Sequestration of cerium(III) bromide into mesoporous silica

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ABSTRACT

A variety of surface-functionalized mesoporous silica monoliths were reacted with a cerium(III) bromide molecular complex and a successful scaffold for luminescent materials is demonstrated. The variation in structure of the materials is shown through infrared spectroscopy, and the luminescent properties illustrate the varying coordination environment of cerium(III) bromide.

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1. Introduction

Single crystals of doped metal halides are widely used as scintillators for gamma-ray detection. They can provide high photon yield and good energy resolution at room temperature. The most common material is NaI:Tl [1]. Recently, lanthanide halide compounds including $LaBr_3:Ce^{3+}$ [2] and $SrI_2:Eu^{2+}$ [3] have been developed. They offer the highest photon yields (65 k photons/MeV for LaBr₃:Ce [4], and 120 k photons/MeV for SrI₂:Eu [5], versus 45 k photons/MeV for NaI:Tl [6]) and energy resolution among room-temperature scintillators, and they enable radiation sensors that can not only detect but also identify the type of source material. However, the growth of large high quality single crystals of these hygroscopic materials is difficult and expensive, and a cheaper alternative method would be very beneficial. Inexpensive organic scintillators such as plastics [7] or liquids [8] have significantly lower photon yields and are not useful for gamma-ray spectroscopy. For this reason, lanthanide halide scintillators that can be fabricated by an inexpensive and scalable method are highly desired.

Nanocomposite scintillators in which nano-sized scintillator particles are contained within an optically transparent matrix, have been the focus of numerous studies [9–11]. The primary challenges

in developing a nanocomposite scintillator are 1) achieving a high loading level of the scintillator in order to obtain a gamma attenuation that is competitive with traditional single-crystal scintillators, and 2) maintaining a high degree of optical transparency (low absorption and low scattering) in order to efficiently transport the scintillation light to the photodetector. The second challenge is particularly difficult due to the high refractive index of the inorganic crystals (n > 2 [12–14]) compared with that of most potential matrices. Silica has an index around 1.5 [15], and the resulting large refractive index mismatch between the scintillator and the matrix in a nanocomposite will result in opacity and thus reduced light transport efficiency primarily due to Rayleigh scattering [16]. Particle size has a large impact on scattering [17]; as the scintillator particle size decreases to ~3% of the wavelength, scattering should become negligible even in the presence of some refractive index mismatch [18].

Mesoporous (defined as having pores between 2 and 50 nm [19]) silica was first developed in the 1990s [20] by Mobil, and has been widely used in a variety of applications, such as gas [21] and water [22] treatment, catalysis [23], and even biological applications such as drug delivery [24] and imaging. Mesoporous silica can be modified with a range of functionalities [25], and it has been made with widely tunable properties such as surface area and pore size. Mesoporous silica is an attractive matrix for nanocomposite scintillators because surface functionality can be introduced to bind the scintillator inside the pores. When mesoporous silica is filled with scintillator, the pore size defines the scintillator particle size, which can be sufficiently small to result in potentially low optical scattering.

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Our group has recently developed coordination polymers of cerium(III) bromide with ligands coordinated through a nitrile group [26]. Functionalizing the pore surfaces within the mesoporous silica with a nitrile group should allow cerium bromide to bind to the matrix by forming nitrile coordination compounds at the pore surface. Furthermore, we expect that introducing organic ligands will reduce the net refractive index of the composite material (since organic materials typically have low refractive indices) and therefore decrease scattering. The inclusion of organic material however will decrease the possible loading level of cerium(III) bromide and potentially reduce the possible light output. The goal of the present study is to chemically modify mesoporous silica with cerium(III) bromide to introduce scintillation functionality, and assess the luminescent properties.

2. Experimental

2.1. Preparation of mesoporous silica (1)

Based on a procedure by Zhao [27], 0.8 g Pluronic F127 was dissolved in 1.0 g tetraethylorthosilicate, 8 mL ethanol, and 1 mL 0.2 M HCl. The solution was stirred at room temperature and pressure for 2 h and became transparent. The solution was heated at 0.1 °C/min–70 °C, held for 36 h, and cooled at 0.1 °C/min to room temperature. The resulting monolithic gel was then calcined in air to remove the Pluronic by heating it at 1 °C/min–550 °C, holding for 6 h under ambient pressure, and cooling to room temperature.

2.2. Preparation of hydrolyzed mesoporous silica (2)

The mesoporous silica monolith (1) was soaked in a 10 mL piranha solution (70% H_2SO_4, 30% H_2O_2) overnight and then rinsed with water.

2.3. Preparation of nitrile-functionalized mesoporous silica (3)

1 mL 3-cyanopropyltriethoxysilane was added to 10 mL toluene. The hydrolyzed mesoporous silica monolith (2) was put in solution and was refluxed for 3 h (without stirring, to avoid damaging the monolith). The monolith was then rinsed 3 times with toluene, followed by 3 washes with tetrahydrofuran.

2.4. Preparation of $CeBr_3 \cdot THF$ solution (4)

Based on a method we have previously reported [28], in an argon glovebox, 0.1 g $CeBr_3$ was heated in 10 mL tetrahydrofuran at 50 °C while stirring overnight, then filtered through a coarse glass frit.

2.5. Preparation of mesoporous silica sequestered $CeBr_3$ (5)

In an argon glovebox, a mesoporous silica monolith (1) was heated overnight in $CeBr_3 \cdot THF$ solution (4) at 50 °C, then dried on a watchglass. The monolith remained intact, and the same in appearance to the starting material.

2.6. Preparation of hydrolyzed mesoporous silica sequestered $CeBr_3$ (6)

In an argon glovebox, a hydrolyzed mesoporous silica monolith (2) was heated overnight in $CeBr_3 \cdot THF$ solution (4) at 50 °C, then dried on a watchglass. The monolith remained intact, and the same in appearance to the starting material.

2.7. Preparation of nitrile-functionalized mesoporous silica sequestered $CeBr_3$ (7)

In an argon glovebox, a nitrile-functionalized mesoporous silica monolith (3) was heated overnight in $CeBr_3 \cdot THF$ solution (4) at 50 °C, then dried on a watchglass. The monolith remained intact, and the same in appearance to the starting material.

2.8. Characterization

Fourier Transform Infrared (FT-IR) spectra of the samples in KBr pellets were measured using a Bruker Vertex 80 V FT-IR spectrometer at 4 cm^{-1} energy resolution. Photoluminescence spectra were measured using a Photon Technologies International Timemaster photoluminescence spectrophotometer. Nitrogen physisorption was performed using a Quantachrome Autosorb-1 instrument at −196 °C. Samples were outgassed under vacuum at 523.15 K for at least 48 h prior to analysis. Specific surface areas were calculated according to Brunauer–Emmett–Teller (BET) theory by taking a minimum of five data points of the adsorption branch within the range of 0.05–0.30 relative pressures (P/P$_0$). Pore size distributions were calculated according to Barrett–Joyner–Halenda (BJH) theory using the desorption branch, as well as the equilibrium model for a cylindrical pore shape in silica, based off of non-local density functional theory (NLDFT) calculations. Radioluminescence (RL) spectroscopy was performed using a homemade apparatus featuring a charge-coupled device (CCD) (Jobin-Yvon Spectrum One 3000) coupled to a Jobin-Yvon Triax 180 monochromator as the detection system. Sample excitation was obtained by X-ray irradiation through a Be window, using a Phillips 2274 X-ray tube with a tungsten target operated at 50 kV and producing an effective X-ray energy of ~25 keV with a dose rate of 1.75 Gy/s for 30 s. The data was corrected for the spectral response of the detection system.

3. Results and discussion

3.1. BET

A typical nitrogen physisorption isotherm of a mesoporous silica monolith is shown in Fig. 1. The isotherm exhibits a fast rate of adsorption in the relative pressure (P/P$_0$) range of 0.05–0.60 before reaching a steady-state of adsorption in the P/P$_0$ range of ~0.6–0.95. At P/P$_0$ > 0.95, an uptake is observed that indicates macroporosity. BET specific surface area (SSA) derived from the nitrogen physisorption isotherm (Fig. 1) is presented in Table 1. The pore size distribution presented in Fig. 1, derived from the isotherm, exhibits a narrow monomodal peak at 3.43 nm, which can be attributed to surfactant templating. The pore size distribution as determined from NLDFT shows a larger pore size, with a peak at 4.74 nm is in close enough agreement with the BJH data, given that BJH can underestimate pore size by 20–30% (28% here) for pores smaller than 10 nm [29,30]. Given the derived total pore volume and assuming a silica density of 2.65 g cm^{-3} [31], the pore volume fraction is calculated to 54.9 ± 0.1%. Due to the chemical instability of surface-modified mesoporous silicas at the high outgassing temperature (250 °C), nitrogen physisorption isotherms acquired after silica modification were unsuitable for analysis. Outgassing at lower temperatures for longer times was also ineffective at degassing without decomposition of the material.

3.2. Infrared spectroscopy

A monolith of mesoporous silica was made and the pores were functionalized with a nitrile group in an attempt to facilitate the