Applied Surface Science 286 (2013) 364–370

Contents lists available at ScienceDirect

Applied Surface Science

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

Superhydrophobic and UV-blocking cotton fabrics prepared by layer-by-layer assembly of organic UV absorber intercalated layered double hydroxides

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ARTICLE INFO

Article history:
Received 21 August 2013
Received in revised form
13 September 2013
Accepted 15 September 2013
Available online 21 September 2013

Keywords:
Cotton
Superhydrophobicity
UV protection
Layered double hydroxides
Layer-by-layer

ABSTRACT

A dual-functional coating with both superhydrophobic and UV-blocking properties was prepared on cotton fabric using a hybrid layered double hydroxide (LDH) nanoplatelet intercalated with 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid (HMBS) molecules and an electrostatic layer-by-layer (LbL) assembly technique. The thermal stability of HMBS was greatly enhanced by the host–guest interaction with LDH layers. The as-prepared HMBS@LDH hybrid had a nearly neutral surface charge. To make it carry enough charge for the electrostatic LbL assembly, the HMBS@LDH nanoplatelet was further modified with 3-aminopropyltriethoxy silane. The nanoscale roughness generated by LDH nanoplatelets, together with low-surface-energy fluoroalkylsilane, endowed cotton fabrics with superhydrophobicity. The HMBS@LDH coating showed up to four-fold increase in the UV protection ability of cotton fabrics.

1. Introduction

Cotton is one of the most commonly used natural fibers for textiles. It is soft and comfortable to wear, biodegradable and low cost. However, the abundant hydroxyl groups on the cotton surface make cotton fabrics highly absorbent and therefore easily stained. Recently, superhydrophobic treatment of cotton fabrics has attracted great attention because of the non-sticking and self-cleaning functions originating from the Lotus effect. The superhydrophobicity of lotus leaves derives from the combination of hierarchical nano-to-micro surface structures covered by low-surface-energy substances [1]. Cotton fabrics inherently have a micro-scale rough surface coming from the texture structure. To render cotton fabrics with a superhydrophobic surface, nanoscale secondary structures are often generated on fiber surface using inorganic nanomaterials, such as silica particles [2–4], carbon nanotubes [5,6], ZnO nanorods [7,8], gold particles [9], and copper crystallites [10], combined with a hydrophobic treatment.

Cotton fabrics are widely used in summer, though the UV-blocking ability of native cotton is very limited [11]. Growing awareness on the injurious effects of UV light has increased the demand for UV-protecting treatment of cotton fabrics. Unlike synthetic fibers, where UV absorbers can be applied during the fiber manufacturing process, cotton fibers can only be improved in their UV protection ability through a post-treatment such as surface modification. To prepare a UV-blocking coating on cotton surface, inorganic absorbers such as ZnO and TiO_2 and organic UV absorbers have been used. For instance, nano-scale ZnO with various shapes like dumbbell [12], rod [13], petal [14], and sphere [15–17] has been applied onto cotton fabrics. TiO_2 has been coated on cotton fabrics through sol–gel route [18,19]. Benzophenone-type UV absorber has been applied on cotton fabrics by admicellar polymerization method [20]. Organic UV absorbers with reactive groups capable of forming covalent bonds with cotton have also been reported to improve the UV protective ability of cotton fabric [21].

Layered double hydroxides (LDHs) are inorganic layered materials composing stacks of positively charged hydroxide layers and hydrated anions placed in the interlayer gallery for charge balance. The chemical composition of LDH is broad, and can be expressed by the general formula $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]A^{n-}{}_{x/n}\cdot mH_2O$, wherein M^{2+} and M^{3+} are divalent and trivalent metal ions capable of occupying the octahedral positions of the host layers and A^{n-} is the interlayer anion. The positive charge on the hydroxide layer is due to the partial substitution of divalent metal ions with trivalent ones [22]. In recent years, LDHs have received increasing attention owing to the wide range of metal ions in the host layer and the possibility of encapsulating various guest anions, such as dyes [23,24] and organic UV absorbers [25–27]. Both thermal stability and photostability of the organic guest anions were reported to be greatly enhanced by the host–guest interaction. When these supreme LDH

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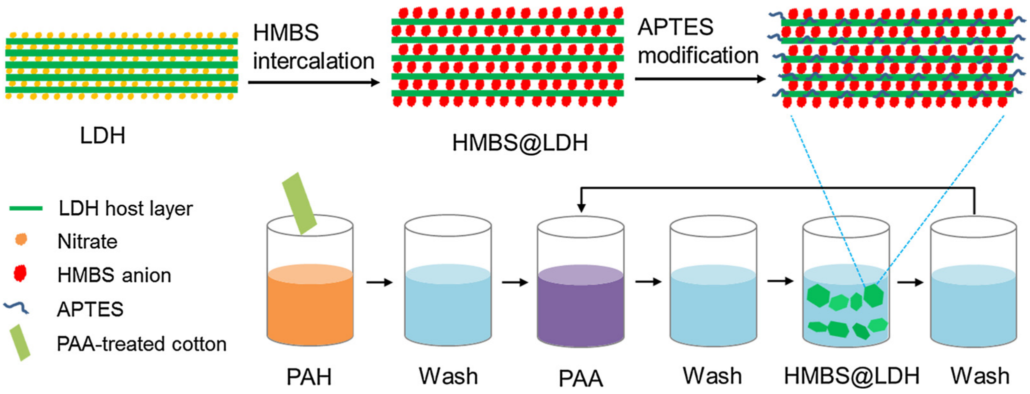
http://dx.doi.org/10.1016/j.apsusc.2013.09.092



Scheme 1. Schematic illustration for the procedure of HMBS@LDH synthesis and LbL coating.

intercalation compounds are applied to textiles, the LDH layers can avoid the direct contact of skin with the organic molecules, thus preventing the organic molecules from being absorbed into the skin. However, as far as we know, there is still no report on using such LDH intercalation compounds for surface modification of cotton fabrics.

In this work, a hybrid LDH with organic UV absorbers being intercalated into the interlayer was used to form a coating with dual-functions of superhydrophobicity and UV-blocking on cotton fabrics. LDH nanoplatelets provide nanoscale roughness that is required for superhydrophobicity. The encapsulated UV-absorbing molecule functions to improve the UV protection ability of cotton fabrics. The intercalation of organic UV absorbers into LDH was accomplished by an ion-exchange method. Since the as-prepared intercalation compound had a nearly neutral surface charge, 3-aminopropyltriethoxy silane was used to modify the LDH surface to increase surface charge for electrostatic layer-by-layer (LbL) assembly. The LbL assembly technique allows easy control of LDH loading and fine tuning of surface roughness through assembly cycles. Moreover, it should be noted that previous reports on combination of superhydrophobic and UV-protective functions on cotton fabrics were based on inorganic UV absorbers (e.g., TiO_2 [28], ZnO [29] and CeO_2 [30]) and hydrophobic treatment with fluoroalkylsilane. Since these metal oxides could cause degradation of fluoroalkylsilane layer and hence losing the superhydrophobicity under UV light, an additional silica layer had to be added between metal oxide and fluoroalkylsilane to suppress the photoactivity [29].

2. Experimental

2.1. Materials

$Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, 3-aminopropyltriethoxy silane (APTES), and poly(allylamine hydrochloride) (PAH, M_w – 56 000) were purchased from Sigma–Aldrich. Poly(acrylic acid) (PAA, M_w – 50 000, 25% aqueous solution) was obtained from Polysciences. UV absorber, 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid (HMBS), was obtained from Riedel-de Haën. Fluoroalkylsilane (FAS, tridecafluorooctyltriethoxysilane, $CF_3(CF_2)_5(CH_2)_2Si(OCH_2CH_3)_3$, Dynasylan F8261) was supplied by Degussa. All chemicals were used as received.

2.2. Preparation of LDH

$Mg_2Al\text{-}NO_3$ LDH (2:1 Mg/Al molar ratio) was prepared by a co-precipitation method [31,32]. Briefly, 6.0 mmol $Mg(NO_3)_2{\cdot}6H_2O$ and 3.0 mmol $Al(NO_3)_3{\cdot}9H_2O$ in 20 mL methanol was added dropwise into 80 mL NaOH (~18 mmol) solution in methanol under refluxing conditions. The mixture was then transferred into a Teflon-lined autoclave and aged at 150 °C for 24 h. The resulting slurries were washed several times by repeated centrifugation, and then re-dispersed in water to hydrolyze the methoxide with constant stirring overnight.

2.3. Preparation of HMBS-intercalated LDH (HMBS@LDH)

HMBS was intercalated into the nitrate form LDH by mixing 30 mL of LDH suspension in water (~0.85 wt%) with 20 mL of HMBS aqueous solution (~32 mmol/L) for 2 h at room temperature. The pH value of the HMBS solution was adjusted to be about 7 with 1.0 M NaOH aqueous solution before use. The obtained solid was washed thoroughly with deionized water by centrifugation.

2.4. Preparation of amino-functionalized HMBS@LDH

HMBS@LDH (0.5 g) was suspended into 20 mL ethanol, followed by adding 2.5 mL APTES. After stirring for 2 h, the product was washed thoroughly by centrifugation.

2.5. Preparation of HMBS@LDH coating on cotton fabrics

The cotton fabric was first treated with poly(acrylic acid) according to our previous report [4]. As illustrated in Scheme 1, the treated fabric was then immersed into a PAH (1.0 wt%) solution, after which $(PAA/HMBS@LDH)_n$ ($n = 1, 3, 5$) multilayers were assembled by alternately immersing the fabric into a PAA (1.0 wt%) solution and a solution containing ~1.0 wt% amino-functionalized HMBS@LDH nanoplatelets. The pH values of PAH and PAA solutions were adjusted with NaOH to about 7.5 and 7, respectively. For each layer, the immersion time was 5 min, followed by washing three times with deionized water. Finally, the treated cotton fabrics were dipped in 2.0 wt% FAS in hexane for 2 h and subsequently dried at 100 °C for 30 min.

2.6. Characterizations

Powder X-ray diffraction (XRD) data were collected on a Bruker D8 Advance diffractometer with CuKa radiation (40 kV, 40 mA) monochromatized with a graphite sample monochromator over the 2-theta range of 1–71°. Scanning electron microscopy (SEM) was conducted on a Zeiss Supra 55VP operated at an acceleration voltage of 5.0 kV. Transmission electron microscopy (TEM) was performed on a JEOL JEM-2100 transmission electron microscope at an acceleration voltage of 200 kV. Atomic force microscopy (AFM) was performed using a Nanoscope IIIa multimode scanning probe microscope (Digital Instruments) operating in tapping mode. Fourier transform infrared (FTIR) spectra were recorded with