Recent Advances in Pen-Based Writing Electronics and their Emerging Applications

Zedong Li, Hao Liu, Cheng Ouyang, Wei Hong Wee, Xingye Cui, Tian Jian Lu, Belinda Pingguan-Murphy, Fei Li, and Feng Xu**

The emerging demand for cost-effective, easily accessible, and rapid prototyping electronics fabrication calls for novel techniques to design and manufacture electronic components and devices for wearable functional sensing, on-skin medical monitoring, and body-worn energy conversion. Inspired by daily hand-writing, innovative and ubiquitously available pens can be employed to write conductive patterns on multiple substrates; such a low-cost, fast, and user-friendly direct writing paradigm has recently aroused remarkable research interest as a promising electronics prototyping strategy. In this review, state-of-art advances in techniques for direct writing of electronics are presented, and pros and cons of each fabrication route are discussed. Emerging applications of pen-based writing electronics are also summarized. Based on these, final conclusions, limitations and challenges, as well as ongoing perspectives are illustrated.

1. Introduction

Nowadays there is a great interest in the development of flexible electronics for widespread applications, such as wearable functional devices,[1,2] medical monitoring systems,[3,4] and flexible energy storage and conversion.[5,6] For instance, a polyester-based tattoo-like integrated epidermal electronic system has been developed that can perform real-time muscle movement, heart activities, and brain-wave detection without the engagement of expensive and bulky medical instrumentations, holding promises to empower doctors to timely monitor vital signs of patients in a simple and efficient way.[3] For these applications, the ideal electronics should be low-cost, easily accessible, high-performance, rapid prototyping, and user friendly etc. Consequently, increasing attention has been devoted to discovering several factors closely related to flexible electronics (e.g., substrates, conductive materials, and manufacturing techniques) for fabricating electronics with increased performance and decreased cost.[7] Among them, the development of fast and cost-effective fabrication strategies has drawn close attentions for realizing low-cost flexible electronics.[8–10]

Recently, various techniques have been developed to fabricate flexible electronics, such as coating,[11,12] sputtering,[13] and printing techniques (e.g., gravure printing,[14] flexo printing,[15] offset printing,[16] inkjet printing,[17] and screen printing[18]). Specifically, printing techniques enable rapid prototyping of components and devices with accurate three-dimensional (3D) structures, thus facilitating achievement of functional 3D electronics.[19–21] Based on a newly developed embedded 3D printing system, the fabrication of strain and pressure sensors has been demonstrated to be viable within highly stretchable silicon polymer substrates, exhibiting huge potential for the production of flexible electronics and wearable devices with arbitrary constructs and unique functions.[6] However, these sophisticated techniques may not live up to the emerging demand of low cost, easy accessibility and rapid prototyping for flexible electronics fabrication, since the long processing period of coating, the high energy consumption of sputtering, and the inevitable enrollment of expensive professional equipment of printing are all intractable issues that can hardly be overlooked.[22,23]

As an alternative technique and inspired from day-to-day hand writing, various writing instruments, such as brush pen,[22,24,25] pencil,[26–29] fountain pen,[30,31] and ball pen,[32–35] have been recently utilized to directly write electronics. Direct writing with a pen is a simple and fast way of depositing electrically conductive materials on substrates to form electronics

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Z. Li, H. Liu, C. Ouyang, X. Cui, Prof. F. Xu
The Key Laboratory of Biomedical
Information Engineering of Ministry of Education
School of Life Science and Technology
Xi'an Jiaotong University
Xi'an 710049, P.R. China
E-mail: fengxu@mail.xjtu.edu.cn

Z. Li, H. Liu, C. Ouyang, W. Hong Wee, X. Cui,
Prof. T. Jian Lu, Prof. B. Pingguan-Murphy,
Dr. F. Li, Prof. F. Xu
Bioinspired Engineering and Biomechanics Center (BEBC)
Xi'an Jiaotong University
Xi'an 710049, P.R. China
E-mail: feili@mail.xjtu.edu.cn

W. Hong Wee, Prof. B. Pingguan-Murphy
Department of Biomedical Engineering
Faculty of Engineering
University of Malaya
50603 Kuala Lumpur, Malaysia

Dr. F. Li
Department of Chemistry
School of Science
Xi'an Jiaotong University
Xi'an 710049, P.R. China

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for emerging applications in fields of biomedical and electrochemical sensing,[36–38] electronic components,[1,26,32,39] and energy storage devices.[24,28,29] Specially, writing with a pen endows end-users the capability to design and realize "on-demand" sensors for specific "on-site" applications.[37] Furthermore, pen-based writing has also been combined with printing techniques, taking both advantages of writing (e.g., simplicity and low cost) and printing (e.g., mass production and high resolution), known as pen-analogue writing, mainly including electrohydrodynamic direct writing[40] and microplasma-based direct writing.[41]

In the past few years, quite a few good reviews on printed electronics[42–44] and pencil-written electronics[27] have been reported. However, the rapid development of truly low-cost flexible electronics appeals for a strong demand for a thorough, state-of-the-art review based on the most recent advances in direct writing of electronics. In this review, we discuss recent research progresses in direct writing electronics and their emerging applications. We first introduce various writing techniques that have been used for manufacturing electronics in Section 2. Then, we discuss emerging applications of written electronics in Section 3. Finally, conclusions, challenges and future perspectives are proposed in Section 4.

Fei Li received her PhD in Electrochemistry in 2008 from the University of Warwick, UK. During 2008–2010, she worked as postdoctoral fellow at Ecole Polytechnique Federale de Lausanne, Switzerland, and then at Temple University, USA, respectively. Since 2011, she is an associate professor at Xi'an Jiaotong University, China. Her current research studies various spectroelectrochemical, electrocatalysis, and biological interfacial processes using electrochemical techniques and scanning probe microscopy.

Feng Xu received his PhD in Engineering in 2008 from Cambridge University, UK and worked as a research fellow at Harvard Medical School and Harvard-MIT Health Science and Technology (HST) during 2008–2011. Currently, he is a full professor at Xi'an Jiaotong University (XJTU) and is also the founding director of XJTU Bioinspired Engineering and Biomechanics Center. His current research aims at advancing human health through academic excellence in education and research that integrates engineering, science biology and medicine with focus on Engineering of Cell Microenvironment and Point-of-Care Technologies.

2. Techniques for Writing Electronics

Writing is one of the most ubiquitous things in people's daily life for helping people communicate through recording signs and symbols. Since the invention of the first writing instrument, writing has greatly accelerated the human civilization with the development of writing facilities. There are four kinds of popular writing instruments nowadays including brush pen, pencil, fountain pen and ball pen, which were invented in the 1st millennium B.C.,[45] the 16th century,[46] the 19th century,[45] and the 20th century,[45] respectively (**Figure 1**). Traditionally, when we use a pen to write, the writing component (e.g., ink, graphite) is released, forming signs and symbols on substrates. Besides the traditional writing function on paper, a series of pen-based writing methods have also recently been developed to fabricate electronics for electronic applications (Figure 1).[32]

The important properties of electronics that affect their performance include their microstructures (e.g., width resolution) and electrical properties (e.g., conductivity), which are summarized in **Table 1**. Each pen-based writing method has its advantages and disadvantages in fabricating electronics. Thus a proper writing method should be chosen based on the required quality of the electronic components and their application fields. In this section, we classify the writing methods for electronics into two types: pen-based writing methods (i.e., brush pen, pencil, fountain pen, and ball pen) and pen-analogue writing methods. The developing history, working principle, advantages and disadvantages, and application examples of each pen-based writing method are reviewed and summarized in the following parts.

2.1. Brush Pen

A brush pen is known as a traditional Chinese writing and painting instrument, which is similar to the paintbrush used in oil painting in the western countries. It was invented before Christ in China,[45] and has been used as the main writing device in eastern countries for over thousands of years. A typical brush pen is fabricated by bonding a bunch of filaments (e.g., bristle, nylon fibrils) to a head of handle (e.g., bamboo, wood). During writing, the brush pen is firstly soaked in an ink container, and then the ink is transferred onto a substrate under handwriting pressure. Specifically, the shear stress and capillary force from the brush deliver the ink onto the substrate to form continuous pattern (**Figure 2**a). Paintbrush is also referred to as the brush pen here, owing to their similar structures.

For fabricating electronics, brush pen has the capability of writing electronics on both soft (e.g., paper, polyethylene terephthalate (PET), cloth) and rigid (e.g., glass, plastic) substrates. Prior to writing, the substrates are often cleaned with a detergent to remove contaminants and treated with plasma or ultraviolet (UV)/ozone to improve the wetting properties of substrates as the inks for brush pen writing are mainly water based solutions.[47,55,56,65,66] During writing, there

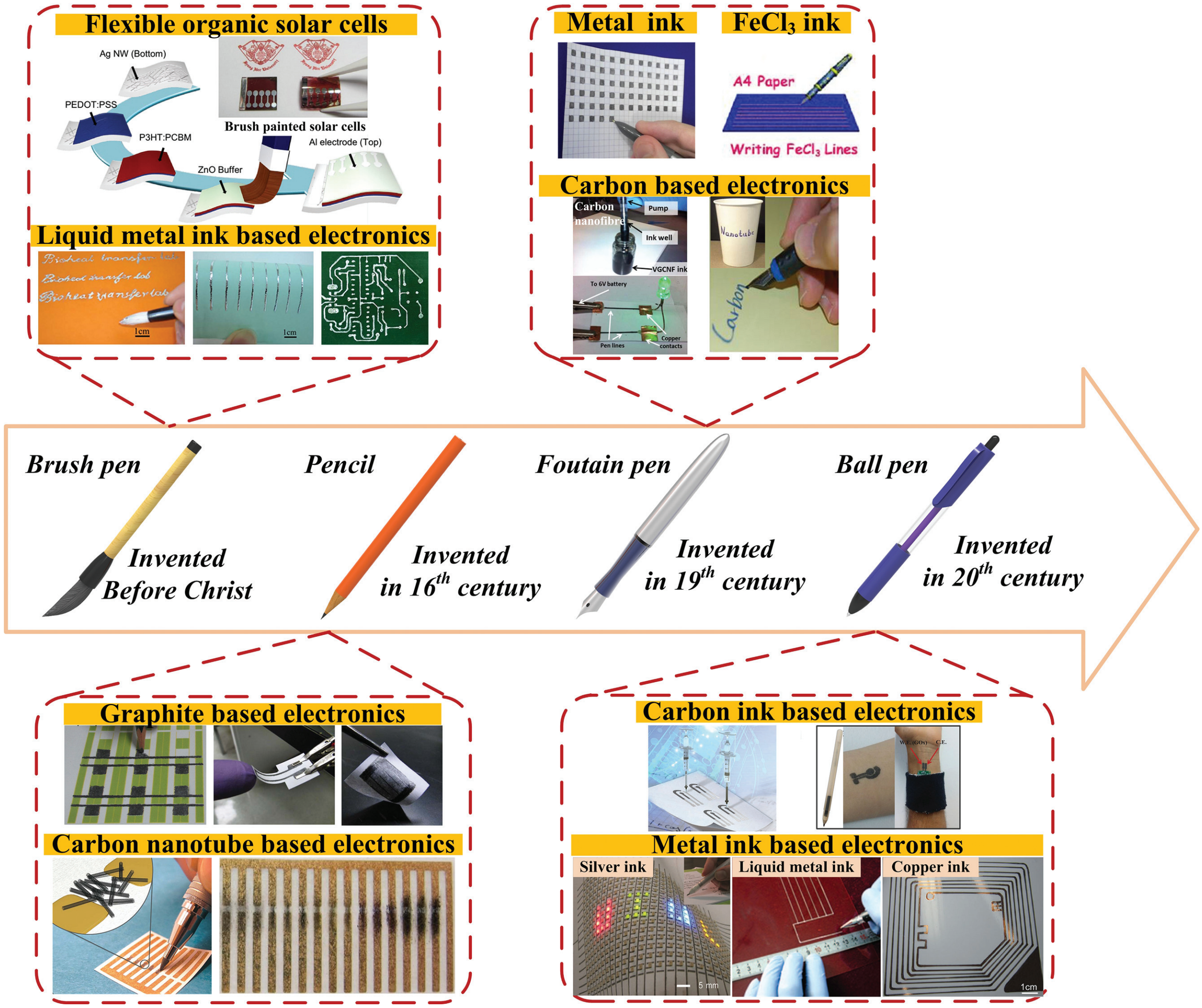

Figure 1. Development in direct-writing electronics. Brush pens have been mainly used to fabricate flexible organic solar cells and liquid metal ink based electronics. Top left: Schematics of the brush writing process for fabrication of solar cells and fabrication of circuits using Gallium-based liquid metal ink. Commercial pencils are adopted to fabricate graphite based electronics and home-made pencils are developed to write materials other than graphite, such as carbon nanotubes. Bottom left: Photographs of graphite based electronics (e.g., paper electrodes, U-shaped strain gauge and chemiresistor) and photographs of carbon nanotube based chemiresistive gas sensors. Top right: The fountain pen is capable of writing various inks, including metal ink, $FeCl_3$ ink and carbon-based inks (e.g., carbon nanofibers and carbon nanotubes). Bottom right: Ball pens have been widely used to fabricate carbon ink based electronics (e.g., paper based electrochemical sensors and epidermal glucose sensors) and metal ink based electronics (e.g., silver circuits, liquid metal conductive tracks and copper antenna). Reproduced with permission.[22] Copyright 2012, Public Library of Science. Reproduced with permission.[25] Copyright 2013, Public Library of Science. Reproduced with permission.[26] Copyright 2014, Nature Publishing Group. Reproduced with permission.[30] Copyright 2014, Elsevier. Reproduced with permission.[31] Copyright 2013, Royal Society of Chemistry. Reproduced with permission.[32] Copyright 2011, Wiley-VCH. Reproduced with permission.[33] Copyright 2013, AIP Publishing. Reproduced with permission.[37] Copyright 2015, Wiley-VCH. Reproduced with permission.[47] Copyright 2014, Elsevier. Reproduced with permission.[48] Copyright 2012, Wiley-VCH. Reproduced with permission.[49] Copyright 2013, National Academy of Sciences. Reproduced with permission.[50] Copyright 2013, American Chemical Society. Reproduced with permission.[51] Copyright 2014, Wiley-VCH. Reproduced with permission.[52] Copyright 2015, Royal Society of Chemistry. Reproduced with permission.[53] Copyright 2013, Springer. Reproduced with permission.[54] Copyright 2014, Elsevier.

is a shear stress applied on the solution existing between the two boundaries, the solution–substrate and the solution–brush interfaces (Figure 2a).[24] The properties of the fabricated electronic patterns are related to writing speed, repeated writing cycles, and substrate temperature. Among them, the writing speed is a key parameter to control the uniformity of the electronic pattern. The writing speed is usually kept at a certain constant value in the range from 1 to 2 cm s^{-1},[24,39,47,55,56,66,67] because a high writing speed will induce an discontinuous film while a low writing speed will cause a non-uniform film (Figure 2b). In addition, the number of writing cycles needs to be optimized since it determines the density of the electronic pattern on the substrates and thus has significant impact on the electrical performance of

Table 1. Summary of key parameters for each pen-based writing method.

Writing techniques	Writing materials	Substrates	Conductivity [S cm^{-1}]	Width [µm]	Ref.
Brushpen	PEDOT: PSS/P3HT/PCBM, silver nanowire ink, CNT ink, V_2O_5 ink, gallium-based liquid metal ink	Glass, PET, ITO, paper	50 – 2.9 × 10^4	50–500	[22,24,39,47,55,56,57]
Pencil	Graphite rod, pencil lead, SWCNT/MWCNT	Paper, salt substrate	20–884	900–1900	[29,48,49,58–80,61]
Ballpen	Silver/copper ink, gallium-based liquid metal ink, enzymatic ink	Paper, PDMS, human skin	5 × 10^3–1 × 10^5	100–800	[33,37,53,62–64]
Fountainpen	Carbon nanofibre ink, CNT ink, $FeCl_3$ ink	Paper	–	770–980	[30,31,50]

Note: Abbreviations as follows: poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT: PSS), poly(3-hexylthiophene) (P3HT), [6,6]-phenyl-C61butyric acid methyl ester (PCBM), carbon nanotube (CNT), single-wall carbon nanotube (SWCNT), multi-wall carbon nanotube (MWCNT).

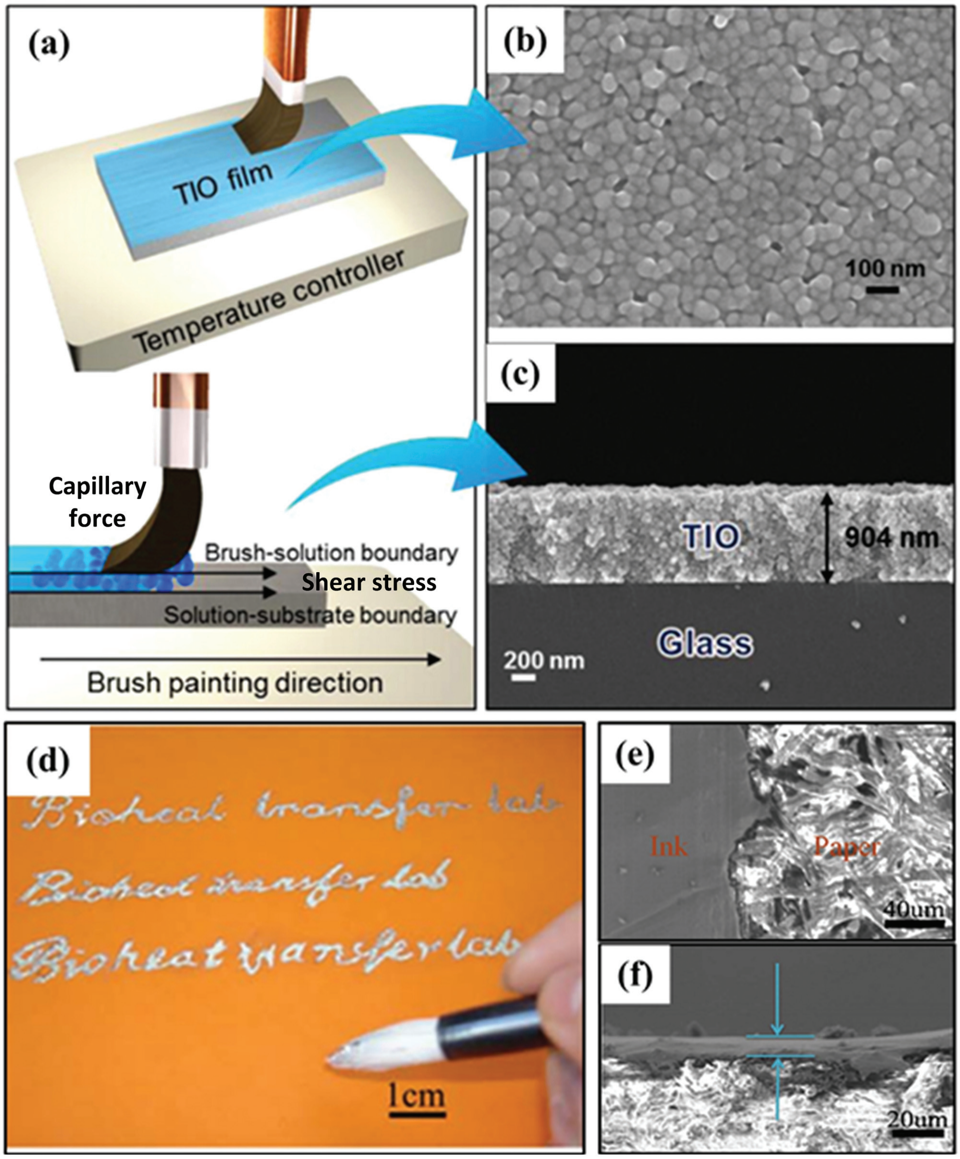

Figure 2. Writing electronics using a brush pen. a) Schematic and working principle of the brush pen writing process to form Ti-doped In_2O_3 (TIO) film on a glass substrate with the controlled substrate temperature. b) Surface and c) cross-sectional field emission scanning electron microscopy (FESEM) images of the brush painted TIO film with 90 nm thickness. d) Optical image of conductive text written on paper by using Gallium-based liquid metal ink. Scanning electron microscopy (SEM) graphs of e) surface and f) thickness of conductive line written on paper by using Gallium-based liquid metal ink. Reproduced with permission.[22] Copyright 2012, Public Library of Science. Reproduced with permission.[55] Copyright 2014, Elsevier.

the final electronics.[47,56,66] Moreover, an appropriate temperature of the substrates is also necessary to control and adjust the viscosity and evaporation speed of the solution to precisely control the width and thickness of the written pattern (Figure 2c).[39,57,65] However, Liu's group wrote Gallium-based liquid metal ink on various substrates (e.g., paper, skin) using a brush pen under room temperature (Figure 2d–f).[22,25,38] The liquid metal is a low viscosity (1.99×10^{-3} Pa s) fluid, which is completely melted at room temperature due to its low melting temperature (≈15.5 °C). Therefore, further heating of the substrate will not have significant effect on its viscosity.[68,69] Additionally, the geometrical structures of the liquid metal patterns can be well maintained with the passivation contribution of the instantaneously formed oxidization skin on the liquid metal surface when exposed to the atmosphere.[10,20,69] Interestingly, such thin skin is proven to have negligible effect on the intrinsic electrical conductivity of liquid metals.[70] In addition, the width of the conductive trace is also affected by the tip size of the brush and the applied writing pressure.[22] Fortunately, the bristles of the brush pen have negligible effect on the roughness of the written pattern. As an illustration, a brush pen made of nylon fibrils has been employed for fabricating a smooth film with a relatively low roughness (2.26 nm).[39] Finally, the amount of ink on the brush and how the ink is delivered may affect the properties of electronics. However, the effect could be minimized by repeated writing.

With the advantages of being simple, fast, cost-effective and compatible with roll-to-roll systems for high throughput production, brush pen writing has been demonstrated to be a promising method for fabricating electronics. Thin conductive and semiconductive films with nanometer-scale thickness have been achieved by controlling the substrate temperature during writing process, which makes it capable for fabrication of multi-layered electronics such as organic thin-film transistors and solar cells in a fast way benefiting from the quick solidification of each layer under appropriate temperature.[39,47] The width resolution for brush pen writing can reach 0.5 mm by using Gallium-based liquid metal ink,[25] which can be improved to ≈50 µm by using a water-based solution.[39] However, during the brush pen writing process, a custom-made mask is usually required to precisely control the geometrical shape of the designed pattern on substrates. In addition, it is still challenging to accurately control the thickness and width of the pattern by hand-writing without appropriate temperature control.

2.2. Pencil

The first pencil was invented in England in the 16th century after the graphite was widely used to mark.[46] A pencil is normally composed of a pencil lead (normally fine graphite powder bound together by clay) and a protective handle to prevent the pencil lead from being broken and to make it easy for user to handle (**Figure 3**a,b). During writing process, the graphite particles of the lead are rubbed off through physical friction between tip of the pencil lead and the writing substrate (Figure 3a), and then the graphite is left on the substrate to form a trace (Figure 3c,d). Based on the good electrical conductivity of graphite (about 0.1–1 S cm^{-1}[71]), both commercial pencils and home-made pencils have recently been developed and used to write electronics (Figure 3e).[26]

2.2.1. Commercial Pencils

Commercial pencils are classified by the hardness and blackness of the pencil leads, which are mostly denoted by the letter "H" (for hardness) and "B" (for blackness) determined by its relative fraction of graphite. Furthermore, the combination of the letter with a number (e.g., 4B, 2H) is employed by pencil manufacturers to indicate the degree of hardness and blackness. For instance, a 4B pencil has a blacker lead than a 2B pencil while the lead of a 4H pencil is harder than that of a 2H pencil. Typically, the HB pencil is popular in our daily life with 60–70% graphite,[27] the lead of which is less hard than an H pencil and less black than a B pencil. Commercial pencils with different grades of hardness and blackness have been used to fabricate various electronics. For instance, the graphite trace written with an HB pencil has been used as the anode and cathode of a paper-based fuel cell,[72] and as the resistor element in fabricating resistor-capacitor filters.[58] The feasibility of fabricating electronics using pencils is based on the electric conductivity of pencil traces composed of graphite particles. Apart from the amount of graphite content, the electric conductivity is also dependent on the quality of the contact between graphite particles in the pencil traces, where mechanical deformation (e.g., expanding or compressing) of the substrate or chemically induced particle re-distribution will induce changes in electric conductivity.[26] Based on this, various grades of pencils have been employed to write sensors based on the resistance change, such as piezoresistive sensors,[73,74] strain gauges, and chemiresistors.[26] In addition, it is found that the traces written by "hard" pencils, such as HB pencils, are more electrically sensitive to substrate deformation for sensing applications.[26,73] But it is also noted that the traces written by pencil with hardness higher than HB pencil may be nonconductive due to its low concentration of graphite. Besides HB pencils, B grade pencils also have been employed to write electronics with good conductivity due to their high graphite content. For instance, 4B pencils have been used to fabricate UV sensors[59,75] and photodetectors,[76] while 3B pencils have been employed to fabricate carbon electrodes for paper-based electrochemical devices.[77,78] In addition to the commercial pencils, commercially available pure graphite rods with higher electrical conductivity have also been utilized to write electronics on paper,[29,79] and even multilayer graphene sheets can be obtained, which are significant for some electronic components (Figure 3d).[29,60,79]

2.2.2. Home-Made Pencils

Due to the fixed properties of commercial pencils (e.g., hardness and graphite content ratio), they cannot meet some specific performance and application demands such as for resistors and sensing. To address this, home-made pencils have been developed and used to write electronics.[1,26,80] For instance, since

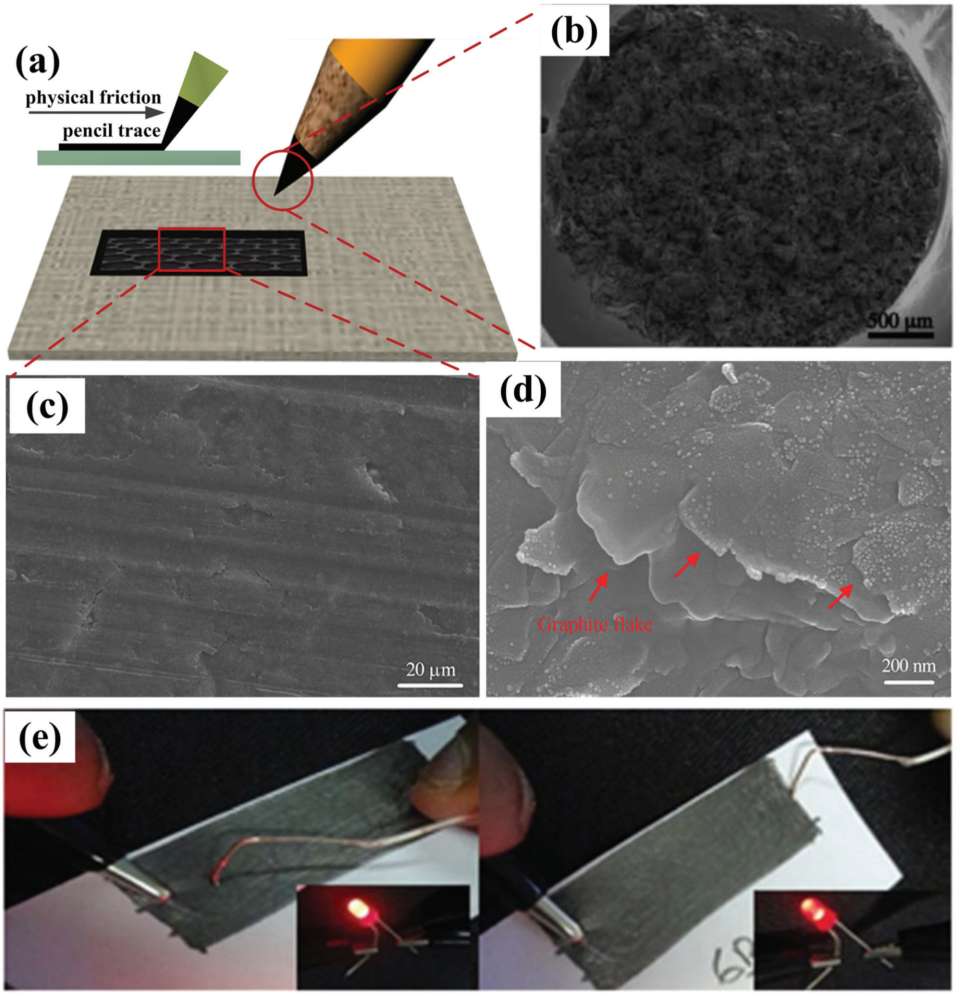

Figure 3. Writing electronics using a pencil. a) Schematic diagram and working principle of writing a conductive trace on cellulose paper using a pencil. b) SEM images of the lead of a pristine graphite rod with 99.999% purity. c,d) FESEM images of the graphite-coated paper using a 2B pencil writing, red arrows indicating the edge planes of the graphitic flakes (e.g., multilayer graphenes and single-layer graphene). e) The brightness of a LED is controlled based on the resistance of the pencil trace. Reproduced with permission.[1] Copyright 2015, Wiley-VCH. Reproduced with permission.[27] Copyright 2013, Royal Society of Chemistry. Reproduced with permission.[29] Copyright 2011, Royal Society of Chemistry.

the chemiresistors with disordered networks of carbon nanotubes (CNTs) show great promise for sensing gases and volatile organic compounds, Swager's group developed a rapid strategy to fabricate carbon-based (CNTs- and graphite-based) chemiresistors through writing with a home-made "pencil".[48,49,81] The "pencil" was fabricated by loading carbon nanomaterials (graphite, single-wall carbon nanotubes (SWNTs) or multiwall carbon nanotubes (MWNTs)) and selectors (designed to interact with specific classes of gaseous analytes) into a die and subsequently compressing the mixed powder into the shape of conventional pencil. The specially designed pencil was used to fabricate gas sensor on paper substrate for ammonia detection. Compared to commercial pencils, the home-made pencil holds the advantage of being capable of writing carbon nanotubes other than graphite and making selective chemiresistive sensors for different analytes. On the other hand, when using commercial pencils to write electrodes of electrochemical devices, the written working electrode is difficult to modify with suitable tailored modifiers for the detection of analytes. And the written carbon pseudo-reference electrode cannot provide stable and well-defined potentials as that applied at a standard reference electrode, such as Ag/AgCl reference electrode. To address this, Dossi et al. created home-made pencils doped with electrode modifiers and with electrochemical deposition of Ag and AgCl, respectively.[82,83] The doped pencils were fabricated by mixing modifiers or Ag/AgCl modified graphite powder with carbon powder as conductive material, sodium bentonite as binding agent and sodium silicate as hardening agent and then extruding the mixtures using a suitable die to form pencils. This method presented a simple and highly reproducible way for the production of stable and durable real-time biochemical sensors.[82,83]

Writing electronics using pencils has been proved to be a simple, rapid and solvent-free technique for the fabrication of carbon based electronics via repeated rubbing pencil lead onto substrates to form thin conductive graphite films. Besides the high conductivity of graphite, the carbon based electronics written by pencil are quite stable against moisture, chemicals, ultraviolet/radioactive radiation and natural aging.[26,60] However, since enough friction force is needed to rub off the graphite from the pencil, the writing should be done along the fiber orientation direction (e.g., of paper) to prevent fraying of substrate surface and thus reduces electrical conductivity of the obtained electronics.[29] Usually, rough surface of substrates is necessary for writing with a pencil due to the need of friction and it is thus difficult to write on smooth surface, such as glass. To address this, Brus et al. developed a simple pencil writing method on arbitrary substrates based on the salt dissolution process.[60] In their work, pencil traces were first written on a salt substrate and then placed on the surface of water to dissolve the salt, finally forming a transferrable graphite film which can be transferred onto arbitrary substrates.[60]

2.3. Fountain Pen

A typical fountain pen normally consists of four parts, including the nib as the contact point with the substrate, the feed under the nib to control the ink flow from the reservoir to the nib, a round barrel on the writing end to hold the nib and feed, and a self-filling soft rubber sac to reserve ink internally. In writing, the nib of the fountain pen contacts with a substrate, then the ink contained in the internal reservoir flows out due to capillary force and gravity action to form a mark on the substrate surface through permeation of liquid ink into the substrate (**Figure 4**a).

Similar to the brush pen-based writing electronics method, the fountain pen-based writing procedure is also based on its nature of a solution processing technique (Figure 4).[30,50] For instance, a light emitting diode (LED) circuit and a chemical sensor were fabricated using a fountain pen with carbon nanotubes as the ink,[84] where circuits were successfully written on different surfaces (e.g., curved surface of paper cup), which maintained their electrical function after a few times of trimming and creasing even under water. In another example, a series of versatile real-time sensors were fabricated for detecting ammonia gas, thermal heat and near-infrared irradiation by writing electronics using a fountain pen.[50] Besides, the sensor types can be further expanded by modifying different “inks” in fountain pen. For example, conductive polypyrrole arrays were written on A4 paper using pyrrole as polymerization agent with $FeCl_3$ through adjusting the polymerization temperature (Figure 4a–c), and the resulting conductive traces proved to be endurable with the bending of the paper substrate with negligible conductance variance (Figure 4d,e), thus further implies its feasibility as electrode (Figure 4f,g).[50] In another example, Polavarapu’s group developed a technique of direct writing surface enhanced raman scatterings (SERS) arrays on paper substrates with a fountain pen loaded with Ag or Au nanoparticle solution.[51] The written sensor has been applied to detect toxic parasiticide molecules on sample substrate with concentration of 20 ppb in a 10 µL sample volume, showing great potential to bring SERS to the real application with low cost and simple preparation protocol.

Direct writing electronics using fountain pen has wide selection range of conductive inks since the evaporation rate of the ink is limited in the reservoir and do not have big effect on the ink to flow out from the nib of fountain pen. Therefore, various conductive metal inks (e.g., Ag nanospheres and Au nanoparticles[51], the saturated $FeCl_3$ polymerized with pyrrole,[50] vapor-grown carbon nanofibers,[85] and carbon nanotube pellets[84]) have been used as the conducting materials for directly writing electronics using fountain pen. For instance, when writing electronics using carbon nanofibers as fountain pen ink, the written patterns achieved good performance on cellulose paper and showed resistance against bending, folding and crumpling stresses due to the good adhesion of nanostructured carbon materials.[84]

Fountain pen with self-supplied conductive inks provides an easy, portable and cheap technique for directly writing electronics. Besides, with the reservoir in the fountain pen, the ink has a highly uniform dispersion of microparticles/nanoparticles that can remain stable for years. Nevertheless, the popularity of writing with a fountain pen is experiencing a rapid downward trend in this decade due to the unexpected instability, discontinuity and splattering during writing, which dramatically impacts the patterning resolution of the conductive traces and further jeopardizes the performance of functional components written through a fountain pen. In addition, the time-consuming post-treatment process in some concrete applications, for example, producing a nominal cheap versatile sensor requires an at least 90-min polymerization procedure to fulfill the compact coverage of conductive polypyrrole on paper substrate and functionalization,[50] also clouds the perspective of fountain pen as a fabricating tool for flexible electronics. In the meantime, a commercial capillary pen, an apparatus with similar working mechanism with fountain pen, has recently presented as a simple and efficient patterning paradigm for the commercialization of low-cost large-area organic electronics.[70,86]

2.4. Ball Pen

A ball pen is named for a tiny metal ball at the tip of it. During writing, this ballpoint rotates to flow ink out of the ink-filling cartridge, in such way, a trace is formed on a substrate (**Figure 5**a (inset)). The ball pen employs a quick-drying ink inspired from the newspaper printing industry, fulfilling the demand for eliminating splatter and smear which often occur in writing with stereotyped quill and fountain pen. Besides, ball pen is disposable, refillable, and durable, providing consumers’ writing with reassurance, fairness and robustness, and thus is simple, practical and typically suitable for convenient and daily use. Benefiting from these excellent properties, the great potential of the ubiquitous ball pen as a portable instrument for writing electronics has gradually been unfolded (Figure 5).[23,32,37,52]

The idea of fabricating electronics with ball pen was firstly demonstrated by Lewis’ group in 2011,[32] in which a ubiquitously available roller ball pen was modified and refilled with electric conductive silver ink and employed to directly write patterns on Xerox paper. Their writing approach as a new ball pen strategy proved to be facile and feasible with the capability of configuring electronics with 3D structures in a low-cost, fast and user-oriented way. Following their work, wide academic interests on pen-based writing electronics have been ignited

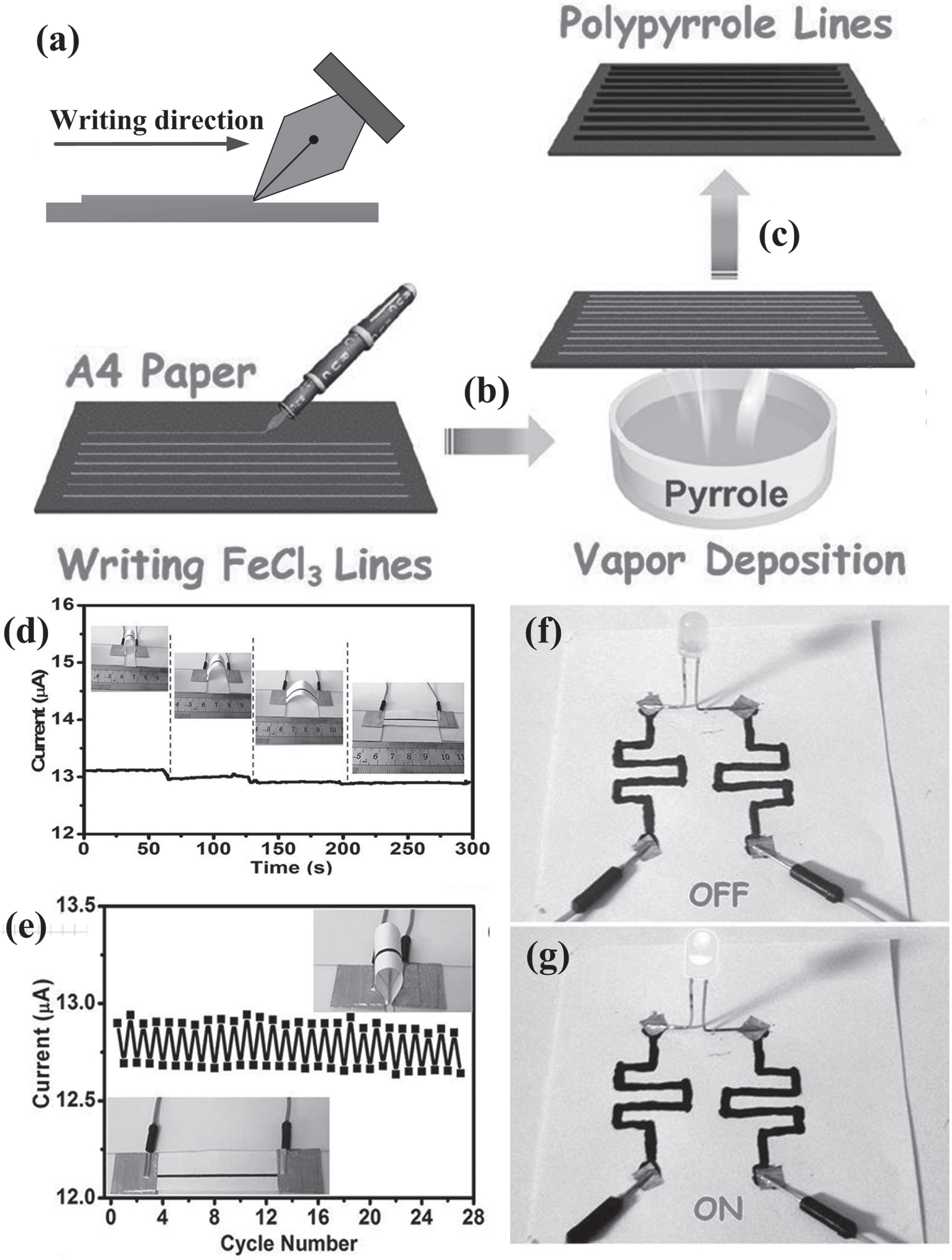

Figure 4. Writing electronics using a fountain pen. a) Schematic diagram of the working principle of the fountain pen writing. b,c) Schematic illustration of a fountain-pen-based writing technique for paper-based flexible electronics fabrication. d) Current–time curve of the fabricated conductor with 1 V applied voltage at several various bending states. e) Electrical performance of the paper conductor: current as a function of bending cycles. Different conditions of LED f) without and g) with applied voltage of 3 V. Reproduced with permission.[50] Copyright 2013, American Chemical Society.

with the increasing number of research reports on enhancing the performance of written electronics[22,33,37,62] and expanding their applications.[33,37,50,53,63,64] For instance, to improve the compatibility of conductive silver inks with paper substrate, a mechanical pressure-assisted method was introduced to reduce the temperature and time of sintering process, which was a necessary step to realize conductive traces with silver inks.[62] In another example, an on-site biocatalytic sensor was fabricated by directly writing electrodes modified with fresh active glucose-oxidase on human skin using a bio-ink filled roller ball pen for the purpose of home-based low-cost diabetes diagnosis.[37] Also motivated to the bio-related target, a pressure-assisted ball pen (**Figure 5**a) was applied to write conductive silver and carbon inks on paper with various formats (Figure 5b,c), and the conductivity of the fabricated paper electronic devices were successfully characterized (Figure 5d,e) which paved the way for its application as an electrochemical detection platform for glucose.[52] Such user-written scenarios are thus expected to provide inexpensive, renewable and so-called do-it-yourself (DIY) paradigms for glucose level monitoring.

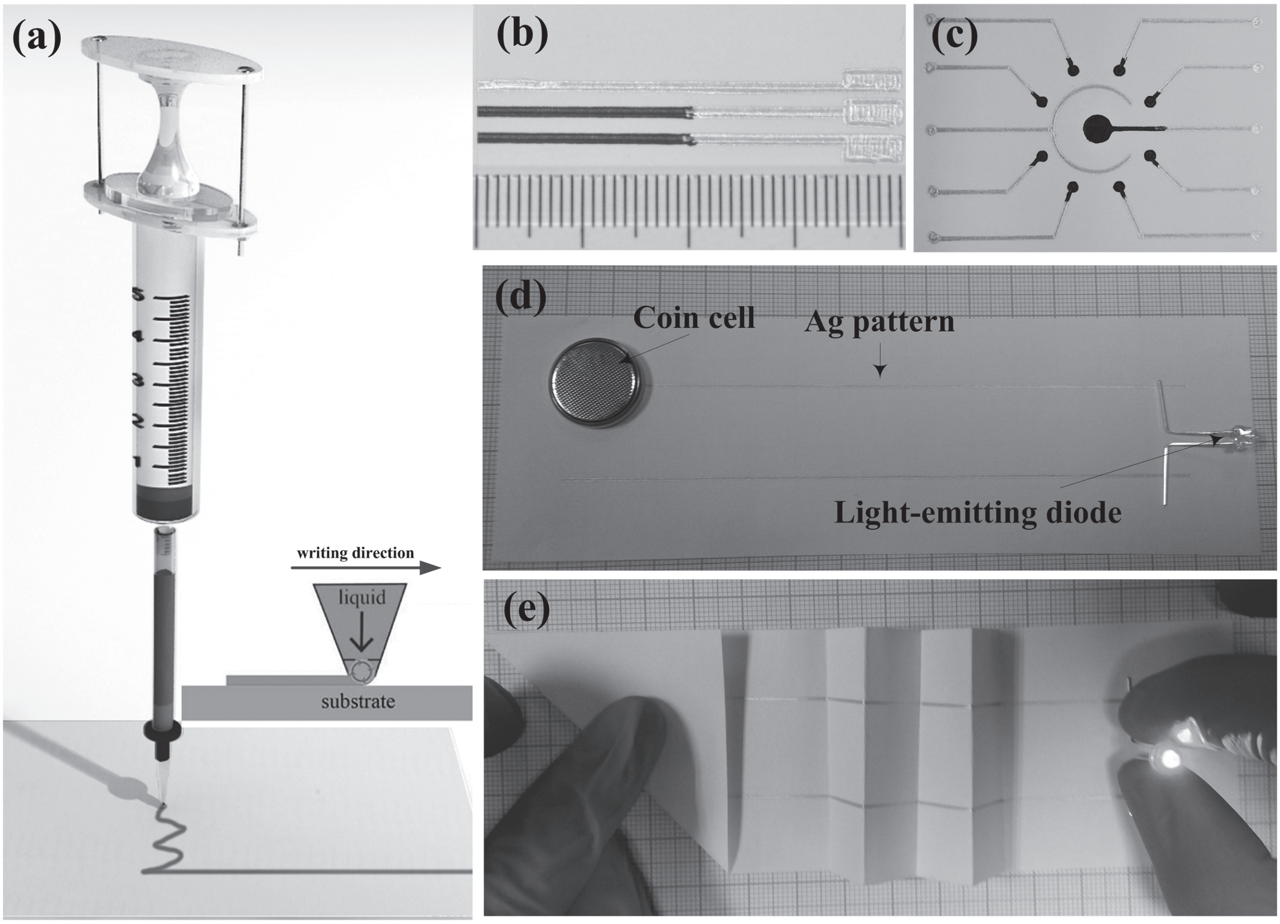

Figure 5. Writing electronics using a ball pen. a) Schematic diagram of direct writing electronics on paper using a pressure-assisted ball pen, the inset showing the working principle of the ball pen writing. b,c) Photographs of fabricated paper based electrochemical devices with b) a three electrode system of a carbon working electrode, silver reference electrode, and carbon counter electrode and c) an eight-electrode array of eight carbon working electrodes, a communal silver reference electrode, and a communal carbon counter electrode. d) The photograph of a closed loop with a coin cell and a LED connected by the written silver traces. e) The LED lights to show that the written silver traces retain conductive even after folding of paper substrate. Reproduced with permission.[52] Copyright 2015, Royal Society of Chemistry. Reproduced with permission.[34] Copyright 2014, Nature Publishing Group.

Thanks to the wide popularity of ball pen in our daily life, pens with various sizes of roller balls (ranging from 250 µm to 1 mm) are commercially available, making it facile to write electronics with variable scales and precisions for different purposes and applications. Meanwhile, unlike the pencil-based writing approach that is only capable to write carbon-related materials with fixed composition and relatively low conductivity, ball pen is compatible with various conductive inks, including the highly conductive liquid metals,[22,33] silver ink,[32,62,87] copper nanoparticles,[53,63,64] organic semiconducting crystals,[88] and enzymatic ink.[37] Silver ink holds the advantage of high conductivity but is subjected to a relatively high cost and the electrical circuit of silver suffers a problem of electro-migration.[53,64] To address this, copper nanoparticles have been considered as an alternative material owing to its high conductivity, low cost, and diminished electro-migration effect.[53,64] However, these metallic inks are associated with the main limitation of demand for high processing temperatures to form conductive patterns, restricting their wide application and compatibility with flexible substrates, such as plastic and poly(methyl methacrylate) (PMMA).[22] Room temperature liquid metal is proposed with the merit of no need for high processing temperature and thus can be extended to more substrates.[22] Further, through adapting the ball pen with multiple "ink sources", a conceptual design of writing electronic patterns with inks of different concentrations or even with diverse types of ink materials could be achieved.[34] It is noteworthy that such a device holds tremendous promise for integrated circuits fabrication where components of various conductivity and functionality are required. In addition, the versatility of the ball pen-based writing method can also be reflected by its capability with various substrate materials with different surface roughness, including paper, glass, plastic, cotton cloth, silicone gel plate and epoxy resin board.[22] Of remarkable note, human skin has now joined this family, as demonstrated by recent work using a modified roller ball pen to write electrochemical sensors on human skin with biocompatible enzymatic inks for real-time glucose monitoring.[37] Meanwhile, directly writing electronics using ball pen is also facing some challenges. For instance, for writing metallic inks such as silver nanoparticles[62,87] and copper nanoparticles,[53,63,64] an extra time-consuming sintering step (≈2 hours) is needed to enhance the conductivity of metallic patterns after being written on substrates, where the need for high temperatures (up to 160 °C[64]) further complicates the whole fabrication process. Even though various conductive traces working as electrodes or interconnects have been successfully written on different substrates using ball pen,[22,33,63,64] more complicated electronic components have not been achieved yet.

2.5. Pen-Analogue Writing Techniques

The limited productivity of handy-writing tools has set a challenge for their long-term perspective in fabricating electronics. Recently, to fulfill the demand of mass production for practical applications, pen-based writing methods have been combined with high-throughput printing technologies, named as pen-analogue writing techniques in this review, to facilitate the commercialization and wide-spread applications of pen-based techniques in electronics manufacturing. The phrase "pen-analogue writing techniques" refers to a family of emerging new direct writing techniques beyond traditional pen-based methods, including electrohydrodynamic direct writing (**Figure 6**)[40,89] and microplasma-based direct writing approaches.[41] The electrohydrodynamic direct writing is a method of fabricating conductive/semiconductive nanofibers, through pulling a fluidic material into liquid jet to form solid patterns using electric field force[90] or centrifugal force.[91] It has been reported to be an economical and rapid way to fabricate various nanofibers with diameters less than 100 nm on different substrates.[40] Additionally, it is compatible with materials with high viscosity (e.g., polyurethane in dimethylacetamide with viscosity of ≈725 mPa m[92]), expanding the selection range of electronic patterning materials. The electrohydrodynamic direct writing method has been utilized to fabricate ZnO nanowires for field effect transistors (FET)[93] and solar cells.[94] To further fulfill the demand of controlled alignment and assembly of semiconducting nanowires for nano-scale optoelectronics, an electrohydrodynamic printer was exploited to fabricate organic FETs with nanoscaled channel length and width (Figure 6a,b). This method presents an effective route for fabricating large area FET arrays with excellent output characteristics and transfer performance and even the integration of inverter array (Figure 6c–f).[21] The other pen-analogue writing technique, microplasma-based direct writing method, is mainly applied to produce electrically conductive metal patterns on polymer surfaces.[41] It involves loading conductive metal ions on substrate surfaces and then exposing the substrates under scanning microplasma process, which induces local reduction reactions between cations in metal film and electrons in plasma to form electrically conductive nanoparticles. The produced nanoparticles nucleate and aggregate to conductive metal particles, forming a percolating network.[41] A recent research reported that the microplasma-based direct writing method could fabricate Ag traces with line width of 300 μm, thickness of 5 μm and sheet resistance of 1–10 Ω sq^{-1}.[41] Recently, a brand new pen-analogue writing technique based on the evaporative deposition of propelled anti-pinning ink droplets (PAPIDs) was proposed for continuous and conformable conductive patterning on flexible substrates even with 3D concave geometry.[95] Such PAPID printing method can provide well-defined deposition of nanometeric materials with controlled thickness gradient and resolution (spacing down to 30 μm),[95] thus it is appealing for future researches on flexible electronics and bio-related technology.

Compared to the pen-based writing electronics, the main advantage of the pen-analogue writing methods is their versatility on the selection of both electronic "ink" and substrate. During conventional writing electronics, the choices of conductors and substrates are dependent on the mechanism of writing process, the wetting behavior, the capillary phenomenon of the nib and the topographical structure of the substrate.[8] Based on the distinct working mechanisms, these pen-analogue methods are suitable for once regarded "non-writable" materials. Unlike other new emerging techniques for fabricating electronics, such as scanning probe lithography,[96] photolithography,[97] and vapor deposition,[98] the pen-analogue direct writing techniques only require simple processes and equipment. Featuring the wider selection of materials and lower facility requirement, the pen-analogue writing techniques hold great potential for the commercialization and mass, wide-spread manufacturing of writing electronics.

3. Emerging Applications of Pen-Based Writing Techniques

3.1. Biomedical and Electrochemical Sensing

For biomedical applications, the most outstanding advantage of direct writing electronics is its capability of patterning self-serviced circuit in bioelectrical detection devices. A strategy of electrocardiogram (ECG) conducted by a skin circuit based on liquid metal ink (e.g., the Gallium-based liquid metal ink) with good conductivity and low toxicity has been reported recently,[38] providing a promising way to address the challenges of coupling performance, discomfort, manufacturing complexity and high cost of the conventional rigid biomedical sensors.

In recent years, the paper-based electrochemical devices have attracted much attention based on its low cost, ease to use, and application in point-of-care testing with low detection limits and high sensitivity. The key component of the paper-based electrochemical devices, the electrode, is usually fabricated on paper by screen printing or sputtering techniques. But these approaches demand professional instruments and skilled operator, thus blocks their applications for point-of-care purposes. Recently, pencils have been proposed to write carbon electrodes of paper-based electrochemical devices.[54,77,78,82,83,99,100] In addition, an enzymatic ink-based ball pen for direct writing of electrochemical biosensors (**Figure 7**a) was recently proposed by Wang et al.[37] The prepared enzymatic-ink pen enables the direct writing of glucose-oxidase on human skin (Figure 7b), which avoids the need of enzyme immobilization on electrodes steps and realizes the one-step fabrication of biocatalytic sensors that can subject to twisting and stretching of skin (Figure 7c,d). Surprisingly, signals detected from such a pen-written sensor displays good correlation with the response of a

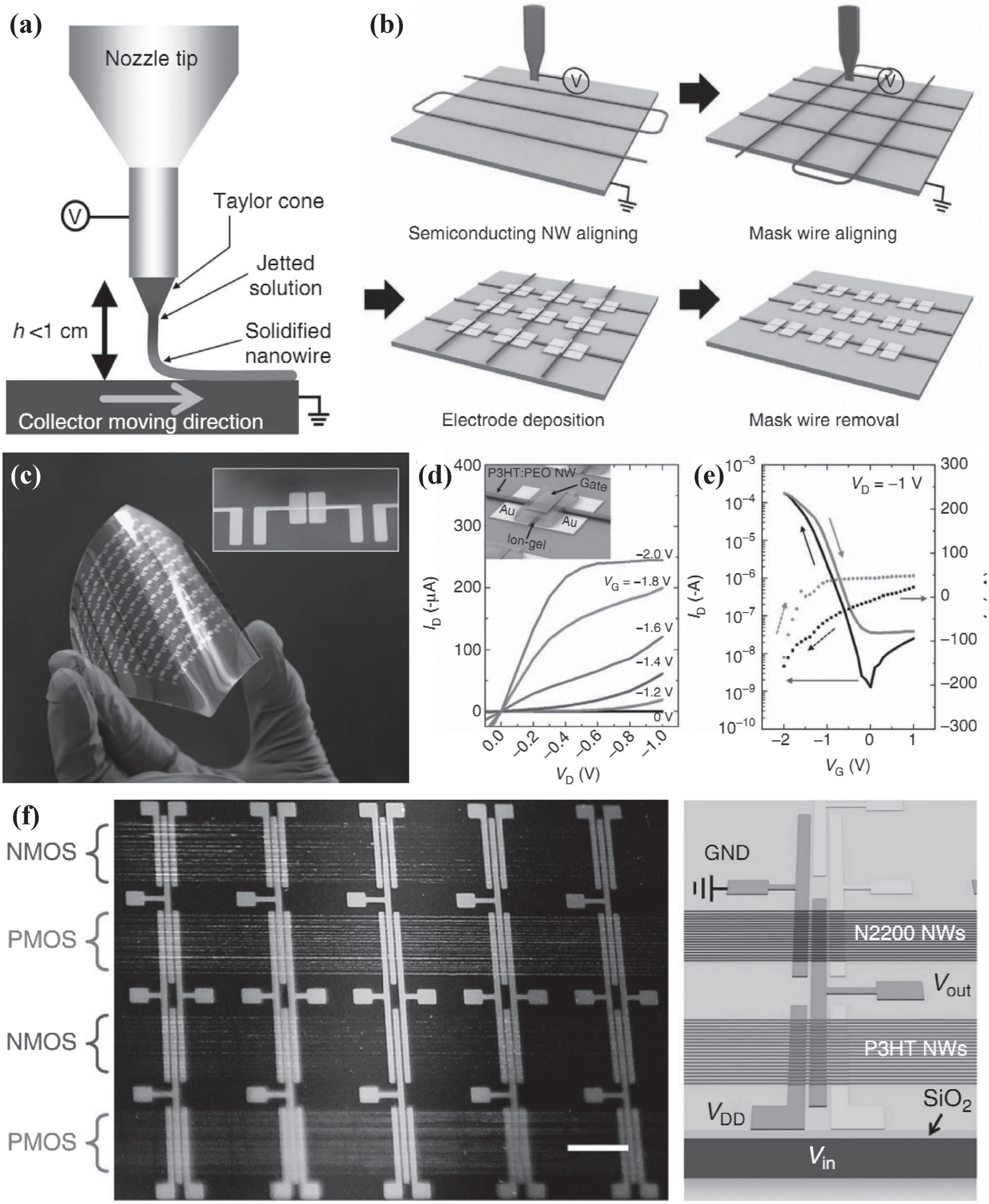

Figure 6. Writing electronics using pen analogue devices. a) Schematic diagram of an electrohydrodynamic writing device. b) Schematic of the fabricating process of organic FET with channel length and width in nanoscale. c) Large-area single poly(3-hexylthiophene):poly(ethylene oxide) (P3HT:PEO) nanowire FET array on plastic. d) Output characteristics curve (inset: device structure) and e) transfer characteristic (solid line) and gate current as a function of gate voltage characteristics (dot line) of the fabricated FET. f) Left: optical image of an array of inverter (scale bar is 2 mm); right: schematic of a single inverter. Reproduced with permission.[89] Copyright 2013, Nature Publishing Group.

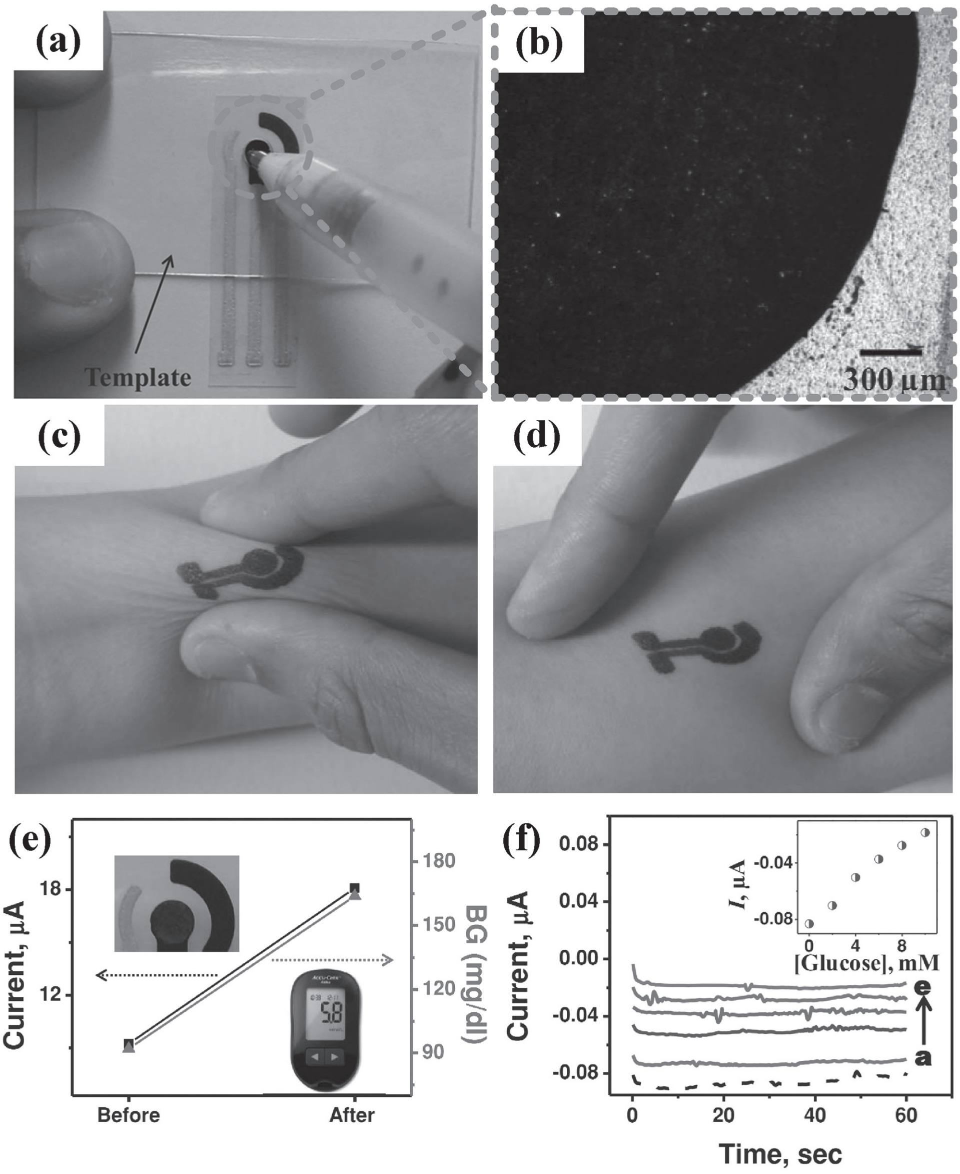

Figure 7. Direct writing of glucose monitoring sensors with a ball pen. a) Writing of the active enzyme layer onto a template to achieve biocatalytic sensors using a glucose oxidase ink-filled pen. b) Microscopic image of the enzymatic sensor surface indicates a uniform coating of enzyme layer written with the modified ball pen. c,d) Epidermal glucose monitors realized by direct writing of biocompatible glucose oxidase ink on skin can endure twisting (c) and stretching (d). e) Data obtained from the pen writing sensor (left arrow) in correlation with the response of a commercial glucose meter (right arrow). f) Ameperometric data, obtained from sensor on skin, for growing glucose levels ranging from 0 (dashed line) to 10×10^{-3} M. Inset is the calibration figure for the on-skin glucose sensor. Reproduced with permission.[37] Copyright 2015, Wiley-VCH.

commercial glucose meter and the responses for different glucose levels are clearly identified (Figure 7e,f).[37]

3.2. Electronic Components

Electronic circuits are generally composed of active components (e.g., transistors, diodes, interconnected circuits) and passive components (e.g., resistors, inducers, capacitors). Conventionally, components are fabricated with complex procedure needing expensive facilities. The emerging writing techniques enable rapid, low cost, and convenient written-by-hand electronics fabrication (**Figure 8**).[1,32] For example, direct writing of resistors, capacitors and inducers have been achieved via writing conductive Gallium-based liquid metal with brush pen[25] and ball pen,[33] such strategies only require simple tool and merely room temperature, enabling paper-based low-cost disposable writing electronics.[25] Furthermore, the commercialization potential of these pen-based writing electronics have been continuously revealed especially in electronic arts and STEM (science, technology, engineering and mathematics) education for pre-school children.[32] In a demonstration, a roller ball pen was applied to draw conductive silver traces on Xerox paper to light up a LED on a Chinese painting.[32]

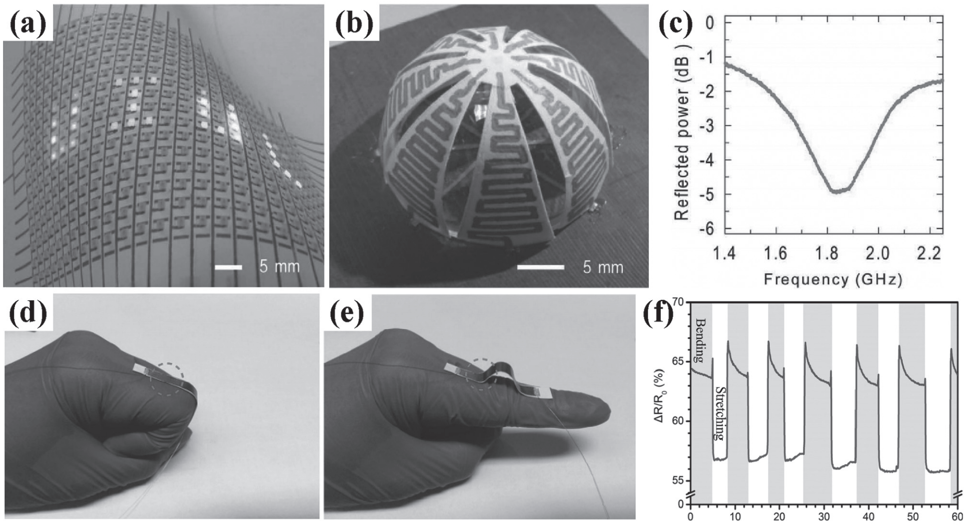

Figure 8. Electronic components and devices manufactured by pen writing. a) Optical image of a flexible paper display containing a LED array with the written conductive silver interconnects. b) Optical image of the 3D antenna achieved by writing conductive silver ink on a sticky paper. c) Performance characterization of the 3D antenna: reflected power as a function of frequency. d,e) The wearable strain sensor attached onto a forefinger for detecting human motion, with the red dotted line circles indicating the deformation section of the device under bending and stretching states of the finger. f) Relative resistance change plot during a 60-second finger bending test, indicating that the strain sensor is able to monitor human motion. Reproduced with permission.[1] Copyright 2015, Wiley-VCH. Reproduced with permission.[32] Copyright 2011, Wiley-VCH.

Organic transistors, possessing superb electrical performance in amorphous or poly-crystalline films, are nominated as the foundation of modern electronics.[88] It is recently reported that solution-processed organic crystals for FETs have been written directly on Si/SiO$_2$ substrate using a roller ball pen.[88] The organic semiconducting crystal grains, dioctylbenzothienobenzothiophenee (C$_8$-BTBT), with widths of several hundred micrometers were deposited on a pre-fabricated Si/SiO$_2$ surface as a channel material by an ordinary roller ball pen filled with C$_8$-BTBT solution. Furthermore, with the assistance of thermally deposited MoO$_3$ and shadow-masked deposited Au acting as source and drain electrodes, this organic FET exhibits a field effect mobility of 0.7 cm^2 V^{-1} s^{-1} and an on/off ratio of more than 10^7.[53]

For functionalization, integration in flexible display (Figure 8a) and manufacturing of three-dimensional functional antennas (Figure 8b,c) both turned out to be compatible with pen-based writing tactics.[32] Furthermore, a body-worn strain sensor for human motion detection (Figure 8d,e) was achieved by drawing graphite traces with pencil on a piece of paper, and the testing results showed remarkable differences under diverse degrees of deformation of human skin (Figure 8f).[1] Additionally, with the conformable PAPID printing of oppositely graded gold nanoparticles as two parallel sensing layers on soft polymers, a flexible linear strain sensor was realized for real-time sensing of position and strain of mechanical deformations in a smart patch.[101]

3.3. Energy Storage Devices

Simple, cost-effective, and eco-friendly energy storage devices have received colossal public attention ever since the start of the new millennium due to their promising application perspectives in some burgeoning areas, such as functional wireless electronic systems[102] and green automobiles.[103] Considering the demand for cost-effectiveness and simple fabrication technique in these application realms, direct writing method has stood out as a simple, rapid and ultra-low-cost strategy, especially for the flexible energy storage devices fabrication.[28,29,61,72]

Pencil rods have been applied to pattern conductive traces of flexible electronics[26] and to write electrodes of power sources (e.g., fuel cells,[72] lithium–air batteries,[28] and supercapacitors[29,61]). With the cooperation of another omnipresent material, paper serving as substrate and separator, pencils have been employed to write directly on it to further reduce the manufacturing cost and enhance the environmentally friendly property in supercapacitors production (**Figure 9**a–c), without sacrificing charge/discharge performance (Figure 9d), areal capacitance (2.3 mF cm^{-2}) (Figure 9e) and long-term cycling performance, which is of nearly zero decay of capacity up to 3000 cycles and 90% capacity retention after 15000 cycles (Figure 9f).[29] In addition, brush pen has also been applied for fabricating flexible organic solar cells in a simple, low-cost and atmospheric process.[47,55,56,66] In particular, thanks to the shear stress provided by the painting brush, conductive inks composing particles (e.g., silver nanowires,[47,66] Ti-doped In$_2$O$_3$ nanoparticles[55] and carbon nanotubes[56]) can pledge well-connected junctions and uniform coating with smooth surface morphologies, contributing to a low sheet resistance (26.4 Ω sq^{-1}[47]) in such devices.

4. Conclusions, Challenges and Future Perspectives

The research on writing conductive and semiconductive patterns onto soft substrates using low-cost, ubiquitous pens is

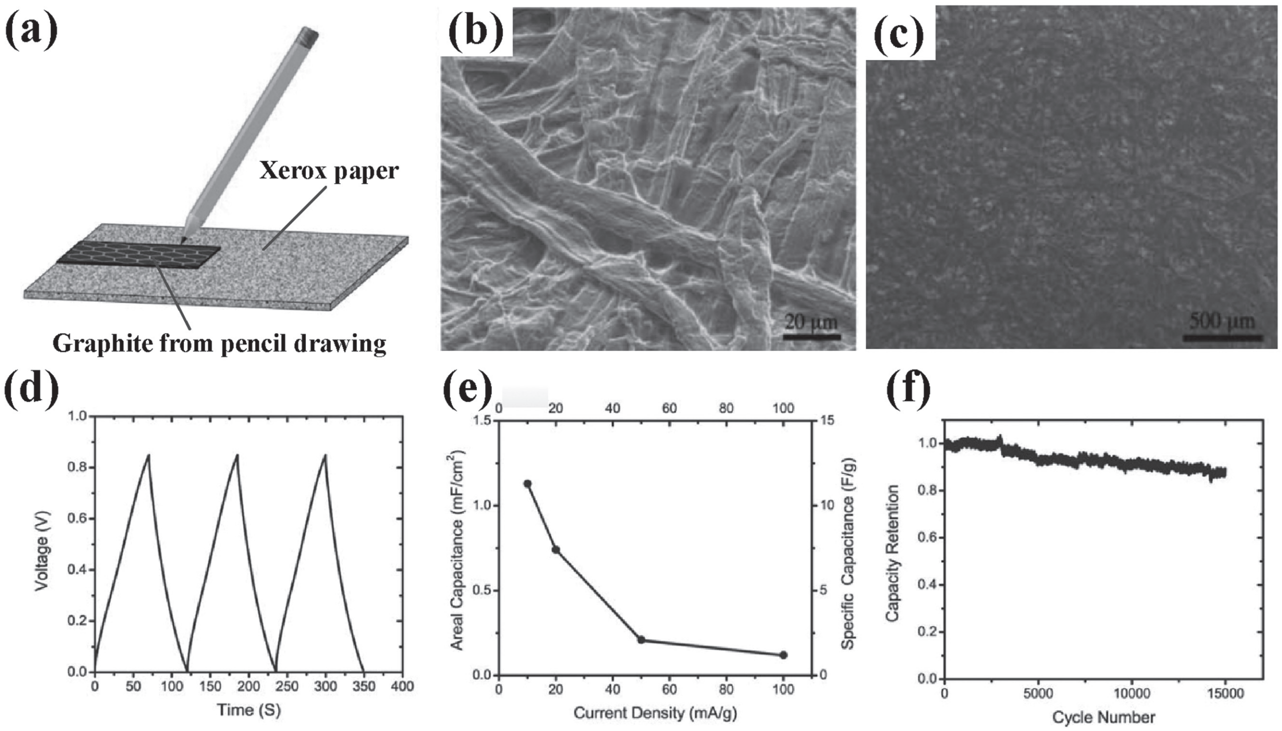

Figure 9. Paper supercapacitors fabricated by pencil writing. a) Schematic of writing conductive electrodes of supercapacitors on a Xerox paper employing a graphite pencil. Surface morphology of Xerox paper b) before and c) after graphitic coating via a pencil. d) Charge/discharge curve of the paper supercapacitor at a current of 200 mA g^{-1}. e) Areal and specific capacitances of the fabricated supercapacitor at various current densities. f) Cycling performance of the supercapacitor. Reproduced with permission.[29] Copyright 2011, Royal Society of Chemistry.

currently undergoing an encouraging development as a promising approach for fabricating flexible electronics in an ideally cost-effective, rapid, and portable manner. Such a combination of basic hand-held tools and modern electronics moves a significant step towards enabling DIY fabrication and desktop manufacturing of wearable electronic devices, body-worn biomedical sensing and diagnostic systems and rechargeable power supplies. Traditional writing instruments including brush pen, pencil, fountain pen and ball pen have all been ingeniously modified as practical apparatus for achieving writing electronics. Recently, a novel pen-analogue technique has been developed to be available to enhance the compatibility with highly viscous inks with the help of professional devices, which further expands the selection range of ink materials.

However, it is worth of notice that although the writing process proves to be rapid and portable, it is a bit far away from an ideally simple and cost-effective method for fabricating electronics, considering the complicated after-treatment procedures. The involved conditions like long time, high temperature, and vacuum atmosphere are essentially required for some specific circumstances. The other evident challenge for pen-based direct writing electronics refers to the present shortage of accessibility with complicated electronic components and devices, and even integrated circuits, which are of crucial importance to electronics industry, despite the success in writing conductors and electrodes.

Hence, it is suggested that more fundamental work is urgently needed to focus on developing new ink materials and applying new technology to reduce time and energy consumption in post-treatment processes, thus perfect the direct writing paradigm. Additional attention should also be paid to enhancing the integrity of the written electronics by fabricating components with advanced functionalities and integrating them with energy storage devices into a fully integrated circuit. Moreover, the issue of massive production of such pen-based writing electronics remains. Although these tactics show remarkably appealing features in cost-effectiveness and rapid prototyping, it is not yet persuasive as practical fabrication tools for real-life electronic applications. Therefore, the combination with printing technology with enhanced productivity, namely the pen-analogue writing technique, is worthy of efforts and investments to boost the sparkling pen-based writing electronics into wide-spread manufacturing. With these upgrades accomplished, the pen-based writing electronics technique can literally transform our whole world into a potential electronic playground.

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