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2D Materials

Ultrafast, Low-Cost, and Mass Production of High-Quality Graphene

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Abstract: *Fast, mass, and low-cost production of high-quality graphene, which is alluring, remains a great challenge, even though some approaches have shown potential for mass synthesis of graphene. Very recently a great breakthrough was made by Tour and co-workers (Nature 2020, 577, 647–651): in just a second, easily exfoliated and highly crystalline graphene was produced from abundant carbon-containing species by cost-effective flash Joule heating with a low energy input of 7.2 kJ per gram graphene. Such an ultrafast, economic, and scalable process for high-quality graphene production can be considered as a milestone in the graphene field and is highlighted in this article.*

The exceptional properties of graphene and its excellent performance in tremendous applications are fascinating.[1] Nevertheless, its widespread usage in practice has to rely on an easy scalable and low-cost synthesis approach. Since a monolayer graphene was first obtained by tape-assisted mechanical exfoliation of graphite in 2004,[2] tremendous scientific endeavors have been devoted to a facile fabrication of graphene, especially high-quality graphene.[3] Currently, the two most extensively used methods for the synthesis of graphene are reduction of exfoliated graphene oxide (GO) and chemical vapor deposition (CVD). However, in spite of the tremendous reduction methods (for example thermal, hydrothermal, chemical, electrochemical or photon-induced reduction, amongst others), a full reduction of GO could hardly be achieved.[4] Besides, a more critical obstacle for the scalable production of graphene from GO is the synthesis of GO itself. The most commonly used Hummer's[5] and modified Hummer's methods[6] for GO production involve highly corrosive agents, produce toxic compounds, and should be followed by tedious washing processes. In contrast, CVD on metal substrates offers intriguing opportunities for the synthesis of high-quality graphene at elevated temperatures (approximately 1000 °C).[7] Nevertheless, the method suffers from a low yield and a high cost.

Some other methods that have been developed in the past years show potential for a mass production of graphene materials. For example, alkali-metal-triggered redox reaction achieved the production of 3D-structured graphene materials from carbon oxides (namely, CO_2 and CO) in a high yield.[8] The reactions are all exothermic and thus able to generate self-propagating high temperatures, which significantly reduces the energy input. Also, gram-scale production of graphene with various structures and qualities were realized by on-site polymerization of liquid/solid hydrocarbons and low-cost carbon-containing materials (for example, biomasses, daily-life wastes, and industrial cast-off) via templated thermal annealing[9] or laser-scribing.[10] However, obtaining high-quality graphene by these routes remains a great challenge. During these fabrication processes, while a high reaction temperature helps reduce the number of defects in the produced graphene, the possibility of obtaining graphite materials as well as the energy input increases with the rising temperature. Laser-scribing is more efficient and lower in cost than the conventional annealing approaches, but it is only able to convert the surface layer of a polymer into graphene. A bulk conversion of a carbon source into high-quality graphene materials with a high efficiency, though highly desired, had never been achieved.

Very recently, in *Nature*, Tour and co-workers reported that various amorphous carbon materials could be converted into highly crystalline graphene within one second by flash Joule heating (FJH).[11] This marks a great breakthrough in the development of scalable synthesis approaches for high-quality graphene materials. The process was simple: A carbon source showing a certain conductivity was compressed between two electrodes in a quartz or ceramic tube (Figure 1 a). Then, after a high-voltage (greater than 90 V) electric shock, which increased the local temperature in the carbon source to over 3,000 K in an instant, and a rapid cooling process, the flash graphene (FG) was formed.

The significance of this finding lies in several aspects. First, a unique type of graphene with super-high quality was synthesized. Turbostratic FG with misoriented layers forming Moiré patterns (Figures 1 b,c) and monolayer graphene showing hexagonal lattice (Figure 1 b,d) were obtained from carbon black and spent coffee grounds, respectively. During

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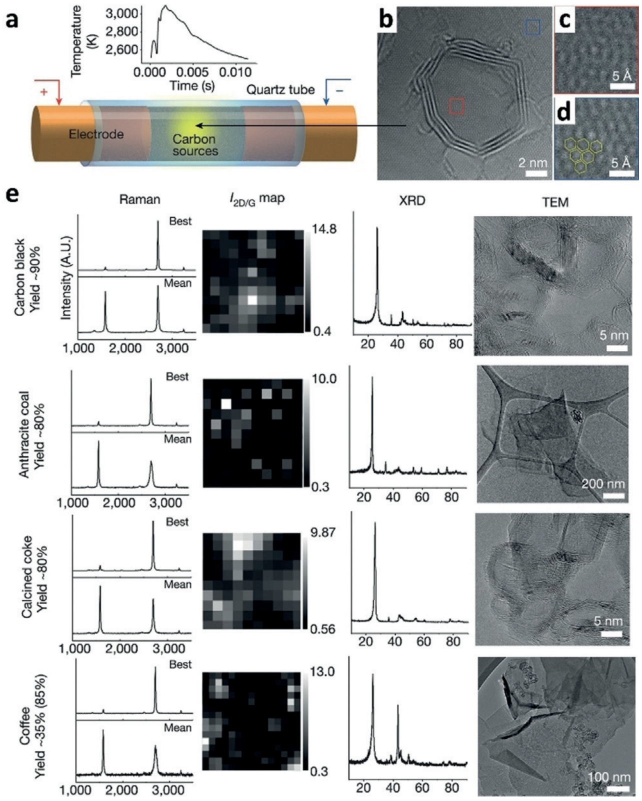

Figure 1. a) Schematic of the FJH process, and plot of the temperature rise versus time during flashing (inset). b–d) HR-TEM image of carbon-black-formed FG on top of a single layer of coffee-derived FG. e) Characterization results, including Raman spectra (showing the best and the mean obtained spectra), XRD spectra, and TEM images of FGs derived from four different carbon sources. Each pixel in the Raman mapping is 4 μm^2 using a 50× magnification. The sample size for the mean Raman spectrum is 10. The small graphene particles in the TEM image of coffee-derived FG came from the carbon black conductive additive.[11] Copyright 2020, Springer Nature.

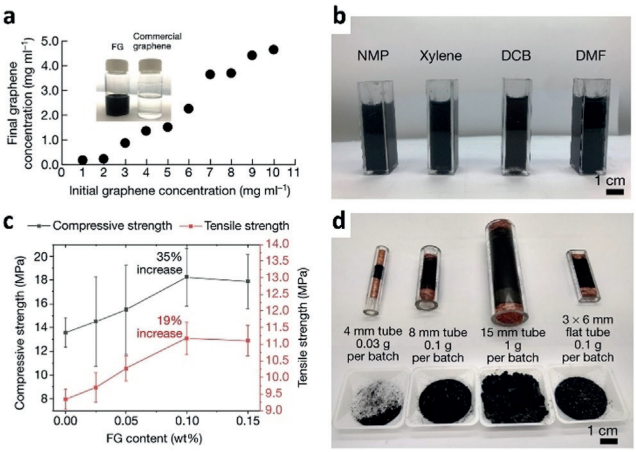

Figure 2. a) FG dispersion in a water–Pluronic (F-127) solution (1%). The inset photograph shows the supernatants of 4 g l^{-1} of CB-FG and of 10 g l^{-1} of a commercial sample after centrifugation. The commercial graphene was not stable as a colloid at this concentration, resulting in a clear liquid in the supernatant after centrifugation. b) FG dispersion in various organic solvents at 5 g l^{-1}. c) Mechanical performance of cement compounded with FG. The error bars represent one standard error ($n=3$). d) FJH quartz tubes of different sizes and shapes, used to synthesize FG. Two separate synthesis processes were conducted with each tube, providing the samples in the tube and those in the plastic dishes.[11] Copyright 2020, Springer Nature.

Raman mapping, the FGs synthesized from four different carbon sources (namely, carbon black, anthracite coal, calcined coke, and coffee) all demonstrated strong 2D peaks with $I_{2D/G}$ exceeding 10 (up to 17) and extremely low D peak intensity in many locations (Figure 1e). The extraordinarily high $I_{2D/G}$ values surpassed those of all other graphene materials reported hitherto, suggesting the distinctive structure of FGs induced by the ultra-high temperature. Meanwhile, the negligible D peaks of the FGs reflected the ultra-small number of defects in their lattice. Moreover, the FGs all possessed a sharp and asymmetric peak at around 26° in their XRD patterns (Figure 1e), corresponding to an expanded periodic interlayer spacing of 3.45 Å, compared to that of graphite (3.37 Å). Thereby, the FGs could be easily exfoliated and were highly dispersible in water/surfactant (Pluronic F-127) and organic solvents (Figures 2a,b). Furthermore, FG showed an appreciable capability in enhancing the mechanical performance of cement (Figure 2c), implying its potential as a building-composite additive.

Second, this is an efficient and low-energy process with a great scaling potential. For each synthesis, 80–90% of carbon in the carbon sources was transformed into graphene. The total yield can be easily scaled up by increasing the quartz/ceramic tube size (Figure 2d). With the different quantities and types of the carbon precursors, the conversion duration could vary, but all within the rage of 0.1–10 s. The high-voltage induced a sudden temperature increase on the carbon source to trigger the reaction. Afterward, the high temperature cooled down quickly because most of the heat exited as black-body radiation (a very bright flash). Even with the internal temperatures exceeding 3,000 K, the external walls of the quartz tubes were just warm (less than 60°C) after the flash. Furthermore, because the high-voltage-induced high-temperature pulse was concentrated on the carbon precursor with minimal energy loss, the electric energy consumption for the production of 1 g FG was merely approximately 7.2 kJ. In fact, the extremely high reaction temperature (greater than 3,000 K) that was reached instantly and the ultra-fast cooling rate of FJH were the keys for the generation of FG with a high degree of crystallinity and purity. The super-high-temperature pulse not only trigged the fast graphitization of the carbon atoms, but also led to a prompt sublimation of the heteroatoms in the carbon precursor. Meanwhile, the rapid cooling avoided the further crystallization of FG into graphitic domains.

Third, a wide range of carbon sources, including discarded food, natural coals, human hairs, biomasses, residual rubbers, and mixed plastic, are valid for the FJH synthesis of graphene. This means that by the low-energy and clean FJH process, many low-value carbon-based substances can be converted into valuable FG. Since the carbon-containing wastes would become CO_2 emission sources when they are disposed of by general combustion or in landfills, conversion of them into FG by FJH also reduces undesired emissions of greenhouse gases.

Furthermore, the properties of the FGs can be further controlled/optimized by adjusting the reaction atmosphere, applied voltage, switching duration, and composition and compression density of the precursor. This allows researchers to explore graphene products with more versatile properties by this efficient approach. These FJH-synthesized graphene materials could then play important roles in a wide range of fields.

Overall, graphene synthesis by flash Joule heating shows a great potential for industrial scale-up. It creates a new direction for inexpensive graphene materials. Of course, a number of difficulties, such as guaranteeing the uniformity of products at a large scale, should be surmounted before the process can be commercialized.

Conflict of interest

The authors declare no conflict of interest.

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