Electronic Supplementary information

Lotus-Inspired Janus Hybrid Film Enabled by Interfacial Self-Assembly and In Situ Asymmetric Modification

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General remarks

The raw nano carbon-based materials were acquired from Chengdu Organic Chemistry Co., Ltd, which are contains the COOH functionalized multi-walled carbon nanotubes (CNTs-COOH) with the diameter about 20−30 nm, length about 10−30 μm, −COOH % about 1.23 wt % and the purity is over 95%; the OH functionalized multi-walled carbon nanotubes (CNTs-OH) with the diameter about 20-30 nm, length about 10-30 μm, -OH % about 1.76% and the purity is over 98%; the NH_2 functionalized multi-walled carbon nanotubes (CNTs-NH_2) with the diameter about 8-15 nm, length about 50 μm and the purity is over 95%; the pure multi-walled carbon nanotubes (CNTs) with the diameter about 4-6 nm, length about 10-20 μm and the purity is over 98% and the graphene with the diameter about 0.5-3 μm, thickness about 0.55-3.74nm and the purity is over 98%. 1H,1H,2H,2H-Perfluorodecyltriethoxysilane (PFDTS) was purchased from aladdin Chemical Reagent Co., Ltd. PDMS substrates were fabricated from Sylgard 184 (Dowcorning, US, the ratio between components A and B was 1:10). Other solvents and reagents were obtained from Sinopharm Chemical Reagent Co., Ltd. and used as received.

Preparation of carbon-based films at the air/water interface

The carbon-based films were prepared according to previous Langmuir–Blodgett assembled methods with some alterations.[1, 2] Typically, 20 mg the different carbon-based nanomaterials (CNTs-COOH, CMTs-OH, CNTs-NH_2, CNTs and graphene) were first dispersed in 200 mL anhydrous ethanol solution, followed by strong ultra-sonication for 2 h using an ultrasonic to form a stable dispersion with appropriate aging time. Subsequently, the resultant uniform dispersion was dropped onto the deionized water surface, the capillary substances like tissue or microporous sponges were selected to put on one side of the interface to quickly siphon water from the system, followed by a prominent decrease of the Langmuir area. Notably, the homogeneous Langmuir layers were closely packed toward the opposite direction of the siphone direction. When the movement of the film stopped and further siphoning could not drive the film, the resulting film was ultimately formed, indicating a closely packed structure.

Preparation of transferred substrate with different hydrophilic and hydrophobic properties

The hydrophobic substrate was prepared by attached the cloth on the slide, and the cloth treated by AC-FAS heptane solution with the concentration as 2 wt % under room temperature 12 h. The superhydrophilic substrate prepared by using plasma under the air condition to treat slide with 2 min. And the raw slide substrate with the water contact angle (WCA) is 60°, PDMS attached slide substrate with the WCA is 108°.

Transfer of the as-formed films and interface modification

In our system, the resulting films can be transferred onto other aqueous solutions interface by flat substrate (such as glass substrate), and organic solvent with lighter than water can be add to the aqueous solutions surface to interface asymmetry modification. As a concept, the prepared CNTs-OH film first transferred onto the water surface. Then, 2 wt % AC-FAS N-heptane solution was added to the film surface. Further, dopamine Tris mixture solution was injected into the water and made the final concentration of dopamine as 2 mg/mL, pH=7.5. Finally, the reaction was allowed to stand for 12 h at room temperature and an asymmetrically modified CNTs film was formed.

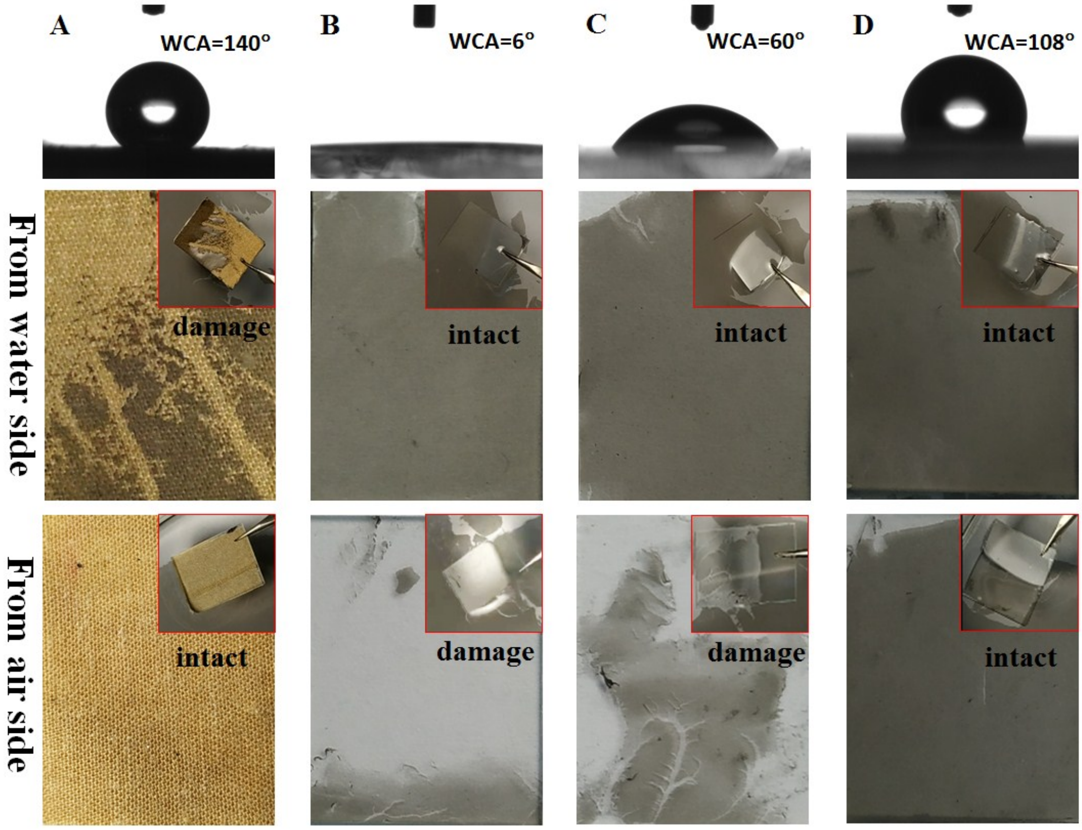

Fig. S1 Transferring CNTs films with different hydrophilic and hydrophobic properties substrates from water side and air side. WCA of the substrates are 140° (A), 6° (B), 60° (C) and 108° (D), respectively. Insets: photo of transfer processing.

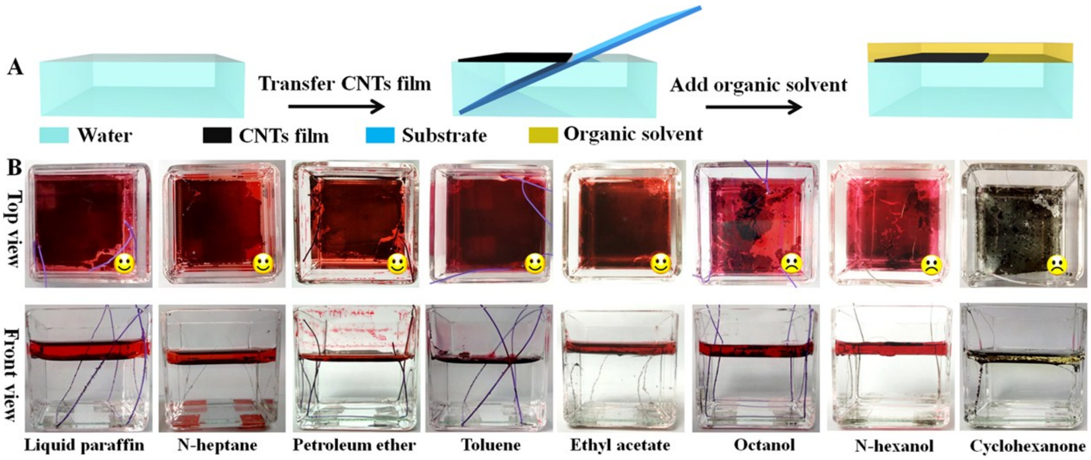

Fig. S2 Investigating the stability of CNTs film at the oil/water interface. A) The schematic illustration of transferring CNTs film onto the oil/water interface. B) Photograph of the CNTs film with aging 72 h at the different organic solvent/water interface by top view and front view after transferred 16 hours.

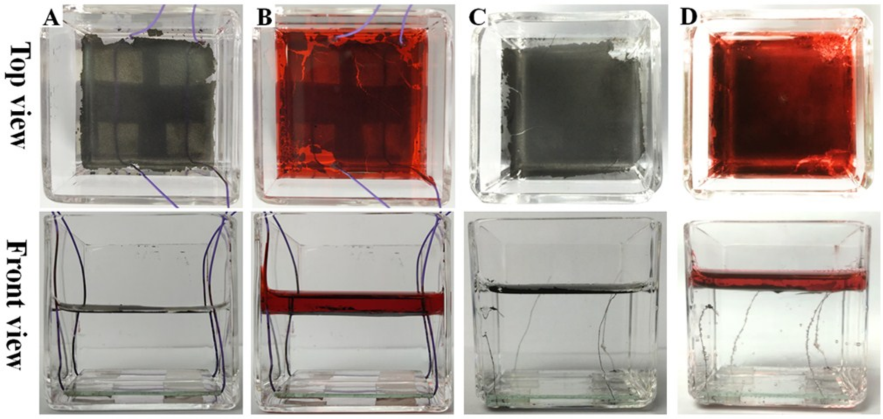

Fig. S3 Photos of the freshly prepared CNTs film A) at air-water interface, B) at oil (ethyl acetate)-water interface. Photographs of the CNTs film after aging procedure C) at air-water interface and D) at oil (ethyl acetate)-water interface.

Table S1 the physical properties of organic solvents[3-5]

	Surface tension at 20˚C (mN/m)	Solubility of organic solvent in water (wt %.)	Solubility of water in organic solvent (wt %)
Liquid paraffin	~35	insoluble	insoluble
N-heptane	20.35	0.0003%	0.0082%
Petroleum ether	-	-	-
Toluene	28.53	0.05%	0.0543%
Ethyl acetate	23.75	8.7%	2.94%
Octanol	26.06	0.096%	5.31%
N-hexanol	23.75	0.59%	8.97%

Cyclohexanone	34.50	2.3%	8.0%
Pentane	18.7	0.004%	0.0101%
Hexane	20.3	0.0014%	0.009%

Characterization

Static water contact angles (WCA) measurements were measured at room temperature using an OCA-20 DataPhysics instrument. The water (Milli-Q) droplet volume was 3 µL, and an average of three measurements was made to determine the surface wettability. Scanning electron microscopy (SEM) was performed to observe the micromorphology with a Hitachi S-4800 cold field emission SEM at an accelerating voltage of 8 kV. X-ray photo-electron spectroscopy (XPS) analysis was performed on a Shimadzu Axis Utltra DLD spectroscope, using Mg Kα as radiation resource. Energy dispersive spectroscopy (EDS) measurements were measured by FEI Quanta FEG 250 thermal field emission SEM.

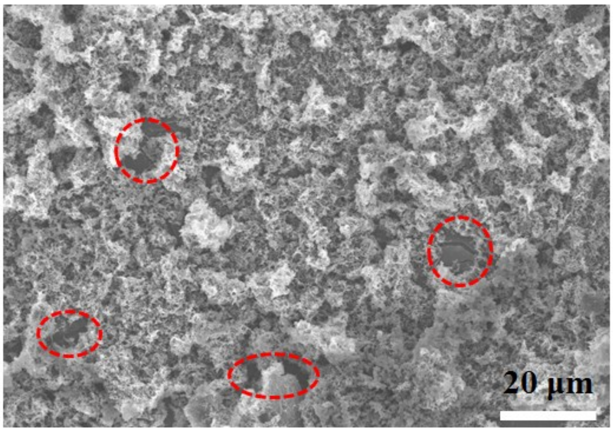

Fig. S3 PDA modified side SEM image of the CNTs-OH film.

Table S2 Atomic/mass concentration of different films

	Atomic Concentration %				Mass Concentration %			
	F 1s	O 1s	N 1s	C 1s	F 1s	O 1s	N 1s	C 1s
Air side of CNTs film	0	5.96	0	94.04	0	7.79	0	92.21
water side of CNTs film	0	7.38	0	92.62	0	9.6	0	90.4
PDA modified side	18.7	13.52	5.33	62.45	25.43	15.48	5.35	53.73
PFDTS modified side	52.98	6.5	0.44	10.08	62.98	6.5	0.39	30.14

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