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Integration of a patterned conductive carbon nanotube thin film with an insulating hydrophobic polymer carpet into robust 2D Janus hybrid flexible electronics†

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Despite CNTs based flexible electronics showing promising applications in numerous fields, they are still weak against harsh environments. Herein, we present our recent advancement in the integration of patterned conductive CNTs thin films with an insulating hydrophobic polymer carpet into 2D Janus hybrid thin films for robust flexible electronics. Due to the introduction of the hydrophobic polymer as the water proof layer, our strategy could be considered as a new electronic packaging technique to protect conductive 2D CNTs thin films at a molecular level. The obtained polymer carpet grafted 2D CNTs thin films have potential application as flexible, transparent electronics with highly robust environmental stability.

Introduction

Two-dimensional (2D) carbon nanotubes (CNTs) thin films[1] have received a great deal of attention because of their unique properties, such as high optical transmittance, excellent thermal conductivity, chemical sensitivity and good mechanical flexibility.[2–6] They are thus the most reliable candidates for flexible, transparent, and conductive materials that complement indium tin oxide (ITO) for various applications, including field-effect transistors, chemical sensors, smart windows, and flexible electronics.[7–12] It is known that solution based wet processes, including dip-coating,[13,14] spin-coating,[15] spray-coating,[16,17] vacuum filtration[18] and Langmuir–Blodgett (LB) deposition,[19] are cost-effective ways to fabricate large-area thin films of CNTs. Furthermore, free-standing 2D CNTs thin films achieved on the air/liquid interface may open new opportunities for several applications since they can be easily transferred to various target substrates. Among these abovementioned wet processes, the LB method has been demonstrated as the most popular way to achieve freestanding 2D CNTs thin films on a liquid surface.[20] Combined with lithographic techniques, the CNTs thin films could be also achieved in a patterned fashion for use as building blocks in electronic devices.[21,22] Despite the flexible electronics having shown promising applications in many fields, they are still weak against harsh environments, which requires an electronic packaging technique as a necessary process to protect the conductive network.[23] However, the challenge for the CNTs thin film packages process currently is that it usually requires sophisticated facilities and time-consuming multistep procedures. Therefore, more simple and reliable thin film packaging approaches for free-standing 2D CNTs thin films with both conductivity and environmental resistance are still highly required.

Inspired by the carpet for floor protection, there was a recent report about a polymer carpet by Jordan and co-workers,[24,25] who made freestanding polymer brushes fabricated by surface initiated polymerization from a cross-linked 1 nm-thick monolayer as polymer carpets. The solid-supported polymer carpets were found to be mechanically robust and hydrophobic and had the potential for developing a polymer carpet as the protecting layer by polymer grafting from conductive thin films. Grafting a polymer layer from a 2D thin film resulted in the formation of 2D Janus hybrid materials that could be transported from one environment to another one without losing their structural integrity, which provided new opportunities for 2D chemistry.[26] There are several current efforts for fabricating polymers from carbon based thin films. For example, Sharp *et al.*[27] reported the direct chemical modification of graphene by photopolymerization with styrene occurring at existing defect sites and that there is no detectable disruption of the

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graphene basal plane conjugation. This method thus offers a route to define graphene functionality without degrading its electronic properties. We have previously covalently attached hydrophobic polymer onto CNTs membrane to achieve superhydrophobic polymer/CNTs hybrid materials, which could be used for oil/water separation.[28,29] For further strengthening and protecting the 2D CNTs films against harsh conditions, polymer asymmetric grafting on the top layer of the films with controllable thickness was supposed to be an effective way. Other than the homogenous modification of the CNTs, the unidirectional modification endows the resulting hybrids with both comparable conductivity and excellent environmental resistance.

In this article, we present our recent advancement in integrating patterned conductive CNTs thin films with insulating hydrophobic polymer carpets into 2D Janus hybrid thin films for robust flexible electronics. 2D CNTs thin films on the surface of water could be achieved by the Langmuir–Blodgett method and then be further transferred onto other substrates in a patterned fashion in combination with lift-up lithography. Photoactive HO– groups on CNTs could be initiated to grow hydrophobic polymer brushes by self-initiated photografting and photopolymerization (SIPGP)[30] from the CNTs network, which allows the fabrication of a 2D Janus hybrid thin film in a simple strategy. Due to the introduction of hydrophobic polymer as the waterproof layer, our strategy could be considered as a new electronic packaging technique for conductive 2D CNTs thin films at a molecular level. The obtained polymer carpet grafted 2D CNTs thin film has potential applications as flexible, transparent electronics with highly robust environmental stability.

Experimental section

Materials

The raw carbon nanotubes (CNTs) (diameter, ~32–35 nm; length, about 10–30 μm; –OH%, about 2 wt%) with a purity of over 90% were acquired from Chengdu Organic Chemistry Co., Ltd and were rinsed thoroughly with anhydrous ethanol and dried in a stream of nitrogen before use. General chemicals in chemical reagent grade were used as received from Sinopharm Chemical Reagent. Styrene was obtained from Alfa Aesar China (Tianjin) Co., Ltd, which was purified by a neutral Al_2O_3 column and dried with a 0.4 nm molecular sieve at room temperature for 3 days. Silicon wafers were cleaned in a mixture of H_2O_2/H_2SO_4 (1 : 3, v/v) at 80 °C (''piranha solution'') for 2 h and washed thoroughly with Milli-Q-grade water (**Caution**: Piranha solution reacts violently with organic matter!).

Preparation of the LB-based CNTs film

The carbon nanotubes were first dispersed in an anhydrous ethanol solution, followed by strong ultrasonication for 2 h to form a stable dispersion with appropriate aging time. Finally, a centrifugation step was conducted to further purify the sample. A modified LB technique was employed to construct the self-assembly CNTs films. The ethanol-assisted carbon nanotubes suspension was injected dropwise onto the water surface for an appropriate volume. It was noted that it was necessary to employ a relatively slow drop speed to achieve a homogenous spread. Due to the intense Marangoni effect induced spread, Langmuir monolayers were finally preformed on the air/water interface. Surface pressure was monitored using a tensiometer attached to a Wilhelmy plate. The film was compressed by Teflon barriers at a 15 cm^2 min^{-1} speed, resulting in a uniform CNTs film with a faint black color at the end of the compression.

Fabrication of CNTs micropatterns

In our system, the resulting film was transferred using the horizontal transfer method, followed by a N_2 drying procedure. The PDMS stamp with features of box-shaped structures of ~10 μm in lateral size, spacing of ~4.5 μm and ~1 μm in depth was first placed onto the as-formed film surface with an appropriate pressure for 20 s. Subsequently, a quick lift-up speed was employed to selectively transfer the contacted substances, resulting in an integrated grid-shaped film in high-quality with large areas.

Self-initiated photografting and photopolymerization (SIPGP)

The polymer carpets were synthesized following a procedure and the solid supported patterned hybrid was submerged in ~2 mL of distilled and degassed bulk monomer and irradiated with an UV fluorescent lamp with a spectral distribution between 300 and 400 nm distribution (intensity maximum at λ = 365 nm with a total power of ~240 mW cm^{-2}) for the required time (PS for 1 h). Following SIPGP, the functionalized films were exhaustively rinsed with different solvents (toluene, ethyl acetate, and ethanol for styrene) following extremely mild ultrasonication for several minutes in order to remove any physisorbed polymer and finally it was dried using N_2 gas.

Fabrication of freestanding PS carpet grafted films

The polymer carpet grafted CNT films were cleaved from the silicon surface by immersing the silicon wafer in NaOH solution (1 M). After several hours (usually for 6–8 h), the film was easily released from the substrate. Due to the intensely hydrophobic property of the grafted PS brushes and the better wettability of the unreacted CNTs bottom layer, the resulting film floated smoothly and flatly at the air/water interface with the polymer carpet toward the air phase. In order to have direct contact between the unmodified CNTs side of the hybrid and the Au electrodes, in our experiments, the substrate with patterned Au electrodes was horizontally placed to transfer the film. Finally, the resulting film was exhaustively rinsed with deionized water for several times and dried in an N_2 atmosphere.

Characterization

Field Emission Scanning Electron Microscopy (FE-SEM) images were obtained with a FE scanning electron microanalyzer (Hitachi-S4800, 4 kV). Transmission electron microscopy (TEM) was recorded by a JEM-2100F, transmission electron microscope with a 200 kV accelerating voltage. TEM samples

were prepared by dropping a diluted aqueous solution of CNTs onto carbon-coated copper grids and drying in air. Atomic force microscopy (AFM) images were taken by a multimode AFM (Being Nano-Instruments, Ltd) operating in the contact and/or tapping mode using silicon cantilevers (spring constant: 0.15 Nm^{-1}, resonant frequency: 12 kHz for cantilever of contact mode, spring constant: 3–40 Nm^{-1}, resonant frequency: 75–300 kHz for the tapping mode cantilever). Optical images were acquired by polarized optical microscopy (Olympus, BX 51TF Instec H601). The Raman scattering measurements were performed at room temperature on a Raman system (inVia-reflex, Renishaw) using confocal microscopy. The solid-state diode laser (532 nm) was used as an excitation source with a 3200–1000 cm^{-1} frequency range. Electrical measurements for the devices were performed with a semiconductor parameter analyzer (Keithley 4200). Static water contact angles were measured at room temperature using the sessile drop method and image analysis of the drop profile. The instrument (OCA-20, Dataphysics) used a charge-coupled device (CCD) camera and an image analysis processor. The water (Milli-Q) droplet volume was 2 μL, and the contact angle was measured after the drop was stable on the sample. For each sample, the reported value is the average of the results obtained on three droplets.

Results and discussion

Our approach of fabricating robust 2D Janus hybrid flexible electronics *via* the integration of a patterned conductive CNT thin film with an insulating hydrophobic polymer carpet is schematically illustrated in Fig. 1. A LB technique is first employed to prepare a free-standing and flexible 2D CNTs thin film (Fig. 1a), which could be transferred further to a Si/SiO_2 substrate. Using a square patterned PDMS stamp to contact tightly with the homogenous CNTs thin films covered silicon wafer (Fig. 1b), a continuous grid CNTs thin film patterns formed on the surface of wafer could be achieved upon a quick lift-up procedure with the PDMS stamp (Fig. 1c). The chemical groups of CNTs offered the photoactive sites for growing hydrophobic polymer brushes finally by SIPGP of styrene from one side of the patterned CNTs thin films (Fig. 1d and e). Due to the strong hydrophobic properties of the polymer covered layer, the resulting 2D hybrid thin film could be easily released from the supported substrate using the alkaline media as an etching agent (Fig. 1f). The as-prepared freestanding 2D Janus hybrid thin film could be transferred onto any substrate or electrode for further particular applications as flexible electronics (Fig. 1g).

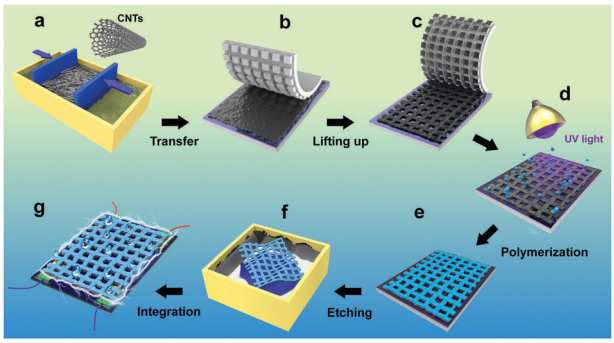

Fig. 1 Schematic of fabricating robust 2D Janus hybrid flexible electronics *via* integrating a patterned conductive CNT thin film with insulating hydrophobic polymer carpets. (a) Fabrication of a 2D free-standing CNTs thin film *via* the LB method. (b) Using a square patterned PDMS stamp to contact tightly with the transferred homogenous CNTs thin films covered silicon wafer (c) continuous grid CNTs thin film patterns on the water surface could be achieved with a quick lift-up procedure of the PDMS stamp. (d and e) Growing hydrophobic polymer brushes finally by SIPGP from photoactive sites on CNTs thin films (f) releasing the 2D CNTs hybrid thin film from the silicon surface using an alkaline solution, resulting in an integral film floating on the water surface. (g) The as-prepared freestanding 2D Janus hybrid thin film could be transferred onto any substrate or electrode for further particular applications as flexible electronics.

The commercially available CNTs with 1.5 wt% of HO– groups could be homogenously dispersed in ethanol solvent to form a stable suspension (Fig. S1, ESI†). The TEM image in Fig. 2a shows the feature of approximate 32–35 nm diameter and 15–30 μm length. Through a modified LB technique, the CNTs can experience prominently interlocked entanglement, which ensures the required strength and stability into a uniform film (Fig. 2b). After the transfer of the floating CNTs thin film from the water surface, a continuous CNTs film on glass with good transmittance was eventually formed (Fig. 2c). Further characterization of the transferred CNTs thin film on a silica wafer (Fig. 2d) by optical microscopy proved the homogeneity of the assembled film, which provided a favorable platform for further micro-sculpture (Fig. 2e). The lift-up method is an important technique of soft lithography and it can be utilized to realize refined control over the microstructures.[31] Given the kinetic control of adhesion, a simple and highly efficient transfer could occur in only 30 seconds without pre/post treatment of the sample.[32] Specifically, a structured PDMS stamp with ~10 μm cubic features and a ~4.5 μm distance was placed on the CNTs film surface at an appropriate pressure, followed by a fast delamination process to selectively remove

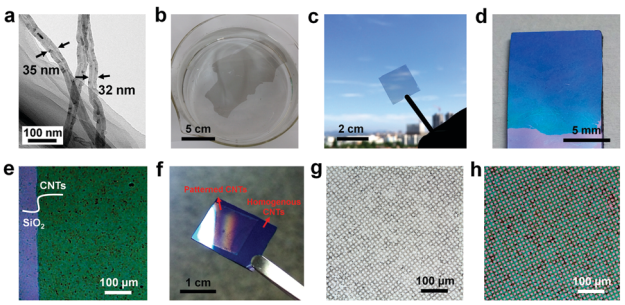

Fig. 2 (a) TEM image of the morphology of CNTs. (b) Image of the uniform assembled CNTs film transferred onto the air/water surface, indicating high strength and stability. (c and d) The obtained film transferred onto glass and SiO_2 substrates, respectively. (e) Optical image of the as-formed CNTs film, showing a uniform and high-qualified property. (f) Image of the patterned CNTs film *via* the lift-up method, demonstrating a prominent color change compared with the original homogenous film. (g and h) Optical images of CNTs grid-shaped patterns with features ~4.5 μm wide at a ~10 μm distance on glass and SiO_2 surfaces.

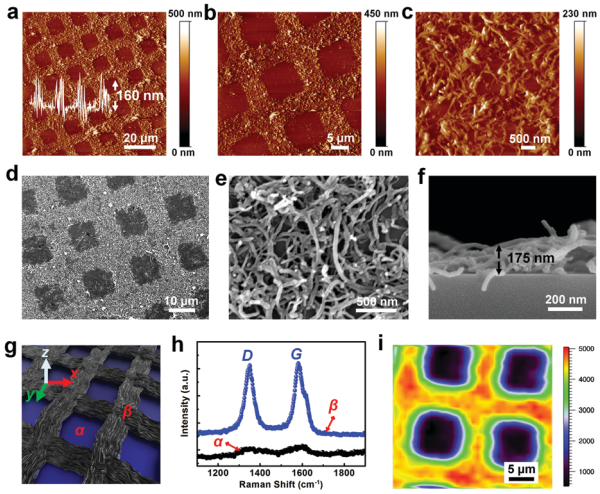

Fig. 3 (a) AFM image of grid patterns (90 × 90 μm). (b) The enlarged AFM image of CNTs patterns (40 × 40 μm). (c) The refined morphology of the assembled CNTs film with closely packed structures (4 × 4 μm). (d) SEM image of the grid patterns on a silicon substrate. (e) The enlarged SEM image of (d), showing densely condensed structure. (f) The SEM cross-section image of the CNTs patterns. (g) Schematic of the CNTs pattern. (h) Raman spectra of micropatterns with and without CNTs coverage. (i) Raman mapping information of the grid patterns. The color gradations represent the value of I_G, which are collected from a 30 × 30 μm area.

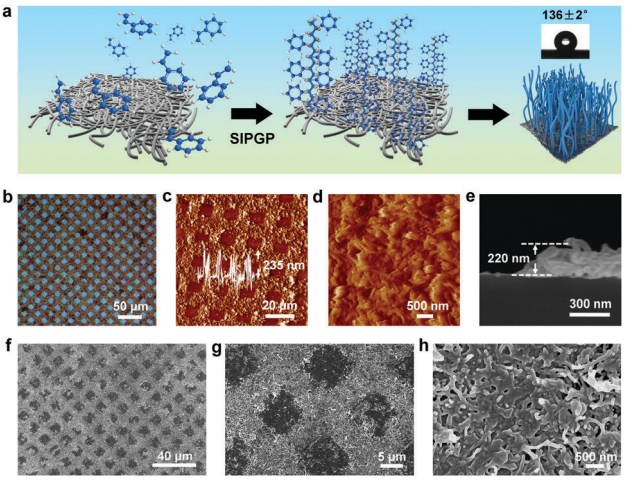

Fig. 4 (a) Schematic procedure of polystyrene grafted onto the CNTs surface *via* the SIPGP approach. (b) Optical image of the polystyrene grafted CNTs patterns, showing an intense color contrast from original green color to final brown one. (c) AFM morphology of the resulted PS grafted patterned CNTs thin film (90 × 90 μm). (d) The enlarged AFM image of the surface morphology of the hybrid. (e) The cross section image of the resulted hybrid, demonstrating an obvious increase of the thickness compared with CNTs thin film in Fig. 3g. (f–h) SEM images of detailed morphology information of the 2D PS grafted patterned CNTs thin film.

the contacted CNTs. As displayed in Fig. 2f, a remarkable color change could be easily observed with the naked eye. The optical image in Fig. 2g and h further demonstrate the patterned 2D CNTs thin film after a fast delamination process of the contacted stamp has a very controlled grid network structure over a large scale.

More refined morphology and structural information was characterized by AFM and SEM imaging. As shown in Fig. 3a, well-defined CNTs micropatterns with about 160 nm thickness are exhibited, which suggests that about five-layers of CNTs were stacked together to form a closely packed film. It could be seen that there was almost no residue left on the contacted region of PDMS (Fig. 3b). The higher magnified image in Fig. 3c prominently reflects the random entanglement of the CNTs network, which ensured a good conductive path. Moreover, scanning electron microscopy (SEM) was also used to confirm the well-aligned architectures and controlled thickness of approximately 175 nm, which was in good agreement with the AFM analysis (Fig. 3d–f). Moreover, for acquiring more structural information of the patterned films, locally recorded Raman spectra were collected from the regions with and without CNTs coverage. As shown in Fig. 3g, compared with the low intensity of that in contacted regions, the CNTs patterns showed a pronounced characteristic of the D and G bands. To further investigate the homogeneity of the patterns, Raman mapping was performed using I_G as a reference, in which the intensity of the G band strongly illustrated the amount of CNTs. The Raman maps in Fig. 3i and Fig. S2 (ESI†) show ordered color gradations, which evidently represent the successful and high-quality transfer technique for well-defined architectures.

The achieved CNTs conductive circuit at the moment is not suitable for some harsh circumstances such as extreme humidity and chemical environments, which may dramatically deteriorate the stability and sustainability of electrical performance. Alternative electronic packaging precisely along the conductive pathway is of significance to retain the original geometry and ensures that the current will flow smoothly along the designated circuit to effectively prevent any short-circuits. Polystyrene (PS), widely used as an electrical insulation material, has favorable hydrophobicity and excellent insulativity, which is preferred to unidirectionally functionalize the CNTs film, thus maintaining considerable conductivity *via* SIPGP (Fig. 4a). After polymer amplification, the surface wettability exhibited a remarkable water contact angle (WCA) increase to 136° ± 2°.[28] Moreover, attributed to the change in thickness, the resulting hybrid characterized by optical imaging presents a prominent color transition from green to brown (Fig. 4b). Further AFM characterization in Fig. 4c demonstrates well-defined microarchitectures with a remarkable thickness increase to about 235 nm. The amplified AFM image clearly showed that the top layers of the CNTs were fully covered with polymers (Fig. 4d). Moreover, the cross section and morphology information was also ascertained by the SEM images in Fig. 4e–h, which significantly demonstrated the successful grafting of uniform hydrophobic polymer layers and showed their potential as highly qualified protectors.

Free-standing 2D hybrid thin films could be achieved with alkaline media as an etching agent and then be transferred onto receiving targets for specific device applications. After the etching, a transparent PS grafted CNTs thin film could be observed floating on the water surface, which is robust enough

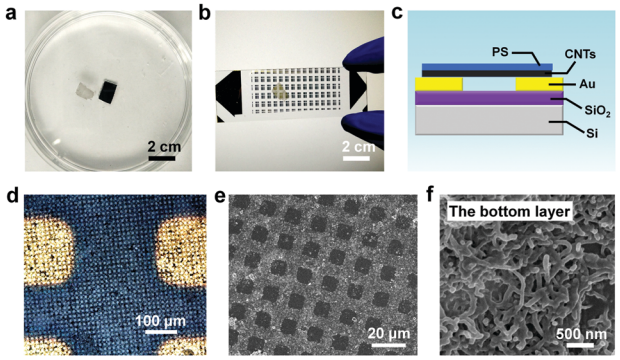

Fig. 5 (a) Image of the etched patterned 2D PS grafted CNTs thin film floating on the alkaline solution surface. (b) Image of the hybrid thin film transferred onto the Au electrodes surface. (c) The profile of the hybrid on Au electrodes. (d) The optical image, indicating clear and structured patterns in high-quality even after alkaline etching, solvent rinsing and final mechanical transfer. (e) SEM image of the transferred patterned hybrid. (f) SEM morphology of pure CNTs as the bottom layer of the PS-grafted CNTs hybrid.

to resist the surface tension without any fracture (Fig. 5a). Then, it can be easily transferred onto the Au electrodes surface after drying by N_2 flow for further characterization (Fig. 5b). The profile in Fig. 5c clearly displays the structure of the transferred hybrid, illustrating the conducting layer contacting tightly with the electrodes. Optical and SEM images further demonstrated that the transferred free-standing film maintained an integrated state without remarkable breakage (Fig. S3 (ESI†) and Fig. 5d and e). Significantly, the morphology of the bottom layer was also characterized. As displayed in Fig. 5f, compared with the smooth morphology of the top layer, the presence of abundant bare CNTs strongly proves the Janus structure and ensures good conductivity for the final hybrid.

For an environment-resistance electronic device, electronics packaging offers the conducting circuit with an insulating layer against some extreme environments. Our strategy of fabricating an insulating PS grafted conductive CNTs thin film, provides a new electronics packaging method for PS layers on a CNTs network at the molecular level. With the protection layers, the antielectric leakage behavior of the top hydrophobic PS carpet layer was measured using an *I–V* curve, and a maximum absolute current of about 8.0 pA was determined, demonstrating a high resistance to prevent potential short-circuits with other electrical systems (Fig. 6a and Fig. S4, ESI†). In comparison with the good insulativity of the polymer carpet, the bottom one exhibited good conductivity with the maximum absolute current of about 64 nA at −1.0 and 1.0 V bias values. Furthermore, it is worth noting that the stability of the hybrid is of great importance. Transient response towards a square-shaped pulse with a 60 ms width and 1.0 V amplitude is shown in Fig. 6b, which exhibited good reproducibility, indicating an excellent electrical stability.

Further experiments were performed to investigate the environmental resistance of the insulating PS as the carpet grafted conductive CNTs thin films under harsh conditions. As displayed in Fig. 6c, the conductive CNTs thin film without

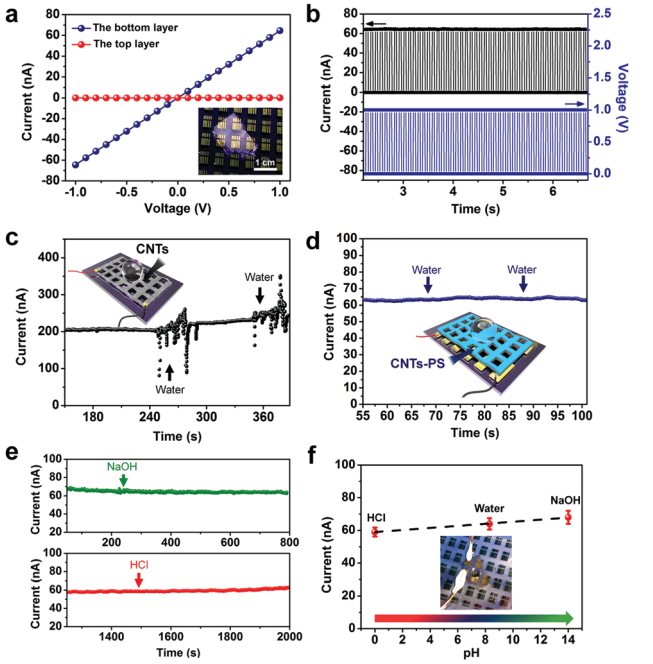

Fig. 6 (a) Current–voltage curves of the top insulating PS and bottom conductive CNTs layers of the free-standing 2D Janus PS grated CNTs hybrid thin film, individually. Inset: Image of transparent patterned CNTs film transferred onto an Au electrode surface. (b) *I–t* and *V–t* curves of transient response at 60 ms for each cycle. (c) Current–time curve of the patterned CNTs film in the circumstances of the absence and presence of water. (d) Current–time curve of the resulting PS grafted CNTs hybrid thin film in the absence and presence of water, demonstrating a good electrical stability to the presence of water. (e) Current–time curves of the patterned PS grafted CNTs hybrid thin film in the harsh circumstances of alkaline (1 M NaOH) and acid (1 M HCl) solution. (f) Current–pH curve, demonstrating high resistance to harsh chemical conditions.

polymer modification experienced drastic fluctuation in the presence of water dropped on the film surface, indicating a poor resistance to harsh circumstances even to a mild condition of deionized water. However, throughout the entire dropping and removing water process, the PS carpet grafted CNTs were highly stable and demonstrated a significant enhancement with waterproof capability (Fig. 6d and Fig. S5, ESI†). Furthermore, tests performed on the hybrid even under acid and alkaline conditions were also conducted. Fig. 6e shows that the PS grafted CNTs hybrid thin film behaved with excellent stability in extremely low or high pH. There was no more conductivity variation of the 2D PS grafted CNTs Janus hybrid thin film under harsh conditions in the pH regions ranging from 0 to 14 (Fig. 6f). The high-resistance to harsh environments presents a promising potential in micro/nano electronic devices of high-performance under extreme conditions.

Conclusions

In conclusion, we developed a novel electronic packaging strategy to alternatively functionalize a conducting CNTs microcircuit on a molecular level. The unidirectionally polymer carpet wrapped

CNTs network demonstrates both considerable conductivity and excellent insulativity even under harsh environments. Other than the conventional electronic packages with sophisticated and expensive facilities, this technique presents a new idea to provide a grafted polymer carpet protection precisely along the patterned conductive network without the need of rigorous photolithography in a cost-effective and reliable way. The integration of the insulative polymer carpet and conducting circuits provides promising applications as flexible electronics in harsh circumstances.

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