Perovskite optoelectronics

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Hand-drawing perovskite devices

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New conductive and perovskite inks enable hand-drawing of optoelectronic devices with a ballpoint pen on a variety of daily substrates, including paper, textiles and other irregular surfaces.

Emerging electronic systems such as displays, smart textiles, wearables and bioelectronics, among others, require the integration of active electronics, optoelectronics and sensing components onto diverse substrates including fabrics, plastics and elastomers[1,2]. These innovations aim to redefine our interaction with electronic devices, with applications spanning healthcare, robotics and the Internet of Things[3–5]. Conventional device fabrication approaches[6], such as transfer printing, screen printing or gravure printing, often involve heterogeneous integration, cumbersome alignment and calibration steps, and dedicated equipment, making them time-consuming and difficult to implement on dynamic or irregular surfaces.

Given the limitations of these printing techniques, the direct implementation of relevant components on the target substrate, including on the human body, offers a straightforward and effective alternative. A simple, yet powerful method is based on hand-drawing devices, which involves the deposition of relevant layers of materials by a handheld writing tool. Although the method has been applied to the fabrication of electronics and sensors directly on human skin for health monitoring and therapeutic functions[7], optoelectronic devices have yet to be realized on diverse substrates using this approach.

Now, writing in *Nature Photonics*, Zhao and colleagues develop a hand-drawing method to fabricate perovskite optoelectronic devices on paper, textiles and other irregular surfaces[8]. The fabrication relies on layer-by-layer hand-drawing with ballpoint pens filled with multiple conductive inks and perovskite inks for the realization of perovskite light-emitting diodes (PeLEDs) and perovskite photodetectors (PePDs), offering exciting possibilities for flexible electronic displays, human–machine interfaces and wearable bioelectronics.

The key requirements for hand-drawing such optoelectronic devices on various surfaces include: (1) the raw materials of the hand-drawing ink should be in the form of liquid precursors with appropriate rheological properties to flow from pen tips; (2) the first layer of the device should exhibit self-flattening properties to produce a relatively uniform thin film on rough surfaces; (3) different ink layers should not blend into each other; and (4) the resulting film should maintain suitable optical transparency and good optoelectronic properties. Metal-halide perovskite solutions are particularly well suited to these tasks owing to their liquid state, their compatibility to make versatile polymer composites and their ability to adjust their bandgap by swapping halide elements[9].

As fabricating films on fibrous paper can result in a rough morphology and absorbance of the solution into the paper, the resulting film may have uneven thickness and be more susceptible to current leakage. To address this issue, Zhao and colleagues developed a composite ink consisting of poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate) (PEDOT:PSS) and poly(ethylene oxide) (PEO) and optimized their weight ratio to planarize the paper substrate. This composite ink serves as the bottom layer of the devices. For the active layers, the authors developed a library of halide perovskite inks composed of either methylammonium lead halide ($MAPbX_3$) or butylammonium group-based quasi-two-dimensional Ruddlesden–Popper perovskite.

The team first explored the writability and performance of the conductive and perovskite inks on a variety of substrates. The $MAPbBr_3$ ink was drawn onto a paper substrate on top of the composite PEDOT:PSS layer, followed by drawing of polyethylenimine, acting as a buffer layer, and silver nanowires, acting as a top electrode to form a green PeLED, as shown in Fig. 1a. Multiple perovskite inks were drawn into a logo on aluminium foil which, upon irradiation under ultraviolet light, emitted red, green and blue colours. To demonstrate the electroluminescence of the perovskite inks on different substrates, the authors fabricated PeLEDs on vinyl gloves, the interior sidewall of a glass vial, a spherical latex balloon and plastic films; the devices remained functional even under a biaxial stretch of 40%- (balloon) and 180%-fold (plastic film). Furthermore, the PeLEDs could be fabricated as e-textiles on cotton, voile, organza and chiffon fibres.

As the hand-drawing process could potentially result in the formation of pinholes within the films, it was especially important to optimize the formulations of all the inks. Adding 30 wt% PEO to the PEDOT:PSS ink increased the viscosity and contact angle, allowing for smooth patterning. The hand-drawing resolution could be reduced below 200 μm if pens with finer tips were used owing to this ink modification. As the PEO slowed the ink penetration into the paper substrate, it also allowed for the formation of an electrode layer that also self-planarized. The resulting film exhibited an optical transparency of 63.51%, was 852 μm wide and had a sheet resistance of 166 $\Omega\ sq^{-1}$, making it suitable as a transparent conductive electrode. PEO was also added to the perovskite inks to improve their rheological properties. In the case of PeLEDs, the addition of polystyrene improved the perovskite crystal arrangement, producing a brighter emission with a lower leakage current. For the PePD fabrication, the perovskite inks were mixed with the polymer polymethyl methacrylate to reduce grain boundaries, facilitating the transport of photocarriers.

The PeLEDs drawn on untreated paper were compared with those fabricated on planarized polydimethylsiloxane (PDMS)-coated paper (Fig. 1b). Although the PeLEDs drawn on pristine paper had a slightly rougher morphology, the threshold voltage was lower (2.9 V) and the brightness (600 cd m^{-2} at 3.6 V) is sufficient for low-power displays. In addition, the PeLEDs on pristine paper produced a maximum luminance of 3,980 cd m^{-2} at 6.6 V. The devices also showed excellent durability by withstanding 5,000 bending cycles with a minimal drop in luminance. These performance metrics are noteworthy, considering the less-controlled fabrication on the rougher substrate, and demonstrate the great potential of the hand-drawing approach.

The hand-drawing approach was also used to fabricate PePDs in vertical photodiode and lateral photoconductor configurations (Fig. 1c,d). The vertical photodiode, characterized in the dark and under 532 nm illumination, showed a high on–off ratio of 1.1×10^4 at −0.5 V bias.

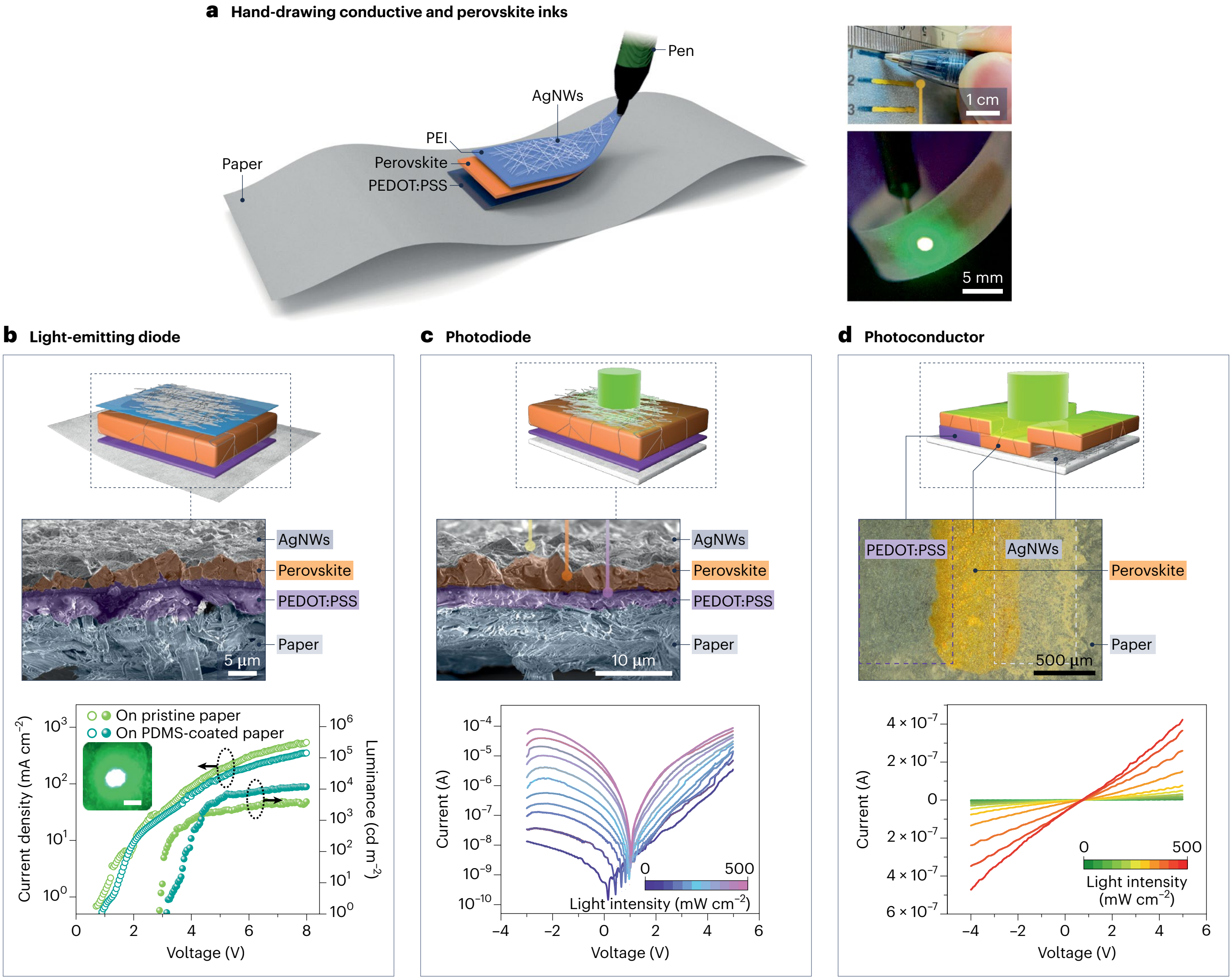

Fig. 1 | Hand-drawing perovskite optoelectronic devices on various surfaces. **a**, Schematic illustration of hand-drawing perovskite optoelectronic devices in a layer-by-layer fashion on a paper substrate (AgNWs, silver nanowires; PEI, polyethylenimine). Top right: layer-by-layer hand-drawing of PeLEDs. Bottom right: an image of the electroluminescence emitted from a hand-drawn green PeLED on a sheet of pristine paper. **b**, Schematic and corresponding cross-sectional scanning electron microscope image of the hand-drawn PeLED on untreated paper and planarized PDMS-coated paper and their current efficiency–voltage performance. The inset graph shows a picture of an emitting hand-drawn $MAPbBr_3$ green LED. Scale bar, 500 µm. **c**, Schematic and corresponding cross-sectional scanning electron microscope image of a hand-drawn vertical photodiode and current–voltage characteristics. **d**, Schematic and the optical image of a hand-drawn lateral photoconductor and its current–voltage characteristics. Figure adapted with permission from ref. 8, Springer Nature Ltd.

The lateral photoconductor showed increasing photoresponse with higher light intensity, with polymer additives having little influence on light absorption.

Overall, the direct hand-drawing approach proposed by Zhao and colleagues with new conductive and perovskite inks is a simple, useful and viable method to fabricate high-performance optoelectronic devices on rough and deformable substrates. Although the method holds considerable potential for the fabrication of on-demand low-cost perovskite optoelectronics, the necessity for non-toxic, lead-free and long operational stability in practical devices still needs to be addressed for applications directly related to human health. Future efforts could involve expanding the library of inks to enable more functions, implementing mask-based patterning to afford higher resolution and developing wireless power schemes for portability. The development of a comprehensive all-hand-drawn circuit system will also allow the integration of various components such as LEDs, photodetectors, energy-harvesting photovoltaics, transistors and sensors into the same device. This will pave the way for low-cost and customized electronic fabrics (e-textiles), digital paper (e-paper), intelligent packaging, biomedical diagnostic tools and wearable bioelectronics.

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Competing interests

The authors declare no competing interests.