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Regular Article

Eco-friendly functionalized superhydrophobic recycled paper with enhanced flame-retardancy

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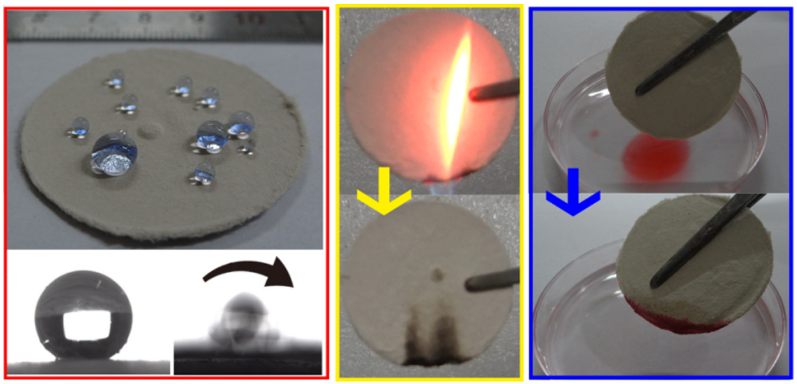
GRAPHICAL ABSTRACT

Eco-friendly functionalized recycled paper with superhydrophobicity and flame-retardancy has been demonstrated which can put up with the invasion of water and fire. What is more, this multifunctional recycled paper display great self-cleaning and anti-fouling ability and can be used to oil-water separation. Surprisingly, the absorbed oil or organic can be reused as fuel via simple combustion method for multiple cycles.



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ABSTRACT

Recycled paper with superhydrophobicity and flame-retardancy has been demonstrated here due to the synergistic action of dopamine-silica trimethylsilyl modified gel powder and stearic acid modified Mg$(OH)_2$. This multifunctional recycled paper displays great self-cleaning and anti-fouling ability and can be used for oil-water separation. Surprisingly, the absorbed organic can be reused as fuel via simple combustion method for multiple cycles. This work will not only expand the usable range of paper but also ease the energy and environment crisis.

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1. Introduction

Papermaking industry is an increasingly important part of the global circular economy chain. Simultaneously, paper is an essential common product in our daily life as well as industry. However, just like a double-edged sword, traditional papermaking industry has also brought up some issues related to energy consumption, air-water pollution and ecosystem destruction [1–5]. With the development of science and technology, most of these issues have been overcome. Especially in recent years, recycled paper must be the optimal choice to solve these problems more completely. Based on the statistics data and analyses, recycled paper can reduce 40% energy consumption and cause 35% less water pollution, 74% less air pollution compared with virgin pulps [6,7]. In addition, short service life and fast dissipation of paper are other reasons making these issues even worse.

It is well known that water and fire are the two leading killers of paper. The strength of paper will be damaged significantly due to the decrease of fiber-to-fiber bonding in paper by water molecules [8]. Then the practicality and aesthetic property will be both influenced. As a highly inflammable commodity, the consequences of fire are far more destructive of paper. Thus, flame-retardant treatment on paper that can delay ignition and hinder flame propagation is necessary to prolong its service life and reduce the risk of fires [9–12]. On the other hand, superhydrophilicity and inflammability greatly limit the applications range of paper, especially in packaging, crafts and transportation fields.

Superhydrophobic surface, inspired by lotus leaves, have always been a research hot point for recent decades [13–17]. For its high water contact angle (WCA) (>150°) and low water sliding angle (SA) (<10°), superhydrophobic surface possesses wonderful waterproof ability and self-cleaning, anti-fouling abilities [18]. As the theory research moves along, nano- and micro-hierarchical roughness and low surface energy are identified as the key to achieve superhydrophobicity, which is a powerful heuristic to create waterproof paper. However, low energy modifiers are generally fluorine-contained substances that has significant shortcomings in highly-toxic and highly-cost [19–22]. These shortcomings must restrict its wider applications. Similarly, flame-retardant materials have become one of the research focuses now [23–25]. Halogenated flame retardants are the most common choice by now but its bioaccumulate and toxicity make it invalidate here. For the moment, to develop eco-friendly flame-retardant and superhydrophobic paper is still a huge challenge [26].

Inspired by nature and traditional papermaking method, we present an eco-friendly superhydrophobic & flame-retardant recycled paper successfully by taking advantage of the synergistic action of dopamine–silica trimethylsilyl modified gel powder (DTMGP for short) and stearic acid modified $Mg(OH)_2$ (STA-MH for short). The superhydrophobic & flame-retardant recycled paper not only can be used as paper package material with self-cleaning and anti-fouling abilities but also has the potential to be absorbent for water-oil mixture separation. It's worth mentioning that the absorbed oil can be removed through simple combustion method and then the superhydrophobic & flame-retardant recycled paper can be reused for several times

2. Experimental

2.1. Materials

3-Hydroxytyramine hydrochloride (dopamine hydrochloride, 99.5%) was purchased from Sigma-Aldrich. 1,1,1,3,3,3-hexamethyl disilazane (HMDS, 98%) was obtained from Shanghai KEFENG Chemical Reagent Co. Lnc, China. Magnesium hydroxide ($Mg(OH)_2$, 98%) and stearic acid (chemical pure) were purchased from Xilong Chemical Co., Ltd, China. All other chemicals were analytical-grade reagents and used as received. Millipore water (resistivity ~18 MΩ cm) was used throughout this study.

2.2. Preparation of hydrophobic $Mg(OH)_2$

The hydrophobization process of $Mg(OH)_2$ belongs to the acid-base reaction between stearic acid (STA) and $Mg(OH)_2$ via simple one-step immersion method. 0.3 g $Mg(OH)_2$ was soaked in 30 ml ethanol solution of STA (5 mM) under wild stirring for 2 h at room temperature. After filtered and washed with deionized water and ethanol respectively, and dried at 60 °C for 3 h. Then, the hydrophobic STA modified $Mg(OH)_2$ (STA-MH) was obtained.

2.3. Preparation of dopamine-silica trimethylsilyl modified gel powder (DTMGP)

The preparation of superhydrophobic SiO_2 gel powders was carried out through sol-gel and solvothermal method as described by previous work of our group [27]. Typically, 5 mL tetraethoxysilane (TEOS) was dissolved in 10 mL methanol, then a mixture of 7.5 mL NH_4OH (0.02 M) and 10 mL CH_3OH was added into this solution with stirring. 3.5 mL of HCl (0.1 M) was added dropwise to this mixture. Now, pH of this system was close to 5. 0.02 g dopamine hydrochloride was added and kept stirring for 3 h. Then, 1.5 mL NH_4OH (25–28%) was dropwise slowly to turn pH into 8–9. After aging for 12 h, the brown opaque DOPA-silica gel was formed. DOPA-silica gel, 50 mL of *n*-hexane and 7.5 mL of 1,1,1,3,3,3-hexamethyl disilazane (HMDS) were added into autoclave together and kept 80 °C for 10 h. After filtered and washed with *n*-propanol twice, the dopamine-silica trimethylsilyl modified gel powders were obtained. Whitey-brown dopamine-silica trimethylsilyl modified powders were consisted by the silica colloid particles of around 30 nm in size covered with $-OSi(CH_3)_3$ (see Fig. 1S and the optical image was shown in Fig. 2S, Supporting Information).

2.4. Preparation of Superhydrophobic & flame-retardant recycled paper via papermaking method

Waste paper fragments 0.3 g was immerged into deionized water 60 mL under vigorous stirring conditions at 80 °C. After 3 h, an aqueous suspension of rough cellulose fibers pulp was obtained. After filtered and washed with deionized water and ethanol twice, respectively, cellulose fibers pulp was re-dispersed into ethanol 30 mL under gentle agitation at room temperature for 30 min. Different weight ratios of HMH and SSGP on the basis of the weight of waste paper fragments were added into this system. After stirring for 30 min, wet cake-like STA-MH@SSGP@ cellulose fibers was get after filtered. Dried at 60 °C in air condition for 2 h, finally, the "dry pulp cake" was pressed into paper using Tablet press under 5 MPa. Then the superhydrophobic & flame-retardant recycled paper is final formation.

2.5. Characterization

Field emission scanning electron microscope (FESEM) images were obtained on JSM-6701F, both with Au-sputtered specimens. X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi) measurement using the Al Kα line as the excitation source. Transmission electron microscopy (TEM) measurements were carried out with a TechnaiG20 (FEI) operating at 300 kV. The UV–visible spectra were obtained with a Cary 60 scan spectrophotometer. TG/DTA measurements were done with NETZSCH STA 449 C using a dynamic heating rate of 10 °C min^{-1}. Fourier transformer infrared spectra (FTIR) spectroscopy was