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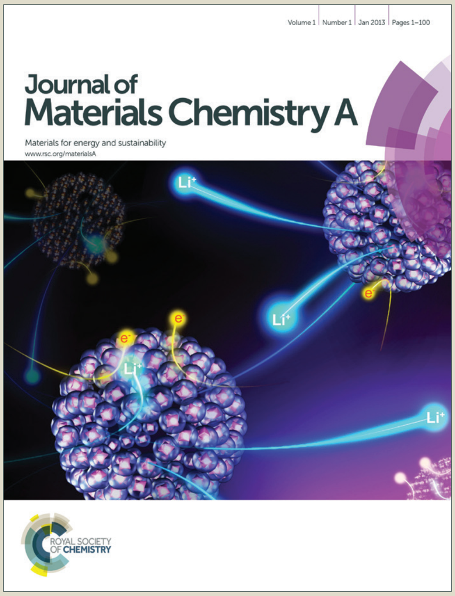

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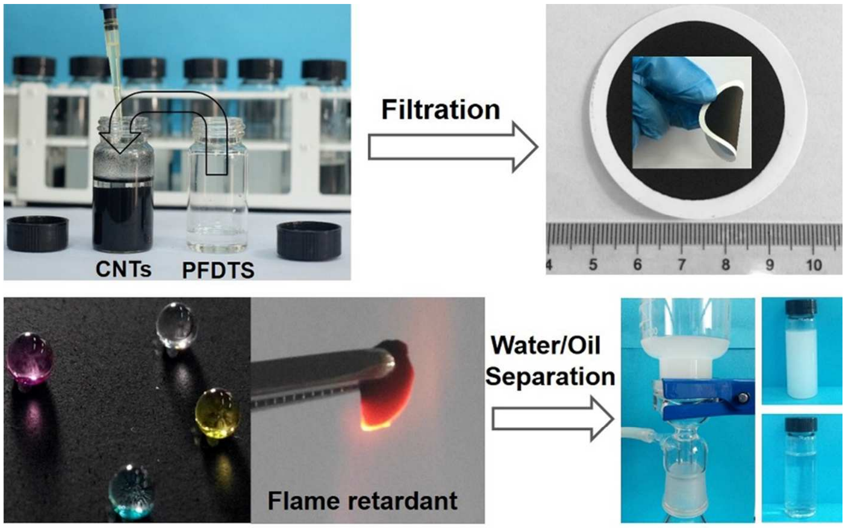

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Controlled Functionalization of Carbon Nanotubes as Superhydrophobic Materials for Adjustable Oil/Water Separation

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A robust strategy for fabricating superhydrophobic carbon nanotubes (CNTs) based hybrid materials as separation membrane through the covalent attaching fluorine-bearing organosilane of 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (PFDTS) onto -OH funcitonalzied CNTs is proposed. This resulted PFDTS/CNTs superhydrophobic materials with controlled functionalzaition could be used to effectively separate various surfactant-stabilized water-in-oil emulsions with high separation efficiency and high flux. It even maintain stable superhydrophobicity and high separation efficiency under extreme conditions including high or low temperature, strong acidic or alkaline solutions, and show fire-retardant properties.

Inspired by the self-cleaning and water-repellent properties of lotus leaf in natural world, artificially bioinspired superhydrophobic surfaces have aroused wide interest[1-7] due to their potential applications in fluid transportation, environmental remediation, or oil/water separation etc. [8-14] As one of the important oil/water separation materials, carbon nanotubes (CNTs) have attracted tremendous interests because of their low density, high porosity, extraordinary mechanical strength and hydrophobic properties.[15-24] Shi et al. reported that single-walled CNTs network films could be used for the separation of emulsified oil/water mixtures with a higher flux than commercial filtration membranes.[25] Dong et al. found that the hybrid foam of graphene and CNTs can selectively remove organic solvents from water with high absorption capacity.[21] We have reported previously that polymers could be covalently attached onto the surface of CNTs to achieve polymer/CNTs hybrid membrane, which can effectively separate various surfactant-stabilized oil/water emulsions with high separating efficiency.[26-27] Although many CNTs based membranes have been created for oil/water separation, challenges still exist for simple preparation technique, full scale fabrication, recyclability and durability in severe processing environment. Thus, a versatile and efficient approach to produce CNTs based superhydrophobic materials are still highly desired.

Organosilanes have been widely used as effective surface-modifying agents for different OH-terminated substrates because of the strong Si-O linkage between silane and the substrates or between adjacent silane molecules.[28-29] This motivates us to present a simple applicable method towards fabricating robust and durable CNTs based superhydrophobic hybrid membranes by attaching fluorine-bearing organosilane of 1H,1H,2H,2H-perfluordecyl-triethoxysilane (PFDTS) onto -OH funcitonalzied CNTs. The as-prapared superhydrophobic PFDTS/CNTs hybrid membranes show excellent separation properties for various surfactant-stabilized water-in-oil emulsions. The fabricating procedure is schematically shown in **Fig. 1**. A simple mix of CNTs and hydrophobic PFDTS leads to the spontaneous deposit of the PFDTS layer onto CNTs (**Fig. 1A**). [28-29] The PFDTS modified CNTs were then filtrated through a poly(vinylidene fluoride) (PVDF) membrane to achieve superhydrophobic PFDTS/CNTs membrane (**Fig. 1B**-**1D**). The morphology and surface wettability of the PFDTS/CNTs membrane are adjustable according to the feed volume ratio of PFDTS to CNTs. With proper volume ratio of PFDTS to CNTs, superhydrophobic PFDTS/CNTs membranes can be obtained, which show excellent separation properties for various surfactant-stabilized water-in-oil emulsions, and kept stable superhydrophobicity and high separation efficiency under extreme conditions including high or low temperature, strong acidic or alkaline solutions. Furthermore, the PFDTS/CNTs membranes inherit the intrinsic flame retardant nature of PFDTS. With simple preparation process, stable superhydrophobicity, flame retardancy and effective separation performance, the PFDTS/CNTs membranes contribute to the development of oil/water separation materials and will have great potential for practical oil/water separation.

The functionalization of PFDTS onto CNTs improved the film forming ability of pure CNTs, which was shown by the photographs in **Fig. S1**. There was a significant difference between the CNTs membrane and the PFDTS/CNTs membrane. Before the addition of PFDTS, the CNTs membrane cracked largely during the membrane drying process (**Fig. S1A**). Upon the mixing of PFDTS with CNTs, PFDTS could act as glue to stick the CNTs together during the formation of the strong Si-O linkage between silane and the substrates or between adjacent silane molecules.[28-29] Free-standing PFDTS/CNTs membranes with a large size of the diameter at 4.0 ± 0.1 cm could be easily obtained (**Fig. 1B** and **Fig. S1B**). The PFDTS/CNTs membrane is able to maintain the complete and uniform state even after drying, which is strong enough to be manipulated by tweezers (**Fig. 1C**) or by hands (**Fig. S1C**), indicating the excellent mechanical properties of the resulted PFDTS/CNTs membrane. The as-prepared PFDTS/CNTs hybrid memberane showed a superhydrophobic properties(**Fig. 1D** and **Movie S1**).

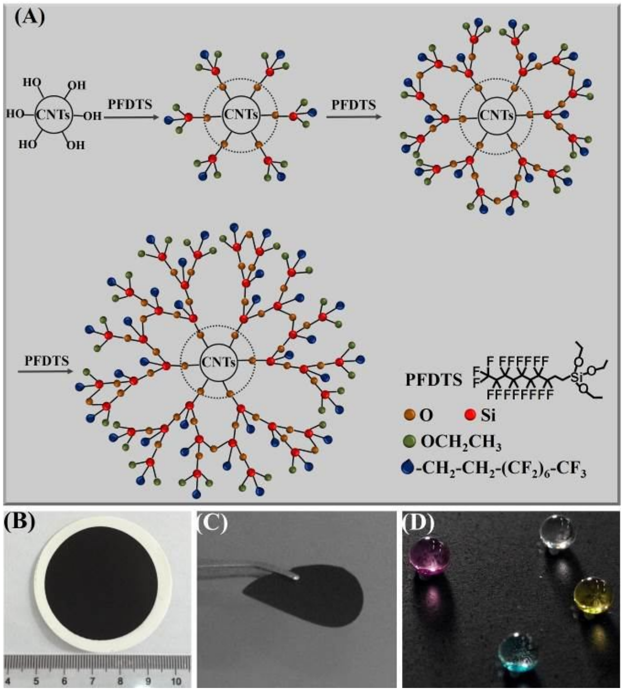

Fig. 1 (A) Schematic illustration of the fabricating superhydrophoic PFDTS/CNTs hybrid membrane. Photograph of (B) A PFDTS/CNTs membrane prepared on PVDF membrane substrate by filtation process. (C) A free-standing PFDTS/CNTs membrane etched from the PVDF membrane substrate bended by tweezers. (D) An as-prepared superhydrophobic PFDTS/CNTs membrane with water droplets on the surface (water was dyed with $KMnO_4$, $CuSO_4$, and $FeCl_3$, respectively).

Scanning electronic microscopy (SEM) and transmission electronic microscopy (TEM) were applied to characterize the surface morphology of the CNTs membrane before and after the hydrophobic modification by PFDTS. As shown in **Fig. 2, Fig. S2** and **Fig. S3**, after the modification with PFDTS, the diameter and microstructure of the PFDTS/CNTs are totally different from that of the original CNTs network membrane. (**Fig. 2A-2D**). Using the feed ratio of 1.25 as the example, the diameter of the CNTs has a double increase changed from original diamter at ~28 nm (**Fig. 2A-2C**) to ~59 nm (**Fig. 2B-2D**). The TEM results not only are consistent with the SEM results, but also show the details and large shell thickness increase (**Fig. 2C-2D**). Both the SEM and TEM images illustrate that PFDTS is uniformly grafted onto the surface of CNTs and there is almost no agglomeration among CNTs. In order to investigated the relationship between the diameter of CNTs and the various feed ratio of PFDTS to CNTs, a detailed research was carried out (**Fig. S2-S3**), which is summaried in **Fig. 2E**. It was shown that the diamater of the modified CNTs by PFDTS could be tunably controlled from the original ~28 nm to a balanced state at ~70 nm. Upon the ratio is above 1.25, there is no more change in diameter, showing a modification saturation (**Fig. 2Ea**). These results confirm that our robust strategy of coating PFDTS onto CNTs in mild reactions did not damage the original structure and morphology of the CNTs, yet did package evenly on the surface of CNTs by PFDTS.

The corresponding surface wettability of the as-prepared PFDTS/CNTs membranes with various feed ratio were also investigated (**Fig. S4** and **Fig. 2Eb**). It is well known that the intrinsic hydrophobicity can be adjusted both by chemical functionality and surface roughness. Functionalization of hydrophobic PFDTS onto CNTs with high roughness (**Fig. 2A-2B**) endows the possibility of PFDTS/CNTs membrane with superhydrophobic properties. The water contact angle (WCA) of the original -OH functionalized CNTs membrane is 62 ± 3° **(Fig. S4A)**. After the modification with PFDTS, WCA of CNTs membrane increases with the increasing feed volume ratio (**Fig. S4B-S4F**). According to the Arkles theory[30], PFDTS are covalently attached onto CNTs through the reaction of fluorine-bearing organosilane molecules of PFDTS with hydroxyl groups of CNTs, which converse highly polar hydroxyl to low polarity ether bond (**Fig. 1A**). Therefore, the CNTs surface become hydrophobic because of the formation of a covalently attached fluoroalkylsilane layer on rough CNTs surface (**Fig. 2A-2B**) which significantly reduces the surface energy of the membrane and increases the WCA.[31] The membrane reached a superhydrophobicity state when the feed volume ratio of PFDTS to CNTs is 1.0 (**Fig. S4D**). The sliding angle of the membrane for water droplet is about 3.0 ± 0.6° (**Fig. S5,** and **Movie S2**), which suggested furtherly that the superhydrophobic PFDTS/CNTs membrane exhibits excellent self-cleaning ability.

The chemical composition of the attached PFDTS was confirmed by X-ray photoelectron spectroscopy (XPS). As shown in **Fig. 2F**, **Fig. S6** and **Table S1**, compared with CNTs membrane (**Fig. 2Fa**) XPS spectrum of PFDTS/CNTs surface reveals a new F1s peak at about 686 eV(**Fig. 2Fb**), which can be assigned to the F element of PFDTS. Since F is the characteristic element of PFDTS, the XPS results provide direct evidence of the successful covalent attachment of PFDTS onto the surface of CNTs.

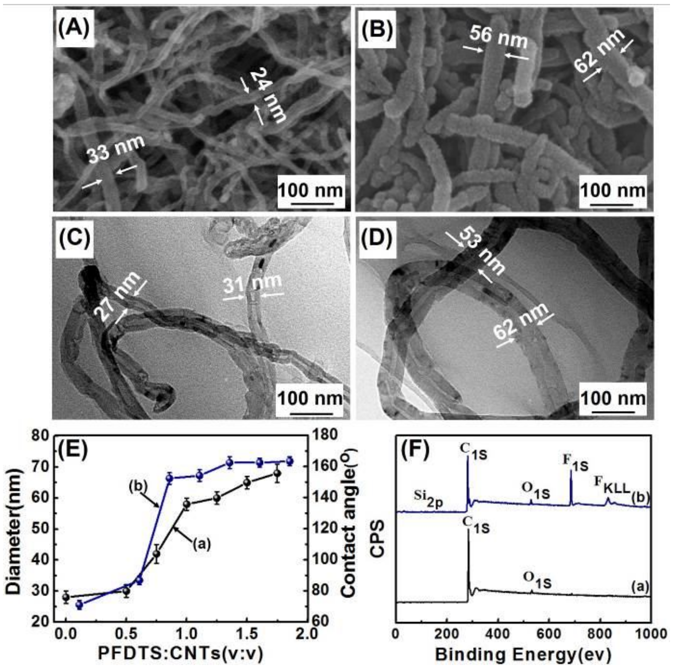

Fig.2 SEM images of (A)CNTs membrane, (B)PFDTS/CNTs membrane. TEM images of (C) CNTs, (D) PFDTS/CNTs membrane.

(E)Diameter(a) and WCA(b) of PFDTS/CNTs membrane versus the volume ratio of PFDTS to CNTs. (F)XPS spectra of (a)CNTs membrane and (b)PFDTS/CNTs membrane. Notice: as to Fig. 2B, Fig. 2D and Fig. 2F, the volume ratio of PFDTS to CNTs is 1.25.

There are various reports about the separation materials with special wettability that can effectively separate oil and water mixture, however, most of these materials are useful for separating immiscible oil-water mixtures, but are not effective at removing oil drops with small diameters from oil/water emulsions, especially for surfactantstabilized emulsions with droplet sizes below 20 μm, even nanosized oil drops.[25,33] As discussed above, our roubust strategy for fabricating the PFDTS/CNTs hybrid membrane shows a superhydrophobicity property, which provides excellent basis for its application in separating oil/water emulsions. In this work, oil/water separation was carried out at 0.09 MPa with a vacuum driven filtration system (**Fig. 3A**). If there was no PFDTS/CNTs deposited on the supported membrane of PVDF, the PVDF membrane also shows hydrophobicity with a WCA 120 ± 2°(**Fig. S7**). However, this non-superhydrophobic materials cannot separate the oil/water mixtures (**Fig. S8A, S8B** and **Movie S3**). The PFDTS/CNTs membrane can effectively separate oil/water mixtures (**Fig. S8C** and **Movie S4**), indicating PVDF membrane just act as a substrate to the PFDTS/CNTs membrane, and the oil/water separation performance is exhibited by the PFDTS/CNTs only.

A series of surfactant-stabilized water-in-oil emulsions were prepared to evaluate the separation capability of the membrane (**Table S2**). **Fig. 3** gives the separating results of using span80-stabilized water-in-toluene (S-1) emulsions as example. Emulsion droplets could be de-emulsified once touching the PFDTS/CNTs membrane, toluene immediately may be permeated through the membrane and water was retained above the membrane (**Movie S5**). As shown in **Fig. 3B-3C**, the collected filtrate (down) is transparent compared with the original milky white feed emulsion (upon). Optical microscopy was used to examine the separation effectiveness by comparing the feed with its collected filtrate. In the feed solution, there are densely-packed droplets flood the entire view and the size of the droplets is about 200 nm (**Fig. 3D-3F**), and no droplets are observed in the collected filtrate in the whole view (**Fig. 3E-3G**), indicating the excellent separating properties of the PFDTS/CNTs membranes. The purity of oil was also calculated by measuring the water weight percentage in the filtrate using a Karl Fischer analyzer. As shown in **Table S3**, the purity of oil is about 99.89%, indicating an extremely high separation efficiency of the PFDTS/CNTs membrane. Similar effective separations are also achieved for other emulsion systems including water-in-chloroform (S-2), water-in-hexane (S-3) (**Fig. S9, Fig. S10**, and **Table S3**).

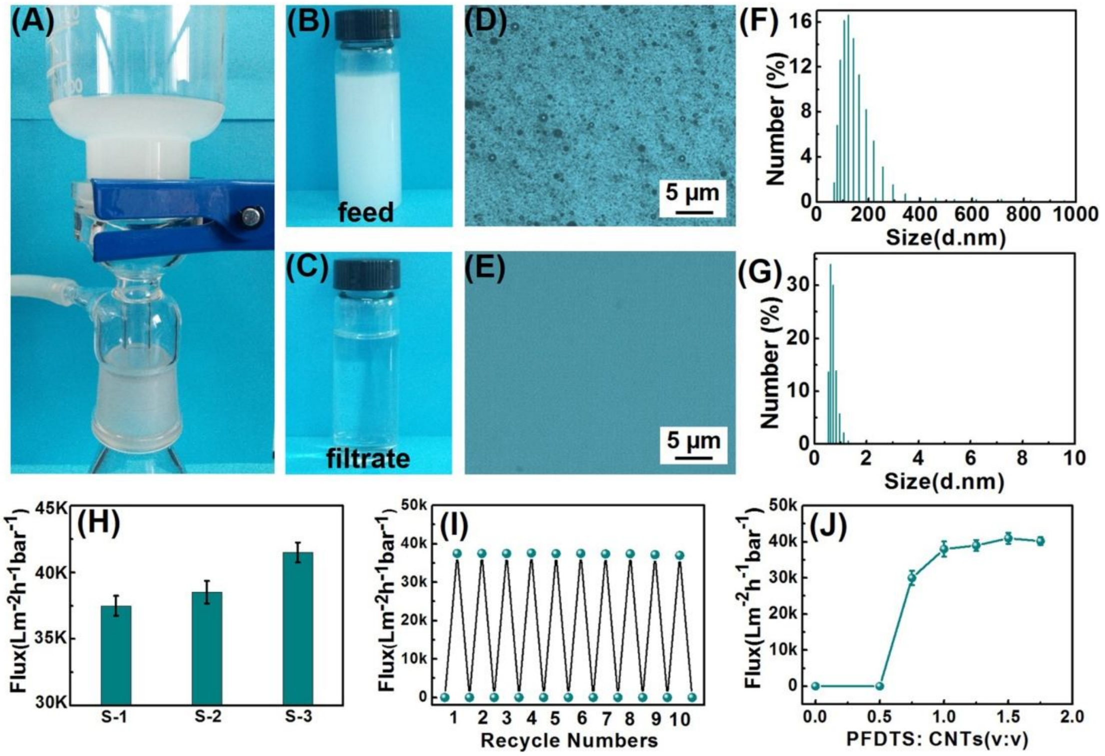

Fig. 3 (A) A photograph of separating water-in-toluene emulsion where toluene selectively permeates through the PFDTS/CNTs membrane. Photographs and DLS data of water-in-toluene emulsion before (B, D, F) and after (C, E, G) filtration. (H) Permeate flux for various emulsions of the PFDTS/CNTs membrane. S-1, S-2 and S-3 represent water-in-toluene, water-in-chloroform, water-in-hexane, respectively. (I) The fluxes of water-in-toluene emulsion passing through PFDTS/CNTs membrane versus the recycle numbers of filtration process.(J) Flux of PFDTS/CNTs membrane versus the volume ratio of PFDTS to CNTs. Notice: from Fig. 3A to 3I, the volume ratio of PFDTS to CNTs is 1.25.

The fluxes of various emulsions that permeate through the membranes were also measured (obtained by calculating the flow volume in the unit time from the valid area of the membrane). With regard to water-in-oil emulsions, the permeate flux of the membrane depends on the viscosity of the oil. Consequently, it is reasonable that membrane flux is higher for oils with lower viscosity(**Fig. 3H**). Since toluene is the most viscous subject (0.587 mPa s) among the oils selected in this work (**Table S4**), the membrane presents the lowest flux of

37530 ± 631 L m^{-2} h^{-1} bar^{-1} for water-in-toluene(S-1), and flux of 38620 ± 734,41880 ± 655 L m^{-2} h^{-1} bar^{-1} are achieved for water-in-chloroform (S-2) and water-in-hexane (S-3), respectively. The reliability of the PFDTS/CNTs membrane was tested by carrying out cyclic experiments for the treatment of water-in-toluene emulsion (S-1). In every cycle, the PFDTS/CNTs membrane was washed by 5 mL ethanol. As shown in **Fig. 3I**, the membrane maintains the high flux even after 10 recycle numbers, which indicates good cyclic performance of the PFDTS/CNTs membrane. **Fig. 3J** also shows that the flux could be controlled with a various value with the change of the feed volume ratio of PFDTS to CNTs. With the increasing volume ratio of PFDTS to CNTs, the flux increased first and finally reach a plateau. If the volume ratio of PFDTS to CNTs continue increases, the flux may decrease slightly, which might be caused by the decrease of effective pore size of CNTs membrane with more PFDTS coated on CNTs.[25]

Since most superhydrophic surfaces have poor durability because of chemical oxidation, strong light, or physical rubbing.[32] Therefore, it is an important criteria to evaluate the recyclability and durability of the PFDTS/CNTs membrane for practical applications. When the PFDTS/CNTs hybrid membrane was placed in an environment with a temperature of 0°C for 30 h, its WCA remain unchanged within experimental error and the separation efficiency for the toluene/water emulsion is almost constant (**Fig. 4A**). Similarly, the PFDTS/CNTs membrane does not lose superhydrophobicity, and the separation efficiency is unaffected after exposure to an extremely hot environment at 100 °C for 30 h (**Fig. 4B**). Thus, the PFDTS/CNTs membrane shows rather stable superhydrophobicity toward high or low environment temperature. The chemical durability of the PFDTS/CNTs membrane was also studied by immersing them in strong acidic or alkaline solutions. As shown in **Fig. 4C**, there is no obvious change of the WCA when the PFDTS/CNTs membrane was immersed into the strong acidic (pH = 1) or alkaline (pH = 13) solutions for 30 h, and the PFDTS/CNTs membrane is still capable of effectively separating oil/water mixtures after the chemical treatment. These results demonstrate that the obtained PFDTS/CNTs membrane is tolerant to hot, cold, acid and alkaline conditions.

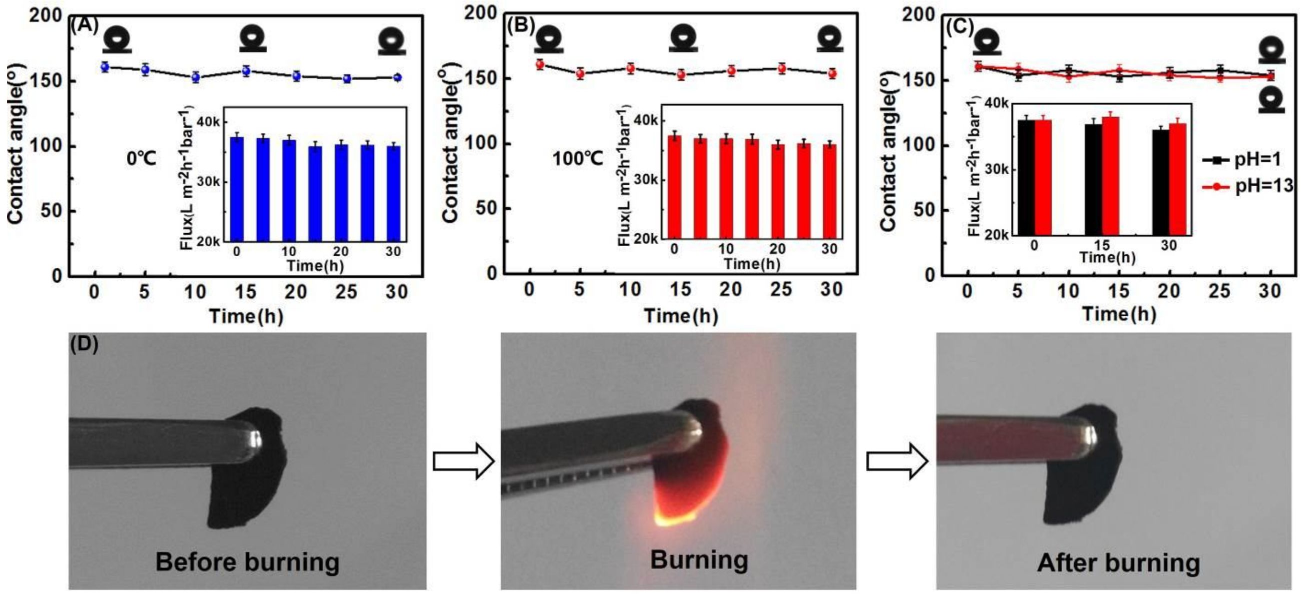

Fig. 4 Variation of WCA of the superhydrophobic FDTS/CNTs membrane (A) at 0 °C, (B) at 100 °C, (C) exposed to acidic (pH = 1) and alkaline solutions (pH = 13), Insets are the corresponding separation efficiencies for the water-in-toluene emulsions. (D) The combustion process of the superhydrophoboc PFDTS/CNTs membranes (10 min). Notice: from Fig. 4A to 4D, the volume ratio of PFDTS to CNTs is 1.25.

Since most organic solvents and crude oil are highly flammable and could be extremely dangerous when caused on fire, therefore flame retardant property is another important criterion for practical applications. The combustion behavior of the obtained PFDTS/CNTs membrane was investigated and shown in **Fig. 4D** and **Movie S6**. The flame on the PFDTS/CNTs membrane is very weak and vanishes within a few seconds, and the WCA of the membranes remain unchanged within experimental error after burning for 10 min (**Fig. S11**), which indicate the PFDTS/CNTs membranes inherit the flame retardant property of PFDTS. Therefore the PFDTS/CNTs membrane is the promising flame retardant candidates to remove flammable oils and organic solvents.

Conclusions

In summary, a facile and robust strategy for fabricating superhydrophobic carbon nanotubes (CNTs) based hybrid materials as separation membrane through the covalent attachment of fluorine-bearing organosilane of PFDTS onto -OH funcitonalzied CNTs surface has been presented. The morphology, surface wettability and flux are adjustable according to the feed volume ratio of PFDTS to CNTs. The as-prepared membranes can effectively separate various water-in-oil emulsions with high separation efficiency and high flux. Furthermore, the PFDTS/CNTs membranes maintain stable superhydrophobicity and high separation efficiency under extreme conditions including high or low temperature, strong acidic or alkaline solutions, and also show fire-retardant properties. The simple preparation process, stable superhydrophobicity, flame retardancy and effective separation performance make the PFDTS/CNTs membranes promising candidates in various practical applications such as fuel-purification and commercially-relevant oil/water separation.

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Notes and references

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