Shutter luminous fibres based on rare-earth materials for real-time thermal response

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Abstract

Rare earth luminescent materials (RELMs) are commonly used in optics and products intended for safety and decoration. However, there is still a great challenge to alternate the emission performance after the RELMs are activated. In this work, a novel shutter luminous fibre (SLF) was developed using a water-spin method with polyacrylonitrile (PAN) as the filament material. The emission performance of the RELMs SLFs could be alternated at near-ambient temperatures. A heat-sensitive thermochromic pigment composed mainly of 7-Anilino-3-diethylamino-6-methyl fluoran (TF-BL1) served as the shutter material. The emitting properties, shielding effect, and the temperature response behaviour of RELMs SLFs with primary colour-emitting properties (Sr2ZnSi2O7: Eu3+, Dy3+; SrAl2O4: Eu2+, Dy3+; and Y2O2S: Eu3+, Mg2+, Ti4+) were investigated. The quinoid structure of TF-BL1 blocked the light of primary colours at low temperatures. At high temperatures, the lactone structure of TF-BL1 allowed the light of the RELMs to emit. SLFs with real-time responding behaviour have great potential as electronic skin in soft robotics, flexible electronics, and camouflage applications.

1. Introduction

In nature, alternating luminescence is a useful skill for survival. Animals attract prey, deter predators, and attract mates by luminescence. These animals inspire us. For example, displays change colour and light to communicate information in human-machine interfaces [1]. Functional fibres that respond to ambient stimuli such as mechanical force, electricity, and temperature are gathering growing scientific and commercial interest [2, 3]. Smart luminous fibres that exceed human expectations have been widely researched because of their ability to display invisible signals [4]. Therefore, luminous fibres find applications in smart clothing and wearable devices.

Inorganic phosphor is very important luminescent material which has widely used in electroluminescence and photoluminescence [5–7]. Rare earth luminescent materials (RELMs) have attracted great interest because they can emit light for a long time after being excited by ultraviolet (UV) radiation [8, 9]. RELMs are outstanding materials with a high energy efficiency ratio. Because of their excellent initial brightness and long afterglow, Sr2ZnSi2O7: Eu3+, Dy3+ (SZSO); SrAl2O4: Eu2+, Dy3+ (SAO); and Y2O2S: Eu3+, Mg2+, Ti4+ (YOS) are the most widely used RELMs to obtain blue, green, and red light, respectively [10–14]. The afterglow of YOS can be detected by the human eye for nearly 3 h after a few minutes of excitation [15]. However, the decay time of YOS is shorter than those of SZSO and SAO. The europium ion is usually treated as an activator in semiconductor materials owing to the special electronic structure of rare earth ions [16–18]. Alkaline earth metal oxide materials are endowed with long-lasting luminescent properties by co-doping with dysprosium ions or any other metal ions [19, 20].

There are several ways to trigger luminescence. RELMs can be easily excited under light exposure (e.g., sunshine and UV light). However, once activated, RELMs continue to shine until their eventual decay.
Alternatively, luminescence can be triggered using electricity switches, such as in electroluminescence. However, conventional electroluminescence requires a solid non-flexible power source to be maintained. Therefore, the conventional electroluminescence strategy is not suitable enough for soft and flexible applications such as wearable devices. In several cases, heat is used to directly trigger luminescence, e.g., a heat lamp filament to incandescence. Nevertheless, a thermal-radiation-activated light also requires a solid power source and is a low energy efficiency ratio strategy that generates unbearable heat.

Systems based on thermochromic pigments operating in RELMs are a new strategy to alternate luminescence. Using this strategy, luminescence hidden in a thermochromic soft matrix and heat can trigger the luminescence without a hard power source. The three components of thermochromic pigments include fluoran (7-Anilino-3-diethylamino-6-methyl fluoran) as a colourant, weak acids as the developer, and alcohols as the solvent [21]. These can be mixed to form a reversible thermochromic system [22]. Colour change is driven by the interactions between these components. The developer is an electron acceptor compound, such as bisphenol A and phenols [23]. Typically, the complex is coloured because the fluoran dye has a quinoid structure below the melting point of the solvent. Colour change always occurs at the melting temperature of the solvent [24]. When the solvent melts, the dye-developer complex is destroyed, and the fluoran dye changes to the lactone structure and the system acquires the natural colour [12]. Such a reversible thermochromic system can be encapsulated in a polymer envelope to form a microcapsule which was used as a pigment [25].

In this study, we used a commercial heat-sensitive pigment (TF-BL1) to prepare shutter luminous fibres (SLFs) and studied the influence of TF-BL1 on the luminescence of RELMs in polyacrylonitrile. The microstructure and crystal structure were analysed to determine the basic properties of the SLFs. Absorptivity and emission spectra were analysed to demonstrate the real-time thermal response performance of the SLFs.

2. Materials and methods

2.1. Preparation of SLFs

Polyacrylonitrile (PAN) was purchased from Shaoxing Gimel Advanced Materials Technology Co., Ltd (Shaoxing, China). Dimethyl sulfoxide (DMSO) was purchased from Sinopharm Chemical Reagent Co., Ltd, (Shanghai, China). Commercial Heat Sensitive Black (TF-BL1, with thermochromic temperature of 27 °C, and composed mainly of 7-Anilino-3-diethylamino-6-methyl fluoran) was purchased from Shenzhen Aobo Co. Ltd. TF-BL1 was added to a homogeneous PAN/DMSO spinning dope used as the spinning solution. Wet spinning was carried out using a syringe (needle type: 22 G) and a boost device. The prepared spinning solution was injected into water at room temperature (20 °C–25 °C) at an injection speed of 4 ml min⁻¹ to obtain the SLF. The ratio of PAN/DMSO was 20%w/v. The ratios of TF-BL1 to the PAN/DMSO spinning dope used 1%w/w, 3%w/w, and 5%w/w, and the samples were labelled as SLF 1, SLF 3, and SLF 5, respectively. SZSO, SAO, and YOS were uniformly mixed with the PAN/DMSO spinning dope at a ratio of 10%w/w. The preparation of RELMs was according to the conventional high temperature solid state method described elsewhere [17].

2.2. Characterisation

The microstructures of the SLFs were examined using a Hitachi TM3030 scanning electron microscope. The emission spectra were obtained using a fluorescence spectrophotometer (FS5 Fluorescence Spectrometer, Edinburgh Instruments). The samples were excited at a wavelength of 365 nm for 5 min using a handheld ultraviolet lamp (20 W) before the tests; the slit was 2 nm wide; the excitation wavelengths were in the range of 400–700 nm; the dwell time was 0.2 s. X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Advance (Germany). Absorptivity of the samples was deduced from reflectivity measurements using a Macbeth colour-Eye 7000A spectrophotometer. Differential scanning calorimetry (DSC) was performed using a TA Q200 (US).

3. Results and discussion

3.1. SLF concept

Because SZSO, SAO, and YOS can match diverse colours via trichroism [10], the basic concept of the SLFs was described by demonstrating their shield effect. Figure 1(a) shows the SLF after irradiation with UV light and illustrates the concept of ‘block’ luminescence with a thermally triggered SLF. TF-BL1 and RELMs can be easily added to the polymer to create a soft composite fibre. TF-BL1 effectively blocks most of the luminescence from exiting the composite fibre. Heating the SLF triggers TF-BL1 to transform the structure. Thus, luminescence is allowed to visualise. It behaves like an optical ‘shutter’. Consequently, shutters can be triggered via heat transfer, including at human body temperatures. Many fields, such as soft robotics, wearable devices, and e-skins, could
benefit from alternated coloration for more effective light-based signalling and optical adaptation [1, 26, 27].

Figure 1 (a) also shows the ingredients of the SLFs and explains their working principle.

PAN is an ideal material to load the RELMs and TF-BL1 because of its handleability and simple spinning process. RELMs and TF-BL1 were mixed in PAN to prepare the SLFs. The RELMs and TF-BL1 spinning solutions were extruded from the syringe needle. The resulting SLF was drawn into water following the gravity direction. Figure 1 (a) depicts the shutter effect of the SLFs in both the closed and open states. TF-BL1 worked as a shutter to shield the light. The quinoid structure of TF-BL1 was black with high visible absorption (figure 1 (b)). Luminescence was hidden in the black pigment matrix. Heating led to TF-BL1 opening the shutter, resulting in a change in the luminescence. The lactone structure of TF-BL1 was white with low visible absorption (figure 1 (b)). The emission spectra of the SZSO, SAO, and YOS SLFs are shown in figure 1 (c). Our results showed that TF-BL1 is an efficient light shielding agent that can absorb the emission of SZSO (peak at 480 nm), SAO (peak at 520 nm), and YOS (peak at 626 nm). The advantage of using tricolour systems is to form several colours. The results above demonstrate the effect of TF-BL1 on SZSO, SAO, and YOS.

The reversible thermochromic system was encapsulated in a polymer envelope to form a microcapsule which was used as a pigment [25]. The microcapsules (figure 2(a)) enable the solid–liquid thermochromic system to stay as a solid powder during heating. Therefore, luminescence transmits out of the SLFs.

3.2. Microstructure and crystal structure
The SEM images of the TF-BL1, SZSO, SAO, and YOS SLFs are shown in figures 2(a)–(d). Most of the spherical TF-BL1 microcapsules had diameters <5 μm. The type of RELM showed little effect on the morphology and dimensions of the SLFs. The SZSO, SAO, and YOS SLFs had a uniform and regular cylindrical shape with diameters of ~400 μm (figures 2(b), (c)). Few particles were exposed on the fibre surface, forming nodules, whereas most of them remained buried in the PAN. This arrangement is advantageous to obtain the shutter structure.

Figure 2(e) shows the XRD patterns of the SLFs, RELMs, and TF-BL1. The diffraction peaks of SZSO, SAO, and YOS can be indexed well to tetragonal, monoclinic, and hexagonal crystal systems, with space groups P-421m, P2/m, and P-3m1. The result was in good agreement with the data from the standard Joint Committee on Powder Diffraction Standards (JCPDS) cards. This indicates that the rare earth ions only occupy the chemical substitutional sites of Sr2ZnSi2O7, SrAl2O4, and Y2O2S. However, this occupancy does not disturb the crystal structure. The characteristic peaks of TF-BL1 and RELMs can be found on SLFs, indicating that the crystal
phases of TF-BL1 and RELM were not destroyed during the milling and spinning process. TF-BL1 and RELMs retained their crystal structures in PAN.

3.3. DSC of SLFs

The DSC curves of the SLFs and TF-BL1 are shown in figure 3 to demonstrate the influence of temperature on the phase in the fibre. The endothermic peak of SLFs close to 27 °C corresponds to the phase change of TF-BL1. This peak arises from the melting of the solvent and represents thermochromism [21].

The endothermic peak intensity is directly related to the TF-BL1 content. The curve for the thermochromic pigment showed that the solvent began melting at 25 °C and was completely melted at 35 °C. Additionally, the melting temperature of the solvent matched the thermochromic temperature.

3.4. Thermochromism performance of SLF

To evaluate the thermochromism performance of the SLFs, we placed a roll of SLF (SZSO SLF 3) into water at 35 °C and recorded the experimental phenomenon to demonstrate the brightness real-time temperature response (figure 4 and supplementary video S1 is available online at stacks.iop.org/MRX/7/095702/mmedia).

In the surrounding air, the fibres were black and showed higher absorptivity than the white fibres obtained when submerged in water (figure 4(a)). This indicates that the shutter is easy to alternate, and the rate of colour change is fast. Figure 4(b) shows the absorptivity of the SLFs when the shutter is both open (25 °C) and closed (35 °C). When the shutter is closed, TF-BL1 absorbs all wavelengths of visible light. In this case, the
luminescence was turned off. TF-BL1 becomes white after sufficient heating (35 °C), and then the shutter is turned on. The absorption of TF-BL1 decreased significantly, which indicates that temperature can trigger a switch between two different colours (black and white). Absorption of SLFs decreased with increasing TF-BL1 concentration, which can also be seen from the images of the SLFs in figure 4(a). The colour of SLF 1 was lighter than that of SLF 5. The luminescence in the black ‘shutter’ is either on or off. Colour changing requires heat to trigger. Therefore, the SLFs were able to switch invisible heat signals to visible signals (colour and luminescence).

3.5. Luminescence performance of SLFs
To evaluate the luminescence performance of the SLFs, we placed the SZSO, SAO, and YOS SLFs into water at 35 °C under darkness and recorded the results (figure 5 and supplementary video S2). In surrounding air, the shutter of the SLFs was closed. Most of the light from the RELM was blocked in the fibre. When the SLFs were immersed in water heat transfer occurs. The lactone ring of TF-BL1 was closed (figure 1(a)), and the visible light absorption drastically increased. While the heat-triggered shutter was active, the SZSO, SAO, and YOS SLFs emitted blue, green, and red luminescence, respectively (the luminescence colour depends on the type of RELM). Figures 5(b)–(d) show the emission spectra of the SZSO, SAO, and YOS SLFs. The spectra were obtained at 25 °C and 35 °C. Figure 5(b) shows the emission spectra of the SZSO SLFs. The emission peak at 470 nm is generated by the electronic transition of Eu3+ from 7Fj to 5D1. The emission peak of Dy3+ was not observed, since trivalent dysprosium does not act as a luminescence centre in SZSO.

The emission spectra of the SAO SLFs are shown in figure 5(c). The 520 nm emission peak is the characteristic peak of SAO [28]. The peak of SAO are generated by the representative 5Fl → 5D1 transition from Eu2+. The Dy3+ ion is the co-doping ion that acts as a trap to improve the afterglow. The emission spectra of the YOS SLFs are comprised of several significant emission peaks. These emission peaks are generated from 5D0 → 7Fj (j = 0, 1, 3, 4), 5D1, and 5D2 → 7Fj (j = 0, 1, 2, 3, 4) transitions of Eu3+, and the 5D0 → 5F2 transition of Eu3+. There are no emission peaks of co-doped ions (Dy3+, Mg2+, and Tr4+) because co-doping ions only generate traps to improve afterglow (figure 5(d)). The afterglow decay curves of SZSO, SAO, and YOS were given in supplementary figure S1 to demonstrate long lasting properties of RELMs and SLFs. The results show that SLFs can keep shining for more than 3 h after excited.

The emission spectra show that TF-BL1 has a significant blocking capacity for trichromatic RELMs. Theoretically, the central carbon atom of the spiro forms sp3 hybrid orbitals with other carbon atoms. Therefore, the absorption of fluoruran occurs in the ultraviolet band and the white lactone structure is obtained at 35 °C. After cooling (25 °C), the fluoruran as a proton donor loses the donor and the opened lactone ring transforms into an sp2 hybrid orbital. The enhancement of conjugation causes the absorption spectrum to redshift to the visible band (figure 6) [29]. This indicates that TF-BL1 well serves as an optical mask and light alternate. The emission spectra of the SLFs demonstrated that TF-BL1 did not shift the emission spectra of the RELMs. However, TF-BL1 formed a shutter to alternate the intensity of luminescence. When TF-BL1 has a significant heating, the emission intensity was stronger than that at 25 °C. The luminescence could be easily transmitted by the lactone structure of TF-BL1 because the absorption of TF-BL1 decreased with the reduction of conjugated degrees. The SLFs showed an alternating luminescent capacity, which could be triggered by relatively small amounts of heat. TF-BL1, as a black fluoruran, has better luminescence blocking performance than the other fluoruran compounds [30]. The luminescence blocking effect was affected by the concentration of TF-BL1. The luminescence intensity decreased.

Figure 4. Images of the SZSO SLFs and its thermochromism performance (a). Absorption curves of TF-BL1 SLFs (b).
when the concentration of TF-BL1 increased. Additionally, figure 6 shows the blocking luminescence mechanism. TF-BL1 can form dense shades, such as the shutter of a window. The concentration of TF-BL1 was highly relevant to the density of shades, suggesting that higher concentrations of TF-BL1 can form a denser shade shielding tier.

4. Conclusions

This work introduced RELM SLFs, which can be used as a temperature label. The SLFs were composed of SZSO, SAO, and YOS, PAN, and TF-BL1. RELMs formed uniform dispersions in SLFs, and the crystal structure of
TF-BL1 was stable after water spinning. The DSC results indicate that SLFs could change their colours at 27 °C. However, the thorough colour change occurred at 35 °C. The SLFs were black at 25 °C because the quinoid structure of TF-BL1 can block the light of primary colours at low temperatures. At high temperatures, the lactone structure of TF-BL1 allowed the light of the RELMs to transmit out. Therefore, the heat-induced chemical structure change of TF-BL1 allowed the visual response of the SLFs to external temperature. Furthermore, the temperature-dependent colour change of the SLFs is a promising tuneable ‘shutter’ property. The incorporation of TF-BL1 and RELMs enables the SLFs to serve as a real-time label for temperature sensing applications by transforming the information from heat to a visible signal. The concept of SLFs is particularly interesting because it enables alternate over luminescent materials. After the initial UV excitation, the SLFs shined without external equipment for several hours. Therefore, the RELMs SLFs can potentially be used as e-skins in soft robots, prosthetics, and wearable devices.

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