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Paper supercapacitors by a solvent-free drawing method†

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We designed and fabricated supercapacitors by directly drawing graphite on cellulose paper. The supercapacitors show stable long cycling performance and a high areal capacitance of 2.3 mF cm^{-2}, which is much higher than the literature reported values. This solvent-free deposition technique represents a low cost, highly scalable and versatile fabrication method for integrated paper-based energy devices.

Developing low cost, flexible and environmentally friendly energy storage devices is highly desired for a wide range of applications, including flexible electronics, radio-frequency identification devices (RFID) and wearable gadgets.[1–5] The strong interest in this area has led to a number of works on polymer, paper and textile-based devices.[6–14] Electronically conducting polymers (ECP) such as polypyrrole[10,15] and polyaniline,[14] in addition to carbon nanotubes[7–9,15–17] and chemically derived graphenes, are some of the most commonly used electrode materials.[18–20] Recently, our group also developed energy devices based on conductive paper and textile by conformally coating carbon nanotubes on the surface of macroporous fibers, through a solution-based process. These power devices are highly promising for all-integrated paper and textile electronics.[9,11,21] However, many of these processes involve environmentally unfriendly chemicals and elaborate procedures. The cost of carbon nanotubes is still prohibitive,[22] and most of the graphene supercapacitors reported employ the harsh oxidation–reduction process at high temperature to produce the graphene sheets.[18,19,23,24] Solvent-based processes such as inkjet-printing and Meyer rod coating of carbon nanotubes have been shown to be potentially scalable methods for fabricating flexible electronics and energy storage devices.[25–27] Such processes generally involve dispersing the coating materials in a special solvent with certain type of surfactant, followed by reforming the film on a substrate. Preparation of stable ink with the right rheological properties is critical for successful film formation. After deposition, high temperature annealing or washing is required in order to remove the surfactants and improve conductivity. Plasma treatment of the substrate surface is also generally performed to improve its wettability and enhance film adhesion.[28,29] These requirements on ink properties and the post-treatments pose challenges for a wide range of applications of the solution-based methods. Successful application of low cost, flexible energy devices lies in the development of fabrication methods that are based on inexpensive materials and can be easily scaled up.

Here we demonstrate a simple solvent-free deposition method to fabricate supercapacitors on cellulose paper using graphite rods or pencils. The process is analogous to drawing with regular pencil on paper. Pencil rods are well known to be electrically conductive and have been used to fabricate electrodes for lithium air batteries by drawing on a ceramic separator.[30] The idea here was inspired by the fact that pencil trace on paper is highly conductive and graphite is an

Broader context

Flexible energy storage systems have many applications in roll-up display, flexible electronics and wearable devices. Significant efforts have also been put into developing energy storage devices that are environmentally friendly and based on earth-abundant materials. Among the many types of energy storage technologies, supercapacitors have several advantages, such as quick charge/discharge process, high power density and long cycling life, owing to their non-faradic charge storage mechanism. Flexible supercapacitors based on carbon nanotubes, graphenes or electronically conductive polymers have been previously reported. However, most of the works utilized solution-based processes to fabricate the electrodes, which involved dispersing the active materials in a special solvent, followed by reforming the electrode on a substrate. The use of environmentally unfriendly chemicals and the requirements of post-treatment pose challenges for the wide applications of the techniques. In the present work, we report a new approach to fabricate supercapacitors by drawing with a graphite rod on standard printing paper. The supercapacitors thus fabricated show stable long cycling performance with 90% capacity retention after 15 000 cycles and a high areal capacitance of 2.3 mF cm^{-2}. The drawing approach demonstrated here could be extended to fabricate other types of low cost energy storage devices.

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excellent electrode material for electrochemical double layer formation. In addition, the highly porous paper substrate serves as an excellent separator for the supercapacitor, allowing rapid diffusion of ionic species.[9,10,21] The deposition technique can be potentially extended to fabricate low cost electrodes for circuits, electrodes for lithium ion batteries and other electronic devices.

To demonstrate the concept, a supercapacitor electrode was fabricated by simple drawing with a graphite pencil on Xerox paper (Fig. 1a). For accurate characterizations, the graphite rods used in this experiment were purchased from Sigma Aldrich and had 99.999% purity (metal basis). Ruler-guided drawing in orthogonal directions was repeated three times to form a stripe of uniform coating. Since cellulose fibers in Xerox paper have a global alignment along the long side, the first round of drawing was done in the direction of the fiber orientation. This was important in order to prevent fraying of the paper surface, which would result in a significant reduction in electrical conductivity of the paper electrodes. Fig. 1b shows that the graphite trace is very stable even on bending down to a radius of 2 mm. The electrical resistance of the graphite stripe on paper was measured at different lengths (for a stripe of graphite 2 cm in width). The resistance of the conductive stripe showed a linear correlation with distance, indicating a relatively uniform coating of graphitic materials on the surface (Fig. 1c). Sheet resistance was measured to be around $223\ \Omega\ \square^{-1}$. To fabricate the supercapacitor, a separator (Xerox paper) was sandwiched between two conductive paper electrodes (Fig. 1d). This paper separator was needed in order to prevent potential short-circuiting due to occasional penetration of the deposited graphites. When in-house paper was used as the drawing substrate as discussed later, the same paper is used as the separator and the whole supercapacitor is integrated into a single piece of paper.

Morphological changes of the graphitic materials upon drawing on paper were examined with scanning electron microscopy (SEM). Fig. 2a and b show that the pristine graphite rods are composed of irregular grains, where graphitic flakes are highly stacked to form a compact structure. The rough surface structure of paper enables exfoliation and adhesion of the graphitic materials (Fig. 2c), which not only form continuous conducting paths on the surface, but also provide significant adsorption area for double layer formation (Fig. 2d). In an effort to increase the graphite surface area for supercapacitor application, previous approaches mainly utilized high-energy ball milling for an extensive period of time to produce smaller graphite particles.[31,32] The shear peeling method demonstrated here leverages on the anisotropic mechanical properties of graphite and has been previously shown to produce a variety of graphitic flakes, including small amounts of single-layer graphenes.[33] The binding force between the graphene layers is approximately 2 eV nm^{-1}, which translates to about 300 nN for shearing 1 μm^2 graphene sheet (assuming a friction coefficient of 1).[34] The drawing of graphite on paper produces multilayer graphenes (MLG) with a large portion of edge structures (Fig. 2e).

Raman spectra of both pristine graphite rods and the graphitic materials on paper were measured to study the structural change upon drawing (Fig. 2f). The G band is attributed to the doubly degenerate in-plane E_{2g} vibration mode, while the D and D′ bands are due to the disorder-induced mode from Raman scattering at the

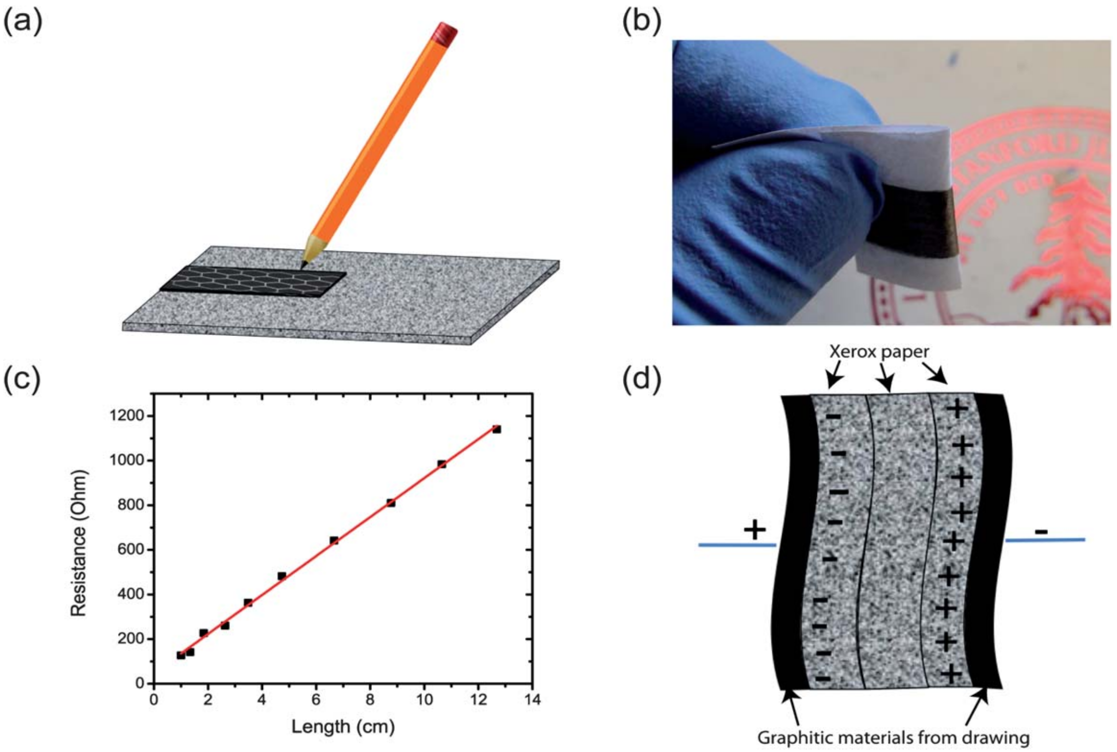

Fig. 1 (a) Schematic diagram of drawing conductive electrode on cellulose paper using a graphite pencil. (b) Digital camera image showing the finished conductive paper electrode from drawing. (c) Resistance measurement of the graphitic coating on paper (width of the graphite stripe is 2.0 cm) over different lengths. (d) Schematic diagram of the paper supercapacitor device.

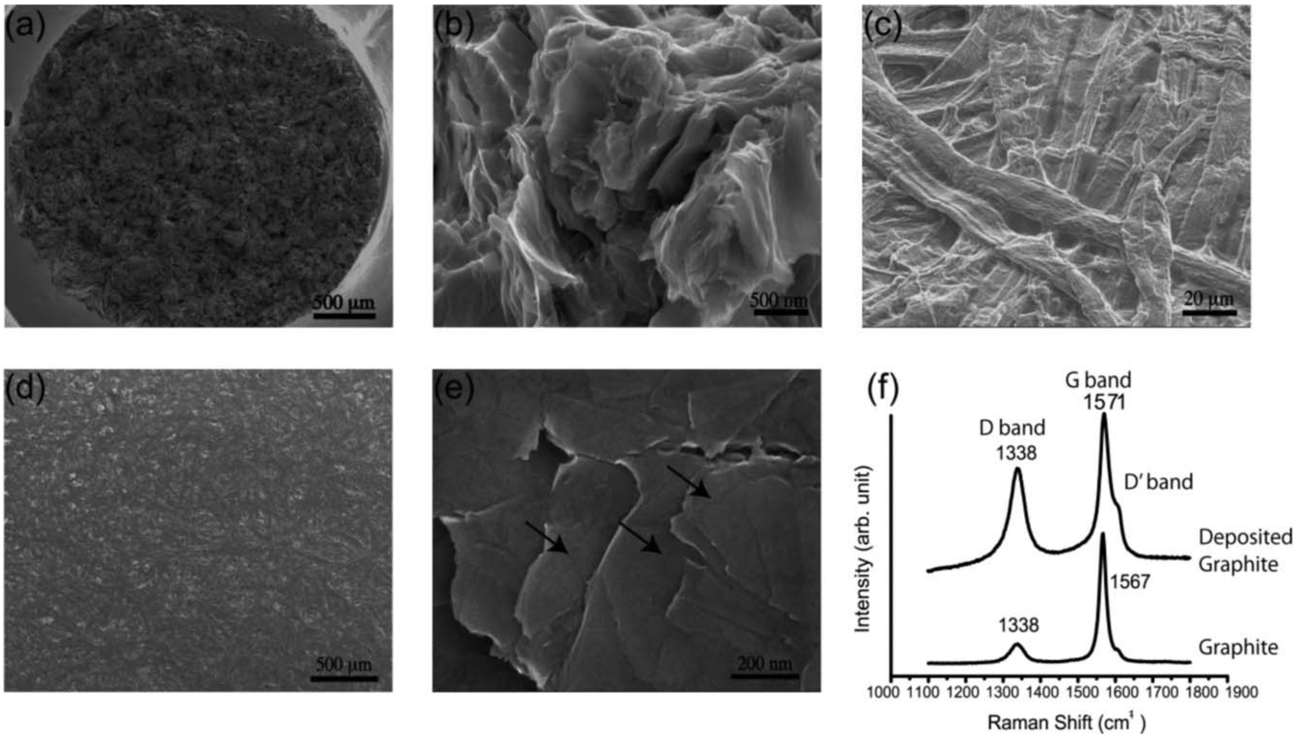

Fig. 2 Morphologies of the graphitic materials before and after deposition on cellulose paper. SEM images of (a and b) pristine graphite rod at different scales, (c) surface morphology of Xerox paper, and (d and e) graphitic materials deposited on Xerox paper. Arrows indicate the edge planes of the graphitic flakes. (f) Raman spectra of both pristine graphite rod and graphites deposited on paper.

graphene edges. The spectra show that in the pristine graphite rods, the intensity of the D band is much weaker than the G band, as compared to the spectrum for the graphitic materials on paper. The higher I_D/I_G ratio for the deposited graphites indicates a high proportion of edge defect features, which are beneficial for electrochemical capacitance. The strong D band intensity could be explained by two factors. First, decrease in the number of stacked graphenes allows more edge planes to be exposed. Second, shearing also causes the AB stacking to be less aligned and increases the degree of disorder in the deposited graphites.[35] Disorder in graphene alignment is important in reducing the anisotropic properties of graphitic materials and thus useful in many practical applications. The blue shift in the G band frequency corresponds to a decrease in the number of graphene layers, which was also reported by a previous study.[36]

For electrochemical testing of the supercapacitors, a small piece of platinum was attached to each electrode. The area overlapped by the active materials on both sides of the paper electrode was 1 cm^2. The supercapacitor was soaked in the aqueous electrolyte (1 M H_2SO_4) for about 10 minutes before being sealed in a polymer bag (Sigma-Aldrich) to form a pouch cell. Mass loading of the supercapacitor was controlled at 0.1 mg cm^{-2} on a single side of the paper. Electrochemical testing was performed using a Bio-Logic VMP3 battery tester. Fig. 3a shows the galvanostatic cycling performance of the Xerox paper supercapacitors at a constant current of 200 mA g^{-1}. The potential between the two electrodes was swept between 0 V and 0.85 V. Specific capacitance is calculated from the slope of the discharge curve and the results show that the as-fabricated supercapacitors have a high areal capacitance of approximately 1.13 mF cm^{-2} (Fig. 3b). This value is ~90 times higher than the previously reported value of 12.4 μF cm^{-2} from thermally exfoliated graphene and sulfuric acid.[37] Areal capacitance is an important indicator of supercapacitor performance in applications such as small scale electronics.[38] Electrodes that have very low mass loading of active materials are likely to achieve very high gravimetric capacitances, but poor areal capacitances.[39,40] Comparison of areal capacitance in the current context is thus more appropriate in light of the low cost and low density of the materials used. The high area-normalized capacitance of the paper supercapacitors could be attributed to both the large amount of graphite edge planes and the hierarchical porous structure of the paper substrate. The graphite edge planes have one of the highest specific double layer capacitances among all the carbon materials. The capacitance of a graphite basal plane is about 3–4 μF cm^{-2}, while the edge structure has a capacitance of about 70–100 μF cm^{-1}.[41] The relatively low basal plane capacitance is due to the space charge contribution to the capacitance C_{sc}, which forms a series capacitor with the Helmholtz double layer electrochemical capacitor. The low C_{sc} results in a small overall capacitance of the basal planes. The edge planes on the other hand do not have the space charge capacitance and hence give a larger overall capacitance. In addition, the residual surface bonds with "dangling valencies" provide ideal sites for the oxidation–reduction process and give rise to significant pseudocapacitance.[42] The oxygen functionalities on the graphite edges also contribute to higher ionic adsorption. The gravimetric capacitance was measured to be around 12 F g^{-1}, which is a reasonable performance for the un-optimized device and it is comparable to some of the literature reported values of supercapacitor performance using active carbon (~12.6 F g^{-1})[43] and untreated carbon nanotubes as electrodes.[44]

High porosity in the paper substrate allows rapid access of electrolyte to the electrode surfaces. In addition, adhesion onto the paper

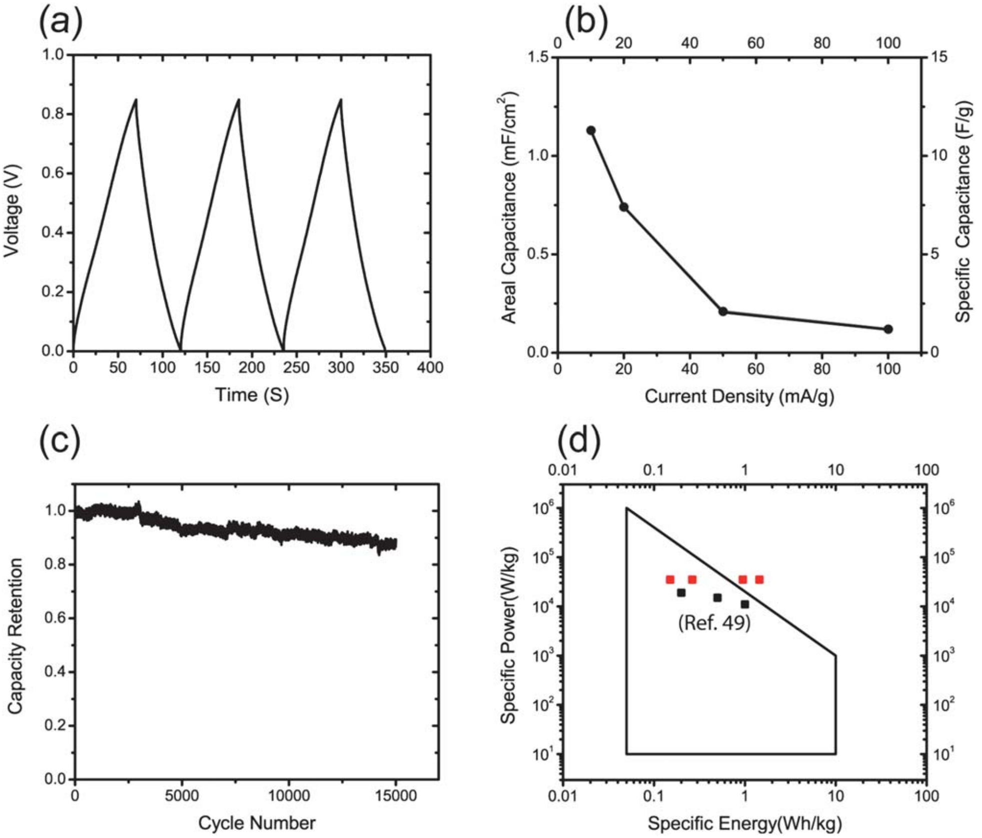

Fig. 3 Electrochemical performance of the as-fabricated supercapacitors. (a) Galvanostatic charge/discharge curve at a constant current of 200 mA g^{-1}, using 1 M sulfuric acid electrolyte. (b) Areal and gravimetric capacitances of the supercapacitor at different current densities. (c) Cycling performance of the supercapacitor. (d) A Ragone plot showing the specific energy and power densities at different current densities for the paper supercapacitors (red). The trapezoid shows the performance of commercial devices from ref. 47. A plot of carbon fabric supercapacitor performance based on 1 M sulfuric acid from ref. 49 is also presented (black).

surface increases the hydrophilicity of graphites and thus wettability of the electrodes. Without the paper substrate, the highly hydrophobic graphite surface[45] will significantly undermine double-layer capacity of the device.

The long term cycling behavior is one of the key parameters in evaluating supercapacitor performance. The as-fabricated paper supercapacitor was cycled at 500 mA g^{-1} in sealed polymer bag with 1 M sulfuric acid electrolyte. Fig. 3c shows the supercapacitor has

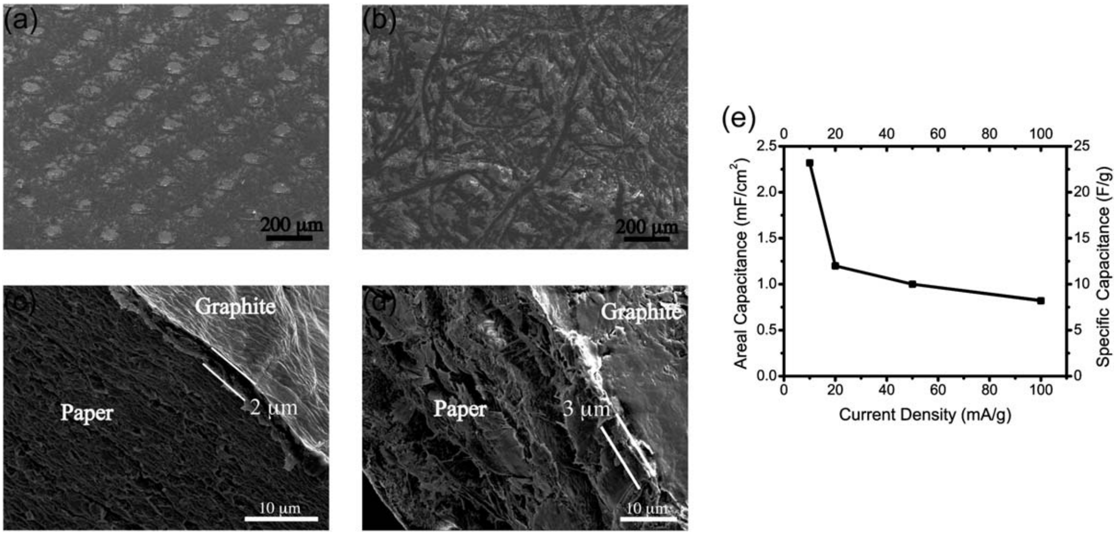

Fig. 4 (a and b) Top view SEM images of in-house paper and Xerox paper deposited with graphites. (c) and (d) 45° tilt view of (a) and (b) respectively, with thickness of the graphite coating indicated. (e) Areal and gravimetric capacitances of the supercapacitors based on in-house paper at different current densities.

excellent cycling performance with nearly 100% retention of capacity up to 3000 cycles. After 15 000 cycles of testing, the capacity was maintained at around 90%. The slow decay was likely due to the oxidation of graphitic surface by sulfuric acid.[46] The Ragone plot (Fig. 3d) shows that the specific energy and power densities of the paper supercapacitors are reasonable as compared to commercial supercapacitor[47,48] and other carbon-based supercapacitors in 1 M sulfuric acid electrolyte.[49]

Further improvement of the supercapacitor performance can be achieved in several manners. Nitrogen plasma treatment is one possible approach as it has been recently shown to improve the performance of graphene-based supercapacitors, due to enhanced ionic adsorption from the nitrogen doping.[50] Controlling graphite deposition on paper is another option, which can be done by modifying the paper surface or controlling the pressure used for drawing with a robotic arm. Surface modification of the paper substrate was explored here to study its effect on the supercapacitor performance.

In-house paper was fabricated using a standard pulp filtration process (see ESI† for details). The surface texture was modified during drying by using an iron mesh, which results in arrays of imprints on the paper. The surface texture of the in-house paper is smoother and more uniform than Xerox paper (Fig. 4a and b). The cross-sectional SEM images show that graphite exfoliation could be improved with the uniform surface texture (Fig. 4c). The thickness of the deposited film was measured to be around 2.0 μm (±0.5 μm). The relatively rougher surface on Xerox paper results in the deposition of bigger graphitic flakes (Fig. 4d) and a thicker film around 3 μm (±1 μm). With the same mass loading of 0.1 mg cm^{-2}, supercapacitors assembled using the in-house paper showed improvement in overall capacitance at different current densities (Fig. 4e). At 200 mA g^{-1}, the areal capacitance is 2.3 mF cm^{-2} for supercapacitors fabricated using in-house paper, as compared to 1.13 mF cm^{-2} using Xerox paper. The gravimetric capacitance was measured to be around 23 F g^{-1}, which also showed improvement over the Xerox paper design.

Conclusions

In summary, we demonstrated the concept of fabricating supercapacitors by directly drawing on cellulose paper with a graphite rod. The shear peeling of graphites produces multi-layer graphenes with a high proportion of edge structures. Electrochemical testing of the supercapacitors showed high areal capacitance and excellent long term cycling performance. The solvent-free method demonstrated here is highly scalable and can be a viable alternative approach for low cost and environmentally friendly energy storage devices. When integrated with other paper-based devices, the paper supercapacitors demonstrated here can potentially lead to the development of all-paper electronics that are low cost and highly versatile.

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