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Layer-by-Layer Assembly Fabrication of Porous Boron Nitride Coated Multifunctional Materials for Water Cleaning

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Cleanup of oil spills and industrial discharge of organic solvents is a global challenge. However, development of the ideal materials for water remediation with a high separation efficiency and low risk of fire is still rather sparse because the material needs to be superhydrophobic/superoleophilic and also flame-retardant. Here, a novel coating material of porous boron nitride nanosheets (BNNSs) and a layer-by-layer assembly technology for tailoring inexpensive cotton fabric and melamine sponge with these desired properties are reported. The BNNS-coated cotton fabric and melamine sponge exhibit high oil/water separation efficiency, selective absorption capacity of oil and organic solvents, and excellent recyclability. Furthermore, the coated materials show an efficient flame-retardant effect which completely stops melamine sponge melt dripping upon exposure to the direct flame from a butane blowtorch within 52 s. The integrated advantages of the high porosity, low water adhesion, compressibility, strong fire-resistance, simple operation, and commercial availability enable the porous BNNS-coated cotton fabric and melamine sponge to satisfy various practical oil/water separation requirements.

1. Introduction

Oil pollution is one of the major global issues because of the large amounts of oily wastewater generated from petrochemical, textiles, food, leathers, and metal industries, as well as frequent offshore oil-spill events during exploration and transportation.[1,2] It has long-term adverse effects on natural environment, ecological balance, and human health.[3,4] Recently, it has been proposed that an ideal absorbent material should possess excellent flame-retardant properties to reduce the risk of fire and explosion because the crude oil and some organic solvents are highly flammable and extremely dangerous once ignited.[5,6] As a result, it is still an arduous challenge on oil/water separation with a technology of high efficiency, good stability, excellent recyclability, simply operation, flame retardancy, and commercially available world widely. There is an extremely urgent and strong demand for multifunctional materials with high absorption capacity and selectivity, thermal stability, lightweight, chemical inertness, low cost, and environmental friendliness for effectively separating oil from water.

Currently, one of the most efficient oil/water separation techniques is using oil-absorbing materials, such as textiles and polyurethane foams at the sites where a large amount of oil spill, for example, Gulf of Mexico.[7] Although textiles and polyurethane foams have some merits, such as high absorption capability, flexibility, low cost and density, as well as high mechanical stability under harsh practical conditions, both of them absorbing water and oil simultaneously lead to a low efficiency of oil absorption.[7–10] Recently, research on fabricating novel 2D nanomaterials to possess simultaneous superhydrophobicity and superoleophilicity has attracted considerable interests in the field of oil/water separation.[11,12] Based on that, many effective 2D absorbent materials, including graphene and boron nitride nanosheets (BNNSs), have exhibited superior absorption capacity and excellent recyclability for organic pollutant adsorption and cleanup of oil spillage.[13–15] Although extensively implemented in research, these materials often have limitations for practical application under different situations because some technical challenges such as the tiny materials are difficult for practical operation and collection completely after usage. Further effort has been made to synthesise 3D materials with interconnected structure and hydrophobic surface through the rational control of surface structures and chemical compositions, such as graphene-based sponges,[16] superhydrophobic-conjugated microporous polymers,[17] and carbon aerogels.[18] Although these materials have high processing capacity and excellent separation efficiency, the difficulty of large-scale fabrication, multistep processes, and high-cost limits their commercial applications.

Inspired by the previous achievements, we hypothesize that if the surface of commercially available and low-cost textiles and polyurethane foams could be modified to be superhydrophobic and superoleophilic, the 2D membranes and 3D foams

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would be fabricated for practical applications in both ocean oil spillage and industry. In our previous paper,[13] we have reported that the porous BNNSs have some advantages over existing technologies for cleanup of oil spillage due to the superhydrophobicity, ultralight, high resistance to oxidation, good chemical inertness, and easy recyclability.[19–24] Importantly, this nanostructured material exhibited a high absorption capacity up to 33 times its own weight in oils and organic solvents while repelling water.

Here, we develop a new fabrication strategy of flexible and multifunctional porous BNNS-based membranes and sponges with superhydrophobic and excellent flame-retardant properties through an easy and versatile layer-by-layer (LBL) assembly process. Both of 2D fabric membrane and 3D melamine sponge with low water adhesion, light weight, high porosity, and robustness were used as a framework for porous BNNS coating, which overcome many fundamental limitations due to their commercial availabilities and low cost. The new BNNS-coated membrane and sponge exhibit ultrafast oil/water separation and simple operation. More importantly, as-fabricated BNNS-coated fabric membrane and melamine sponge absorb a broad range of oils and organic solvents with high selectivity, good recyclability, and excellent absorption capacities approaching 112 times its own weight as well as low risk of fire and explosion. The current study will contribute to the development of advanced oil–water separation materials, promising for water remediation. To our knowledge, these features are novel and have not been reported in the research literature.

2. Results and Discussion

Figure 1a shows the chemical structures of the coating materials and the procedures to prepare superhydrophobic fabrics. In this study, a simple and effective LBL building blocks method[25–27] was employed for coating treatment of fabrics and melamine sponge as described in Figure 1a. The assembly of BNNS and soft base materials is based on electrostatic interaction as driving force and it is easy for BNNS adsorbing on the modified surface of cotton fabric or melamine sponge

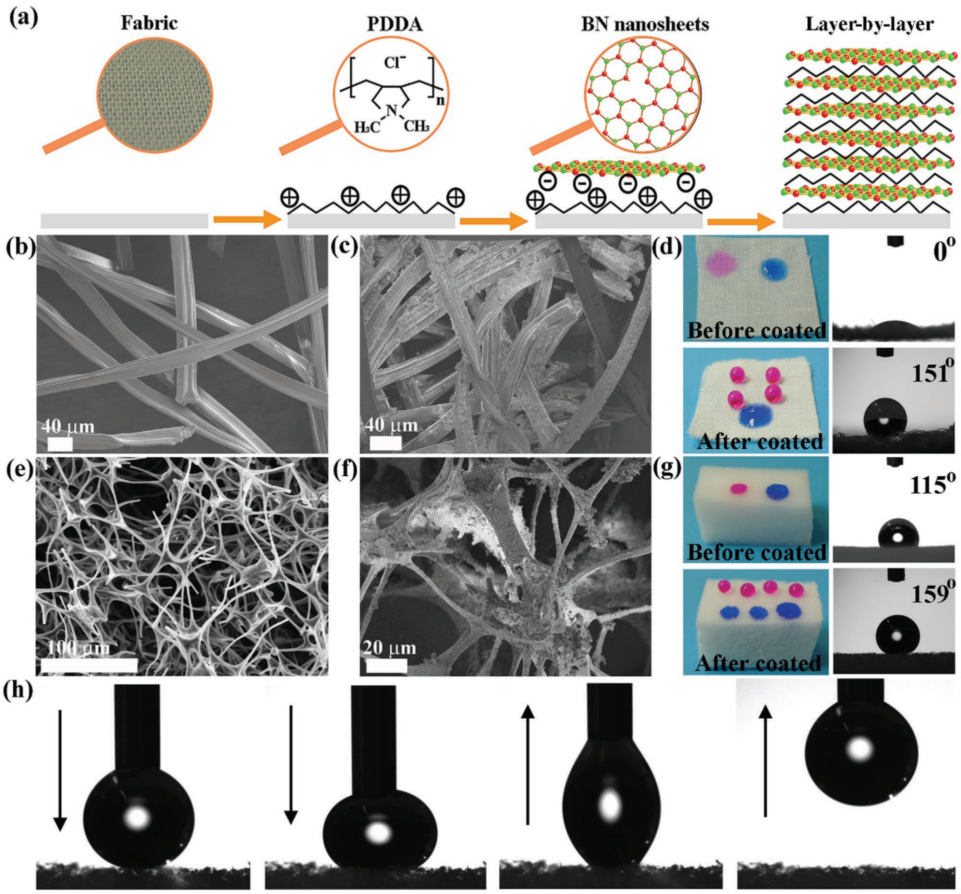

Figure 1. a) Chemical structures of layer-by-layer materials and procedure for LBL treatment, b,c) SEM images of cotton fabrics before and after PDDA and porous BNNSs LBL coating, and d) images of dyes water (red) and oil drops (blue) on the uncoated (upper) and coated (under) fabric, and their water contact-angle images. e,f) SEM images of melamine sponge before and after PDDA and porous BNNSs LBL coating. g) Photographs of dyed water (red) and oil drops (blue) on the uncoated (upper) and coated (under) melamine sponge, and their water contact-angle images. h) Photographs of the dynamic water-adhesion measurements on the coated melamine sponge. A water droplet was used as the detecting probe to contact the surface and then leave. The coated melamine sponge exhibits excellent low affinity to the water droplet.

by cationic polyelectrolyte as the first layer due to hydrogen bonding force. The base material was dipped into the solutions, alternating between the cationic polyelectrolyte and BNNS, with each cycle corresponding to one bilayer. Typical scanning electron microscope (SEM) images of the superhydrophobic fabric and melamine sponge before and after coating treatment are shown in Figure 1b–f. Before the coating, both the fabric and melamine sponge had a smooth surface of a network framework. After LBL coating, a rough surface formed on both the fabric and melamine sponge, indicating that porous BNNSs were assembled on the frameworks of both fabric and melamine sponge. Fourier transform infrared (FTIR) measurements provide a further evidence for the porous BNNSs coating, as shown in Figure S1 (Supporting Information). Compared with uncoated fabric and melamine sponge, the FTIR spectra of the porous BNNS-coated fabric and melamine sponge exhibited strong absorption peaks at 1371 and 791 cm^{-1} assigned to the B—N stretching (in-plane ring vibration) and B—N bending (out-of-plane vibration) (Figure S1, Supporting Information).[13] Figure 1d,g displays the wetting behaviors of water and oil on the surface of the cotton fabric and melamine sponge with and without coating, respectively. It can be seen that the uncoated fabric and melamine sponge can be easily wetted by both water (dyed pink color) and oil (dyed blue color) with a water contact-angle (CA) of 0° and 115°, respectively. After LBL coating, drops of oil completely spread out and was infused into the pores of the fabric and melamine sponge, whereas several stationary water droplets rest on the surface of both fabric and melamine sponge with a water CA of 151° and 159°, respectively, resulting from the wettability property changed from hydrophobic to superhydrophobic. Moreover, the water adhesion test was carried out by using a water droplet as a probe water to contact and leave the surface of porous BNNS-coated 3D melamine sponge. As shown in Figure 1h, the water droplet can completely detach from the surface of porous BNNS-coated 3D melamine sponge without leaving any residue, indicating an extremely low water adhesion.

Since most oils and organic solvents are flammable liquid and could be extremely dangerous when ignited, high thermal stability and flame-retardant properties are another important criterion for practical applications. The combustion behavior of both the porous BNNS-coated 2D fabric membrane and 3D melamine sponge was investigated by using butane blowtorch, as shown in **Figure 2** and Movies S1 and S2 (Supporting Information). For comparison, the same sizes of uncoated fabric membrane and melamine sponge were tested under the same condition. In Figure 2a, a rapid and vigorous combustion is shown on the uncoated fabric membrane once being ignited, it completely burned out within only 5 s. In contrast, the burning time took 9 s after the flame on the porous BNNS-coated 2D fabric membrane (Figure 2b). Different from fabric, melamine sponge has an intrinsic flame-retardant property reported by Ruan et al.[5] The flame on the uncoated melamine sponge is weak and finished within 9 s, leaving one-third of residue (Figure 2c). In contrast, there is no flame on the porous BNNS-coated 3D melamine sponge within the first 11 s after being ignited (Figure 2d). Then, a weak flame occurred and completely went out after 52 s, leaving behind a shrinkage framework of porous BNNS-coated 3D melamine sponge (Figure S2, Supporting Information). The improvement of flame-retardant behavior in porous BNNS-coated sponges is at least six times more than uncoated melamine sponge, indicating its great potential of reducing the risk of fire and explosion due to the strong resistance to oxidation and excellent thermal stability of BN material. Therefore, the porous BNNS-coated fabric and 3D melamine sponge are ideal flame-retardant candidates for inflammable oils and organic solvents.

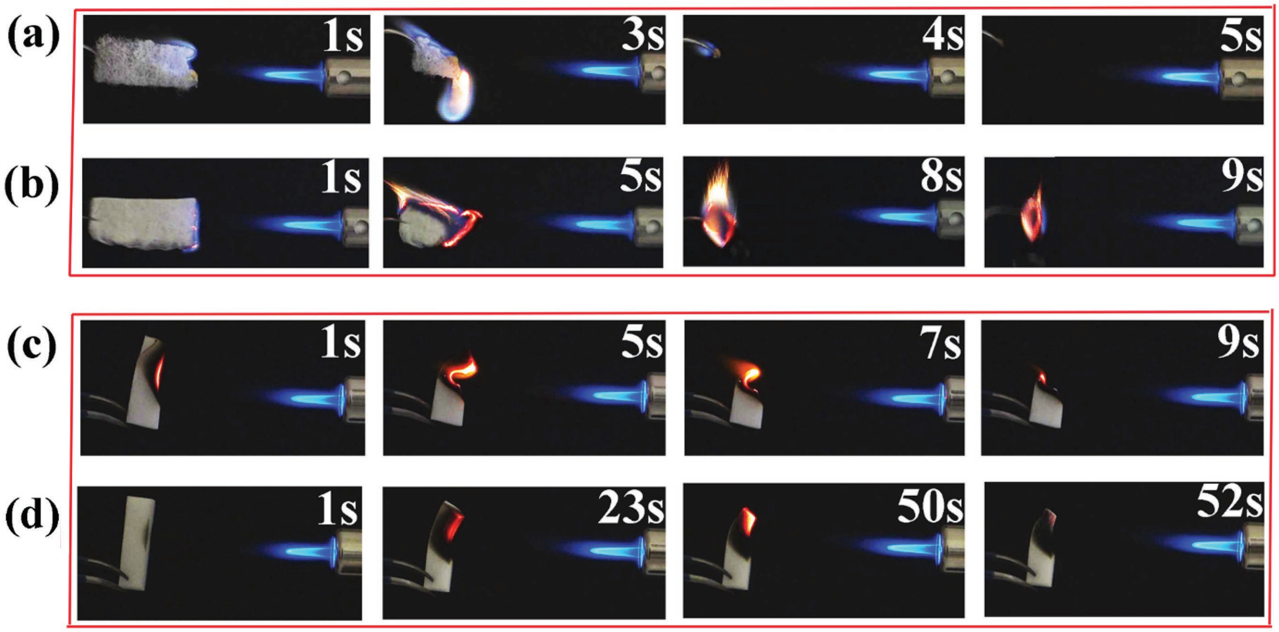

Figure 2. The combustion process of a) uncoated 2D fabric membrane, b) porous BNNS-coated 2D fabric membrane, c) uncoated 3D melamine sponge, and d) porous BNNS-coated 3D melamine sponge using a blowtorch.

The compression experiments were performed to evaluate the mechanical performances of porous BNNS-coated 3D melamine sponge. As shown in **Figure 3**a, the coated sponge exhibits excellent elasticity and flexibility after the compressions even as high as 80%. Figure 3b shows the stress–strain curves of the porous BNNS-coated melamine sponge at a maximum strain of 20%, 40%, 60%, and 80%, respectively. The coated sponge can easily recover without losing porous BNNSs compared to the original morphology after the compressions. Importantly, the stress–strain curve of the 1000th cycle is identical to that of zthe first cycle from 50% of compression strain, with the exception that the compressive stress decreases slightly to 88% of the original value (Figure 3c). The compressive durability endows the porous BNNS-coated melamine sponge with highly stable and robust against various harsh conditions, which is of great significance for practical applications.

Having demonstrated the peculiar wettability toward water and oil, porous BNNS-coated 2D fabric membrane is expected to efficiently separate or absorb insoluble oil from water. As a proof of concept, an oil/water separation experiment using the porous BNNSs-coated 2D fabric as the separation membrane was setup as shown in **Figure 4** and Figure S3 (Supporting Information). The porous BNNS-coated 2D fabric membrane was sandwiched between two glass tubes of the filter apparatus (Figure 4a). The floating pump oil (dyed by red color)/water mixture of 75 mL ($V_{\mathrm{oil}}/V_{\mathrm{water}}$: 1/2) is added to the upper tube (Figure 4b). During the whole separation process, the 25 mL pump oil continuously permeates through the porous BNNS-coated 2D fabric membrane and drops into the beaker by gravity while the water is retained above the membrane due to the excellent superhydrophobicity and low water-adhesion features of the porous BNNS-coated 2D fabric membrane. More importantly, no water is observed in the oil or vice versa after separation, indicating the highly effective separation of the oil from water. The performance of the coated 2D fabric membrane for the underwater dichloromethane separation was also tested (Figure S3, Supporting Information). Once the dichloromethane (dyed by blue color) contacts the membrane, the surface starts to reconfigure (Figure S3c, Supporting Information). Within just 5 s, 50 mL dichloromethane quickly permeated through the membrane while the water was blocked. Moreover, after usage, the coated 2D fabric membrane can be easily regenerated by squeezing or solvent (e.g., acetone) washing and drying. No obvious change in filtration capacity was found after five cycles (Figure S4, Supporting Information). The above results indicate that the porous BNNS-coated 2D fabric membrane has a great potential in the industrial application of oil-polluted water treatments.

The porous BNNS-coated 3D melamine sponge is another potential ideal absorbent for highly efficient separation of oil contaminants from water due to its surface superhydrophobicity, excellent absorption, light weight, high porosity, robustness, and good flame retardancy. The evolvement of absorbing oil is shown in a series of photos in **Figure 5**. The underwater dichloromethane droplet dyed with blue color was completely adsorbed by a piece of porous BNNS-coated 3D melamine sponge within a few seconds, as shown in Figure 5a. When a piece of porous BNNS-coated 3D melamine sponge meets pump oil, which floats in water dyed with blue color, the oil was sucked up into the sponge immediately, resulting in the clean water originally contaminated by the pump oil (Figure 5b). The saturated sponge still floats on clean water surface due to its low density and superhydrophobic nature, which makes them easy to be collected, thereby indicating a facile and useful

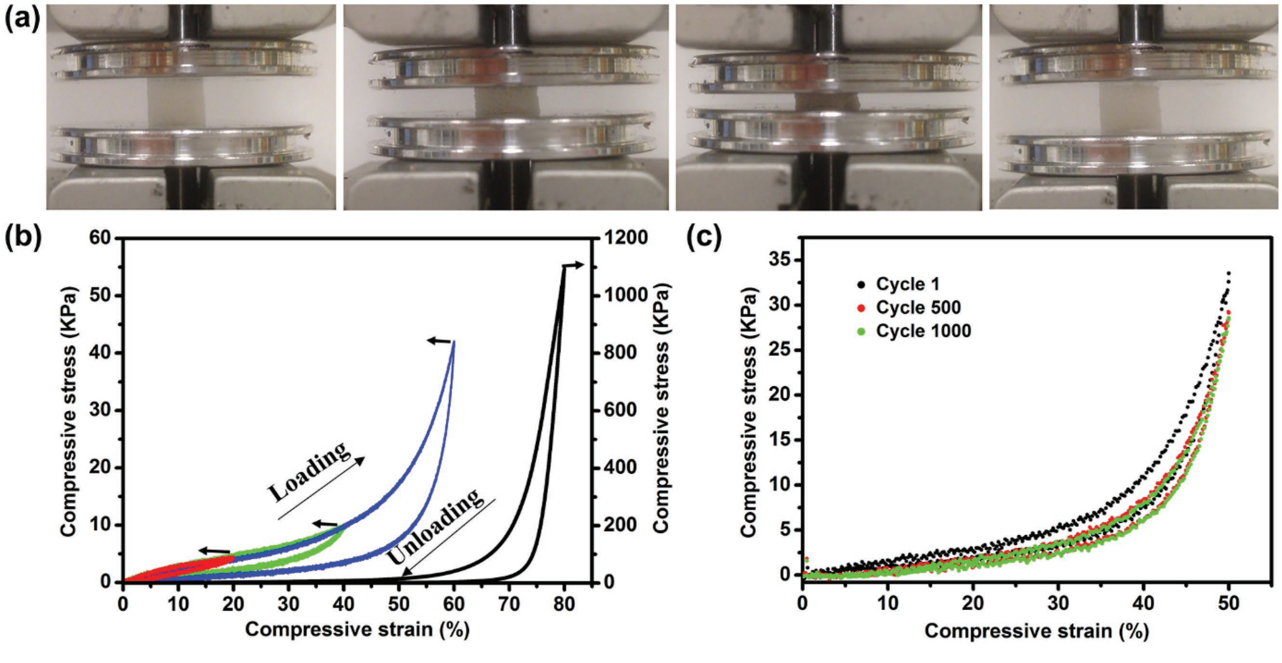

Figure 3. a) The compression–recovery process showing that the porous BNNS-coated 3D melamine sponge recovers their original shape after compression by more than 80%. b) Stress–strain curves of porous BNNS-coated 3D melamine sponge with a different set strain of 20, 40, 60, and 80%, respectively. c) The compressive stress–strain curves of the porous BNNS-coated 3D melamine sponge over 1000 cycles at 50% strain.

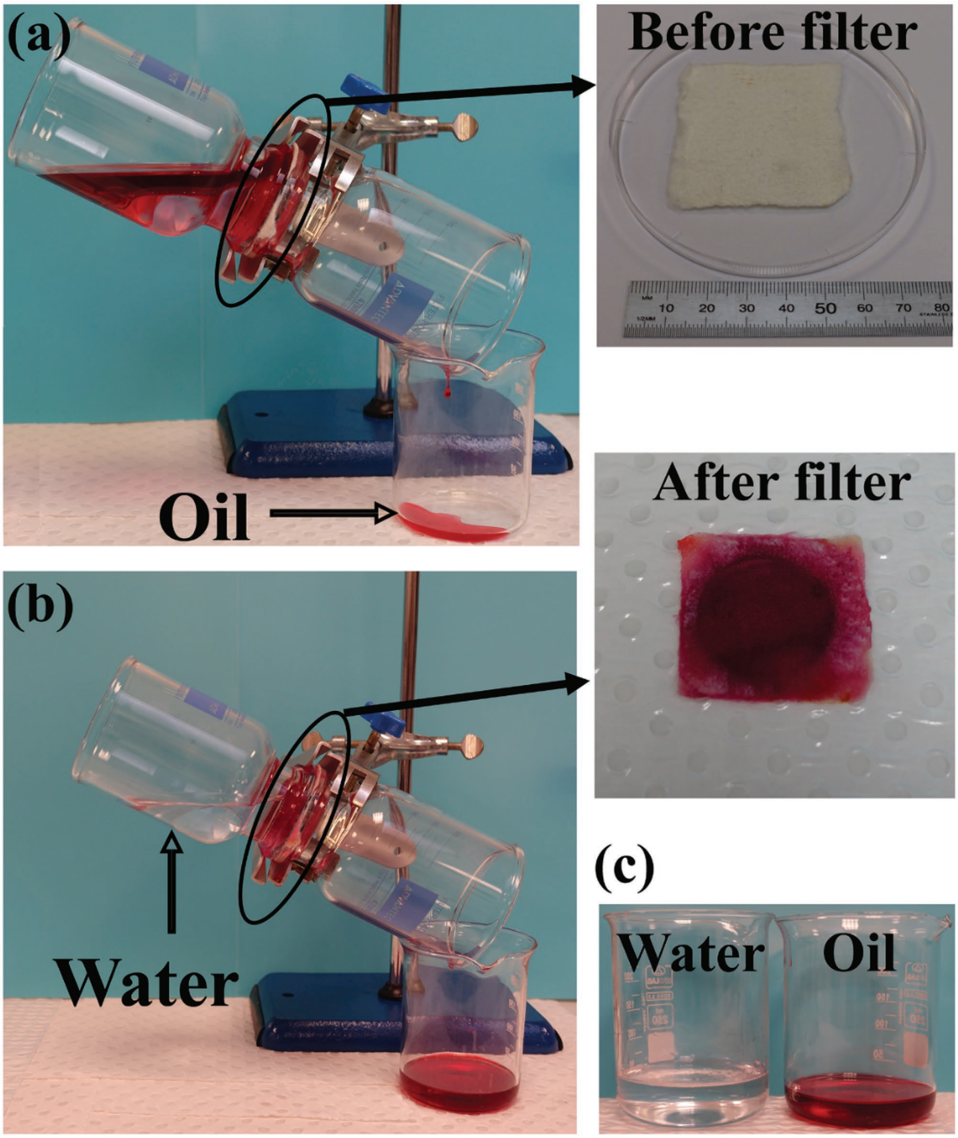

Figure 4. Oil/water separation studies of the porous BNNS-coated 2D fabric membrane. a) The mixture of pump oil (dyed by red color) and water was put into the upper glass tube, the zoom-in shows the coated membrane was fixed between two glass tubes; b) pump oil permeated through the coated membrane, while the water was repelled and kept in the upper glass tube, the zoom-in shows the coated membrane after oil/water separation; and c) photograph shows collected water and pump oil after the separation.

route for cleaning up oil spillage. As a comprehensive sorbent in practical requirements, it should not only effectively separate oil from water, but also possess excellent recyclability and recoverability of the absorbed oil simultaneously. The regeneration of the absorbed oil by porous BNNS-coated 3D melamine sponge was evaluated in this study (Figure 5c). The pump oil can be easily recovered by simply squeezing an oil-absorbed porous BNNS-coated 3D melamine sponge due to its excellent robustness. Most importantly, the coated 3D melamine sponge almost unchanged after ten cycles of the absorption/squeezing tests, which indicates a strong adherence of porous BNNSs to the 3D melamine sponge even after multiple extrusions. In addition, the porous BNNS-coated 3D melamine sponge also exhibits excellent absorption capacity toward a wide range of other organic solvents and oils (Figure 5d), such as ethanol, toluene, and hexane, which are common oily pollutants in daily life or industry. The efficiency of absorption can be referred to weight gain (wt%) defined as the weight of absorbed substances per unit weight of porous BNNS-coated 3D melamine sponge. It was revealed that the porous BNNS-coated 3D melamine sponge exhibited excellent absorption capacity in the range 58–112 times its own. For instance, the absorption capacity toward pump oil, white oil, and chloroform is close to 58×, 91×, and 112×, respectively, which is much higher than porous sponge materials, including porous poly (dimethylsiloxane),[28] polyurethane and iron oxide composites,[29] graphene hydrogels,[30] and nanocellulose aerogels,[31] validating its great potential in water remediation. Importantly, it shows a similar absorption capacity (51×) of pump oil using the coated sponge after 1000 compressions cycles at 50% strain, which not

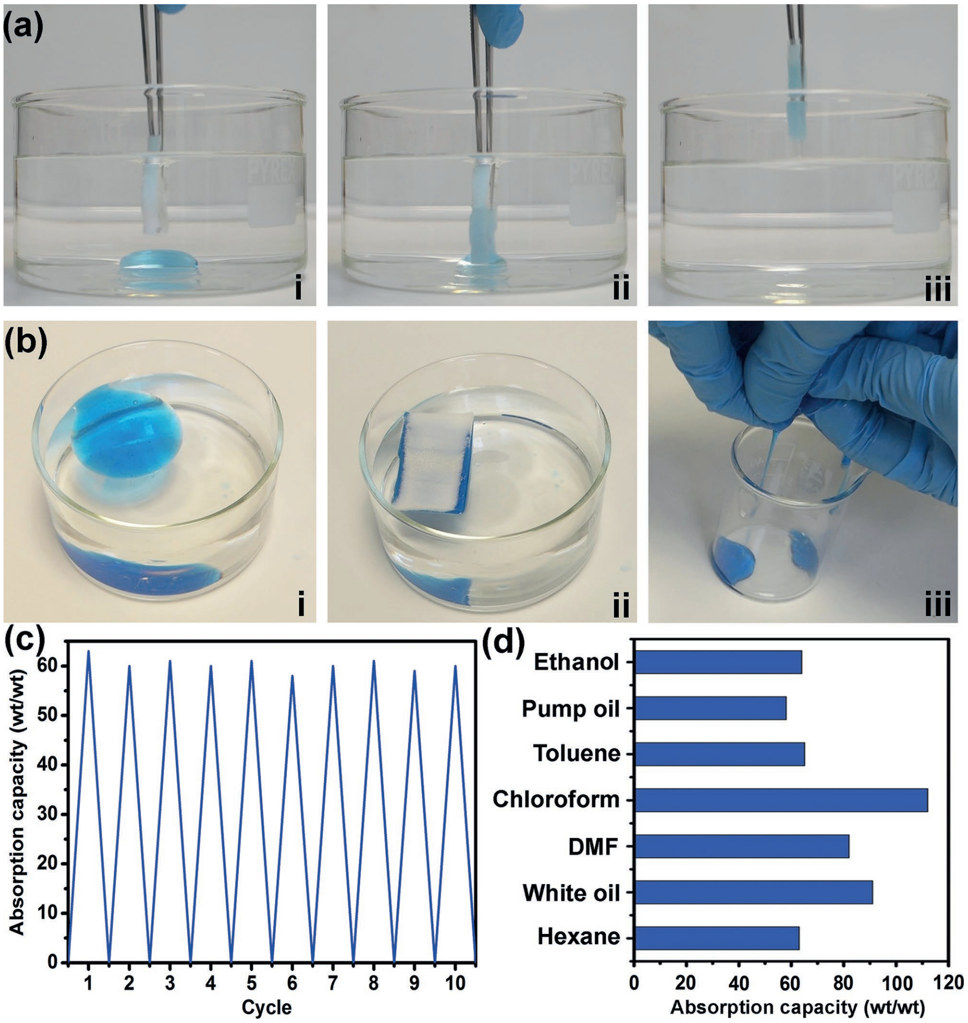

Figure 5. a) Photographs showing the underwater adsorption of dichloromethane (dyed by blue color) by a piece of porous BNNS-coated 3D melamine sponge. b) Photographs showing the absorption/squeezing process of pump oil (dyed by blue color). c) The pump oil absorption capacity of the porous BNNS-coated 3D melamine sponge recycled via squeezing methods. d) The adsorption capacity of porous BNNS-coated 3D melamine sponge toward a variety of organic solvents and oils.

only indicates the strong adhesion between BNNS and the base material but also a promising material with long cycle availability for oil-spill cleanup (Figure S5, Supporting Information).

3. Conclusion

We reported a facile LBL assembled method to coat porous BNNSs onto the commercial cotton fabric and melamine sponge, changing the surface of fabric and melamine sponge framework to be superhydrophobicity and superoleophilicity. Meanwhile, the coated porous BNNSs membrane and sponge show improved flame-retardant upon exposure to flame due to the intrinsic high resistance to oxidation and flame retardancy of BNNSs. Moreover, the oil/water separation tests have been performed, indicating some outstanding features of coated materials: high separation efficiency (superhydrophobic), self-clean (low water adhesion), good adsorption capability (58–112 times its own weight), excellent recyclability (>10 cycles), and simple recycling routes (robustness). We believe that such a simple, low cost, easily scaled up, and effective assembly protocol will provide a new pathway for applications in oil–water separators and cleanup of large-area oil spills.

4. Experimental Section

Materials and Chemicals: Poly dimethyl diallyl ammonium chloride (PDDA, 20 wt%, $M_w \approx 100\,000–200\,000$), chitosan, tetrahydrofuran, dichloromethane, pump oil, white oil, toluene, hexane, and ethanol were obtained from Sigma-Aldrich (Australia). Sylgard 186 silicone elastomer base and Sylgard 186 silicone elastomer curing agent were purchased from Dow Corning (United States). All chemicals were used as received. Deionized water was used during all the experiments. Cotton fabric and melamine sponge were purchased from local stores.

Fabrication of Superhydrophobic Coating (Layer-by-Layer Assembly): The cotton fabric was cut into 5×5 cm^2 followed by washing repeatedly with water and ethanol for three times and dried overnight at room temperature. The as-cleaned cotton fabric was then immersed in aqueous PDDA solution (10 mg mL^{-1}) for 30 min to render its surface positively charged, followed by rinsing with water and drying at room temperature.

For BNNS preparation, boron trioxide and guanidine hydrochloride in a 1:5 molar ratio were mixed in methanol (20 mL) to form a clear, colorless solution.[13] After 24 h under vigorous stirring, a white crystalline powder constituting a complex between boron trioxide and urea had formed. The resulting porous BNNS powder was placed in a quartz boat and heated up to 1100 °C at a rate of 10 °C min^{-1} and held for 2 h under a gas flow of mixture of 15% hydrogen in nitrogen. Finally, the as-synthesized BNNSs were used to prepare a 0.5 mg mL^{-1} porous BNNS aqueous suspension using probe ultrasonic treatment for 2 h at room temperature.

As-above modified cotton fabric was first soaked in 50 mL as-prepared BN aqueous suspension for 30 min under slowly stirring, ensuring the negatively charged porous BNNSs transferred onto the surface of the cotton fabric. The cotton fabric was removed from suspension when the electrostatic absorption completed, and hang-dried at room temperature. 1.25 mL of PDDA aqueous solution (10 mg mL^{-1}) was subsequently spread on the cotton fabric and also hang-dried at room temperature. Repeating the above 16 steps, positive PDDA and negative BNNSs with different layers alternatively formed on the surface of the cotton fabric. The PDDA layer provided a uniformly charged surface and facilitates subsequent electrostatic absorption of BNNSs, therefore the outermost surface layer was always BNNSs.

The surface coating of polydimethylsiloxane (PDMS) was carried out by a dip-coating method. The solution contained 0.909% on weight of bath (o.w.b.) of Sylgard 186 silicone elastomer base and 0.091% o.w.b. of Sylgard 186 silicone elastomer curing agent in tetrahydrofuran. Fabrics were squeezed by a Rapid PA0 pad mangle (Rapid Labortex Co. Ltd., Taiwan) after each bath to remove excess liquor. After padding the solution retained in the fabrics was around 100% w/w to ensure the loading amount of polydimethylsiloxane close to 1% on weight of fabric (o.w.f.). Finally, the treated fabric samples were cured at 65 °C for 5 h.

The porous BNNS-coated melamine sponge was fabricated in a similar way as cotton fabric with minor modification. To further enhance the positive charge of the surface, the melamine sponge was first modified by a cationic solution rather than PDDA. The cationic solution was prepared by adjusting the pH value of deionized water to 4 with acetic acid and then dissolving 0.2 wt% chitosan. This aqueous solution was magnetically stirred overnight as the chitosan was completely dissolved. The cleaned melamine sponge ($3 \times 3 \times 3$ cm^3) was immersed into 20 mL above cationic solution for 30 min. Followed by rinsing with water and drying at room temperature, the sponge immersed into 20 mL porous BNNS aqueous suspension (0.5 mg mL^{-1}) for 30 min and then dried. The assembly of porous BNNSs and chitosan based on electrostatic interaction as a driving force was carried on repeatedly as the cotton fabric and the outermost surface layer was also BNNSs. After coating the desired number of layers, sponge samples were coated by PDMS using the dip-coating method.

Characterizations: SEM was conducted on a Zeiss Supra 55V operating at 110 kV. FTIR spectra were recorded on a Bruker Lumos FTIR Microscope (Billerica, MA, USA) in ATR mode, with an accumulation of 64 scans at 4 cm^{-1} resolution. The contact angle was measured using a contact angle measurement system (CAM101, KSV Instruments Ltd.). Fabric and foam flammability were evaluated through exposure to direct flame from a butane microtorch (Tradeflame, the blue flame temperature is ≈2400 °F).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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