Original Article

Fabrication, Characterization of SiO₂ Nanospheres and SiO₂ Opal Photonic Crystals

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Abstract: In this report, we presented the usage of Stober method to fabricate SiO₂ nanospheres and self-assembly method to make SiO₂ opal photonic crystals based on the fabricated SiO₂ nanospheres. An averaged size of SiO₂ nanospheres was controlled by varying concentrations of NH₄OH and TEOS. Crystal structure and morphology of particles was investigated by using X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. Experimental results showed that SiO₂ nanospheres possess amorphous crystal structure with sizes ranged from 150 to 300 nm. The diffuse reflection spectra show the reflection peaks of the SiO₂ opal photonic crystals from 410 nm to 520 nm.

Keywords: SiO₂ nanospheres; opal photonic crystals, diffuse reflection spectra.

1. Introduction

SiO₂ nanospheres and SiO₂ opal photonic crystals have attracted considerable attention due to their potential applications, such as catalyst materials, electronics, pharmaceuticals and analysis techniques. SiO₂ nanoparticles have been shown to have low specific weight, high heat resistance, high mechanical strength and chemical inertness those led to a wide range of applications such as fluorescence enhancement [1,2], photocatalytic enhancement [3,4], photovoltaic enhancement [5], Raman scattering enhancement [6,7], absorption enhancement [1-7]. In particular, when the SiO₂ nanospheres were arranged orderly and periodically (formed as SiO₂ opal photonic crystals), interesting and superior
properties were exhibited. So SiO$_2$ opal photonic crystals have been used as fluorescence enhancers substrates for materials showing enhanced properties those depended on different directions of excitation wavelength [8,9]. In another way, the SiO$_2$ opal photonic crystals have the role of dispersing metal particles on the surface, avoiding agglomeration, thereby increasing the efficiency of the Raman sensor based on the plasmon resonance effect [10]. Experimentally, the SiO$_2$ nanospheres were usually synthesized by using Stober method in different hydrolysis environments [11]. The SiO$_2$ opal photonic crystals were fabricated by using the self-assembly method from SiO$_2$ nanospheres - an inexpensive and easy method towards large scale structures.

In this report, the experimental procedure was performed as two following steps: (i) SiO$_2$ nanospheres were fabricated in the hydrolysis environment - a mixture of alcohol and water - by using the Stober method; (ii) SiO$_2$ opal photonic crystals were made from SiO$_2$ nanospheres by using the self-assembly method. Our research focused on the effect of NH$_4$OH and TEOS concentrations on size of SiO$_2$ nanospheres, and effect of size of SiO$_2$ nanospheres on the diffuse reflection spectra of the SiO$_2$ opal photonic crystals.

2. Experiments

All the precursors with high purity were provided from commercialized distributors: Tetraethyl-orthosilicate (C$_8$H$_2$O$_4$Si – TEOS 99%), Ethanol (C$_2$H$_5$OH 99,7%) Ammonium hydroxide (NH$_4$OH 25%) and distilled water. Synthesis of SiO$_2$ nanospheres by using the Stober method was carried out as follows: 85 ml of Ethanol was firstly dissolved into 15 ml of distilled water under magnetic stirring, 2-5 ml of TEOS solution and 7.5 ml of NH$_4$OH solution were then added drop by drop into the mixture, respectively. The mixture was stirred at a temperature of 30°C for 4 h. The resultant white precipitates (SiO$_2$) were purified using centrifuge and redispersed in 10 ml of ethanol. Fabrication of SiO$_2$ opal photonic crystals was carried out as followings: 10 ml of a solution containing the SiO$_2$ nanospheres was poured into a Teflon flask (d = 1.5 cm). Then, materials were evaporated at a temperature of 35°C by hot plate. In this evaporation process, the SiO$_2$ nanospheres were converted into SiO$_2$ opal photonic crystals.

Crystal structure of the synthesized products was analyzed by X-ray diffraction (XRD) using an X-ray diffractometer Siemens D5005, Bruker, Germany, with Cu-K$_\alpha$ ($\lambda = 1.54056$ Å) source. Surface morphology of the samples was observed by using a field emission scanning electron microscope (FE-SEM) Nova NANO-SEM-450, FEI. The composition of the samples was determined by an energy-dispersive X-ray spectrometer (EDS) Oxford ISIS 300 attached to a JEOL-JSM5410 LV scanning electron microscope. Diffuse reflection spectroscopy measurements were carried out on a VARIAN UV-VIS-NIR Cary 5000 spectrophotometer, the spectra were recorded at room temperature in the wavelength region of 200-900 nm.

3. Results and Discussion

3.1. Crystal Structure and Surface Morphology

Figure 1(a) presents XRD pattern of SiO$_2$ nanospheres. The results shows that the sample has an amorphous structure with the characteristic diffraction peak of SiO$_2$ is located in the 20 range of 20°-30°, the EDS spectrum given in Figure 1(b) reveals the fact that the product contains only Si and O elements. Figure 1(c) exhibits a SEM image of SiO$_2$ nanospheres. The SiO$_2$ nanospheres were observed to be uniform and the average size was estimated to be about 200 nm. Finally, Figure 1(c) exhibits a SEM image of SiO$_2$ opal photonic crystals those were self-arranged from SiO$_2$ nanospheres. The average
size is then found to be remain ~200 nm. In principle, observations of the triangular arrangement could attribute to either a (111) surface of a fcc system or a (001) surface of a hexagonal close packed hcp.

![Figure 1](image1)

**Figure 1.** X-ray diffraction spectrum (a) and energy-dispersive spectrometer (b) of SiO$_2$ nanospheres. SEM images of SiO$_2$ nanospheres (c), top view SEM images of SiO$_2$ opal photonic crystals (d).

3.2. Effect of TEOS Concentration on the Average Size of SiO$_2$ Nanospheres

![Figure 2](image2)

**Figure 2.** (up row) SEM images, and (down row) corresponding historic diagrams of SiO$_2$ nanosphere distributions with various TEOS concentrations.

The effects of TEOS concentrations on the average size of SiO$_2$ particles size were reported in previous researches. Stöber et al. [11] found that TEOS concentration had negligible effect on the final particle size, while Helden et al. [12] reported that high TEOS concentrations tended to produce larger SiO$_2$ particles. The SEM image and size distribution of the SiO$_2$ nanospheres prepared under the conditions of 85 ml C$_2$H$_5$OH: 15 ml H$_2$O: 7.5 ml NH$_4$OH with TEOS concentrations varied from 2.5 to
5 ml are presented in Figure 2. Our results show that when the TEOS concentration increases, the average size of the SiO$_2$ nanospheres increases as well. The average size of the SiO$_2$ nanospheres is observed to be ~ 170 nm, 230 nm, 290 nm corresponding to the TEOS concentrations of 2, 3 and 5 ml, respectively. The possible origin of these observations might be attributed to the reaction rate, in which the faster hydrolysis and condensation were achieved when the TEOS concentration increased. Thus, the total number of formed nuclei would be decreased and the resultant spheres will also be enlarged.

3.2. Effect of NH$_4$OH Concentration on SiO$_2$ Nanospheres Size

![Figure 3. SEM image of samples with different NH$_4$OH concentrations](image)

Figure 3 is SEM image of the samples prepared under the conditions of 85 ml C$_2$H$_5$OH: 15 ml H$_2$O: 2 ml TEOS with different NH$_4$OH concentrations. The results in Figure 3 show that a decrease in the size of SiO$_2$ nanospheres from about 300 nm to 180 nm when increasing ammonia concentration in the range 2.5 - 7.5 ml, respectively. The similar result has been observed in previous reports [13] This phenomenon can be explained as follows when NH$_4$OH low concentration lead to high water concentration, a high nucleation rate occurs and a lot of sub-particles are produced during a short period. But the hydrogen bond of SiO$_2$ sub-particles is stronger at higher water concentration compared to lower water concentration, because of excess water. As a result, the agglomeration causes the formation of large particles

3.4. Optical Properties

In order to optically characterize these structures, the reflection spectrum measurements were performed. In Figure 4 is the reflection spectrum of the four different opal samples made of spheres with different size from 200 to 270 nm. We found that with sample of 200 nm particle diameter, the reflecting peak is at 408 nm. As the size particles increases, the reflecting peaks tend to increase. Given the 270 nm size sample, the reflecting peak is at 522 nm, This properties can be explained as follows: As shown by the SEM image, opal structure consist of equally sized SiO$_2$ spheres arranged in periodic order, thus can be considered as a crystal lattice and can apply Bragg diffraction formula to calculate [14]
\[ \lambda_{\text{max}} = 2 \ast \left(\frac{2}{3}\right)^{1/2} \ast a(n_a^2 - \sin^2 \phi)^{1/2} \]  \[1\]

Where \( a \) is the lattice constant (the closest distance between two particles in the (111) plane), corresponding to the diameter of the \( \text{SiO}_2 \) spheres, \( \lambda_{\text{max}} \) is the maximum reflected wavelength. Formula [1] shows that if \( \phi \) and \( n_a \) is constant, then changes when \( \lambda_{\text{max}} \) the size of \( \text{SiO}_2 \) spheres change. It notice that \( \lambda_{\text{max}} \) depends on \( a \) and \( \phi \), if \( a \) is constant, by changing \( \phi \) we obtain different \( \lambda_{\text{max}} \), so \( \text{SiO}_2 \) opal can be used as wavelength rejection optical filters. The rejected wavelength can be tuned by using particles with different sizes or by changing the angle \( \phi \) between the incident light and the normal to the surface of the filter. The results of Figure 4 give us the prediction that, if we apply \( \text{SiO}_2 \) Opal substrates as SERS substrates, the laser wavelength and the absorption wavelength of the metal nanoparticles on SERS substrate should be different with reflected region of \( \text{SiO}_2 \) Opal substrates.

![Figure 4. Reflection spectrum of \( \text{SiO}_2 \) Opal substrates with \( \text{SiO}_2 \) particle size change.](image)

4. Conclusion

The \( \text{SiO}_2 \) nanospheres with fairly uniform have been successfully synthesized by Stober method. Effect of \( \text{NH}_4\text{OH} \) and TEOS concentration on particle size and morphology of \( \text{SiO}_2 \) nanoparticles were systematically investigated. Results show that, to some extent, the \( \text{SiO}_2 \) particle size increased with the increase of TEOS concentration and they decreased with the increase of \( \text{NH}_4\text{OH} \) concentration, that may allow us to control the particle size of the \( \text{SiO}_2 \) nanoparticles over a wide range of various reaction conditions. \( \text{SiO}_2 \) opal crystals have also been successfully synthesized by self-assembly method from the suspension of spherical particles of \( \text{SiO}_2 \). The reflected spectrum of \( \text{SiO}_2 \) opal crystals shows characteristic reflection peaks depending on the size of the spheres. \( \text{SiO}_2 \) opal substrates can be used to enhance optical signal for sensor.

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