SYNTHESIS AND CHARACTERIZATION OF COMMON OPAL

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Abstract: In this work, synthesis of common opal by sol-gel method under acid catalyzed condition was presented. The main objective of this article is to study effect of tetraethyl orthosilicate (TEOS) concentration, precursor molecule for opal synthesis. The process preparation of the synthetic opal includes; mixing different concentrations of TEOS with ethanol, nitric acid and distilled water to form the clear sol and gel. After drying and heating the gel, synthetic common opal was obtained. Scanning Electron Microscope (SEM) and Fourier transform infrared (FTIR) spectroscopy were performed for determining microstructure and chemical composition of the opal, respectively. Experimental results indicate that the size and packing of silica sphere increase with increasing TEOS concentration and infrared spectra of our synthetic common opals were similar with natural common opal.

Introduction: Natural opal is a gemstone made of hydrated amorphous silica which can be classified as precious opal, common opal and fire opal depending on their visual appearances. Precious opal exhibit a play-of-color, phenomenon of changing spectral hues produced by the diffraction of white light through a microstructure of orderly arrayed silica sphere. Common opal is mostly opaque and do not exhibit the play-of-color while fire opals are transparent or translucent opal with a yellow to red body color. Opal is a valuable gemstone for use in jewelry on the world market. To meet the rising demand for opal, synthetic opals were produced in laboratory conditions. However, the synthesis of opal is very complicated. In the last few years, there have been a number of articles published on the formation and properties of synthetic precious opal which most cases were performed based in a method originated by Stober *et al*.[1,2] Stober *et al.* developed the controlled growth of spherical silica particle by means of hydrolysis of alkyl silicates and subsequent condensation of silicic acid in alcoholic solutions.[3] By Stober's method, precious opal was successful synthesized by using tetraethyl orthosilicate (TEOS) as precursor material, ethanol as solvent, and ammonia as catalyst.[1,2] In this article, we present a preliminary study of the sol-gel method for synthesis of common opal. The article emphasized on study effect of TEOS concentration. The comparison between microstructure of the natural and our synthetic common opals were observed by using Scanning Electron Microscope (SEM) and those of chemical structures were studied by Infrared spectroscopy.

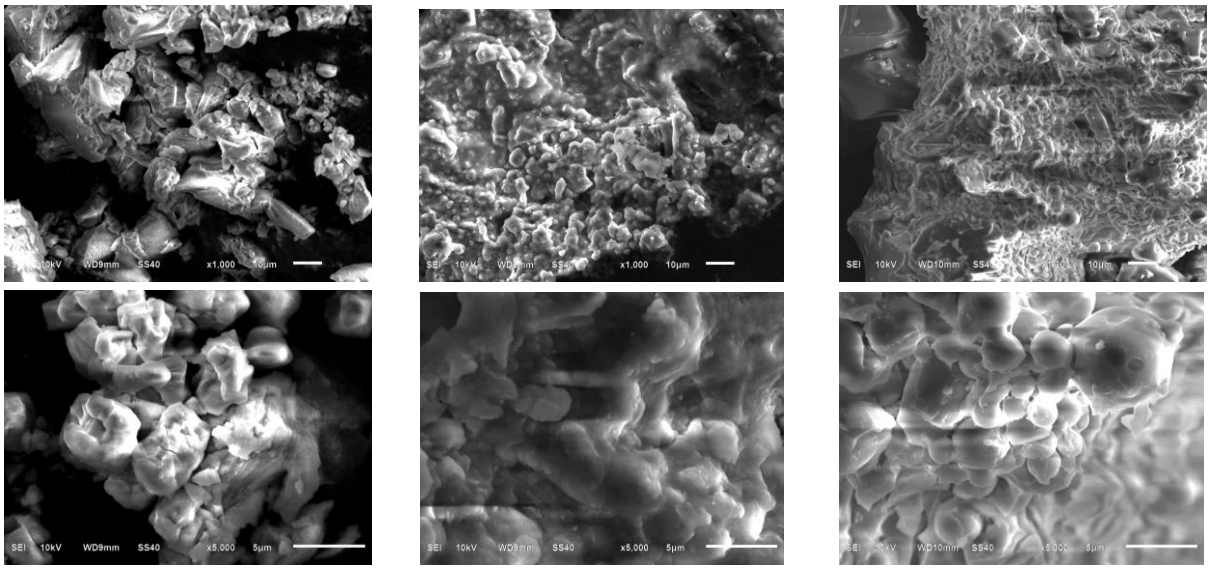
Methodology: The materials required for the synthesis of common opal are tetraethyl orthosilicate (TEOS 98%), concentrated nitric acid, and absolute ethanol 99%. The TEOS's concentrations were varied for 0.1, 0.4 and 0.6 M at ratio of ethanol : nitric acid constant. For synthesis, solution containing appropriate quantities of absolute ethanol, nitric acid and deionized water were mixed and stirred for 4 hour to obtain a homogeneous reaction mixture. Thereafter, TEOS is carefully added to homogeneous mixture to obtain a clear sol. The sol was stored at room temperature to obtain a wet gel. The gel is dried at 100^{o}C to obtain a transparent material and then heat treated at 800^{o}C to improve its hardness. After thermal treatment, the microstructures of the opals were observed by using JEOL JSM-6510A

Scanning Electron Microscope. The infrared spectra measurements were performed by KBr pellet method, using Thermo scientific NICOLET iN10 MX FTIR infrared microscope. Spectra were recorded in the mid infrared region with 64 scans at a resolution of 4 cm^{-1}. The spectra of unheated and heat treated opal (at 800^{o}C) were monitored for determining their spectral change.

Results, Discussion and Conclusion: The SEM images of our synthetic common opal prepared with an embodiment of this article are shown in Figure 1. The figure shows that the silica particles were aggregated and their particle size increases with TEOS concentration ranging from 0.1 to 0.6 M while nitric concentration and alcohol solvent were fixed. When TEOS concentration is increased; both the rate of hydrolysis and condensation become faster.[4-5] This is because the ethoxy group of TEOS reacts with the water molecule to form intermediate $[Si(OC_2H_5)_{4-x}(OH)_x]$ with hydroxyl group substituting ethoxy group during the hydrolysis reaction. The chemical reaction is expressed as follows[1,6]:

$$Si(OC_2H_5)_4 + xH_2O \rightarrow Si(OC_2H_5)_{4-x}(OH)_x + xC_2H_5OH$$

As a result, when TEOS concentration increased, the intermediate $[Si(OC_2H_5)_{4-x}(OH)_x]$ will be increase rapid and the final particle size of synthetic silica will be relative larger under the constraint of the same total solution.[1] Therefore, the higher TEOS concentration, the greater silica particle aggregation exhibited. Moreover, the result shows that the hardness of the opal increased when TEOS concentration increased and heat treatment was performed. The opal synthesized under 0.6 M TEOS show obvious silica sphere packing (Figure 1c) which exhibit better feature than the microstructure of natural common opal (Figure 2). It can be concluded that the synthetic condition with 0.6 M TEOS is suitable for synthesis of common opal in our experiments.



(a) 0.1 M TEOS (b) 0.4 M TEOS (c) 0.6 M TEOS

Figure 1. SEM images of the synthetic common opal obtained with keeping nitric acid and ethanol constant and varying TEOS a) 0.1 M, b) 0.4 M and c) 0.6 M TEOS.

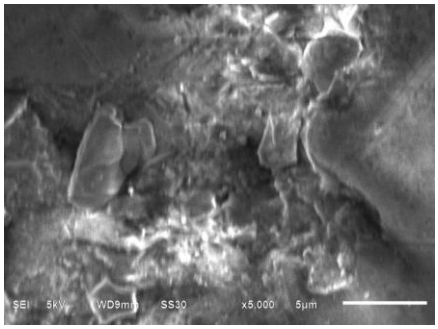


Figure 2. Representative SEM image of natural common opal

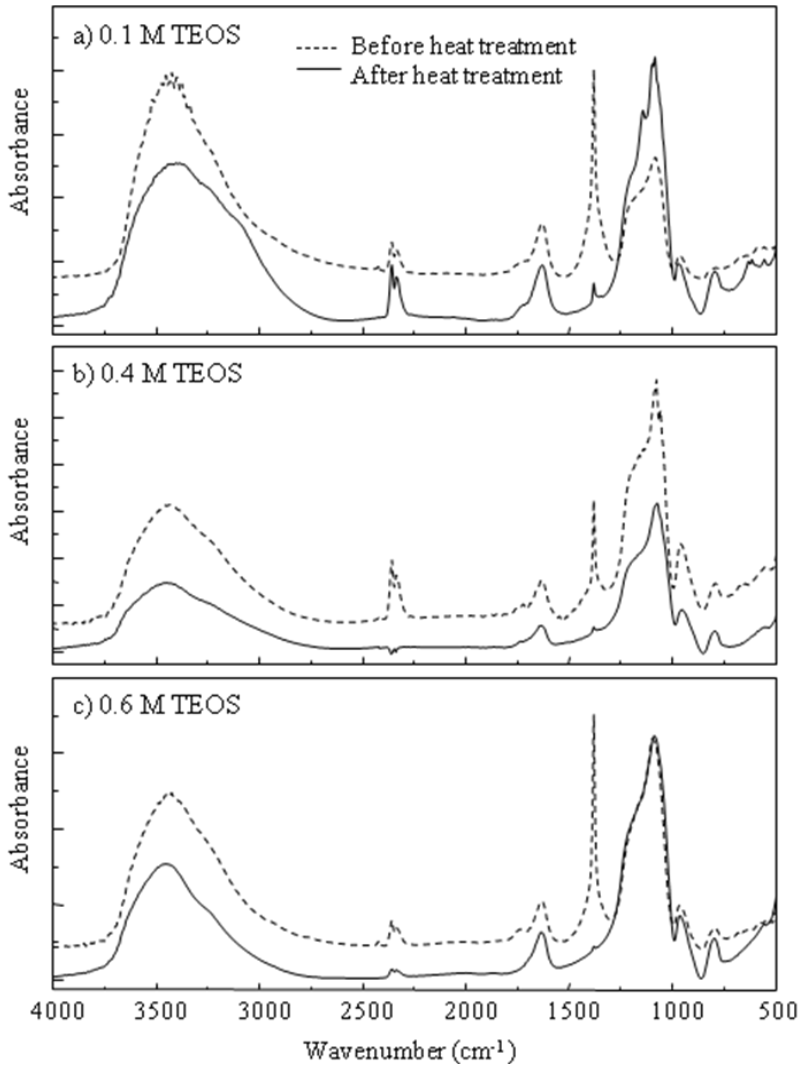


Figure 3. FTIR spectra of our synthetic common opal at different concentration of TEOS; a) 0.1 M; b) 0.4 M; and c) 0.6 M TEOS.

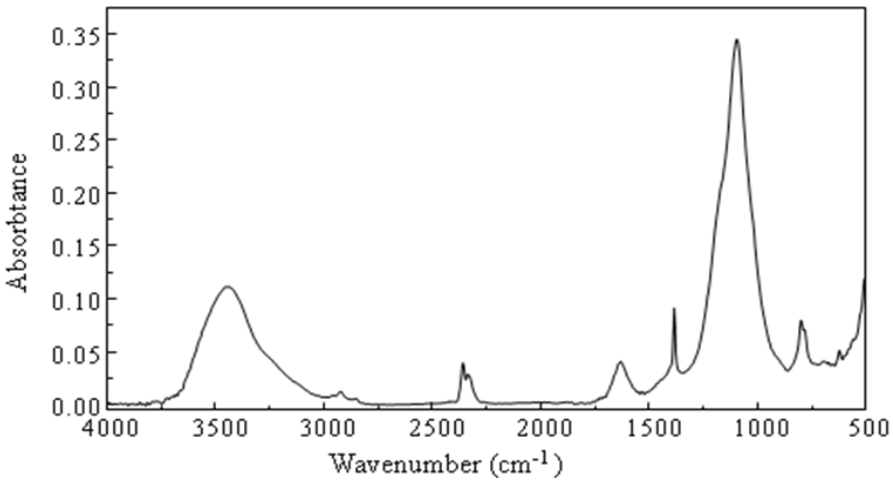


Figure 4. FTIR spectra of the representative natural common opal

To observed chemical structure of our synthetic opal prepared with different TEOS's condensations, FTIR spectra of those opals; including before and after thermal treatment, were determined, as shown in Figure 3. There are three major bands observed at around 470, 796 and 1,100 cm^{-1} which can be assigned to O-Si-O and Si-O-Si bending and Si-O asymmetric stretching vibration, respectively. The presence of intense absorption peak centered at 1,100 cm^{-1} (Si-O-Si bonds) confirms the formation of a network structure inside the opal.[7] In case of the opal synthesized by adding 0.6 M TEOS (Figure 3c), infrared spectrum of the heat treated opal show very sharp peak at 1,100 cm^{-1}. It indicated that the degree of crystallinity in this opal is higher than the opals synthesized by other conditions. The peak at around 1,600 cm^{-1} is due to H-O-H bending vibration of molecular water related to two water species, H_2O and SiOH group. The absorption band around 3,400 cm^{-1} is due to the Si-OH group.

Comparison between infrared spectra of unheated and heated opal in Figure 3, absorption of OH group at 3,400 cm^{-1} and that of bending of C-H bonds at 1,376 cm^{-1} decrease when the opal sample were sintered at 800^{o}C . Moreover, shoulder absorption band at 1,747 due to C=O of reactant disappeared because of decomposition of solvent. As shown in the Figure 3 and 4, infrared spectra of all synthetic opals after heat treatment present the spectral feature similar with those of natural common opal. However, small absorption band at 950 cm^{-1} attributed for Si-OH stretching (silicate form) present only in our synthetic opals. It can be imply that this band can use for distinguishing between natural and our synthetic common opal.

Figure 5. Example of our synthetic common opal synthesized under 0.6 M TEOS condition

Figure 5 shows example of our synthetic common opal. Herein, synthesis of common opal was successful performed by using TEOS reactant and acid catalyst. Unlike the synthetic opal synthesized under base catalyst condition, our synthetic opal does not show play-of-color. From this result, it can be imply that the synthesis of common opal (no play-of-color phenomenon) appropriately performed by sol-gel method under acid catalyzed condition. In conclusion, the experimental result indicated that the TEOS's concentration affect to particle size and packing of silica sphere for synthetic opal. Future works include study of acid catalyst (nitric acid) and water concentration for synthesis of common opal.

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