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Original Article

Fabrication, Characterization of SiO_2 Nanospheres and SiO_2 Opal Photonic Crystals

Nguyen Duy Thien[1,*], Nguyen Ngoc Tu[2], Nguyen Quang Hoa[1], Sai Cong Doanh[1] and Le Van Vu[1]

[1]*VNU University of Science, 334 Nguyen Trai, Thanh Xuan, Hanoi, Viet Nam*

[2]*Sao Do University, 24 Thai Hoc, Sao Do, Chi Linh, Hai Duong*

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Abstract: In this report, we presented the usage of Stober method to fabricate SiO_2 nanospheres and self-assembly method to make SiO_2 opal photonic crystals based on the fabricated SiO_2 nanospheres. An averaged size of SiO_2 nanospheres was controlled by varying concentrations of NH_4OH 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 SiO_2 nanospheres possess amorphous crystal structure with sizes ranged from 150 to 300 nm. The diffuse reflection spectra show the reflection peaks of the SiO_2 opal photonic crystals from 410 nm to 520 nm.

Keywords: SiO_2 nanospheres; opal photonic crystals, diffuse reflection spectra.

1. Introduction

SiO_2 nanospheres and SiO_2 opal photonic crystals have attracted considerable attention due to their potential applications, such as catalyst materials, electronics, pharmaceuticals and analysis techniques. SiO_2 nanoparticles have been shown to have low specific weight, hight heat resistance, hight 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 SiO_2 nanospheres were arranged orderly and periodically (formed as SiO_2 opal photonic crystals), interesting and superior

*Corresponding author.
Email address: thiennd@hus.edu.vn

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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 - aninexpensive 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_4OH 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 ($C_8H_{20}O_4Si$ – TEOS 99%), Ethanol (C_2H_5OH 99,7%) Ammoniumhydroxit (NH_4OH 25%) and distilled water. Synthesis of SiO_2 nanospheres by using the Stober method was carried out as followings: 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_4OH 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-Kα (λ = 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 2θ 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.

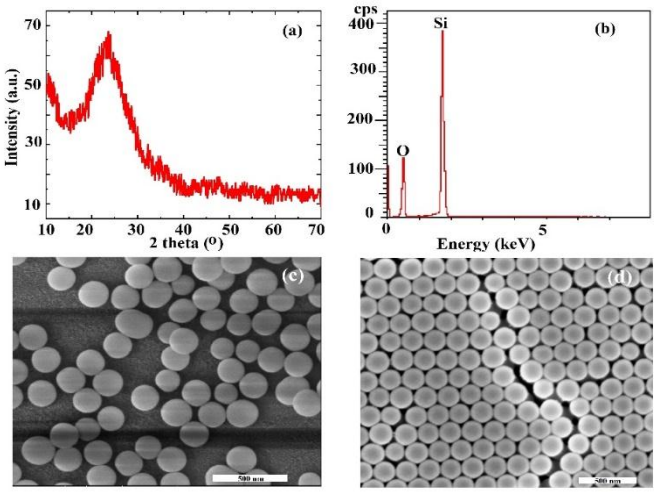

Figure 1. X-ray diffraction spectrum (a) and energy-dispersive spectrometer (b) of SiO_2 nanospheres SEM images of SiO_2 nanospheres (c), top view SEM images of SiO_2 opal photonic crystals (d)

3.2. Effect of TEOS Concentration on the Average size of SiO_2 Nanospheres

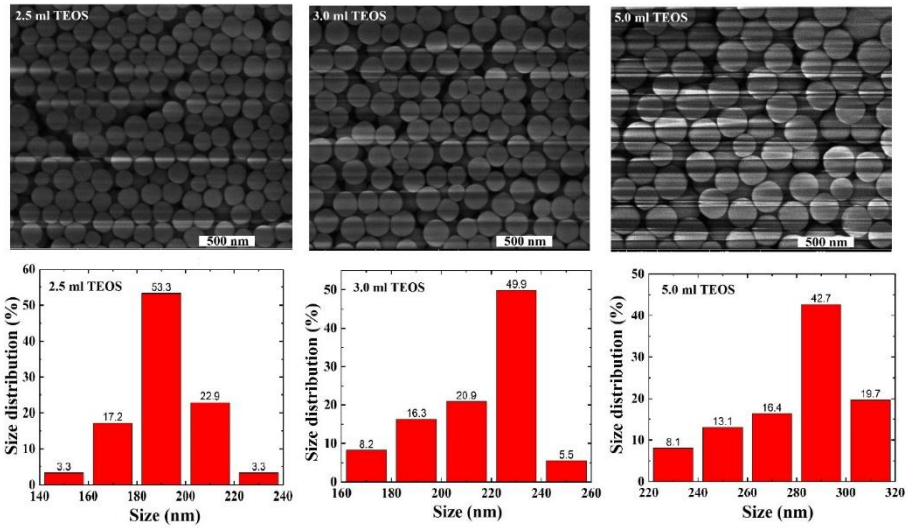

Figure 2. (up row) SEM images, and (down row) corresponding historic diagrams of SiO_2 nanosphere distributions with various TEOS concentrations.

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 distributionof the SiO_2 nanospheres prepared under the conditions of 85 ml C_2H_5OH: 15 ml H_2O: 7.5 ml NH_4OH 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 sizeof the SiO_2 nanospheres increases as well. The average size of the SiO_2 nanospheres is observed to be ~ 170 nm, 230 nm, 290nm 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_4OH Concentration on SiO_2 Nanospheres Size

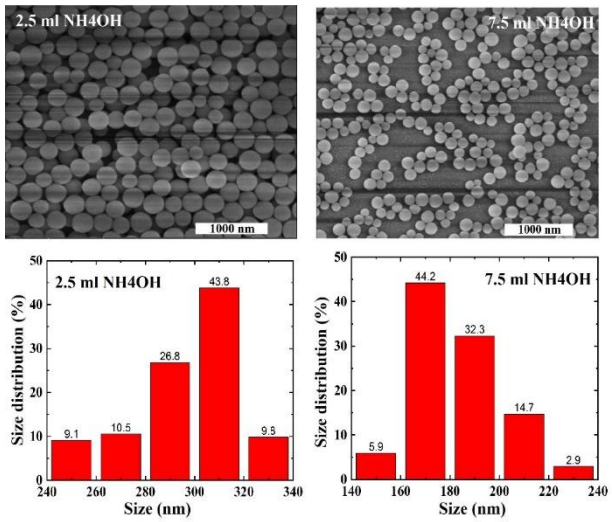

Figure 3. SEM image of samples with different NH_4OH concentrations

Figure 3 is SEM image of the samples prepared under the conditions of 85 ml C_2H_5OH: 15 ml H_2O: 2 ml TEOS with different NH_4OH 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_4OH 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]

$$\lambda_{max} = 2^* \left(\frac{2}{3}\right)^{1/2} {}^*a(n_a{}^2 - \sin^2 \phi)^{1/2} \qquad [1]$$

Where a is the lattice constant (the closest distance between two particles in the (111) plane), corresponding to the diameter of the SiO_2 spheres, λ_{max} is the maximum reflected wavelength. Formula [1] shows that if ϕ and n_a is constant, then changes when λ_{max} the size of SiO_2 spheres change. It notice that λ_{max} depends on a and ϕ, if a is constant, by changing ϕ we obtain different λ_{max}, so 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 ϕ 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 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 SiO_2 Opal substrates

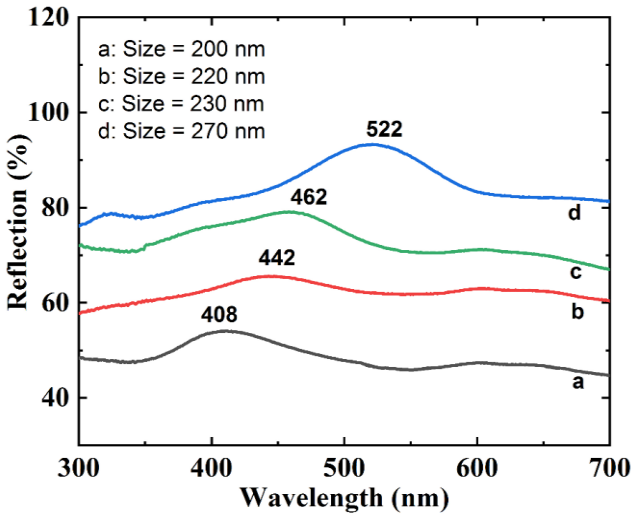

Figure 4. Reflection spectrum of SiO_2 Opal substrates with SiO_2 particle size change.

4. Conclusion

The SiO_2 nanospheres with fairly uniform have been successfully synthesized by Stober method. Effect of NH_4OH and TEOS concentration on particle size and morphology of SiO_2 nanoparticles were systematically investigated. Results show that, to some extent, the SiO_2 particle size increased with the increase of TEOS concentration and they decreased with the increase of NH_4OH concentration, that may allow us to control the particle size of the SiO_2 nanoparticles over a wide range of various reaction conditions. SiO_2 opal crystals have also been successfully synthesized by self-assembly method from the suspension of spherical particles of SiO_2. The reflected spectrum of SiO_2 opal crystals shows characteristic reflection peaks depending on the size of the spheres. SiO_2 opal substrates can be used to enhance optical signal for sensor

Acknowledgments

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