Luminescent mesoporous colloidal silica: A nanoporous substrate for photosensitization of lanthanide ions

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Nearly monodisperse, mesoporous, colloidal silica spheres were treated with aminopropyltriethoxysilane and subsequently calcined to generate luminescent mesoporous colloidal silica (LMCS), with broad bimodal visible emission and high surface areas exceeding 700 m²/g. The combination of high surface area and localization of luminescence centers at the surface provides opportunities for exploring new efficient photophysical/photochemical relaxation processes with the metal-free/dye-free luminescent silica sol–gel materials. Addition of LMCS to solutions of TbCl₃ or EuCl₃ results in efficient lanthanide sensitization. The enhancement in lanthanide emission is accompanied by a quenching of LMCS emission.

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1. Introduction

Metal-free/dye-free luminescent silica sol–gel materials are a promising environmentally friendly class of phosphors resulting from the carboxylic acid catalyzed condensation of alkoxysilane or aminopropyltriethoxysilane precursors [1]. In recent years, modifications of this procedure have led to nearly monodisperse luminescent colloidal silica spheres, which are potentially useful for applications where conventional dye-doped colloidal spheres have been used such as biological imaging [2,3]. Monodisperse, luminescent colloidal silica spheres are synthesized by the co-condensation of tetraethoxysilicate (TEOS) and aminopropyltriethoxysilane (APTES) in basic ethanolic conditions, and subsequently calcined at temperatures greater than or equal to 200 °C for a few hours [4]. Various other procedures for the synthesis of metal-free/dye-free luminescent colloidal silica have also been developed recently, all leading to a broad emission (~3 eV, 400 nm) with modest quantum yields of 5%–10% [5–7].

While photoluminescent applications continue to drive the research in this field, the potential to do photochemistry or other photoexcited state processes is particularly intriguing due to the ubiquitous and general biological inertness of silica. However, useful processes such as photo-induced electron transfer or resonance energy transfer require very small distances of nanometers or less for efficient interactions between surface adsorbed molecules and localized fluorescence centers. Assuming a uniform distribution of luminescence centers throughout the luminescent colloidal silica, a sphere with a diameter of 500 nm would have less than 3% of its luminescent centers within 5 nm of the surface for possible energy transfer processes. To realize the potential of luminescent colloidal silica as a substrate for photophysical/photochemical processes, we have developed a simple synthetic procedure for very high surface area, luminescent mesoporous colloidal silica (LMCS), that maximizes the amount of accessible luminescent centers. Ordered mesoporous silicates with very high surface areas can be grown via sol–gel processes utilizing appropriate surfactants [8], and their advantages as optical material substrates have been reviewed [9]. Under certain conditions, it is possible to generate nearly monodisperse, mesoporous colloidal silica spheres [10,11].

In this manuscript, we describe the synthesis and photoluminescent properties of LMCS, and demonstrate the subsequent photosensitization of lanthanide ions from solution with LMCS. Lianos and coworkers previously synthesized hybrid europium doped aminosilica films with high-efficiency europium phosphorescence resulting from europium ions distributed throughout the matrix during the sol–gel process [12]. By contrast, LMCS can be used as a nanoporous substrate capable of photosensitization and interaction with species in solution, providing new opportunities for sensing or photochemistry applications.

2. Experimental conditions

Mesoporous colloidal silica spheres were grown via the condensation of TEOS in basic ethanolic solution with C₁₆TMABr
Mesoporous colloidal silica (1 g), toluene (30 mL), and aminopropyl-triethoxysilane (APTES, 3 g) were added to a reaction vessel under anaerobic conditions. The mixture was stirred at 200 rpm for 24 h at 100 °C. The aminosilica spheres were isolated by centrifuge, then rinsed with ethanol and diethyl ether and dried at 70 °C for 1 h. The reaction mixture was allowed to stir for 24 h. The mesoporous colloidal silica was recovered by filtration and rinsed with copious amounts of ethanol, 1 M HCl to remove the surfactant, ethanol/water, and finally ether. Once dried, the mesoporous colloidal silica was reacted with APTES using a method reported by Descalzo [13]. Mesoporous colloidal silica (1 g), toluene (30 mL), and aminopropyl-triethoxysilane (APTES, 3 g) were added to a reaction vessel under anaerobic conditions. The mixture was stirred at 200 rpm for 24 h at 100 °C. The aminosilica spheres were isolated by centrifuge, then rinsed with ethanol and diethyl ether and dried at 70 °C for 1 h. The procedure yields ~1.3 g of low polydispersity, aminopropyl modified, mesoporous colloidal silica spheres with an average diameter of 377 nm (relative standard deviation = 3%) (Fig. 1). The spheres were then baked at 200 °C for 48 h to become luminescent (Fig. 2).

3. Results and discussion

The broad luminescence exhibited by luminescent mesoporous colloidal silica (Fig. 2) is largely dependent on calcination times and conditions, but generally consists of two Gaussian distributions centered at ~400 nm (high energy component) and a distribution centered at ~450 nm (low energy component). Varying the calcination time and/or temperature has a significant effect on the relative contribution of each component [14]. The luminescence results are consistent with the results for other types of APTES modified silica sol–gel materials. Carlos and coworkers attribute the bimodal distribution to charge transfer processes between nitrogen centers in the silica lattice (low energy component) which EPR evidence indicates is a peroxy radical attached to a Si center with two oxygens and one organic substituent [15].

The LMCS possess a very high surface area as consistent with their mesoporous nature. The surface area and porosity of the spheres following calcinations were studied using a Micromeretics ASAP 2020 Surface Area Analyzer with N2 gas as the adsorptive. A surface area of 728±16 m2/g (BET) and an average pore width of 20.6 Å were obtained for the LMCS following calcination. The high surface area in conjunction with the localization of all fluorescent sites on the surface via the two-step synthesis provides the potential for significant photochemistry to occur with LMCS.

Figs. 3 and 4 show clear evidence of lanthanide photosensitization in solution using the LMCS as host. Fig. 3 shows the PL spectrum of three solutions excited under identical conditions at 320 nm with 2 nm band-pass slit-widths. The first solution (light gray line) contains 1 mg of LMCS suspended in 3 g of a 30/70 ethanol/toluene mixed solvent. The solvent ratio was chosen to minimize scattering effects with the spheres by refractive index matching. The second solution (black line) consists of 0.1 mg of EuCl3 dissolved in 3 g of 30/70 ethanol/toluene mixture, for clarity the intensity has been multiplied by 10. The third solution contains both the EuCl3 and the LMCS (0.1 mg and 1 mg respectively) dissolved in 3 g of the ethanol toluene mixture. Addition of the LMCS results in an increase in Eu luminescence by more than a factor of 20. Fig. 4 shows that a similar enhancement was obtained when TbCl3 (0.1 mg) was combined with LMCS (1 mg) in a 3 g solvent. In the case of TbCl3, the LMCS sensitized luminescence was increased by more than a factor of 60 over the solution of TbCl3 alone.

A decrease in the LMCS emission is observed along with the 20-fold and 60-fold increase in the lanthanide emissions providing further evidence of the sensitizing nature of the LMCS to the Eu and Tb ions. The significant quenching of the LMCS emission also demonstrates the accessibility of the luminescence centers to the lanthanide ions as expected. The large enhancements in lanthanide emission in these materials can be directly attributed to the two-step synthesis route that ensures (1) high surface area via mesoporous silica formation and (2) localization of the fluorescent centers on the surface via subsequent surface modification.

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**Fig. 1.** SEM image of luminescent mesoporous colloidal silica calcined at 200 °C for 48 h. Imaging performed on a field emission scanning electron microscope, Raith 150 with a Leo Gemini column using an acceleration voltage of 10 kV (bar = 1 μm).

**Fig. 3.** Luminescence of LMCS (light gray), EuCl3 + LMCS (dark gray), and EuCl3 solutions. The intensity of the EuCl3 solution is multiplied by 10 to show detail.

**Fig. 2.** PL spectrum of LMCS (black) excited at 320 nm collected with Jobin_Yvon Fluorolog 3 fluorescence spectrometer. The best theoretical fit is included (gray) consisting of a sum of two Gaussian distributions (identified as a high energy distribution at 400 nm and a low energy distribution at 456 nm).
4. Conclusion

Luminescent colloidal mesoporous silica is able to sensitize Eu$^{3+}$ and Tb$^{3+}$ emission without requiring organic antenna ligands or subsequent heat or chemical treatments of the matrix. This property may lead to new functional materials or devices and could be an important development for the field of lanthanide-containing light-emitting organic–inorganic hybrids [16]. Furthermore, these results demonstrate the potential for using LMCS as a new material for photophysical/photochemical processes because of its high surface area and accessible luminescent sites. Further studies are currently underway to elucidate the mechanism of sensitization in this system.

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