

Assembly of novel Tb³⁺/Eu³⁺ sensitized cellulose gels and their emission behaviors

Jiansheng Huo · Yuhui Zheng · Shuting Pang ·
Qianming Wang

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Abstract In this paper, a novel luminescent hydrogel was successfully prepared by incorporating Tb-HSA (HSA = Human Serum Albumin) complex into cellulose host. The green luminescence intensities of Tb(III) exhibited *on-off* changes in terms of pH variation. At the same time, europium activated phosphor (GdVO₄:Eu³⁺) was immobilized into the cellulose hydrogels through two approaches. The photophysical properties of luminescent gels with the temperature variation were investigated by fluorescence. The new group of soft materials will display task-specific usages in sensing fields.

Keywords Luminescent · Cellulose hydrogel · pH · Temperature · Lanthanide

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J. Huo · Y. Zheng · S. Pang · Q. Wang (✉)
School of Chemistry and Environment,
South China Normal University, Guangzhou 510006,
People's Republic of China
e-mail: rareearth@126.com; qmwang@scnu.edu.cn

Q. Wang
Key Laboratory of Theoretical Chemistry of
Environment, Ministry of Education,
School of Chemistry and Environment, South China
Normal University, Guangzhou 510006, People's
Republic of China

Introduction

Lanthanide-based luminescent materials have been extensively applied in chemical and biological sensing systems that have aroused tremendous interests during the last decade (Mccoy et al. 2006; Camerel et al. 2006; Fages 2006). Compared to other sensor systems, they have unique properties such as long lifetimes, sharp emission peaks, high color purity, and low long-term toxicity (Mitsuishi et al. 2003; Bünzli and Piguet 2005; Bünzli 2006). However, their emissions in aqueous solution were quite weak due to the coordination with hydroxyl groups. Lately, the lanthanide-containing soft materials were emerging as new topics. They can overcome the above drawback of quenching luminescence in water and a relatively facile synthesis makes them broadly applicable (Binnemans and Gorller-Walrand 2002; Seo and Chang 2005; Mukhopadhyay et al. 2003).

Cellulose hydrogels are composed of three dimensional networks and have played essential roles in life science, biological processes and industrial treatment (Chandra and Rustgi 1998; Klemm et al. 2005; Zhou et al. 2007; Kadokawa et al. 2009). The unique polymeric gels have elongated fibrous aggregates with nanometer-scale diameters and micrometer-scale lengths that cross-link into 3D networks. Thanks to its structural properties, they are considered as the excellent hosts for the fabrication of luminescent soft material.

Human Serum Albumin is considered as a primary protein in human body and widely used in cell culture

(He and Carter 1992). In this article, the luminescent cellulose hydrogels (Fig. 1) containing a novel luminescent rare-earth complexes Tb-HSA was prepared through a “one step” method. Until now, this is the first time that the terbium-protein complex was doped into soft matter and their sensing effects were investigated. Interestingly, Tb(III) emission has a good response to the pH change that could be clearly detected in the fluorescence spectra. In order to explore its application in a broad color range, the red emissive europium phosphors ($\text{GdVO}_4\text{:Eu}^{3+}$) were also incorporated into the cellulose hydrogel by way of two different methods and the luminescence properties were extensively studied. Surprisingly, the emission intensity was found to increase with elevated temperature in the range of 10–70 °C. Understanding the gelation of thermo-sensitive or acidic-sensitive hydrogels will establish a new platform in their usages for many important processes such as cell therapy and protein delivery (Lee et al. 2010). Consequently, we successfully obtained novel type of responsive materials with recognition capacities to temperature and pH variation.

Experimental

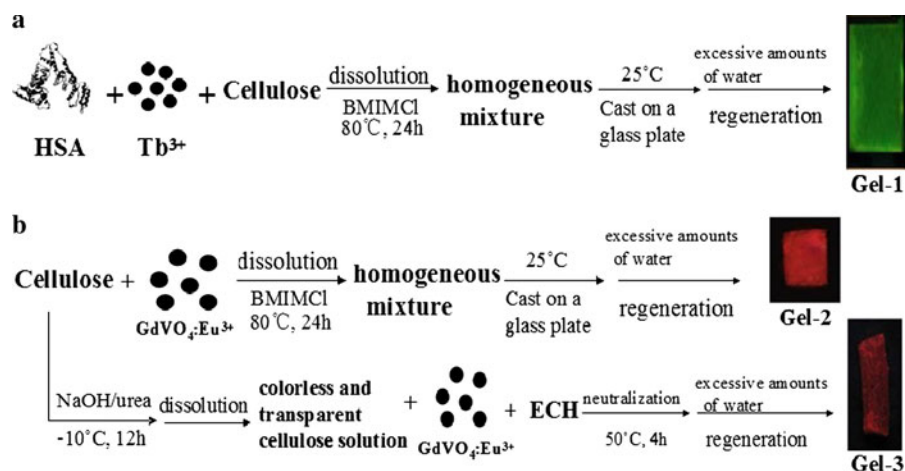
General

Microcrystalline cellulose (refined wood pulp) powder provided by Aladdin Chemistry Co. Ltd was used as the starting reagent. The average molecular weight was determined to be 7.34×10^4 by gel permeation

chromatography (GPC, Waters-ALC-244) according to the reference method (Tang 2000). Analytical grade chemicals of HSA, RE_2O_3 (RE = Gd, Eu, Tb; purity 99.9 %) were purchased by Aladdin Chemistry Co. Ltd. All the other reagents were used as received. Fluorescence spectra were measured with Hitachi F-4500 spectrophotometer with a 150 W xenon lamp as light source. The scan speed was fixed at 300 nm/min. Both the excitation and emission spectra were corrected for the instrument response variations. FT-IR spectra were measured within the 4,000–400 cm^{-1} region on an infrared spectrophotometer Prestingge-21 with the KBr pellet technique. The crystal structures were characterized by means of X-ray diffraction (XRD Y-2000 of Dandong Aolong company, PR China). All of the samples, pre-treated with freeze-drying to remove all the solvents, were characterized by scanning electric microscopy (SEM).

The method used for the synthesis of cellulose gel based on ionic liquid was similar to the literature (Kadokawa et al. 2009). Luminescent cellulose hydrogel containing Tb-HSA hybrid materials was prepared by in situ synthesis. In this typical procedure, $\text{Tb}(\text{NO}_3)_3$ were obtained by dissolving Tb_2O_3 in nitric acid. HSA (50 mg), $\text{Tb}(\text{NO}_3)_3$ (5 mg), cellulose(300 mg) and 1-butyl-3-methylimidazolium chloride (BMIMCl, 1.5 g) were added into the tube consecutively. The mixture was heated at 80 °C to obtain a homogeneous transparent viscous material. The hot viscous material was carefully decanted on glass plates into a thin layer. After the thin layer cooled to room temperature, the excessive BMIMCl was removed by washing with adequate water. Then the transparent cellulose hydrogel film was obtained

Fig. 1 Schematic representation of luminescent cellulose hydrogel



(Kadokawa et al. 2009). For the comparison purpose, the reducing amount of BMIMCl (0.6 g) was also used to prepare the corresponding gel that had been studied by SEM. Gel-2 was prepared by replacing Tb-HSA with $\text{GdVO}_4\text{:Eu}^{3+}$ according to the synthesis of Gel-1. In order to determine the terbium concentration, the gel (the freeze-dried hydrogel) was dissolved in concentrated nitric acid and the resultant solution was titrated by ethylenediaminetetraacetic acid (EDTA) using xylenol orange as the indicator (Yang et al. 1989). The concentration of terbium ions in the dried gel was determined to be 1.2 % (mass ratio).

The method used for the synthesis of cellulose gel containing europium activated phosphor ($\text{GdVO}_4\text{:Eu}^{3+}$) based on NaOH/urea conditions (Gel-3) was modified by the recent publication (Zhou et al. 2007). The phosphor was synthesized by a co-precipitation method (Su et al. 2005). First, Gd_2O_3 and Eu_2O_3 were dissolved in concentrated HNO_3 upon heating treatments. Then the rare earth nitrates $\text{Gd}(\text{NO}_3)_3$ (2 mmol) and $\text{Eu}(\text{NO}_3)_3$ (0.1 mmol) were added together and mixed homogeneously. 2 mmol of NH_4VO_3 dissolved in 30 mL H_2O was added in the above sample and the whole solution was vigorously stirred. The pH was adjusted to 7.0 using $\text{NH}_3\cdot\text{H}_2\text{O}$ solution. The obtained precipitate was separated by centrifugation and washed with deionized water and ethanol twice. Finally, the as-derived solid was dried in vacuum at 80 °C for 4 h before usage.

6 wt% NaOH (6.5 g), 4 wt. % urea (4.5 g) and deionized water (100 mL) were put into a 250 mL beaker. Then, cellulose (3 g) was added into the above solution. The whole mixture was ultrasonicated (200 W) for 1 h. The sample was stored in a refrigerator (−5 °C) for 20 h. Colorless and transparent solution was achieved at room temperature after the solid was thawed. It was subjected to centrifugation at 7,000 rpm for 10 min to remove the un-dissolved samples. In the above solution (20 mL), 1.5 mL epichlorohydrin (ECH) was added, then $\text{GdVO}_4\text{:Eu}^{3+}$ (10 mg in 500 μL water) was dropped into the mixture and stirred for 2 h at 60 °C. The reacted sample was neutralized with 5 wt. % H_2SO_4 and then washed with adequate water three times. So cellulose hydrogels assembled by luminescent species were taken out and stored for further testing. Regenerated cellulose was derived from cellulose/NaOH/urea mixed solution by coagulating with 5 wt. % H_2SO_4 .

Results and discussion

The FT-IR spectra were shown in Fig. S1 for ligand HSA(a), Tb-HSA(b) and Gel-1(c) respectively. The amides I and II bands of protein were located at $1,670\text{ cm}^{-1}$ (C=O stretching vibrations of carbonyl groups) and $1,540\text{ cm}^{-1}$ (C–N stretching vibration couple with N–H bending modes) and they were correlated with structural changes in proteins (Pelton and McLean 2000). Due to the introduction of terbium ions and the formation of the complex, it showed that the peak position of amide I shifted from $1,670$ to $1,642\text{ cm}^{-1}$. In addition, amide II bands also shifted from $1,540$ to $1,405\text{ cm}^{-1}$ (Fig. S1). Before the encapsulation, the pure cellulose hydrogel gave the characteristic signals located at $3,420$, $2,920$ and $1,640\text{ cm}^{-1}$ respectively (Chang et al. 2009). After the immobilization of terbium protein complex, the stretching vibration of hydroxyl groups at $3,420\text{ cm}^{-1}$ shifted to $3,430\text{ cm}^{-1}$ and the band became narrower than the neat sample, suggesting that hydrogen bond interactions in the pure gel had been weakened due to the introduction of the complex (Li et al. 2009) (Fig. S2).

In this report, we tried to use two independent approaches (ionic liquid and NaOH/urea methods) to synthesize Tb(III) or Eu(III) activated cellulose gels. The assembly of Tb-HSA cellulose gel through the cross-linker ECH failed because the green emissions disappeared under the basic environment. Therefore, we carefully investigated the characteristic physical properties of the luminescent cellulose hydrogels based on ionic liquid method (1-butyl-3-methylimidazolium chloride). The curve in Fig. 2 showed the excitation spectrum ($\lambda_{\text{em}} = 545\text{ nm}$) and emission spectrum ($\lambda_{\text{ex}} = 249\text{ nm}$) of Gel-1 at room temperature. The excitation spectra exhibited a broad band between 220 and 400 nm with the maximum peak at 249 nm, while the emission spectra exhibited the narrow bands from $4f \rightarrow 4f$ transitions within Tb^{3+} ions in the region of 450–650 nm. It was clearly seen that there were four obvious bands at 489 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_6$), 545 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_5$), 585 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_4$) and 624 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_3$). $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition was the most prominent one, showing the typical green emission of terbium(III). Furthermore, the pH variation responsive ability of Gel-1 were studied by measuring the changes of the Tb(III) emission ($\lambda_{\text{ex}} = 249\text{ nm}$). As shown in Fig. 3, fluorescence intensity sharply

decreased at pH 4.0, then it remained to be relatively stable less than pH = 3.0. Figure 4 shows the pH dependent variation of the emission intensity at $\lambda_{\text{em}} = 545$ nm. It has been found that the increasing pH value also did not affect the resultant green emissions. Although the drawback of this sensor had the narrow dynamic range compared to the literature (Lin et al. 2000; Niu et al. 2005), it had terbium long lifetime photoluminescence which generally falls in the range of micro-seconds and mille-seconds that can eliminate interference signals (Li and Selvin 1995). More interestingly, it had enough photostability and can be repeatedly used. When pH value shifted from 3.0 to 4.0, the luminescence could be recovered after 5 cycles (Fig. 5). This result indicated that the luminescence changing behavior may be applicable in the design of pH-dependent “on–off” switchers.

As far as the internal structures were concerned, the published papers reported that the solvents or temperature would result in the rearrangements of the packing modes in cellulose matrices (Gavillon et al. 2008; Adel et al. 2010). Accordingly, we studied the effects of ionic liquid concentration on the morphology. At lower concentration of 1-butyl-3-methylimidazolium chloride (0.6 g), the diffusion of particles appeared and all the components were agglomerated (Fig. S3). Under the direction of increasing amount of BMIMCl, numerous fibers bundles with relatively smooth surface were the most commonly observed organizations with low size distributions (Fig. 6a). Similar fiber bundles with highly compact structures could be

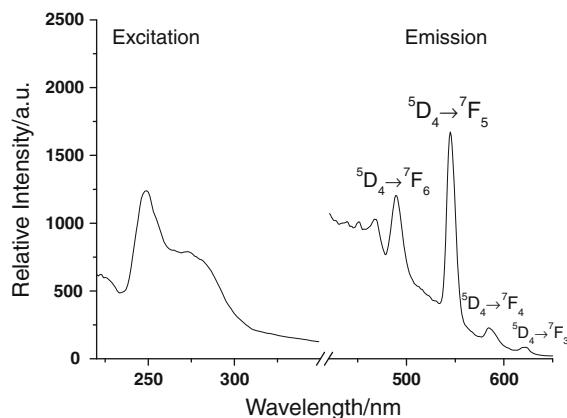


Fig. 2 Excitation ($\lambda_{\text{em}} = 545$ nm) and emission spectra ($\lambda_{\text{ex}} = 249$ nm) of Gel-1

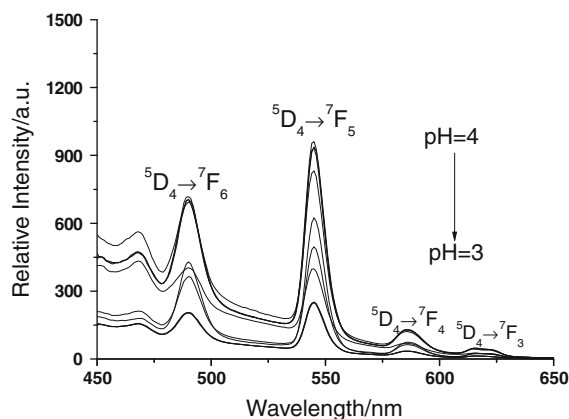


Fig. 3 Emission spectra of Gel-1 ($\lambda_{\text{ex}} = 249$ nm) between pH = 3 and 4

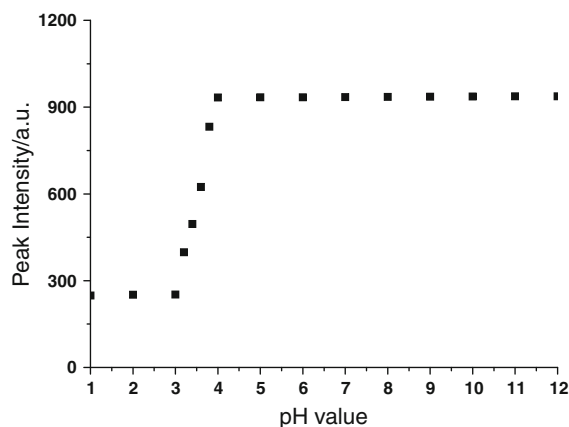


Fig. 4 Correlation between emission peak intensities at 545 nm and pH values (pH = 1–12)

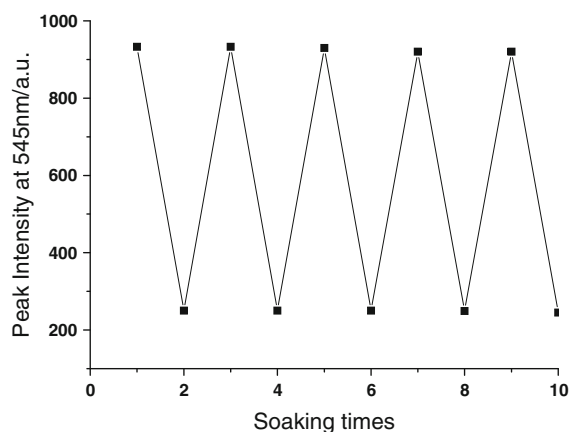


Fig. 5 Emission peak intensities of Gel-1 by alternative soaking with acid and base, data in odd and even numbers refer to the values after basic and acidic treatments respectively. Peak intensities were recorded at 545 nm

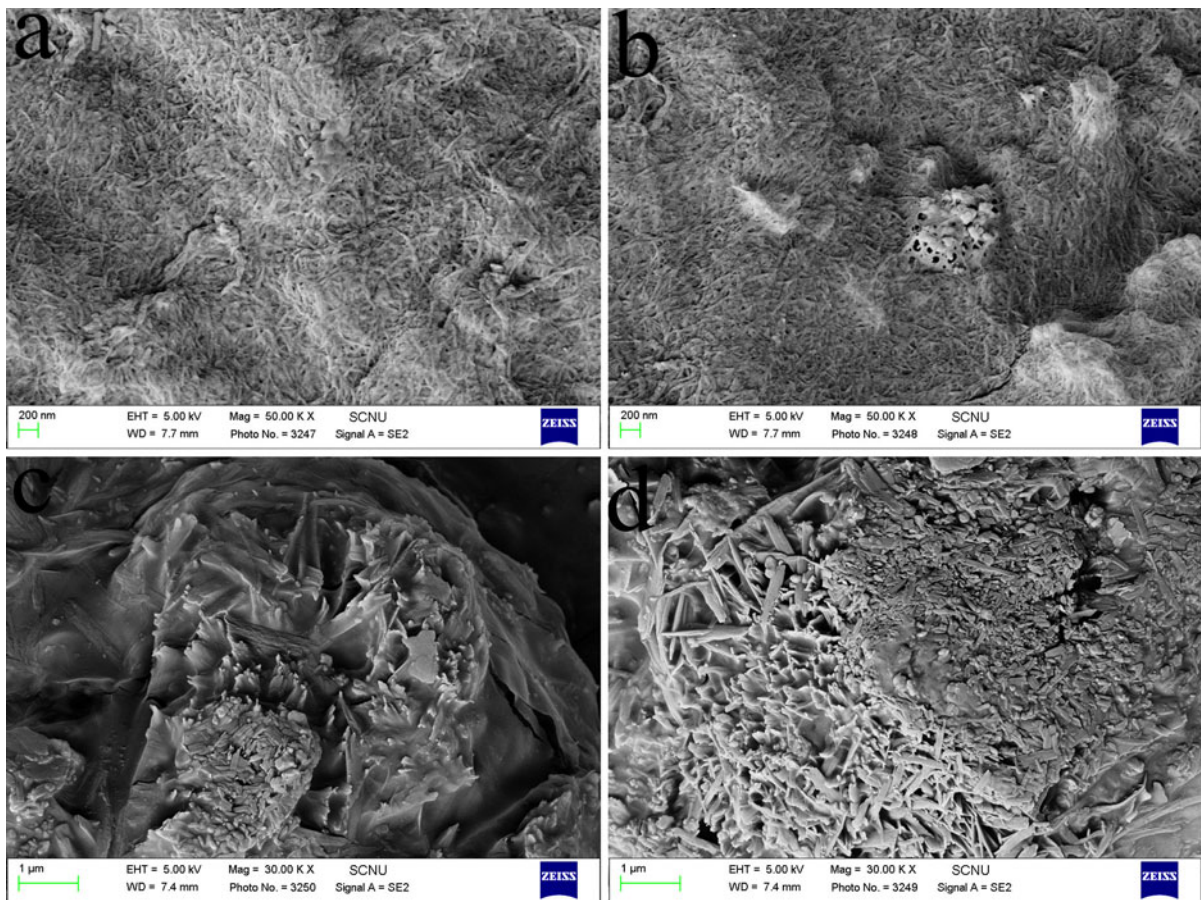
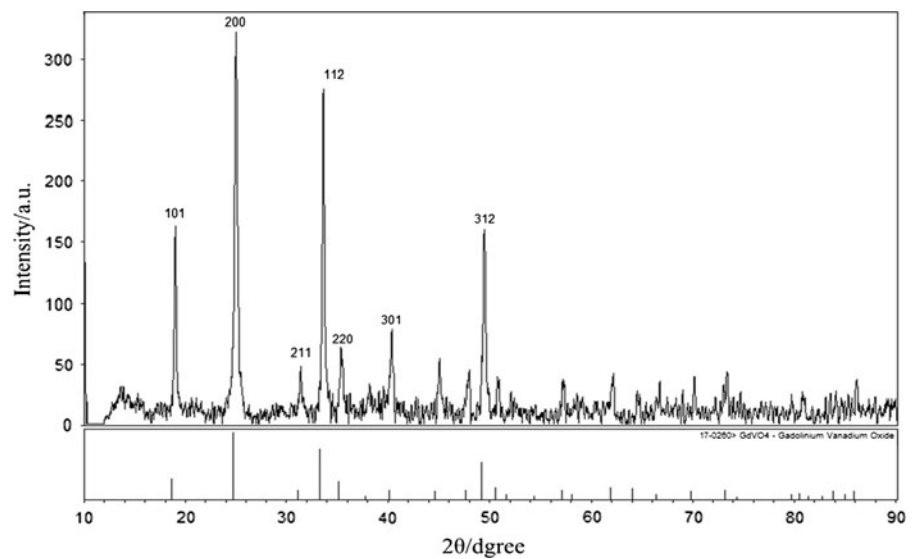


Fig. 6 Morphology of luminescent cellulose hydrogels. **a** SEM images of Gel-1, **b** SEM images of Gel-2, **c** and **d** SEM images of Gel-3

Fig. 7 XRD pattern of $\text{GdVO}_4:\text{Eu}^{3+}$



obtained when Tb-HSA complex was replaced by the phosphor $\text{GdVO}_4\text{:Eu}$ 5 % (Fig. 6b). But if we used epichlorohydrin, the 3D network with high roughness was achieved (Fig. 6c, d). The images showed that the nanocrystals tended to aggregate into rods or columns. So the changes in morphologies maybe related to specific template directing property and assembly features of the phosphors in cellulose.

For the case of europium doped systems, we successfully prepared hybrids by introducing the Eu^{3+} activated phosphors ($\text{GdVO}_4\text{:Eu}^{3+}$) into cellulose hydrogel by different methods. The crystal structure of $\text{GdVO}_4\text{:Eu}^{3+}$ was examined by X-ray powder diffraction (XRD). From Fig. 7, the XRD data were consistent with the standard card of JCPDS17-0 260, suggesting the obtained samples crystallized well and have the ZrSiO_4 structure. No obvious diffraction peaks of impurities were detected. At room temperature, the excitation spectra of Gel-2 and Gel-3 showed the similar features. By monitoring the emission peak at 618 nm, both of them had a broad band between 220 and 350 nm in Fig. S4. Upon the excitation at 280 nm, the spectra displayed the electronic transitions from $^5\text{D}_0$ of Eu(III) to $^7\text{F}_j$ ($j = 1, 2, 3$ and 4) levels. The primary band $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (electric dipole transition) located at 618 nm showed pure red luminescence, indicating the europium ion occupies a site without an inversion center (Ferhi et al. 2009) (Fig. 8). Moreover, it was clearly seen that Gel-2 had much higher emission than Gel-3. This result indicated the particles morphological properties would have certain influence on the resultant photoluminescence. The published work proved that organized structures led to new emissions in the longer wavelength within the polymeric network (Surin et al. 2004). Here in our report, it was found that well-defined and highly compact structures (Gel-2) may restrict the unexpected scattering and reflections and contribute to the luminescence enhancement. The coarse surfaces and non-organized structures in Gel-3 would easily interfere with the optical features.

In fact, cellulose derivatives incorporated by various fluorescent additives have already been paid much attention in view of their optical applications (Chang et al. 2009; Karakawa et al. 2007). However, the reported quantum dots or organic dyes have broad band emissions and short excited lifetimes. The trivalent lanthanide ions with their forbidden 4f shells have gained several advantages over other fluorescent

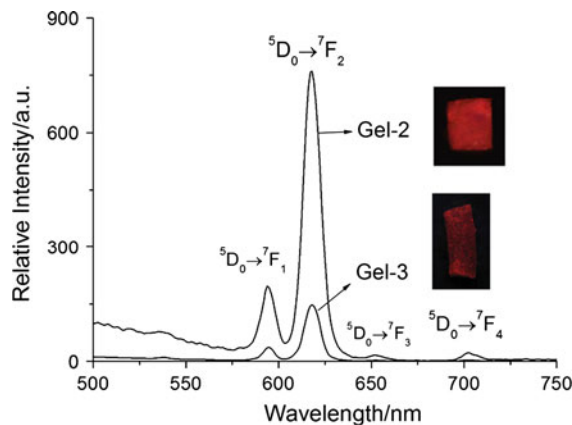


Fig. 8 Emission spectra ($\lambda_{\text{ex}} = 280$ nm) of Gel-2 and Gel-3. Inset photos Gel-2(up) and Gel-3(down) excited by UV light at 254 nm

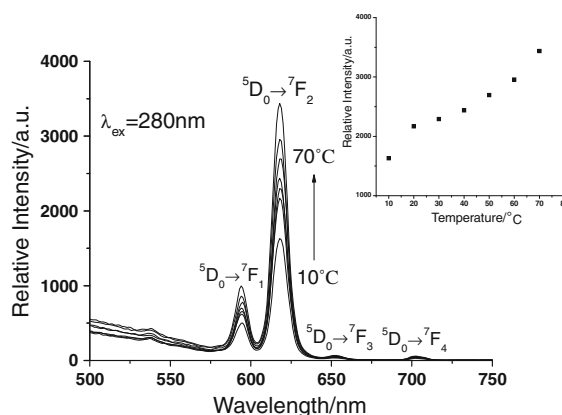


Fig. 9 Temperature dependence of the emission intensity of cellulose/ $\text{GdVO}_4\text{:Eu}^{3+}$ + composite hydrogels ($\lambda_{\text{ex}} = 280$ nm). Inset: Peak intensities at 618 nm versus temperature changes

systems. Their long lived excited states and narrow line emissions would allow them to minimize the influence of auto-fluorescence and noise signals (Park 2000).

The temperature dependence of the Gel-2 was studied in terms of photoluminescence changes. The fluorescence intensity ($\lambda_{\text{ex}} = 280$ nm) increased upon heating treatments ($10^\circ\text{C} \rightarrow 70^\circ\text{C}$, 5°C/min , water-retention rate 85 % at 70°C) (Fig. 9). This intriguing result would be significant in industrial uses for the design of new temperature sensor. The reason for the variation of emission intensity could be explained as follows: evaporation of water in hydrogels due to the elevated temperature would weaken the coordination bonds between hydroxyl groups (H_2O) and lanthanide

ions, therefore, partial emissions from Eu(III) ions were recovered as the result of the released solvent molecules.

Conclusions

In the present research, cellulose was compounded with Tb-HSA complex affording a composite material that featured green luminescence. Unexpectedly, we found reversible *on-off* switch signal changes based on pH variation. In europium (III) series, the luminescent hydrogel was prepared by embedding the GdVO₄:Eu5 % powder into the soft host by two different methods. Interestingly, the Eu(III) emission in hydrogel gave a distinguished enhancement with the increase of temperature. Consequently, these novel findings demonstrate the lanthanide luminescent cellulose hydrogels as appealing soft matters will find potential applications in a wide range of fields.

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