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Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Full Length Article

Self-organized dysprosium-directed alginate hydrogels and its chemical features

Qianmin Ma^b, Jinwei Gao^d, Huojun Peng^b, Qianming Wang^{a,b,c,*}

^a Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, School of Chemistry and Environment, South China Normal University, Guangzhou 510006, PR China

^b School of Chemistry and Environment, South China Normal University, Guangzhou 510006, PR China

^c Guangzhou Key Laboratory of Materials for Energy Conversion and Storage, Guangzhou 510006, PR China

^d Institute for Advanced Materials, Academy of Advanced Optoelectronics, South China Normal University, Guangzhou 510006, PR China

ARTICLE INFO

Article history:

Received 9 November 2015

Received in revised form

28 April 2016

Accepted 2 May 2016

Available online 7 May 2016

Keywords:

Soft materials

Structure

Lanthanide

Luminescence

ABSTRACT

Rational use of self-organized materials may contribute in developing new structures and devices in practical technology. Synthetic metallo-supramolecular gels are generally designed with transitional metal-directed process. However, the assembly of both lanthanide and sodium alginate in macro-molecular systems would find a new way of utilizing its physical properties. The stimuli-responsive molecule (alginate) could firmly form stable hydrogels upon the encapsulation of dysprosium ions. In addition, the immobilization of YVO₄: Eu³⁺ nanoparticle in the soft matrix has been achieved and it has never been explored in the fabrication of phosphor-incorporated luminescent alginate gels. The key feature of the present soft matter is that its red emission could be switched off in the presence of sodium ascorbate and the results may have a tremendous impact on the extension of photophysical application based on soft nanoscale devices.

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1. Introduction

The design and exploration of new molecular optical probes for the detection of various kinds of guest species have attracted considerable attention and received ever-increasing interests in recent years [1,2]. In addition to outstanding optical application of these devices, some fluorescent molecular switches could provide practical applications in measuring and monitoring chemicals within biological field at the level of single molecule in solution and for the real-time visualization of cellular events [3–5]. They represent a versatile group of materials which own remarkable selectivity and high sensitivity based on their luminescence signals [6]. Optical changes could be achieved through interactions with strong chemical bond (covalent), hydrogen linkage or weak intermolecular forces [7]. Currently, the influence of redox processes on emission properties of molecular switches has been developed to engender widespread concerns in this field. These molecular probes were mainly derived from different metal complexes or organic compounds, such as ruthenium complexes

with 1,4-phenylenediamine ligands, typical organic couple (quinone/hydroquinone), tetrathiafulvalene (TTF) and free-base porphyrin [8–10]. However, the construction of well-organized luminescent architectures established on lanthanide elements has been very rare [6]. As far as we know, lanthanide ions have intriguing electronic and optical characteristics based on 4f electrons. They can avoid the influence from background signals due to the large Stokes shifts and long excited states lifetimes [10,11,13].

In order to search suitable vehicles to assemble the emissive centers, inorganic backbone (SiO₂), carbon-related materials and polymeric chains have been extensively investigated [12]. Except the above mentioned hosts, the new supramolecular soft matters with high biocompatibility and flexibility have gained much attention [14,15]. Among many smart soft building blocks, alginate, with linear block co-polymers comprised of α -L-gulonate and β -D-mannuronate monomers [16,17], has been used to synthesize biologically active materials which could be applied in the controlled release of drugs, cosmetics, biological catalysis, and enzyme transport in detergents [18,19]. Previous reports demonstrated that bivalent ions of alkaline-earth cations and several transition metal cations, such as Cu²⁺, Ca²⁺, Co²⁺ and Mn²⁺ were employed for the fabrication of metal-assisted gel networks [20–23]. But the use of lanthanide ions to construct the stable alginate-based hydrogels was very limited [24–26].

* Corresponding author at: Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, School of Chemistry and Environment, South China Normal University, Guangzhou 510006, PR China. Tel.: +86 20 39310258; fax: +86 20 39310187.

E-mail address: qmwang@scnu.edu.cn (Q. Wang).

In this work, we have investigated the relationship between alginate structures and lanthanide ions during gelation process. $\text{YVO}_4: \text{Eu}^{3+}$ nanoparticles were incorporated into the soft matrix. Subsequently, Dy^{3+} induced the formation of stable hydrogel beads. Previously we have reported the fabrication of lanthanide phosphor containing polyelectrolyte gels (polyacrylamide and polyacrylic acid) and their templates effects on emission properties [27]. Although the polyelectrolytes were relatively non-toxic, their functional units such as acrylamide might be closely related to toxicological studies and would be carcinogenic and lead to cancers [28]. Especially it could be absorbed through dermal exposure [29]. In general, the residual amounts of monomers might increase the concerns about their risks in health and environment [30]. Therefore, the new design and naturally-derived materials would be expected. Alginate as a suitable polymer was abundant in nature and extracted from brown algae and has been fully explored in numerous biomedical applications due to its high biocompatibility, low toxicity, low cost and easy gelation properties with cations under mild conditions [14,15]. In this case, the utilization of alginate hydrogels as scaffolding materials has been studied. Moreover, it was well accepted that ascorbate as the essential component in food played critical roles in many biochemical channels and it can be found in a wide range of fluids, drinks, drugs and juices [31]. The major strategy for the detection of ascorbate requires electrochemical assay [31] and the search for new alternatives such as redox-active principles will provide more choices for the rational design. Here we reported the detailed studies on chemical structures and photophysical features of the alginate gels. Moreover, this soft matter with intense red emission was specifically responsive to the addition of sodium ascorbate due to redox process. To our knowledge, it would be the first case study of a remarkable effect that ascorbate has on the europium luminescence within hydrogels.

2. Experimental

2.1. Materials

Eu_2O_3 (99.9%), Dy_2O_3 (99.9%) and NH_4VO_3 were purchased from Shanghai Yuelong company (China). Europium nitrate and Dysprosium nitrate were prepared by dissolving Eu_2O_3 and Dy_2O_3 in concentrated nitric acid. Sodium alginate (LVG, 100 kDa, > 65% guluronic acid) and sodium ascorbate were purchased from J&K Scientific.

2.2. Synthesis of $\text{YVO}_4: \text{Eu}^{3+}$ nanoparticle

10 mL $\text{Y}(\text{NO}_3)_3$ (0.1 mol) and 5 mL $\text{Eu}(\text{NO}_3)_3$ (0.01 mol) aqueous solution were mixed, then 10 mL NH_4VO_3 (0.1 mol) was added. It was stirred at room temperature for 30 min at pH=8, then moved into a Teflon bottle held in a stainless steel autoclave, sealed, and maintained at 160 °C for 12 h. When cooled to room temperature naturally, the precipitates were washed with ethanol and deionized water for three times, and dried in air at 80 °C for 12 h.

2.3. Gelation test

$\text{YVO}_4: \text{Eu}^{3+}$ nanoparticle was dispersed in aqueous solution, then $\text{YVO}_4: \text{Eu}^{3+}$ (10^{-5} M) aqueous solution was mixed with 5.0% (w/v) sodium alginate aqueous solution. The hydrogel was prepared by slowly dropping the mixed solution into 0.01 M $\text{Dy}(\text{NO}_3)_3$ 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 ± 0.01 mm). The gelation reaction was proceeded at room temperature for 6 h

at pH=7.0. The fluorescence titration experiments were carried out by adding sodium ascorbate at different concentrations in aqueous solution.

2.4. Characterizations

FT-IR spectra were measured by using a Shimadzu Prestige-21. Scanning electron microscopy (SEM) was measured by using a Zeiss Ultra 55 scanning electron microscope. Fluorescence emission spectra were recorded on a computer controlled HITACHI F-2500 fluorescence spectrophotometer. The X-ray powder diffraction was investigated on a Bruker D8 diffractometer with $\text{Cu K}\alpha$ radiation ($k=0.1541$ nm) in the range of $2\theta=20\text{--}80^\circ$.

3. Results and discussion

Currently, the utilization of metal ions or organic chromophores in controlling luminescence through the establishment of gels has been paid much attention. But the major drawbacks such as short lifetimes and light scattering in biological environment significantly restrict their application in health or medical uses. New alternatives to these transitional metal ions were the preparation of lanthanide based materials with typical line-like emissions. Therefore we have developed several kinds of metal containing hydrogels derived from Eu^{3+} , Tb^{3+} , Ca^{2+} and Dy^{3+} ions. The results demonstrated that the employment of Eu^{3+} (or Tb^{3+}) and Ca^{2+} would lead to translucent gels (Fig. 1). Only by incorporating Dy^{3+} into the host, we were able to achieve regular and transparent hydrogel beads (Fig. 1). In particular, the use of dysprosium ions has a striking effect on the size of the beads. The corresponding hydrogel dimension (ca. 4 mm) is much larger than its counterparts (Eu^{3+} and Ca^{2+} beads, Fig. 1). The variable diameter effect might be related to different affinities of Ca^{2+} , Eu^{3+} and Dy^{3+} . The stronger electrostatic attraction between cationic dysprosium ions and anionic alginate segments would lead to the larger dimensions. These interaction difference may affect the capability of Dy^{3+} to cross-link the alginate functional groups. Consequently, the alginate gelation potentials, as well as the inherent features of gel network would be altered, in this way, the size of the formed beads has been changed.

In view of observation, the combination of Eu^{3+} (or Tb^{3+}) and alginate would exhibit red or green emissions, these signals may severely interfere with the luminescence of $\text{YVO}_4: \text{Eu}^{3+}$. Therefore, we selected Dy^{3+} to trigger the formation of metal assisted hydrogels. The detailed gelling process was given in Fig. 2. When

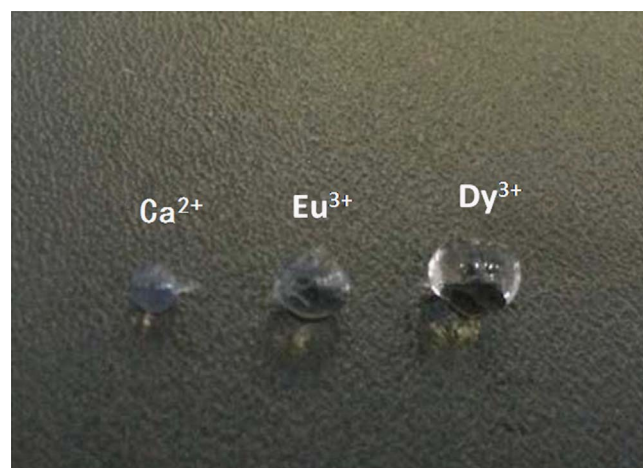


Fig. 1. Digital photos of the hydrogel beads gelling by Ca^{2+} , Eu^{3+} and Dy^{3+} .

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