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Lanthanide induced formation of novel luminescent alginate hydrogels and detection features

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ABSTRACT

Responsive photo-luminescent soft matters have led to the design of optical sensors and switches. In this research, two new organic–inorganic type hybrid hydrogels have been fabricated by the self-assembly of sodium alginate and lanthanide elements. The incorporation of europium ions (Eu^{3+}) (or terbium ions (Tb^{3+})) was required for the gelation of the dissolved alginate and thermally stable gels were formed. It has been found that red/green emissions derived from lanthanide ions were clearly identified in pure aqueous media through the metal coordination interactions with assembled alginate. These supramolecular structures could partially prevent the Eu^{3+} (or Tb^{3+}) from being attacked by high frequency vibrations. More importantly, the lanthanide luminescence could be switched "off–on" in the presence of the anthrax biomarker sodium dipicolinate (NaDPA). The detection limits (for NaDPA) were determined to be 8.3×10^{-8} M and 9.0×10^{-8} M based on Eu(III) and Tb(III) gel, respectively.

1. Introduction

Responsive aggregations of supramolecular structures have been intensively studied in gel industry and biomedical fields. It is well accepted that these organized soft materials with high biocompatibility and flexibility have been used in a wide range of applications (Kim, Bae, & Okano, 1992; Sakai & Kawakami, 2007). Gelation features can be realized through changes in temperature, light, pH, sound and stress (Zhao, Benjamin Beck, Rowan, & Jamieson, 2004; Naota & Koori, 2005; Camerel, Bonardi, Schmutz, & Ziessel, 2006). Recently, there have been extensive interests in the utilization of metal–ligand interactions as efficient synthesis ways to assemble gels (Weng, Beck, Jamieson, & Rowan, 2006; Fages, 2006). Numerous organic molecular moieties or low molecular weight gelators that are able to immobilize organic solvents have been developed (Camerel et al., 2007; Jang, Jiang, & Aida, 2000; Mohmeyer & Schmidt, 2007). However, designing a metal assisted gel that could be easily formed in pure aqueous media, while being functional and practical, remains a real challenge. Previous examples of such metal-stimuli hydrogelators were developed by the special sea alginates that bear natural polysaccharides units (Agulhon, Robitzer, Habas, & Quignard, 2014). These linear block co-polymers comprised of α-L-guluronate and β-D-mannuronate monomers have excellent biocompatibility, low toxicity and low costs (Zimmermann et al., 2005; Lee & Mooney, 2001). In this field, alkaline-earth cations and several transition mental cations, such as Cu^{2+}, Ca^{2+}, Co^{2+} and Mn^{2+} were employed for the fabrication of metallo-supramolecular architectures (Topuz, Henke, Richtering, & Groll, 2012; Swamy & Yun, 2015; Straccia, d'Ayala, Romano, & Laurienzo, 2015; Yang et al., 2013). But the use of incorporated ions to induce visible light emissions in alginates through the linkage of metal complexation needs further exploration.

As for the selection of cations, the charge dense lanthanide ions with large ionic radius have high coordination numbers and will be of prime importance in binding multiple carboxylate groups. Second, the lowest energy excited states of these cations have the radiative lifetimes of the order of milliseconds which may demonstrate difference from the short-lived background fluorescence (generally life time in the range of nanoseconds) or light scattering. Third, the narrow line emissions of lanthanide ions are very unique (normally full width at half maxima around 10 nm) and color purity is high (Tan & Wang, 2011; Peng et al., 2010; Bunzli, 2010). Therefore, these elements have provided new choices due to their unique photophysical properties (Oerlemans et al., 2013; Liu et al., 2008). Generally, lanthanide luminescence would be quenched by water or high frequency vibrations. In the present study, two kinds of

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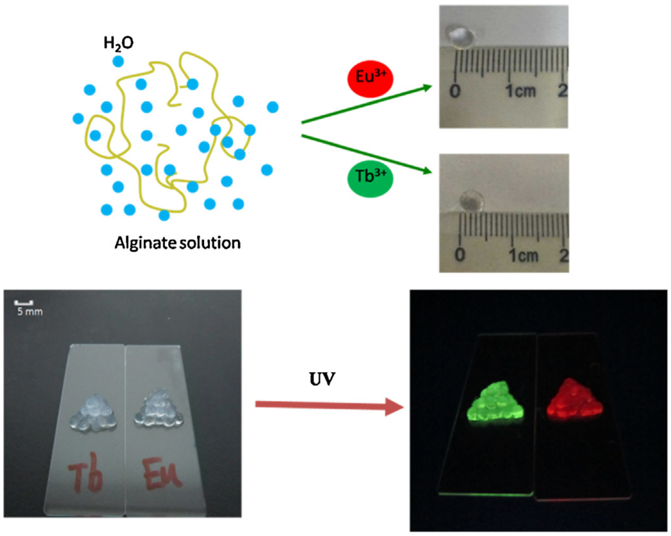

Fig. 1. Lanthanide alginate hydrogels and excitation under the UV light at 254 nm.

novel hydrogels stimulated by Eu^{3+} and Tb^{3+} with red or green luminescence have been synthesized in the presence of pure alginates aqueous solution (Fig. 1). In previous literature, the results also demonstrated that lanthanide activated alginate gels could give characteristic emissions or mixed colors (Liu et al., 2008). However, the development of hydrogel-type sensors or receptors for different analytes has received considerable interests due to their indispensable roles in biological or environmental processes. As far as the target chemical species were concerned, bacillus anthracis that was closely related to anthrax disease has received much attention (Lu & Eychmuller, 2008). The anthracis spores can be considered as biological warfare agents that would lead to death within 1–2 days (Wang et al., 2009). Dipicolinate acid is a main constituent of the bacterial spores and normally it can bind with calcium or other metals in equivalent molar ratio. Ten percent of its dry weight of bacillus anthracis spores is calcium dipicolinate (CaDPA) (Scott & Ellar, 1978). The convenient, rapid and real-time detection of this unique biomarker has been explored (Cable, Kirby, Soarasaenee, Gray, & Ponce, 2007; Tan, Wang, & Zhang, 2011). Our team has already developed a carbon nanotube based terbium inorganic–organic network and it could recognize CaDPA by the modulation of the emissions (Tan et al., 2011). But the analytical media was a mixture of organic solvent (DMSO) and water in terms of the solubility restrictions. Here we are able to achieve optical sensing in pure water by appropriately encapsulating a hydrophilic soft matter host (alginate) into the system. The alginate is capable of forming gels by interactions with terbium as well as europium ions (Fig. 1). Accordingly, lanthanide containing hydrogels with optical active features have been developed through extensive cross-linking process. Moreover, Tb(III) and Eu(III) emissions exhibited obvious enhancements in pure water depending on the CaDPA concentrations. The demonstration of detection behavior in aqueous media will be critical for the design of lanthanide based soft materials sensors used in clinical environments.

2. Experimental

2.1. Materials

Eu_2O_3 (99.9%) and Tb_4O_7 (99.9%) were purchased from Shanghai Yuelong company (China). Europium nitrate and terbium nitrate were obtained by dissolving Eu_2O_3 and Tb_4O_7 in concentrated nitric acid. Sodium alginate (LVG, 100 kDa, >65% guluronic acid) and Dipicolinate acid were purchased from J&K Scientific.

2.2. Gelation test

Sodium alginate was dissolved at 5.0% (w/v) in deionized water. The hydrogel was prepared by slowly dropping the sodium alginate solution into 0.01 M $Eu(NO_3)_3$ and 0.01 M $Tb(NO_3)_3$ at a speed of 0.2 ml/min. The preparation of spherical beads has been performed by using a plastic syringe equipped with a needle (diameter 0.8 mm). Gel spheres were thus achieved (4.5 ± 0.01 mm). The gelation reaction was proceeded at room temperature for 6 h at pH = 7.0. We have determined the lanthanide concentrations (Eu^{3+} and Tb^{3+}) by ethylenediaminetetraacetic acid (EDTA) titration method by using xylenol orange as an indicator. The collected results were measured to be 1.7% for terbium hydrogel gel and 1.3% for europium hydrogel.

The gelation properties of the lanthanide gels were investigated at a concentration (alginate concentration) of 5% (w/v) in solvents experiments (Table S1). It can form regular hydrogel beads within pure water and H_2O/EtOH (9/1; v/v). Upon further addition of ethanol in the mixed solvents, it was unable to obtain spherical shape beads and only stable hydrogels were achieved (named as alcogel). It has also been found that water is the most effective solvent for the gelation process and Ln–alginate could not form hydrogel in pure ethanol.

2.3. Methods of characterization

Fourier transform infrared spectra (FT-IR) were measured using a Shimadzu Prestige-21. Scanning electron microscopy (SEM) was measured using a Zeiss Ultra 55 scanning electron microscope. The hydrogel beads was pre-freezing for 5 h within a freezer, and then freeze-dried 12 h at −40 °C by a LABCONCO FreeZone lyophilizer. The dried samples were cut and attached to the stubs with conductive paint and sputter-coated with a thin layer of gold (10 nm). The samples were measured under SEM at an accelerating voltage of 5 kV. Fluorescence emission spectra were recorded on a computer controlled HITACHI F-2500 fluorescence spectrophotometer. Luminescence lifetimes were recorded in an Edinburgh FLS920.

3. Results and discussion

3.1. FT-IR spectra analysis

To prove chelation between rare earth cations and alginate, we have carried out FT-IR analysis in Fig. 2. It showed the vibration spectra of pure alginate, the chelation of Tb^{3+} and the presence of NaDPA. In the spectrum of the alginate, the broad band at 3370 cm^{-1} corresponded to hydroxyl groups, the symmetric and asymmetric stretching vibrations of COO^-groups were indicated by the peaks of 1600 cm^{-1} and 1410 cm^{-1}. It has been found that some nitrates (band at 1350 cm^{-1}) still remained in the gel system. The bands around 1030 cm^{-1} was attributed to the saccharide structure of alinate, and the peak located at 1085 cm^{-1} was related to characteristics signals of —CH—OH. When coordinated with Tb^{3+}, the peaks of the COO^- groups at 1600 cm^{-1} and 1410 cm^{-1} was shifted to 1613 cm^{-1} and 1428 cm^{-1}. These changes suggested that COO^- groups of alginate participated into the coordination reaction with Tb^{3+}. Moreover, the frequency signal below 500 cm^{-1} would provide useful information concerning metal–ligand vibrations (Kostova, Peica, & Kiefer, 2006). The new peak at 420 cm^{-1} can be assigned to be the Tb–O coordination interactions. After the addition of NaDPA, the major vibration band appearing at 1588 cm^{-1} could be derived from carboxylate of dipicolinate and