Fabrication and characterization of FITC-modified naturalbased silica nanoparticles using sol-gel method

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Abstract. This research aimed to synthesize fluorescent silica nanoparticles (SiFITC) modified with the fluorescein isothiocyanate (FITC) dye using sol-gel method. The FITC dye was used as the fluorophore to produce fluorescent silica nanoparticles. The precipitate from geothermal power plant containing SiO_2 was used as a precursor and added with NaOH at 90°C generating sodium silicate. FITC solution was added with various concentrations ranging from 0.1, 0.2, 1, 5 to 10 mg/mL and the mixture was allowed to age for 18 hours. Characterization of SiFITC was measured using fluorescence spectrophotometer to obtain the fluorescence intensity, Fourier Transform Infra-Red (FT-IR) spectroscopy to determine the functional group of SiFITC, Brauner Emmett-Teller (BET) adsorption method to calculate the specific area of the nanoparticles, and X-ray diffraction (XRD) to analyze the crystallographic phases. Fluorescent intensity showed that SiFITC with 1 mg/mL of FITC had the lowest fluorescence intensity indicating self-quenching mechanism due to the overloading of the dye in the silica matrix. The FT-IR spectra showed vibration at wavenumber of 956 (Si-O); 1073 and 798 (Si-O-Si); 3396 (OH) and 1631 cm^{-1} (Si-OH). BET analysis showed that the specific surface of the SiFITC 480 m^2/g and XRD results showed that the samples were in amorphous phase with uniform pore distribution. The results showed that the FITC-modified silica nanoparticles have great potential for further investigation in biosensing applications, particularly fluorescence or optical based detection of antibiotic resistant bacteria.

1. Introduction

Nanoparticle-based bionanotechnology is currently on a steep upward trajectory due to its vast applications for bioanalytics, biotechnology, and biomedical systems. Silica nanoparticles make up the major section of the latter research due to its advantageous properties, such as low toxicity and high stability. The geothermal waste contains high amount of amorphous silica, which is potentially applied as silica precursors in nanoparticle fabrication [1]. One of the geothermal waste resources in Indonesia is from the geothermal power plant in Dieng, Central Java with the production amount of about 3,000 tonnes per year of precipitate silica. [2]

In bioanalysis, dye-doped silica nanoparticles have critical preferences over single dye labeling. The incorporation of dye molecules inside the silica matrix protects the dye from leaching to the environment, possesses increased photostability and more importantly, provides signal enhancement due to an increase in the number of dye molecules per nanoparticle [3]. Fluorescent silica nanoparticles can be generated by incorporating organic molecules such as fluorescent dyes within the silica matrix. When fluorescent dyes are assembled within the silica pores, the fluorescence properties

of such dye change [4]. There are some methods to synthesize silica nanoparticles. One of them is the sol-gel method due to its simplicity, low temperature requirement, and low cost [5]. The synthesis of silica-based fluorescent nanoparticles has been developed in recent years. Jenie et al. [6] has synthesized fluorescent silica nanoparticles with sol-gel process based on natural silica for bioimaging were modified with rhodamine 6G as dye. The result showed that the fluorescent nanoparticles has increased fluorescence intensity.

In this study, we report the fabrication and characterization of fluorescent silica nanoparticles derived from geothermal silica modified with fluorescein isothiocyanate (FITC) via sol-gel method. FITC was chosen as the model dye because it is generally inexpensive and broadly used in physical sciences and bio-sciences [7]. The fluorescein-based dye is also known for its pH affectability and the self-quenching effect when encapsulated in the nanoparticles matrix as described in the literature [8]. The samples were characterized with fluorescence spectrophotometer, FTIR, surface area analysis, and XRD analysis.

2. Materials and method

2.1. Material

The materials used in this study were geothermal sludge as the source to produce silica, supplied from Geodipa Dieng Geothermal Power Plant, Central Java, Indonesia. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) and Fluorescein isothiocyanate (FITC) was purchased from Merck Chemicals. Deionized water was obtained from the Research Center of Chemistry, LIPI.

2.2. Synthesis of Fluorescent Silica Nanoparticles

A total of 10 g washed silica geothermal was mixed with 400 mL of 1.5 N NaOH at 90°C under constant stirring for 60 min. The mixture was then filtered through filter paper to obtain the sodium silicate (Na_2SiO_3) solution from the solids. Sodium silicate was added with varied concentration FITC from 0.1 to 10 mg/mL, stirred, and then the mixture was titrated with 2 N HCl to form a gel phase until the pH is 4. The gel was settled for 18 hours, then filtered and neutralized with deionized water until the pH was 7. The neutralized gel was dried overnight at 100°C. The obtained dried powder was named SiNP-FITC.

2.3. Fluorescence Measurements

The fluorescence intensity of SiNP-FITC was optimized by comparing the fluorescence intensity emitted from a different concentration of FITC dye within the nanoparticles. A total of 5 mg for each variety of SiNP-FITC was dispersed in 5 mL of deionized water. The nanoparticle solution was transferred into a cuvette. Then the fluorescence emission was recorded employing a fluorescence spectrophotometer Cary Eclipse (Agilent, Singapore) over the extent of 480 - 600 nm at an excitation wavelength of 436 nm.

2.4. Characterization of Nanoparticles

The SiNP-FITCs were characterized using the Fourier Transfer Infrared (FTIR) Spectroscopy, surface area analysis Brunauer–Emmett–Teller (BET) method and X-ray diffraction (XRD). The 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 accumulating average of 40 scans to determine the functional group. Nitrogen adsorption-desorption isotherms were conducted on Micrometritics Tristar II 3020 2.00 porosimeter at 77 K to obtain the BET surface area. The XRD pattern of the SiNP-FITC were recorded using a Rigaku miniflex 600 with Cu Kαradiation on 2θ = 5-90º at 40 kV and 15 mA.

3. Result and Discussion

3.1. Fluorescence Intensity of SiNP-FITC

The synthesis of FSNP using sol-gel method was derived from geothermal waste and modified with FITC dye. In this research, we investigate the effect of FITC concentration towards the optical properties of the SiNP-FITC. The fluorescent intensity were measured by the fluorescent spectrometer with excitation wavelength at 436 and a broad emission peak with a maximum at 515 nm.

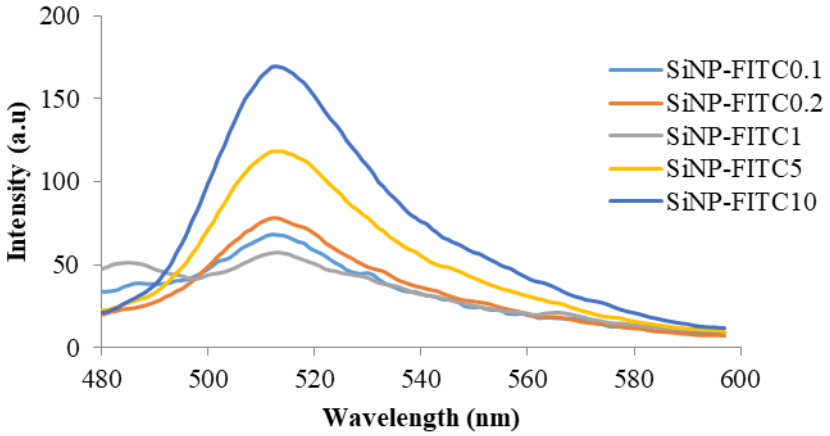

Figure 1. Fluorescent spectra of SiNP-FITC in various concentrations of FITC.

Figure 1 showed that the concentration of FITC dye from 0.1 to 0.2 mg/mL exhibits a gradual increase in maximum peak intensity but still in a low range, whereas dye concentration of 5 and 10 g/mL showed a significant increase of maximum emission. At a dye concentration of 1 mg/mL, the emission decreased due to self-quenching phenomena [7]. The SiNP-FITC with dye concentration of 1 mg/mL was chosen as the optimum sample due to this self-quenching effect which may further be used for detection applications.

3.2. Surface Chemistry

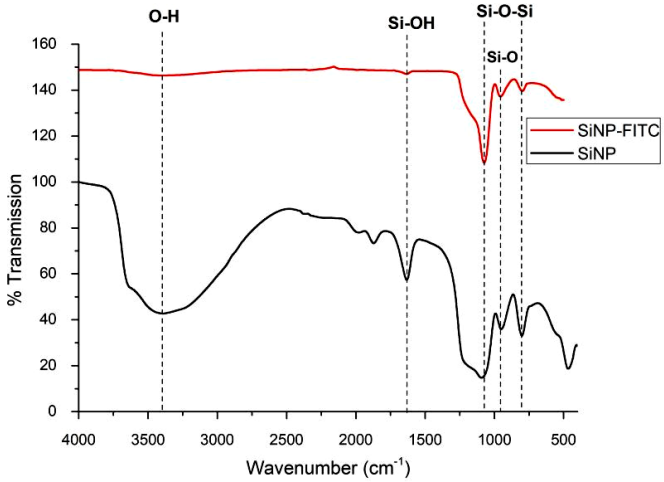

Figure 2. FTIR spectra of SiNP-FITC and SiNP.

The FTIR spectra of the non-modified silica nanoparticles (SiNP) and SiNP-FITC1 is shown in figure 2. The SiNP spectrum showed a peak at 1631 cm^{-1} which was assigned to the bending vibration of water molecules bound to the silica lattice (Si-OH). The broad absorption band at 3396 cm^{-1} is due to the stretching vibration of –O–H bonds from the silanol groups. Both the SiNP and SiNP-FITC1 spectra showed peaks at 1073 cm^{-1} and 798 cm^{-1} which were assigned to the asymmetric and symmetric stretching vibrations, respectively, of the silica (Si–O–Si) network. The peak at 956.15 cm^{-1} indicated the stretching band of Si–O confirming the presence of silica oxide in the nanoparticles. The modification of SiNP to SiNP-FITC with varied concentrations of FITC dye showed a decrease of intensity in the Si-OH peak, indicating that the fluorescein dye may have reacted covalently with the silica surface through the hydroxyl functional group.

3.3. Specific Surface Area

We further analyzed the specific surface area of SiNP-FITC1 with 18 hours aging time through nitrogen adsorption-desorption isotherms. Table 1 shows specific surface area of SiNP-FITC1. In the BET calculation of the adsorption-desorption isotherm, the specific surface area of SiNP-FITC1 with 18 hours aging time was 480 m^2/g. The titration method in synthesizing fluorescent silica nanoparticles could produce a larger surface area than those without the titration method was 190,22 m^2/g [9]. The optimum aging time obtained was the same as, which is 18 hours. The result of specific surface area tended to increase over 6 to 18 hours. The longer the aging time could also cause the synthesized silica nanoparticles to agglomerate, producing a large material and reducing the final product's surface area. In addition, it could also cause the strength of the gel tissue bond to get stronger so that it can cause shrinkage of the pore cavity. The smaller pore cavity, the smaller result of surface area.

Table 1. Specific surface area of SiNP-FITC1 at reaction temperature of 90 °C and aging time of 18 h.

Specification	Value
Surface area	480 m^2/g
Pore size	6.15 nm
Pore volume	0.73 cm^3/g
Nanoparticle size	12.49 nm

3.4. Crystallinity

Figure 3 shows the diffraction pattern for SiNP-FITC1 (red) and SiNP (black). The nanosilica pattern presented a broad peak at 2θ =22º, which indicated that the FSNP is in its amorph phase [10]. The sharp peak was observed at 2θ = 20-30° and 2θ = 27.4; 31.7; 45.4; 56.4; 66.2; and 75.2°, indicated the formation of SiO_2 and Na_2SiO_3 crystallite according to Joint Committee on Powder Diffraction Standard (JCPDS 05-0628). The SiNP-FITC1 showed lack of sharp peak than SiNP, indicating the lack of crystalline phase. The reduction of the crystallinity of SiO_2 was due to addition of SiNP-FITC1.

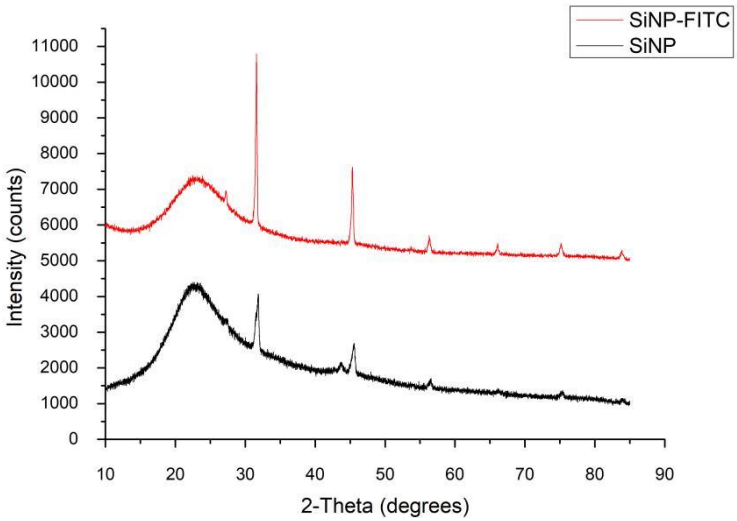

Figure 3. XRD pattern of SiNP-FITC and SiNP.

4. Conclusion

The synthesis of fluorescent silica nanoparticles from geothermal silica using FITC dye was successfully obtained through the sol-gel method. The effect of varying the dye concentration affected the fluorescence intensity of the SiNP-FITC. The optimized SiNP-FITC exhibited strong fluorescent and the FITC was physically entrapped in the pores of the silica nanoparticles. The specific surface area was at 480 m^2/g in its amorphous phase.

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