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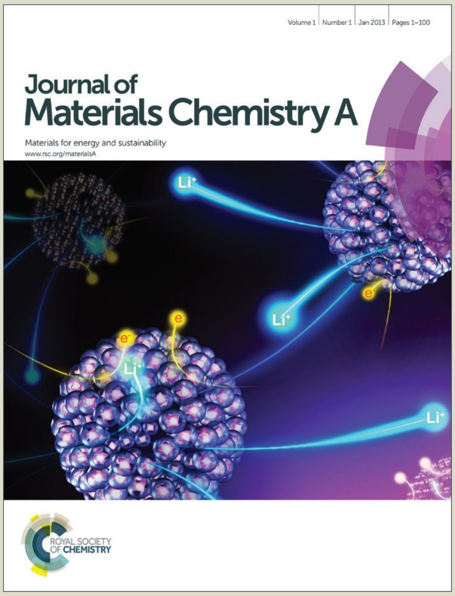

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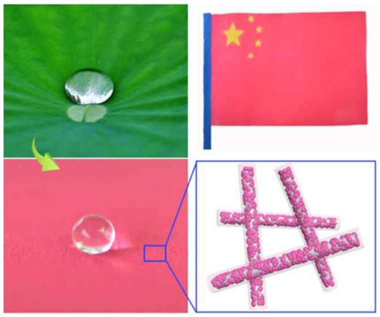
Durable and self-cleaning biomimetic superhydrophobic pigments of various colours were fabricated.



Journal Name

ARTICLE

From Maya Blue to Biomimetic Pigments: Durable Biomimetic Pigments with Self-Cleaning Property

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The inferior stability of most Maya Blue-like pigments to ancient Maya Blue seriously hinders their practical applications. Inspired by self-cleaning and water-repellent properties of the lotus leaf in the natural world, biomimetic superhydrophobic pigments with high contact angles and ultralow sliding angles for various aqueous solutions were fabricated by the combination of palygorskite, cationic dyes and organosilanes. Superhydrophobicity of the pigments is closely related to their topography and chemical composition, which can be regulated simply by changing the concentrations of organosilanes. The superhydrophobic pigments feature excellent self-cleaning property and high stability under various conditions owing to the air cushion at the solid-liquid interface and the shielding effect of the chemically inert coating based on organosilanes. Moreover, durable superhydrophobic pigments of various colours can be easily prepared using different cationic dyes and applied onto various substrates via the same procedure.

Introduction

Maya Blue is a famous hybrid pigment composed of palygorskite (PAL) and indigo from the leaves of añil plant, which was widely used in mural paintings and ceramic pieces in Yucatan by Mayan.[1] The extraordinary stability of Maya Blue against acidic, alkaline and organic corrosions and biodegradation has attracted much attention of researchers in the fields of material, chemistry and archeology in the past decades.[1d, 2] It is believed that the interactions between PAL and indigo contribute preponderantly to the amazing stability of Maya Blue, but the real nature of the interactions remains controversial. The most acknowledged interactions between PAL and indigo encompass hydrogen bonding, van der Waals forces, steric shielding as well as interaction between indigo and octahedral cations of PAL.[3]

Inspired by Maya Blue, various organic dyes (or pigments) and clays have been exploited to prepare Maya Blue-like pigments and to study the host-guest interactions between clay and dye (or pigment).[1b, 1d, 2d, 4] A series of Maya Blue-like pigments with different colors has been successfully prepared using methyl red, alizarin, murexide, Sudan red, cationic red X-GRL, methylene blue and methyl violet.[5] Besides PAL, other clays including sepiolite and zeolite have also been used as hosts for the preparation of Maya Blue-like pigments.[6] Although the results are helpful to clarify the host-guest interactions, all these Maya Blue-like pigments show inferior stability to ancient Maya Blue,[7] which hinders their practical applications. Thus, the preparation of durable Maya Blue-like pigments with different colors is still very challenging, which pushes us to explore a novel, efficient and widely applicable strategy for the preparation of Maya Blue-like pigments with excellent stability.

Wettability issues are among the most frequently encountered problems for scientific research and our daily life.[8] Wettability of a solid surface (or powder) by a liquid (*e.g.*, water) depends on both surface microstructure and surface tension of the solid surface (or powder).[9] Wetting of a solid surface (or powder) by a liquid is essential for the interaction and/or reaction between them. Thus, the inferior stability of the above-mentioned Maya Blue-like pigments is partly ascribed to the fact that these pigments are hydrophilic and can be completely wetted by various aqueous solutions. Consequently, the dyes (or pigments) loaded on clays can be gradually eluted by the aqueous phase. On the contrary, the stability of traditional Maya Blue-like pigments may be improved by making them hydrophobic. Inspired by self-cleaning and water-repellent properties of the lotus leaf in the natural world, superhydrophobic coatings with water contact angle (CA) >150° and sliding angle (SA) < 10° have attracted great interests over the past few years.[10] Superhydrophobic coatings can trap a thin layer of air cushion at the solid-liquid interface, which effectively prevents the direct contact between them. Xue et al. designed colorful

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Electronic Supplementary Information (ESI) available: alytical data, images and videos for products see DOI: 10.1039/x0xx00000x superhydrophobic textiles with high stability by chemical etching followed by conventional dying or transfer printing before hydrophobization.[11] It is expected that the stability of Maya Blue-like pigments can be greatly enhanced by introducing a durable superhydrophobic coating.

Herein, we report a simple approach for the preparation of biomimetic superhydrophobic Maya Blue-like pigments via adsorption of dyes onto PAL followed by surface modification with versatile organosilanes. Coating of surfaces with organosilanes is well known because of its fine properties, high stability and simplicity.[12] We have prepared a series of superhydrophobic materials with excellent superhydrophobicity and stability using organosilanes.[13] For the fabrication of the superhydrophobic pigments in this study, the hydrophilic PAL/Astrozon Brilliant Red 4G (PAL/ABR) pigment was prepared via adsorption of ABR onto PAL. Subsequently, the PAL/ABR pigment was coated with polymerized organosilanes (POS) by hydrolytic co-condensation of *n*-hexadecyltrimethoxysilane (HDTMS) and tetraethoxysilane (TEOS) via a modified Stöber method (Fig. 1a).[14] The superhydrophobic PAL/ABR@POS pigments feature high CAs and ultralow SAs for various aqueous solutions (*e.g.*, coffee, milk, orange juice, 98% H_2SO_4 and 60% NaOH), excellent self-cleaning property and high stability under various conditions.

Experimental section

Materials

ABR (2-[(E)-2-{4-[(2-cyanoethyl)(methyl)amino]phenyl}ethenyl]-1,3,3-trimethyl-3H-indolium chloride) was purchased from China National Medicines Corporation Ltd. and was used without further purification. Natural PAL, obtained from Xuyi (Jiangsu, China), was crushed and purified by 2% H_2SO_4 to remove quartz and other impurities, such as carbonates. The purified PAL was filtered by passing through a 180-mesh sieve. HDTMS (95%) and TEOS (99.9%) were purchased from Gelest. H_2SO_4 (98%), NaOH, aqueous ammonia (28-30%), HCl, anhydrous ethanol, acetone were provided by China National Medicines Co. Ltd. (Shanghai, China). Glass slides (24 × 50 mm, Menzel, Braunschweig, Germany) were used as the main substrates for spray coating. Other cationic dyes, *e.g.* methylene blue, methyl violet and basic yellow 14 were also purchased from China National Medicines Corporation Ltd. and were used without further purification. Other reagents used were all of analytical grade. All the reagents were used without further purification and all solutions were prepared with distilled water.

Preparation of PAL/ABR

2.00 g of PAL was dispersed in 240 mL of the ABR aqueous solution (1,000 ppm), and then magnetically stirred for 4 h to reach the adsorption equilibrium. Subsequently, the mixture was centrifuged at 10,000 rpm for 10 min to remove the supernatant and the precipitate was dried at 60 °C for 2 h. Then, the PAL/ABR pigment with a m_{ABR}/m_{PAL} of 12 wt% was obtained.

Preparation of PAL/ABR@POS

The PAL/ABR@POS pigments were prepared by hydrolytic co-condensation of HDTES and TEOS in the presence of PAL/ABR via a modified Stöber method.[14] 0.50 g of the PAL/ABR pigment was fully dispersed in 9 mL of ethanol and 1 mL of ammonia saturated ethanol under magnetically stirring for 3 min in a vial. The ammonia-saturated ethanol solution was prepared by passing the ammonia aqueous solution through a drying column and then bubbling it through anhydrous ethanol. The ammonia concentration in ethanol was approximately 3 M. Then, proper amounts of TEOS and HDTMS were charged into the mixture with stirring. The solution was ultrasonicated for 30 min at 50 °C, and then 1.44 mL of water was injected quickly into the solution under ultrasonication. The vial was sealed and ultrasonicated at 50 °C for 1 h. The reaction was allowed to proceed for 24 h at room temperature under magnetically stirring. The products were centrifuged at 10,000 rpm for 10 min to remove the supernatant followed by washing with 30 mL of ethanol for 3 times. Then, the superhydrophobic PAL/ABR@POS pigments were obtained after drying at 60 °C for 2 h. The other biomimetic pigments of various colors were prepared using different cationic dyes via the same procedure.

Fabrication of PAL/ABR@POS Coatings via Spray-Coating. The PAL/ABR@POS coatings can be easily fabricated by spray-coating the pigment on glass slides. Firstly, a piece of glass slide was cleaned by washing with ethanol, acetone, and distilled water in turn, and then dried under a nitrogen flow. 60 mg of PAL/ABR@POS was dispersed in 4 mL of toluene, followed by ultrasonication for 30 min at 30 °C to form a uniform suspension. PAL/ABR was dispersed in ethanol because of its poor dispersibility in toluene. Then, the suspension was spray-coated onto a piece of vertically placed glass slide using an airbrush (INFINITY 2 in 1, Harder & Steenbeck, Germany) with 0.2 MPa N_2 at a distance of 15 cm. Other materials, including wood block, aluminum plate, cotton fabric and A4 paper were also used as substrates for spray-coating according to the same procedure.

Characterization

CAs, SAs and high speed videos (400 fps) were taken using the Contact Angle System OCA 20, Dataphysics (Germany) equipped with a tilting table. The syringe was positioned such that the water droplet (10 μL) contacted the surface of the samples before leaving the needle. The tilting angle of the table was adjustable (0-70°) and allowed the subsequent measurement of SA at the same position on the sample. A minimum of three readings were recorded for each sample. The surface microstructure of the samples was observed using field emission scanning electron microscope (SEM, JSM-6701F, JEOL) and transmitting electron microscope (TEM, TECNAI-G2-F30, FEI). Before SEM observation, a drop of the sample dispersion in toluene was put on an aluminum stub and dried in the open atmosphere, and then coated with a thin layer of gold film ~7 nm. For TEM observation, the samples were prepared as follows. A drop of the samples dispersion in toluene was placed on a copper grid and dried in the open atmosphere. The Fourier Transform infrared (FTIR) spectra of samples were collected on a Thermo Nicolet NEXUS TM spectrophotometer (Thermo, Madison, USA) in the range of 4000-400 cm^{-1} using KBr pellets. Powder X-ray diffraction (XRD) analysis of samples was obtained on X'pert PRO diffractometer with working conditions of Cu Ka, 30 mA and 40 kV (k = 1.54060 Å). The scanning was made at room temperature between 3° and 70° with a scanning speed of 0.02° per second. X-ray photoelectron spectra (XPS) were obtained using a VG ESCALAB 250 Xi spectrometer equipped with a Monochromated AlKaX-ray radiation source and a hemispherical electron analyzer. The spectra were recorded in the constant pass energy mode with a value of 100 eV, and all binding energies were calibrated using the C1s peak at 284.6 eV as the reference.

Results and discussion

Preparation of Biomimetic PAL/ABR@POS Pigments. Once dispersed in an aqueous solution of ABR, the grey PAL will adsorb the ABR molecules and form the scarlet PAL/ABR pigment (Fig. 1a). The weight ratio of ABR to PAL (m_{ABR}/m_{PAL}) in the PAL/ABR pigment is as high as 12 wt%, which is higher than all the state-of-the-art Maya Blue-like pigments. The presence of ABR in the pigment is confirmed by SEM (Fig. 1b-c) and TEM (Fig. 1e-f) images. In an ethanol-water solution with ammonia as the catalyst, HDTMS and TEOS gradually co-condensed onto the surface of PAL/ABR via the Si-O-Si bonds to form the PAL/ABR@POS pigment (Fig. 1a and S1). The surface of PAL/ABR is coated with a dense layer of POS (Fig. 1d and g), which is further evidenced by the appearance of the absorption bands at 2920, 2850 and 1468 cm^{-1} attributed to the hexadecyl group in the FTIR spectrum of PAL/ABR@POS (Fig. 2a). The adsorption of ABR onto PAL and the subsequent modification with organosilanes do not affect the crystalline structure of PAL (Fig. S1).

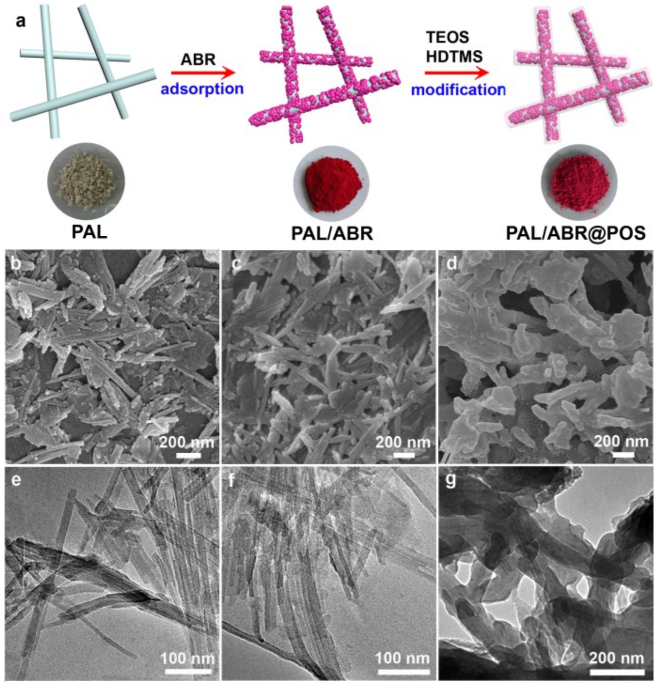

Fig. 1. (a) Schematic illustration for preparation of the PAL/ABR@POS pigments, and SEM and TEM images of (b, e) PAL, (c, f) PAL/ABR and (d, g) PAL/ABR@POS pigments.

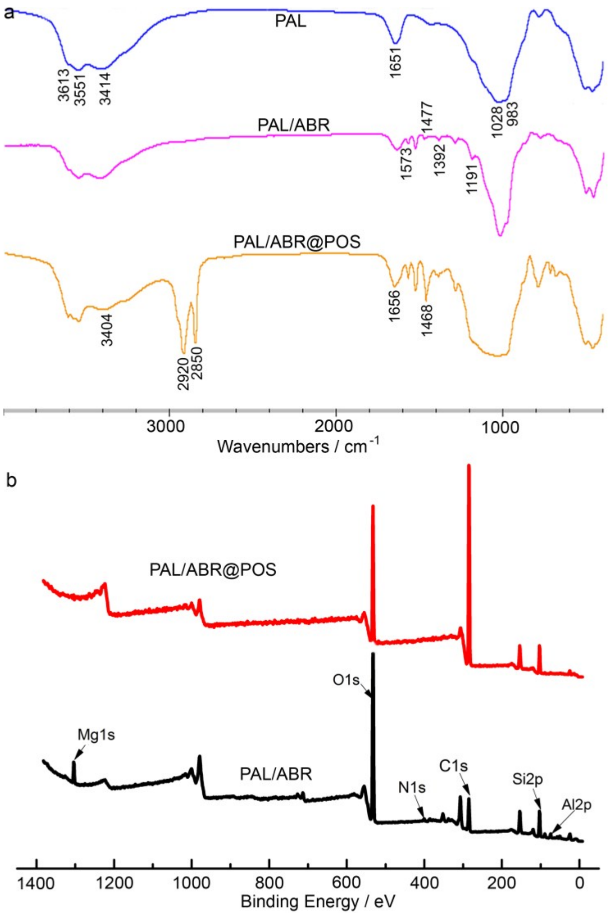

Fig. 2. (a) FTIR spectra of PAL, PAL/ABR (m_{ABR}/m_{PAL}=12%) and PAL/ABR@POS, (b) XPS spectra of PAL/ABR and PAL/ABR@POS. C_{HDTMS} = 0.14 M and C_{TEOS} = 0.14 M.

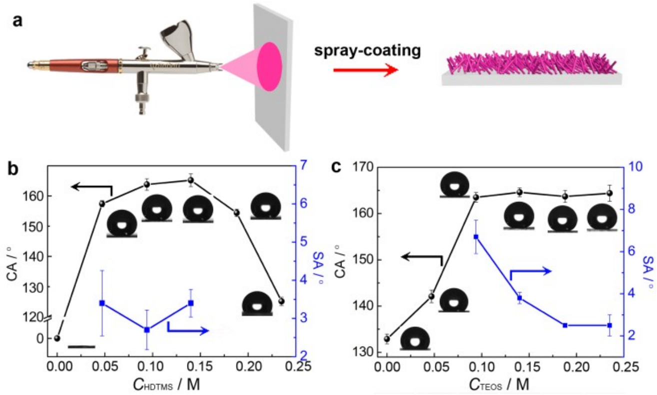

Fig. 3. (a) Schematic illustration for preparation of the PAL/ABR@POS coatings via spray-coating, variation of the CAs and SAs of water droplets on the PAL/ABR@POS coatings with (b) C_{HDTMS} and (c) C_{TEOS}.

In order to study wettability of the PAL/ABR@POS pigments, homogeneous suspensions of the pigments in toluene were prepared and spray-coated onto glass slides (Fig. 3a). The pigment prepared with an HDTMS concentration (C_{HDTMS}) of 0.14 M and a TEOS concentration (C_{TEOS}) of 0.14 M shows excellent superhydrophobicity. The PAL/ABR@POS pigment has a rough topography (Fig. 1d) and the hexadecyl groups at the surface of the coating decrease the surface energy according to the XPS spectra (Fig. 2b). Similar conformation of methyl groups of silicone nanofilaments has been proposed by Seeger et al.[9a]

Wettability of the PAL/ABR@POS pigments strongly depends on C_{HDTMS} (Fig. 3b). In absence of HDTMS, the PAL/ABR@POS pigment is superhydrophilic. The CA of water increases significantly to 157.4° with increasing C_{HDTMS} from 0 to 0.047 M. The CA keeps climbing to 165.2° with increasing C_{HDTMS} to 0.14 M, and then decreases to 125.1° with further increasing C_{HDTMS} to 0.235 M. The SA of water is 3-4° and the water droplets could easily roll off the PAL/ABR@POS coatings in the range 0.047-0.14 M C_{HDTMS}, indicating that water droplets are in the Cassie-Baxter state on the coating. A further increase of C_{HDTMS} to 0.235 M results in strong adhesion of water droplets on the coatings, even when the coatings are turned upside down, which indicates transition from the Cassie-Baxter state to the Wenzel state. It was found that the behavior of water droplets on the PAL/ABR@POS coatings is closely related to the topography and chemical composition of the coatings, which can be regulated simply by changing C_{HDTMS}. Without HDTMS, hydrolysis of TEOS formed many hydrophilic silica nanoparticles (Fig. 4a). With increasing C_{HDTMS} to 0.14 M, a uniform layer of POS was coated on the surface of PAL/ABR and the superhydrophobic PAL/ABR@POS pigment with a very rough topography was formed (Fig. 4b). The crystals of PAL could hardly be observed and the roughness decreased with further increasing C_{HDTMS} (Fig. 4c), which is responsible for the decline of the superhydrophobicity. Meanwhile, the intensity of the C 1s peak increases and the intensity of the O 1s peak decreases with increasing C_{HDTMS} according to the XPS spectra of the coatings, which indicate an increment of the hexadecyl groups on the surface of the coating (Fig. 5). This is further confirmed by the stronger absorption bands of the hexadecyl group (2920, 2850 and 1468 cm^{-1}) and the Si-O group (1028 and 983 cm^{-1}) with increasing C_{HDTMS} in the FTIR spectra of the pigments (Fig. S2).[5b, 15]

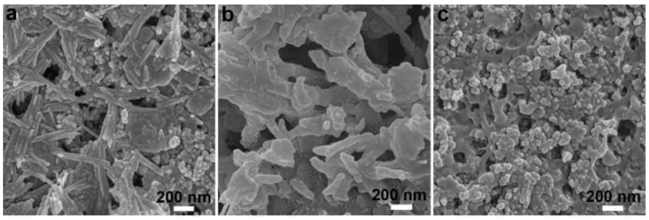

Fig. 4. SEM images of PAL/ABR@POS prepared with a C_{HDTMS} of (a) 0, (b) 0.14 and (c) 0.235 M. C_{TEOS} = 0.14 M.

C_{TEOS} also has a great influence on wettability of the coating (Fig. 3c). The CA is below 145° when C_{TEOS} is less than 0.094 M and the water droplets adhere steadily on the coating. The CA increases to 163.5° and the water droplets could readily roll off the slightly tilted (6.7°) sample with increasing C_{TEOS} to 0.094 M. Further increase of C_{TEOS} to 0.235 M has no influence on the CA but gradually reduces the SA to 2.5°. TEOS acts as a coupling agent, and is helpful for the hydrolytic condensation of HDTMS on the surface of PAL/ABR. Consequently, the PAL/ABR@POS pigments with improved topography were formed. However, the color of the pigments tends to fade at C_{TEOS} above 0.14 M due to excessive silica formed at a high C_{TEOS} (Fig. S3).

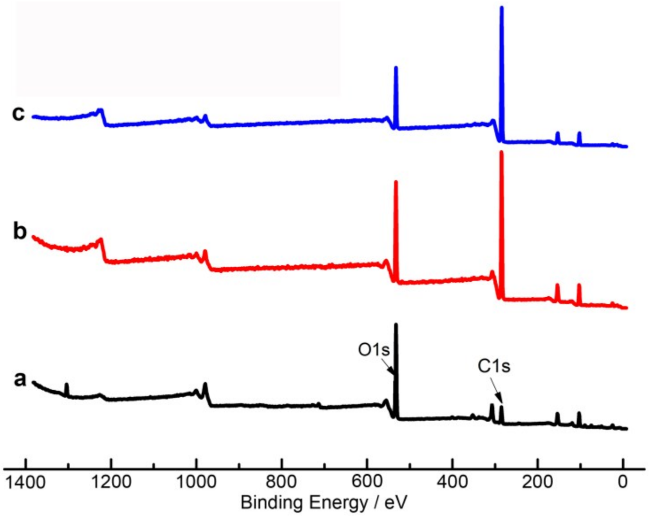

Fig. 5. XPS spectra of PAL/ABR@POS prepared with a C_{HDTMS} of (a) 0, (b) 0.14 and (c) 0.235 M. C_{TEOS} = 0.14 M.

Superhydrophobicity and Self-Cleaning Property of Biomimetic PAL/ABR@POS Pigments. After confirming the relationship between preparation parameters (C_{HDTMS} and C_{TEOS}) and wettability, superhydrophobicity and self-cleaning property of the PAL/ABR@POS pigment were tested, and compared to the PAL/ABR pigment. The PAL/ABR pigment is superhydrophilic (CA = 0°) and can be quickly wetted upon contacting with water (Fig. 6a-b and Movie S1, part 1), whereas the PAL/ABR@POS pigment shows excellent superhydrophobicity. Water droplets are spherical in shape on the PAL/ABR@POS pigment with a high CA of 165.2° and an ultralow SA of 3.4° (Fig. 6c). Moreover, a 10 μL water droplet released from a height of 15 mm (dispensing tip to surface) could bounce more than ten times on the horizontal PAL/ABR@POS coating (Fig. 6d and Movie S1, part 2), implying very weak liquid-solid interaction. The kinetic energy of the water droplet is well conserved by the surface deformation, and the dissipation of the kinetic energy by work of adhesion is very low during the impact against the surface.[16] This is attributed to the existence of the air cushion between the coating and the water droplet.[17] The coating is reflective in water with a silver mirror-like surface and remains completely dry after taken out (Fig. 6e). A jet of water could bounce off the coating without leaving a trace (Fig. 6f and Movie S2). These are direct evidences for the existence of the air cushion which makes the area beneath the water droplet is mainly the liquid-vapor interface. The PAL/ABR@POS coating is also nonwettable by other aqueous liquids such as coffee, milk, orange juice and vinegar. All these liquids have high CAs (~161°) and low SAs (~5°) on the coating (Fig. 6g). Furthermore, the PAL/ABR@POS coating displays self-cleaning property (Fig. 6h). The powdered dirt on the coating can be efficiently washed off by water (Movie S3). This is attributed to the weak interaction of the coating with water and the dirt as well as the rolling motion of water droplets on the coating.

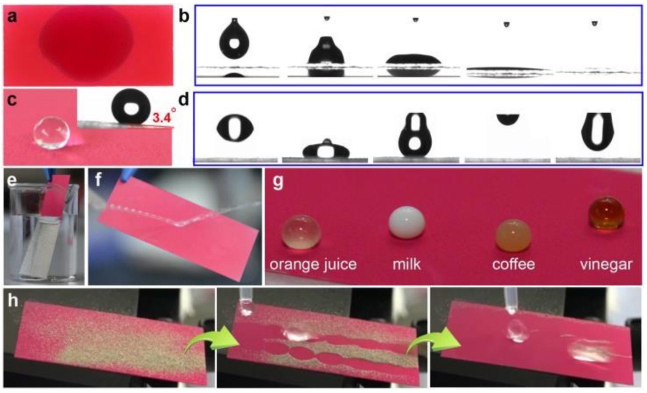

Fig. 6. Images and bounce behaviors of water droplets on the (a, b) PAL/ABR and (c-d) PAL/ABR@POS coatings, images of the PAL/ABR@POS coating (e) in water, (f) with a jet of water bouncing off and (g) with various liquids, and (h) self-cleaning property of the PAL/ABR@POS coating.

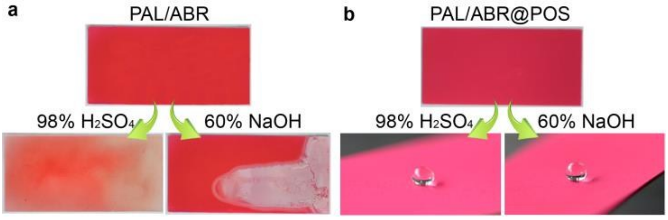

Fig. 7. Digital images of the (a) PAL/ABR and (b) PAL/ABR@POS coatings before and after attacks of 98% H_2SO_4 and 60% NaOH.

Stability of Biomimetic PAL/ABR@POS Pigments. A series of experiments was performed under various conditions to check chemical and environmental stability of the superhydrophobic PAL/ABR@POS pigment. Chemical stability of the PAL/ABR@POS pigment was firstly carried out with 98% H_2SO_4 and 60% NaOH, which are mostly used to evaluate the stability of Maya Blue-like pigments.[1d, 1g, 5a,18] For most Maya Blue-like pigments, a part of dye or pigment was eluted (or decomposed) and the pigments underwent color changes after chemical elution.[1g, 5a] As shown in Fig. 7a and Movie S4 (part 1), the PAL/ABR pigment was immediately wetted and gradually faded once the droplets of 98% H_2SO_4 and 60% NaOH fell on the coatings. Different from the PAL/ABR pigment, the droplets of 98% H_2SO_4 and 60% NaOH are spherical in shape on the PAL/ABR@POS pigment (Fig. 7b). The PAL/ABR@POS pigment was completely dry after the droplets of 98% H_2SO_4 and 60% NaOH rolled off the samples (Movie S4, part 2). The PAL/ABR@POS pigment is also resistant to weak acidic (0.1 M HCl) and basic (0.1 M NaOH) solutions as shown in Table 1. The air cushion at the liquid-solid interface significantly improves stability of the PAL/ABR@POS pigment towards these corrosive aqueous liquids. Although the PAL/ABR@POS pigment can be completely wetted by organic solvents like ethanol and acetone, no influence on superhydrophobicity was observed after evaporation of these solvents. Moreover, different from the discernible discoloration of the PAL/ABR pigment in ethanol, no discoloration of the PAL/ABR@POS pigment was detected after immersed in ethanol for 24 h (Fig. 8). These results demonstrate remarkable stability against organic solvents. The PAL/ABR@POS pigment also showed excellent stability under harsh temperatures (200 °C for 1 h and -196 °C for 1 h) and UV irradiation (200-400 nm, 0.5 h) since the CAs and SAs of water after these treatments were similar to those on the fresh one. The excellent stability against organic solvents, harsh temperatures and UV irradiation is because of the shielding effect of the chemically inert POS layer on the surface of PAL/ABR.

Table 1 CAs and SAs of water droplets on the PAL/ABR@POS coatings after treatments under various conditions.

Treatments	CA / °	SA / °
After preparation	164.3±0.8	3.4±0.6
0.1 M HCl, 1 h	157.7±0.7	6.0±0.0
0.1 M NaOH, 1 h	163.8±1.3	3.2±0.6
Ethanol, 1 h	161.5±1.3	2.7±0.6
Acetone, 1 h	164.4±1.7	2.5±0.6
200 °C, 1 h	161.5±1.0	2.8±0.0
Liquid N_2 (-196 °C), 1 h	163.1±0.6	3.6±0.6
UV(200 W, 200–400 nm, 0.5 h, 10 cm)	163.2±0.7	2.6±0.6

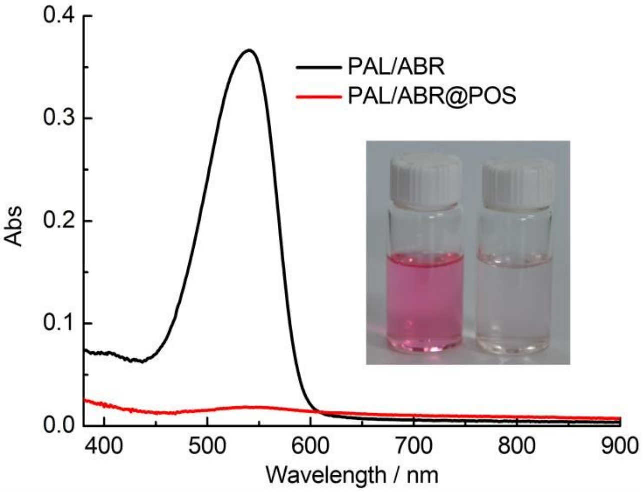

Fig. 8. UV-Vis spectra and digital images of the supernatants of PAL/ABR and PAL/ABR@POS (0.2 g) after attacks of ethanol for 24 h.

Colorful Biomimetic Pigments on Various Substrates. Besides glass slides, the superhydrophobic PAL/ABR@POS pigment can also be spray-coated onto various other substrates, *e.g.*, wood plate, aluminium plate, cotton fabric and paper, etc. (Fig. 9a). Water droplets have very high CAs and could roll off all the slightly tilted PAL/ABR@POS-coated samples regardless of composition and surface structure of the substrates. Moreover, other cationic dyes, *e.g.*, basic yellow 24, methylene blue and methyl violet, can also be used to prepare superhydrophobic pigments with different colors via the same approach (Fig. 9b). Superhydrophobicity and stability of all these pigments are comparable to those of the PAL/ABR@POS pigment, indicating that the method reported in this study is a universal approach for the preparation of durable biomimetic superhydrophobic pigments with self-cleaning property.

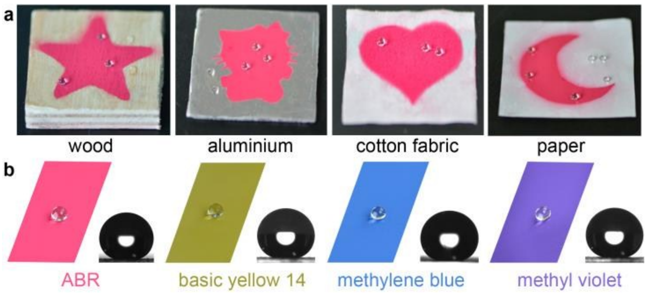

Fig. 9. Images of (a) the PAL/ABR@POS coatings on different substrates and (b) the superhydrophobic pigments prepared with different cationic dyes with water droplets on them.

Conclusions

In summary, we have successfully fabricated biomimetic superhydrophobic pigments by adsorption of ABR onto PAL followed by surface modification using POS via a simple approach. Superhydrophobicity of the pigment is closely related to its topography and chemical composition, which can be regulated simply by changing C_{HDTMS} and C_{TEOS}. The PAL/ABR@POS pigment has high CAs and ultralow SAs for various aqueous solutions, and shows excellent self-cleaning property. Furthermore, compared to traditional Maya Blue-like pigments such as PAL/ABR, the superhydrophobic PAL/ABR@POS pigment features high stability under various conditions owing to the air cushion at the solid-liquid interface and the chemically inert POS layer. We believe that this technique could be used to prepare biomimetic superhydrophobic pigments with novel properties and applied to various fields, as the superhydrophobic pigments of different colors can be easily prepared and applied onto various substrates via the same procedure.

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