ResearchGate

See discussions, stats, and author profiles for this publication at: https://www.researchgate.net/publication/260412860

Resistance-Switchable Graphene Oxide–Polymer Nanocomposites for Molecular Electronics

ARTICLE · MARCH 2014

DOI: 10.1002/celc.201400017

CITATIONS
3

READS
31

7 AUTHORS, INCLUDING:

Gang Liu
Chinese Academy of Sciences
33 PUBLICATIONS **872** CITATIONS

SEE PROFILE

yu Chen
East China University of Science and Techn…
105 PUBLICATIONS **2,251** CITATIONS

SEE PROFILE

Cheng Wang
Wuhan University
20 PUBLICATIONS **184** CITATIONS

SEE PROFILE

Xiaodong Zhuang
Technische Universität Dresden
58 PUBLICATIONS **929** CITATIONS

SEE PROFILE

All in-text references underlined in blue are linked to publications on ResearchGate, letting you access and read them immediately.

Available from: Xiaodong Zhuang
Retrieved on: 03 February 2016

DOI: 10.1002/celc.201300158

Resistance-Switchable Graphene Oxide–Polymer Nanocomposites for Molecular Electronics

Gang Liu,[a, b] Yu Chen,*[a, d] Run-Wei Li,*[b] Bin Zhang,[a, c] En-Tang Kang,*[c] Cheng Wang,[a] and Xiaodong Zhuang[a]

As the thinnest material ever known in the universe, graphene has attracted a tremendous amount of attention in recent years. To switch graphene ON and OFF for memory devices, electroactive polymers, including polyaniline (PANI), polyvinylcarbazole (PVK), triphenylamine-based polyazomethine (TPAPAM), polythiophene (PTh), and others, have been covalently bonded to graphene oxide (GO) to manipulate the processability and to engineer the molecular bandgap of the atomic carbon nanosheets. GO–PANI, GO–PVK, and GO–TPAPAM demonstrate promising bi-stable resistive switching behaviors with small turn-on voltages of less than 2.0 V, low power consumptions of 6.7 nW–221.4 µW, and large ON/OFF ratios exceeding 10^3. With advantages including miniaturized dimensions, mechanical flexibility, and the non-exotic nature of the raw carbon material, GO–polymer nanocomposites promise to have great potential for next-generation information-storage applications.

1. Introduction

With the rapid development of the global information technology (IT) industry over the past decade, electronic devices such as tablet PCs, smart phones, digital cameras, and media players have made a striking impact on our daily lives.[1] However, as the feature size of a transistor (the fundamental circuitry element of modern memory devices) has decreased from 130 nm in 2000 to 32 nm at present,[2,3] a threatening cloud rises from the horizon. Silicon-based semiconductor devices become less stable beyond 22 nm, and the reliability to store and read individual bits of information will be substantially reduced by severe cross-talk issues. Therefore, the current state-of-the-art memory technology is considered as pacing towards the end of the journey (Figure 1) on the International Technology Roadmap for Semiconductors (ITRS).[4] To continue the innovation of electronic industries, efforts should be devoted both to discovering new functionalities of emerging materials and to designing novel data-storage device concepts.[5]

[a] Prof. Dr. G. Liu, Prof. Dr. Y. Chen, Dr. B. Zhang, C. Wang, Dr. X. Zhuang
Key Lay for Advanced Materials, Institute of Applied Chemistry
East China University of Science and Technology
Shanghai 200237(PR China)
E-mail: chentangyu@yahoo.com
[b] Prof. Dr. G. Liu, Prof. Dr. R.-W. Li
CAS Key Lab of Magnetic Materials and Devices
Ningbo Institute of Materials Technology and Engineering
Chinese Academy of Sciences, Ningbo 315201(PR China)
E-mail: runweili@nimte.ac.cn
[c] Dr. B. Zhang, Prof. Dr. E.-T. Kang
Department of Chemical and Biomolecular Engineering
National University of Singapore, Kent Ridge 119260 (Singapore)
E-mail: cheket@nus.edu.sg
[d] Prof. Dr. Y. Chen
The State Key Laboratory of ASIC & System, Fudan University
220 Handan Road, Shanghai 200433 (PR China)

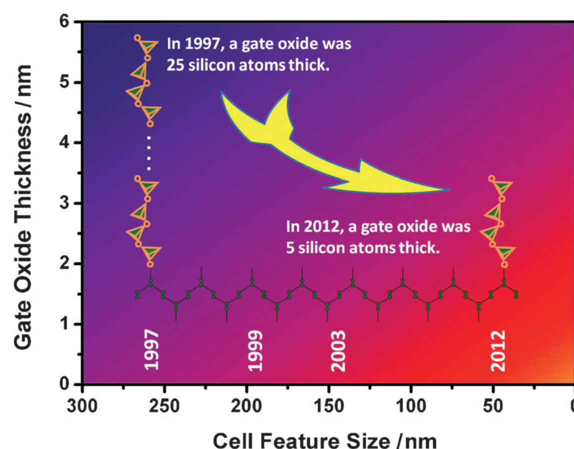
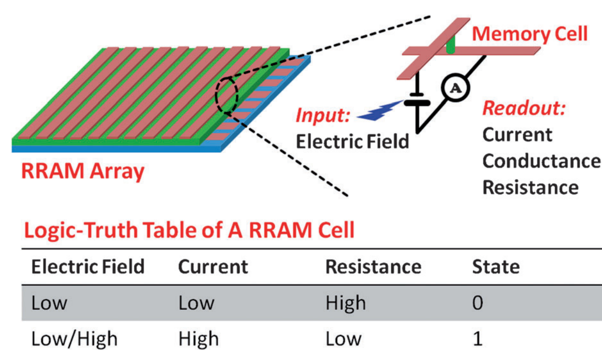


Figure 1. Evolution of the cell-feature size and gate-oxide thickness of state-of-the-art silicon-based transistors and memories.

In modern von Neumann computer systems, all the fetching, decoding, and execution of instructions are based on binary algorithms.[6] Any physical phenomena, such as magnetism,[7] ferroelectricity,[8] phase transition,[9] and others that lead to bi-stable states, can be used to construct random-access memories. Among the emerging memory technologies, resistive random-access memory (RRAM), which stores binary digital data by encoding “0” and “1” as the low (OFF) and high (ON) resistance states in response to the external electric field (Figure 2), is of great importance for the continuous innovation of electronic industries and requires rational design and synthesis of novel functional materials with desired and controllable electronic properties.[10] Since 2005, polymer memories have been proposed to revolutionize electrical applications by providing extremely inexpensive, lightweight, and transparent

 © 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Electric Field	Current	Resistance	State
Low	Low	High	0
Low/High	High	Low	1

Figure 2. Illustration and logic-truth table of RRAMs.

modules that can be fabricated onto plastic, glass, or the top layer of the complementary metal-oxide semiconductor (CMOS) circuits. By using polymer materials as the storage media, flexible and miniaturized memory devices with simple structures can be fabricated with particular ease through solution processing, resulting in a simplified fabrication process and significantly reduced manufacturing cost. More importantly, organic chemistry provides a huge treasure trove of functional molecules that can be used to adjust the electronic properties of the polymers, allowing the device performance to be fine-tuned through molecular design and chemical synthesis.

Since its first successful isolation by Geim and co-workers in 2004,[11,12] graphene has inspired a tremendous amount of research interests. The exceptional crystallinity and extended π-conjugation offer a combination of fascinating properties, among which is the intriguing electronic quality[13–16] together with the potential compatibility with the CMOS circuitry, promise graphene to be an attractive candidate for novel electronic devices and have ignited a revolution in IT industries.[17] However, the zero-bandgap properties of graphene make it unable to be switched OFF, and the minimum conductance of graphene is still too high to produce a sufficient ON and OFF current (I_{on}/I_{off}) ratio for CMOS applications.[18] Therefore, it is necessary to manipulate the current flowing through the graphene layer to effectively switch the carbon atomic sheet ON and OFF.

The chemistry of graphene reported in the literature mainly concerns the chemistry of graphene oxide (GO) with chemically reactive oxygen functionality, including carboxylic acid groups at the edges of GO, and epoxy and hydroxyl groups on the basal planes. Both small molecules and polymers have been covalently attached to GO's highly reactive oxygen functionalities, or noncovalently attached to the graphitic surfaces of chemically modified graphenes (Figure 3).[19,20] For instance, electroactive polymers can be attached to these reactive oxygen functionalities to scatter the ballistic transport of charge carriers on the graphitic surface and to introduce a significant bandgap into graphene crystals. Moreover, the solution dispersibility and processability can be greatly enhanced in the GO–polymer composites, resulting in simple and low-cost device fabrications. Recently, a series of GO–electroactive polymer nanocomposites, with polymers such as polyaniline

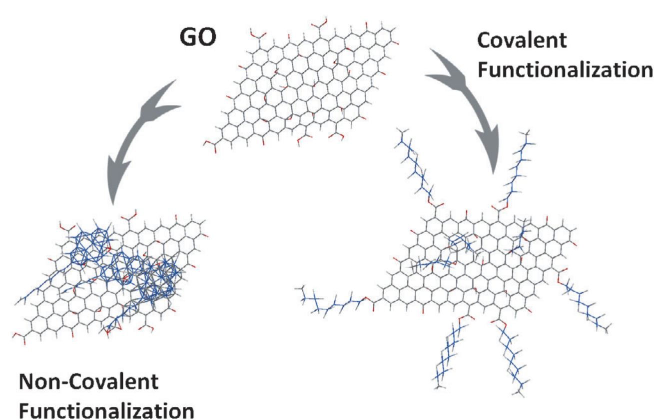


Figure 3. Functionalization routes of GO.

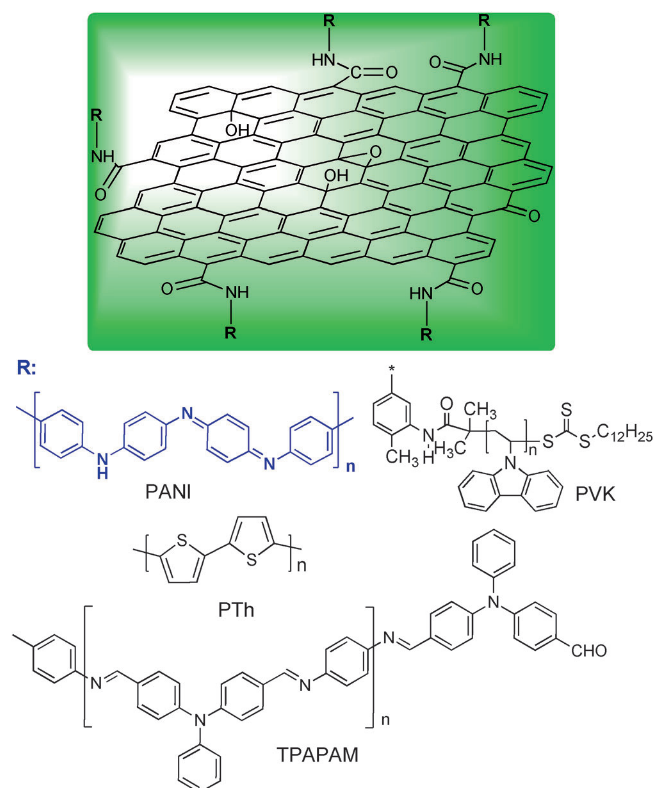


Figure 4. Chemical structures of GO–PANI, GO–PVK, GO–TPAPAM, and GO–PTh nanocomposites.

(PANI), polyvinylcarbazole (PVK), triphenylamine-based polyazomethine (TPAPAM), and others (Figure 4), have been developed to demonstrate promising memory characteristics. In this contribution, the recent progress on using GO–polymer nanocomposites as the storage medium to construct RRAM, as well as the challenges and future designs for innovative memory devices, will be addressed.

2. Results and Discussion

Similar to the carbon nanotube allotrope, chemical modification through carboxylic-acid-based esterification or an epox-

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

ide-based ring-opening reaction is expected to play a key role in tailoring the structure, solubility, processability, and properties of GO nanosheets. By selecting the correct grafting strategy and the grafted polymers, electroactive GO–polymer nanocomposites can be obtained with various functional polymers. The "grafting from" method, which refers to the in situ synthesis of covalently attached polymer chains from the basal plane and edge of GO nanosheets, is able to produce thick and dense polymer graft layers or brushes with minimized steric effects. As a prominent intrinsically conducting polymer, PANI has been, and is still being, studied extensively because of their good environmental and thermal stability, biocompatibility, low cost, ease of synthesis, high reversible pseudocapacitance, and good electrochemical activity.[21] Most PANI–graphene composites have been prepared by using the noncovalent approaches [e.g. doping graphene with PANI, in situ polymerization approaches of aniline (An) in the presence of GO or reduced GO (RGO), and others]. In this work, a new PANI-functionalized GO derivative (GO–PANI) was prepared through the in situ oxidative graft polymerization of An on the surface of GO.[22] PANI coats the GO sheets and acts as a tunneling barrier for electrons moving from one GO sheet to another. A GO-based electron-transfer system is constructed for data-storage devices.

For a low-cost but high-performance memory material, it must be electroactive. With the presence of both electron-donating (PANI) and electron-accepting (GO) entities, the resulting donor–acceptor complex is expected to generate a significant bandgap through charge-transfer interaction between the two entities, exhibiting bi-stable electrical switching and memory effects. The electrochemical behavior of the GO–PANI nanocomposites demonstrates well-defined redox properties (Figure 5 a). The hybrid system can be oxidized to the excited state at 0.91 V versus Ag/Ag^+, which corresponds to +1.2 V versus a saturated calomel electrode (SCE), and reduced to the ground state at −0.85 V versus Ag/Ag^+, which corresponds to −0.56 V versus SCE. Therefore, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), which correspond to the valence and conduction bands of a semiconductor, respectively, are derived to be −5.33 and −3.57 eV, accordingly. The significant energy bandgap of 1.76 eV, as well as the reversible redox behavior of the nanocomposites, provide the fundamental driving force that can switch the GO–PANI memory device ON and OFF, repeatedly.

GO–PANI nanocomposites demonstrate a bipolar resistive switching behavior at room temperature, as evaluated through the direct current (dc) current–voltage measurements of an Al/GO–PANI/indium–tin oxide(ITO)/glass device with an active device area of 0.16 mm^2 (Figure 5 b). The biased sweeping voltage was applied to the top Al electrode, and the current flowing through the sandwiched structure was recorded. The conductance of the as-fabricated device, initially low, increases gradually when subjected to a negatively biased sweeping voltage. The current remains low until the switching threshold voltage of −1.3 V is reached. At the threshold voltage, the current increases abruptly from 10^{-8} to 10^{-5} A (Sweep 1), suggest-

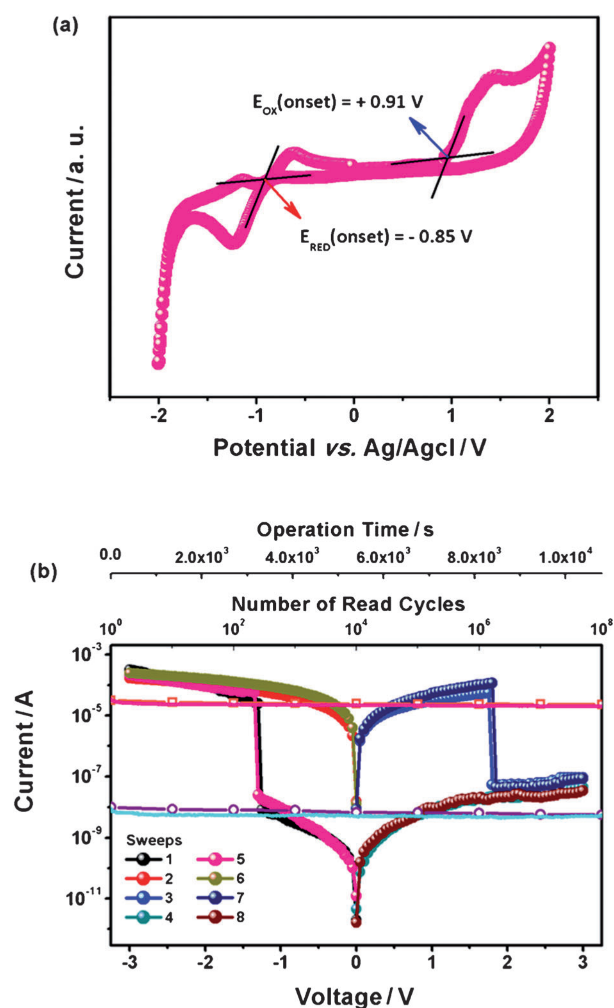


Figure 5. a) Electrochemical and b) electrical properties of the GO–PANI nanocomposite.

ing device transition from the low-conductivity (OFF) state to the high-conductivity (ON) state. This transition, from the OFF to the ON state, serves as the writing process for a memory device. The ON state can be maintained after removing the power supply (Sweep 2), and is characteristic of a nonvolatile memory device. With a sufficient magnitude of reversed voltage (+1.8 V, Sweep 3), the conductance of the device can be programmed back to the initial OFF state, thereby erasing the information stored during the writing process. By sweeping the voltage in the direction of 0→3→0→−3V→0→3 V (Sweeps 1 to 8), GO–PANI can be switched continuously between the two resistance states with uniformly distributed threshold voltages of approximately −1.3 V (write) and +1.8 V (erase), and a stable ON/OFF ratio of approximately 10^3 (read at −1 V), thus completing the write–read–erase–read–rewrite cycles of a RRAM. The large ON/OFF ratio is also sufficient for a low misreading rate through the precise control of the ON and OFF states. The Al/GO–PANI/ITO/glass device was characterized under ambient conditions, in which the presence of air or moisture may influence the intrinsic and interfacial properties of the nanocomposites/electrode heterostructures. It can

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

be expected that the minor variation in the switching cycles can be avoided upon proper device encapsulation, which is beyond the scope of the present study. Nevertheless, both states can be sustained for more than 3 h or 100 million cycles. Upon integrating the voltage with the current readout at the corresponding operation point, a low power consumption of approximately 6.7 nW, 33.3 nW, 97.6 μW, or 221.4 μW can be derived for the room-temperature read (OFF state), write, read (ON state), or erase operation of the GO–PANI-based memory device. Devices based on PANI–gold nanoparticles have also been reported to demonstrate nonvolatile memory behaviors with a switching threshold of approximately 3.0 V.[23] By using GO as a larger electron acceptor to enhance the charge-transfer interaction with the PANI donor, resistance switching is expected to occur easier and earlier in the present GO–PANI nanocomposites. Thus, the GO–PANI-based memory devices show much lower turn-ON voltages of approximately −1.3 V, and consequently a lower device power consumption.

The static electronic scenario is also simulated to better understand the switching mechanism of the GO–PANI nanocomposites (Figure 6). Initially, GO is electrically insulating, whereas

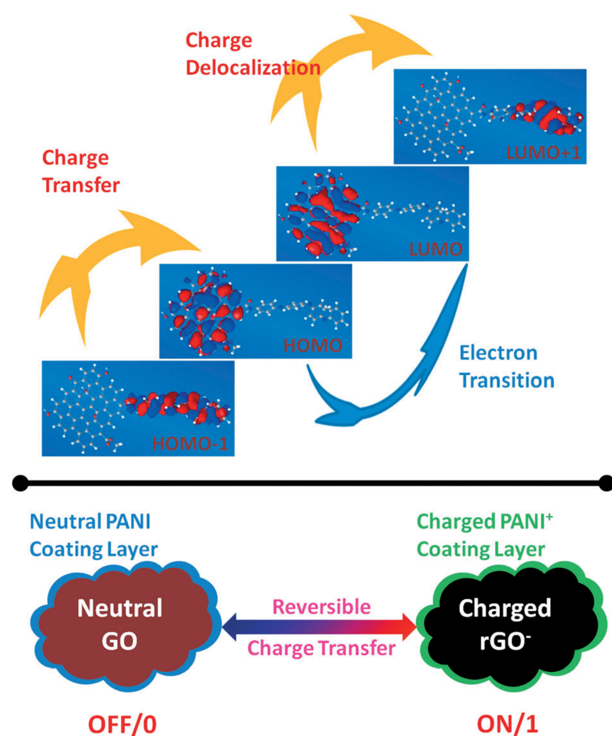


Figure 6. Simulated electronic scenario and schematic switching mechanism of the GO–PANI nanocomposite.

the grafted PANI serves as a coating layer and a tunneling barrier that prevents electron hopping from one GO nanosheet to another. The distribution of electrons on the HOMO overlaps with that on the LUMO, and is beneficial for charge excitation across the artificial energy bandgap. At the switching threshold voltage, electrons transit readily from HOMO to LUMO within the GO sheets, causing excited neutral state of the nanocomposites. As the difference between the energy level of HOMO−1 and HOMO is only 0.115 eV, a charge-transfer interaction between the peripheral PANI donor entities and the central GO plane can occur easily. Electrons residing on the imine nitrogen of PANI gain enough energy to surmount the energy barrier between HOMO−1 to HOMO, and are further delocalized on the LUMO and LUMO+1. The delocalized electrons among the large π-conjugation system reduce the GO to RGO, on which electrons can propagate with less scattering and enhanced conductance.[24] Covalent functionalization of GO with electroactive PANI is thus an effective and versatile approach to tuning the electronic properties of GO. The facile engineering of the GO energy bandgap through polymer functionalization also provides an alternative route to supplement the lithographical patterning of graphene sheets into low-dimensional nanostructures and chemical modification of graphene nanoribbons. In addition, the conductance of PANI can be further manipulated by ionic doping with minerals and organic acids, demonstrating a great potential for the development of novel ionic electronics.

The other prerequisite for GO–polymer-based memory materials is the ease of solution processing. The incorporation of polymer chains into the nanocomposites leads to a much enhanced compatibility with organic solvents, and GO–polymer composites can be well-dispersed in solutions. Figure 7 shows

Figure 7. Images of GO and GO–PTh nanocomposite dispersions in DMF. From left to right: GO, and GO–PTh samples prepared at 70 °C over 24 h, 12 h, 4 h, and prepared at 50 °C and room temperature over 24 h, respectively.

the GO–polythiophene (GO–PTh) samples dispersed in dimethylformamide (DMF) that were prepared under different conditions. All of these GO–polymer nanocomposites exhibit memory characteristics. For instance, reversible addition-fragmentation chain-transfer (RAFT) polymerization allows the growing of poly(*N*-vinylcarbazole) (PVK) from the surface of GO with narrow molecular weight distributions and well-defined compositions.[25] The relatively large bandgap of 2.15 eV leads to slightly increased writing and erasing voltages of −1.7 V and +2.6 V, respectively. When the "grafting from" approach is employed, polymers that cannot be synthesized in situ can be tethered onto the GO surface or edge easily. Another soluble

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

nanocomposite, consisting of triphenylamine (TPA)-based polyazomethine covalently grafted to GO (GO–TPAPAM), was used directly for fabricating memory devices.[26] With efficient hole injection, high carrier mobilities, and the low ionization potential of TPA polymer chains, the devices exhibit bi-stable electrical switching and nonvolatile rewritable memory effects, with a small switch-ON voltage of about −1 V and an ON/OFF current ratio of more than 10^3. When RGO–polymer nanocomposites are employed as memory materials, larger ON/OFF ratios of 10^4 are achieved from the recovered crystalline quality and electronic structures of RGO.[27,28]

3. Conclusions

In recognizing the significance of new materials, structures, and mechanisms, extensive efforts have been devoted to the exploration of the memory function of graphene nanosheets over the last ten years. With the elimination of the third electrode in the RRAM architecture, as well as the ultrathin thickness of less than 1 nm, devices based on single-layer graphene materials are potentially capable of increasing the data-storage density by 50 times, as compared to the 45 nm flash memories.[29] By using either sheet-based or roll-to-roll printing techniques, such as inkjet, screen, gravure, offset, flexographic, micro-contact printing, and even nano-imprint lithography, both high-volume and high-quality production of the three-dimensional flexible and transparent arrays of memories and memristors can be made possible. The launch of graphene memory or memristor-based artificial-neural networks, achieved through mimicking the synaptic learning and logic processing functionalities of human neuromorphic cells, may not completely replace the present silicon technology, but provides supplementary solutions to the existing microelectronic industries. Nevertheless, advanced nanofabrication and characterization techniques including E-beam lithography and scanning probe microscopy will further extend the graphene memories or memristors into real molecular devices. Ultimately, a single molecule is a memory.

Experimental Section

Preparation of GO–An

This material was prepared through an amidation reaction by using 1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide (EDC)/N-hydroxysuccinimide (NHS) as the condensing agent. GO sheets (200 mg) were dispersed into dry DMF (100 mL). After 30 min of ultrasonication, a well-dispersed solution was formed. Then, the reaction system was kept at 0 °C by using an ice–water bath. NHS (1.15 g) and 1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide hydrochloride (EDC·HCl, 1.92 g) were added to the solution. After stirring for 2 h at 0 °C, An (1.08 g) was added, and the solution was stirred overnight at room temperature. The crude product was collected by filtration using a polycarbonate film ($\varphi = 0.45$ μm), and washed sufficiently with water and ethanol. The obtained GO–An composite (210 mg) was vacuum-dried at room temperature overnight.

Synthesis of GO–PANI

GO–PANI was prepared through oxidative graft polymerization of An on the surface of GO. Typically, GO–An (100 mg) was dispersed into 1.0 M HCl (80 mL) with the aid of ultrasonication for 30 min. Then, An (1 mL) was added and stirred at 0 °C for 30 min. $(NH_4)_2S_2O_8$ (0.6 g, 2.6 mol), which was dissolved in 1.0 M HCl (20 mL), was slowly added into the above reaction mixture. The oxidative polymerization was performed at 0 °C for 6 h under vigorous stirring. The crude GO–PANI composites were collected by filtration. The free PANI in the crude product was converted to the neutral emeraldine (EM) base by treatment with excess 0.5 M NH_4OH, and then centrifuged at 8000 rpm. After that, the GO–PANI composites were washed with *N*-methylpyrrolidone (NMP, a good solvent for the EM base) and centrifuged at 12 000 rpm. This process was repeated several times to ensure the complete removal of the PANI homopolymer. The obtained GO–PANI (145 mg) was thoroughly vacuum-dried at 50 °C for 12 h. Other GO–polymer nanocomposites can be prepared similarly.

Memory Device Fabrication, Characterization, and Simulation

The Al/GO–PANI/ITO/glass device was fabricated by spin-coating a thin layer of the nanocomposites from NMP solution, followed by thermal-evaporation of the aluminum electrode through a shadow mask. Electrical characterization was carried out on a Hewlett–Packard 4155B semiconductor parameter analyzer under ambient conditions. Calculations of the electronic properties of the basic unit of the GO-based polymers were carried out on a supercomputer by using the Gaussian 03 program package and density functional theory at the B3LYP/6-31G(d) level.[30]

Acknowledgements

The authors are grateful for the financial support of the State Key Project of Fundamental Research of China (973 Program, 2012CB933004), the National Natural Science Foundation of China (51333002, 21074034, 51303194, 61328402), the Fundamental Research Funds for the Central Universities (WA0913004), the State Key Laboratory of ASIC & System of Fudan University (11KF007), Ningbo Science and Technology Innovation Team (2011B82004) and Ningbo Natural Science Foundation (2013A610031).

Keywords: graphene oxide · memory · nanostructures · polymers · resistive switching

[1] C. Kincaid, Electronics: New Gadgets = New Growth in *Area Development Online.* **2007**, Oct. http://www.areadevelopment.com/HighTechNanoElectronics/oct07/electronics.shtm l?Page = 1.
[2] ICT Result: Next-Generation RAM: Remembering the Future. *Science Daily.* **2007**, Dec. 21. http://www.sciencedaily.com/releases/2007/12/071221174912.htm.
[3] R. F. Service, *Science* **2003**, *302*, 556 – 557.
[4] Executive summary. In: the International Technology Roadmap for Semiconductors (ITRS). 2009 ed. Austin, TX: Semiconductor Industry Association, International Sematech; **2009**. 1 – 85.
[5] R. Waser, *Nanoelectronics and Information Technology: Advanced Electronic Materials and Novel Devices, 2nd ed.*, Wiley-VCH, Weinheim, **2005**.
[6] J. von Neumann, First Draft of A Report on the EDVAC, **1945**.
[7] C. Chappert, A. Fert, F. N. Van Dau, *Nat. Mater.* **2007**, *6*, 813 – 823.

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

[8] R. Guo, L. You, Y. Zhou, Z. S. Lim, X. Zou, L. Chen, R. Ramesh, J. Wang, *Nat. Commun.* **2013**, *4*, 1990.
[9] M. Wuttig, *Nat. Mater.* **2005**, *4*, 265 – 266.
[10] R. Waser, M. Aono, *Nat. Mater.* **2007**, *6*, 833 – 840.
[11] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, *306*, 666 – 669.
[12] A. K. Geim, K. S. Novoselov, *Nat. Mater.* **2007**, *6*, 183 – 191.
[13] I. Meric, M. Y. Han, A. F. Young, B. Ozyilmaz, P. Kim, K. L. Shepard, *Nat. Nanotechnol.* **2008**, *3*, 654 – 659.
[14] Y. Zhang, T.-T. Tang, C. Girit, Z. Hao, M. L. C. Martin, A. Zettl, M. F. Crommie, Y. R. Shen, F. Wang, *Nature* **2009**, *459*, 820 – 823.
[15] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, A. K. Geim, *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 10451 – 10453.
[16] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, A. A. Firsov, *Nature* **2005**, *438*, 197 – 200.
[17] B. Standley, W. Bao, H. Zhang, J. Bruck, C. N. Lau, M. Bockrath, *Nano Lett.* **2008**, *8*, 3345 – 3349.
[18] F. Schwierz, *Nat. Nanotechnol.* **2010**, *5*, 487 – 496.
[19] D. R. Dreyer, S. Park, C. W. Bielawski, R. S. Ruoff, *Chem. Soc. Rev.* **2010**, *39*, 228 – 240.
[20] S. Park, R. S. Ruoff, *Nat. Nanotechnol.* **2009**, *4*, 217 – 224.
[21] A. G. MacDiarmid, *Angew. Chem.* **2001**, *113*, 2649 – 2659; *Angew. Chem. Int. Ed.* **2001**, *40*, 2581 – 2590.
[22] B. Zhang, Y. Chen, L.-Q. Xu, C. Wang, C.-X. Zhu, K.-G. Neoh, E.-T. Kang, *Chem. Eur. J.* **2013**, *19*, 6265 – 6273.
[23] R. J. Tseng, J. Huang, J. Ouyang, R. B. Kaner, Y. Yang, *Nano Lett.* **2005**, *5*, 1077 – 1080.
[24] D. C. Elias, R. R. Nair, T. M. G. Mohiuddin, S. V. Morozov, P. Blake, M. P. Halsall, A. C. Ferrari, D. W. Boukhvalov, M. I. Katsnelson, A. K. Geim, K. S. Novoselov, *Science* **2009**, *323*, 610 – 613.
[25] B. Zhang, Y. Chen, L. Xu, L. Zeng, Y. He, E. T. Kang, J. Zhang, *J. Polym. Sci. Part A* **2011**, *49*, 2043 – 2050.
[26] X. D. Zhuang, Y. Chen, G. Liu, P. P. Li, C. X. Zhu, E. T. Kang, K. G. Neoh, B. Zhang, J. H. Zhu, Y. X. Li, *Adv. Mater.* **2010**, *22*, 1731 – 1735.
[27] B. Zhang, G. Liu, Y. Chen, L. Zeng, C. X. Zhu, K. G. Neoh, C. Wang, E. T. Kang, *Chem. Eur. J.* **2011**, *17*, 13646 – 13652.
[28] B. Zhang, Y. Chen, G. Liu, L. Q. Xu, J. Chen, C. X. Zhu, K. G. Neoh, E. T. Kang, *J. Polym. Sci. Part A* **2012**, *50*, 378 – 387.
[29] Y. Li, A. Sinitskii, J. M. Tour, *Nat. Mater.* **2008**, *7*, 966 – 971.
[30] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

Received: September 17, 2013
Revised: October 15, 2013
Published online on November 22, 2013

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim