



## Superhydrophobic coating of silica with photoluminescence properties synthesized from rice husk ash



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### ABSTRACT

Water penetration into concrete can cause the degradation of concrete strength, leading into structure failure. Superhydrophobic coatings on concrete received tremendous attention in the recent years as these coatings repel water like lotus leaves. In this work, rice husk ash (RHA) was used to prepare the superhydrophobic coating. Rice husk was calcined at 550 °C and 650 °C to form silica particles with a small amount of carbon residue. RHA 550 sample showed slightly higher photoluminescence (PL) intensity than RHA 660 sample as shown in fluorescent images and PL spectra. Such difference could be related to the variation of carbon content measured using scanning electron microscope-energy-dispersive X-ray spectroscopy. The carbon residue in nano size was detected in transmission electron microscope images. RHA with PL properties was further mechanochemically modified using 1H,1H,2H,2H-perfluorodecyltriethoxysilane (HFDS) or stearic acid in ethanol. However, PL properties of RHA 550 was slightly reduced due the successful grafting of hydrophobic groups on silica particles. The modified RHA in ethanol was later spray coated on a layer of commercial adhesive to form superhydrophobic coatings on glass slides and concrete. The superhydrophobic coating on concrete with the water contact angle as high as 157.7° was recorded.

### 1. Introduction

The ingress of water into concrete not only causes the destructive expansion, but also results in the penetration of corrosive chloride ions. Hence, concrete degradation and structure failure due to the ingress of water into the hydrophilic concretes with pores and micro-cracks should be prevented. Different types of water resistant materials can be used to alter the surface energy on the concrete surface, pores and cracks for reducing concrete wetting. In the recent years, superhydrophobic coatings with water contact angles larger than 150° have been promoted since the superhydrophobic coatings can repel water droplets, dew drops and even dust particles [1]. The superhydrophobic coatings enhanced the anti-wetting, anti-corrosion, anti-icing, anti-contamination and self-cleaning properties of concrete to combat the adverse weather conditions [2–5].

A wide range of hydrophobic chemicals can be used to reduce the surface energy of concrete, including silane, siloxanes and silicones [6]. These silicon based chemicals contains the hydrophobic alkyl groups to prevent wetting. However, the water repellence of superhydrophobic

coatings at Cassie-Baxter state requires the creation of surface roughness to capture a thin layer of air which can minimize water contact [1]. Many roughness creation methods such as sol-gel [7], self-assembly [8], templating [9], lithographic patterning [10], chemical etching [11], electrospinning [12] and chemical vapour deposition [13] have been reported. The addition of nanoparticles remains to be popular since it is time and cost saving. Expensive equipment or rigorous condition is not required as well. Hence, the popular formulation of superhydrophobic coatings usually consists of the hydrophobic polymer and the inorganic nanoparticles dispersed in the solvent. Various types of hydrophobic polymers were recently studied in the development of superhydrophobic coatings [14]. The superhydrophobic thin film made of polyvinylidene fluoride (PVDF) and SiO<sub>2</sub> nanoparticles with fluoroalkyl groups was successfully coated on the glass surface using the surface functionalizing agent, aminopropyltriethoxysilane [14]. The superhydrophobic PVDF coating not only exhibited the satisfactory durability, the surface hydrophobicity was maintained even after UV irradiation. Incorporating the TiO<sub>2</sub> nanoparticles with fluoroalkyl groups into PVDF coating, the superhydrophobic surface could be easily turned into

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hydrophilic under UV irradiation [15]. Thermal treatment could be used to restore the superhydrophobic surface of PVDF/TiO<sub>2</sub> coating. In order to improve the durability of superhydrophobic coating, Wang et al. [16] utilized polydimethylsiloxane (PDMS) which is a common sealant to bond a mixture of SiO<sub>2</sub> nanoparticles and fluoroalkylsilane coating on glass slide via spray coating. The commercial adhesive containing hydrocarbon resin had also been used to attach the hydrophobic silica nanoparticles on substrate strongly without the requirement of heat treatment at high temperature [5,17].

Besides looking into the chemical selection and roughness creation, the sustainability of superhydrophobic coatings was further studied. The SiO<sub>2</sub> nanoparticles in waste ash [18–21] could be used to improve the sustainability of superhydrophobic coating as reported in our previous work [5]. Meanwhile, the cost effective and safe chemicals such as fatty acids were used to modify the silica nanoparticles which were later applied as the concrete admixture [22,23]. The green solvent, water was even promoted by selecting the water soluble fluoroacrylic copolymer as the hydrophobic agent [24]. Pantoja et al. [25] emphasized that the solvent selection is important to disperse the nanoparticles for roughness creation. The higher water contact angle was achieved by using white spirit instead of ethanol or ethanol-water to form the superhydrophobic bentonite coating. Moreover, the superhydrophobic coating with satisfactory transparency was successfully synthesized by dip-coating a mixture of SiO<sub>2</sub> and methyltrimethoxysilane on polyurethane (PU) surface [26]. The PU/SiO<sub>2</sub> coating with three-dimensional networking structure allowed the light transmittance as high as 94.38%. The multiple layer of silica coatings followed by the chemical vapour deposition of 1H,1H,2H,2H-perfluorooctyltriethoxysilane also resulted in the superhydrophobic coating with excellent transparency [27]. The mesopores in silica nanosheets and the hollows in silica nanospheres reduced the refractive index and increased the light transmission. On the other hand, the photocatalytic properties of the near superhydrophobic sol-gel coating of TiO<sub>2</sub>-SiO<sub>2</sub> on bricks was investigated [28]. This coating degraded at least 70% of methylene blue strains within 4 h of light irradiation. Besides transparency and photocatalysis, the luminescence of coating is interesting to be studied since it is useful in safety signs and markings. Phosphors are the most commonly used luminescent materials as they can convert energy into electromagnetic radiation, generally in the visible energy range [29]. In other words, phosphors emit photons when they are energized by an external energy source such as sun light. The incoming radiation can be converted to visible light by the presence of phosphor during dark. Photoluminescent SiO<sub>2</sub> materials were recently reported due to their wide applications in the bioanalytical assays, labelling, chemical sensing, lighting, drug delivery and etc. [30]. The luminescent silica can be chemically produced from alkoxy silanes as well as physically doped with the expensive dyes or metal activators [29]. Due to the trapped carbon in the silica framework, rice husk ash (RHA) exhibited photoluminescence (PL) as well [31]. Fluorescence sensing and imaging could be helpful in the detection or analysis of corrosion in reinforced concrete using these photoluminescent materials available in abundance and low cost [32].

The major aim of this work is to synthesize superhydrophobic coating with PL. The PL can be a useful indicator of coating presence and even durability. The photoluminescent SiO<sub>2</sub> nanoparticles from RHA were used to engineer the superhydrophobic coating for concrete. The effects of calcination temperature on the properties of RHA was first studied. The effects of fluoroalkyl silane and stearic acid (SA) on RHA and coating properties were further investigated. Furthermore, the superhydrophobic coating was applied on the concrete cube.

## 2. Experimental

### 2.1. Materials

The raw rice husk was collected from Padiberas Nasional Berhad,

located at Kuala Selangor, Malaysia. Citric acid and ethanol were purchased from Merck, Malaysia. On the other hand, 1H,1H,2H,2H-perfluorodecyltriethoxysilane (HFDS) from Gelest Inc. and SA (C<sub>18</sub>H<sub>36</sub>O<sub>2</sub>) at the analytical grade with 95% purity from Sigma Aldrich were used as the hydrophobic modifier. The commercial adhesive, 3M Spray Mount™ Artist's adhesive was used in spray coating.

### 2.2. RHA preparation and characterization

The rice husk was chemically washed according to literature [33]. The raw rice husk was first washed with tap water, then it was further rinsed with distilled water up to 3 times. After drying at 110 °C for 24 h, 20 g of rice husk was immersed in 500 ml of citric acid solution (5 wt. %) and stirred for 2 h at 50 °C. The rice husk was then filtered, rinsed and dried before calcination. In order to generate the photoluminescent silica, the washed rice husks were calcined in a muffle furnace (Carbolite) at two different calcination temperatures, 550 °C and 650 °C for 6 h under the heating rate of 10 °C/min and atmospheric condition as reported by Liu et al. [31]. RHA calcined at 550 °C was denoted as RHA 550 while RHA calcined at 650 °C was denoted as RHA 650 (Table 1). The RHA samples were examined using scanning electron microscope equipped with energy-dispersive X-ray spectroscopy (SEM-EDX, Quanta FEG 450) which was operated at an accelerating voltage 5 kV and transmission electron microscope (TEM, CM200 FEG Philips). RHA samples were sonicated in ethanol, dispersed onto a carbon grid and air dried prior to TEM imaging.

### 2.3. Silica modification, coating and characterization

The RHA samples calcined at 550 °C were further modified using HFDS and SA and they are designated as RHA 550 HFDS and RHA 550 SA, respectively. The modification involved mechanochemical grafting which was conducted in the ball milling machine (PM 100, Retsch, Germany). The chemical grafting and size reduction occurred simultaneously by grinding 2 g of RHA in the HFDS/ethanol mixture (volume ratio 1:50 ml) for 1 h or 50 ml of SA/ethanol solution (8 mM) for 5 h at 600 rpm. The unmodified and modified RHA samples were also characterized using Fourier Transform Infrared (FTIR) spectroscopy (Nicolet Nexus 670, Thermo Scientific, USA) in order to investigate the chemical properties. The spectra were generated from 32 scans within the wavenumber range of 425–4000 cm<sup>-1</sup> at a resolution of 4.00 cm<sup>-1</sup>. The fluorescent and microscopic images of these RHA samples were recorded using a fluorescence microscope (365 nm, Olympus BX53, Japan). RHA samples dispersed in ethanol at a concentration of 0.1 g/ml were used to prepare the slides for imaging. Meanwhile, PL intensity of the unmodified and modified RHA samples was quantified using a spectrofluorometer (Perkin Elmer Lambda S55 spectrofluorometer using a Xe lamp). The PL measurement was conducted using RHA samples dispersed in ethanol at a concentration 4.5 × 10<sup>-9</sup> mg/ml. The spectra were scanned under 365 nm light excitation.

The superhydrophobic coating was formed by spray coating the ethanol solution containing the modified RHA on a layer of adhesive which was pre-coated on the glass slide. A layer of adhesive coating was sprayed on the glass slide before the ash coating was applied. The same coating method was applied on the concrete cubes

**Table 1**  
Description of all RHA samples applied in this work.

Sample	Description
RHA 550	Calcined RHA at 550 °C
RHA 650	Calcined RHA at 650 °C
RHA 550 HFDS	Calcined RHA at 550 °C and grafted with HFDS
RHA 550 SA	Calcined RHA at 550 °C and grafted with SA

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