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Superhydrophobic and luminescent cotton fabrics prepared by dip-coating of APTMS modified $SrAl_2O_4:Eu^{2+},Dy^{3+}$ particles in the presence of SU8 and fluorinated alkyl silane

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Abstract: An organic-inorganic composite dip-coating method was adopted in order to obtain ideal water repellent cotton fabrics. To be specific, a dual-functional coating with both superhydrophobic and luminescent properties was prepared on cotton fabric by using a dip-coating solution comprising (3-aminopropyl) trimethoxysilane (APTMS) modified $SrAl_2O_4:Eu^{2+},Dy^{3+}$ particles, SU8, and fluorinated alkyl silane (FAS). The micro/nano-scale roughness generated by $SrAl_2O_4:Eu^{2+},Dy^{3+}$ particles, together with low-surface-energy FAS, rendered the cotton fabric superhydrophobic with a water contact angle of about 160° and a sliding angle as small as 2°. The coated fabric could withstand at least 100 cycles of standard laundry. The emission spectra of the coated fabric showed two emission peaks at 440 and 520 nm, which belonged to the blue and yellow-green color areas, respectively. The afterglow duration of the coated fabric was mainly influenced by the different depths of the trap levels in the $SrAl_2O_4:Eu^{2+},Dy^{3+}$.

Keywords: superhydrophobicity; luminescent properties; $SrAl_2O_4:Eu^{2+},Dy^{3+}$ particles; cotton fabric; dip-coating; rare earths

Recently, cotton fabrics have been becoming the most commonly used natural fabric because of their soft feel. They are expected to have abundant hydroxyl groups on the cotton surface, which makes the fabrics highly absorbent and therefore easily stained. As such, superhydrophobic surfaces with a self-cleaning property have been added to the cotton fabrics. To create the superhydrophobicity, both nano/micro-scale roughness and low surface free energy are usually needed. Some inorganic nanomaterials such as silica particles[1–3], gold particles[4], carbon nanotubes[5,6], ZnO nanorods[7,8] and copper crystallites[9] have been used to generate the desired roughness.

More attention has been payed to the area of dual-functional coating with both superhydrophobicity and an additional intelligent property. Combined with a hydrophobic treatment, a range of techniques have been developed to impart cotton fabrics with ultraviolet blocking property[10], electrical conductivity[11], or physiology, health and safety[12,13]. In addition, the superhydrophobic surfaces have been made by several methods, such as dip-coating, spin-coating, sol-gel process, plasma, gas phase deposition, electrospinning, and so on. Among them, the dip-coating method is most widely used and has a low cost to achieve the goal.

Moreover, functional textiles can also be made using long afterglow rare earth materials for photoluminescence applications. Since strontium aluminate luminescent material ($SrAl_2O_4:Eu^{2+},Dy^{3+}$ phosphor powder) has high afterglow intensity, favorable physical and chemical properties and long duration time (more than 2000 min), it has attracted great attention as a novel photoluminescence material[14–16]. However, as the $SrAl_2O_4:Eu^{2+},Dy^{3+}$ particles are small in size and easy to aggregate, it is difficult for them to disperse evenly in the polymer matrix and the fluorescence intensity is thus greatly weakened. In order to realize even dispersion of the luminescent particles in coating solution, (3-aminopropyl) trimethoxysilane (APTMS) was used to modify the surface of $SrAl_2O_4:Eu^{2+},Dy^{3+}$ phosphor particles.

In previous work, low durability exists on most superhydrophobic surfaces. Herein, effective measures should be taken to improve the durability which includes the way of cross-linking the coating layer. SU8 is a novolac epoxy-based photoresist, and is highlighted by the range of applications, such as micro electro mechanical systems (MEMS)[17], sensors[18], tissue repair[19], microlenses[20], and precursor of carbon nanofibers[21]. It has also been used together with SiO_2 particles to generate superhydrophobicity on fabric surface[22], or together with carbon nanotubes to form a conducting composite for inkjet printing purpose[23].

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In this work, we synthesized the $SrAl_2O_4:Eu^{2+},Dy^{3+}$ particles via a solid-state method and the as-prepared particles were then coated with APTMS. An acetone solution consisting of APTMS modified $SrAl_2O_4:Eu^{2+},Dy^{3+}$ particles, SU8 resin and fluorinated alkyl silane (FAS) was applied onto cotton fabric by a dip-coating process. The surface morphology of coated fabrics was observed by using scanning electron microscopy (SEM). Static and sliding contact angles were measured to characterize the non-wetting property of the coated fabrics. To study the luminescent property, excitation and emission spectra were measured. Furthermore, the afterglow properties of the coated fabrics were evaluated.

1 Experimental

1.1 Materials

$SrCO_3$, Al_2O_3, Eu_2O_3, Dy_2O_3 and H_3BO_3 were purchased from Sinopharm Chemical Reagent Co., Ltd. (3-Aminopropyl) trimethoxysilane was purchased from Sigma-Aldrich. Tridecafluorooctyltriethoxysilane (Dynasylan F8261, FAS) was supplied by Plastral Pty Ltd. SU8 was obtained from Microchem Corporation. All chemicals were used as received. Ultrapure (100%) cotton fabric (plain weave, 180 g/m^2), supplied by Hejiang Xiyifang Industrial Co., Ltd., China, was used as substrate.

1.2 Synthesis of APTMS modified $SrAl_2O_4:Eu^{2+},Dy^{3+}$ phosphor powder

$SrAl_2O_4:Eu^{2+},Dy^{3+}$ phosphor powder was prepared through a solid-state reaction by using $SrCO_3$, Al_2O_3, Eu_2O_3, Dy_2O_3 and H_3BO_3 of analytical reagent (A.R.) grade as the starting materials[24]. Appropriate amounts of raw materials were mixed and dissolved in appropriate amounts of absolute ethanol, followed by ultrasonic dispersion for 30 min in order to get a homogeneous mixture, then dried at 90 ºC for 24 h and milled thoroughly. The mixtures were finally heated to the optimum calcination conditions with high temperature 1300 ºC for 4 h under a reducing atmosphere, and the reducing environment was obtained by using the H_2(5 vol.%)+N_2(95 vol.%) gas flow[25], then the sintered products were re-milled and sieved to get the desired samples.

The dried $SrAl_2O_4:Eu^{2+},Dy^{3+}$ powder (0.5 g) was dispersed in 3 mL of absolute ethanol by 30 min of ultrasonic homogenizing. The ethanol solution was then added with 3 wt.% APTMS, followed by ultrasonic dispersion for 2 h in order to get a homogeneous mixture. After this reaction, the powder was centrifuged for separation from the liquid, then washed three times with ethanol, and dried at 90 ºC for 24 h.

1.3 Coating process

The cotton fabric was rinsed with ethanol and distilled water separately several times and dried at 90 ºC for 1 h. To prepare the coating solution, SU8 (2%) was dissolved in 10 mL acetone, and magnetically stirred in the darkness until a homogeneous solution was obtained. The cotton fabric sample, APTMS modified $SrAl_2O_4:Eu^{2+},Dy^{3+}$ phosphor powder (2.5%) and FAS (3%) were added in sequence to the SU8/acetone solution. After 1 h ultrasonic disperse process and 30 min of magnetic stirring, the treated fabric was subsequently dried at room temperature for 15 min. Fig. 1 illustrates the chemical structures of the coating materials and the coating process. The obtained samples were irradiated by UV light for 10 min and then further cured at 130 ºC for 15 min.

1.4 Characterization

The microscopic morphologies of all the samples were observed using a Supra 55VP SEM under a 5 kV acceleration voltage. X-ray diffraction (XRD) patterns were recorded on a D8 Advance X-ray diffractometer. Fourier transform infrared (FT-IR) spectra were recorded with a Bruker Vertex 70 FT-IR spectrometer in the range of 400–4000 cm^{-1}. The contact angles were measured by using a contact angle goniometer (KSV CAM 101). The water drop for the test was 5 μL in volume. The washing

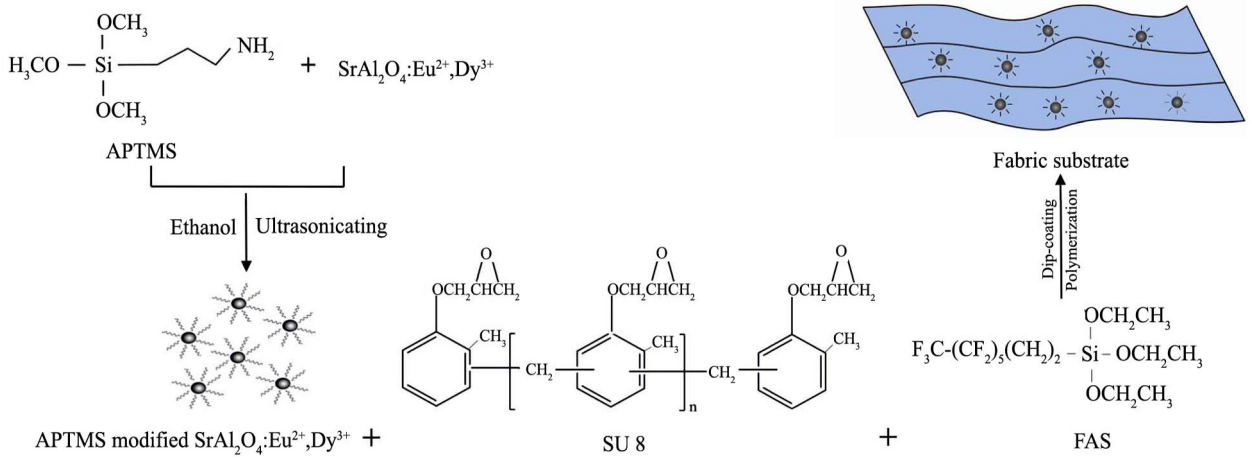

Fig. 1 Chemical structures of coating materials and the coating process