Transferable and Flexible Label-Like Macromolecular Memory on Arbitrary Substrates with High Performance and a Facile Methodology

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Future electronic modules are expected to possess advanced functionalities such as portability, flexibility, wearability, stretchability, and transparency.[1] Those advanced electronic systems will be built up on a flexible substrate by multiple crucial devices such as logic, memory, and power supply. Organic electronics, including organic light-emitting diodes, transistors, memories, and solar cells, have been widely proposed as the building blocks for those functional electronics due to their unique advantages, such as flexibility, low-temperature fabrication, and roll-to-roll printability.[2] Macromolecular memory

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(polymer or organic memory), with simply an active layer sandwiched between two electrodes, has been considered as a promising storage element in those electronic modules due to its exceptional merits such as facile processes, low-cost, mechanical elasticity, flexibility, and 3D-stacked capability.[3] However, the devices have been fabricated only on rigid, flat, and smooth substrates, such as metal, glass, plastic and silicon, which limits the promising utilization of organic memories. Moreover, due to the fact that organic films are often fabricated by solution processes (i.e., spin-coating or ink-jet printing method), there exists a great hurdle in constructing multiple organic electronics in stack or 3D architecture, because the use of solution processes can result in a severe damage to the bottom organic devices arising from the solvent used for the fabrication of the subsequent devices.[4] Therefore, for future applications, it is essential to establish a proper fabrication scheme for organic memory on diverse substrates or devices in order to expand more possible applications.

Traditional fabrication approaches, including well-established semiconducting techniques and organic solution processes, involve first depositing the electrode such as metal or graphene on the selected rigid, flat, or smooth substrates, and then carrying out the fabrication procedures on the conventional substrates using a bottom-up fabrication scheme.[3] In those approaches, the substrate is pre-determined and restricted by the processing conditions, chemical solvent compatibility, and handling requirements.[5] Such restrictions lead to the difficulty in fabricating devices on arbitrary non-conventional substrates for more advanced applications. Alternatively, a promising strategy is to carry out the well-established fabrication processes on a conventional planar substrate and then transfer the as-prepared devices onto the desired substrates such as soft plastic, non-planar substrates, functional devices or integrated circuits for avoiding unsuitable fabricating processes. In terms of organic memory researches, this approach scheme can open new routes for storage devices in novel applications such as flexible paper-like displays, wearable computers, and epidermal electronics. However, to date, there is no report regarding a transferable organic memory for applications on arbitrary non-conventional substrates.

Graphene, a single-atom-layer of continuous 2D crystal, has received great attention both in fundamental research and practical applications due to its high carrier mobility, ultrahigh mechanical strength, and optical transparency.[6] Utilization of its superior electrical properties as well as its excellent elasticity, flexibility and low-cost features, graphene sheet has been

successfully used as flexible and stretchable transparent conductors.[7] In particular, taking the advantages of both organic materials and graphene electrodes have been considered as promising technologies components for flexible and stretchable electronic devices.[8] The success of growth graphene films on supporting metalic films (Cu or Ni) by chemical vapor deposition (CVD) methods enables to efficiently transfer graphene sheets on to arbitrary substrates with lage area after etching away the underlying supporting metal.[9] Moreover, based on its excellent mechanical properties and ultrastrong interfacial adhesion to the substrates with strong attractive intersurface forces, i.e., Van der Waals (adhesive energy of 0.45 Jm^{-2} on SiO$_2$),[10] the graphene sheet enables to direct interfacing onto different rugged surfaces.[9] Accordingly, with the inherent excellent electrical and mechanical properties together with its strong adhesion force, graphene is a remarkable candidate for transferable sticker-type devices functioned as the flexible bottom electrode and adhesive face for various types of surfaces.

In this communication, we demonstrate, for the first time, a facile and practical strategy to fabricate a newly designed transferable and flexible sticker-type macromolecular memory based on CVD-derived graphene electrode; *graphene macromolecular memory label* (GMML). Our approach uses poly(methyl methacrylate) (PMMA). PMMA is a material commonly used to minimize the damage to CVD-derived graphene during the stripping process from the metal foil; therefore we choose the PMMA as the insulator of the memory active layer, which means that the PMMA is functions as the protective layer during the CVD-graphene transferring processes as well as one of the active materials in our label-like memory devices. After choosing the insulating polymer of PMMA, the semiconducting macromolecular poly(3-butylthiophene) (P3BT) polymer is selected as another crucial charge storage media in the active layer. The polythiophene-family P3BT with relatively high conductivity serves as a charge-trapping and carrier transporting medium, whereas PMMA acts as the charge blocking material for the label-like organic memory. The composite of the active layer of PMMA and P3BT in the GMML exhibits excellent stability and reproducibility under air conditions. Moreover, the composite of the two blending macromolecular polymers also reveals satisfactory flexibility and good thermal robustness for various memory applications. It is worth noting that saving the steps for the chemical treatment of washing away the PMMA from CVD-graphene enables the 3D-stacked organic memories, the vertical integration with other organic devices, and the fabrication on arbitrary non-conventional substrates to be realized. This is because using acetone to wash away the protective layer from the CVD-graphene electrode severely damages the flexible plastic substrates and the bottom organic materials once it is vertically integrated with other flexible organic devices. The blending composite of PMMA and P3BT is then spin-coated onto the obtained CVD-graphene film on the supporting copper foil followed by the top aluminum (Al) electrode deposition onto the active layer. After etching away the supporting metal, we can simply transfer the pre-fabricated label-like organic memory onto desired non-conventional substrates or functional devices for various purposes. We firstly transfer the label-like memory onto polyethylene terephthalate (PET) substrate for characterization, and then apply it to different substrates and

devices, including a vial, glove, medical wristband, coin, silicon wafer, and organic diode. Notably, in our strategy, harsh synthesis and inappropriate fabrication steps can be avoided, and the GMML can be transferred onto desired substrates with a simple one-step transfer process, which will be largely beneficial to a range of advanced electronic applications such as flexible, wearable computers, and epidermal electronics. Moreover, since our novel GMML can be simply transferred onto desired substrates including organic devices, it thus paves a promising way for stacking organic electronics and creating flexible 3D circuitries. The methodology shown here is simple and useful. Based on the capability of roll-to-roll fabricating process of CVD graphene,[11] our proposed GMML is suitable for industrial mass manufacturing.

Figure 1a shows the schematic fabrication process for the GMML. The large area of graphene film was grown on copper foil using CVD technique. Detailed synthesis of the CVD-derived graphene film can be found elsewhere.[11] The obtained monolayer graphene film with few defects was confirmed by Raman spectroscopy (Figure S1 in Supporting Information) and the sheet resistance of the film was ~1.1 kΩ/sq. by the four-point probe method.[11] The mixture of PMMA and P3BT serves as the active layer of the memory as well as the protective layer of graphene film during removing the copper foil. The existence of the P3BT in PMMA matrix was confirmed by the absorption measurements (Figure S2). The distinct phase-separated P3BT is expected in the film due to the different polarity of P3BT and PMMA (Figure S3).[12] The graphene/P3BT:PMMA structure exhibits high transmittance exceeding 60% through the entire visible spectrum (Figure S4). The GMML was firstly transferred onto a flexible PET substrate for the memory performance tests. In order to perform the I–V measurement, a contact metal (Ni) was pre-deposited on the border of the PET and partially contacted with the graphene film. In this configuration, graphene sheet serves as the flexible bottom electrode and the adhesion face for transferring the GMML on desired substrates. Figure 1b demonstrates the high flexibility feature of the GMML transferred onto a PET substrate. Figure 1c illustrates the schematic drawing of the measurement along with the chemical structures of PMMA and P3BT used in the active layer.

We evaluated the electrical switching and memory effects of the GMML both on flat and under bending conditions. **Figure 2**a shows the memory characteristics of the GMML on flat condition. The arrows denote the voltage sweeping direction. Initially, as the bias swept from 0 to +2.2 V, the as-fabricated device was in a low-conductivity state (OFF-state, stage I) with the currents in a quite low level of 10^{-11}–10^{-10} A. Once the applied voltage exceeded a turn-on voltage of +2.2 V, a rapid increase in the current flow was observed (stage II), indicating a switch from the low- (OFF) to the high-conductivity (ON) state with a high ON/OFF current ratio of ~10^6 (inset in Figure 2a). The transition from the OFF- to ON-state is equivalent to the "writing" command in digital storage devices and the high ON/OFF current ratio promises a low misreading probability in data access. Compared to other different types of graphene-based memory devices, the GMML reveals a relatively lower writing voltage, suggesting a promising application for low power consumed memory.[13,14] The programmed device
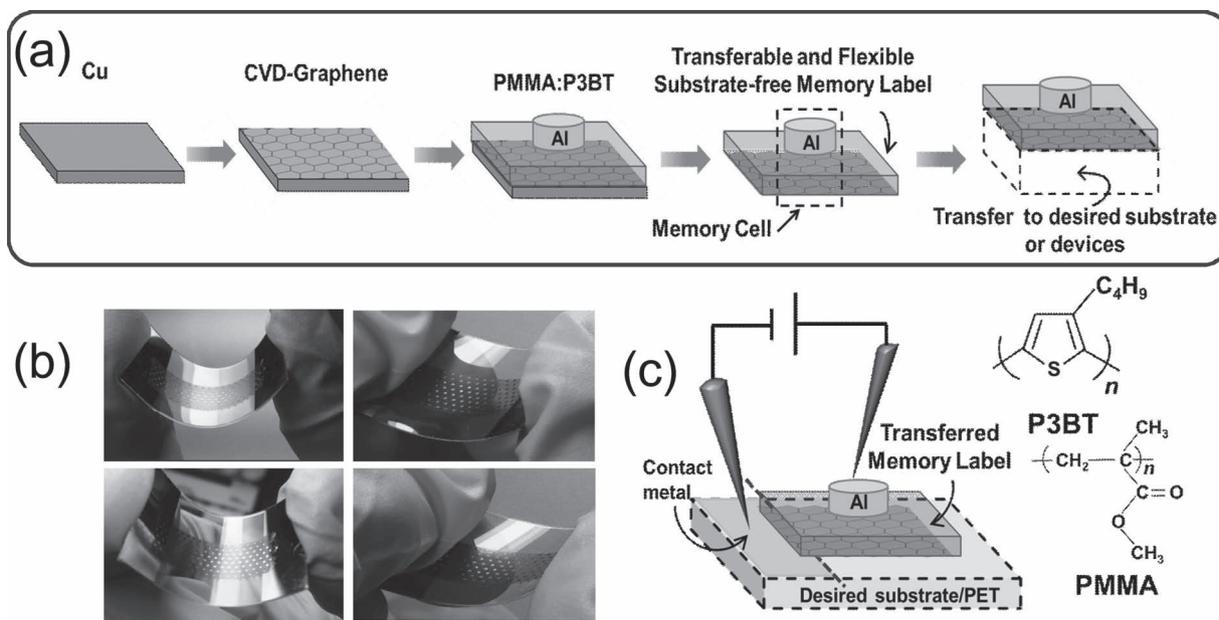
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Figure 1. (a) Schematic diagram for the fabrication process of the memory label. (b) Photographs of as-prepared GMML under repetitive bending. (c) Measurement arrangement of the GMML along with the chemical structures of PMMA and P3BT.

retained this high-conductivity state in the following scans (stages III and IV). Additionally, this high-conductivity state remained even when the power was off, indicating a nonvolatile feature of the memory effect. The high-conductivity state is not retrievable by applying the reverse bias scans (stages V and VI), indicating that the GMML exhibits a characteristic of write-once-read-many-times (WORM)-type memory.[3] Note that the memory effects were not observed from those P3BT-free and low P3BT concentration devices, indicating that the presence and the concentration of P3BT play key roles in the observed memory effects (Figure S5).

Besides the low writing voltage and low misreading probability, the device stability, including data retention and stimulus effect of continuous pulse reading stress, is also an important character in practical WORM-type memory applications.[3] For testing the data retention ability, the ON/OFF state was probed at regular intervals using the reading voltage of +1 V. As shown in Figure 2b, the OFF and programmed ON state were remained in the same order of magnitude without significant degradations after considerable duration for 10^4 sec. This excellent electrical stability without applying a constant stress bias indicates good applications in nonvolatile memory. The GMML also showed excellent data retention even at high temperature up to 85 °C (Figure S6). Further temperature-dependence of the coded state can be found in Figure S7. For exploring the effect of the pulse reading stress, the device was initially started from the OFF- (or ON-) state and continuously read out under a successive pulse reading biases of +1 V with a pulse duration of 3 μs and a period of 5 μs. As shown in Figure 2c, the coded information was fairly stable even under 10^7 continuous reading pulses. From the application perspective, the stable performance of the GMML provided a promising commercial potential for a broad variety of memory applications, for example portable disks, low-cost electrical labels, and radio-frequency identification (RFID)

tags. Regarding the cell-to-cell performance variation, we had randomly selected 25 cells from the GMML and those cells exhibited similar ON (OFF) current levels and turn-on voltages as a result of good uniformity (Figure S8). This also suggests that our approach is controllable and feasible for large-area applications.

Next, the GMML was further characterized under bending condition and the results were compared with that of the flat case. The GMML was bent into a concave with bending radius of 10 mm (inset in Figure 2d). The procedure for the electrical measurement is identical to that of the flat condition. As depicted in Figure 2d, the bent GMML revealed the similar WORM-type memory behavior with the similar current level as that of the flat condition. These memory features were reproducible and stable after repetitive bending. Figure 2e shows the associated data retention ability of the GMML under bending condition. Similarly, the programmed state can be manifestly distinguished with a high ON/OFF current ratio of $\sim 10^6$ and can be sustained over 10^4 s without any degradation. And, the coded information can be correctly accessed even after reading more than 10^7 times (Figure 2f). Clearly, the excellent data retention and stability properties of the GMML were not affected by the bent situation. More experiments about memory characteristics of the GMML under various bending conditions have been performed and the results were presented in Figure S9. The similar performance of the GMML at different bending conditions indicates that the performance of the GMML is reliable regardless of its physical presentation.

After confirming the excellent performances of the GMML on the PET substrate with various geometric deformation, we tried to transfer the GMML onto various challenging nonconventional substrates. **Figure 3**a shows the free-standing GMML after removing the supporting copper foil. This free-standing GMML is ready to be transferred onto diverse
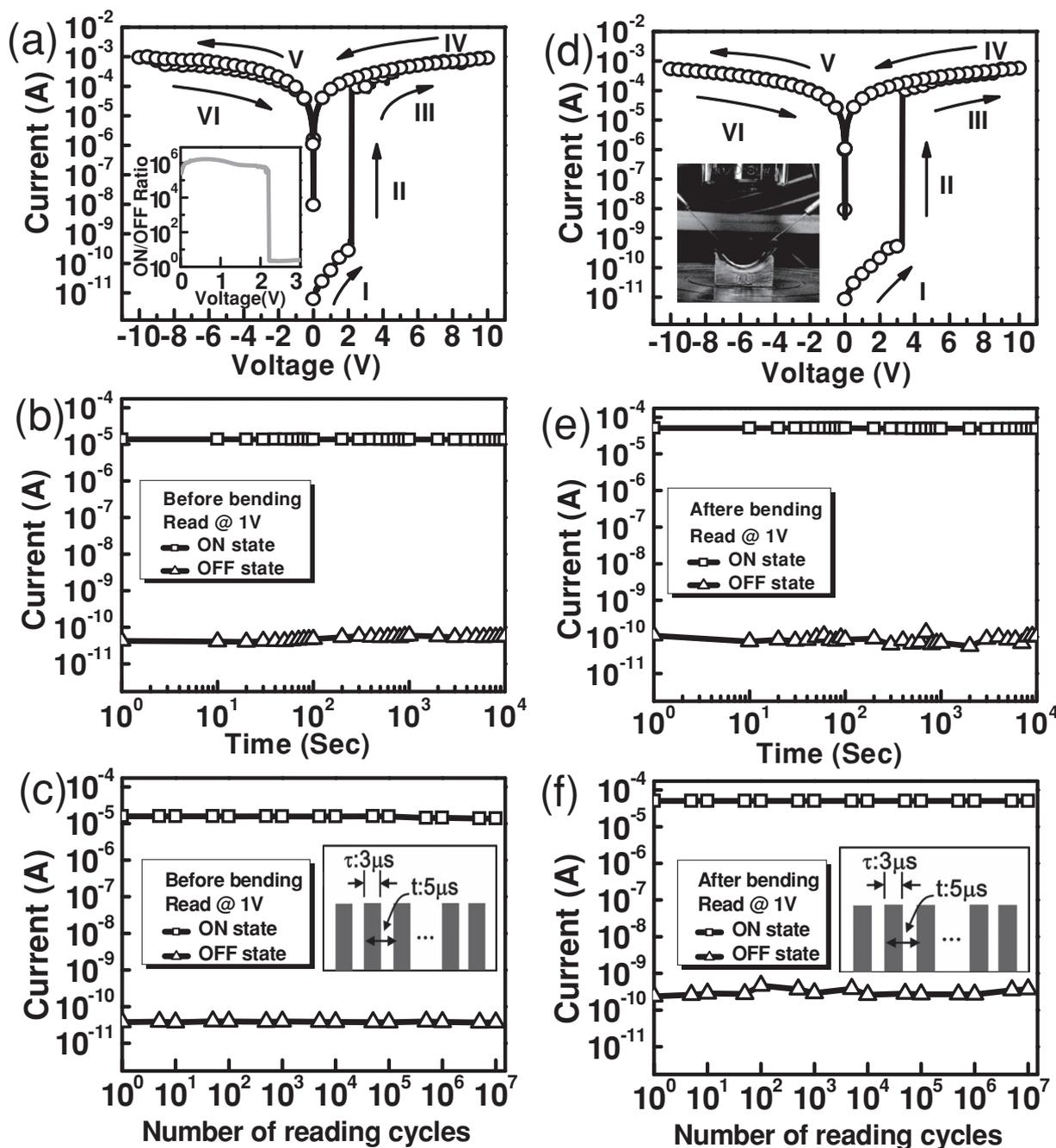
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Figure 2. Electrical properties of the memory cell: (a), (d) *I–V* characteristics for the device on flat and bending conditions (bending radius R = 10 mm), respectively. The inset in (a) shows the ON/OFF ratio as a function of forward voltage while that in (d) presents a photograph of the GMML bent at R = 10 mm. (b), (e)The programmed data retention ability at the reading voltage of +1 V before and after bending, respectively. (c), (f) Effects of a succession of pulse reading bias of +1 V on the written ON (OFF) state before and after bending. The inset shows the pulses used for the measurement.

substrates, both rigid and soft ones. Identical fabrication and measurement procedures were used for these transferred devices as mentioned on PET substrate (Figure S10). The corresponding I–V characteristics were presented alongside the photos of the transferred GMML. First, we have succeeded in transferring the GMML onto a rigid cylindrical vial (with a diameter of 20 mm) (Figures 3b and S10b). The result indicates that the GMML can be easily transferred onto non-planar surfaces

and exhibits similar memory behaviors. Next, we attempted to transfer the GMML onto a wearable and stretchable PVC glove (Figure S10c). As shown in Figure 3c, the memory cells still performed normally, which provides an exciting opportunity for developing wearable electronics. The GMML also works on a bent medical wristband (Figures 3d and S10d), suggesting a possible real world flexible electronic applications. We have also tried a rougher and conductive coin surface for memory
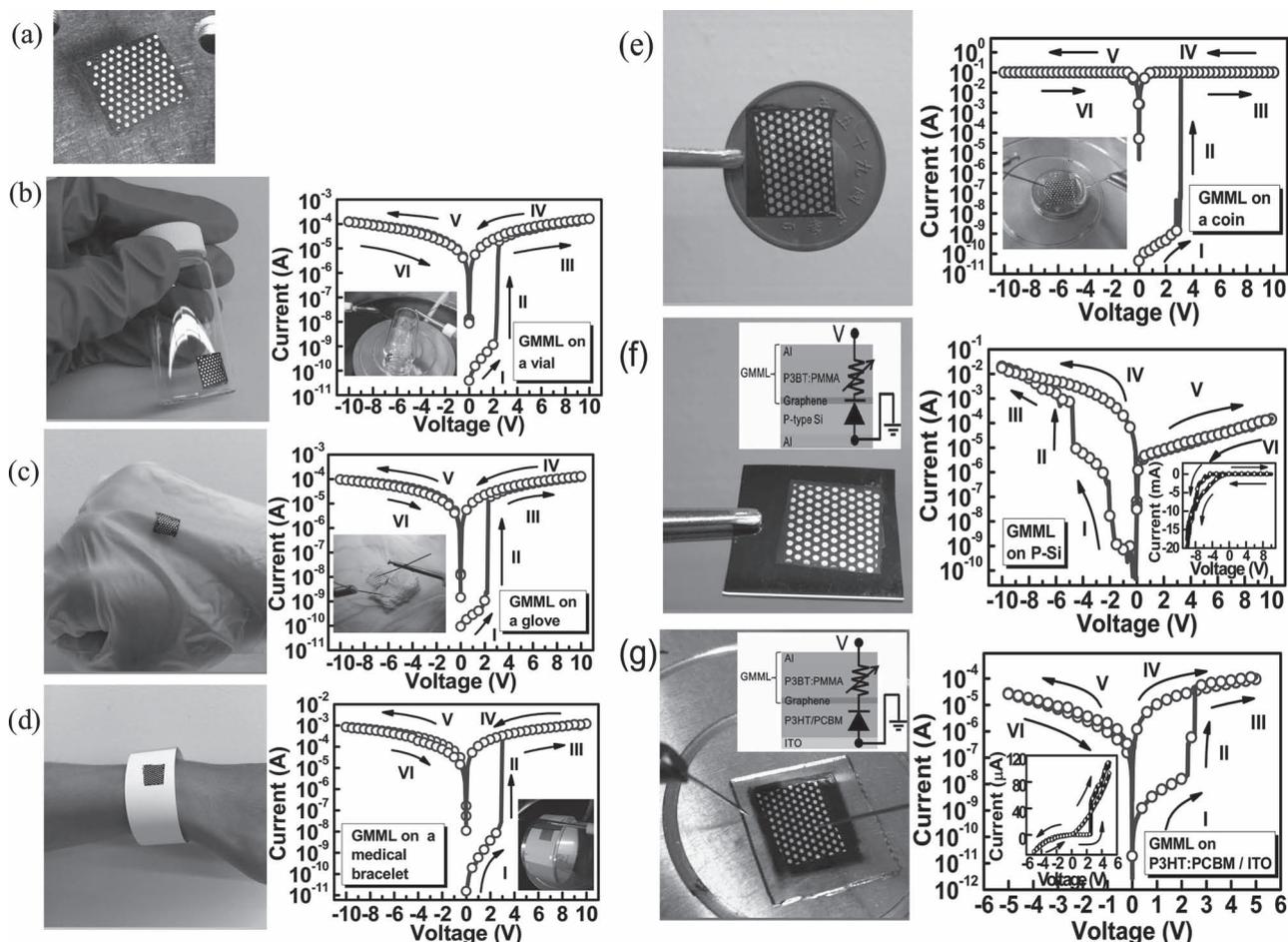
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Figure 3. (a) Free-standing GMML after etching away the copper foil. (b~g) Photographs with the corresponding I-V curves alongside for the GMMLs transferred onto various non-conventional substrates, including on the outside surface of a cylindrical vial (b), a glove (PVC) (c), a medical wristband (d), a coin (e), a P-type silicon (f), and an organic diode (g). (The size of GMML is about 1 cm^2.)

behavior test (Figures 3e and S10e). The result shows that the ON-state current is higher than other substrates, which might be attributed to the full coverage of the graphene film by the conductive copper surface of the coin resulting in lower in-plane resistance. Subsequently, we have transferred the GMML onto a P-type Si wafer to form a 1D-1R configuration (Figures 3f and S11).[15] In this configuration, for switching the rectified GMML at forward bias (relative to P-type Si), we started with negative biases applied to the Al electrode and obtained WORM-type memory effect (Figure S12). At a read voltage of ±1 V, the ON-state currents in the forward and reverse biases are ~10^{-4} and ~10^{-6} A, respectively, achieving a rectification ratio of approximately two orders of magnitude for the hybrid memory device in the ON-state. The rectifying effect can be attributed to the Schottky diode formed by graphene-P-Si junction.[16] It is known that a hybrid-type device consisting of an inorganic Si-based diode and an organic memory can efficiently eliminate the cross-talk interference in high-density array-type memories for accurately sensing the coded state.[15] Thus, our novel GMML with simple one-step transfer fabrication is promising for high-density memory development when it is integrated with most industry-compatible silicon IC techniques. Finally,

we have demonstrated an organic-based tandem diode-memory device (Figures 3g and S13). The rectifying characteristics of this tandem device comes from the bottom organic diode with a rectification ratio of about one order of magnitude at a read voltage of ±1 V (Detailed discussion in SI.13). This rectifying effect of the organic diode could be further improved by tuning the work function of the graphene electrode through chemical doping before transferring the GMML or introducing an electron transport layer at the bottom diode device.[17] Accordingly, our strategy shows a significantly facile transferring method for stacked 1D-1R organic electronic modules without harsh synthesis and arduously depositing another rigid middle electrode for isolating the organic materials.

From the above demonstrations, our GMML can be easily transferred onto diverse unconventional substrates, including soft, flexed ones or functional organic/inorganic devices with 100% fidelity. Besides, even being stored under ambient conditions for more than 5 months or rinsing with water (500 ml/min), the transferred GMMLs still reveal good adhesion to the receiver substrates (Figures S14 and SI. Multimedia). Based on these results, the GMML behaves like a sticker, which can readily be applied to arbitrary surfaces including a circuit

board or flexible functionalities electronic modules, resulting in greatly diversifying organic memory applications, especially for the development of integrating the GMML with other organic-based advanced electronics in a stacked circuitry.

To understand the carrier transport mechanisms of the GMML, the measured I–V curves were analyzed by appropriate charge transport models: the Schottky emission (SE), and space-charge-limited current (SCLC) for the OFF-state; the Ohmic current for the ON-state (Detailed discussion in SI.15).[18] The results imply that the injected carriers from the electrode are captured in the P3BT molecules and act as space charges at a high applied bias in the OFF-state. After the device was switched to the ON-state, the P3BT molecules are completely filled up with carriers and the following injected carriers are able to move through the active layer, resulting in a current flow between the bottom and top electrodes. We tried to study the impacts of P3BT concentrations and top-electrode materials on the memory effects. As the composite films made from solutions containing greater than 4 mg/mL of P3BT, a distinct distinguishable switching characteristic can be observed (Figure S5), indicating that the electrical switching of GMML is originated from the presence of P3BT with proper loadings. With the replacement of top electrode by noble Pt and Ni, both types of devices exhibit the similar WORM-type memory effects (Figure S16), suggesting that the top electrode materials is not involved in the observed memory effects. It can also be used to rule out the possibility that the filament formation is responsible for the switching behavior in our devices. In addition, according to the temperature dependent measurement (Figure S7), the conduction in the programmed ON-state follows the Arrhenius relationship (Figure S17). It implies that the conduction of charge carriers is dominated by the activation process arising from charge trapping. A more detailed description of the underlying mechanism has been included in Supporting information 18.

Compared to previous reports,[3] our transferable and flexible GMML offers numerous advantages. Firstly, the GMML following well-established processes can be easily transferred onto desired substrates; hence harsh synthesis and unaccustomed fabrication steps on non-conventional substrates can be avoided. Secondly, the transferability onto organic devices of our GMML can minimize the possible solvent damage issue suffered from traditional solution-phase techniques. This unique transfer feature could advance the development of 3D-stacked memories or multiple organic electronics modules. Thirdly, there is a freedom to transfer entire GMML on substrates of various types, including rigid, flexible, stretchable, non-planar, rough, etc. The versatile substrate selection advantage could greatly broaden memory applications in advanced electronics such as flexible, wearable or epidermal electronics. Finally, considering the cost-effective production, the presented approach is simple and high-yield; moreover, the integration of the flexible graphene bottom electrode and the polymer memory composite is suitable for roll-to-roll industrial manufacturing.[11]

In summary, we have successfully demonstrated a transferable and flexible label-like organic memory based on graphene electrode through a significantly simple and cost-effective strategy. The entire GMML can be readily fabricated on a CVD-derived graphene with solution-process. By etching away the supporting metal foil of the graphene film, the as-fabricated GMML is freely to be transferred onto desired substrates, which can function independently or can be integrated with other components in a circuitry for diverse applications. The newly designed GMML exhibits an excellent performance and a good stability regardless of its physical presentation. The proposed strategy is the first report demonstrating the transferable organic memory on nonconventional substrates. We believe that our approach may promote memory devices for diversified applications in advanced functional electronics and open up a simple scheme for organic memories in flexible 3D-stacked circuits and multiple-stacked electronics modules.

Experimental Section

Material Preparation and Device Fabrication: A polymer solution composed of poly (3-butylthiophene) (10 mg, Sigma-Aldrich), chlorobenzene (0.5 mL), and poly (methyl methacrylate) (0.5 mL, 950k A4, Micro-Chem) was stirred at 50 °C for 1 day. The resulting solution was dropped on the graphene sheet for 10 min before starting the spin coating process at a rate of 2500 rpm for 20 sec (~120 nm by alpha step). To complete the device fabrication, an aluminum layer (300 nm) was thermally deposited on top of the organic film at a pressure of 2×10^{-6} torr. The Al electrodes were circular patterns with a diameter of 0.54 mm and the typical active area defined by the overlapping of graphene and Al electrodes was 0.23 mm^2. Finally, the sacrificial Cu foil was removed by immersing the device into an aqueous solution of iron nitrate ($Fe(NO_3)_3$) (0.05 g/mL) for ~4 hours. Then, this graphene/PMMA:P3BT/Al memory label was transferred to DI water to wash away the Cu etchant followed by being transferred to the polyethylene terephthalate (PET) substrate or other desired substrates and dried naturally.

Device Measurement: The electrical characterizations of the bistable GMML were measured by an Agilent 4156C semiconductor parameter analyzer equipped with an Agilent 41501B. All electrical properties were characterized at room temperature and ambient conditions, unless otherwise stated.

Supporting Information

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

Acknowledgements

[1] D. H. Kim, N. Lu, R. Ma, Y. S. Kim, R. H. Kim, S. Wang, J. Wu, S. M. Won, H. Tao, A. Islam, *Science* **2011**, *333*, 838.

[2] S. R. Forrest, *Nature* **2004**, *428*, 911.

[3] B. Cho, S. Song, Y. Ji, T. W. Kim, T. Lee, *Adv. Funct. Mater.* **2011**, *21*, 2806.

[4] A. Hadipour, B. de Boer, J. Wildeman, F. B. Kooistra, J. C. Hummelen, M. G. R. Turbiez, M. M. Wienk, R. A. J. Janssen, P. W. M. Blom, *Adv. Funct. Mater.* **2006**, *16*, 1897.

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[5] K. Chung, C. H. Lee, G. C. Yi, *Science* **2010**, *330*, 655.

[6] A. K. Geim, K. S. Novoselov, *Nat. Mater.* **2007**, *6*, 183.

[7] K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, J. H. Ahn, P. Kim, J. Y. Choi, B. H. Hong, *Nature* **2009**, *457*, 706.

[8] X. Huang, Z. Zeng, Z. Fan, J. Liu, H. Zhang, *Adv. Mater.* **2012**, *24*, 5979.

[9] A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, M. S. Dresselhaus, J. Kong, *Nano Lett.* **2008**, *9*, 30.

[10] S. P. Koenig, N. G. Boddeti, M. L. Dunn, J. S. Bunch, *Nat. Nanotechnol.* **2011**, *6*, 543.

[11] S. Bae, H. Kim, Y. Lee, X. Xu, J. S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. R. Kim, Y. I. Song, *Nat. Nanotechnol.* **2010**, *5*, 574.

[12] G. Lu, H. Tang, Y. Huan, S. Li, L. Li, Y. Wang, X. Yang, *Adv. Funct. Mater.* **2010**, *20*, 1714.

[13] S. M. Kim, E. B. Song, S. Lee, J. Zhu, D. H. Seo, M. Mecklenburg, S. Seo, K. L. Wang, *ACS Nano* **2012**, *6*, 7879.

[14] A. J. Hong, E. B. Song, H. S. Yu, M. J. Allen, J. Kim, J. D. Fowler, J. K. Wassei, Y. Park, Y. Wang, J. Zou, *ACS Nano* **2011**, *5*, 7812.

[15] B. Cho, T. W. Kim, S. Song, Y. Ji, M. Jo, H. Hwang, G. Y. Jung, T. Lee, *Adv. Mater.* **2009**, *22*, 1228.

[16] C. C. Chen, M. Aykol, C. C. Chang, A. Levi, S. B. Cronin, *Nano Lett.* **2011**, *11*, 1863.

[17] Z. Liu, J. Li, Z. H. Sun, G. Tai, S. P. Lau, F. Yan, *ACS Nano* **2011**, *6*, 810.

[18] S. M. Sze, *Physics of Semiconductor Devices*, 2nd ed. John Wiley & Sons, New York **1981**.