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Original Research Article

Preparation and characterization of hydrophobic cotton fiber for water/oil separation by electroless plating combined with chemical corrosion

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In this study, cotton fibers were coated with nickel film using a simple electroless plating process, followed by chemical corrosion and stearic acid treatment, to develop hydrophobic cotton fibers for oil/water separation. The effects of chemical corrosion and stearic acid treatment on the contact angle of the resulting cotton fibers were discussed. The hydrophobic cotton fibers were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photo electron spectroscopy (XPS). The adsorption capacities of petrol and soybean oil were measured. The results show that the surface contact angle reached approximately 138° when the nickel-coated cotton fibers were immersed in Cu^{2+} solution for 30 min and treated with stearic acid for 5 h. The SEM and XRD results indicate that microroughness formed on the surface of the resulting cotton fibers, causing the hydrophobicity of the surface. The adsorption capacities for petrol and soybean oil were 14.98 and 7.52 g/g, respectively. The results suggest that this work provides a new and feasible method for developing cotton fiber-based materials for oil/water separation.

Key words: Cotton fiber, electroless plating, chemical corrosion, hydrophobicity, oil adsorption

INTRODUCTION

In recent years, water pollution resulting from natural and anthropogenic oil spillage has been frequently reported. It is known that oil pollution can cause serious environmental disasters and even harm ecological security. Conventional methods for cleaning up spilled oil include chemical degradation, bioremediation (Lin et al., 2014), mechanical extraction, combustion, and adsorption (Said et al., 2009; Chin et al., 2014; Liu et al., 2014). However, secondary pollution may be caused by the toxic by-products of some of these processes. It has been found that oil adsorption by sorbent materials is a simple and efficient method for cleaning oil spills. Oil sorbent materials such as carbon nanotubes (Gui et al., 2011), nanocomposites (Tao et al., 2011), and foams (Zhu et al., 2011, 2013) have been developed. However, their high cost limits their further application in oil removal. Therefore, finding a novel, low-cost sorbent is necessary.

Bio-based sorbent materials have attracted attention for oil removal because of their renewability and abundance. However, biomass consists of cellulose, hemicellulose, and lignin. Cotton is a kind of the biomass. Cotton fiber has a affinity to some pollutants. Therefore, it can be used as an sorbent material and easily recycled. But its hydrophilic nature leads to a low affinity with non-polar oil. Therefore, surface modification is required to fabricate a hydrophobic and coarse surfactant structure by introducing roughness combined with a coating with low-surface energy molecules.

Several studies have been conducted on cotton fibers. Superhydrophobic cotton textiles were prepared using a superhydrophobic composite thin film containing modified ZnO nanoparticles and polystyrene (Zhang et al., 2013). The

Table 1: Composition and Operation Conditions of Electroless Plating

Chemicals	Content (g/L)
$NiSO_4 \cdot 6H_2O$	30
$NaH_2PO_2 \cdot H_2O$	32
Complexing agent	35
NH_4Cl	20
pH	8.0
Temperature (°C)	70

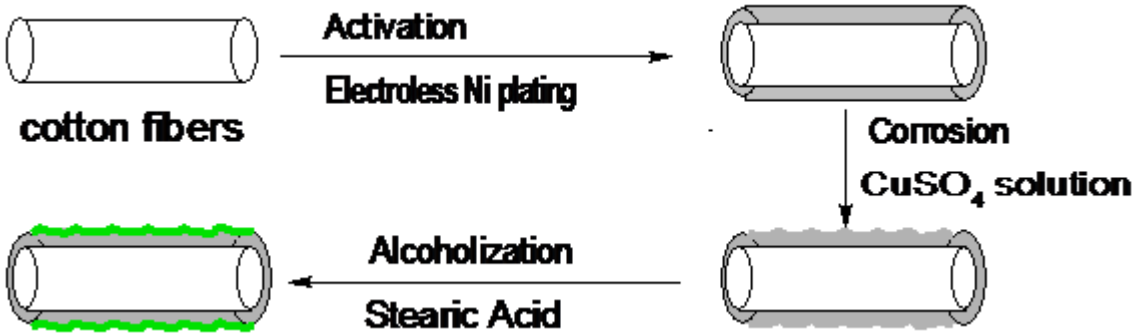

Figure 1: Schematic illustration of the procedure for the preparation of the hydrophobic surface of cotton fiber

combination of SiO_2 nanoparticles on cotton fiber surface octadecyltrichlorosilane modification was successfully used to prepare superhydrophobic/superoleophilic cotton fibers for water/oil separation (Liu et al., 2014). However, that modification method is complicated. Electroless plating is an effective process for obtaining metal film on the surface of biomaterials. The film is uniform and continuous. To the best of our knowledge, electroless plating combined with chemical corrosion has not been reported in the modification of cotton fiber for obtaining a hydrophobic surface.

In this work, cotton fiber was coated with nickel film using a simple electroless plating process, followed by chemical corrosion and stearic acid treatment. The effects of chemical corrosion and stearic acid treatment on the contact angle of the resulting cotton fiber were investigated. The hydrophobic cotton fibers were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photo electron spectroscopy (XPS).

MATERIALS AND METHODS

Materials

Cotton fibers were purchased from a local store. Nickel sulfate ($NiSO_4 \cdot 6H_2O$), copper sulfate ($CuSO_4 \cdot 5H_2O$), ammonium chloride (NH_4Cl), sodium hypophosphite ($NaH_2PO_4 \cdot H_2O$), stearic acid ($C_{16}H_{32}O_2$), ethanol (C_2H_5OH), hydrochloride (HCl), $PdCl_2$-$SnCl_2$ and ammonia ($NH_3 \cdot H_2O$) were purchased from Tianjin Kermel Chemical Reagents Development Center. All chemicals were of analytical grade.

Activation and plating procedure

The activation process was as follows: cotton fibers were dipped in $PdCl_2$-$SnCl_2$ solution for 6 min at room temperature, then immersed into HCl solution for 1 min and hung in the air for about 1 min. After that, the activated cotton fibers were placed into the plating bath for electroless plating for 10 min.

The composition of the electroless bath and the operation conditions are shown in Table 1. The pH of the bath was regulated using $NH_3 \cdot H_2O$.

Corrosion procedure

The plated cotton fibers were immersed into $CuSO_4$ solution (0.25 M) for a set amount of time, followed by washing with water to remove residues, and then dried in an oven at 90 °C for 3 h.

Alcoholization procedure

After chemical corrosion, the cotton fibers were treated in 0.3 M stearic acid-ethanol solution for a set amount of time, then hung in the air for approximately 1 min and dried in an oven at 120 °C for 3 h. The schematic illustration of procedure is shown in Figure 1.

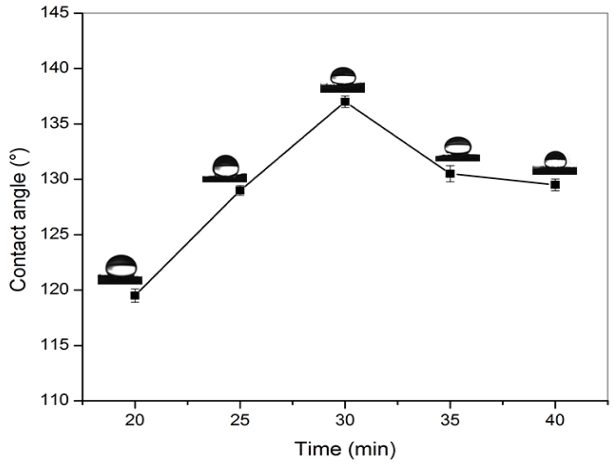

Figure 2: Effects of corrosion time on contact angle

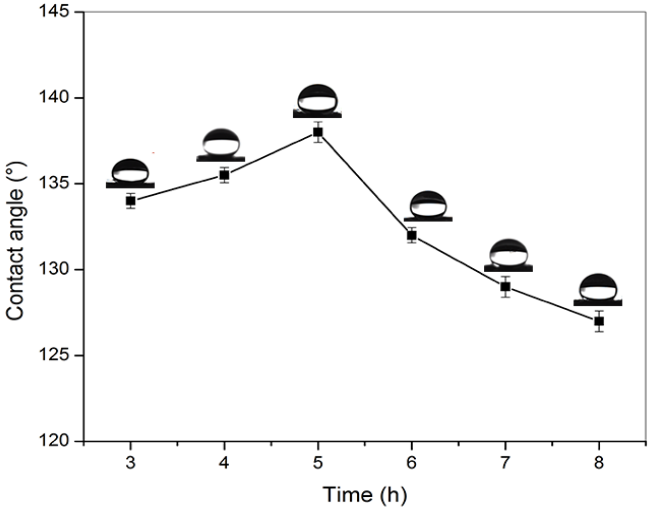

Figure 3: Effect of stearic acid-ethanol soak time on surface contact angle (soak volume 25 mL; temperature 30 ℃)

Characterization Methods

The surface morphology and elemental compositions of the pristine resulting cotton fibers were determined using scanning electron microscopy (SEM, Quanta 200, Philips-FEI Co., The Netherlands). The accelerating voltage was 12.5 kV. The phase structure of the cotton fibers under different treatment conditions was investigated using X-ray diffraction (XRD, D/max2200 diffractometer, Rigaku, Japan) using a Cu K_α radiation generator operated at 1200 W (40 kV×30 mA). XPS was used for chemical state analysis of the copper coating. XPS signals were recorded with a K-Alpha XPS Analyzer (ThermoFisher Scientific Company) using an Al K_α source.

Measurement of contact angle

The wettability of the cotton fibers was determined by the sessile drop method using a contact angle measurer (OCA20, Dataphysics Company, Germany). Twenty microliters of distilled water were dropped onto the surface of the films. The angle between the drop and the surface of the film was measured.

Oil absorption test

To further investigate the cotton fibers' hydrophobic performance, soybean oil and petrol were selected for sorption experiments. The sorption experiment was carried out as follows: the samples were immersed in the oil-water mixture (200 mL) for approximately 30 min, then hung in the air for 30 s to let the surface residual liquid drip away before being weighed. All tests were performed at room temperature.

The sorption capacity of the sample was expressed in terms of grams of oil absorbed per gram of cotton (g/g), according to Equation 1:

$$Q_t = (M_t - M_0)/M_0 \quad (1)$$

Where Q_t (g/g) is the sorption capacity of the as-prepared cotton at a certain time t (s); M_t (g) is the weight of the as-prepared cotton after absorption, and M_0 (g) is the initial weight of the as-prepared cotton.

RESULTS AND DISCUSSION

Effect of $CuSO_4 \cdot 5H_2O$ corrosion time

The plated cotton fibers were decomposed with Cu^{2+} to fabricate roughness on the surface. Corrosion time is a key factor. As shown in Figure 2, the surface contact angle increased from 119.5 to 137° with an increase in corrosion time from 20 to 30 min, then decreased from 137 to 129.5°. The maximum value occurred at 30 min. The purpose of chemical corrosion is to obtain roughness by breaking the continuous nickel film. Suitable corrosion time can result in a rough microstructure for the fabrication of the hydrophobic surface. Longer corrosion time may transform more nickel film to Ni^{2+} into the corrosion solution, which leads to the fabrication of rough surface failure.

Effect of stearic acid-ethanol soaking time

Stearic acid ($C_{17}H_{35}COOH$) is a hydrophobic material with low surface energy. A layer of stearic acid formed on the surface of the rough nickel coating on the cotton fibers after treatment with stearic acid ethanol solution, which further improved the hydrophobicity of the resulting cotton fibers. As shown in Figure 3, the contact angle increased from 134 to 138° when treatment time was increased from 3 to 5 h. However, the contact angle decreased with treatment times longer than 5 h. This may be because the shorter treatment times prevented the formation of a continuous hydrophobic layer of stearic acid. On the contrary, excessive treatment

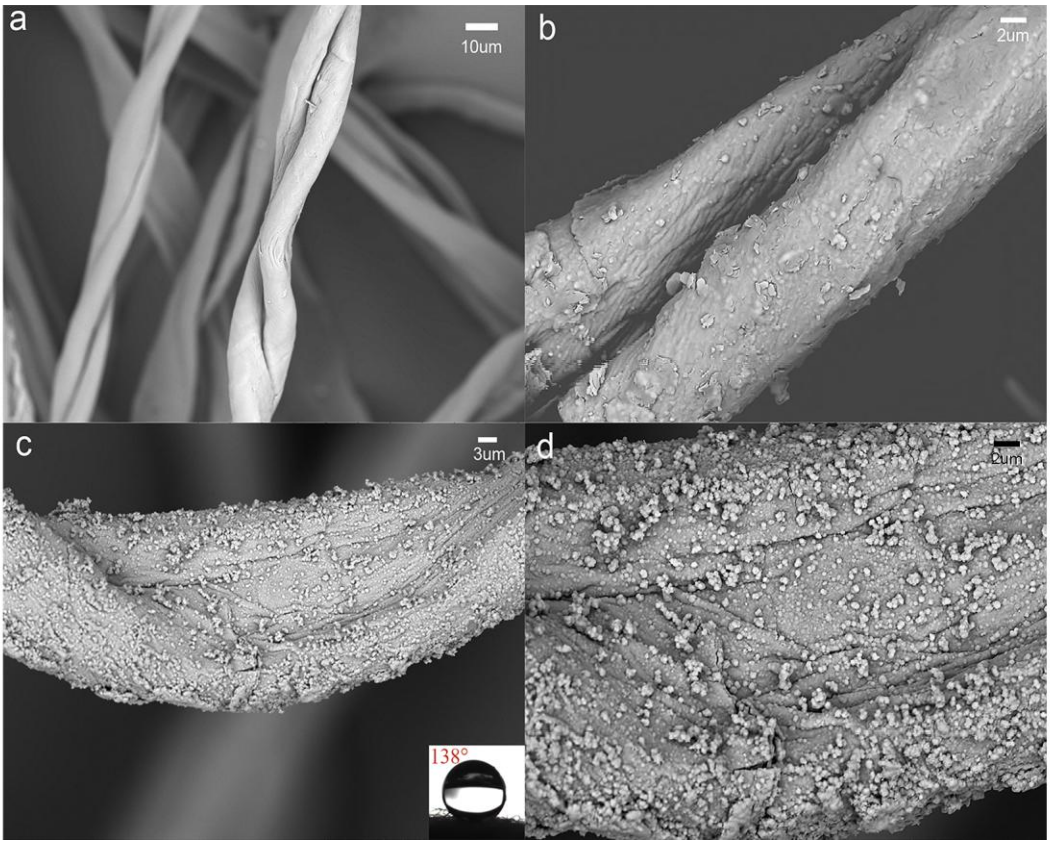

Figure 4: SEM photographs of (a) the pristine cotton fiber; (b) the plated cotton fiber; and (c, d) the as-prepared cotton fiber

durations resulted in a thicker layer of stearic acid, which reduced the surface roughness and therefore decreased the contact angle. According to the results, a treatment time of 5 h is suitable.

Surface morphology

The surface morphologies of the pristine cotton fiber, nickel-coated cotton fiber, and the as-prepared cotton fiber were observed using SEM and are shown in Figure 4. The surface of the pristine cotton fiber, with a fine-wrinkle structure, is smooth and clean. After being plated with a layer of nickel, the surface was continuous and compact. A few little flake formed on the surface of the nickel layer. Moreover, the wrinkle structure of the cotton fiber remained intact after being plated. After chemical corrosion, the surface changed noticeably. The microroughness of the surface was successfully developed on the surface. This surface structure is the base of hydrophobicity.

XRD analysis

Figure 5 shows the XRD patterns of pristine cotton and as-prepared cotton fibers. The strong peak at 2θ=22.43° is a characteristic peak of cellulose in cotton fibers. In the case of cotton fibers coated with a nickel layer, two peaks, at 2θ=44.64° and 51.58° (Kong et al. 2002), can be attributed to Ni (111) and Ni (200), which indicates the face-centered cubic phase of nickel. Moreover, the peak at 2θ=22.43° became weaker, which indicates that the cellulose was entirely covered by the continuous nickel layer. After chemical corrosion, the characteristic peak of cellulose became slightly stronger, which shows that the continuous surface of the nickel layer was broken, and roughness formed. After treatment with stearic acid, a series of new peaks at 2θ=21.75° and 36.58° occurred, indicating the ordered structure of stearic acid on the decomposed surface (Lodha and Netravali 2005). All XRD results are in agreement with those observed from SEM photographs.

XPS analysis

XPS analysis was used to provide further information about the chemical state of the surface of the Ni-P coating before and after corroded. A typical XPS wide spectrum is shown in Figure 6, which indicates that nickel, phosphorus, carbon, oxygen elements were detected. The peaks at 859.33 eV, 876.67 eV, and 1014 eV are attributed to $Ni2p_{3/2}$, $Ni2p_{1/2}$, and Ni 2s, respectively. The peaks at 114.67eV, 284.67 eV, and 530.67 eV are attributed to P, C, and O, respectively (Table 2). The results imply that Ni-P alloy coating was

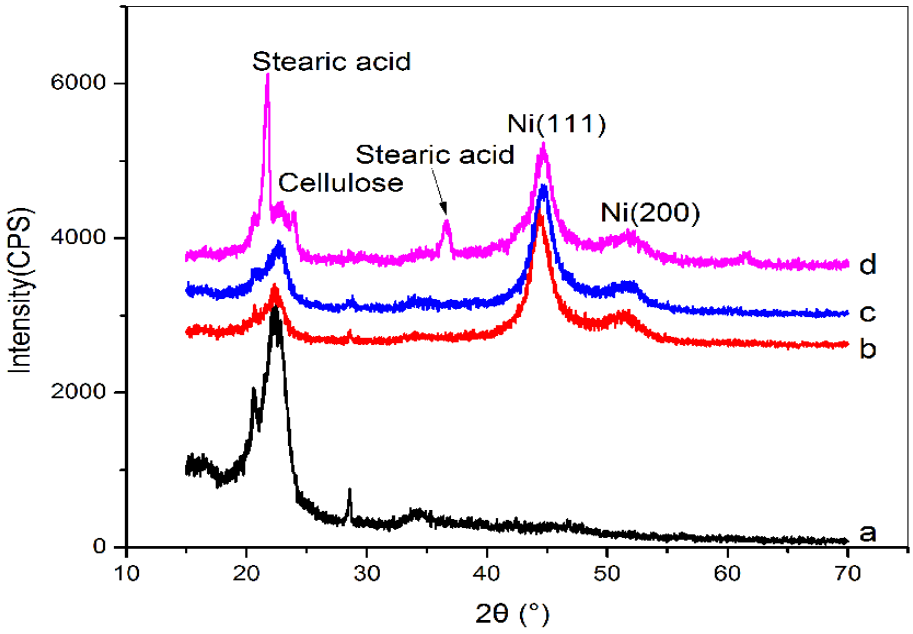

Figure 5: XRD patterns of (a) the pristine cotton; (b) the plated cotton fiber; (c) the corrosion cotton fiber; and (d) the as-prepared cotton fiber

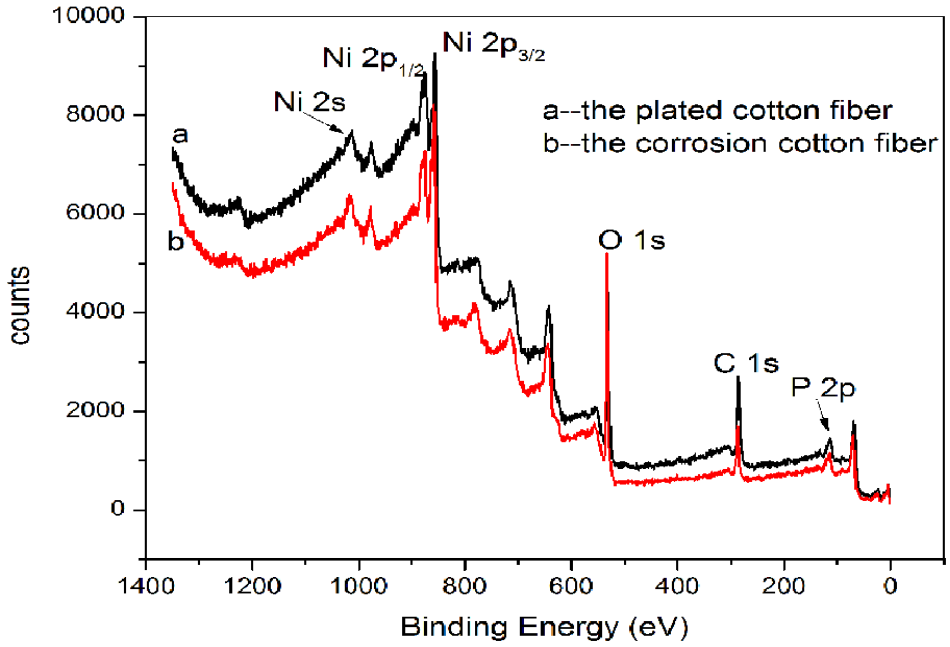

Figure 6: XPS spectrum of Ni-P coated cotton fibers before and after corrosion

successfully deposited on the surface of the cotton fibers. Nickel and phosphorus co-deposited in the plating process, as written below:

$H_2PO_2^- + H_2O \rightarrow H_2PO_3^{2-} + H^+ + 2H$

$Ni^{2+} + 2H \rightarrow Ni^0 + H_2$

$H_2PO_2^- + H \rightarrow P + H_2O + OH^-$

XPS can only detect to a depth of several nanometers, which is far less than the thickness of the Ni-P coating. Therefore, O and C peaks indicated that the contaminants really existed on or in the coating.

After Cu^{2+} corrosion, the intensity of the peaks of Ni decreased, however, those of C and O increased, which indicated that Ni metal transformed to soluble Ni^{2+} and went into the corrosion solution so that the surface of the Ni-P coating became rough and the thickness of the corroded position became thinner. So, the C, O of cotton

Table 2: The Elemental Composition Obtained from XPS Measurements

Elemental composition	Binding Energy (eV)
P 2p	114.67
C 1s	284.67
O 1s	530.67
Ni $2p_{3/2}$	859.33
Ni $2p_{1/2}$	876.67
Ni 2s	1014

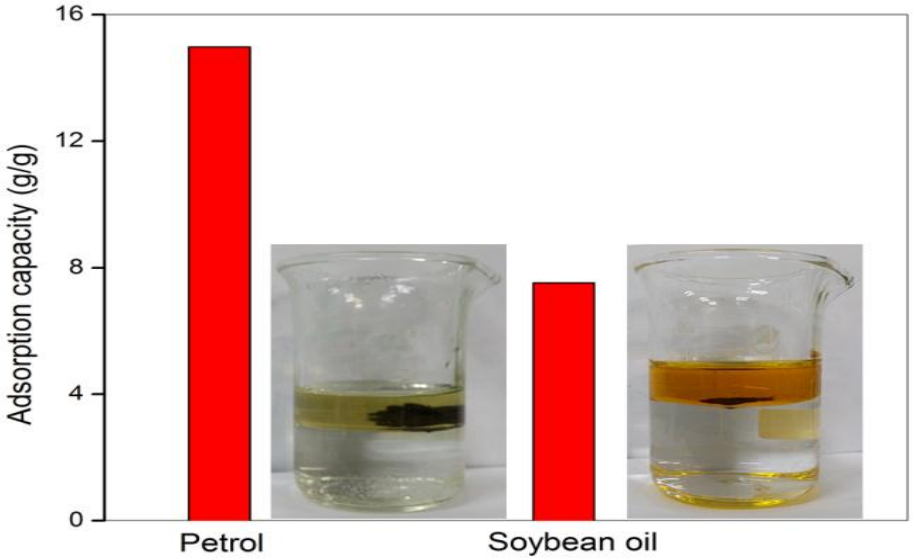

Figure 7: Photo of the affinity to oil and adsorption capacity of the as-prepared hydrophobic cotton fibers

fibers were detected. Those indicated roughness formed on the surface of the coating. The results further proved the XRD analyses.

Adsorption of oil

The aim of this study was to fabricate hydrophobic cotton fibers for oil/water separation. The oil absorption capacity was measured in a mixture of water and oil. As shown in Figure 7, the pristine cotton fibers have a high affinity with water and cannot absorb oil into the mixture. However, the as-prepared cotton fibers absorbed the oil layer, indicating that they have high hydrophobicity and an affinity with oil. The adsorption capacities for petrol and soybean oil were 14.98 and 7.52 g/g, respectively. Modification of cotton fibers with metal greatly increased the total weight. Therefore, the adsorption capacities were a little low. The results still confirm that hydrophobic cotton fibers were successfully prepared for oil/water separation.

Conclusions

1.Hydrophobic cotton fibers were successfully prepared by electroless nickel plating combined with chemical corrosion, followed by stearic acid treatment.

2.Corrosion and stearic acid treatment had observable effects on the surface hydrophobicity of cotton fibers. The results showed that the surface contact angle reached approximately 138° when the nickel-coated cotton fibers were immersed in Cu^{2+} solution for 30 min and treated with stearic acid for 5 h.

3.SEM and XRD results indicated that microroughness formed on the surface of the cotton fibers, which is the reason for their surface hydrophobicity.

4.The adsorption capacities for petrol and soybean oil were 14.98 and 7.52 g/g, respectively.

5.The as-prepared cotton fibers have potential in applications for oil/water separation, and therefore cleaning oil pollution.

Conflict of interest

No conflict of interest exits in the submission of this manuscript.

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