

is compatible with conventional device manufacturing processes<sup>8</sup>; doping processes that can assure stable, high electrical conductivity over long periods<sup>9</sup>; a method to improve the environmental stability of graphene electrodes against moisture and chemicals in the air<sup>10</sup>; and a method to decrease the contact resistance between electrodes and active materials<sup>11</sup>.

One issue, in particular, with CVD-grown graphene is that it must be transferred to a perfectly flat surface. Most electronic devices, however, have an interconnected, multilayered structure. Although this is not a problem for ITO, as it can be sputtered onto irregularly shaped surfaces, the device architecture needs to be customized for two dimensions when using graphene electrodes. This limits the immediate replacement of ITO by graphene. Because of this, we anticipate that applications to flat and simple structures

such as touch screens, smart windows, electromagnetic interference shields, lighting and transparent heaters<sup>12</sup> will be the first to be realized, whereas applications to flexible displays and microelectronic devices will follow some years later.

We expect that the market for flexible electronics will become larger than that for non-flexible electronics in about 10 years. Although there are many candidates for ITO replacement — including metal meshes and silver nanowires whose sheet resistances are as low as  $\sim 10 \Omega \text{ sq}^{-1}$  at  $\sim 90\%$  transmittance<sup>2</sup> — none of them are as flexible as graphene. For example, the conducting properties of graphene can remain stable up to  $\sim 11\%$  extension<sup>1</sup>, and its initial sheet resistance persists for  $\sim 300,000$  cycles at 3% bending strain<sup>7</sup>, whereas a silver nanowire breaks easily at strains of less than 1%<sup>13</sup>.

Resolving the above-mentioned challenges will bring closer the advent of

flexible electronics, in which graphene technology will be as stretchable as our imagination. □

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## Electrifying inks with 2D materials

Felice Torrisi and Jonathan N. Coleman describe how graphene can be used in conductive inks to print electronic circuits.

**P**rinted electronics<sup>1,2</sup> has recently emerged as an important new direction for electronics beyond conventional silicon-based technologies. Electronic devices, including radiofrequency identification

tags, light-emitting diodes, batteries and transistors, can be built by printing liquid-dispersed functional materials such as organic polymers, nanoparticles and nanotubes. Techniques including inkjet, roll-to-roll and

spray deposition can pattern these materials on either rigid or flexible substrates, at low temperature and over large areas, and most importantly at very low cost. However, the performance of printed devices is limited by the quality of the materials contained in the inks and how these are arranged on the target substrate. Graphene and other two-dimensional (2D) materials are solution-processable and have useful physical and chemical properties. Can they make an impact on printed electronics?

Electronic inks are mixtures of a functional material, stabilizers and rheology modifiers. Different inks are needed to print the different elements of devices: semiconducting inks (the functional materials) in the active layer, insulating materials for dielectrics, and conducting materials for electrodes. They must be stable, cheap and print easily on appropriate substrates to produce devices with high charge-carrier mobility and long lifetime, without the need for aggressive post-treatments. Finding materials that fulfil these requirements is difficult. For example, conducting inks often contain metallic nanoparticles that may require sintering at high temperatures to maximize conductivity, which is problematic for polymeric



substrates. Furthermore, polymer-based inks often lack stability whereas nanotube inks are generally unsuitable for semiconducting applications owing to the presence of both metallic and semiconducting nanotubes.

Graphene has the potential to fulfil most requirements for use in conducting inks thanks to its high carrier mobility, mechanical robustness, environmental stability and potential for low-cost production. Before an ink can be produced, graphene must first be dispersed as nanosheets in a liquid. Graphene suspensions can be produced from graphite by oxidation to produce graphene oxide, or by liquid-phase exfoliation in solvents to give few-layer nanosheets<sup>3</sup>. Without high-temperature or aggressive chemical processing, however, it can be hard to achieve high conductivities in films produced from graphene oxide nanosheets. On the other hand, large quantities of pristine nanosheets, typically hundreds of nanometres across and ~1 nm thick, can be produced quickly and easily by liquid-phase exfoliation in readily printable liquids such as water and organic solvents<sup>4</sup>. The resulting ink is stable, processable in ambient conditions, and has high batch-to-batch reproducibility as well as good rheological properties for printing and coating<sup>5</sup>. Continuous networks of graphene nanosheets have been produced by methods such as spraying, filtration and rod coating, and tend to have conductivities of up to  $10^4 \text{ S m}^{-1}$  (ref. 6), even without high-temperature or chemical treatments<sup>7–9</sup>. They have performed well in applications such as electrodes for supercapacitors, as well as transparent electrodes for liquid-crystal displays, thin-film transistors and smart windows<sup>5,8,9</sup>. Patterned networks, with features as small as 30  $\mu\text{m}$  (ref. 10), have been produced by inkjet printing<sup>5,7</sup> and gravure coating<sup>10</sup>, and have shown promise in applications from supercapacitors<sup>11</sup> to antennae<sup>12</sup>.

Although graphene can be used in flexible interconnects or as an active material in printed supercapacitors or

composite devices<sup>5,9</sup>, its lack of a bandgap means that it cannot replace conjugated polymers<sup>2</sup> as the semiconducting material in printed electronic devices. In addition to graphene, however, liquid-phase exfoliation can produce suspensions of a range of other 2D nanosheets, including  $\text{WS}_2$ ,  $\text{MoO}_3$  and BN (ref. 3). These 2D materials have diverse properties, with some being semiconductors or insulators and some electrochemically active, making their inks suitable for a wide range of applications as active materials in printed electronics. Spray coating<sup>13</sup> or inkjet printing<sup>14,15</sup> of  $\text{MoS}_2$  nanosheets have been recently reported for supercapacitor and sensing applications.

But the most exciting applications of 2D materials in printed electronics will come from printing devices where two or more nanomaterials are integrated together in well-defined structures. All-inkjet-printed heterostructure photodetectors and transistors have already been produced by sequential printing of graphene and  $\text{WS}_2$ ,  $\text{MoS}_2$  or BN (refs 7,16). It is likely that many developments will stem from these pioneering works.

Nevertheless, a number of important hurdles remain before these developments can lead to commercialization of 2D material-based inks. For example, although nanosheets can be made in large quantities by liquid-phase exfoliation, the yield of monolayers is still low, typically on the order of 5–25%, and the flake size is poorly controlled. For inkjet printing, the nanosheet size and the rheological properties of the suspension must be carefully tuned<sup>5</sup>. Furthermore, the high aspect ratio of nanosheets generally results in low-concentration suspensions (~0.01–1 wt%), which is problematic for some printing techniques. Electrical performance is another issue. Printed devices will consist of networks of either graphene or inorganic nanosheets, and charge transport will be limited by junctions between the sheets, resulting in mobilities typically two orders of magnitude lower than in individual

nanosheets<sup>17</sup>. This will limit the achievable conductivity of graphene interconnects, and reduce the performance of devices based on semiconducting nanosheets. On the other hand, as  $\text{MoS}_2$  nanosheets have mobilities of hundreds of  $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , production of  $\text{MoS}_2$  networks with mobilities of a few  $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  might be possible, making them competitive with printed conjugated-polymer-based devices<sup>2</sup>.

We believe that the future is bright for printed devices based on 2D materials, although many challenges remain. As new materials combinations are demonstrated, the range of printed devices and applications will expand. Moreover, as the scaling up of ink production proceeds, costs will fall, eventually allowing the best 2D material-printed devices to compete with traditional technologies on cost and possibly performance.  $\square$

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## Charging graphene for energy

Energy storage is a grand challenge for future energy infrastructure, transportation and consumer electronics. Jun Liu discusses how graphene may — or may not — be used to improve various electrochemical energy storage devices.

**G**raphene has captured the imagination of researchers for energy storage because of its extremely high theoretical surface area (2,630  $\text{m}^2 \text{ g}^{-1}$ )

compared with traditional activated carbon (typically below 1,500  $\text{m}^2 \text{ g}^{-1}$ ), excellent electrical conductivity, high mechanical strength and potential for low-cost

manufacturing. These properties are very desirable for achieving high capacity and energy density, and fast charge and discharge rates. Graphene sheets used in energy