



(Proceedings of 2011 Shanghai International Nanotechnology Cooperation Symposium, SINCS 2011, Published online 10 January 2012)

A Facile Fabrication of Carboxyferrocene Nanorods with Cavities and Its Properties

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Abstract: In the paper, a typical carboxyferrocene nanorod with cavities were presented by a simple sonication method, using PEG400 as a template in the process. The scanning electron microscope (SEM) shows the nanorods have lengths of 5~10 μm , and the diameter about 200 nm. To characterize the as-obtained nanomaterials, X-ray diffraction patterns were carried out, which indicate that the products keep the original crystal structure as bulk materials. Further research on optical properties of the products is characterized by FT-IR and UV spectrometer, which are different from bulk materials. With these features, the nanorods would have wide applications in the field of electrochemistry and biosensor.

Keywords: Ferrocene-carboxy; Nanorods; Sonication

Citation: Tiejian Zhu, Qingsheng Wu and Xinlin Zhou, "A Facile Fabrication of Carboxyferrocene Nanorods with Cavities and Its Properties", Proceedings of Shanghai International Nanotechnology Cooperation Symposium, 114-116 (2011). <http://dx.doi.org/10.3786/sincs2011.27>

Introduction

1-D nanomaterials are of great attractive because of their marvelous electrochemical and optical properties [1,2]. For example, Jaehyun, Moon group has fabricated nanofibers of Pd-TiO₂ as highly sensitive gas sensors [3]. Of 1-D nanomaterials, nanorods are obtained more attention due to their significant application. Qin Y, X group has fabricated tungsten oxide nanorods with quicker response characteristic and higher response value to the same concentration of NO₂ gas [4]. However, in the process, complicated steps are employed or a great amount of power is consumed. Thus, it is significant to explore some feasible routes for preparation of nanorods.

Recent years, organometallic compounds become hot point due to its outstanding catalysis. As typical organometallic compounds, ferrocene and its derivatives have been widely researched because of their promising applications in electrochemistry [5, 6] catal-

ysis [7], life science and medicine [8] and optics [9]. With sandwich structure, ferrocene consists of a pair of cyclopentadiene with an iron atom squeezed between them. Electrons transfer more easily inside the molecule due to the π conjugated bond. Therefore, ferrocene and its derivatives are especially used as catalysts for asymmetric synthesis [10], biosensor [11], etc. It is supposed that nanomaterials of organometallic compounds will provide greater significance. However, few investigations have been done on these typical organometallic nanomaterials on account of its instability.

In this work, nanorods of carboxyferrocene were successfully prepared via a simple sonication method with PEG400 as a soft template. SEM images of the samples show that the morphology of the samples are nanorod. Related optical properties are characterized by FT-IR and UV spectrometer. This method can also be applied in the preparation of other similar compound nanomaterials.

Experimental section

Reagents and equipment

Commercial carboxyferrocene (98%) was purchased from Shanghai Quanyu chemical Co. Ltd. Powder X-ray diffraction (XRD) pattern of the sample was measured on 1710 X-ray diffraction with Cu K_{α} radiation ($\lambda=0.54184$ nm) (Netherlands). Scanning Electron Microscopy (SEM, Philip XL30, Holand) measurements were performed on 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).

Preparation of carboxyferrocene nanorod

Carboxyferrocene bulk materials (0.1 g) were mixed with 20 ml water, and then 1 ml polyethylene glycol 400 (PEG 400) was added to the suspension system. Following dilute NaOH (5 mmol/L) solution was dropped to above mixture until suspending solution become transparent. Exposed to sonication, the resulted transparent solution was introduced dilute HCl at the speed of about one drop per second. Yellow color precipitation would appear after 15 min, at which pH value was decreased to 5.0. The dropping of HCl do not stopped until the pH value of the solution reached 3. After that, ultrasonication was continued for another 10 min. The products were separated by centrifugation. The resulted precipitate was washed by pure water for 5 times, and dried under vacuum.

Results and discussion

Morphologies and structures

SEM images in Figure 1A, B show the nanorods with cavities have a length of about $5\ \mu\text{m}$ and diameter of 200 nm. With some cavities, the as-obtained 1-D nanomaterials like a prism seen from figure 1B. It is supposed that the soft-template, PEG400 control the crystal growth direction. Sule Erten-Ela et al have prepared ZnO rods using PEG400 as surfactant under microwave irradiation. Xie Y et al have obtained ZnO nanorods

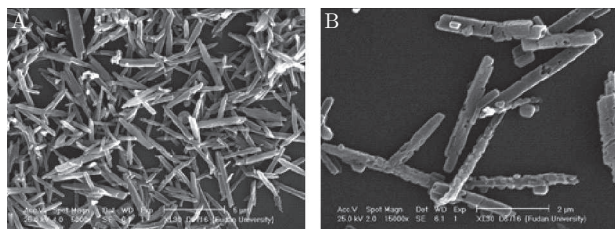


Fig. 1 The SEM morphology of as-obtained products (A and B).

under PEG400 synergistic effect. Figure 2 shows the XRD patterns for the as-prepared product and bulk material, which are in good agreement, revealing that the nanorod products well maintain the original crystal structure.

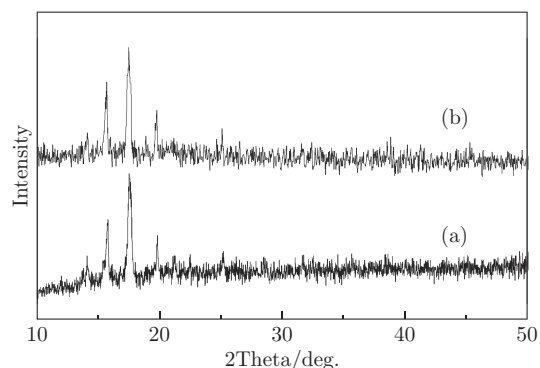


Fig. 2 XRD patterns of (a) bulk material and (b) as-obtained products (acidity of 0.03 mol/L, PEG400 of 10 mg).

Optical properties of the products

IR spectra for bulk materials and samples carboxyferrocene products are showed in Figure 3. The absorption peaks between 3000 cm^{-1} and 3450 cm^{-1} in spectrum b, correspond to the two peaks at 3500 cm^{-1} and 3000 cm^{-1} in spectrum a, are attributed to the stretching vibration of O-H of free water. The peak at 1700 cm^{-1} and 1480 cm^{-1} in spectrum b, corresponding to peaks at 1750 cm^{-1} and 1476 cm^{-1} in spectrum a, are assigned to the stretching modes of carboxyl (C=O), respectively. Therefore, compared to peak positions of the bulk materials (spectrum a), the ones for the samples (spectrum b) exhibit blue shift to some extent on the IR spectrum. The UV spectrum of the as-obtained products (Fig. 4(b)) present a distinct blue shift comparing to bulk material (Fig. 4(a)), which should be ascribed to the quantum size effect of nanomaterials.

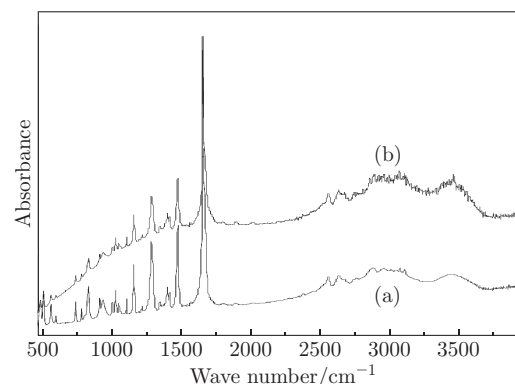


Fig. 3 IR spectra for (a) bulk material and (b) as-obtained product.

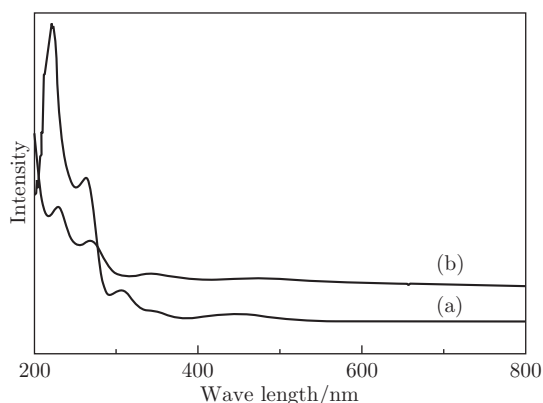


Fig. 4 UV-vis spectra for (a) bulk material and (b) as-obtained product.

Possible mechanism

To explore the formation mechanism of carboxyferrocene nanorods, PEG400 was replaced with polyvinylpyrrolidone (PVP) and hexadecyl trimethyl ammonium bromide (CTAB) as surfactant in the experiment. The as-obtained products in rectangular (Fig. 5A) and multi-branch nanorods (Fig. 5B) could be obtained respectively.

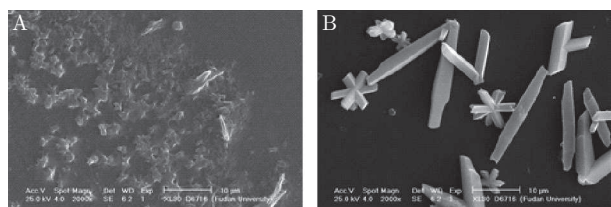


Fig. 5 The morphologies for the products prepared with surfactant PVP (a) and CTAB (b).

So it is surfactant that plays a key role during the nanorod formation. Possible mechanism of nanorods formation are supposed as following:

First, carboxyferrocene molecules are absorbed by PEG400 under H-bond interactions. The crystal facets with higher density of OH groups are preferable to attach on -OH group of PEG400 molecules. Explored to ultrasonication, carboxyferrocene nanorods start to generate along the PEG400 chains when dilute HCl was dropped to the above solution. Finally, surfactants were brushed off by continuous ultrasonication and water washing, and nanorods were obtained.

Conclusion

Here carboxyferrocene nanorods are firstly prepared by combining ultrasonication and pH value adjustment. The nanorods have a promising application in the fields of electrocatalysis, biosensor and so on. In addition, only deionized water and a small amount of surfactants are used in the preparation thus our method has the advantages of environmental friendliness and low cost. Further investigation on their properties and applications are still under progress in our group.

Acknowledgements

We acknowledge the financial support of the National Natural Science Foundation (No. 51072134) of China, the Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials (No. 2012MCIMKF03) and Chang jiang Delta Union Project (No. 10140702017).

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