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Stable Colloidal Silica Particles Doped with a Fluorescent Dye

Tomiris Mulikova¹, Laura Khamkhash², Kanat Dukenbayev³, Anara Molkenova¹, Timur Sh. Atabaev¹

¹Department of Chemistry, Nazarbayev University, Astana 010000, Kazakhstan

²Nazarbayev University Core Facilities, Astana 010000, Kazakhstan

³Electronic and Computer Engineering Department, Nazarbayev University, Astana 010000, Kazakhstan

timur.atabaev@nu.edu.kz

Abstract. In this study, we described the quick synthesis strategy of stable colloidal silica particles encapsulated with a fluorescent dye. Atomic Force Microscopy AFM, Fourier-Transform Infrared Spectroscopy FTIR, and Fluorescence Spectroscopy FS were utilized to characterize the obtained silica particles. AFM analysis revealed that obtained silica particles have a spherical shape with a mean size of 210 ± 13 nm. FS analysis showed that fluorescent dye was successfully incorporated into a silica matrix. In particular, eye-visible green fluorescence emission with a peak maximum at 526 nm was detected. The emission stability of prepared particles was tested in a biologically-relevant pH range, under constant UV irradiation and at different storage time intervals.

1. Introduction

To date, various organic fluorescent dyes are widely utilized for bioimaging thanks to their good optical properties and nontoxicity [1]. On the other hand, organic dyes have several drawbacks such as chemical instability, temperature and pH sensitivity, and quick fluorescence quenching [2, 3]. To address these issues, a fluorescent dye can be incorporated into a protective media. For example, indocyanine green dye (ICG) can be successfully encapsulated within the polymeric and silica nanoparticles [4, 5]. However, encapsulation of organic dye in a polymer matrix is still a challenging task because of the low incorporation process. From this point of view, silica is an ideal material for introducing the fluorescent molecules thanks to the preparation simplicity, low-cost, chemical inertness, and biocompatibility [3]. Silica matrix can be an effective barrier protecting the dye from the surrounding environment. Furthermore, biocompatible silica particles with excellent optical properties can be of great interest for biomedical imaging, sensing and security applications [3, 6-8]. Therefore, one of the objectives of this study was the development of a quick and user-friendly synthesis of colloidal silica particles encapsulated with a fluorescent dye. In addition, we also studied the photostability of the prepared sample in terms of storage time and pH range.

2. Materials and Methods

For the synthesis of colloidal SiO₂ particles encapsulated with a fluorescent dye, 30 ml of ethanol (96% purity) was mixed with 10 ml of deionized (DI) water. Later on, 5 mg of 2, 7 – dichlorofluorescein dye (~ 90% purity) and 0.5 ml of tetraethyl orthosilicate (TEOS, 99.999% purity) were added. The obtained solution was heated to 30 °C and vigorously stirred (700 rpm) for 5 min. Next, 300 µl of



NaOH (0.5 M) was added and left to react for 2 hours. Formed silica particles were collected using centrifugation (4000 rpm), washed several times with DI water and dried.

Atomic Force Microscope (AFM, SmartSPM 1000) was used to analyze the morphology and size of prepared SiO₂ particles. IR transmission measurements were carried out using a Fourier-transform infrared spectrometer (FTIR, Nicolet iS5). The optical properties of nanoprobles were examined using a fluorescence spectrophotometer (Agilent Cary Eclipse). All measurements were performed at room temperature 23 ± 1 °C.

3. Results

AFM was utilized to analyze the size and shape of prepared silica particles. Figure 1 shows that synthesized particles have a spherical morphology with a mean size of 210 ± 13 nm. In some cases, small clusters consisting of several particles can be observed as well. The colloidal solution prepared from silica powder can be stable for 2-3 days. After that, the precipitation process can be observed. However, one can disperse the precipitated particles by simple sonication process for 5-10 seconds.

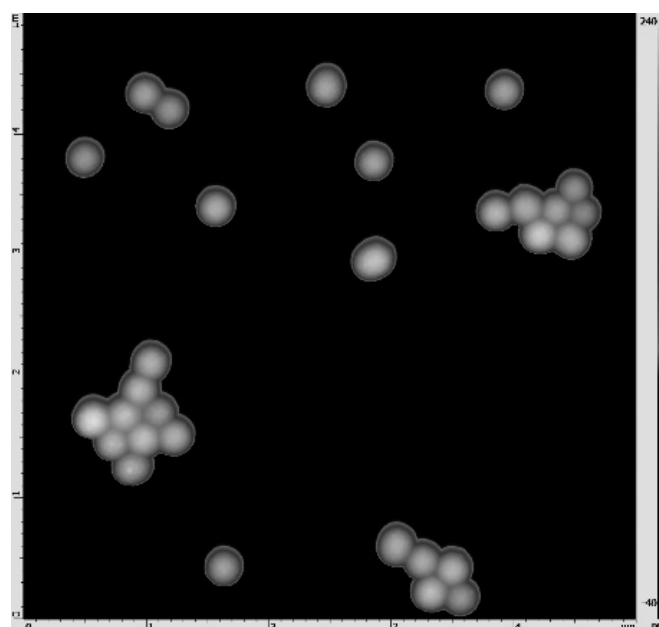


Figure 1. AFM image of prepared fluorescent silica particles.

Figure 2 shows the FTIR analysis of the prepared particles. Strong absorption bands at 800 and 1076 cm⁻¹ confirmed the formation of SiO₂ structure. The band near 800 cm⁻¹ arises from symmetric stretching vibration of Si-O-Si bond [9, 10]. The characteristic band at 1076 cm⁻¹ was assigned to the asymmetric stretching vibrations of Si-O-Si bond in the SiO₄ tetrahedron [9, 10].

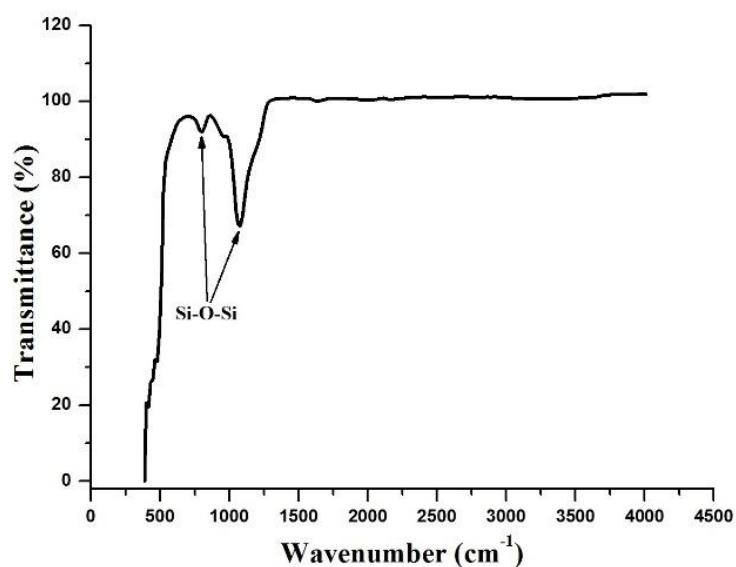


Figure 2. FTIR analysis of prepared fluorescent silica particles.

Figure 3 shows the fluorescence excitation and emission spectra of the silica particles. One can notice that the emission and excitation spectrum consist of two well-resolved peaks. The maximum of the excitation was detected at 336 nm, while the maximum of emission peak was detected at 526 nm. One can notice that the emission peak is nearly similar to those of the parent 2, 7 – dichlorofluorescein dye (529 nm in 0.1 M Tris pH 8.0).

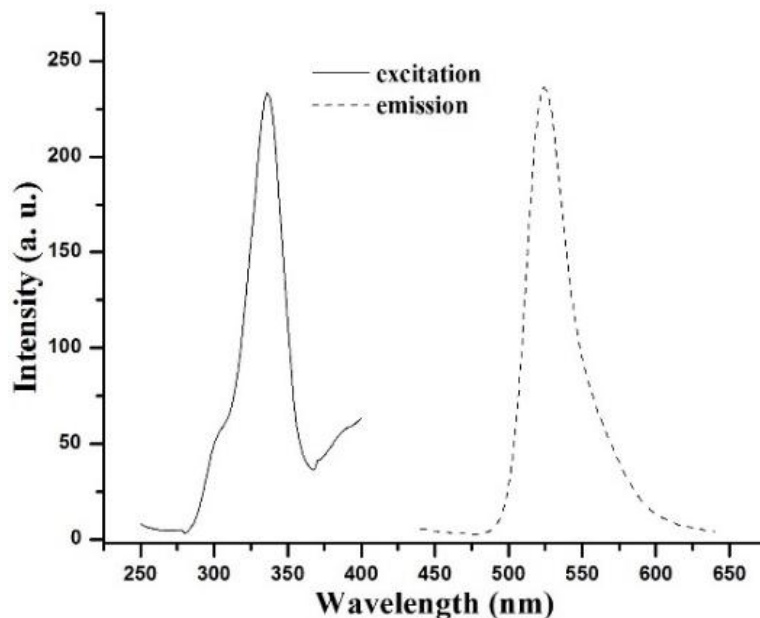


Figure 3. Excitation and emission curves of prepared fluorescent silica particles.

The fluorescence stability is an important parameter for numerous applications such as bioimaging, sensing, and security. The photostability of prepared silica particles was investigated in biologically-relevant pH range of 4-8 (figure 4). It was found that these silica particles can provide a stable emission in the pH range of 6-8, and decreased at lower pH range.

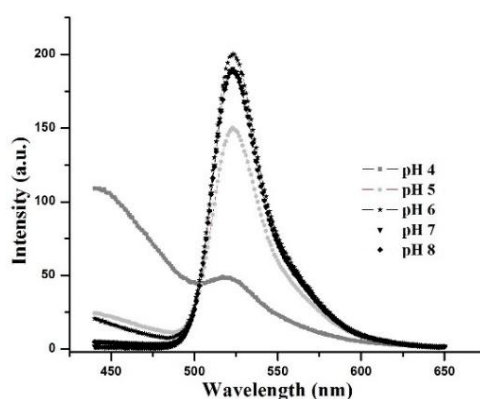


Figure 4. pH-dependent emission of prepared fluorescent silica particles.

4. Discussion

This study proposed a quick synthesis strategy for the preparation of stable fluorescent silica particles. We showed that prepared silica particles have a spherical morphology with a mean diameter of 210 ± 13 nm. FTIR analysis further confirmed the formation of pure silica structure. Interestingly, no traces of absorbed water or 2, 7 – dichlorofluorescein dye on the surface of silica particles were detected. The prepared dye-doped silica particles have yellowish-orange color, while undoped silica particles have a white color. Also, FS analysis reveals that the dye-doped silica particles are fluorescent and the emission pattern was similar to that of the bare dye. Therefore, it can be concluded that the dye molecules were successfully incorporated into silica particles. Incorporation of the dye inside the silica can be quite beneficial in terms of the preservation of the organic dye from the surrounding environment. It was also found that the silica particles are photostable in the range of 6-8 only. It can be explained by partial etching of the amorphous silica matrix in acidic conditions. Figure 5 shows the UV irradiation stability of silica particles measured at pH 7. UV lamp ($\lambda=365$ nm) with a power 6 W was used as an irradiation source. One can notice that the emission intensity slightly decreasing with the UV irradiation time. Deterioration of the emission signal is mainly related to the UV-induced degradation of 2, 7 – dichlorofluorescein dye in a silica matrix. Nevertheless, around 67.3 % of initial intensity was still preserved after 30 min of harsh UV irradiation.

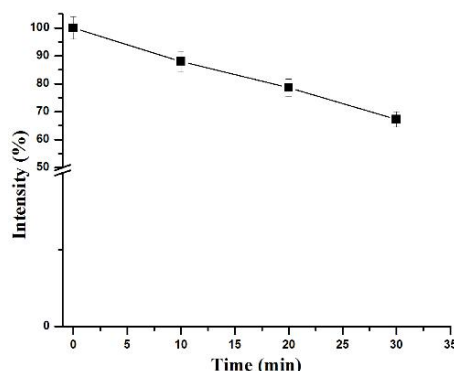


Figure 5. Emission stability of prepared fluorescent silica particles under UV-irradiation.

We also found that prepared silica particles can be stable in terms of storage time. Prepared dried particles were kept in the dark at ambient conditions ($T = 22 \pm 2$ °C, humidity 30 – 40 %) for 1 month, and colloidal solutions of silica particles with the same concentrations were prepared every 10 days. The experiments were repeated three times for each trial. Figure 6 shows that no significant fluorescence quenching was observed in all cases. The fluorescence intensity deviation was negligible (± 3.7 %). Thus, it can be concluded that fluorescent silica particles can be stored safely for some time without significant fluorescence loss.

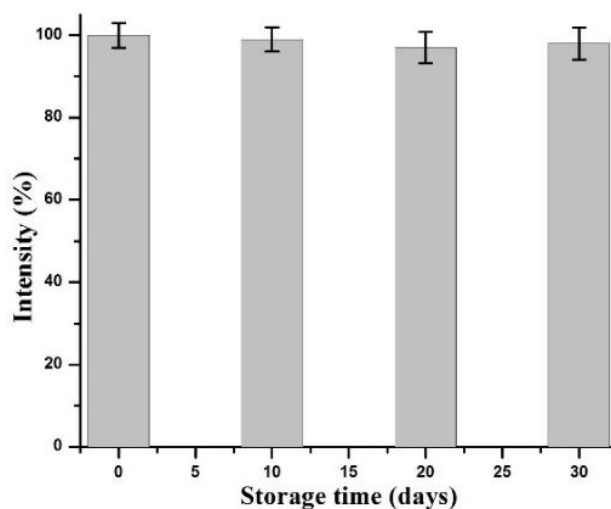


Figure 6. Storage time-dependent emission of prepared fluorescent silica particles.

5. Conclusions

In this study, we describe the one-pot synthesis method for the preparation of fluorescent silica particles with the mean diameter of 210 ± 13 nm. FS revealed that these particles have strong emission with a maximum at 526 nm. We found that prepared silica particles are photostable in the pH range of 6-8. In addition, we also found that the sample is photostable in terms of storage time. Thus, prepared fluorescent silica particles can be utilized for bioimaging, sensing and security applications.

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