A Coral Reef-like Structure Fabricated on Cellulose Paper for Simultaneous Oil–Water Separation and Electromagnetic Shielding Protection

Tongcheng Zhang, Danyang Wang, Ruoting Liu, Yanjun Xie, Jian Li, and Lijuan Wang*  

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**ABSTRACT:** The functional design of paper-based material surfaces with renewable functions and environmentally friendly properties is prevalent nowadays. Herein, a superhydrophobic surface with a coral reef-like structure was prepared on filter paper by electroless copper plating, rapid silver nitrate etching, and facile 1-hexadecanethiol impregnation. After low-surface-energy thiol treatment, this unique coral reef-like structure surface showed excellent superhydrophobicity with a water contact angle of 163.8° and superoleophobicity with an oil contact angle of 0°, which could be used for oil–water separation and had a separation efficiency above 89.17% after 12 consecutive oil–water separations. Because the copper layer and silver nanostructure are both excellent conductive materials, the modified paper exhibited excellent electromagnetic shielding properties, and the electromagnetic interface shielding effectiveness exceeded 63 dB from 9 kHz to 1.5 GHz. The modified paper also had excellent self-cleaning properties and a better corrosion resistance. The unique three-dimensional interweaving structure between the cellulose fibers in the filter paper is fully utilized, and the substitution reaction between the silver ion and the copper coating produces a coral reef-like structure, which provides a new strategy for promoting the wide application of paper-based materials.

**INTRODUCTION**

As one of the most widely distributed and most abundant polysaccharides in nature, cellulose fibers are affordable, easily degradable, and renewable. The presence of hydroxyl groups makes cellulose fibers easy to be modified by various chemicals through covalent bonds. Paper-based materials with high porosities and low densities in a nonwoven mat inheriting the superiority of cellulose fibers and displaying unique features have been used to make electrodes,† smart detection devices,‡ paper-based robots,§ and paper-based plastics,∥ which has encouraged the application and development of paper-based materials.

Special surfaces in nature, such as lotus leaves, cicada wings, gecko feet, fly eyes, and water strider legs, are non-sticking because of the combination of a low surface energy and surface roughness. Functional materials with special wettability have been used in oil–water separation, metal anticorrosion, self-cleaning, droplet-oriented transportation, antibacterial applications, intelligent drug release, antithrombotic formation, human damp heat management, and efficient fog collection.

Materials with micro/nanostructured surfaces have allowed for great progress in oil–water separation and oil recovery. Commonly used substrates for oil–water separation are metal mesh-based materials, fabric-based materials, sponge and foam-based materials, carbon and its derivative materials, and particles and powdery materials. Paper-based substrates are relatively rare as substrates for oil–water separation. As a simple technology, electroless deposition technology is often used to build multiscale roughness to obtain superwetting surfaces for oil–water separation. Pal et al. prepared superhydrophobic surfaces on various substrates by chemical reduction of copper acetate with hydrazine hydrate at room temperature. Wang et al. prepared oil–water separation membrane by chemical deposition of Ag nanoclusters on nanofibrous membrane, and Wang et al. reported that acicular papillae-like structures can be prepared by copper deposition. Although these studies have yielded superhydrophobic surfaces for oil–water separation, complex substrate preparation processes, slow electroless plating processes or time-consuming low-surface-energy modification...
procedures have limited their large-scale application.15,16,29,42–46

Recently, conductive materials with porous structures that can dissipate rapidly and attenuate electromagnetic waves can eliminate secondary pollution that is caused by electromagnetic wave reflection, which provides the opportunity for the development of shielding materials.47–49 Li et al. prepared a high heat-resistance bioplastic foam with excellent electromagnetic interface (EMI) shielding properties by phase separation.50 Zhang et al. fabricated ultralight cellulose porous composites with a manipulated porous structure by ice-template freeze-drying.51 Extensive progress has been made to prepare electromagnetic shielding materials with substrates with renewable capabilities. Jeong et al. fabricated silver nanowire (Ag NW)-coated cellulose papers with a high (EMI) shielding effectiveness.52 However, it remains challenging to prepare efficient porous-structure EMI shielding materials that are based on regenerable materials and that combine lightweight, corrosion-resistant properties. Studies on the construction of paper-based materials with a combination of oil–water separation and electromagnetic shielding functions by electroless plating have not been reported.

Herein, we fabricated a coral reef-like structure on cellulose paper for simultaneous oil–water separation and electromagnetic shielding protection. We simulated the coral reef structure in the ocean and downsized it to the micrometer range to form a reasonable roughness to meet the geometrical structure required for superhydrophobicity. A layer of copper was deposited on a filter paper substrate by traditional electroless plating technology to metallize the cellulose skeleton. Silver etching and low-surface-energy modification were performed to form a coral reef-like structure. The long-chain alkyl group of 1-hexadecanethiol can be fixed on the coral reef-like structure by Ag–S bonding. With this modified paper, leaking oil can be collected by filtering oil–water pollutants, and modified paper also has good self-cleaning and thermal stability properties. Because of the excellent conductivity of the plated metal and unique three-dimensional interweaving structure of the filter paper, this modified paper can provide an excellent EMI shielding effectiveness (SE).

**RESULTS AND DISCUSSION**

**Surface Modification of Filter Paper.** Future industries focus on developing a facile, efficient, and environment-protecting strategy to achieve high value-added use of paper. Functional filter paper surfaces have gained substantial attention. ECP-Ag-SH-40 preparation is shown in Scheme 1. Paper subjected to constant mass treatment was immersed in a salt-based colloidal palladium solution for activation, and after degumming in dilute hydrochloric acid solution, electroless copper plating was performed. With the progress of electroless plating, the filter paper changed slowly from white to fuchsia. The final sample was black because nanosilver particles were generated on the surface, but the color did not change after thiol modification.53,54

**Electrical Performance of ECP-Ag-SH-40.** Copper is an excellent conductive material so that electroless copper plating can impart an electrical conductivity to non-conductive filter paper. Figure S1a shows that the thickness and mass increment of the copper-plated paper increase with an increase in plating time, and the increase is fastest in the first 40 min. An RTS-9 double-electric four-probe tester was used to test the sheet resistance ($R_s$) and electrical conductivity, showing that the $R_s$ dropped rapidly in the first 40 min (Figure S1b) and reached 99.22 mΩ/sq at 40 min (electrical conductivity of 218.11 S/cm). The resistance was sufficiently small, and a reduction in filter paper resistance was not obvious with an extended plating time. The surface microstructure was perfect; hence, ECP-40 was selected as the standard in subsequent experiments. The inset in Figure S1a shows that ECP-40 and ECP-Ag-SH–40 can act as wires in the circuit without affecting the normal illumination of the small bulbs, and their luminous intensity was almost the same, which shows that etching of the copper coating by the silver nitrate was slight without changing the continuity of the copper layer, and thiol modification did not affect the ECP-Ag-SH-40 conductivity.

**Characterization of Morphology and Chemical Composition.** Scanning electron microscopy (SEM) was used to analyze the sample surface morphology at different stages to prepare ECP-Ag-SH-40, including filter paper, ECP-40, ECP-Ag-40, and ECP-Ag-SH-40, and the morphologies of ECP-SH-40 and ECP-SA-40 as control specimens were also characterized. Figure 1a–c shows that the filter paper has a unique three-dimensional hierarchical structure with a micron-scale rough structure, in which micropores with different sizes were formed by irregular interlacing of cellulose fibers. After plating for 40 min, a layer of copper was plated evenly and densely on the cellulose fibers (Figure 1d). The filter paper surface became smooth, and some fine streaks on the cellulose fiber surface disappeared. The micropore size formed by the interweaving of cellulose fibers did not change much, and the original unique three-dimensional structure was maintained. The good combination of copper and cellulose fiber surfaces was conducive to the formation of a good conductive network. Although many holes remained in the filter paper after copper plating, ECP-40 still had a high conductivity with a sheet resistance of 99.22 Ω/sq, which contributed the rapid transmission of electrons. ECP-Ag-40 was prepared by replacing a layer of copper with silver, which covered the surface with an irregular polygonal nanosphere structure with a diameter of several hundreds of nanometers (Figure 1g). The enlarged diagram (inset in Figure 1g) shows that the structure was similar to that of the coral reef in the ocean, which makes the surface of the copper-plated filter paper rough and leads to
the formation of nanoscale structures. In summary, this micro-/nano-multiscale hierarchical structure formed by an electroless copper plating reaction and the displacement reaction met the superhydrophobic geometric configuration, which ensured that a large amount of air could be trapped on the contact surface to act as an air cushion, increased the contact angle, and prevented water penetration. After further thiol modification, ECP-Ag-SH-40 (Figure 1h) still exhibited the same surface

Figure 1. SEM images of (a−c) filter paper (showing the filter paper cross section), (d) ECP-40 (along with its inset), (e) ECP-SH-40 (along with its inset), (f) ECP-SA-40 (along with its inset), (g) ECP-Ag-40 (along with its inset), and (h) ECP-Ag-SH-40 (along with its inset). (i) Digital images of ECP-SA-40, ECP-SH-40, and ECP-Ag-SH-40 from left to right.

Figure 2. (a) Water contact angle and rolling angle of ECP-SH-40, ECP-SA-40, and ECP-Ag-SH-40; droplet images on corresponding modified surface are shown in insets. (b) Model of a water droplet on the ECP-Ag-SH-40 surface.
The morphology remained unchanged, which was consistent with research results in the literature.54,55

**Figure 1f** shows that, after treatment with stearic acid for 20 h, many flower-like clusters appeared on the surface of the copper-plated paper, which was similar to the structure described in some research16,46,56 and indicates that copper on the filter paper surface underwent a corrosion reaction to generate low-surface-energy salt copper stearate. This flower-like structure could roughen the ECP-SA-40 surface and generated nanoscale structures. **Figure 1i** shows that lots of blue substance was generated on the ECP-SA-40 surface. Compared with the surface morphology of the ECP-40, the surface morphology of ECP-SH-40 (**Figure 1e**) after thiol treatment remained almost unchanged. **Figure 1i** also shows that, after immersing ECP-40 in 0.01 M 1-hexadecanethiol ethanol solution for 20 h, the ECP-SH-40 color remained consistent with that of the original ECP-40.

The coral reef-like micro/nanostructures in the SEM images meet the geometry requirements for superhydrophobicity, and the thiol modification created a low-surface-energy surface.16,45 Contact angles with 10 μL of water droplets and rolling angle were tested to verify the superhydrophobicity of ECP-SA-40, ECP-SH-40, and ECP-Ag-SH-40 (**Figure 2a**). The contact angles of ECP-SA-40, ECP-SH-40, and ECP-Ag-SH-40 were 152.3°, 140.5°, and 163.8°, respectively, and their corresponding sliding angles were 11.3°, 58.8°, and 3.7°, respectively. The contact angle and sliding angle test showed that ECP-Ag-SH-40 preparation was the most effective and timesaving. This phenomenon also proves that the Ag–S bond was more stable and easier to form than the Cu–S bond as described in the investigation.57 Because copper in the stearic acid ethanol solution cannot form a chemical bond with stearic acid, only copper stearate was formed on the surface of the copper layer.46,56 This copper salt compound was scooped off easily, which resulted in a relatively poor hydrophobicity. In summary, an effective and rapid method to prepare superhydrophobic surfaces was found through comparison.

Diesel (8 μL) was used in the oil contact angle test. Once the diesel droplets contact the ECP-Ag-SH-40, it diffuses and penetrates the ECP-Ag-SH-40 surface rapidly with an oil contact angle of 0°, which indicates that ECP-Ag-SH-40 had excellent superlipophilicity. We also tested the wetting behaviors at different stages during the preparation process, including the water contact angle and oil contact angle of the filter paper, ECP-40, and ECP-Ag-40, and they were all 0° (**Figure S2**).

X-ray photoelectron spectroscopy (XPS) analysis was used to study the surface chemical composition of samples at different processing stages. The XPS wide-scan spectrum in **Figure 3a** shows two main characteristic peaks that belong to O1s and C1s of the filter paper, which correspond to the features of the cellulose. Five pure copper characteristic peaks (Cu3d, Cu3p, Cu3s, Cu2p3/2, and Cu2p1/2) and two silver characteristic peaks (Ag3d5/2 and Ag3d3/2) of ECP-40 and ECP-Ag-40 confirmed that a layer of copper was coated on the filter paper and a displacement reaction occurred on the copper surface, which can also be proven from change in
morphology of the SEM image (Figure 1g). The S2p and S2s spectra of ECP-Ag-SH-40 verified the introduction of thiol groups of 1-hexadecanethiol.

Peak-fitting graphics of the main peaks are listed in Figure S3a-e. A peak matching of the C1s strong peak of the filter paper was performed, where the C1s core-level spectrum can be divided into three peaks (284.6 eV corresponds to C−C or C−H, 286.4 eV corresponds to C−O, 287.9 eV corresponds to O−C−O) (Figure S3a) that are assigned to cellulose. In Figure S3b, high-resolution core-level spectra of Cu2p could be fitted into a double peak at binding energies (BE) of 932.4 eV (Cu2p3/2) and 952.2 eV (Cu2p1/2) and were attributed to pure copper with few impurities.34 Two strong signal peaks (Figure S3c) at BEs of 368.4 eV (Ag3d5/2) and 374.4 eV (Ag3d3/2) meant that silver nanoclusters were formed and fixed on the copper surface.15,58,59 Figure S3d,e shows the existence of fitting peaks of S2p and C1s that belong to the Ag−S bond and a long-chain alkyl group from ECP-Ag-SH-40. The S2p core-level spectrum can be fitted into two peaks, one of which is at a BE of 162.2 eV and corresponds to the S−Ag bond.59 The remainder at a BE of 163.4 eV is attributed to free thiols.58 The strong core-level spectrum at a BE of 284.8 eV from C1s was caused by the alkane group of 1-hexadecanethiol.15

The surface composition of ECP-Ag-SH-40 was investigated by energy-dispersive X-ray spectroscopy (EDS). As shown in Figure 3b, Ag, Cu, O, and C elements from 1-hexadecanethiol present mainly on the ECP-Ag-SH-40 surface, whereas S element was not observed because of the small content. The red dots show a uniform distribution in the EDS element map (Figure 3c), which indicates that the immersion of ECP-40 in the silver nitrate solution can cover the Cu surface with a layer of silver nanoparticles.

The X-ray diffraction (XRD) spectra of the filter paper, ECP-40, and ECP-Ag-40 are listed in Figure 3d to characterize the crystal structure. The diffraction peaks at 2θ = 14.9°, 16.4°, and 22.7° are attributed to cellulose (JCPDS: 50-2241) that corresponds to filter paper. Three sharp peaks at 43.5° (111), 50.6° (200), and 74.4° (220) are attributed to face-centered cubic crystalline copper (JCPDS: 04-0836),32,24 which confirms that a dense copper layer was constructed. Copper deposition lead to a decrease in cellulose peak. No silver peaks were found in the XRD curve of ECP-40, which shows that the content of silver was low and silver etching did not destroy the copper layer continuity. The above analysis shows that the construction of a coral reef-like structure on the filter paper was successful.

Superhydrophobicity of ECP-Ag-SH-40 and Its Applications. A syringe needle was used to drag water droplets (8 μL) on the ECP-Ag-SH-40 surface, as shown in Figure S4a. The dragged water droplets showed no hysteresis during the advancement process, and no water residue remained on the surface, which indicates that the surface provided excellent water repellency.

The water contact angle of ECP-Ag-SH-40 at different pH values is shown in Figure S4c. ECP-Ag-SH-40 exhibited good superhydrophobicity in a pH range of 1−14. All contact angles exceeded 157° at different pH values.

ECP-Ag-SH-40 combined with a unique nanostructure that imitates a coral reef, and low-surface-energy modification is often associated with self-cleaning properties. Dust on the surface of ECP-Ag-SH-40 can be cleaned easily by a single stream of water as depicted in Figure S4b, which shows an excellent self-cleaning performance. After impacting the ECP-Ag-SH-40 surface from the side with a stream of water, the water stream bounced and the surface remained dry, which shows again the sample’s outstanding hydrophobicity (Movie S1).

ECP-Ag-SH-40 with a coral reef-like structure has excellent superhydrophobicity and superlipophilicity so that an oil−water separation test was conducted.

The boat (Figure S5a) prepared by ECP-Ag-SH-40 can float freely on the water surface. The separation efficiency was calculated from the mass ratio of the collected oil from the mixture to the original oil. Figure S5a shows that 40 mL of gasoline and 100 mL of deionized water were mixed to simulate an oil−water mixture in a marine oil spill accident, in which the gasoline was dyed red and the deionized water was dyed blue. When the boat was placed in an oil−water mixture, gasoline could wet the boat rapidly and infiltrate it by gravity and capillary action, whereas the water phase was excluded. A plastic dropper was used to absorb the gasoline that penetrated the boat. After absorbing a part, the oil continuously penetrated the boat until the gasoline had been absorbed completely (Movie S2). Because the dense stacking of cellulose fibers in ECP-Ag-SH-40 resulted in a relatively small pore size, the permeation speed was slow, and it took ~20 min to collect all the floating oil. To test the cyclic collection performance of the ECP-Ag−SH−40, the above separation process was repeated 12 times, and the last collection efficiency reached 89.17% (Figure S6b). Because of the complex composition of the oil phase in marine oil spill accidents, other mixtures of light oil (diesel and toluene) and water were also used to test the separation capability of the ECP-Ag-SH-40. After 12 separation cycles, the final separation efficiencies were 95.44 and 92.9% (Figure S6b), respectively.

Besides the separation of light oil and water, ECP-Ag-SH-40 was used for the separation of a heavy oil (chloroform) and water mixture containing ~35 mL of chloroform and 10 mL of water into a small boat on a beaker, as shown in Figure S5b. Chloroform was filtered from the boat continuously while the water phase remains on the boat (Movie S3). No water went into the beaker, which showed the excellent separation ability. After 12 cycles, the final separation efficiency of chloroform for ECP-Ag-SH-40 was 89.91% (Figure S6b). The decrease in separation efficiency may be due to the volatilization of the oil phase and the adsorption of oil into the pores of the boat. After 12 cycles, the boats were washed with ethanol solution and dried at 60 °C for 30 min to test the water contact angle. The results in Figure S6a show ECP−Ag−SH−40 still exhibited a high hydrophobicity. Because ECP-Ag-SH-40 is lighter than the hydrophobic copper mesh,56 it can be directly placed at the oil spill sites for continuous oil filtration and collection, which could improve the collection efficiency, therefore reducing the cost of oil spill cleanup.

Electromagnetic Interface (EMI) Shielding Property of ECP-Ag-SH-40. With the advent of the 5G information age, requirements for the precision and sensitivity of electronic components have become more stringent. Because of its inherent non-conductivity, the electromagnetic interface shielding effectiveness (EMI SE) of filter paper is close to 0 dB. Compared with traditional metal-based shielding materials, electroless plated filter paper has advantages of a high flexibility, low mass density, adjustable shielding effects, and better renewable capacity and high thermal stability compared with conductive polymer-based shielding materials. As shown in the SEM image (Figure 1a), because filter paper has a
unique three-dimensional void structure, a three-dimensional conductive network can be constructed easily by electroless copper plating, which is effective for attenuating current. In particular, the interspersed voids can alleviate the impedance mismatch of microwave propagation between the material and the voids, which results in effective electromagnetic energy attenuation capabilities and eliminates secondary pollution that is caused by microwave reflections. The EMI shielding mechanism of this modified paper is shown in Figure 4a, and the EMI SE values of the ECP-40 and ECP-Ag-SH-40 are shown in Figure 4b. From 9 kHz to 1.5 GHz, the SE values exceeded 63 dB. This SE value is higher than the target value of EMI SE (20 dB) for practical applications, which shows excellent shielding properties.

Figure 4b shows that the EMI SE curves of ECP-40 and ECP-Ag-SH-40 are almost the same, and the SE of the ECP-40 is slightly higher than that of the ECP-Ag-SH-40. Therefore, silver ion replacement by copper was slight and did not destroy the continuity of the copper coating.

Stability and Corrosion Resistance of ECP-Ag-SH-40. Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) curves are shown in Figure S7a,b to analyze the thermal stability. Filter paper had the same thermal degradation behavior as common cellulose materials, and the profile could be divided into three segments. Volatilization of water (≤100 °C) occurred during the first stage. At approximately 200 °C, cellulose underwent dehydrogenation, and significant mass loss occurred in the third stage (~340 °C) because of cellulose pyrolysis. ECP-40, ECP-Ag-40, and ECP-Ag-SH-40 showed different thermal degradation behaviors in the final stage compared with filter paper, which experienced intense pyrolysis at 300 °C in advance. This phenomenon was caused by cellulose degradation in alkaline solutions during the electroless copper plating process and the catalytic effect of copper on cellulose at elevated temperatures. The small decrease in thermal decomposition temperature is acceptable in practical applications. In the DTG curve of ECP-Ag-SH-40 at 240 °C, a small peak drawn by red dotted circles may be related to the degradation of Ag-bound thiols because the formed Ag–S chemical bond can improve the thermal stability of the 1-hexadecanethiol. The final pyrolysis residual rates of filter paper, ECP-40, ECP-Ag-40, and ECP-Ag-SH-40 at 700 °C were 2.78, 48.44, 47.08, and 51.75%, respectively, which shows that electroless copper plating could lead to an increase in residual amount, whereas silver treatment and 1-hexadecanethiol modification had little effect. The DTG curves also show that the temperature at the fastest pyrolysis rate had the highest peak position, which is consistent with the TGA curves.

The ECP-Ag-SH-40 was immersed in an ethanol solution and sonicated for 30 min to investigate the robustness of the hierarchical multiscale coral reef-like structure. A typical SEM image of the ECP-Ag-SH−40 after sonication is shown in Figure S7d. Although a small portion of the unstable coral reef-like structure fell off, the ECP-Ag-SH-40 surface retained a large contact angle of 156.1°, which indicates that this structure can withstand ultrasonic damage and has good stability.

Superhydrophobic coatings with excellent water repellency can isolate metals from electrolyte solutions through air cushions and can be used in the field of metal corrosion protection. Tafel plots were obtained in a 3.5 wt % NaCl electrolyte solution at −2 to 2 V and a scan rate of 10 mV/s. The corrosion current density (Icorr) and corrosion potential (Ecorr) that were measured by the Tafel linear extrapolation method are shown in the inset of Figure S7c. A higher Ecorr and smaller Icorr on the polarization curves indicate that the tested samples have a better anticorrosive performance. Figure S7c shows that, compared with ECP-40 and ECP-Ag-40, after modification by 1-hexadecanethiol, the Ecorr of ECP-Ag-SH-40 moved significantly in the positive direction. The Icorr of ECP-Ag-SH-40 was also smaller than those of ECP-40 and ECP-Ag−40, which indicates that superhydrophobic treatment can inhibit ECP-Ag-SH-40 corrosion. Compared with ECP-40, the Ecorr of ECP-Ag-40 decreased slightly and became negative because silver nanoparticles and a copper-plated layer could constitute battery systems that cause electrochemical corrosion in electrolyte solutions.

■ CONCLUSIONS

In summary, modified filter paper with excellent water repellency and good EMI shielding properties was prepared by facile, scalable chemical copper plating, silver ion etching, and long alkyl chain thiol modification. Multiscale roughness was achieved by imitating coral reefs and combining with the unique three-dimensional skeleton structure of paper to provide ECP-Ag-SH-40 with a good oil–water separation ability and cycle stability. Electroless copper plating for 40 min
allowed the ECP-Ag-SH-40 to achieve high electrical conductivities ($R_e$ of 99.22 mΩ/sq) with a slight decrease in thermal stability. ECP-Ag-SH-40 showed an excellent self-cleaning and anticorrosive performance. The preparation of ECP-Ag-SH-40 enriched the functionalization of paper, which has allowed for the exploration of ways to make paper specific from the bionics perspective and has speeded up the use of renewable paper.

## EXPERIMENTAL SECTION

**Chemicals and Reagents.** Qualitative filter paper (model: 102) was purchased from Hangzhou Fuyang Beimu Pulp & Paper Co., Ltd. Boric acid ($H_3BO_3$, ≥99.5%), copper(II) sulfate pentahydrate ($CuSO_4·5H_2O$, ≥99.0%), trisodium citrate dihydrate ($Na_3C_6H_5O_7·2H_2O$, ≥99.0%), methylene blue ($C_{16}H_{18}CN_3S_3·H_2O$, ≥98.5%) silver nitrate ($AgNO_3$, ≥99.9%), stearic acid ($C_{18}H_{36}O_2$), sodium hypophosphite monohydrate ($NaH_2PO_2·H_2O$, ≥99.0%), nickel sulfate hexahydrate ($NiSO_4·6H_2O$, ≥98.5%), sodium chloride ($NaCl$, ≥99.5%), sodium hydroxide ($NaOH$, ≥98.0%), silver nitrate ($AgNO_3$, ≥99.0%), nickel sulfate hexahydrate ($NiSO_4·6H_2O$, ≥98.5%), methylene blue ($C_{16}H_{18}CN_3S_3·H_2O$, ≥98.5%) silver nitrate ($AgNO_3$, ≥99.9%), stearic acid ($C_{18}H_{36}O_2$), sodium hypophosphite monohydrate ($NaH_2PO_2·H_2O$, ≥99.0%), nickel sulfate hexahydrate ($NiSO_4·6H_2O$, ≥98.5%), sodium chloride ($NaCl$, ≥99.5%), and sodium hydroxide ($NaOH$, ≥98.0%) were purchased from Tianjin Yongda Chemical Reagent Co., Ltd. Palladium chloride ($PdCl_2$, ≥99.0%) was purchased from Damao Chemical Reagent Plant. Chloroform (HPLC grade) and toluene used as received without further purification. Hydrophobic Modiﬁcation of Copper-Plated Paper. Electroless copper-plated paper was cleaned with ethanol for 2 min. Then, it was immersed in a silver nitrate solution (0.005 M) for 1 min to replace a layer of copper on the copper-plated paper surface followed by 1-hexadecanethiol (0.010 M) in ethanol for 5 min and denoted as ECP-Ag-SH-X. To investigate the effect of silver ion etching on hydrophobicity, two samples were prepared without silver nitrate etching. ECP-SA-X means immersing the electroless copper-plated paper in 0.01 M stearic acid in ethanol for 20 h without other treatment. ECP-SH-X means that the electroless copper-plated paper was immersed in a 0.01 M solution of 1-hexadecanethiol in ethanol for 20 h.

**Construction of a Hydrophobic Boat.** The superhydrophobic ECP-Ag-SH-40 (6.0 cm × 5.0 cm) was folded into a topless boat (4 cm × 3 cm × 1 cm). In order to prevent the folded boat from rebounding into a flat shape, the four corners of the boat were glued with 502 glue, as shown in Figure S5b.

For easy distinction, water and oil were dyed with methylene blue and Sudan III, respectively.

## ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01666.

- Electroless copper plating on filter paper; (Table S1) composition of electroless copper plating solution; characterization; (Figure S1) mass and thickness increment of electroless copper-plated paper with electroless plating time, sheet resistance decrease with electroless plating time, and opposite trend for electrical conductivity; (Figure S2) water contact angle of filter paper, ECP-40, and ECP-Ag-40 and oil contact angle of the filter paper, ECP-40, and ECP-Ag-40; (Figure S3) XPS C1s spectra for filter paper, Cu2p core-level spectrum for ECP-40, Ag3d core-level spectrum for ECP-Ag-40, and C1s and S2p core-level spectrum for ECP-Ag-SH-40; (Figure S4) water droplet of 8 μL guided by a syringe on the ECP-Ag-SH-40 surface, dust-loaded ECP-Ag-SH-40 surface can be cleaned by moving water droplets, and water contact angle recorded for ECP-Ag-SH-40 over a wide range of pH values; (Figure S5) pictures for separation of gas–water mixture and boat floated freely on the oil–water mixture surface and images for separation of chloroform–water mixture; (Figure S6) water contact angle recorded for ECP-Ag-SH-40 after 12 separation cycles of oil–water mixture and separation efficiency of ECP-Ag-SH-40 for multiple oil–water mixtures for different number of cycles; (Figure S7) TGA and DTG curves from 20 to 700 °C, Tafel plots of ECP-40, ECP-Ag-40, and ECP-Ag-SH-40, and SEM image of ECP-Ag-SH-40 after sonication (PDF)

Movie showing that, after impacting the ECP-Ag-SH-40 surface from the side with a stream of water, the water stream bounced and the surface remained dry, which shows again the sample’s outstanding hydrophobicity (MP4)

Movie showing that, after absorbing a part, the oil continuously penetrated the boat until the gasoline had been absorbed completely (MP4)

Movie showing that chloroform was filtered from the boat continuously while the water phase remains on the boat (MP4)

## AUTHOR INFORMATION

**Corresponding Author**

Jian Li — Key Laboratory of Bio-based Materials Science and Technology of Ministry of Education, Northeast Forestry University, Harbin 150040, P. R. China; orcid.org/0000-0001-7805-084X; Email: donglinwlj@163.com

**Authors**

Tongcheng Zhang — Key Laboratory of Bio-based Materials Science and Technology of Ministry of Education, Northeast Forestry University, Harbin 150040, P. R. China

Danyang Wang — Key Laboratory of Bio-based Materials Science and Technology of Ministry of Education, Northeast Forestry University, Harbin 150040, P. R. China

Ruoting Liu — Key Laboratory of Bio-based Materials Science and Technology of Ministry of Education, Northeast Forestry University, Harbin 150040, P. R. China

Yanjun Xie — Key Laboratory of Bio-based Materials Science and Technology of Ministry of Education, Northeast Forestry University, Harbin 150040, P. R. China

**Supporting Information**

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Notes
The authors declare no competing financial interest.

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