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Blue shift of photoluminescence of Al_2O_3–morin nanocomposites

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Using $AlCl_3$ and ammonia as starting materials, Al_2O_3 nanoparticles were fabricated by the chemical precipitation method. Morin was chemically bound on the surface of Al_2O_3 nanoparticles by the ultrasonic method, and the Al_2O_3–morin fluorescent nanocomposite was obtained. Because of interaction between the morin molecules and the surface atoms of Al_2O_3 nanoparticles, a blue-shift of the photoluminescence was observed for the nanocomposites compared with that of morin.

Key words: *nanocomposite; ultrasonic method; morin; photoluminescence blue shift*

1. Introduction

Aluminum oxides are most commonly used as adsorbents, catalysts and catalyst supports [1]. At the same time, the preparation and properties of Al_2O_3 nanomaterials have been extensively investigated [2–5]. Nanocomposite materials have also been very thoroughly investigated, as they can be widely used in the field of luminescence [6, 7], sensors [8] and catalysts [9], etc. A large amount of dangling bonds and vacancies on the surface of nanoparticles makes it possible to prepare, by surface reaction, nanocomposite materials with excellent properties. For example, ZrO_2–morin nanocomposites were successfully fabricated by a simple heat refluxing method and a photoluminescence enhancement phenomenon was observed [10].

At the same time, morin, as a kind of O,O-donating chelating regent, is most frequently used as an analytical reagent, especially as a fluorescent reagent [11]. It is only weakly fluorescent by itself but forms highly fluorescent complexes with Al^{3+}, thus it is a very sensitive reagent for the fluorometric determination of aluminum: its sensitivity limit is of the order of several parts per billion [12, 13]. In addition, the Al_2O_3 composites [14–16] have also been widely investigated. To our best knowledge, there have been no reports on Al_2O_3 / morin nanocomposites till now.

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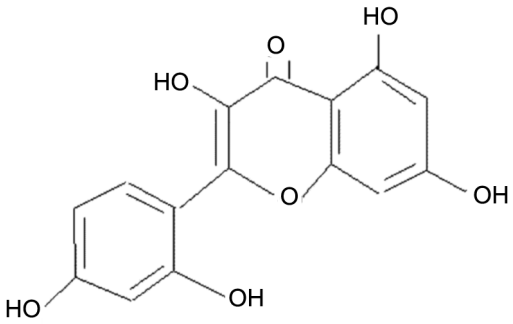
In this paper, Al_2O_3 nanoparticles were synthesized by the chemical precipitation method, using $AlCl_3$ and ammonia as starting materials. Furthermore, the nanoparticles were used as the precursors for synthesizing Al_2O_3–morin nanocomposite fluorescent materials by the ultrasonic irradiation method.

2. Experimental

Materials. The starting materials are $AlCl_3$ (A.R.), ammonia (25–28%, A.R.), deionized water, anhydrous ethanol and morin (Scheme 1). The material was purchased from E. Merck, Darmstadt.



Scheme 1. The structure of the morin molecule

Synthesis of Al_2O_3 nanoparticles. Under vigorous stirring, $AlCl_3$ solution (0.5 mol/dm^3) and ammonia were added slowly to a 500 cm^3 beaker with 100 cm^3 deionized water, and pH was fixed at 8. After continuous stirring for 1 h, a precipitate was obtained which was then filtered and washed with deionized water and five times with alcohol. The obtained powder was dried in an oven at 120 °C for 3 h. Finally, the product was heated at 1100 °C for 3 h, and white nanoparticle Al_2O_3 was obtained.

Synthesis of Al_2O_3–morin nanocomposites. Four aliquots of 2.0 g Al_2O_3 nanoparticles were firstly added to four beakers, and then mixed with 50 cm^3 morin alcohol solutions of various concentrations: 1×10^{-5}, 1×10^{-4}, 5×10^{-4} and 1×10^{-3} mol/dm^3. All samples were ultrasonically treated at 50 °C for 8 h. Thus obtained aqueous Al_2O_3 –morin nanocomposites were filtered for several times with alcohol to remove the excessive morin molecules. Finally, the nanocomposites were dried in an oven for 6 h at 50 °C

Characterization. The photoluminescence spectra of the samples were obtained with a WGY-10 fluorescent spectrometer. The morphology of the samples was tested using a JEM-100CX II transmission electron microscope (TEM) with an accelerating voltage of 150 kV. Fourier transform infrared spectroscopy (FTIR) measurements of the samples were collected on an Avata330 spectrometer with a spectral resolution of 4 cm^{-1}. The samples were mixed with KBr, for which the weight ratio of sample to

KBr was 1:100, and pressed into pellets for characterization. All measurements were carried out at room temperature.

3. Results and discussion

The TEM photograph of the synthesized Al_2O_3 nanoparticles is shown in Fig. 1. It was found that the size of the Al_2O_3 nanoparticles was distributed uniformly the average particle size being ca. 20 nm. The XRD pattern of the Al_2O_3 nanoparticles is shown in Fig. 2. All the sharp peaks in the figure can be assigned to Al_2O_3.

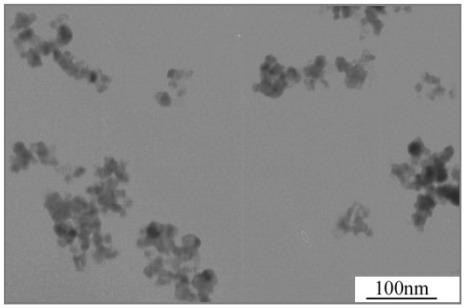


Fig. 1. TEM photograph of Al_2O_3 nanoparticles

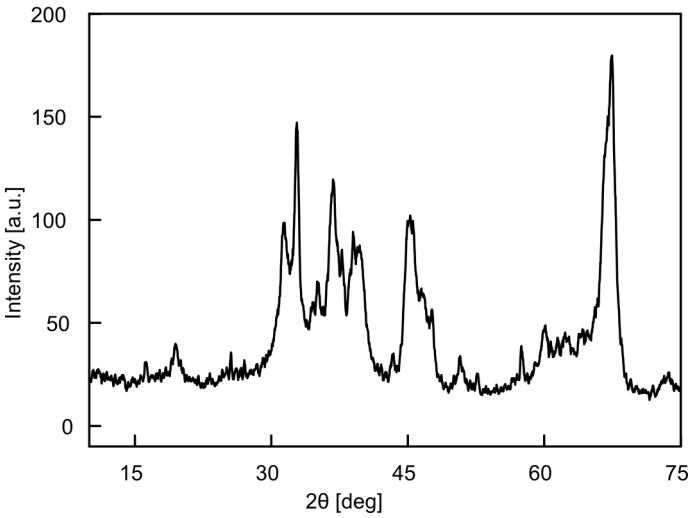


Fig. 2. XRD pattern of Al_2O_3 nanoparticles

Figure 3 shows the FTIR spectra of the nanocomposite, morin and Al_2O_3 nanoparticles in the range of 1680 cm^{-1} to 1160 cm^{-1}. In this figure, the major absorption peaks of Al_2O_3 nanoparticles are located at 1627 and 1398 cm^{-1} (curve a), while the peaks at 1652, 1509 and 1247 cm^{-1} in curve c can be attributed to the stretch vibration mode of C=O in the =C=O group, the vibration of C=C in benzene rings, and the

asymmetric stretching vibration of C–O–C, respectively. The peaks at 1204 and 1174 cm^{-1} have been assigned to the stretching vibration of C–O in 1, 2, 3, 4, 5 ≡C–OH group. The other peaks at 1607, 1573, 1469, 1450 cm^{-1} originate from the vibration of the C=C bond in benzene rings, and those at 1353, 1328 and 1309 cm^{-1} are attributed to the vibration of OH groups [17]. It can seen that the peaks at 1353 cm^{-1} (O–H), 1247 cm^{-1} (C–O–C) and 1174 cm^{-1} (C–O in 1, 2, 3, 4, 5 ≡C–OH group), which originate from the absorption of morin, shift to 1367, 1238 and 1183 cm^{-1}, respectively, in the nanocomposites. This result indicates that complex bonds may form between Al atom of Al_2O_3 nanoparticles and the O atom of ≡C–OH and –C–O–C– groups [18, 19], thus the corresponding FTIR absorption peaks change.

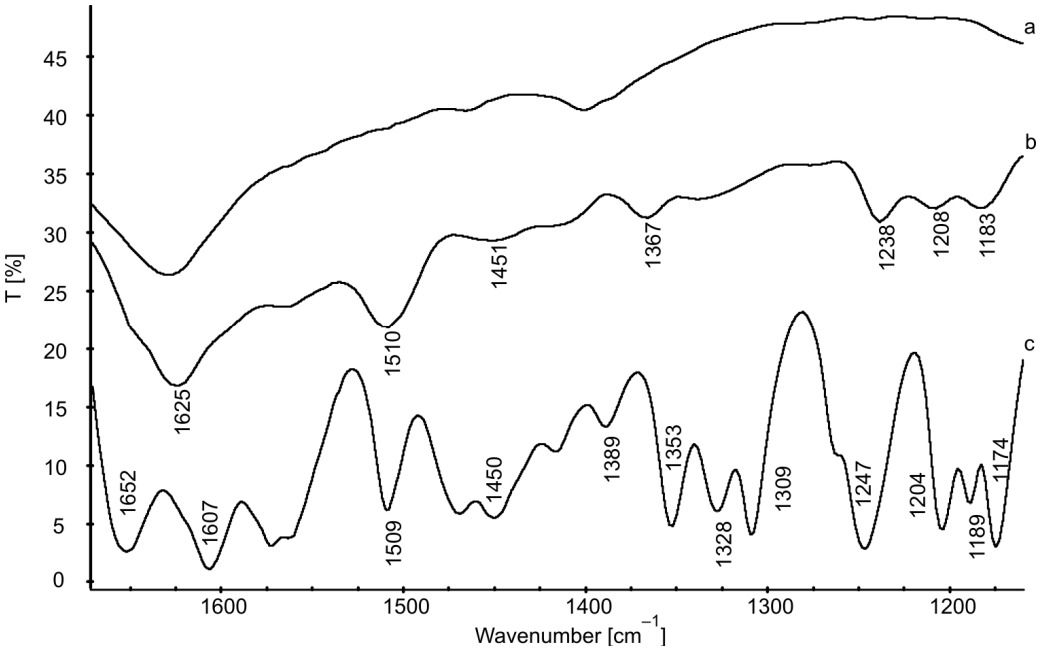


Fig. 3. FTIR spectra of samples: a) Al_2O_3 nanoparticle, b) the nanocomposite and c) morin

Figures 4 and 5 show the photoluminescence (PL) spectra of morin solution and the nanocomposites under the excitation of 430 nm. From Figure 5, it is clear that as the morin concentration increases, the PL intensity increases at first and subsequently decreases. At the same time, the peak positions show a red shift from 516 to 524 nm. At low concentrations, morin molecules can be sufficiently dispersed on the surface of Al_2O_3 nanoparticles. With the increase in the morin concentration, more and more morin molecules contribute to the PL intensity. On the other hand, if too many morin molecules are adsorbed on the surface of Al_2O_3 nanoparticles, they will combine with each other, and dimers or aggregates will be formed. As a result, the energy band gap of the molecules decreases and the interaction between electrons and phonons in-

creases [20], and this phenomenon directly causes a red shift of the peak wavelength and the decrease in the PL intensity.

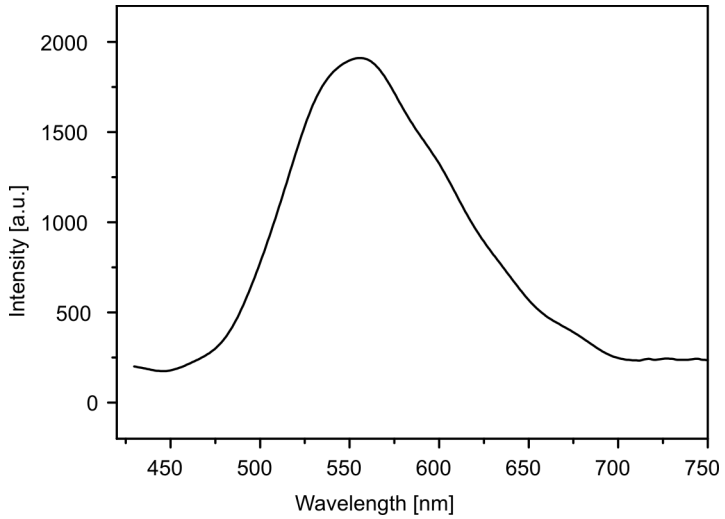


Fig. 4. Photoluminescence spectrum of morin solution (1.0×10^{-3} mol/dm^3)

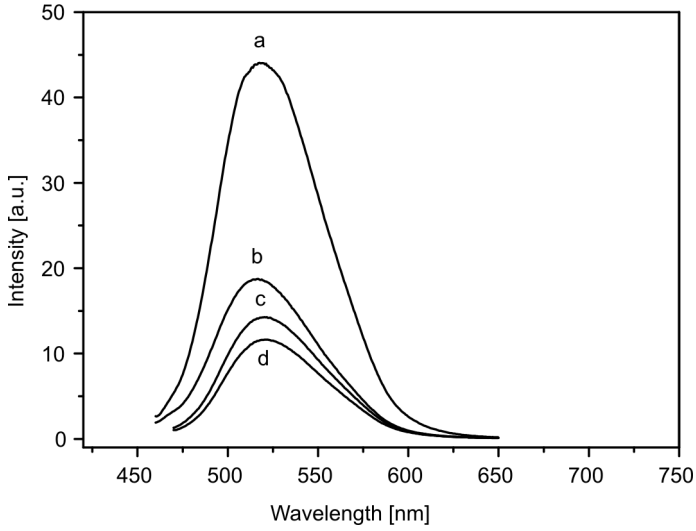


Fig. 5. Photoluminescence spectra of Al_2O_3–morin nanocomposites:
a)1.0×10^{-4} mol/dm^3, b) 1.0×10^{-5} mol/dm^3, c) 5.0×10^{-4} mol/dm^3 and d) 1.0×10^{-3} mol/dm^3

In addition, by comparing Figs. 4 and 5 it is visible that the peak of the naocomposite at 516 nm shows a blue shift of 40 nm with respect to that (556 nm) of morin particles. It is well known that the luminescence of a dye depends strongly on its concentration in solution. The PL intensity becomes weaker when the molecules become too concentrated. In other words, the more the dye molecules are dispersed, the more effi-

cient the luminescence. From the above results, it is known that the morin molecules are adsorbed on the surface of Al_2O_3 nanoparticles, thus the interaction between the morin molecules decreases and a good dispersion of dye molecules is obtained. As a result, a blue shift of the peak wavelength of the nanocomposites is observed [20].

4. Conclusions

Al_2O_3 nanoparticles were synthesized by a chemical precipitation method, using $AlCl_3$ and ammonia as starting materials. Using the synthesized Al_2O_3 nanoparticles as the precursor, Al_2O_3–morin nanocomposite fluorescent materials were synthesized by the ultrasonic method. A blue shift of 40 nm of the PL peak was observed in the nanocomposites with respect to that of morin.

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