption peaks

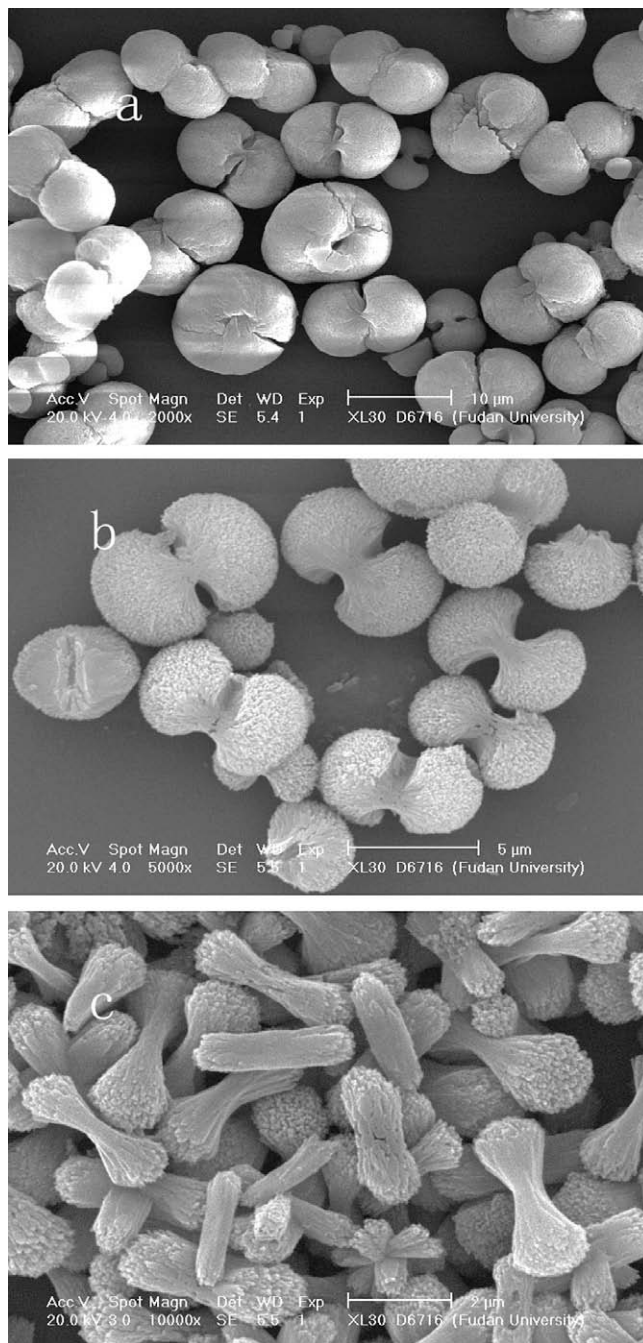


Fig. 2. The SEM morphologies of as-obtained products PVP: 50 mg, (a) HCl concentration/mol/L: 0.12, (b) 0.06, (c) 0.03.

of PVP at 3400 cm^{-1} and 1700 cm^{-1} , due to very strong stretching modes of N–H and N–C=O(C=O), do not appear in the spectrum of the product, which indicates that PVP template is not remained in as-obtained product. UV absorption spectra of bulk materials and as-obtained products are shown in Fig. 5. Comparing with bulk materials, the as-obtained products have shown obvious blue shift due to quantum effect.

3.3. Effect factors on morphologies

3.3.1. Effect of the concentration of the HCl on morphologies

We have investigated the influence of acidity on the morphologies of the samples. The reactions can be formulated as follows:

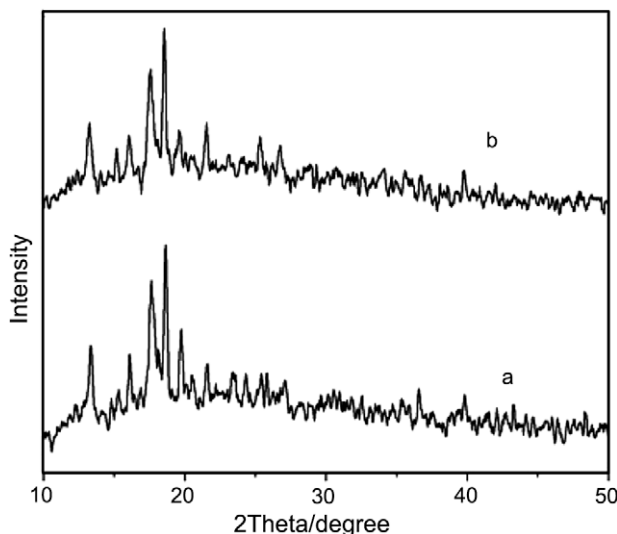


Fig. 3. XRD (a) bulk materials, (b) as-obtained products (HCL concentration: 0.06 mol/L, PVP: 50 mg).

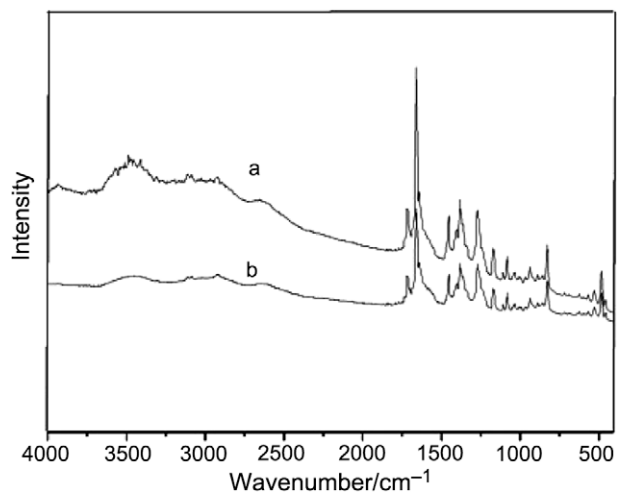


Fig. 4. IR spectrum (a) bulk materials, (b) as-obtained products (HCL concentration: 0.06 mol/L, PVP: 50 mg).



When HCl was dropped into transparent solution of (3-carboxy-1-acyl-propyl)-ferrocene ion, (3-carboxy-1-acyl-propyl)-ferrocene precipitated and was adsorbed by the long chain of PVP because of H-bond site and static effect.

The speed of forming particle becomes faster with higher acidity, and at the same time much more crystal nucleus produced. Here the two polars's distance ("waist") becomes shorter. On the contrary, at lower acidity the crystal has more time to self-assemble. Thus, under this condition the waist becomes longer (Fig. 2b and c). It is supposed that potential energy and kinetic energy commonly decide the superstructure morphologies of products. Under higher acidity condition, kinetic energy is dominant, and the nanorods self-assembled faster (kinetic energy determinism). The potential energy (repulsion between nanoparticles) is secondary factor. That is why the waist of the superstructure (Fig. 2a–c) changes shorter as the acidity rises (from about 4 μm to about 0.5 μm).

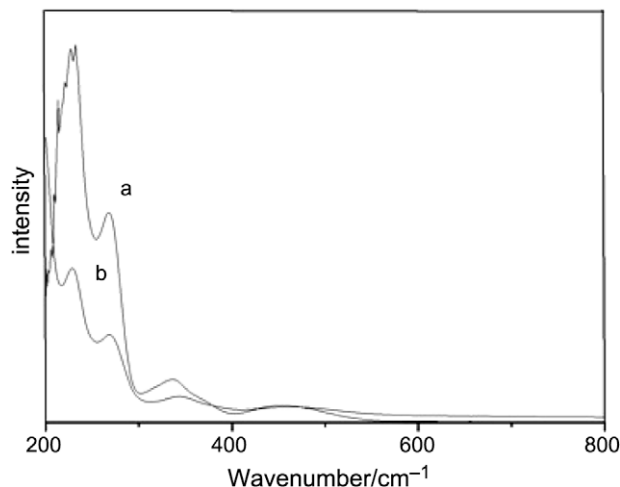


Fig. 5. UV spectrum (a) bulk materials, (b) as-obtained products (HCL concentration: 0.06 mol/L, PVP: 50 mg).

3.3.2. Effect of the additives on morphologies

It is well-known that using a polymer-assisted reaction to control the nucleation and self-assembling is a simple but effective method. Some recent researches show that the capping organic molecules in the reaction system could modulate the kinetics of the crystal growth and determine the subsequent morphology of the product. For example, Yang et al. have prepared SnS₂ submicron particles [29] and Zheng et al. have prepared β-MnO₂ nanotubes in the presence of PVP [30].

In order to further study how PVP influence the formation process of the dumbbell-like superstructure, various amounts of PVP were used under the same conditions. When no PVP, 1 mg, 10 mg, 50 mg PVP were used under the same condition, different morphologies were obtained (Fig. 6a–d). When no PVP was added but other experimental condition was kept the same, the product was regular rectangle patch (Fig. 6a). Fig. 6b shows that the morphology becomes curl patch when the amount of PVP was down to 10 mg. Even so, the curl patch was also self-assembled with nanorods. Dumbbell-like products were obtained when more than 10 mg PVP was employed in this reaction system. The above experiments reveal that optimum amount of is 10–50 mg.

Comparative experiments were done to confirm the indispensable function of PVP in the formation of dumbbell-like superstructure. PVP was substituted by polyethylene glycol (PEG400) and hexadecyl trimethyl ammonium bromide (CTAB) under the same experimental conditions. The result is fully different (Fig. 7a and b).

3.3.3. Effect of ultrasonic on morphologies

In order to investigate the influence of ultrasonic, parallel experiment was done without sonication. The dumbbell-like superstructures (Fig. 8) were also obtained. Yet it is just not so regular. Therefore, it is ultrasonic that modulates the shape of dumbbell-like structures. Those unorderly-produced nanoparticles will be brushed off due to weak bond under ultrasonic effect.

3.4. Possible mechanism

In order to explore the nanosuperstructure formation mechanism, relevant experiments and theories are collected. The details are as follows:

- (1) Nanorod products are presented in Fig. 9 and many nanoparticles can be seen on the nanorods' tips. It implies that the product was self-assembled by nanoparticle under the template inductive effect of PVP.

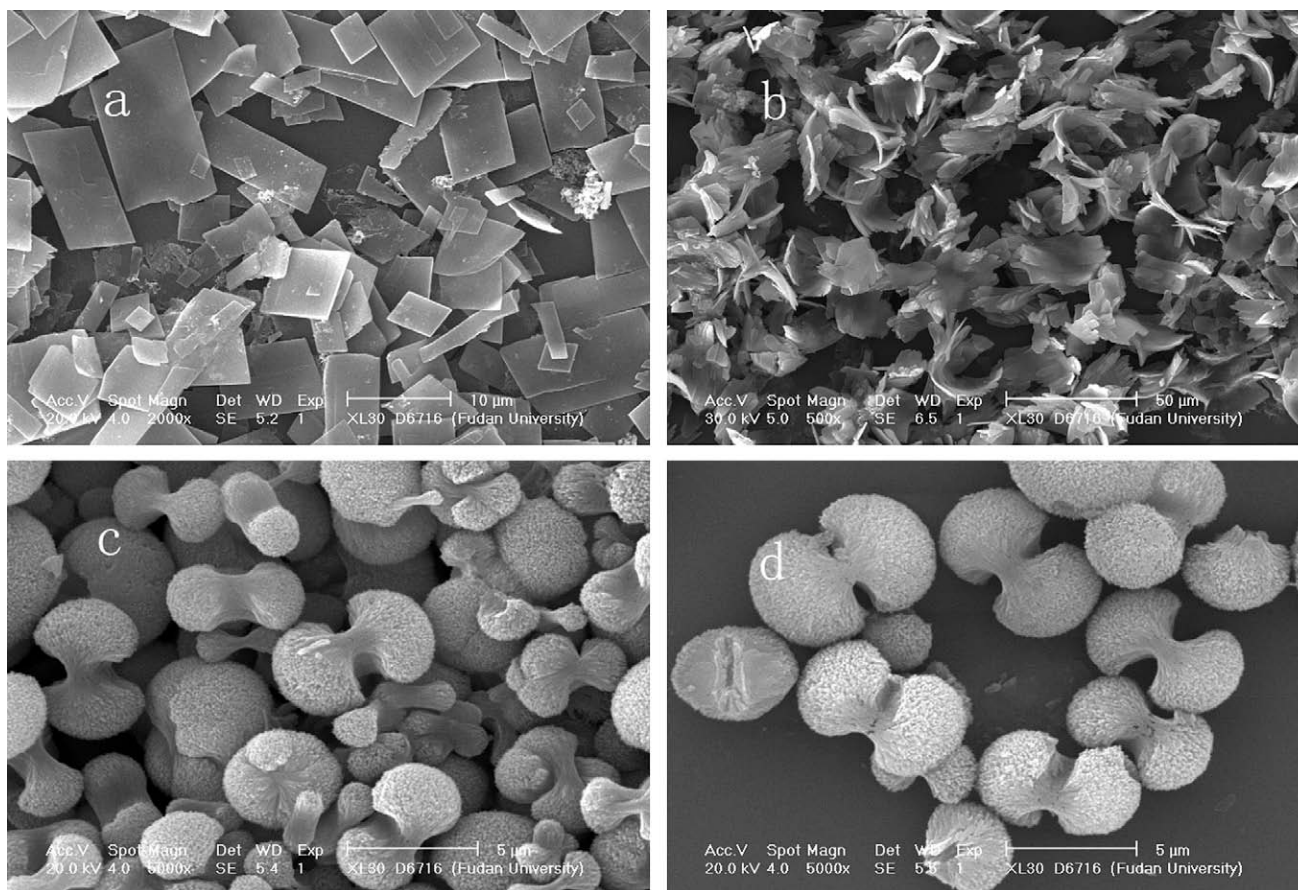


Fig. 6. The morphologies of as-obtained products by SEM, (HCl concentration: 0.06 mol/L), PVP/mg (a) 0, (b) 1, (c) 10, (d) 50.

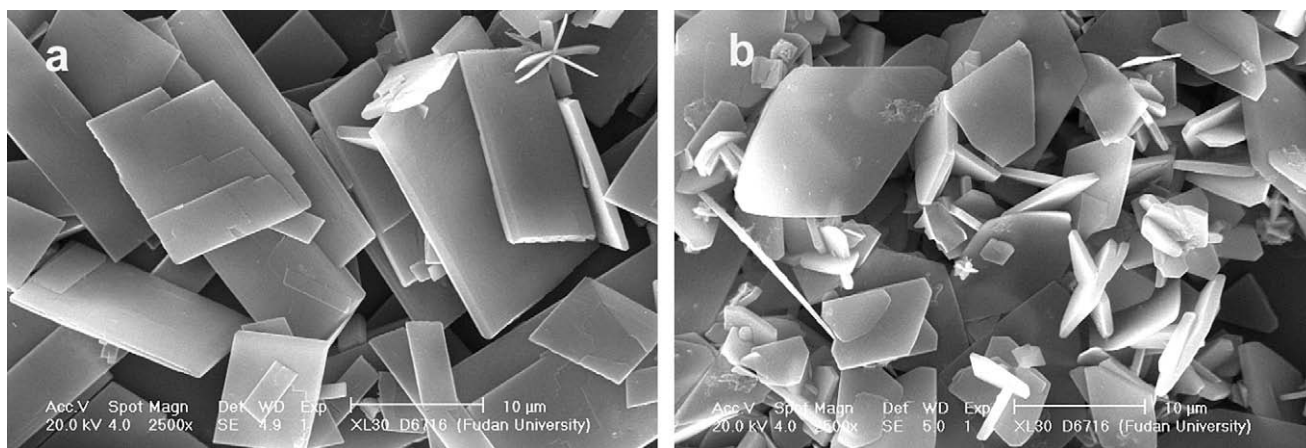


Fig. 7. The morphology of as-obtained product by SEM (a) PEG400 as surfactant, (b) CTAB as surfactant.

(2) Changing HCl concentration from 0.12 mol/L to 0.03 mol/L, the waists (Fig. 2) of the as-obtained products are also different. It shows that acidity affects both the speed of particles self-assembly and the self-assembly mode of these molecules. At higher acidity, many molecules are precipitated from the solution in short time, which results in the change of direction of H-bond. Therefore, the waist of dumbbell-like nanosuperstructure materials becomes shorter. At lower acidity, reverse result would be obtained.

(3) Three kinds of surfactants were employed in experiments, however, dumbbell-like superstructure can be obtained only when PVP was employed (Figs. 6 and 7). It is owing to the particular molecular structure of PVP (Fig. 10a). There are lots of naked O and N atoms in the particular long chain of PVP, which can form H-bond with the (3-carboxy-1-acyl-propyl)-ferrocene. Moreover, there are many caves in the chain because of pyrrolidone rings. The nanoparticles only self-assemble along the PVP chain to nanorods, because the pyrrolidone rings of PVP restrain the rest assembling

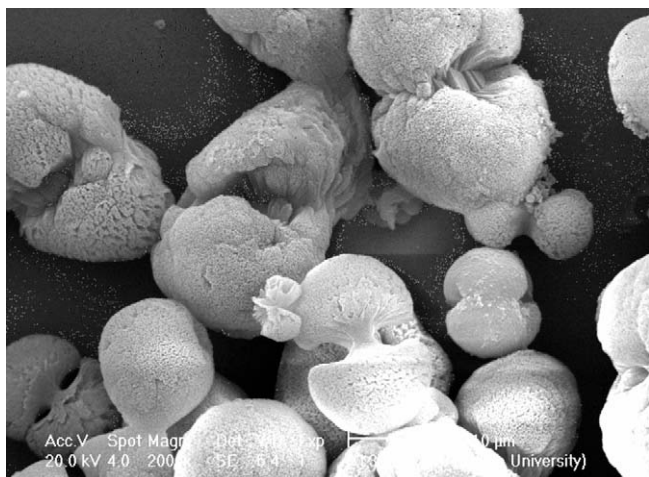


Fig. 8. The SEM of morphology as-obtained product (without sonication).

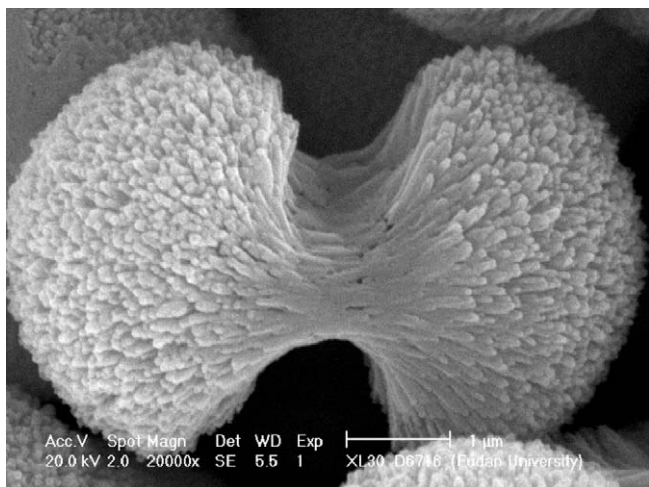


Fig. 9. SEM of as-obtained products (HCl concentration: 0.06 mol/L, PVP: 10 mg).

direction. PEG400 (Fig. 10b) and CTAB (Fig. 10c) do not have such particular structure as that of PVP, so dumbbell-like superstructure can not be obtained.

- (4) It is known that there are fewer PVP molecules, much more dangling bond, larger specific surface area, higher energy, and more active sites on the two polar of the micelle.

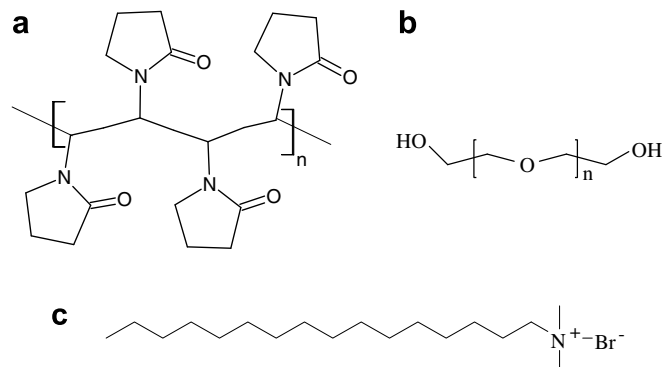


Fig. 10. (a) PVP molecular structure, (b) PEG molecular structure, (c) CTAB molecular structure.

- (5) Yu et al. once produced a stable dispersion of uniform and amorphous selenium particles with size of 100 nm in the presence of PVP [31]. This paper pointed out that PVP, as a polymer surfactant, played an important role in the synthesis of one-dimensional nanorods and nanowires of selenium.

Based on above facts and theories, possible process of the dumbbell-like superstructure formation is described as below:

Firstly, (3-carboxy-1-acyl-propyl)-ferrocene ion solution becomes supersaturated fluid when dilute HCl solution was added into it. Then (3-carboxy-1-acyl-propyl)-ferrocene molecule is separated out and congregates near PVP micelle chains. As the precipitate increases the crystal nucleus is formed. According to Fig. 4, the stretching vibration of hydroxyl of nanosuperstructures has changed in some degree comparing with bulk materials. It implied that H-bond exist between molecules in the as-obtained products. These molecules not only stack to each other firmly but also are easily attached with PVP molecules due to H-bond.

Next, precipitate of derivatives of ferrocene tended to orientation self-assembly under the control of the directivity of H-bond and inducing effect by PVP. This is different from what happened in ferrocene without carboxyl, in which only nanoparticles can be obtained [20].

Then, from Figs. 1 and 9, we can see there are some similarity between the molecule and the as-obtained products. According to principle of fractal geometry (the objective has self-similarity of multilevel structure), these precipitate will further self-assemble in accordance with itself molecule structure.

Lastly, lots of nanoparticles keep on assembling and finally the dumbbell-like superstructures are formatted.

In generally, the process may be described as Fig. 11.

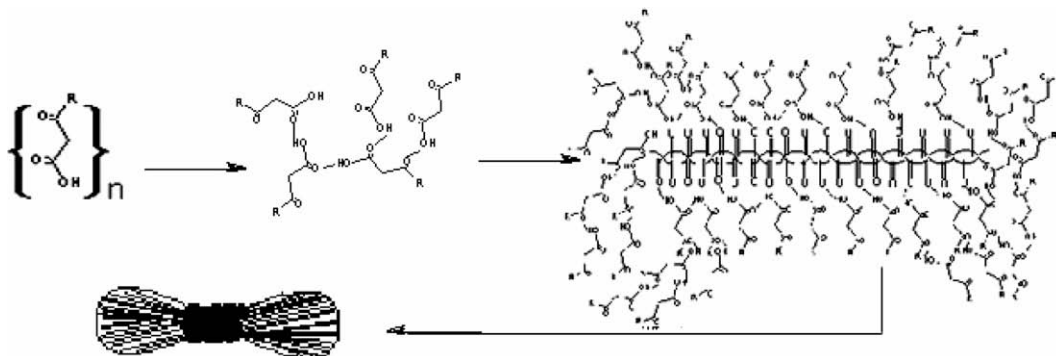


Fig. 11. A schematic illustration of dumbbell-like nanosuperstructure (R=Fc).

4. Conclusion

(3-Carboxy-1-acyl-propyl)-ferrocene with dumbbell-like morphologies is first successfully prepared by ultrasonic and controlling pH value in this paper. The superstructure materials will be of great importance in the application fields of electrocatalysis, nano-devices, biosensor and so on. The fully novel method only used deionized water and little surfactant. Therefore, it will have potential applications in preparing this kind of organic metal compounds by virtue of its convenient operation, environmental friendliness, and low energy consumption. The properties and applications of this novel material with nanosuperstructure will be investigated in our further work.

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References

- [1] S.Y. Ng, W.K. Leong, L.Y. Goh, R.D. Webster, *Eur. J. Inorg. Chem.* 46 (2007) 463–471.
- [2] L.E. Hagopian, A.N. Campbell, J.A. Golen, A.L. Rheingold, C.J. Nataro, *Organomet. Chem.* 691 (2006) 4890–4900.
- [3] H.F. Song, X.H. Li, Y.T. Long, G. Schatte, H.B. Kraatz, *Dalton Trans.* 39 (2006) 4696–4701.
- [4] P. Jego-Evanno, J.P. Hurvois, C. Moinet, *J. Electroanal. Chem.* 507 (2001) 270–274.
- [5] S. Adhikari, S. Adhikary, H. Uchida, *Surf. Rev. Lett.* 13 (2006) 789–793.
- [6] J.G. Seitzberg, C. Dissing, I. Sotofte, P.O. Norrby, M. Johannsen, *J. Org. Chem.* 21 (2005) 8332–8337.
- [7] L. Li, J.L. Shi, J.N. Yan, X.G. Zhao, H.G. Chen, *Appl. Catal. A* 263 (2004) 213–217.
- [8] D.R. Burri, I.R. Shaikh, K.M. Choi, S.E. Park, *Catal. Commun.* 8 (2007) 731–735.
- [9] Y. Jie, Ma, Wen-Fei Dong, Mark A. Hempenius, Mohwald Helmuth, Vancso G. Julius, *Nat. Mater.* 5 (2006) 724–729.
- [10] Kristy M. Jurchen, L. Lo, J. Xu, G. Waston, Kenneth N. Raymond, *Blood* 1 (2002) 100. Abstract No. 1729.
- [11] M. Salmain, G. Jaouen, *C.R. Chim.* 6 (2003) 249–258.
- [12] T. Ireland, G. Grossheimann, C. Wieser-Jeunesse, P. Knochel, *Angew. Chem., Int. Ed.* 38 (1999) 3212–3215.
- [13] C. Genet, S.J. Canipa, P. O'Brien, S. Taylor, *J. Am. Chem. Soc.* 128 (2006) 9336–9337.
- [14] T. Kimura, R. Shoda, N. Taniguchi, K. Kamikawa, et al., *Inorg. Chim. Acta* 357 (2004) 1829–1835.
- [15] A. Garcia, C. Peniche-Covas, B. Chico, B.K. Simpson, R. Villalonga, *Macromol. Biosci.* 7 (2007) 435–439.
- [16] G.S. Xuan, M.C. Kim, D.S. Her, H.L. Lee, *Chin. J. Chem.* 24 (2006) 546–550.
- [17] F. Arslan, A. Yasar, E. Kilic, *Russ. J. Electrochem.* 42 (2006) 137–140.
- [18] V.S. Tripathi, V.B. Kandimalla, H.X. Ju, *Biosens. Bioelectron.* 21 (2006) 1529–1535.
- [19] J.F. Nigel, C.F. Nicola, E.F. Jane, T.L. John, *Bioconjugate Chem.* 15 (2004) 137–144.
- [20] P. Chen, Q.S. Wu, Y.P. Ding, *Small* 3 (2007) 644–649.
- [21] X. Wang, Y.D. Li, *Inorg. Chem.* 45 (2006) 7522–7534.
- [22] Z.J. Gu, T.Y. Zhai, B.F. Gao, G.J. Zhang, D.M. Ke, Y. Ma, J.N. Yao, *Cryst. Growth Des.* 7 (2007) 825–830.
- [23] J. Sharma, B.A. Kakade, N.K. Chaki, S. Mahima, V.K. Pillai, *J. Nanosci. Nanotechnol.* 7 (2007) 2139–2150.
- [24] S.Y. Glazov, S.V. Kryuchkov, *Semiconductors* 35 (2001) 444–446.
- [25] S. Magdassi, M. Ben Moshe, *Langmuir* 19 (2003) 939–942.
- [26] K. Eunsang, O. Hidetoshi, K. Hitoshi, N. Hachiro, *Cryst. Growth Des.* 7 (2007) 600–602.
- [27] B. Li, T. Kawakami, M. Hiramatsu, *Appl. Surf. Sci.* 210 (2003) 171–176; B. Li, T. Kawakami, M. Hiramatsu, *Appl. Surf. Sci.* 210 (2003) 85–88.
- [28] H.B. Fu, J.N. Yao, *J. Am. Chem. Soc.* 123 (2001) 1434–1439.
- [29] H.M. Yang, C.H. Huang, X.H. Su, *Mater. Lett.* 60 (2006) 3714–3717.
- [30] D.S. Zheng, S.X. Sun, W.L. Fan, H.Y. Yu, C.H. Fan, G.X. Cao, Zh.L. Yin, X.Y. Song, *J. Phys. Chem. B* 6 (2005) 16439–16443.
- [31] J.M. Song, J.H. Zhu, S.H. Yu, *J. Phys. Chem. B* 110 (2006) 23790–23795.