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Facile fabrication of hydrophobic paper by HDTMS modified chitin nanocrystals coating for food packaging

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ABSTRACT

Paper is an inherent hydrophilic material due to the hydroxyl groups contained in cellulose, which limits its applications in packaging materials. This study proposed a simple one-step method for preparing hydrophobic paper by introduction of chitin nanocrystals (ChNCs) and hexadecyltrimethoxysilane (HDTMS). The surface chemistry and morphology of coated paper were studied in detail. The 2%ChNCs/HDTMS coated paper was highly hydrophobic with a water contact angle greater than 130°, mainly due to the low surface energy provided by HDTMS. Compared with uncoated paper, the hydrophobic paper's tensile strength and water vapor barrier were significantly improved due to the addition of ChNCs. Meanwhile, the hydrophobic paper showed excellent environmental tolerance and mechanical stability. The survival rate of L929 cells on the modified paper was more than 80% by CCK-8 assay, which proved that the nanocoating was safe. In addition, the obtained hydrophobic coated paper can hold water, cola, green tea, milk, coffee, and orange juice for a long time and can be used as a straw to absorb liquid. This work prepared high-performance and green hydrophobic paper, which exhibits wide applications in food packaging.

1. Introduction

With the release of the government's Plastic Limit Order Policy of China and the development of green chemistry in the world, the research of new biodegradable materials from renewable biomass resources has been widely concerned. For example, paper-based packaging materials have appeared on the market to reduce the use of disposable plastic products in daily life, such as paper bags, paper cups, and paper straws. The paper, fabricated by chemical and mechanical pulping of cellulose and lignin from trees, is sensitive to water and can absorb moisture due to its hydrophilic nature of hydroxyl groups and highly porous structure (Deshwal, Panjagari, & Alam, 2019; Rhim, 2010). The paper is easily damaged when it contacted with water, which limits its practical application (He, Chowdhury, Tong, Reynolds, & Ni, 2019). Laminate paper with high barrier performance by introduction petroleum-based plastic film or aluminum is a common way to improve the water-resistance of paper-based materials. Unfortunately, the paper will lose its recyclability because it is difficult to separate the paper wool from the metal or plastic film (Li & Rabnawaz, 2018). Therefore, preparing biodegradable, renewable, and waterproof paper-based packaging materials is necessary.

To obtain hydrophobic paper with suitable antifouling, self-cleaning, and mechanical stability, the cellulose paper was modified by chemical grafting (Wu et al., 2018), phase separation (Obeso et al., 2013), chemical vapor deposition (Li, Xie, Zhang, & Wang, 2007), rapid expansion of supercritical CO_2 (Olin et al., 2015), plasmas etching (Balu, Breedveld, & Hess, 2008), etc. However, these cellulose modifications often require various chemical reagents, expensive instruments, or complex processes, which are also not suitable for contact with the human body due to the toxicity of the used chemicals. As a result, it is essential to develop a simple, efficient, low-cost, green, and safe hydrophobic paper-based material.

The dip-coating method is always effective for modifying the surface property of various substrates and can be considered a simple and green method since no complicated chemical reaction is involved. Typically, when preparing a hydrophobic paper, an organic solution such as polysiloxane dissolved in toluene was employed for dip-coating the paper. The hydrophobic paper can be prepared after drying the solution (Li et al., 2021). The dip-coating method of mixing all the modifiers in a solution has the advantages of simplicity, high efficiency, low cost, and suitability for industrial scale-up. The prepared paper has excellent hydrophobic properties on both sides. For example, Tang et al. (2019)

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developed a simple poly dopamine-assisted one-pot approach to modify the filter paper. The modified paper can be reused in the process of oil-water separation without apparent loss of surface characteristics. Li et al. (2021) soaked the filter paper in a mixture of beeswax and ethanol for 2 min and took it out to dry. The prepared super-hydrophobic paper had high adhesion toward water droplets similar to rose petals.

Introduction of different nanomaterials on papers can improve the surface roughness and the barrier performance of the paper, which can also be used to fabricate (super) hydrophobic paper. Recently, inorganic nanocoatings such as TiO_2, ZnO, and Fe_2O_3 (Zhou et al., 2019) have been incorporated into the paper matrix to produce two-dimensional roughness. These systems have apparent drawbacks, such as non-biodegradability and high instinct toxicity. Hence, hydrophobic coatings fabricated by natural and biodegradable materials from renewable resources are highly needed (Bayer, 2020; Hubbe, Tyagi, & Pal, 2019). Previously, a series of liquid-repellent surfaces and coatings were prepared using natural extracts and bio-based polymers (e.g., cellulose, natural waxes, fatty acids, proteins, resins). In addition, green packaging materials with improved barrier performance and mechanical stability can be achieved by using nanoparticles, such as cellulose nanofibers (Asim, Badiei, & Mohammad, 2021). Chitin nanocrystals (ChNCs) mainly exist in the exoskeletons of crabs and shrimps, have biocompatibility, biodegradability, high modulus, high aspect ratio, and rich amino active groups, which are the second largest reinforced filler after cellulose nanocrystals (Yang, Liu, Pei, Zheng, & Tang, 2020; Zhu et al., 2019). Like cellulose nanofibers, ChNCs are structural materials in living organisms, which have been studied as a nanoscale reinforcement for various matrixes because of their availability and intrinsic mechanical characteristics (Ifuku & Saimoto, 2012; Zeng, He, Li, & Wang, 2012). Shi, Wu, Chen, Song, and Wang (2020) used ChNCs as the building blocks to prepare ChNCs/poly(vinyl alcohol) composite films with improved mechanical and barrier properties, which proved ChNCs played an important role. Recent research has shown that raw ChNCs can be used as a coating on printed paper to improve water retention (Gao, Jing, Ni, & Jiang, 2021). Besides, ChNCs can be functionalized by grafting reactions with various silane, which was reported in our previous work (Ou, Cai, Tian, Luo, & Liu, 2020).

In this study, we prepared hydrophobic paper by dip-coating ChNCs and long chain alkyl silane water/ethanol solution. The surface wettability and mechanical performance of coated papers were measured. The water vapor barrier and tolerance of paper samples were studied, and the bio-safety of the coating was evaluated. Finally, the feasibility of the obtained hydrophobic paper in food packaging materials, such as paper cup and straw, was assessed. This work prepared high-performance and green hydrophobic paper, which exhibits wide applications in daily life.

2. Materials and methods

2.1. Materials

Crab shells were provided by Wuhan Hezhong Biochemical Manufacturing Co., Ltd., China. Filter paper with medium-speed filtration was obtained from Hangzhou General Electric Biotechnology Co. Ltd., China. Hexadecyltrimethoxysilane (HDTMS) was purchased from Aladdin Industrial Corp., China. Other chemical reagents were supplied by Sinopharm Chemical Reagent Co., Ltd, China. Milli-Q integral water purification system provided deionized water.

2.2. Preparation of ChNCs

ChNCs was prepared on the method reported by Revol and Marchessault with slight modifications (Revol & Marchessault, 1993). Briefly, 20 g clean crab shells were added into 500 mL 3 mol/L HCl solution at 104 °C for 4 h under vigorous stirring. Then, the mixture was centrifuged at 8000 rpm for 10 min and washed with deionized water three times to remove excess acid. The precipitate was resuspended by deionized water under ultrasound and dialyzed in deionized water until the pH value of suspension remained unchanged. Finally, the ChNCs suspension was lyophilized at −58 °C for 24 h in the vacuum freeze-dryer (Ningbo Scientz Biotechnology Co., Ltd., China) to obtain ChNCs powder.

2.3. Preparation of coated filter paper

A certain amount of ChNCs powder was first dispersed in deionized water with ultrasonic treatment for 30 min in an ice-water bath to prepare 0.5, 1, 2, 4 wt% dispersion. Meanwhile, HDTMS was added to the anhydrous ethanol at a concentration of 1.25, 2.5 and 5 wt% under magnetic stirring at room temperature for 30 min. Then the homogenized ChNCs suspension and HDTMS solution were blended with the volume ratio of 1:1, followed by sonication for 15 min to ensure mixing uniformity. Afterward, the medium filter paper was immersed into the as-prepared mixed suspension for 5 min and then was pulled out. The dip-coated paper was dried at room temperature for 2 h and then dried in an oven at 60 °C for 6 h. Coated papers were prepared in 0.5%ChNCs/2.5%HDTMS, 1%ChNCs/2.5%HDTMS, 2%ChNCs/2.5%HDTMS, 4% ChNCs/2.5%HDTMS, 2%ChNCs/1.25%HDTMS, and 2%ChNCs/5% HDTMS water/ethanol dispersion. In order to simplify, 0.5%ChNCs/2.5%HDTMS, 1%ChNCs/2.5%HDTMS, 2%ChNCs/2.5%HDTMS and 4% ChNCs/2.5%HDTMS coated papers were abbreviated as 0.5%, 1%, 2% and 4% coated paper, respectively. The original filter paper was named as uncoated paper.

2.4. Characterization

A scanning electron microscope (SEM, Quanta400FEG, FEI, USA) at 15.0 kV was used to observe uncoated and coated papers' morphology. Before observation, a layer of gold was sputtered on them to make them conductive. An energy dispersive X-ray spectroscopy attached to the SEM was carried out for elemental mapping. Topographical surface images of uncoated and coated paper were conducted by atomic force microscopy (AFM, BioScope Catalyst NanoScope V, Bruker Instruments Ltd., USA) with a contacting model. To characterize the effect of coating on the crystalline structure of paper, X-ray diffraction (XRD) patterns of the uncoated, 0.5%, 1%, 2%, and 4% coated paper were recorded by a Miniflex 600 (Rigaku Corp, Japan) with Cu Kα radiation. The samples were scanned at diffraction angles from 5° to 50°. The Fourier transform infrared spectroscopy (FTIR) of uncoated, 0.5%, 1%, 2%, and 4% coated paper was conducted using thermos FTIR (Nicolet iS50, Thermo Fisher Scientific Co. Ltd., USA) in the wavenumber range of 400–4000 cm^{-1} to characterize the interactions that occurs between the coating and the paper.

2.5. Surface wettability

To investigate the effects of coating on surface hydrophilicity of paper, water contact angle (WCA) was carried out using a contact angle instrument (DSA100, Kruss Ltd., Germany) at room temperature, and the volume of tested water was 5 μL. Each data was reliably obtained by measuring the sample five times.

The water absorption of the papers was calculated based on the gravimetric method (Wang, Jia, Liu, & Lin, 2021). Each paper was weighed in a dry state and then immersed in deionized water. After immersing for a specific time, the paper was taken out, cleaned with the excess water with wet filter paper, and weighted. The water absorption was calculated using Eq. (1):

$$\text{Water absorption } (\%) = \frac{W_S - W_0}{W_0} \times 100\% \quad (1)$$

where W_s is the weight of paper after absorbing the free water (g), W_0 is the initial weight of the paper (g).

2.6. Mechanical properties

Tensile strength testing of the papers was conducted on a universal testing machine (AGS-X, Shimadzu, Japan) with a 2 kN load cell. The papers were cut into rectangular strips with dimension of 15 × 80 mm. For testing the properties in a wet state, the paper samples were immersed in water for 8 h. The tensile experiments were carried out at room temperature, and the strain rate was set as 50 mm/min. Three tested strips of each sample were used, and the data were obtained from the average of the three replicates.

2.7. Barrier property

The water vapor permeability (WVP) represented the moisture transmission rate of paper samples. The WVP of the paper samples was measured using the inverse cup method according to the standard of ASTME-96 with some modifications. A paper was sealed on the top of a bottle containing pre-dried anhydrous silica gels and weighted. Then, the bottle was placed in desiccator containing different saturated salt solutions (K_2SO_4, 97% RH, NaCl, 76% RH, and K_2CO_3, 44% RH) at 20 °C. The weight of the bottle was monitored every 12 h for a period of 72 h. The WVP was calculated using Eq. (2):

$$\text{WVP}\ \left(g \cdot m \,/\, m^2 \cdot Pa \cdot h\right) = \frac{\Delta m \times L}{\Delta t \times A \times \Delta P} \tag{2}$$

where Δm is the weight change of the bottle (g), L is the thickness of paper (m), Δt is the time change during the testing process (h), A is the area of the top of the bottle (m^2), ΔP is the difference of the water vapor pressure between two sides of the paper (Pa).

2.8. Antibacterial adhesion performance

Two essential food pathogenic bacteria (*E. coli* and *S. aureus*) were used to assess the potential antimicrobial adhesion of the coated paper. The capacity of the bacterial adhesion on the surface of the sample papers was explored according to the method of Hizal et al., 2017 with some modifications. The paper samples was cut into a square size of 1 × 1 cm and sterilized under ultraviolet irradiation for 2 h (1 h each side). Then, the bacterial suspensions (20 μL) with the concentration of 10^7 CFU/mL adjusted by sterile normal saline were placed onto the samples' surfaces for a 4 h. After that, the tested papers were rinsed with sterile normal saline three times to remove the non-adherent bacteria. Subsequently, the papers were immersed in LB medium and shaken at 180 rpm at 37 °C for 4 h. After shaking, the resulting suspension was diluted to an inevitable multiple, and 100 μL dilution was seeded on LB agar plate to aerobic incubate at 37 °C for 24 h. Finally, visible colonies were obtained, and the numbers of bacterial colonies were counted.

2.9. Thermal property

The thermal stabilities of uncoated and 2% coated paper were carried out by a thermogravimetric analysis (TG) instrument (Mettler Toledo, Switzerland). About 8 mg of the paper sample was put in a crucible. The samples were heated from 30 to 800 °C under N_2 atmosphere at the heating rate of 10 °C/min. The derivative form of TG (DTG) also was analyzed. The thermal behavior of the paper was also demonstrated by the vertical flame test. The test was carried out according to the test standard. The sample papers were cut into a rectangular size of 3 × 9 cm, and the burning behavior was recorded by photographing.

2.10. Cytotoxicity test

Based on previous studies on human skin safety (Oberdörster et al., 2004), we selected the mouse fibroblast cell line L929 as an in vitro cell model. The cytotoxicity of the papers was tested, and the results were evaluated by the cell counting kit 8 (CCK-8) assay. The cytotoxicity test was studied with the liquid extract of the 2% coated paper and 2% ChNCs/2.5%HDTMS suspension. The L929 cells were inoculated (3×10^4 cells/mL, 100 μL/well) in a 96-well plate at 37 °C for 24 h in a 5% CO_2 atmosphere for cell adherence. Using the medium as a control, the cells were treated with 100 μL/well coated paper extracting liquid with the concentration of 20% (v/v), 40% (v/v), 60% (v/v), 80% (v/v) and 2%ChNCs/2.5%HDTMS suspension with the concentration of 25, 50, 100, 200 μg/mL. After treating 24 h or 48 h, the cells were added with 10 μL CCK-8 solution and incubated for further 4 h. The absorbance was measured using a microplate reader (Bio-Tek, Hercules, USA) at 450 nm and each experiment was read in triplicate. The cell viability was calculated using Eq. (3):

$$\text{Cell viability}\ (\%) = \frac{A_{test}}{A_{control}} \times 100\ \% \tag{3}$$

where A_{test} and $A_{control}$ are the absorbance values of the test and control groups, respectively.

The death/live cells were evaluated by acridine orange/ethidium bromide (AO/EB) staining, in which the live cells became green and the dead cells appeared red. Briefly, 0.5 mL L929 cells (3×10^4 cells/mL) were inoculated in a 36-well plate at 37 °C overnight and then treated with a particular concentration of extracting liquid or ChNCs/HDTMS suspension, respectively. After incubated for 24 or 48 h, the culture supernatants were removed and washed twice with PBS. Then 0.5 mL staining solution (AO: EB: PBS = 1:1:100) was added, followed by a 10 min incubation at room temperature without light. Subsequently, the staining solution was removed and wetted with 100 μL PBS. The cells were observed by fluorescence microscope (XDY-2, Guangzhou Liss Optical Instrument Ltd., China).

2.11. Application

The 2% coated paper was folded into a boat and placed on the water for 24 h. It was also made into a cup or straw to conduct a simulation experiment. Furthermore, the hydrophobic paper was written or drawn to investigate the printability.

2.12. Statistical analysis

The data of all experiments were expressed as mean ± standard deviation. Data analyses were conducted using IBM SPSS Statistics 22 software (SPSS Inc., Chicago, USA). The significance of the differences between data was established using a one-way analysis of variance (ANOVA) followed by Duncan's multiple range test. Statistical significance was set at a level of $P < 0.05$.

3. Results and discussion

3.1. Characterization of ChNCs/HDTMS coated filter paper

Fig. 1a is the schematic showing the preparation process of ChNCs/HDTMS coated filter paper. As we know, filter papers have many hydroxyl groups on their surface, which leads to superhydrophilicity. ChNCs have hydroxyl and amide groups which have high compatibility with hydroxyl groups on cellulose fiber surfaces via hydrogen bonding. HDTMS will tend to condense with hydroxyl groups in cellulose and hydroxyl and amide groups of ChNCs to form a firm covalent bonding between them and bring a low-surface-energy compound to the filter papers. As shown in Fig. 1b, FTIR spectrums of uncoated paper and coated paper with 2.5% HDTMS and different content of ChNCs confirmed the presence of the ChNCs and HDTMS. The uncoated paper showed the broad bands at 3276-3340 cm^{-1} attributing to the stretching of hydroxyl groups and the intensity reduced after coating with ChNCs

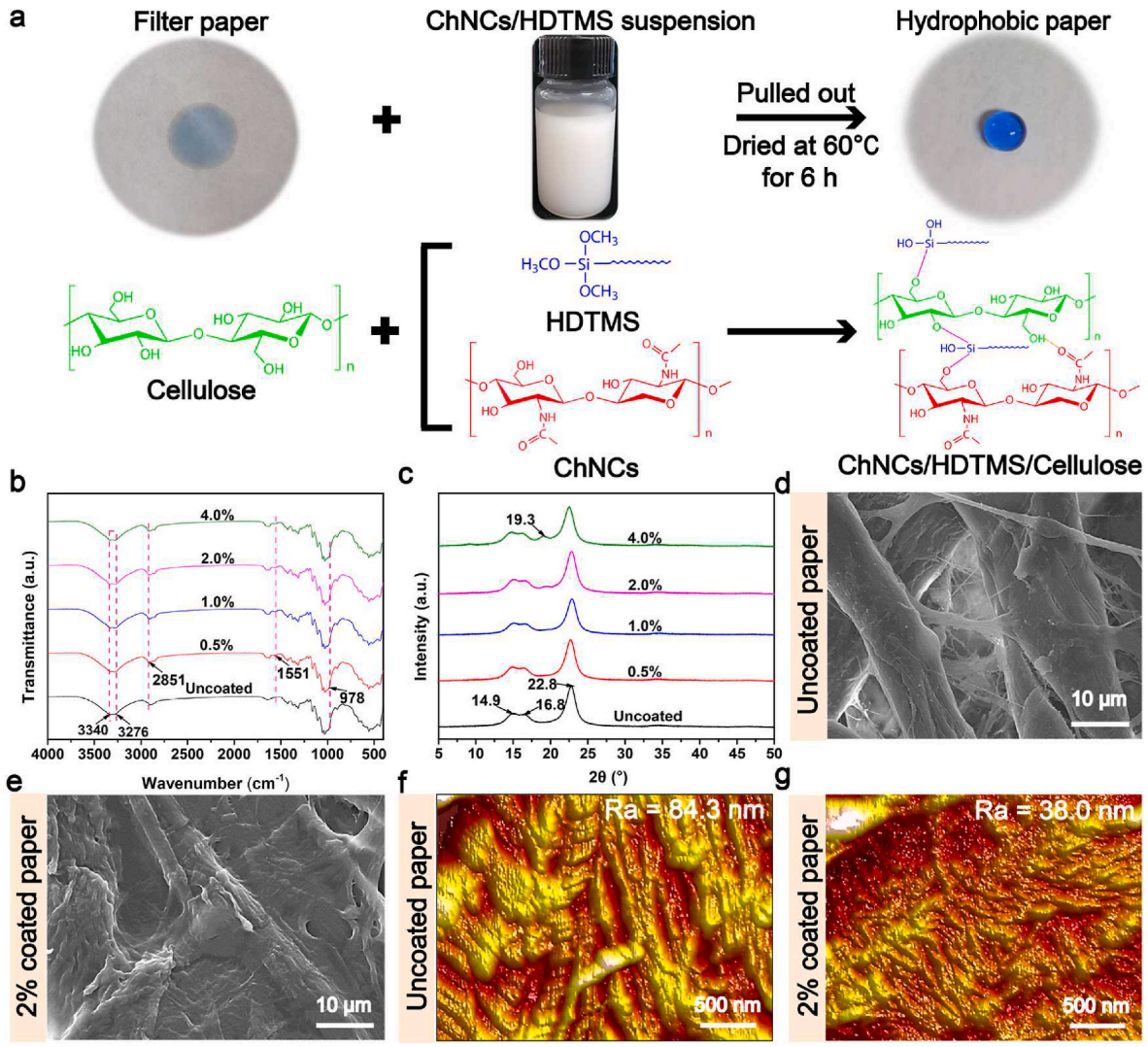

Fig. 1. Schematic representation of the preparation process of ChNCs/HDTMS coated paper (a); FTIR spectra (b) and XRD patterns (c) of uncoated paper and coated papers with 2.5%HDTMS and different content of ChNCs; SEM and AFM images of the uncoated paper (d, f) and 2% coated paper (e, g).

and HDTMS. A new peak at 1551 cm^{-1} corresponds to the amide group of ChNCs. The peaks of coated paper at 2851 cm^{-1} and 978 cm^{-1} were assigned to $–CH_2–$ symmetric vibrations and Si–O–C scissoring, respectively (Sun et al., 2020). The results indicated that the successful anchor of ChNCs and HDTMS onto the surface of filter paper.

XRD pattern in Fig. 1c confirmed the changes in crystallinity of the cellulose fiber. All the samples exhibit three diffraction peaks at 2θ of 14.9°, 16.8°, and 22.8°, which were assigned to the crystal planes of cellulose fiber (Musikavanhu et al., 2019). When the ChNCs content in ChNCs/2.5%HDTMS coating is not higher than 2%, the XRD pattern was quite similar to the uncoated paper. It may be because the coated content of ChNCs was too small to be detected by XRD. Further increasing the ChNCs content, a new diffraction peak attributed to ChNCs at 2θ of 19.3° was observed. This result suggested that ChNCs were successfully coated onto the surfaces of the paper. There is no diffraction peak of HDTMS, since HDTMS is an amorphous phase without a crystal structure.

SEM was carried out to understand further the hydrophobicity of the coated paper. The surface morphology of uncoated and 2% coated papers was shown in Fig. 1d and e. The filter paper showed a rough surface with many visible interlaced cellulose fibers with a diameter of 8–25 μm and some pores. After being impregnated with ChNCs/HDTMS, the pores filled with ChNCs and HDTMS and bridging between adjacent cellulose fibers were observed, resulting in a uniform and smooth surface. This observation was in agreement with our previous study (He, Li, Fei, & Peng, 2021), in which a carboxymethyl cellulose/cellulose nanocrystals immobilized silver system were deposited on cellulose fibers surfaces. In addition, surface elemental mapping analysis of 2% coated paper was performed (Fig. S1). The elements of N and Si were uniformly distributed in the paper, demonstrating that ChNCs and HDTMS were successfully coated on the paper surface. The 3D-morphological features of paper surfaces were further evaluated by AFM images (Fig. 1f and g). Compared to the uncoated paper, arithmetic average roughness (R_a) of 2% coated paper decreased significantly from 84.3 nm to 38.0 nm. The reason may be that ChNCs filled the low-lying parts of fiber surface and HDTMS covered on the surface, resulting in the surface of paper becoming smooth. This finding can be explained by the fact that ChNCs did not construct a rougher and multi-layered structure on the paper surface. Therefore, the coated paper was not superhydrophobic, which was in agreement with the research results of Liu et al. (2018).

3.2. *Surface wettability*

Cellulose paper is highly hydrophilic and can be easily wetted by water due to a large number of hydroxyl groups. When water droplets with different pH values drip on the uncoated paper, the water droplets

are quickly absorbed (Fig. 2g). The surface energy can significantly affect the surface wettability of paper (Liu et al., 2018). When the paper was coated with 2% ChNCs and different amounts of HDTMS, the paper surface became hydrophobic. As shown in Fig. 2b, the WCA was 128.4° when the HDTMS concentration was 1.25%. After increasing the concentration of HDTMS to 2.5%, the WCA increases by about 7°. However, the WCA changed little when the content was further increased, so 2.5% of HDTMS can be considered the optimal silane content. Increased hydrophobicity of the ChNCs/HDTMS-coated paper is mainly due to HDTMS rather than ChNCs. However, excess ChNCs (4%) will aggregation on the coated paper surface, which reduces the hydrophobicity slightly (Fig. 2a).

To further investigate that the influence of ChNCs/HDTMS coating on the wetting behavior of the paper surface, the water absorption of uncoated and 2% coated paper was shown in Fig. 2c. It was found that the water absorption of both papers increased obviously after immersing in water for one day, as free hydroxyl groups interacted with water to display swelling (Zheng et al., 2021). After four days, the water absorption of uncoated paper was up to 150.5% and nearly reached an equilibrium because of the fully swelling of the uncoated paper. The 2% coated paper gave a lower water absorption ratio (~30.0%) than the uncoated one, indicating that the coatings may have potential applications in a wet state.

3.3. Mechanical and optical properties

As shown in Fig. S2, the thickness of papers before and after coating was different. Compared with uncoated paper, the thickness of 0.5% coated paper increased significantly ($P < 0.05$), indicating the ChNCs/HDTMS coating on the paper surface. After adding different contents of ChNCs, the thickness of ChNCs/HDTMS coated paper had no significant differences compared with that of 0.5% coated paper ($P > 0.05$). This indicated that the ChNCs and HDTMS were penetrated into the pores of the paper.

The mechanical strength of papers describes their ability to withstand mechanical damage during handling, storage, and transportation. It also assesses the ability of papers to retain their identity in packaging applications (Indumathi & Rajarajeswari, 2019). The ChNCs demonstrates both high aspect ratio and high elastic modulus, which are highly desirable to be a nanomaterial for enhancing mechanical properties of polymers. Fig. 2d showed the tensile strength of papers coated with 2.5% HDTMS and different contents of ChNCs. The tensile strength of coated paper continuously increased with the increase of ChNCs amount. This was due to the formation of hydrogen bonding between fibers and ChNCs. While, there is no significant difference in the strength between the 2% and 4% coated paper ($P > 0.05$), which may be because the aggregated ChNCs on the paper surfaces lead to weak interfacial bonding.

In addition, the influence of 2% ChNCs and different contents of HDTMS on the tensile strength of coated paper was also investigated (Fig. 2e). It can be observed that different contents of HDTMS had no significant effect on the strength of coated paper ($P > 0.05$). The results show that the addition of ChNCs is the main factor for improving the mechanical strength of paper.

In daily applications, the strength of the hydrophobic paper not only maintains well in dry conditions but also adapts to conditions soaked in liquids. To broaden the future applications of the prepared hydrophobic paper, the tensile strength of the paper was tested after soaking in water for 8 h at room temperature, and the results are shown in Fig. 2f. Interestingly, the 2% coated paper demonstrated higher tensile strength (51.5 MPa) than the uncoated paper (2.2 MPa) after soaking in water for 8 h. The tensile strength of 4% coated paper was slightly lower than 2% coated after soaking, but there is no significant difference ($P > 0.05$). The water resistance is slightly lower than 2% coated, which is consistent with the WCA results. Fig. 2h further showed its mechanical water resistance that after immersing in water for 30 s, the 2% coated paper could still load with a 200 g weight for more than 20 s, while the uncoated paper was immediately pulled off (Video 1).

Supplementary video related to this article can be found at https://doi.org/10.1016/j.foodhyd.2022.107915.

For the hydrophobic modification of paper, it is crucial to maintain the appearance and basic properties such as apparent color (He, Wan, et al., 2019). UV–vis transmittance spectra of uncoated and 2% coated paper was displayed in Fig. S3. The 2% coated paper showed slightly higher transmittance in the UV–visible light region, which may explain that ChNCs formed a transparent film when covering the fiber surface and filling the low-lying areas of the fiber surface. Meanwhile, the illustration showed that although the wettability of the uncoated and 2% coated paper was completely different, there was no difference in appearance. It could be seen that both methods and reagents used for hydrophobic modification are mild.

3.4. Self-cleaning and antifouling properties

The self-cleaning and antifouling of the hydrophobic paper is of practical significance in removing solid surface pollution. In order to investigate the self-cleaning performance, a layer of methylene blue dye as a pollutant was placed on the uncoated and 2% coated paper surfaces, and the self-cleaning test procedure was shown in Fig. S4a and Video 2. The paper was stuck on a glass slide, and the dye was placed on the surface of the paper. When the water droplets were dropped on the coated paper surface, they immediately rolled away from the paper carrying away the dye, finally making the coated paper clean, indicating excellent self-cleaning properties. On the contrary, the surface of the uncoated paper was entirely soaked by water droplets and polluted by a dye. The antifouling ability of the papers before and after coating was also tested, and the result was shown in Fig. S4b and Video 3. After being immersed in methylene blue dyed water for 10 s, the uncoated paper was wetted and stained by the dyed water. The coated paper remained clean and dry, suggesting the excellent anti-fouling performance of the 2% coated paper. The surface of 2% coated paper may not be easily adhered by other water-soluble substances, which indicated that the coated paper has potential application in straw and cup.

Supplementary video related to this article can be found at https://doi.org/10.1016/j.foodhyd.2022.107915.

3.5. Durability

The durability of the coated paper is one of the most important performances. Hydrophobicity can be easily destroyed by various harsh external conditions (such as environmental and mechanical) (Zhang, Li, Wang, Wang, & Qin, 2019). This work studied the environmental durability and mechanical robustness of 2% coated paper (Fig. 3). We carried out the acid/alkaline resistance test to determine its pH stability. The coated paper was immersed into aqueous solutions with pH values of 1–13 for 1 h. The WCA as an evaluation of pH value was exhibited in Fig. 3a. When the pH value is not higher than 11, the WCA was almost unchanged, indicating that the 2% coated paper has excellent stability in this environment. However, the hydrophobicity of the 2% coated paper declined obviously when the pH reached 13. This phenomenon may be due to the solid alkaline environment that could swell the filter paper and ChNCs (Warwicker & Wright, 1967), separating the coating and the substrate. This result provides the possibility for the chemical degradation of paper. Thus, the coated paper of 4 × 4 cm was placed in 2 mol/L NaOH solution, and a commercial paper cup of the same size served as a comparative. As shown in Fig. S5, the commercial paper cup was slowly soaked and turned yellow, while the coated paper was on the solution surface due to its hydrophobicity. In the experiment, magnetic stirring was employed to make the papers entirely in contact with the NaOH solution. After stirring for 1 h, the coated paper was utterly dispersed in the solution, and the commercial paper cup was dispersed into two parts: bulging filter paper and plastic film. It is well known that

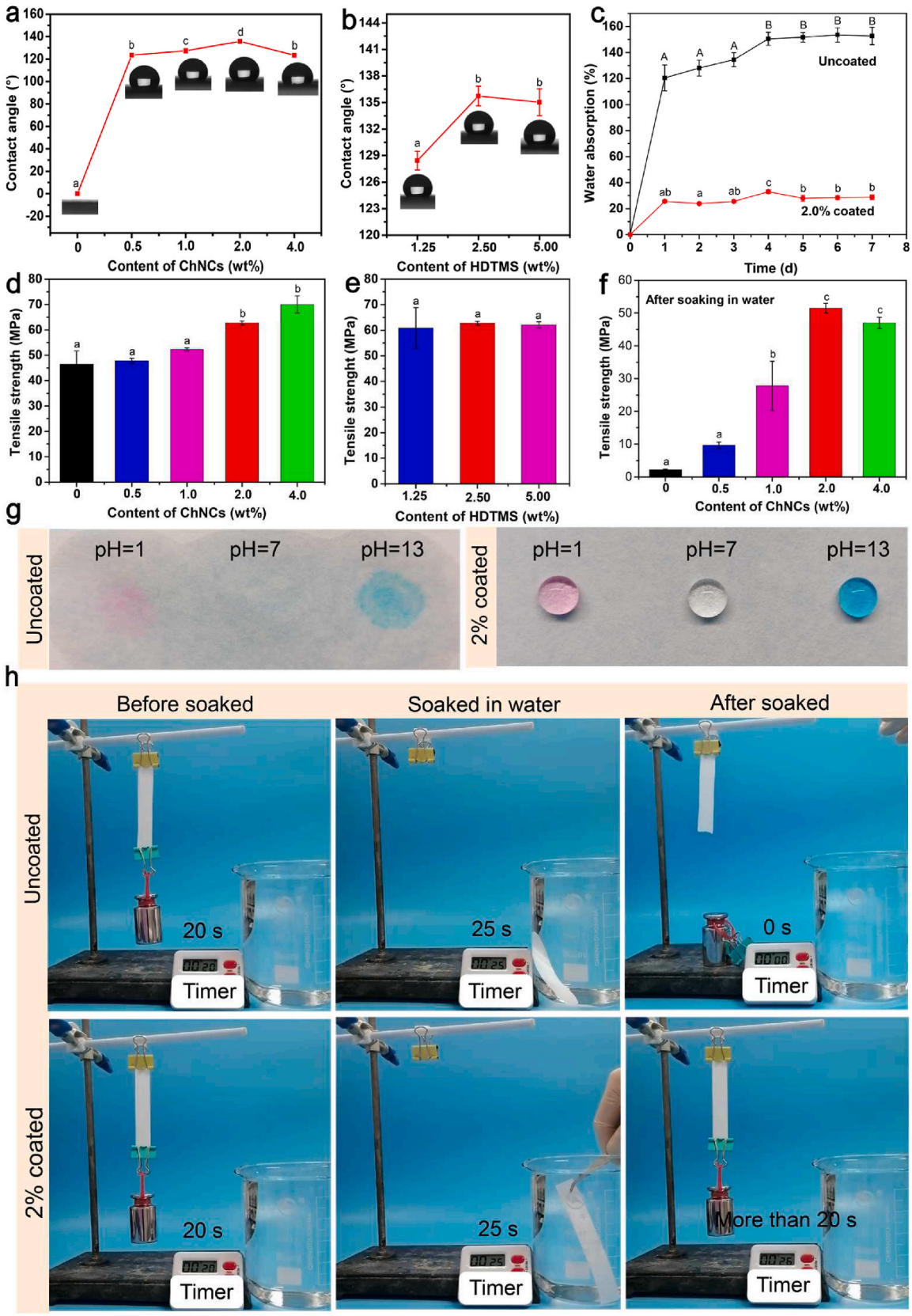

Fig. 2. The influence of ChNCs and HDTMS content on the water contact angle of coated paper (a and b); Water absorption of uncoated and 2% coated paper varying with the time (c); The influence of ChNCs and HDTMS content on the tensile strength of coated paper (d and e); Tensile strength of uncoated and coated paper after soaking in water (f); Photographs of water droplets with different pH values on the 2% coated paper surface (g); Photographs of affording a 200 g weight by the uncoated and 2% coated paper before and after soaking (h).

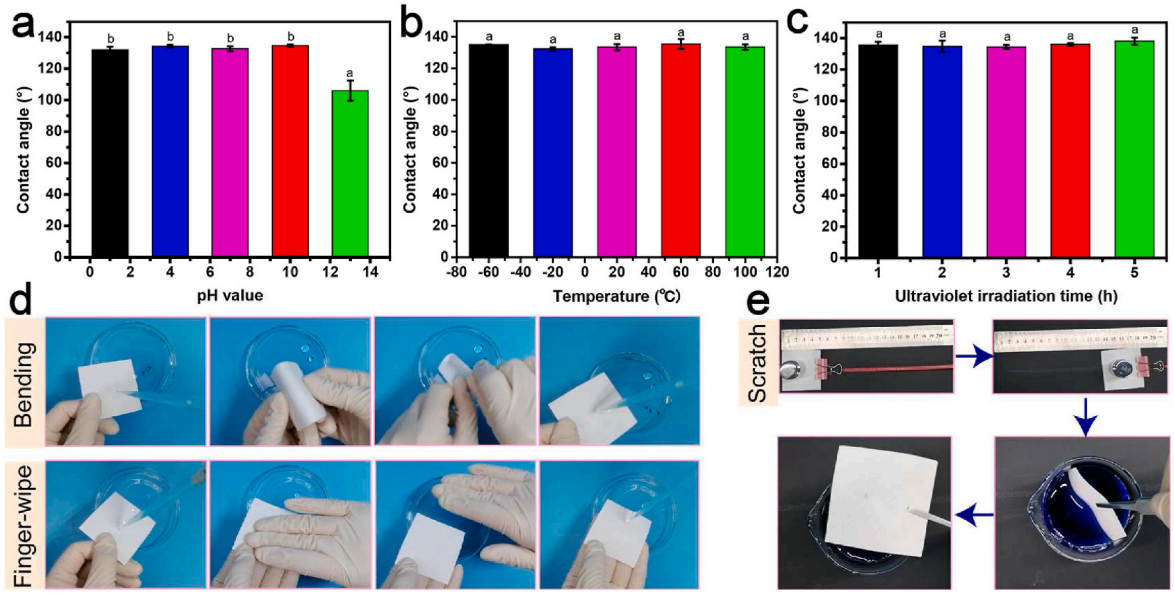

Fig. 3. WCA of 2% coated filter paper treated with different pH aqueous solution for 1 h (a), treated at different temperatures for 1h (b), and treated by ultraviolet irradiation for different time (c); Photographs of the bending and finger-wipe tests by 50 times of the 2% coated filter paper (d); After scratching, the 2% coated paper was immersed in methylene blue dyed water (e). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

plastic films on commercial paper cups are listed as white pollutants because they are not degradable, making coated paper a promising alternative to commercial paper cups. The hydrophobic modification of filter paper by HDTMS may influence the biodegradability and/or composability, and the detailed degradation experiment should be done in further study.

The coated paper may be exposed to different temperature environments in practical applications. Fig. 3b shows the changes in WCA after the hydrophobic paper was exposed to −60 °C–100 °C for 1 h, respectively. WCA is stable above 130° because low or high temperatures will not significantly damage the surface of the paper sample ($P > 0.05$). In addition, ultraviolet irradiation tests were performed to evaluate the ultraviolet durability of the 2% coated paper (Chen & Guo, 2018). The 2% coated paper sample was irradiated under the ultraviolet lamp at a distance of 8 cm. The WCA of coated paper showed no significant change when the paper was continuously irradiated by ultraviolet for 5 h (Fig. 3c) ($P > 0.05$). Considering that the ultraviolet intensity in sunlight is much lower than in the test, the 2% coated paper can be expected to have better ultraviolet durability under natural conditions.

The mechanical robustness of the 2% coated paper was evaluated through the wettability test after suffering from various mechanical forces, including bending, finger-wipe and sandpaper. A bending cycle is a pattern bending back and forth between −90° and 90°. Fig. 3d and Video 4 showed that after 50 times bending or finger-wipe tests, the water droplets quickly fall off from the surface of the coated paper, revealing good durability against bending and finger-wipe. Fig. 3e and Video 4 showed the sandpaper abrasion test of the coated paper under the weight of 100 g. Although the fibers on the paper surface was partly damaged after rubbing with sandpaper, the coated paper still maintained excellent antifouling performance, proving that the obtained paper had excellent abrasion resistance.

Supplementary video related to this article can be found at https://doi.org/10.1016/j.foodhyd.2022.107915.

3.6. Barrier and thermal properties

The water vapor barrier of the film is essential for food packaging applications and should be as low as possible (Saha et al., 2016). The effect of before and after coating on WVP at different relative humidity (RH) of paper samples was investigated (Fig. 4a). Under a high RH of 97%, the WVP of uncoated paper was found to be 14.96×10^{-3} g·m/m^2·Pa·h, which was highly permeable to water vapor since the porous structure of paper, as observed in the SEM image. When 2% ChNCs/HDTMS was coated on the paper surface, the WVP decreased to 11.37×10^{-3} g·m/m^2·Pa·h, significantly ($P < 0.05$). The reason for the decrease in WVP was that the ChNCs/HDTMS coating could reduce the number and size of the paper's pores. Besides, hydrogen and covalent bonding between coating and fiber formed a tighter structure with the paper to further reduce the WVP (Shankar & Rhim, 2018). Under other RH of 76% and 44%, the changing trend of the WVP of papers was similar to those at the RH of 97%. The WVP of the obtained coating decreased by 30.7% at RH of 76% as a function of adding ChNCs. This finding indicated that the ChNCs/HDTMS coating in this study could effectively improve the water vapor barrier property of paper.

Analysis of the thermal properties of a material is essential to characterize its processing thermal limits and applications. TG and DTG were used to investigate the thermal property of the paper before and after coated (Fig. 4b and c). As shown in Fig. 4b, the coated paper had a similar decomposition temperature to uncoated paper, with an initial weight loss and a major thermal decomposition step. The initial weight loss at temperatures of about 100 °C was because of the evaporation of moisture from the paper. The major thermal decomposition step at temperatures between 281 and 421 °C was due to the thermal decomposition of cellulose paper. In Fig. 4c, the maximum weight loss rate temperature of uncoated paper (360 °C) was lower than that of 2% coated paper (368 °C), which may be ascribed to the thermal stability of ChNCs being better than cellulose. Moreover, the charred residue percentage of uncoated paper at 800 °C was 1.33%, lower than coated paper (7.98%). These results supported that the coating of ChNCs/HDTMS improved the thermal property of the paper. It can be understood that ChNCs had better thermal stability than cellulose, besides ChNCs, HDTMS and cellulose paper have strong interfacial interactions.

The actual burning behavior of paper samples was displayed in Fig. 4d and Video 5. It can be seen that the uncoated paper was ignited easily and burned up completely, leaving about 0.15% ash (Fig. 4e). Although the burning behavior of coated paper was similar to that of uncoated paper, the burning time was longer, leaving more ash (2.86%).

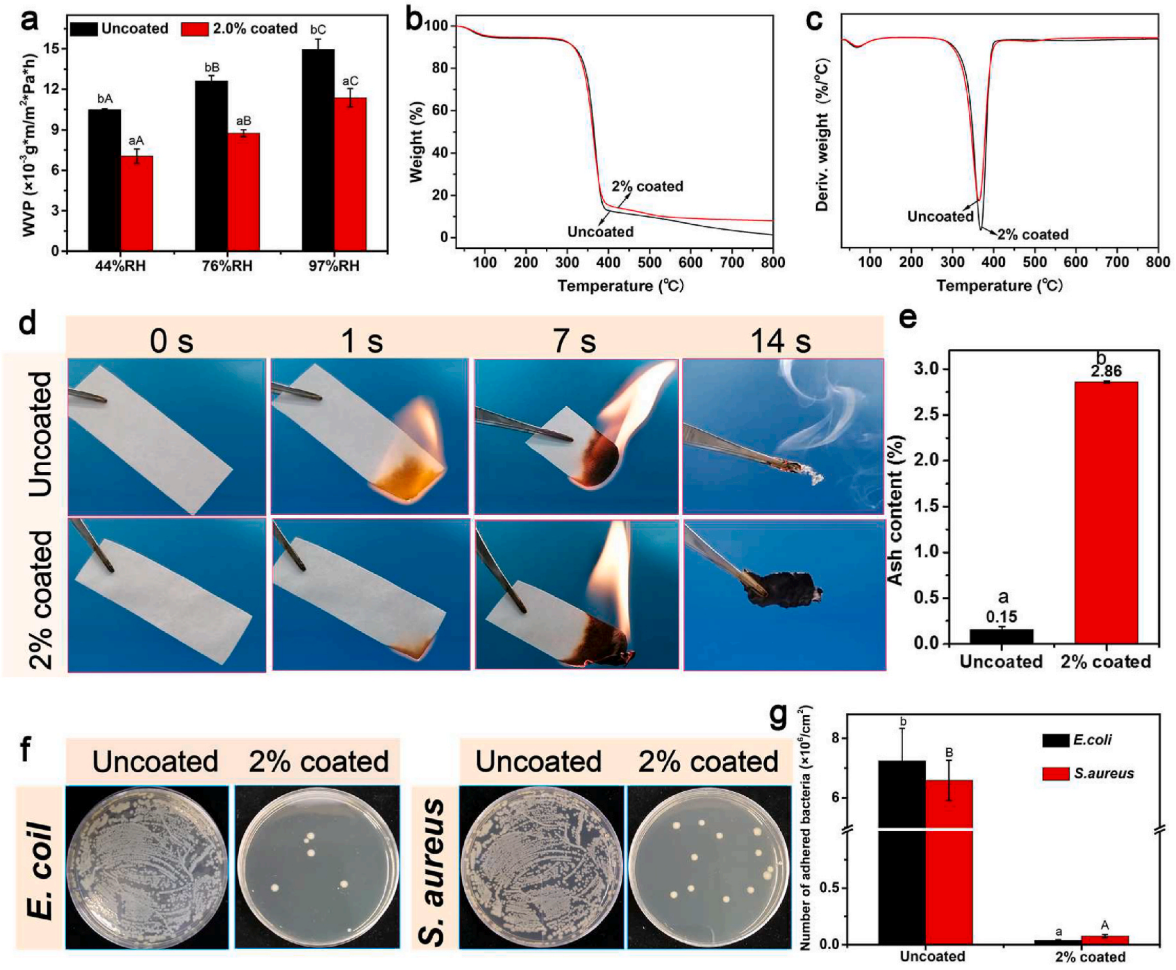

Fig. 4. WVP of uncoated and 2% coated paper (a) ([a, b] Different letters in before and after coating paper indicate significant difference ($p < 0.05$). [A, B, C] Different letters in each humidity indicate significant difference ($p < 0.05$)); TG (b) and DTG (c) curves of the uncoated and 2% coated papers; Burning (d) and ash content (e) of uncoated and 2% coated filter papers; Photos of antibacterial adhesion (f) and number of bacteria adhesion (g) and of paper before and after coated after 4h incubation at 37 °C.

This phenomenon can be interpreted as the fiber paper's inherent flammability due to its chemical composition with C, H, and O elements. On the contrary, ChNCs are rich in nitrogen, which shows inherent fire retardancy as ammonia is formed during the combustion process (Ghanadpour, Wicklein, Carosio, & Wågberg, 2018; Riehle et al., 2019).

Supplementary video related to this article can be found at https://doi.org/10.1016/j.foodhyd.2022.107915.

3.7. Antibacterial adhesion performance

Paper materials are easily polluted by the adhesion of pathogenic microorganisms, which leads to a severe shortening of service life. Hydrophobic surfaces also have antibacterial adhesion because they have interface repellency to water, which limits the contact of bacteria on hydrophobic surfaces (Jalil et al., 2020). In this study, the bacterial adhesion test was executed with *E. coli* and *S. aureus* on the surfaces of uncoated and coated papers, respectively. As shown in Fig. 4f, many *E. coli* and *S. aureus* colonies grew on the agar plates obtained from uncoated surfaces. In contrast, the agar plates obtained from coated paper surfaces hardly showed any bacterial colonies. The number of *E. coli* and *S. aureus* adhered from uncoated paper surfaces $7.237 \times 10^6/cm^2$ and $6.583 \times 10^6/cm^2$, respectively (Fig. 4g). In contrast, the 2% coated paper surface exhibited excellent antibacterial adhesion activity with significantly lower numbers of both *E. coli* and *S. aureus* ($P < 0.05$). The antibacterial adhesion rate of the coating to *E. coli* and *S. aureus* was over 98%. The result indicated that the 2% coated paper could effectively inhibit bacterial adhesion on the surface, which have great potential in food package materials (Wang, Wang, Lu, Parkin, & Zhang, 2020).

3.8. Cytotoxicity test

As a promising daily-used paper, the bio-safety and cytocompatibility of obtained paper is critical. To evaluate the physiological adaption, the cytotoxicity tests of coated paper were measured by CCK-8 assay with L929 cells. L929 cell is most widely used cell line in cytotoxicity experiments for food packaging materials (Indumathi et al., 2019; Neo et al., 2013). In brief, the coated paper extract with the concentration of 20%, 40%, 60%, and 80%(V/V) and 2%ChNCs/2.5% HDTMS suspension with the concentration of 25, 50, 100, 200 μg/mL were cultured L929 cells for 24 h or 48 h. After treatment, the cell viability was detected by CCK-8 assay, and the results were shown in Fig. 5a and b. After 24 h incubation, the cell viability did not change significantly with the increase of the samples concentration ($P > 0.05$), while it decreased significantly after 48h incubation ($P < 0.05$). But the cell viabilities were still higher than 80%, which meets the bio-safety requirements (Cheng et al., 2019). To further study the influence of coating on cells, the live/dead cell staining was executed after being cultured for 24 h or 48 h, and the corresponding fluorescence microscope images had displayed in Fig. 5c and d. The cell density of the

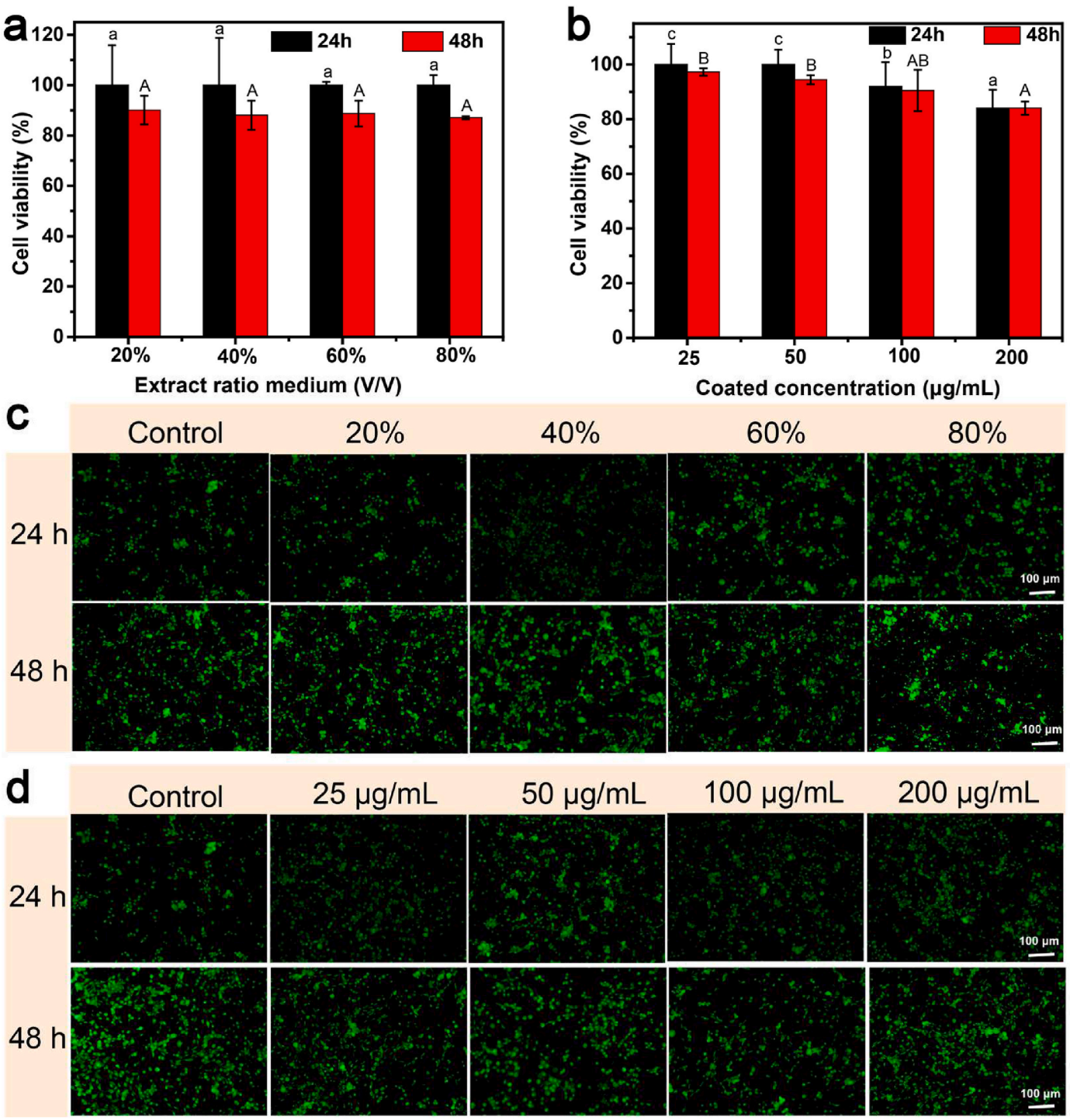

Fig. 5. Viability of L929 cells in the culture mediums containing different concentrations of the 2% coated paper extracts (a) and 2%ChNCs/2.5%HDTMS coating (b); Corresponding LIVE/DEAD staining images of L929 cells cultured for 24 h and 48 h (c, d).

treatment group was similar to that of the control group, the cells were evenly distributed, and the living cells continued to proliferate during the culture process. Thus, the 2% coating on paper has good biocompatibility, which shows a wide range of applications in daily life.

3.9. Application

We folded the paper into a boat and placed it on the water to demonstrate the practical utility of the obtained hydrophobic paper in daily life. It can be seen in Fig. 6a, that the uncoated paper slowly sank under the water due to its hydrophilicity. In contrast, the 2% coated paper still floated on the water after 24 h due to its good hydrophobicity and water resistance. The boat experiment indicated that coated paper could be folded into the desired shape without losing its properties, which provided a possibility for the application of coated paper in paper cups and straw. Firstly, the contact angle of common liquids on the 2% coated paper surface was tested, and the results were shown in Fig. 6b. The contact angle of cola, green tea, milk, coffee, and orange juice was slightly significantly lower than the water ($P < 0.05$), which may be that the liquids have a specific viscosity reducing the interfacial repulsion.

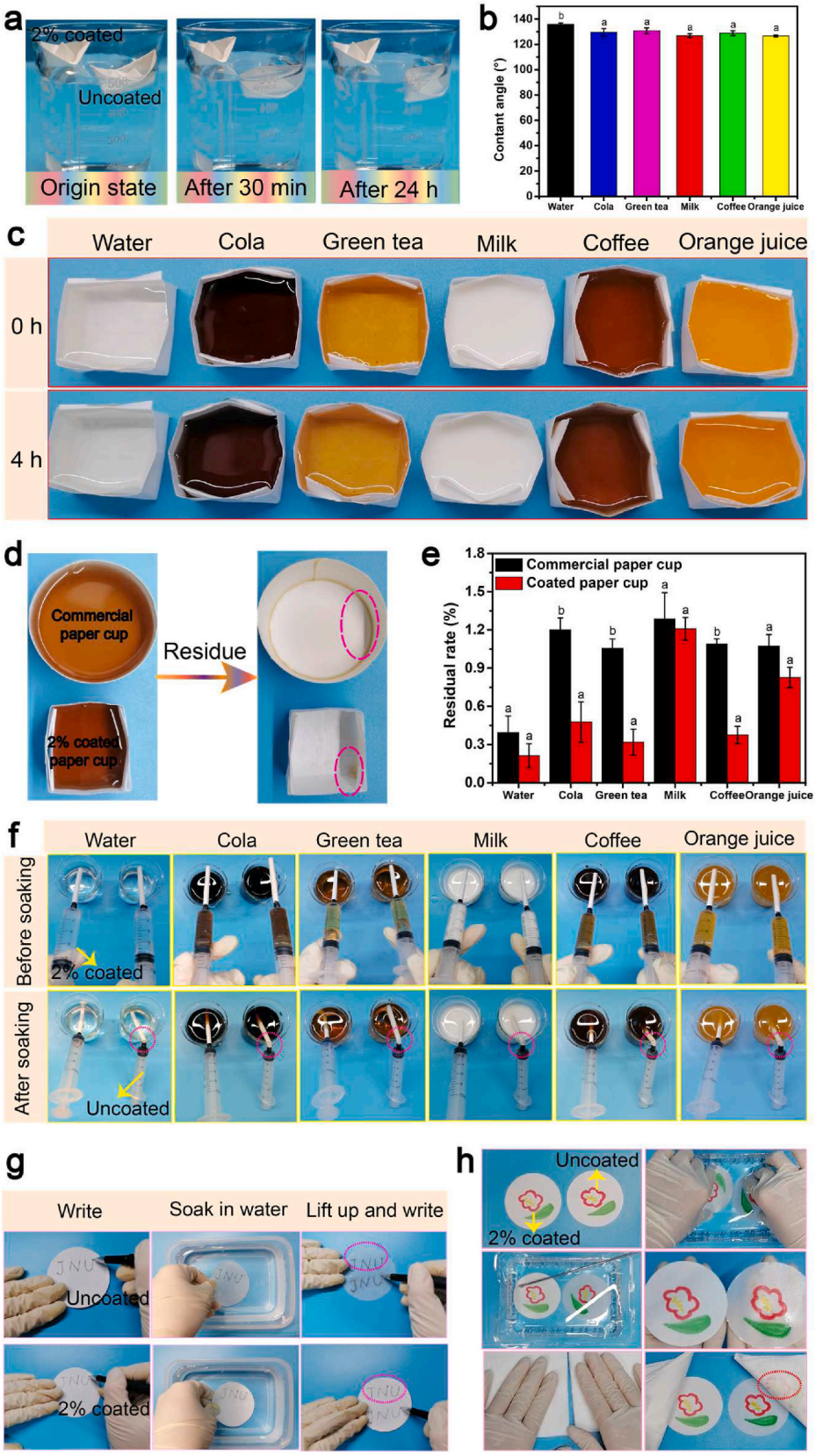

Fig. 6. Appearance of uncoated and coated paper immersed in water for a certain time (a); Contact angle of variety of droplets on the coated paper surface (b); The application in cup (c), drinking straw (f), writing (g) and watercolor protection (h) of the hydrophobic paper; The residue of cola in cups (d); The amount of residue of various liquids in commercial paper cups and coated paper cups (e).

We then folded the coated paper into paper cups to simulate the process of filling liquids. As seen from Fig. 6c, the paper cups can load a variety of drinks, and no deformation or leakage occurred after 4 h in the paper cups. After pouring out the liquids, both commercial and coated cups had some liquid residue (Fig. 6d). By weighing the liquid residue in the cups, we found that the liquid residue rate of the coated paper is lower than that of commercial paper cups (Fig. 6e). Among them, cola, green tea, and coffee significantly reduced ($P < 0.05$). It can be suggested that the obtained coated paper effectively reduces liquid waste from products consumed daily, which is expected to become an alternative to commercial paper cups. Moreover, the coated paper was rolled into a straw to simulate the experiment of sucking liquids, using the uncoated paper as a control, as shown in Fig. 6f and Video 6. With the extension of repeated suction and immersion time, the uncoated straws fully absorbed water and softened, and broke near the pinhole due to gravity. However, the coated straws still play an excellent role in absorbing liquid and maintains its inherent hardness and hydrophobicity. The coated straws are mainly made of biodegradable fiber and will be expected as a substitute for plastic straws. We did not test the potential migration of coating materials to food products due to the hazardous substances content of HDTMS in 2% coated paper is negligible (about 0.46 mg/cm^2), and the cytocompatibility results in Fig. 5 indicates it to be safe as food packaging materials.

Supplementary video related to this article can be found at https://doi.org/10.1016/j.foodhyd.2022.107915.

Simultaneously, we expect to write or draw on cups or straws that are not affected by ambient humidity. Fig. 6g showed writing with a signature pen on the uncoated and coated papers, and there was no apparent difference. After soaking the paper in water for a while, take it out and continue writing on the paper. The ink on the uncoated paper was found to spread. However, the coated paper was not significantly different from before soaking. That is mainly because the coated paper is hydrophobic, and water droplets hardly adhere to the surface after soaking. Similarly, drawing on papers with water-soluble colors and soaking the papers in water, the color on uncoated paper was easy to be peeled off, while the coated paper can keep the pattern intact Fig. 6h. These results suggest that the 2% coated paper can effectively protect water-soluble ink and color. The 2% ChNCs/HDTMS coated paper exhibits wide applications as package materials, protective materials, and containers in daily life since they show water resistance, enhanced mechanical property, thermal-resistance, antibacterial adhesion property, and biocompatibility.

4. Conclusions

The filter paper was dip-coating a layer of ChNCs and HDTMS to prepare hydrophobic packaging materials. SEM and AFM showed that hydrophobic 2% ChNCs/HDTMS coating on the paper's surface forms a film to improve the water vapor barrier of coated paper. Compared with uncoated paper, the coated paper's tensile strength and thermal resistance increased due to the strong hydrogen bond and covalent bond between cellulose fiber and the coating. In addition, the 2% coated paper has good water resistance, bio-safety, and antibacterial adhesion properties. The L929 cell survival rates were more than 80% on the hydrophobic paper, and the *E. coli* and *S. aureus* can hardly grow on the hydrophobic paper surfaces. The hydrophobic paper can be used as cups to load different liquids, straws, and protective coating for calligraphy and painting. This work designed high-performance and environmental-friendly hydrophobic paper in the safe range using renewable chitin bioresources and silane, which will show great potential in green food packaging materials.

Author statement

Yunqing He: Conceptualization, Investigation, Data curation, Writing - original draft. **Youquan Zhou:** Investigation, Formal analysis. **Jiabing Cai:** Investigation, Software. **Yue Feng:** Formal analysis, Validation. **Binghong Luo:** Writing - review & editing. **Mingxian Liu:** Conceptualization, Supervision, Validation, Writing - review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodhyd.2022.107915.

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Supplementary Material

Facile fabrication of hydrophobic paper by HDTMS modified chitin nanocrystals coating for food packaging

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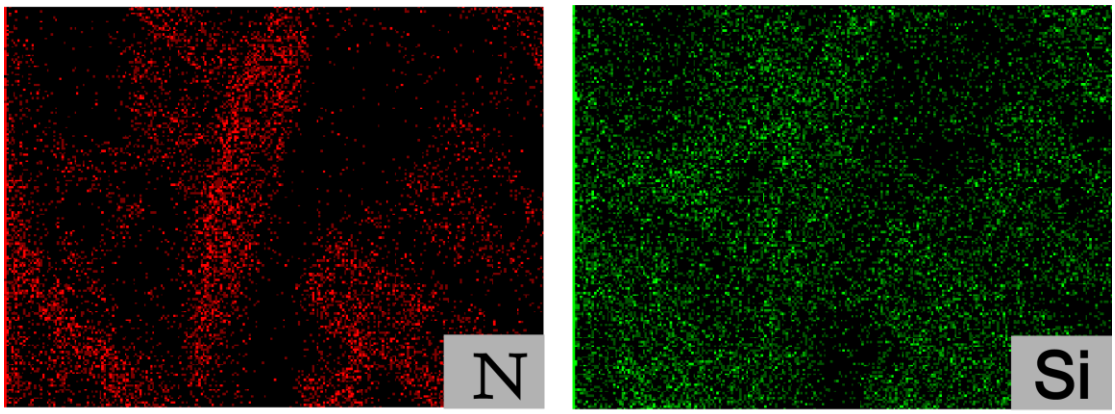

Fig. S1. Views of elemental mapping of the 2% coated paper sample.

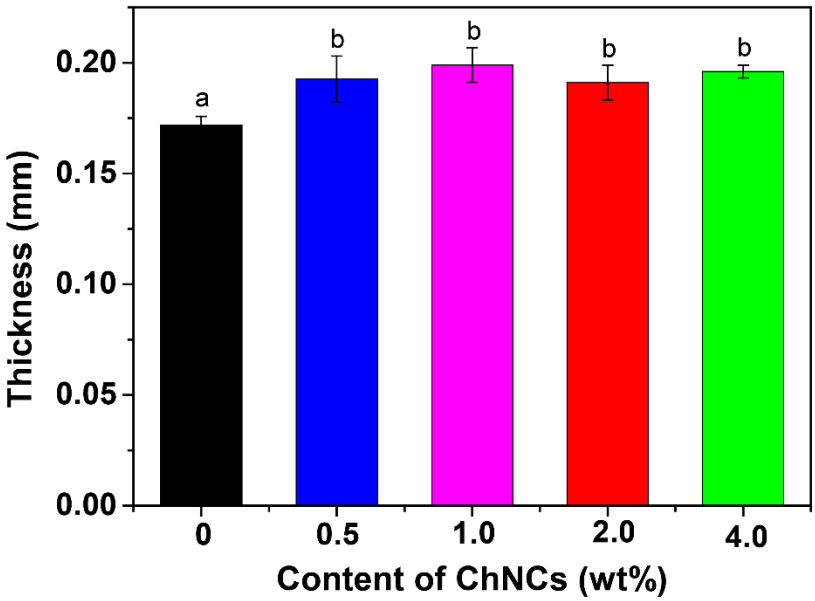

Fig. S2. Dependence of thickness on the content of ChNCs.

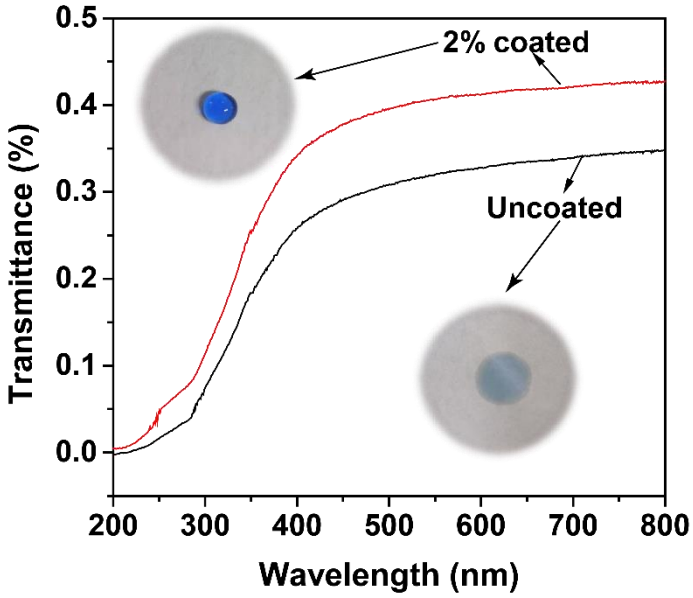

Fig. S3. The UV-vis transmittance spectra of uncoated and 2% coated papers.

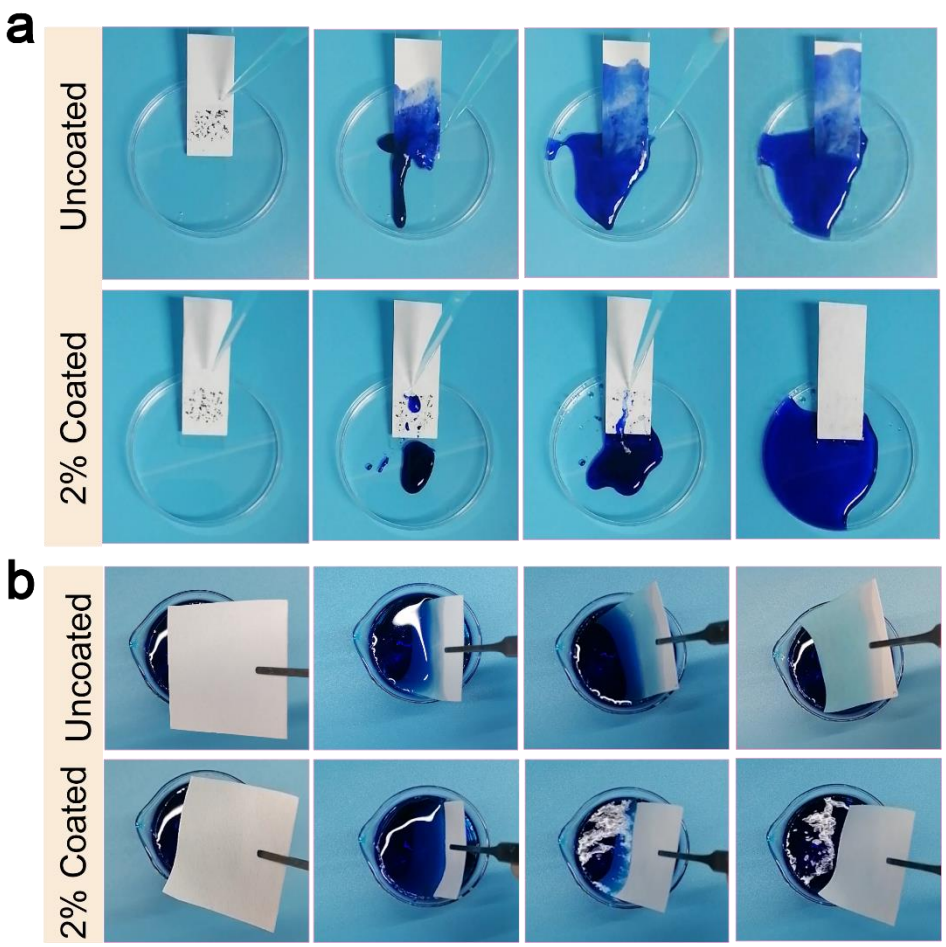

Fig. S4. Photographs of sequential snapshots of self-cleaning properties on the uncoated and coated paper (a); Photographs of uncoated paper and 2% coated paper before and after immersion in methylene blue dyed water (b).

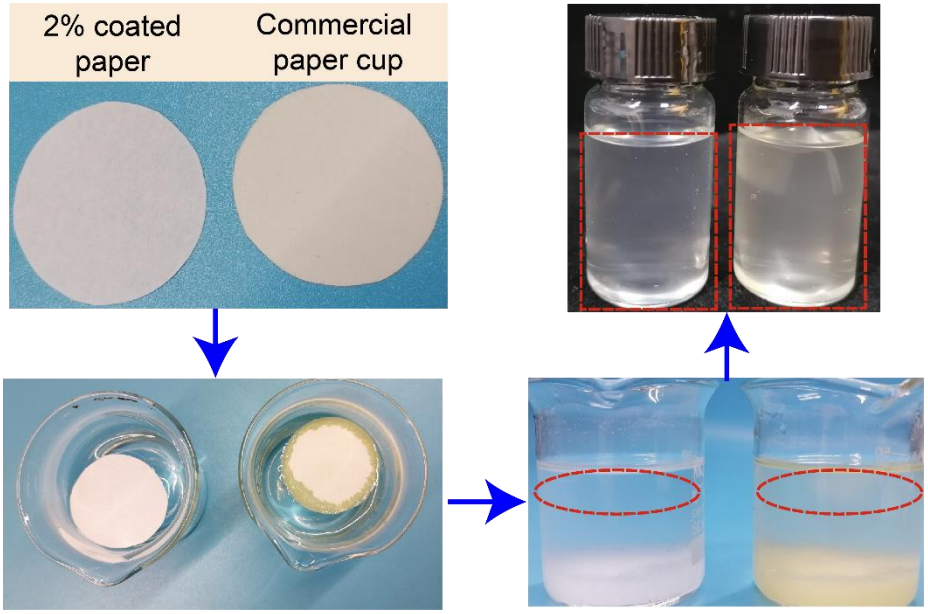

Fig. S5. Chemical degradation of 2% coated paper and commercial paper cups.