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Solvent-etching preparation and enhanced emission of acetylferrocene organometallic nanoparticles

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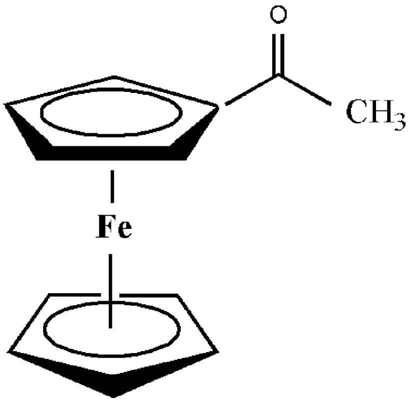
A new type of acetylferrocene organometallic nanoparticles with the diameter of about 70 nm was prepared by a simple solvent-etching method and characterized by scanning electron microscope, transmission electron microscope and X-ray diffractometer. Their optical properties were presently studied by FT-IR, UV–visible absorption spectra and fluorescence spectra. The fluorescence intensity was increased in the nanoparticles compared with that of bulk materials in solid state. The formation mechanism of the nanoparticles along with their optical properties is discussed. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: acetylferrocene; nanoparticles; fluorescence intensity; formation mechanism

Introduction

Over the past decade, inorganic semiconductors and metals nanoparticles have attracted considerable research interest from experimentalists and theoreticians owing to their unique optical, electronic, magnetic and mechanical properties, which are significantly different from those of bulk materials.[1–3] These inorganic nanoparticles were prepared and extensively investigated for various potential applications, such as lasers,[4] biological labels,[5] light-emitting diodes[6] and photovoltaic cells.[7] Compared with inorganic nanoparticles, organic nanoparticles demonstrate novel functions in electronic and optical properties that are fundamentally different from those of inorganic semiconductors and metal nanoparticles, because of the presence of weak van der Waals intermolecular interaction or hydrogen-bonding interaction.[8] Recently, there has been a tendency to extend the research of nanoparticles from semiconductors and metals into general organic compounds in materials synthesis and nanoparticle preparation due to the diversity and complexity of organic molecules, and a few kinds of organic nanoparticles have been reported.[9–12] However, little attention has been paid to the preparation of organometallic nanoparticles, to say nothing of that of metallocenes nanoparticles.

So far, several methods have been developed to prepare organic nanoparticles, such as ion-association technique,[13] vapor-driven self-assembly method,[14] reprecipitation method[15] and laser ablation.[16] Among them, the reprecipitation method involves rapidly injecting microamounts of the solution in a good solvent into macroamounts of a poor solvent. In this process, the sudden change in the surroundings of organic molecules causes the precipitation. At present, the method is widely used for the preparation of organic nanoparticles.[17–20] Moreover, in order to better control the different sizes, size distributions, shapes and structures of organic nanoparticles, many researchers have varied experimental conditions including temperature, precipitation time, monomer concentration and adding cosolvents or surfactants. Although these measures have limited success to a certain extent, it is still a challenge to control the sizes, shapes and structures of organic nanoparticles in a desired pattern. In addition, laser ablation has been applied to the preparation of organic nanoparticles,[21,22] but the preparation method is complex and expensive, so it is strongly expected that more facile and versatile methods will be exploited for preparing organic nanoparticles and further investigating their physical and chemical properties.



Scheme 1. Molecular structure of AFc.

Ferrocene and its derivatives have become the focus of much attention due to their exceptional properties[23,24] and potential applications[25–27] since its accidental discovery in 1951.[28] Until now, numerous efforts have been reported concerning the synthesis of various ferrocene derivatives. Acetylferrocene (AFc; Scheme 1), as a kind of ferrocene derivative, has been identified as an important intermediate and starting material in various

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fields. However, to the best of our knowledge, the preparation of AFc nanoparticles has not yet been reported. Herein, we report the preparation of AFc organometallic nanoparticles by a solvent-etching method and investigate their photoluminescence properties. This method is simple for preparing organometallic nanoparticles in aqueous solution and no organic cosolvents or surfactants are needed.

Experimental

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

The AFc nanoparticles were prepared as follows. AFc bulk material (0.1 g) was dissolved completely in the absolute ethanol (5 ml). To the resulting organic solution was added dropwise water (50 ml) at the rate of 5 ml/min with stirring, and the mixed system was further stirred for 20 min. The system was then centrifuged for 10 min, and received the precipitate. The precipitate was dried and the yellow AFc nanoparticles were obtained.

The microstructures and morphologies of AFc nanoparticles were analyzed with a Hitachi model 800 transmission electron microscope (TEM) and a Philips XL-30E scanning electron microscope (SEM). The crystal structure was measured on a Bruker D8-advance X-ray diffractometer (XRD) with Cu Kα radiation ($\lambda = 0.154056$ nm). IR spectra were measured on a Nexus FT-IR spectrophotometer using KBr pellets. UV–visible absorption spectra were recorded on an Agilent 8453 spectrophotometer. Photoluminescence spectra were carried out on a RF-5301 spectrophotometer.

Results and Discussion

Morphology and structure

The AFc nanoparticles were prepared with stirring by the solvent-etching method (see Experimental section). The morphology of the AFc nanoparticles was studied by TEM and SEM. Figure 1 shows the SEM image of the AFc nanoparticles. The diameter of the nanoparticles is about 70 nm, which can be confirmed by TEM image in Fig. 2. The internal structure of the nanoparticles was determined by XRD measurements (Fig. 3), which indicate that the structures of the nanoparticles and the AFc bulk materials are identical and AFc is not decomposed in the preparation. The peaks at 2θ values of 13.44°, 18.04°, 18.84°, 19.39°, 21.48° and 23.81° correspond to the *d*-spacing of 6.58, 4.91, 4.71, 4.57, 4.13 and 3.73 Å, respectively, which is in agreement with the reported values.[29] Moreover, the AFc crystals are in the monoclinic space group $P2_1/c$ at room temperature.[30,31]

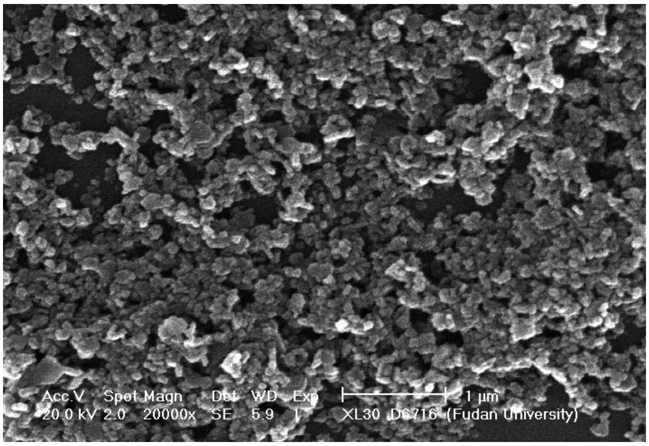

Figure 1. SEM image of AFc nanoparticles.

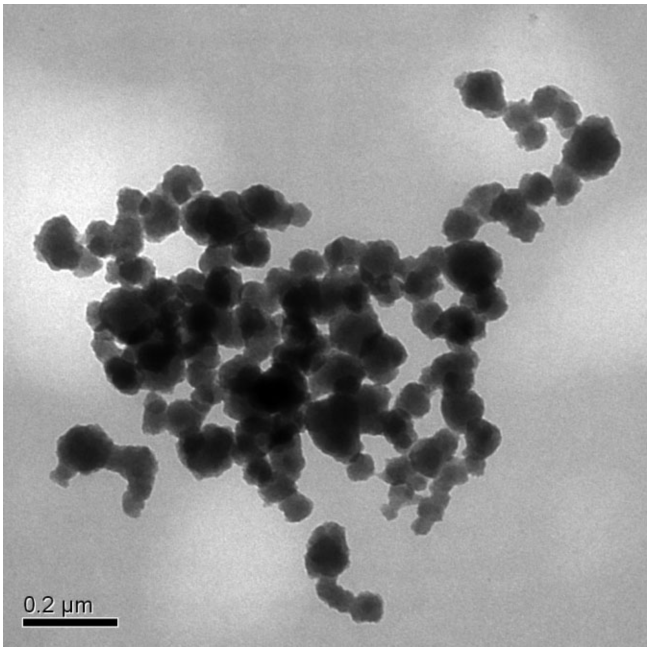

Figure 2. TEM image of AFc nanoparticles.

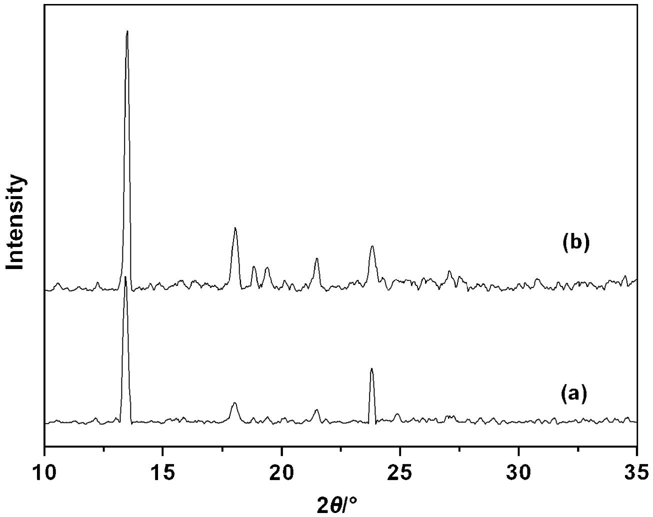

Figure 3. XRD patterns of (a) AFc bulk materials and (b) AFc nanoparticles.

The IR spectra of the bulk materials and the AFc nanoparticles were recorded in the range 4000–400 cm^{-1} as shown in Fig. 4. The IR spectra peaks of the nanoparticles are consistent with those of the bulk materials, which provides further support for the results discussed in the XRD patterns. An infrared absorption spectrum showed a peak at 1660 cm^{-1} which is characteristic of a carbonyl

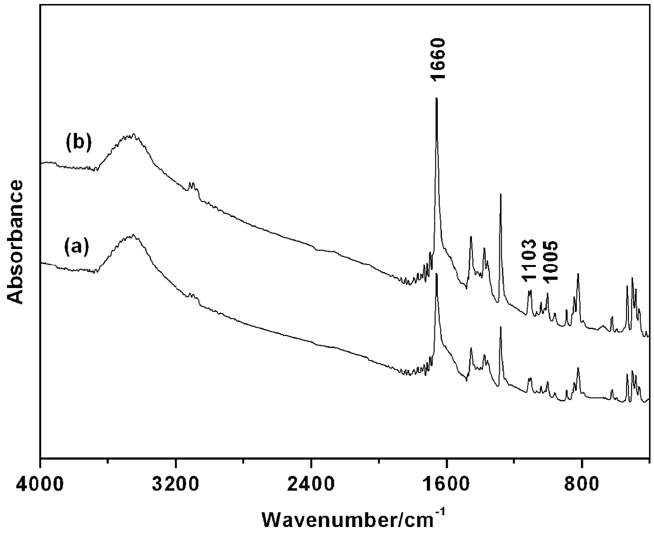

Figure 4. IR spectra of (a) AFc bulk materials and (b) AFc nanoparticles.

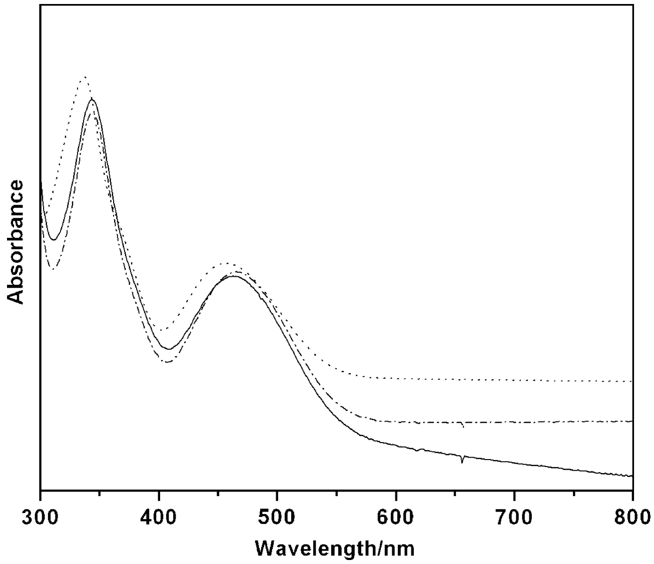

Figure 5. UV–vis absorption spectra of AFc solution in ethanol (dotted line), and AFc bulk materials (dash dot line) and AFc nanoparticles (solid line) dispersed in water.

group. Also peaks were observed at 1103 and 1005 cm^{-1}, which are characteristic of monosubstitution derivates of ferrocene.[32]

UV–vis absorption spectra

The UV–vis absorption spectra of the AFc solution in ethanol, and the AFc bulk materials and the AFc nanoparticles dispersed in water, are shown in Fig. 5. In absolute ethanol, AFc is molecularly dissolved. As shown in Fig. 5, there are two clearly resolved peaks at 337 and 457 nm which are assigned to the $\pi - \pi^*$ and $n - \pi^*$ transitions, respectively. The two peaks are observed to shift to the longer wavelength region at 343 and 462 nm, respectively, in the absorption spectrum of the AFc nanoparticles (Fig. 5). To explain the optical size-dependent property of organic nanoparticles, two reasons were considered by Kasai *et al.*[33] One is the change in 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 may be due to the polarizable environment of the surrounding AFc, which lowers the energy of the transition.[34] For comparison, the absorption spectrum of the AFc bulk materials, which has two resolved peaks at 344 and 466 nm, is also shown in Fig. 5. It was found that the absorption spectrum of the AFc nanoparticles is slightly blue-shifted compared with that of the AFc bulk materials, and the blue shift of optical absorption spectra is the result of quantum size effects.

Emission spectra

Figure 6 displays the fluorescence emission spectra of the AFc bulk materials and the AFc nanoparticles. The excitation wavelength was 423 nm. Two emission peaks at 560 and 639 nm were observed in the emission spectra of the AFc bulk materials [Fig. 6(a)]. Compared with that of the bulk materials, the fluorescence emission of the AFc nanoparticles has two peaks at 540 and 636 nm [Fig. 6(b)]. Furthermore, it can be seen that the nanoparticles emission is higher than the weak emission of the AFc bulk materials. A blue shift of the spectrum and an increase in the emission intensity were found. In recent years, a few cases of enhanced emission in the solid of specific organic molecules have been reported and interpreted in terms of the intra- and intermolecular effects exerted by fluorophore aggregation.[35–39] Intramolecular effects on fluorescence enhancement are simply explained by the conformational changes of chromophores. It is supposed that the twisted conformations of chromophores in solution tend to suppress the radiative process, whereas planar ones of chromophores induced in the solid state activate the radiation process.[40,41] Intermolecular effects in π-conjugated organic chromophores also influence the fluorescence changes, which are correlated with the aggregation structures such as H- and J-aggregates. In our case, this fluorescence enhancement property of the AFc nanoparticles differs from the intra- and

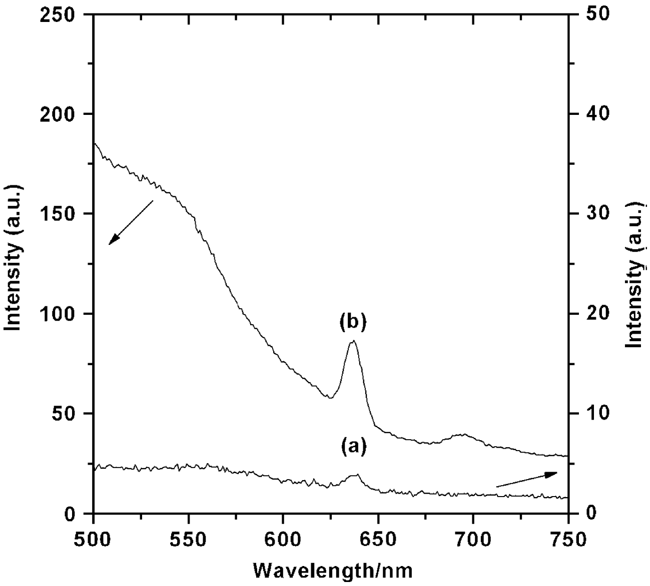

Figure 6. Fluorescence emission spectra of (a) AFc bulk materials and (b) AFc nanoparticles.

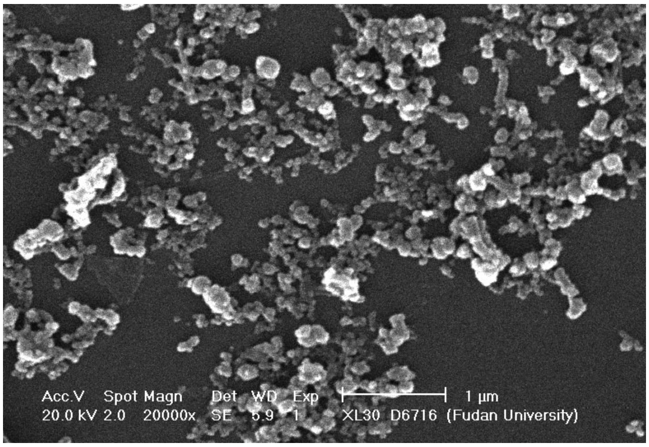

Figure 7. SEM image of the products prepared with stirring by adding dropwise 20 ml of water.

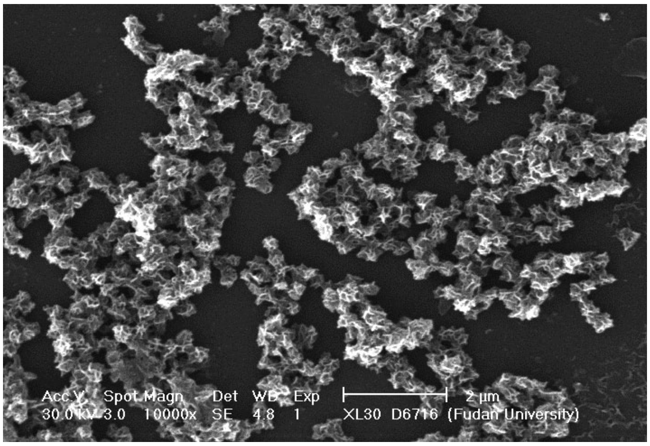

Figure 8. SEM image of AFc nanomaterials prepared under ultrasonic irradiation by adding dropwise 20 ml of water.

intermolecular effects because the intra- and intermolecular effects are observed in organic nanoparticles that are dispersed in water. The blue shift of the spectrum and the increase in emission intensity in our experiment seem to be related to the size of particles and are attributed to the quantum confinement effect.

Choice of the experimental conditions

Many experiments were carried out in order to determine the optimal experimental conditions for the preparation of AFc nanoparticles. The dropping rate of water was found to affect the morphology of the products. Figure 2 shows the TEM image of the AFc nanoparticles prepared at the dropping rate of 5 ml min^{-1} with stirring. However, when the dropping rate of water was more than 12 ml min^{-1} and other experimental conditions were fixed, the size of the products was larger and its morphology was irregular (not shown here). Furthermore, we also observed the effect of the quantity of water added on the products. Figure 7 displays the SEM image of the products prepared with stirring by adding dropwise 20 ml of water. Compared with Fig. 2, it can be seen that the shape and size of the products are different.

In addition, mechanical power also had considerable effects on the formation of the products. As shown in Fig. 8, the larch-fruit-like AFc nanomaterials were prepared under ultrasonic irradiation used in our group[42] by adding dropwise 20 ml of water. The average size was about 260 nm. It was found that the sizes and morphologies of the products were different under different mechanical power. In conclusion, the dropping rate of water, the quantity of water added and mechanical power can affect the sizes and morphologies of AFc nanomaterials. Therefore, in our experiments, the experimental conditions (see Experimental Section) were selected for acquiring large amounts of AFc nanoparticles.

Formation mechanism of the AFc nanoparticles

A possible formation mechanism of the AFc nanoparticles may be as follows. In our experiments, AFc was 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 at a certain rate with stirring, the ethanol is gradually dissolved into the water and the ethanol-rich environment of the AFc molecules is progressively replaced by the bulk water, then the concentration of AFc molecules in the mixing solution reaches supersaturation. After this process, the AFc molecules are surrounded with a complete water shell. In this case, the AFc molecules exposed in the poor solvent tends to aggregate together. This process leads to the formation of amorphous particles, having a range of sizes.[39] With increasing quantity of water, the particles with different sizes are tailored and etched by the poor solvent to control their shape and size. In addition, aggregation is energetically favorable, while the introduction of an interface is unfavorable, so there is a balance between the two processes.[40] According to Li *et al.*,[39] in general, for the reprecipitation system in which the organic molecule is poorly soluble in water, an equilibrium spherical shape will be formed to minimize the interfacial energies. Therefore, AFc nanoparticles with a diameter of about 70 nm were prepared.

Conclusions

In summary, a new type of acetylferrocene organometallic nanoparticles with the diameter of about 70 nm has been successfully prepared by a simple solvent-etching method and characterized by SEM, TEM, XRD, FT-IR, UV–visible absorption and fluorescence spectra. The redshift was found in the AFc nanoparticles compared with that in solution in UV–vis absorption spectra. The enhanced fluorescence emission and the blueshift in the AFc nanoparticles are attributed to the quantum confinement effect. This work provides a useful way to prepare the AFc nanoparticles and the nanoparticles may have potential applications as ultraviolet absorbent or in optoelectronic devices. We believe that this method could be developed further for the preparation of other organometallic nanoparticles.

Acknowledgments

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