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# Self-cleaned photoluminescent viscose fabric incorporated lanthanide-organic framework (Ln-MOF)

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## ABSTRACT

Photoluminescent textiles emitted light in ultraviolet (UV)-radiation region has advanced a variety of applications including military and police clothes. The current study reports the preparation of photoluminescent viscose fabrics incorporated lanthanide metal-organic framework (Ln-MOF) and their applications for self-cleaning. In situ growth of Ln ($Eu^{3+}$, $Tb^{3+}$) MOF into viscose fabrics were achieved using Ln $(NO_3)_3$ and 1,2,4,5-benzenetetracarboxylic dianhydride as organic ligand. The in-growth Ln-MOF within fabrics were characterized using X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscope, energy dispersive X-ray, and fluorescence spectroscopy. Under the UV lamb (345 nm), Eu-MOF@viscose fabric and Tb-MOF@viscose fabric visually emitted red and green color, respectively. The excitation-emission spectra showed the spectra for the $^5D_0 \rightarrow {}^7F_{0\text{-}4}$ transitions and $^5D_4 \rightarrow {}^7F_5$ transitions in case of Eu-MOF and Tb-MOF@viscose fabrics, respectively. The photoluminescent properties of Ln-MOF@viscose fabrics were enhanced after reactive dying process. The self-cleaning functions of Ln-MOF@viscose fabrics were estimated through studying the photo-degradation of Rhodamine B (RhB) dye over the fabrics. After 120 min irradiation time, the photo-degradation of RhB dye was 85–97%, indicating high performance of Ln-MOF@viscose fabric. The materials are promising for advanced applications including protective clothing, textile-based sensors, smart tagging and tickets.

## 1. Introduction

Textiles made from cellulosic materials have unique and desirable properties including softness, breathability, high moisture regime, good mechanical properties, heat-resistant quality, and easy to degrade [1]. Consequently, the demand for cellulosic textiles is ever-growing by consumers. As a result, addition of new or intelligent functionality to textiles based cellulose is a great of interest to be valuable. Therefore, cellulosic textiles with characteristic functions were widely produced over the world and millions of people wearing functionalized cellulosic textiles daily. Some of the most applied functionalized textiles are antimicrobial [2–8], UV-protective [9–11], and water repellent [12,13]. Antimicrobial textiles are originally applied specially in hospitals as surgical gowns, masks, gloves, surgical coats, sheets, curtains, etc. While, UV-protective and water repellent textiles are commonly used for the normal people as outdoor garments protect from solar radiation or rains. On the other hand, other functional textiles are named smart or intelligent textiles due to its smart and non-familiar use including electrically conductive textiles [14–16]. These textiles shield or diffract the harmful electromagnetic radiation, and consequently applied as a liner in microwave or outdoor cloths in or near by radio and television stations and mobile phone stations. One from the smart textiles is photoluminescent (PL) textiles, which can sense and change its color once exposure to UV radiation or emitting light in the dark. According to their unique properties in the dark or under UV light, production of PL textiles have strongly attracted the attention of researchers and

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scientists in the last decades. As the color is a visual observation and can differentiate between peoples by using colored textiles. So, photoluminescent textiles based on Ln, are quite important for smart applications especially in cloths of army forces and police officers. By wearing such PL garments, differentiation between soldiers and enemies, and between policemen and criminals, can be easily realized through using an ultraviolet radiation source in the form of gun or shooter as an applied example.

There are several kinds of PL materials which are visible in poor lighting conditions and consequently, applied in items such as sporting goods, plastic toys, watch, clock and paper currencies [17]. One of the most required PL materials is PL pigments/dye which are characterized by property of 'glow in the dark' [17,18]. These coloring PL materials are applied in the security applications, such like the tickets, passports, cards, coding of bank cheques and on bank notes [17,18]. In addition, PL pigments/dye are widely used in textile industry field in different ways [19–25]. PL nanoparticles (NPs) such as carbon NPs and gold NPs were also used to produce highly PL cotton fibers [26,27]. Moreover, some polymers can be used to enhance the PL properties, as cellulose powder which was grafted with conducting polymers (fluorene and 3-hexylthiophene) to become more fluorescent [28].

There are several PL materials which are visible in poor lighting conditions and consequently, are applied in items such as sporting goods, plastic toys, watches, clock and paper currencies [17]. PL dye are characterized by property of 'glow in the dark' [17,18]. These coloring PL materials are applied in the security applications, such as the tickets, passports, cards, and coding of bank cheques/notes [17,18], and textile industry [19–25]. It was found that nanoparticles (NPs) such as carbon NPs [26,27], gold nanoclusters [26,27], and conducting polymers [28] also improve the photoluminscene properties of cellulose-based materials. Among these materials, lanthanides (Ln)-based metal-organic frameworks (MOFs) are another class from PL materials which are advantageous with poor visible extinction, highly absorbing energy and emitting color light in UV radiation [29–34]. Strontium aluminate containing Ln ($Eu^{2+}$, $DY^{3+}$,$Yb^{+3}$) has attracted attention owing to its high glow intensity [35–37], and they recently prepared in solid form followed by applied onto cotton textiles to be luminescent [38]. Lanthanides-based metal organic frameworks (Ln-MOFs) offer many advantages such as high luminescent performance such as sharp emissions with relatively long lifetime, high optical purity with high quantum yields, and tunable pore size structure [29–32,39–41]. However, a very few reports were focused on the implementation of Ln-MOF into the textile as PL constituents [41].

Herein, Ln-MOF (Ln refer to $Eu^{3+}$ and $Tb^{3+}$ ions) were prepared into viscose fabrics via in situ growth using Ln $(NO_3)_3$ ($Eu^{3+}$ and $Tb^{3+}$) as metal source and 1,2,4,5-benzenetetracarboxylic di-anhydride as organic linker. The prepared Ln-MOF@viscose fabrics were characterized by different instrumental analysis including infrared spectroscopy, scanning electron microscope, energy dispersive X-ray and X-ray diffraction. The effect of dying process on the Photoluminescent properties of Ln-MOF@viscose fabrics was tested. Self-cleaning property for the prepared Ln-MOF@viscose fabrics was studied through the photo-degradation of Rhodamine B (RhB).

## 2. Experimental

### 2.1. Chemicals and materials

$Eu(NO_3)_3{\cdot}6H_2O$ (99.9%, Aldrich), $Tb(NO_3)_3{\cdot}6H_2O$ (99.9%, Aldrich), 1,2,4,5-benzenetetracarboxylic acid (99.9%, Aldrich), 1,2,4,5-benzenetetracarboxylic dianhydride (99.9%, Aldrich), *N, N*-dimethylsulfoxide (DMSO, 99.9%, Aldrich), *N, N*-dimethylformamide (DMF, 99.9%, Aldrich) and Rhodamine B (RhB, 99.9%, Aldrich) were all analytical grade and used without further purification.

Plain-woven viscose fabrics (145 $g/m^2$) were kindly supplied from Lenzing AG (Lenzing, Austria).

### 2.2. Syntheses of lanthanide-organic framework (Ln-MOF)

Ln-MOFs based on Eu and Tb were synthesised according to the reported method in literature with minor modification [29,30]. A mixture of Ln $(NO_3)_3{\cdot}6H_2O$ (0.25 mmol, Ln = $Eu^{3+}$ and $Tb^{3+}$), and 1,2,4,5-benzenetetracarboxylic acid (0.50 mmol) were placed in a 20 mL of Teflon-lined stainless steel vessel with 6 mL of mixed-solvent of DMSO and $H_2O$ (V/V = 1:1), and the mixture was heated up to 120 °C within 4 h. After three days of reaction between mixtures, the reaction system was cooled down slowly to room temperature, filter the mixture and the solids were then dry on air for at room temperature. The dried powders (Ln-MOF) were collected and kept in ambient conditions prior to analysis and characterization.

### 2.3. Synthesis of Ln-MOF@viscose fabric

In-situ growth of Ln-MOF within viscose fabrics was taken a place by using solvothermal method. A solution of Ln $(NO_3)_3{\cdot}6H_2O$ (Ln = $Eu^{3+}$ and $Tb^{3+}$, 183 mg) and 1,2,4,5-benzenetetracarboxylic dianhydride (109 mg) were prepared in 50 mL of DMF. A piece of viscose fabric ($8 \times 8\ cm^2$) was added to the solution under continuous stirring for 30 min. Then, the mixture was heated on open air until complete evaporation of DMF. The reaction vessel was cooled down to room temperature and the produced Ln-MOF@viscose fabrics were rinsed five times by tap water to remove the excess and un-reacted materials. The product was dried at 75 °C over night prior to use and analyses.

### 2.4. Dyeing process

Untreated viscose and Ln-MOF@viscose fabrics were dyed with the CI reactive blue 19 dye. The dyeing process was performed by immersing fabric samples in 3% (owf) dying solutions using 1:50 of material to liquor ratio. At 40 °C, 30 g/L of sodium sulfate was added to dyeing bath, and 20 g/L of sodium carbonate was step wisely added after 30 min. Afterwards, the temperature of solution was elevated up to 60 °C. After 60 min, the dyed samples were rinsed two times with tap water and then air dried prior to analyses.

### 2.5. Characterization of materials

The diffraction of X-ray (XRD) were recorded for the powder Ln-MOF, viscose fabrics and Ln-MOF@viscose fabrics by subjecting samples to PXRD, X'Pert PRO PANalytical diffractometer (Cu Kα X-radiation at 40 kV, 50 mA and $\lambda = 1.5406$ Å) at room temperature. The data of diffraction angles were collected in the range of $2\theta° = 4°–50°$ with a 0.02° step size and 1 s scanning rate.

Topographical structure of viscose fabrics before and after in-growth of Ln-MOFs modification were examined under field emission scanning electron microscopy (Hitachi TM-3000, Japan). The elemental compositions were analyzed by using energy dispersive X-ray analysis unit conducted to the same microscope.

Infrared spectra were characterized for viscose fabrics before and after in-growth of Ln-MOF by using Fourier transform infrared spectroscopy (FTIR). The samples were conducted to Varian 610-IR FT-IR spectrometer, from UK and the absorption spectra were collected in the range of 4000–400 $cm^{-1}$.

### 2.6. Photoluminescent properties

The digital images for viscose and Ln-MOF@viscose were performed by inside the box containing UV lamp (output 4 W, AC/DC input 230 V AC) and the emitted samples were taken upon excitation at 285 nm. The images were picked up by cell phone camera of Sony Xperia C3 model with 8 MP EXMOR R.

The photoluminescence spectra through viscose and Ln-MOF@viscose fabrics in the visible spectral ranges were recorded with a modular