Facile Synthesis and Luminescence Properties of Silica Submicron Rods

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Abstract. Silica submicron rods were conveniently synthesized through a simple sol-gel method at room temperature. The SEM images demonstrated that the obtained silica submicron rods had high purity and uniform diameter of about 380-400 nm. The XRD results showed the obtained silica submicron rods were amorphous. Furthermore, the silica submicron rods exhibited blue emission under UV light excitation, which is relevant to the surface-associated defects.

Introduction

Amorphous silica as an important optical candidate material has been investigated for a long time, due to its unique physical and chemical stability and efficient photoluminescence emission [1]. Especially one dimensional silica materials, such as tubes [2], rods [3], wires [4], and fibers [5] have attracted a lot of attentions during the past decades because of their potential wide-ranging applications, for example drug delivery [6], catalysis [7], controlled release [8] and biological filed [9]. Among these materials, the silica rods are easily incorporated with a lot of nanomaterials because of the large surface area and the high biocompatibility, which makes them exhibit particular properties suitable for drug and gene delivery and so on [10]. So it is of interest to synthesis silica rods using simple method and instruments. Recently many people have devoted numerous efforts to prepare silica materials of sizes from nanometers to micrometers and different methods have been used, such as thermal evaporation method [11], hydrothermal method [12], anodized aluminum oxide(AAO) method [13] and sol-gel method [14]. Thermal evaporation method and hydrothermal method require high temperature, high pressure and expensive equipment. The AAO method needs to use a uniform diameter AAO membrane as template, and it is very difficult to control the diameter and length of the products via this method. Above all, sol-gel method has been an attractive method as for it can avoid these problems and can be achieved easily [10].

In contrast to traditional fluorescent materials in biological field such as organic dyes and quantum dots, the novel defect-related luminescent materials such as silica materials may be the promising fluorescent materials due to their good optical properties, high chemical stability and low toxicity. The photoluminescence properties of such silica rods may be of great interest for fundamental research and semiconductor full-color displays. It is significant to synthesis silica materials to explore the further applications. Based on these, we conveniently synthesized silica rods via the sol-gel process and the photoluminescence properties were investigated in detail by emission spectra in this study.

Experiment

Materials

Sodium citrate, polyvinylpyrrolidone (PVP), 1-pentanol, absolute ethanol and ammonia (28% aqueous solution) were bought from Beijing Chemical Reagents Co. TEOS (99 %) was purchased

from Internet Aladdin Reagent Database Inc. All materials were analytical grade reagents and used directly without further purification.

Preparation

2 g of polyvinylpyrrolidone (PVP) was dissolved in 20 ml of 1-pentanol. When all PVP had been dissolved, 2 ml of absolute ethanol, 0.56 ml of ultrapure water and 0.5 ml of 0.18 M sodium citrate solution was added to the mixture. Subsequently, 0.45 ml of ammonia and 0.2 ml of tetraethyl orthosilicate (TEOS) were added to the mixture under magnetic stirring. After standing in air overnight, the obtained precipitate was centrifuged and washed with distilled water and ethanol for several times, and then the products were dried in the oven at 80 ℃. Finally the dried products were calcined at 700 ℃ for 2 h at a heating rate of 2 ℃ /min.

Characterization

X-ray powder diffraction measurements were carried out on a Rigaku D/max-B II X-ray diffractometer with Cu Ka radiation. The field emission scanning electron microscope (FESEM) images were observed by S-4800, Hitachi. The PL measurements were determined using Jobin Yvon FluoroMax-4 luminescence spectrophotometer equipped with a 150 W xenon lamp as the excitation source. All the measurements were performed at room temperature.

Result and Discussion

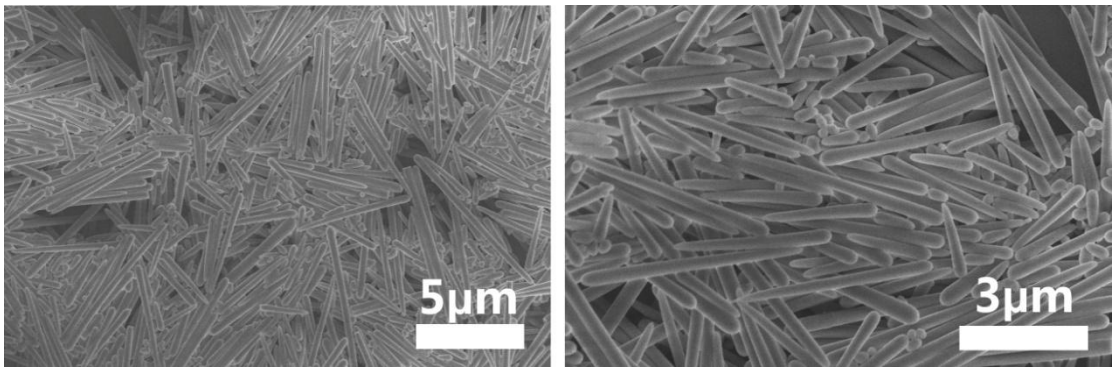

Fig.1 SEM images of silica submicron rods

SEM images clearly showed the morphology and the dimension distribution of silica submicron rods. As seen from Fig.1, the obtained silica submicron rods have a good dispersion and a high yield. The high-magnification SEM image showed that the submicron rods have uniform diameters of 380-400 nm and were remarkably clean and smooth.

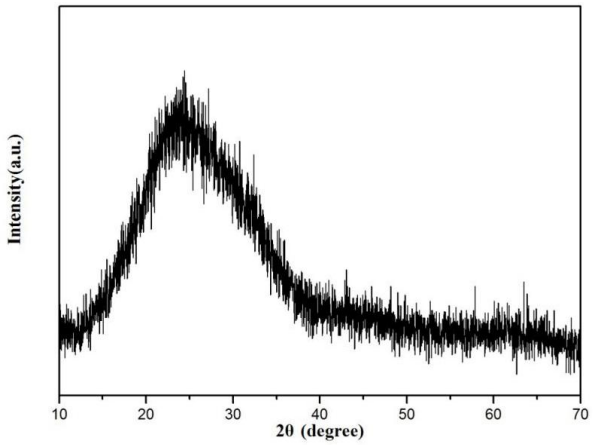

Fig.2 The XRD patterns of silica submicron rods

The XRD pattern of silica submicron rods was shown in Fig.2. Not sharp but weak and broad crystal diffraction peaks at $2\theta = 22°\sim23°$ were observed, which could be assigned to the characteristic diffraction of the amorphous silica [15]. This means that the obtained silica submicron rods were amorphous.

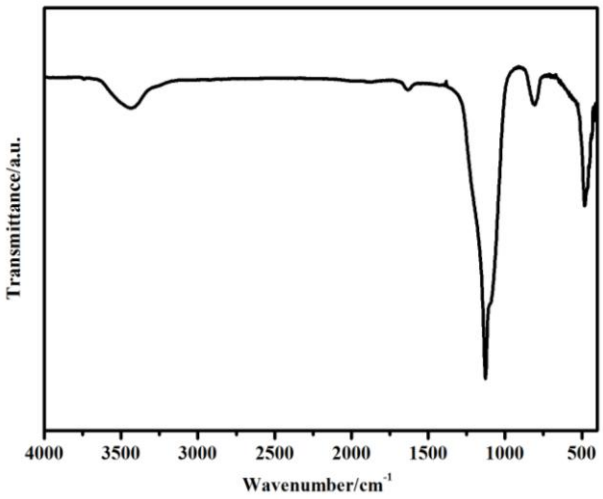

Fig.3 FT-IR spectra of silica submicron rods

The FT-IR spectra of silica submicron rods was shown in Fig.3. The sharp peak at 1132 cm^{-1} could be assigned to the characteristic absorption of Si-O-Si. The peaks at 801 cm^{-1} and 470 cm^{-1} were the bending and rocking vibration of Si–O. The weak peak at 3437cm^{-1} was due to the –OH asymmetric streching of the absorbed water. All the results above were proved that the obtained silica submicron rods were pure because no other obvious peak was observed.

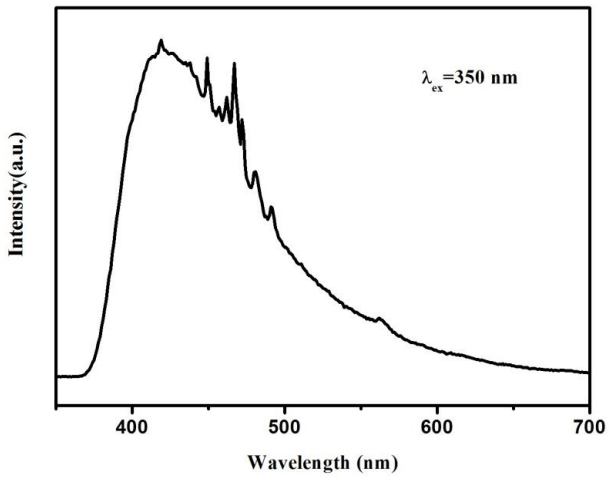

Fig.4 Emission spectra of silica submicron rods

The photoluminescence spectra of silica submicron rods were shown in Fig.4. It was seen that there was a wide emission peak at 419nm under the excitation light of 350 nm, which located in the blue wavelengths of visible light. Several kinds of surface defects, such as nonbridging oxygen hole centers, ≡Si-O• in silica matrix, oxygen-deficient center and self-trapped excitons [16, 17] are responsible for this luminescence band. Uchino and co-workers have proposed a defect pair model that co-condensed by dioxasilirane(=Si(O_2)) and silylene(=Si:)) and a density functional theory. This theory has shown that the photoluminescence excitation wavelength of this defect pair is in the range of 240-364nm, which is in agreement with the photoluminescence excitation wavelength of silica gel at 350nm. Based on this we measure the photoluminescence emission wavelength of silica submicron rods and from Fig.3 we can easily see that the silica submicron rods exhibited blue light

[18], which is in agreement with the result of the literature. And we can conclude that the blue emission of the obtained silica submicron rods is caused by the surface-associated defects.

Summary

In conclusion, silica submicron rods were successfully synthesized through the simple sol-gel method at room temperature. The obtained silica submicron rods had high purity and uniform diameter of about 380-400 nm. The XRD results showed the obtained silica submicron rods were amorphous. Furthermore, the photoluminescence of silica submicron rods was blue and it is relevant to the surface-associated defects. The uniform size and luminescent property of the silica submicron rods are expected to broaden the potential applications in phosphor for lighting, displays, sensing, and biomedical engineering.

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