ACS APPLIED MATERIALS & INTERFACES
Research Article
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Bioinspired Lotus-like Self-Illuminous Coating

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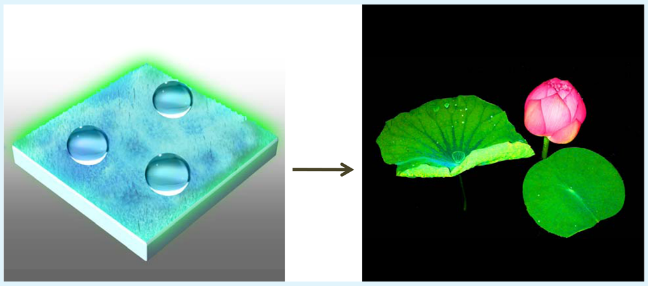
Supporting Information

ABSTRACT: The sensitivity of long persistent phosphor materials (LPP) to moisture greatly limits their applications especially in humid environments, which cause the hydrolysis of LPP and shorten their lifetime. In this work, a facile, environmentally friendly, and low-cost method was developed to prevent the infiltration of water or moisture to the LPP by doping LPP with SiO_2 nanoparticles to form a superhydrophobic coating. The superhydrophobic coating provided a stable environment to the self-illuminous system, which not only can resist the infiltration of water but also can have good self-cleaning property, similar to the lotus leaf effect. This facile method will be very beneficial for expending further application of LPP especially in high humidity.



KEYWORDS: *long persistent phosphor, superhydrophobic, water resistant, self-illuminous,* SiO_2

INTRODUCTION

Long persistent phosphor materials (LPP) are environmentally friendly and energy efficient.[1−3] The materials can release absorbed energy in the form of visible light, and the afterglow duration can last from seconds to hours; these materials have been widely used for emergency indication, illumination, displays, solar cells, in vivo imaging, and so on.[4−7] Host materials of LPP are mainly aluminates or silicates phosphor, which have bright afterglow intensity and long afterglow time.[8] However, most LPP has poor water resistance owing to hydrolysis with long exposure to water.[9] This greatly limits its utility especially under humid conditions. Various methods were developed to protect LPP from water or moisture, for example, by encapsulation with various inorganic materials, including silica, alumina, magnesia, and so on.[9−12] However, most of these approaches involve complicated chemical processes or encapsulation with organic materials, such as alkaline earth fluorides, which have good moisture impervious properties by reaction between inorganic fluorides and LPP materials;[9,13] however, hazardous gas HF can be formed during the preparation processes of fluoride coating. In this study, a facile, environmentally friendly, and low-cost method was developed to prevent the infiltration of water or moisture by preparing the superhydrophobic coating.

The lotus leaf, with an ultrahigh water contact angle (CA) and low sliding angle (SA), is widely known as a model superhydrophobic surface. The highly structured micro-/nanocomposite surface results in super water repellency and endows water to slip away easily from the superhydrophobic coating.[14−17] Nowadays, the fabrication of micro-/nanocomposite coating has been a popular way to prepare the superhydrophobic surface.[18−21] In this work, inspired by the lotus leaf, a self-illuminous lotus-like superhydrophobic coating was prepared, by doping the superhydrophobic SiO_2 nanoparticles into polydimethylsiloxane (PDMS) containing LPP. This coating has good self-illuminous property owing to the LPP; with the increasing of silica contents, the surface is gradually covered by silica nanoparticles and micro-/nanocomposite structure is formed. The final surface was superhydrophobic, and it was observed that water can roll off the surface easily and the surface was also self-cleaning. This coating not only can resist the infiltration of water and prolong the lifetime of LPP but also has good self-cleaning properties, which will be very beneficial for the application of LPP especially under high humidity conditions.

EXPERIMENTAL SECTION

Materials. The long persistent phosphor (LPP) $SrAl_2O_4$:Eu was purchased from Dalian Lu-ming Light Co., Ltd.; polydimethylsiloxane

Received: May 23, 2015
Accepted: August 4, 2015
Published: August 4, 2015

DOI: 10.1021/acsami.5b04499
ACS Appl. Mater. Interfaces 2015, 7, 18424−18428

(PDMS) was purchased from Dow Corning; superhydrophobic SiO_2 nanoparticles modified by dimethyl dichlorosilane were purchased from Shanghai Dike Industrial Co., Ltd. (R972, Evonic Industries). All other reagents were purchased from Beijing Chemical Works.

Preparation of the Coating. The characterization of the LPP material was shown in the Supporting Information. The XPS and XRD patterns of the phosphor were well-matched with the monoclinic $SrAl_2O_4$ phase pattern (Supporting Information, Figure S1).[22] The greenish emission with broadband spectrum centered at ca. 512 nm (Figure 7) corresponded to the transition between the 5d and 4f orbital gaps of Eu^{2+} in the host matrix $SrAl_2O_4$. First, 1.0 g of $SrAl_2O_4$:Eu was added into 1.0 g of unconverted PDMS (monomer:initiator = 10:1) and stirred vigorously to ensure $SrAl_2O_4$:Eu was well dispersed in PDMS. Then a certain amount of SiO_2 nanoparticles were added into unconverted PDMS solution to ensure the contents of SiO_2 in PDMS were 0%, 10%, 20%, 30%, 40%, and 50%, and 1 mL of hexane was added and vigorously stirred to ensure its fluidity and uniformity, and the mixtures were spin coated on a glass slide and solidified under 80 °C for 2 h to form the uniform LPP film.

Method of the Abrasion Test. A 10,000-mesh sandpaper served as an abrasion medium. The coating was glued to a 500 g weight and then was kept in close contact with the sandpaper. Then the surface was dragged back and forth with a speed and abrasion length of 0.5 mm s^{-1} and 10 mm, respectively.

Characterization. SEM images were obtained by a field emission SEM (JEOL JSM-4800, Tokyo, Japan). The contact angle was captured by contact angle analyzer (Kruss, DSA 100). The sliding angles of the drops (10 μL in volume) were measured by inclining the surfaces at room temperature and were recorded by the optical CCD of the system. The XRD pattern was characterized by X-ray diffraction (XRD) using a Rigaku X-ray diffractometer with graphite monochromatized Cu Kα irradiation (λ = 1.54056 Å; Rigaku, D/max-2550 PC). The XPS spectrum was captured by X-ray photoelectron spectrometer (ESCALab220i-XL). The pH value was recorded by pH meter (Sartorius, PB-10). The photographs were captured by digital camera (Nikon, D90). The luminescence spectrum of $SrAl_2O_4$:Eu was characterized by F-4500 fluorescence spectrophotometer (Hitachi, Tokyo, Japan) with the lamp turned off and illuminated by sunlight modulator for 5 min. The power of the sunlight modulator power was characterized by light intensity meter (FZ-A). The surface roughness of the coatings was measured using a roughness profilometer, Wyko NT 9100 (Veeco, Plainview, NY, USA). The abrasion test was obtained using sandpaper as an abrasion medium. The tilting angle was characterized by a protractor.

■ RESULTS AND DISCUSSION

The schematic illustration of the preparation process and property of the superhydrophobic self-illuminous coating is given in Figure 1. $SrAl_2O_4$:Eu and SiO_2 nanoparticles were successively added into unconverted PDMS (monomer, initiator, and solvent hexane) and vigorously stirred, and then the mixtures were spin coated on glass slides and solidified to form the uniform superhydrophobic self-illuminous coating. The addition of PDMS not only can ensure the formation of uniform coating but also can enhance the interactions between particles and the substrate, which is beneficial for the mechanical stability of coating. The coating possesses good self-illuminous property, which can emit visible light in the dark owing to the long afterglow property of $SrAl_2O_4$:Eu. Besides, after the addition of a certain amount of SiO_2 nanoparticles modified by dimethyl dichlorosilane, SiO_2 nanoparticles were about 15 nm in diameter (Supporting Information, Figure S2), $SrAl_2O_4$:Eu particles were gradually surrounded by SiO_2 nanoparticles, and micro-/nanocomposite structure was formed in the coating. The coating possesses good superhydrophobic property, as well as the self-cleaning property, which is similar to the lotus leaf's microstructure. Besides, this coating can effectively resist the infiltration of water or moisture to $SrAl_2O_4$:Eu and the contamination of dust to the coating, which is also similar to the property of the lotus leaf.

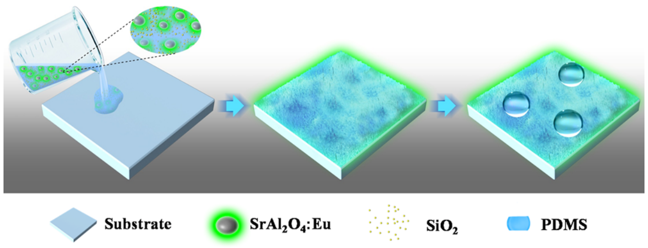


Figure 1. Schematic illustration of the preparation process and properties of the self-illuminous coating, which possesses lotus-like superhydrophobic property and can prevent the infiltration of water or moisture to $SrAl_2O_4$:Eu.

In order to establish the optimal contents of SiO_2 nanoparticles to form the superhydrophobic coating, the contact angles of the coatings with different contents of SiO_2 nanoparticles were characterized, in which the contents of $SrAl_2O_4$:Eu and PDMS were constant. As was shown in Figure 2, in the absence of SiO_2 nanoparticles (Figure 2a), the coating was prepared by doping LPP into PDMS, and the contact angle of coating was 120°, which was hydrophobic owing to the hydrophobicity of PDMS. With the improvement of the contents of SiO_2 nanoparticles, the hydrophobicity of the coating increased as well. As was shown in Figure 2e,f, when the content of SiO_2 nanoparticles was improved from 40% to 50%, the contact angle of coating increased from 150° to 165°, the coating presented a superhydrophobic state. Meanwhile, the sliding angles of coatings decreased from 55° to 5°, which were 55°, 41°, 32°, 15°, 7°, and 5° respectively. When the content of SiO_2 was further improved, many cracks formed in the coating with the volatilizing of the solvent, and water can leak into the cracks and the LPP cannot be protected.

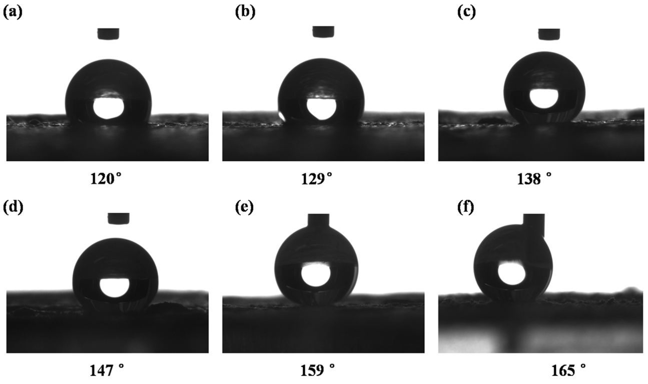


Figure 2. (a−f) Contact angles of surfaces coated with 0%, 10%, 20%, 30%, 40%, and 50% SiO_2 nanoparticles, respectively. The contents of PDMS and $SrAl_2O_4$:Eu were constant.

Figure 3 was the SEM images of the self-illuminous coating with and without SiO_2 nanoparticles. $SrAl_2O_4$:Eu particles were about 10 μm (Figure 3a) and were surrounded by SiO_2 nanoparticles to ensure the superhydrophobicity of the coating (Figure 3b), in which the content of SiO_2 nanoparticles reached 50%. The results suggested that the SiO_2 nanoparticles and $SrAl_2O_4$:Eu particles were well dispersed in the PDMS polymer

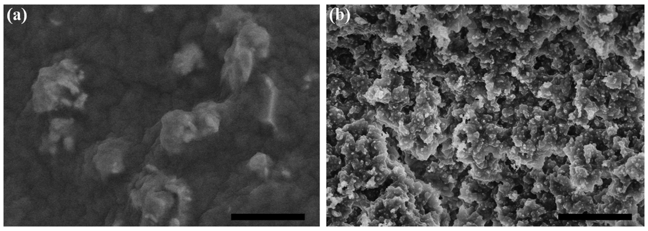


Figure 3. SEM images of the self-illuminous coatings without and with 50% SiO_2 nanoparticles (a, b). Scale bar was 5 μm.

film and formed the micro-/nanocomposite surface. The film thickness of the superhydrophobic coating was about 75 μm (Supporting Information, Figure S3).

Meanwhile, the three-dimensional morphology and surface roughness of the coating without SiO_2 (Figure 4a) and with 50% SiO_2 (Figure 4b) was characterized by profilometer. The coating in Figure 4a fluctuated markedly because of the large particles of $SrAl_2O_4$:Eu. The contact angle of the coating is 120°, the presented Wenzel state, which can propel close contact between solid−liquid interfaces, inducing the pinning of a water droplet and high adhesion. With the increase of SiO_2, $SrAl_2O_4$:Eu particles were surrounded by nano-SiO_2, and the micro-/nanocomposite structure was formed (Figure 4b). By combining both nanostructure and microstructure, a high ratio of trapped air appeared in the interface between the solid and liquid, a water droplet can be suspended due to the multilevel discontinuous three-phase contact line, and low adhesion exists,[23,24] which is similar to the case of the lotus leaf.

To investigate the superhydrophobicity and self-cleaning properties of the coating, $CuSO_4$ was dissolved into water, and then a droplet of solution was dripped onto the surface of the coating. The tilting angle of the coating was fixed to be 35°. Figure 5a was a demonstration of a water droplet sliding off the coating (Figure 5a_1−a_3). It was concluded from the pictures that water cannot slip off the hydrophobic coating owing to the adhesive property as well as the low hydrophobicity of PDMS; while for the superhydrophobic coating, in which the content of SiO_2 was 50% (Figure 5b_1−b_3), water can move easily off the surface immediately. Meanwhile, the superhydrophobic surface of Figure 5b has good self-cleaning properties and low adhesive property; the water droplet can move easily away from the surface while taking off contamination (Figure 5c_1−c_3), which means the LPP can prevent the infiltration of water and the contamination of dirt.

To investigate the moisture-resistance stability of the superhydrophobic coating, the superhydrophobic coating, in which the content of $SrAl_2O_4$:Eu particles was 0.1 g, was immersed into 10 mL of deionized water at room temperature. Another 0.1 g $SrAl_2O_4$:Eu particles was used as control, and the pH value variation of the solutions was monitored. The variation of pH value is due to the hydrolysis of LPP in water, which results in the formation of OH^-.[9,13] In the solution of hydrophilic $SrAl_2O_4$:Eu particles, the pH value increased from 6.74 to 11.72 in 5 days, a layer of white particle thin film was formed on the top of the suspensions, and the precipitate in the bottom still presented a self-illuminous property, while the emission light shifted to blue color.[25] The pH values variation of the superhydrophobic coating turned out to be a more gentle process than that of $SrAl_2O_4$:Eu particles, which increased from 6.74 to 7.39 (Figure 6). Therefore, it was obvious that the water-resistance stability of LPP had been improved to a great extent owing to the superhydrophobicity of the coating, which can resist the infiltration of water and greatly slow the hydrolysis of LPP.

Meanwhile, the mechanical stability of the coating was characterized through the abrasion test by using sandpaper as an abrasion medium. As was shown in the Supporting Information, Figure S4, after 200 times' abrasion cycles, the micro-/nanocomposite structure of the coating kept well, and the contact angles indicated that the coating still possessed good superhydrophobicity (Supporting Information, Figure S4, inset). By applying the coating on other different substrates, such as plastic, Al foil, mica, and Al alloy, the coating also possessed superhydrophobicity after the abrasion test (Supporting Information, Figure S5), which indicated that the coating had good mechanical stability on different substrates.

Figure 7 showed the emission spectra of $SrAl_2O_4$:Eu particles uncoated (black line) and coated (red line) by 50% content of SiO_2 nanoparticles in the PDMS coating; the content of LPP was kept consistent. No remarkable changes appeared in the

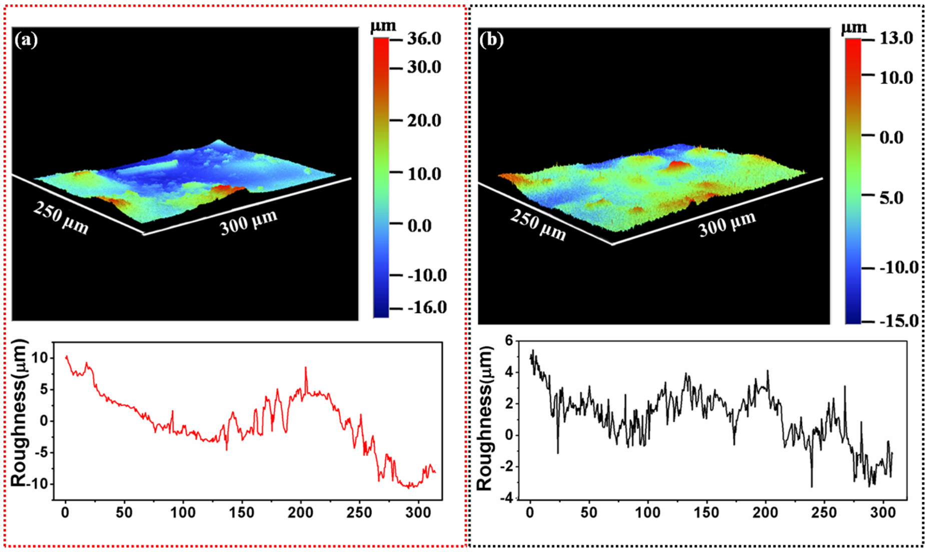


Figure 4. 3D morphology and roughness of the coating without SiO_2 (a) and with 50% content of SiO_2 (b).

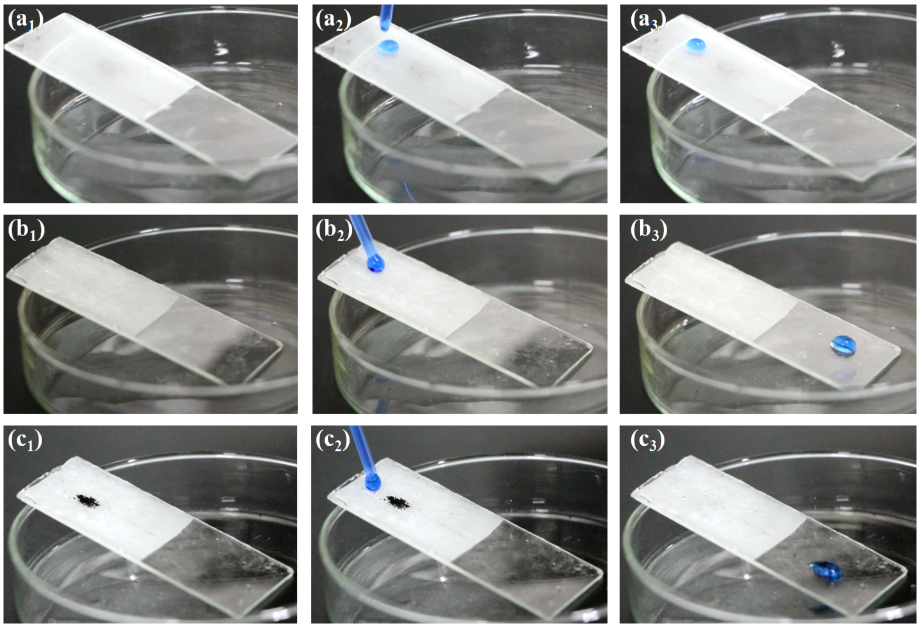


Figure 5. Demonstration of the superhydrophobicity and self-cleaning properties of the surfaces in the absence of SiO_2 (a_1−a_3) and with 50% contents of SiO_2 (b_1−b_3). The water droplet was adherable to the hydrophobic coating, while it can move easily away from the superhydrophobic coating and take off the dirty easily (c_1−c_3).

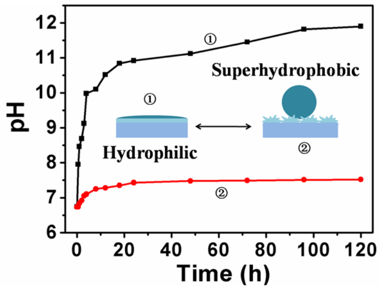


Figure 6. pH value variation of the superhydrophobic coating and the LPP (hydrophilic) versus time when it is immersed into water.

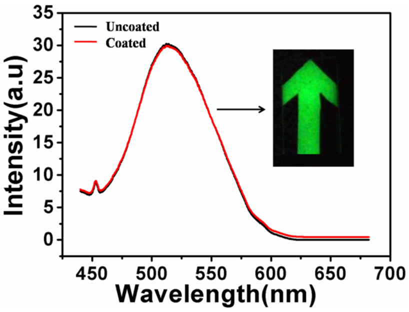


Figure 7. Emission spectra of $SrAl_2O_4$:Eu particles and $SrAl_2O_4$:Eu particles coated in superhydrophobic coating, inset was the self-illuminous property of the superhydrophobic coating under water.

emission spectra of coated and uncoated phosphor (black and red lines in Figure 7). They all showed a broad band centered at 512 nm. Besides, the superhydrophobic coating still maintained self-illuminous property while it was immersed into water (Figure 7, inset), which can be called a self-illuminous lotus leaf because of its analogous nature to the lotus leaf's structure in the superhydrophobic and self-cleaning properties.

■ CONCLUSIONS

In this work, a facile and low-cost method was developed to prevent the infiltration of water or moisture to the LPP by mixing with superhydrophobic SiO_2 nanoparticles to prepare the superhydrophobic self-illuminous coating. The coating can effectively prevent the infiltration of water or moisture to the LPP and possess stable self-illuminous property under water; meanwhile the coating possesses superhydrophobic and self-cleaning properties, which will be very beneficial for future application of LPP under hazardous and moist environment and prolong its lifetime.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b04499.

XPS and XRD characterization of LPP material, the preparation of coating, and the preparation of solution (PDF)

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Author Contributions

⊥X.S. and R.D. contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge financial support from the 2015 Science and Technology Commission of Shanghai Municipality for Yangfan Program (Grant 15YF1400700), the 2014 National Nature Science Foundation of China (Grant 51473032), the

2015 Fundamental Research Funds for the Central Universities (Grant 2232015D3-12), and the Shanghai Municipality Research Project (Grant 13520720100). K.J.S. thanks the National Scientific Foundation (Grant DMR-1308363).

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DOI: 10.1021/acsami.5b04499