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Uranyl fluorescence lifetime in nanoporous silica gel: The influence of pore size, pH, and water

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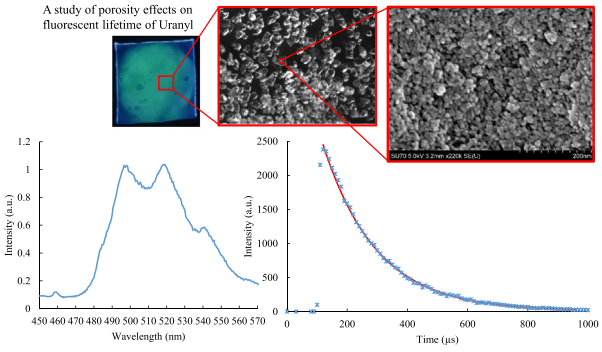
HIGHLIGHTS

- Uranyl fluorescence lifetime increased by 20 μs when silica gel pore size was decreased to 2.2 nm
- A blue shift and increase in lifetime was observed and is indicative of quantum confinement.
- Fluorescence lifetime changed with pH due to a change in the complex that is formed
- When silica gel is removed from water, the fluorescence lifetime decreased by approximately 40 μs

GRAPHICAL ABSTRACT



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ABSTRACT

The fluorescence lifetime of uranyl adsorbed within nanoporous silica gel was measured as a function of pore size at two different pH values and both wet and dry. It was determined that for uranyl adsorbed within pores larger than 4 nm, the lifetime is relatively independent of pore size, whereas below 4 nm, the lifetime increases with decreasing pore size. A blue shift in the emission spectra was observed at the smallest pore size (2.2 nm) and is believed to be caused by quantum confinement. The lifetime was found to be longer at a neutral pH than in an acidic pH, and this is caused by the formation of a uranyl hydroxyl complex at higher pH values. The presence of water within the pores is found to increase the fluorescence lifetime at all pore sizes and pH values studied in this paper; this is caused by the formation of a uranyl silicate bond in the absence of water. An understanding of the parameters that influence the fluorescence lifetime of uranyl within silica gel is important for the development of more sensitive detection methods.

1. Introduction

Uranium is a natural radioactive element found in mineral deposits and ground water. Elevated levels in water can be associated with industrial agriculture, mining, and nuclear fuel manufacturing and disposal [1–4]. Uranium in drinking water can pose a threat to human health but is challenging to detect in the field [5]. This has prompted a drive to develop new field measurement methods that will be able to rapidly detect uranium in water at low concentrations.

The most common and bioavailable form of uranium found in water is the uranium dioxide ion known as uranyl UO_2^{2+} [4,6,7]. The bond length between the uranium and oxygen atoms has been reported to be in the range on 0.15 nm–0.2 nm with the common values between 0.17 nm and 0.18 nm [8,9]. Uranyl has been known for its unique visible green emission for over 150 years [10–12]. This visible emission, with wavelengths ranging from 345 nm to 600 nm, has distinct peaks associated with the vibrational harmonics of the oxygen atoms vibrating

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Table 1
Physical properties of silica gels.

Item	Company	Pore size (nm)	Particle size (μm)	Surface area (m^2/g)
1	Sigma-Aldrich	10.0	63–200	300
2	Acros Organics	6.0	40–60	550
3	Acros Organics	4.0	40–60	750
4	Sigma-Aldrich	3.0	75–150	480
5	Sigma-Aldrich	2.0	75–650	800

Table 2
Spectrometer settings from spectral scans.

Parameter	Value	Unit
Excitation	310	nm
Emission	470–575	nm
Step size	0.25	nm
Delay 1	108	μs
Int. time	0.3	μs
Averages	10	
Shots	10	
Frequency	200	Hz

around the uranium atom [2,3,13,14]. The intensity of the fluorescent emission has been used as a method to determine the uranium concentration in water samples [15–18]. However, at low concentrations, the fluorescence is difficult to detect, particularly in an aqueous environment, since water can both quench and attenuate the uranyl fluorescence [10]. In order to improve the uranyl detection threshold in water, many strategies have been employed such as optimizing the pH and temperature and through chemical complexation. Silica has been used to enhance the fluorescence of uranyl and other compounds including Rhodamine B, Eu^{3+}, $La_4Ti_9O_{24}$, and alpha fetoprotein [16,19–21]. In this paper, nanoporous silica gel is used to collect, concentrate and enhance the fluorescence intensity and increase the fluorescence lifetime of uranyl in water samples.

Hydrophilic, nanoporous silica gel has a very high surface area and can collect and accumulate uranyl ions because the positively charged ions bind to the negatively charged surface sites of the silica. These properties of silica gel have been used for ion removal and desiccant refrigeration [16,22,23]. Silica gel also increases the fluorescent lifetime of the uranyl ion. The lifetime of uranyl in water is about 14 μs, but when adsorbed onto the surface of silica, the lifetime can be increased by more than an order of magnitude [24]. Increasing the fluorescence lifetime is useful for detection and identification because most natural fluorophores have a very short lifetime and can, therefore, be rejected using time gating techniques. This technique, along with investigations of kinetics of uranyl transport into silica gel, are being used to develop a field instrument to detect trace amount of uranium in environmental waters [15,25]. It has been shown that different uranyl complexes are predominant at different pH values, resulting in a variation in fluorescence lifetime with pH [24]. Gabriel et al. showed that at low pH (4.01–6.7), uranyl in complex with silica will form UO_2SiO_2 with a lifetime of 170 μs whereas UO_2SiO_2OH is formed at higher pH (7.35–8.87) with a lifetime of 360 μs [24]. Leung et al. showed that the fluorescent lifetime increases with temperature from 4 K to 293 K [26]. In this paper, the effect of silica gel pore size on the fluorescent lifetime was investigated. Additionally, tests were performed to determine how the pH of the solution alters the fluorescent lifetime and the uranyl species. The influence of the solution, DI water, and air present within the nanopores was examined by measuring the lifetime and observing the spectra after removal and reintroduction of the water. The results show that the presence of water within the silica gel increases the fluorescence lifetime of uranyl-silica compounds by as much as 40 μs and that very small pores can further enhance the lifetime by as much as 20 μs. We also report a blue shift in the emission spectrum for the smallest pore size and hypothesize that the shift could be the result of quantum confinement and a corresponding adjustment of the energy levels for emission.

2. Experimental methodology

2.1. Sample preparation

The silica gel was acquired from Sigma Aldrich and Acros Organics with pore sizes ranging from 2.2 nm to 10 nm, particle sizes from 40 μm to 650 μm, and surface areas from 800 m^2/g to 300 m^2/g as reported by the manufacturer. The list of the manufacturer reported average pore size, particle size range, and specific surface area for the silica gels used in this work are shown in Table 1.

The silica gel was placed in custom-made 1-in. square mesh packets made of nylon fiber mesh that was purchased from McMaster-Carr. The mesh had 28 μm size openings with equivalent fiber diameters. Using a Fisher-Scientific accu-124 balance, 250 mg of silica was measured and transferred to the nylon packets. One example of the silica gel and the samples made are shown in Fig. 1 below.

The solution used in this project was 0.01 M aqueous uranyl nitrate in pure deionized water. The uranyl nitrate was purchased from American Master Tech.

2.2. Full spectra measurements

Baseline fluorescence emission measurements were performed using a QuantaMaster-3 Spectrofluorometer with a Xenon flash lamp excitation source. The spectrometer settings for the spectral scans are shown in Table 2.

All measurements were performed in the spectrometer chamber using quartz UV transparent cuvettes into which the silica gel packets were folded and placed.

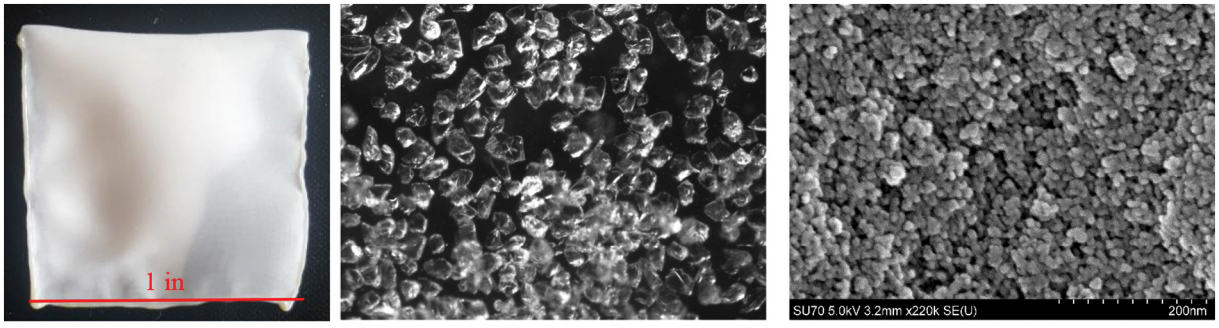

Fig. 1. a) Nylon mesh bag containing silica gel, b) optical microscope image of silica-3 particles, c) SEM image of silica-3 pores.