The Effect of Rhodamine B on the Properties of Fluorescent Nanoparticles Derived from Geothermal Silica

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ABSTRACT

Rhodamine B can be used as a fluorophore to produce fluorescent silica nanoparticles derived from geothermal sludge. The purpose of this research is to synthesize fluorescent silica nanoparticles (FSNP) modified with rhodamine B and cetyl trimethyl ammonium bromide (CTAB) using sol-gel method. Geothermal waste was used as a precursor and added with NaOH at 90°C to generate sodium silicate. Rhodamine B, as the fluorescent dye were added with concentration variations ranging from 0.156 mg/g to 10 mg/g. CTAB was used as template and HCl 2N was applied as gelling catalyst with aging time of 18 hours. Characterization of FSNP was measured using spectrofluorometer to identify the fluorescent intensity, fourier transform infrared (FT-IR) to determine the functional group of FSNP, Brauner-Emmett-Teller (BET) adsorption to calculate the specific area of the particles, X-ray diffraction (XRD) to analyze the crystallographic phases, and transmission electron microscopy (TEM) to analyze the surface morphology of the FSNP. FT-IR and fluorescent intensity results showed that FSNP with 2.5 mg/g of rhodamine B had the optimum characteristics. The FSNP was in amorphous phase with uniform pore distribution. BET analysis showed that the specific surface of the FSNP was 190.22 m²/g.

Keywords: fluorescent silica nanoparticles, rhodamine B, cetyl trimethyl ammonium bromide, sol-gel, geothermal.

INTRODUCTION

Geothermal sludge is a waste material generated from geothermal power plants which has been reported to reduce the productivity hence should be removed. The geothermal waste contains high amount of amorphous silica which is potential to be modified into silica nanoparticles. Using the geothermal silica to generate silica-based nanomaterial provides a way to solve the waste problem. Silica is a non-toxic and functionable material with the general formula of SiO₂ consisting silicon and oxygen [1]. Conventionally, silica was synthesized from either silicate solution or silane reagents [2]. There are some methods to synthesize silica nanoparticles one of which is the sol-gel method due to its simplicity, low temperature requirement and low cost [3].

Fluorescent silica nanoparticle can be modified by the incorporation of organic molecules such as fluorescent dyes within the silica matrix through sol-gel process. When fluorescent dyes are assembled within the silica pores, the fluorescence properties of such dye changes [4].

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This phenomenon leads to the enhanced properties of the incorporated dye, including excellent photostability [5] and long fluorescence lifetime [6].

The synthesis of silica based fluorescent nanoparticles have been developed in recent years. A recently report by Jenie et al [7] has synthesized fluorescent silica nanoparticles with sol gel process based on natural silica for bioimaging. The silica nanoparticles were modified with rhodamine 6G as dye. The result showed that the FSNP has increased fluorescence intensity and therefore applied for the bioimaging of *E. coli* under UV lights.

Herein, we report the synthesis and characterization of fluorescent silica nanoparticles (FSNP) derived from geothermal silica which is modified with Rhodamine B and CTAB via sol-gel methode. Rhodamine B was chosen in this study due to its spectroscopic properties and its capability to form a fluorescent dimer [8]. CTAB was applied to generate uniform pore sizes of the FSNP. The samples were characterized with fluorescence spectrophotometer, FTIR, surface area analysis, TEM and XRD analysis.

**EXPERIMENT**

**Materials**

The materials used in this study were geothermal sludge as the source to produce silica, supplied from PLTP Geodipa Dieng, Central Java, Indonesia. Sodium hydroxide (NaOH) and hydrochloric acid 37% (HCl p.a.) were purchased from Merck Chemicals, Rhodamine-B was purchased from Sigma-Aldrich, cetyl trimethyl ammonium bromide (CTAB) were purchased from Sigma-Aldrich and deionized water.

**Synthesis of Fluorescent Silica Nanoparticles (FSNP)**

A total of 20 g of washed silica powder was mixed with 800 mL of 1.5 N sodium hydroxide (NaOH) in a beaker glass to form sodium silicate. The mixture was then stirred using a magnetic stirrer for 60 minutes and heated at 90 °C. The mixture was filtered through filter paper to separate the solution with solids. The sodium silicate solution was added with varied concentration of Rhodamine-B from 1.56 mg/g to 10 mg/g and stirred until homogeneous, then titrated with 2.0 N HCl to form the gel until pH 5. The formed gel was added with 2% of CTAB. The formed gel was allowed to stand for 18 hours and washed with aquadest until pH 7 and dried in an oven at 100 °C, overnight.

**Characterizations of Fluorescent Silica Nanoparticles (FSNP)**

The FSNP samples were analyzed using several characterization techniques. Fluorescent intensity was recorded with fluorescence spectrophotometer (Agilent, Singapore) at excitation wavelength of 553 nm and recording the emission at 530 – 750 nm. FTIR spectra were recorded on a FTIR Prestige-21 (Shimadzu, Japan), with transmittance mode at 4 cm⁻¹ resolution, over the range of 400-4500 cm⁻¹ and an accumulating average of 40 scans to determine the functional group. The XRD pattern of the FSNP were recorded on 2θ = 5-90° using a Rigaku miniflex 600, with Cu Kα radiation at 40 kV and 15 mA. Nitrogen adsorption-desorption isotherms were conducted in 77 K on Micrometrics Tristar II 3020 2.00 porosimeter to obtain the BET surface area. The FSNP were degassed at 300°C and 10⁻⁴ Torr pressure. TEM examination was performed using TEM Tecnai G-2 S-Twin 200 kV (FEI, USA) to analyze the surface morphology of the FSNP.
RESULT AND DISCUSSION

Synthesis and fluorescent intensity of FSNP

The synthesis of FSNP using sol-gel method was derived from geothermal waste and modified with Rhodamine B [9]. The silica nanoparticle without the fluorescent dye are obtained from the following reactions:

$$\text{SiO}_2 + \text{NaOH} \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O} \quad (1)$$
$$\text{Na}_2\text{SiO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{SiO}_2 + \text{H}_2\text{O} \quad (2)$$

Previous research reported the optimum gelling time of the silica was 18 h with concentration of NaOH of 1.5 N [1]. In this research, we investigated the effect of rhodamine B concentration towards the optical properties of the FSNP. The fluorescent intensity was measured by the fluorescent spectrometer with excitation wavelength of 553 nm and the maximum emission was observed at wavelength of 580 nm. Figure 1 showed that the concentration of rhodamine B from 0.156 mg/g to 1.25 mg/g exhibits a gradual increase in maximum peak intensity but still in a low range, whereas at dye concentration of 2.5 mg/g and 5 mg/g showed a significant increase of maximum emission. At dye concentration of 10 mg/g the emission decreased which was attributed to self-quenching phenomena [10]. Considering the fluorescent spectra, FSNP with 2.5 mg/g of rhodamine B was selected as the optimal FSNP sample.

![Fluorescent spectra of FSNP in various concentration of rhodamine B.](image)

**Surface chemistry**

The FTIR spectra of the FSNP and SiNP is shown in Figure 2. The peaks at 486 and 950 cm\(^{-1}\) indicate the stretching band of Si-O. The peaks at 1093 and 802 cm\(^{-1}\) are due to the Si-O-Si asymmetric and symmetric stretching vibrations respectively. The absorption band observed at 1631 cm\(^{-1}\) indicate the bending vibration Si-OH. The broad absorption band showed a peak at 3410 cm\(^{-1}\) is due to stretching vibration of O-H bonds from the silanol groups. The modification of SiNP to FSNP with rhodamine-B showed no additional peak which hence rhodamine B was not chemically bound to the silica geothermal nanoparticles but only
physically entrapped to the pores of the silica [7]. The additional band only showed at 2933 and 2864 cm$^{-1}$ indicated the bending of CH$_2$ and CH$_3$ of the CTAB surfactant [11]. The CTAB surfactant was not removed in the final step of the reaction due to the high melting point of CTAB. Removal of CTAB will result in the removal of rhodamine B dye in the FSNP sample.

Figure 2. FTIR spectra of SiNP (black), FSNP of rhodamine B concentration of 10 mg/g (red), 5 mg/g, 2.5 mg/g (blue), 1.25 mg/g (pink), 0.625 mg/g (grey), 0.313 mg/g (yellow), 0.156 mg/g (purple).

Specific surface area and morphology
We further analyzed the specific surface area of the optimum FSNP through nitrogen adsorption-desorption isotherms. Table 1 showed specific surface area of the optimum FSNP. From the BET calculation of the adsorption-desorption isotherm, the specific surface area of the FSNP was 190.22 m$^2$/g.

| No | Specification      | Value     |
|----|-------------------|-----------|
| 1  | Surface area      | 190.22 m$^2$/g |
| 2  | Pore size         | 27.88 nm  |
| 3  | Pore volume       | 1.326 cm$^3$/g |
| 4  | Nanoparticle size | 31.541 nm |

Table 1. Specific surface area of the optimum FSNP at reaction temperature of 90 °C and aging time of 18 h.

Figure 3 show the TEM micrographs of FSNP. TEM analysis showed that FSNP has a uniform pore distribution. This was correlated due to the addition of CTAB during the synthesis of FSNP. The amount of 2% of CTAB was chosen as the best concentration based on research
of Le et al [11]. The surfactant, CTAB with concentration of 2% generated a homogenous pore size of the FSNP and the samples were dispersed completely in deionized water.

![Figure 3. TEM micrographs of FSNP](image)

**Crystallinity**  
Figure 4 showed the diffraction pattern for SiNP (red) and FSNP (black). The FSNP pattern presented a broad peak at 2θ =22° which indicates that the FSNP is in its amorph phase [12]. The sharp peak of the SiNP were observed at 2θ = 30-35° and 2θ = 40-45°, indicates the formation of SiO₂ and sodium silicate crystallite according to Joint Committee on Powder Diffraction Standard (JCPDS). The FSNP showed lack of sharp peak than SiNP indicating the lack of crystalline phase. The reduction of the crystallinity of SiO₂ is due to addition of rhodamine B.

![Figure 4. XRD pattern of SiNP (red) and FSNP (black)](image)
CONCLUSION

The synthesis of fluorescent silica nanoparticles from geothermal silica using rhodamine B as dye and CTAB as the surfactant was successfully obtained through the sol-gel method. The effect of varying the dye concentration effected the fluorescence intensity of the FSNP samples, resulting an optimized dye concentration of 2.5 mg/g in the FSNP samples. The optimized FSNP possessed strong fluorescent and the rhodamine B was physically entrapped in the pores of the silica nanoparticles. The specific surface area was at 190.22 m²/g in its amorphous phase and showed uniform pore distribution.

CONFLICT OF INTEREST

Authors declare no competing interest

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