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Durable superhydrophobic cotton filter prepared at low temperature for highly efficient hexane and water separation

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ABSTRACT

A composite of ZnO and cotton fabric (ZnO–CF) with a superhydrophobic surface was successfully synthesized with Teflon-lined stainless steel autoclave at low temperature 100 °C. X-ray diffraction (XRD) results indicated that the fabricated ZnO–CF had a uniform stacked hexagonal slice structure without any impurities. The fabric surface firmly bonded with ZnO through chemical bonding and possessed superhydrophobicity with a surface water contact angle (WCA) greater than 150°. The rough structure of ZnO and the enhancement of nonpolar functional groups on the composite surface gave ZnO–CF its superhydrophobicity. ZnO–CF showed a stable and robust self-cleaning property. When applied to separate a mixture of water (dyed with methylene orange) and organic solvent (hexane), ZnO–CF achieved a separation efficiency of over 99% that decreased only insignificantly even after several cycles. Therefore, this outstanding separation performance demonstrates the strong potential of ZnO–CF for practical applications such as wastewater treatment and water purification.

1. Introduction

Selective separation technologies for organic solvents and aqueous solution containing organics have become global concerns along with the huge increases in wastewater volume requiring proper treatment. Conventional separation methods, such as oil skimming [1], centrifuging [2], and flotation [3], are limited by numerous disadvantages, such as low separation efficiencies, high costs and complicated equipment requirements [4]. There are several publications reported on the organic solvents and aqueous solution separation with outstanding methods [5–7]. Recently, superhydrophobic filters are promising candidates for organic solvents/water separation if they have high efficiency, low cost and environmentally friendly properties. The superhydrophobic filters with water contact angle (WCA) higher than 150° and organic solvent contact angle less than 5° [8–12] could become the potential candidates for the selective separation of organic solvent/water because they can absorb organic solvent only while repelling water.

Inspired by the water repellency ability of lotus or taro leaves, various superhydrophobic materials have been developed for organic solvent/water separation. For instance, the PMIA/SiO_2 membrane with a dense silicone nanofilament layer was prepared to separate water from light oil (canola oil) and heavy oil (carbon tetrachloride, CCl_4) [13]. A fabrication method of the superhydrophobic filter paper was also developed via colloidal deposition [14]. Superhydrophobic copper mesh filters were fabricated via a hydrothermal method to separate diesel from water [15]. However, only a few studies have reported the utilizations of cotton fabric to make the superhydrophobic filter.

Cotton fabric is well known as a porous, rough, flexible and hydrophilic surface with extremely high water absorption ability. As a result, cotton fabrics cannot be used for organic solvents–water separation in their original form because they strongly absorb water and other organic solvents. Thus, prudent chemical modifications are required to control the selectivity and wettability of cotton textiles. Also, maintaining good stability of the cotton fabric-based material and coating with non-toxic chemicals are essential for large-scale practical application.

In this study, we attempted to fabricate superhydrophobic surfaces that can exhibit the superhydrophobicity by the ZnO particles deposition on the cotton fabric surfaces via a very simple hydrothermal method at low temperature. ZnO was selected as the functional material due to its superior biochemical abilities: ZnO is biocompatible, biodegradable and bio safe for environmental applications [16,17]. Furthermore, ZnO is expected to exhibit more advanced controllable wettability due to the ease with which the surface structure can be developed [18,19]. ZnO has abundant structures: hexagonal, wurtzite, rod, pillar, wire, belt, flake, and

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flower-like [20–23]. The WCA can be enhanced by using ZnO's microstructure or nanostructure to change in the surface roughness of the cotton fabric. The goal of the present study is to fabricate a ZnO coating on a cotton fabric surface (ZnO–CF) capable of satisfying the criteria for water superhydrophobicity. The properties of fabricated ZnO–CF were sufficiently studied and the results showed that ZnO–CF have excellent superhydrophobicity, mechanical stability and reusability. After that, it was used to selectively absorb hexane while repelling water completely. The relationship between the surface properties and the wettability of the fabrics was also discussed in detail.

2. Experiments and methodologies

2.1. Materials

Zinc acetate dihydrate ($Zn(CH_3COO)_2•2H_2O$), zinc nitrate hexahydrate ($Zn(NO_3)_2•6H_2O$), ammonium hydroxide (NH_4OH) and hexamethylenetetramine (HMTA, $C_6H_{12}N_4$) were all purchased from Samchun Pure Chemical Co., Ltd, Korea. All chemicals were reagent grades and used as received without further purification. Deionized water was used for all experiments.

Cotton fabric was purchased from a local store in Ulsan, Korea. The cotton fabric was cut into 10×10 cm pieces, cleaned in an ultrasonic bath for 2 h with a mixture of methanol and water, were washed several times with deionized water and dried in an air oven at 50 °C for 24 h.

2.2. Fabrication process

2.2.1. Preparation of ZnO crystal nucleus

In a typical process to prepare the cotton fabric loaded with Zn^{2+}, as an initial step, $Zn(CH_3COO)_2•2H_2O$ was dissolved in water at a concentration of 0.03 M. A piece of cotton fabric was then immersed into the prepared zinc acetate solution. NH_4OH was then slowly added into the solution with stirring maintained for 3 h at 50 °C. Cotton fabric with Zn^{2+} nucleus was dried in an air oven at 50 °C for 12 h.

2.2.2. Preparation of ZnO-coated cotton fabric (ZnO–CF)

A 1:1 molar ratio mixture of 0.025 M $Zn(NO_3)_2•6H_2O$ and 0.025 M HMTA was prepared with constant stirring for 3 h. A piece of cotton fabric loaded with Zn^{2+} nucleus was immersed in this transparent mixture in a 200 mL Teflon-lined stainless steel autoclave. The autoclave was heated in a laboratory oven at a constant temperature of 100 °C for 6 h. After that, the autoclave was taken out from the oven and cooled down at room temperature. The fabric was cleaned several times with deionized water and dried in an air oven at 50 °C for 24 h.

2.3. Material characterizations

The surface morphology and chemical composition of the original cotton fabric and ZnO–CF were characterized by using field emission-scanning electron microscopy (FE-SEM, JEOL 6500), X-ray diffraction (XRD, AXS D8 ADVANCE) and X-ray photoelectron spectroscopy (XPS, Thermofisher Scientific K-Alpha).

The surface roughness was evaluated by confocal fluorescence microscopy (Keyence VK-X200) with a sample magnification of 50 times. The static WCA was measured using a Smart drop contact angle system maintained by a computer-controlled device with the 5 µL droplet. The fabric samples were enclosed on glass slides with double-side tape before the confocal and WCA analysis. The WCA test was conducted at least five times at different areas on each sample. The Young's equation (Eq. (1)) can be applied to calculate the WCA on the fabric surface.

$$\cos\,\theta = (\gamma_{s-v} - \gamma_{s-l})/\gamma_{v-l} \quad (1)$$

where $\gamma_{s\text{-}v}$ is the solid-vapor interfacial energy, γ_{s-l} is the solid-liquid interfacial energy and γ_{v-l} is the vapor-liquid interfacial energy.

The advancing WCA measurements including sliding WCA and shedding WCA were also carried out in order to confirm the superhydrophobicity of the surface [24]. All the equipment was placed on a balance table under ambient condition in order to minimize the experimental error. The sliding WCAs at 1° to 10° at intervals of 1° were also measured using the experimental unit shown in Fig. S1(a). For the shedding WCA measurement, the measurements were carried out as some reported studies [24]. The fabric sample was placed on a tilting base and the measurements were started at an inclination angle of 50° (Fig. S1(b) and (c)). The syringe was kept at 2 cm far away from the sample surface and the volume of the drop was controlled at 5 µL. If all droplets run off from the fabric surface, the angle was reduced by 1° and the experiment finish until the drop cannot completely run off the surface. The lowest angle at which all the drops completely come out from the fabric surface was noted as the shedding WCA.

2.4. Separation test

In the separation test, 20 mL of water (dyed with methylene orange) and 20 mL of hexane taken by a mess cylinder were mixed vigorously. After that, the hexane-water mixture was poured onto the fabrics. The separation of hexane from water was performed as shown in Fig. 1. The same experiment process was also carried out with other types of oil (including toluene, octane, chlorobenzene, kerosene and diesel) in order to check the oil-water separation ability of fabricated ZnO–CF.

In this experiment, the effect of the hexane mass on the separation efficiency was not evaluated due to its penetration into the fabric and its ease of in evaporation. The separation capacity of cotton fabric was calculated depending on the mass of water according to Eq. (2):

$$\text{Separation capacity} = \frac{M}{M_0} \times 100\% \quad (2)$$

where M_0 and M are the weights of water before and after separation, respectively. The value of M_0 was measured before water was mixed with hexane and the value of M was measured immediately after the separation process. The average value of 10 separation experiments was used. Some procedural and instrumental errors could be involved in the transfer process of the liquid mixture into different apparatuses, the subjective view in the mess cylinder and the balancing process. However, the total measurement error was less than 3%, thus the accuracy of the data is acceptable. UV–Vis spectrometry (UV–Vis, USA Model GENESYS 10S) with a quartz cuvette was used to confirm the purity of the water after the separation process. The scan range was 200 to 800 nm, using baseline correction with a medium scan rate and a data point interval of 1 nm.

The flow separation flux (J) was determined by calculating as the following equation:

$$J = \frac{V}{A \times T} \quad (3)$$

where V is the volume of the permeated solution, A is the separation area and T is permeated time.

2.5. Stability and reusability test

The durability or mechanical stability and the reusability of a material are very important for practical applications. To the

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