Dyes and Pigments 130 (2016) 202–208

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Rapid fabrication of angle-independent structurally colored films with a superhydrophobic property

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ARTICLE INFO

Article history:
Received 7 February 2016
Received in revised form
10 March 2016
Accepted 13 March 2016
Available online 18 March 2016

Keywords:
Structural color
SiO_2 NPs
Angle-independent
PDMS
Superhydrophobic

ABSTRACT

Structural colors with anti-photo bleaching character have attracted great attentions in energy-saving reflective displaying. However, the brilliant color will disappear once the film is wet, due to the decreased refractive index contrast.

Generally, hydrophobic colored films are produced from hydrophobic nanoparticles, three-dimension ordered macroporous structures or spray coating of hydrophobic treated silica NPs. But the process of the three-dimension ordered macroporous structures is time consuming and this ordered array will lead to iridescent colors. Besides, it has been recognized that some fluorochemicals have potential risks to human health and environment.

In this work, we report the angle-independent structurally colored films with a superhydrophobic property fabricated by spray coating of SiO_2 NPs and PDMS. The as-prepared films exhibit a high contact angle (~165°) and a low roll-off angle (<2°). The combination of non-iridescent structural color and superhydrophobicity is significant for potential applications in outdoors.

1. Introduction

Chemical pigments used in industries produced from organic or inorganic chemicals are easy to fade over time or upon exposure to light [1–4]. Recent years, structural colors that originate from interference, diffraction, or scattering of visible light, with the anti-photo bleaching character have attracted great attentions in energy-saving reflective displaying [5–13]. Commonly observed structural colors could be divided into two classes: one is the iridescent colors from periodic nano- and microstructures, as illustrated in butterfly wings and beetle scales [14–16]; and another one is the non-iridescent color from amorphous photonic structures (APSs), as illustrated in feathers of many birds which are produced by quasi-random arrays of air vacuoles in the medullary keratin [17,18].

Non-iridescent structural color is originated from amorphous photonic structures (APSs), in which the interference condition does not vary with orientation, and the color is independent of the viewing angles., non-iridescent structural colors have attracted great attentions in potential applications due to the requirement of broad viewing angle, such as building skins, textiles, display boards, print media, cosmetics, colorimetric sensors, and optical devices [6,19–22]. Active research has been conducted on creating angle-independent structural color by packing colloidal crystals into APSs through a variety of approaches such as spin coating, drop-casting, and spray coating [12–19]. Among them, spray coating offers the benefits of rapid patterning and mass production over a large area on both planar and curved surfaces. Ge et al. prepared a composite film consisting of a thin layer of quasi-amorphous array of silica nanoparticles embedded in bulk elastomeric PDMS [23]. However, the colors emitted from colloidal APSs are very pale since incoherent light scattering across the entire visible region is very strong. To reduce the contribution of multiple-scattered light to the overall scattering spectrum, black component with the character of a high absorption across the entire visible region has been mixed into the spray coating solution [24–26].

However, the commonly used SiO_2 are typically hydrophilic and negatively charged, and brilliant structural colors will disappear once the films are wet due to the decreased refractive index contrast within the films [27]. This disadvantage limits their applications only in a dried environment. Superhydrophobic surfaces with contact angle greater than 150° and slide angle lower than 10° have received great interests within the scientific community as

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http://dx.doi.org/10.1016/j.dyepig.2016.03.022
0143-7208/

well as the industrial world over the last two decades [28–31]. Inspired by nature, such as the wings of the Morpho butterfly, a peacock feather and beetle shells, which still maintain brilliant colors even under wet conditions [32]. Thus, it is useful to apply a thin layer of transparent low-surface energy coating on the generated rough surface to prepare superhydrophobic surfaces. [33–35], Method such as post-treat the colored films with fluoroalkyl silane or alkyl silane were utilized to make superhydrophobic films previously [36–39]. However, most of them were achieved by vapor deposition under vacuum or by solution casting, in which the post-treatment step is time consuming and may not be desirable for applications in consumer [12]. Tang et al. reported a simple fabrication of colloidal crystal structural color films with good mechanical stability and high hydrophobicity [40]. They also prepared a heat-resistant photonic crystal structural color films fabricated by assembling microspheres of methyl methacrylate (MMA) and methacrylic acid (MAA) through a vertical-lifting process [41]. But the key to superhydrophobic surfaces lies within the combination of surface chemical compositions and topographic structures [28].

Recently, Ge et al. reported superhydrophobic and angle-independent colored films prepared by spray coating of fluorosilane functionalized SiO_2 [27]. However, it has been recognized that some fluorochemicals have potential risks to human health and environment [42]. PDMS is a typical elastomeric material with low surface energy of about 20 mN/m has many excellent properties, such as hydrophobicity, low toxicity, long-term endurance, and transparency, make it an attractive material for outdoor applications [43–47].

There are two general strategies to create superhydrophobic surfaces: (1) introduction of surface roughness or porosity on a low surface energy material, and (2) creation of roughness on surface, followed by deposition of a low surface energy material on top of it. The second approach is simple, low-cost, and versatile.

In this article, we report the structurally colored films with excellent superhydrophobic property by spray coating of monodisperse SiO_2 nanospheres and PDMS solution. The fabricating process is very simple and suitable for mass production over a large area on both planar and curved surfaces. Moreover, the stop-bands could be easily tuned by adjusting the size of SiO_2 nanospheres. This structurally colored film exhibited a high contact angle (~165°) and a low roll-off angle (<2°).

2. Experimental section

2.1. Materials

Tetraethoxysilane (TEOS), ethanol, and ammonia (28%) were purchased from Sinopharm Chemical Reagent Co., Ltd of China. Polydimethylsiloxane (PDMS, Sylgard 184 Silicone Elastomer Kit with components of PDMS base and curing agent) was purchased from Dow Corning. Tetrahydrofuran (THF), ethanol (EtOH) was commercially obtained without further purification. Deionized water (18.2 MΩ cm resistivity) was used in all experiments.

2.2. Synthesis of SiO_2 nanospheres

Monodispersed silica nanoparticles (NPs) were synthesized according to the modified Stöber method. In a typical procedure to synthesize 200 nm silica nanoparticles, 3 mL tetraethoxysilane (TEOS) solution was added into a mixture of 50 mL ethanol solution and 4 mL aqueous ammonia ($NH_3 \cdot H_2O$), dropwisely. The reaction was lasted for 4 h with constant stirring at 40 °C. Finally, the white powder of SiO_2 was purified by centrifuging and re-dispersing first in water and then in ethanol for several times, followed by drying in a 50 °C oven.

For synthesize of 250 nm SiO_2 NPs. A mixture solution consisting of TEOS (3 mL) and ethanol (3 mL) was slowly added to 47 mL ethanol solution containing 4 mL $NH_3 \cdot H_2O$. The reaction at room temperature lasted for 4 h with constant stirring.

For synthesize of 300 nm SiO_2 NPs. A mixture solution consisting of TEOS (3 mL) and ethanol (6 mL) was slowly added to 44 mL ethanol solution containing 4 mL $NH_3 \cdot H_2O$. The reaction at room temperature lasted for 4 h with constant stirring.

2.3. Spray coating of colored superhydrophobic films on glass slides

Glass slides were cleaned by treatment with acetone, deionized water, and ethanol under ultrasonic conditions and dried for use. A base-coat solution of epoxy resin was prepared by dissolving 0.15 g DGEBA and 0.1 g polyimide resin into 30 g of THF. A PDMS solution was prepared by dissolving 0.1–0.7 g of PDMS and 0.02–0.14 g of curing agent into 10 g of THF solution.

Glass substrates were first spray-coated with the epoxy resin base-coat solution and cured at 80 °C for 10 min. Then the epoxy coated substrates were spray-coated with the ethanol solution containing SiO_2 (10 wt%) and carbon black (0.5 wt %) and dried at 80 °C. Under these conditions, the ethanol solvent rapidly volatilized, resulted in amorphous arrays of SiO_2 deposited onto the substrates. This spray coating was repeated 5 times.

Spray coating of PDMS on SiO_2 films. PDMS precursor part-A (Sylgard 186 elastomer base, 0.1–0.7 g) was dissolved in THF (10 g) and ultrasonicated for 20 min to form a PDMS solution. PDMS precursor Part-B (sylgard 186 curing agent, 0.02–0.14 g) was added into THF solution and stirred for 1 h. Finally, the SiO_2 coated substrates were spray-coated with PDMS solution, and cured at 150 °C for 1 h to obtain A stable superhydrophobic films.

PDMS solutions in different concentration were used to coat the samples in order to find out the best concentration. The weight (wt %) of PDMS was determined according to the following equation:

$$W(wt\%) = \frac{W_1}{W_1 + W_0} \times 100$$

whereW_1 andW_0 are the weights of the PDMS and THF solution, respectively.

2.4. Characterization

The morphology of SiO_2 particles and the spray-coated films were imaged using a field emission scanning electron microscope (FESEM) (Hitachi, FE-SEM S4800).

Samples for SEM analysis were prepared by placing 0.1 mL of ethanol dispersion of the sample on an aluminum sheet, letting it dry and then sputter-coating it with gold. The reflection spectra of the colloidal crystals were performed using a Cary 5000 UV–vis–NIR spectrometer (Agilen).

The topography of superhydrophobic surface was observed using an atomic force microscope (Multi Mode, NanoScope IIIa) operating in contact mode. The static contact angle (CA) of water on the surfaces was measured with a contact angle meter (OCA 20, Dataphysics, Germany). A droplet of water (10 uL) was placed onto the films. The CA was measured on five different sites for each sample. The mean value was taken as the final result. Double-distilled water with a measured surface tension of 72 mN m^{-1} was used in these analyses. The sliding angle was also measured.