Fluorine speeds up two-dimensional materials growth

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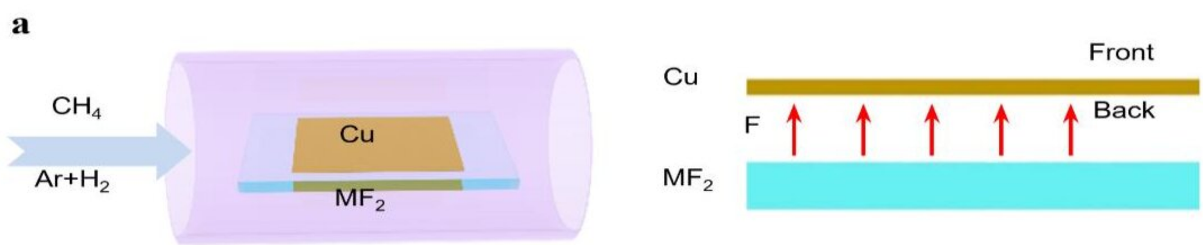
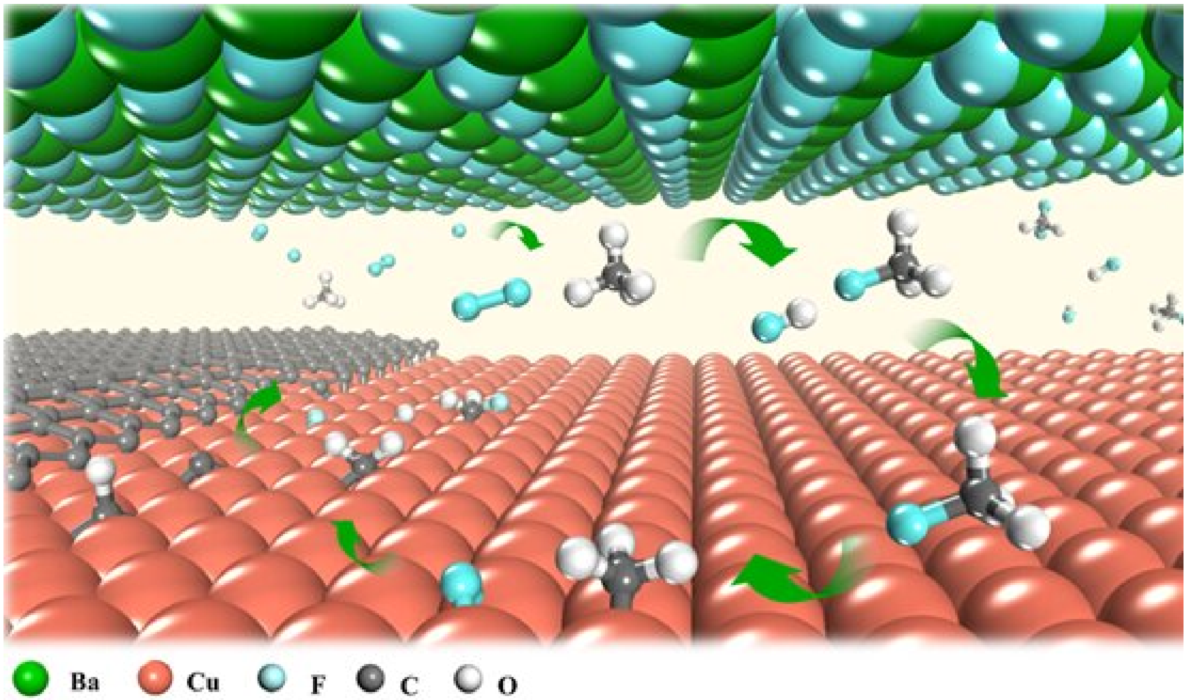


Schematic diagrams of the experimental design for locally introducing fluorine for graphene growth. Credit: IBS

Back in 2004, the physics community was just beginning to recognize the existence of truly two-dimensional (2-D) material, graphene. Fast-forward to 2019, and scientists are exploring a breadth of 2-D materials to uncover more of their fundamental properties. The frenzy behind these new 2-D materials lies in their fascinating properties—materials thinned down to only a few atoms work very differently from 3-D materials. Electrons packed into the thinnest-ever layer show distinctive characteristics apart from being in a "loose net." Also being flexible, 2-D materials could feature distinctive electrical properties, opening up new applications for next-generation technologies such as bendable and wearable devices.

Then, what is the catch? Many parameters such as temperature, pressure, precursor type and flow rate need to be factored into the CVD synthesis of 2-D materials. With multiple reactions involved, it is extremely difficult to optimize all these factors during the reactions and find their best combinations. That being said, 2-D material synthesis is difficult to control. Scientists have tried to accelerate the growth of 2-D materials by adopting different substrates, feedstocks and temperature. Still, only a few types of 2-D materials can be synthesized into large-area, high-quality films.

Scientists from the Center for Multidimensional Carbon Materials (CMCM), within the Institute for Basic Science (IBS) at the Ulsan National Institute of Science and Technology (UNIST) and collaborators demonstrated that fluorine, having the strongest tendency to attract electrons (i.e. electronegativity) in all elements, can speed up the chemical reaction to grow three representative 2-D materials; graphene, h-BN, and WS2. Fluorine requires only one electron to attain a high stability. Also, having seven electrons in the outermost orbit of an atom, the distance at which these valence electrons reside is the minimum compared with other elements. This means the valence electrons of fluorine are bound to the atom more strongly than any other atom, making fluorine the most active element in the periodic table.

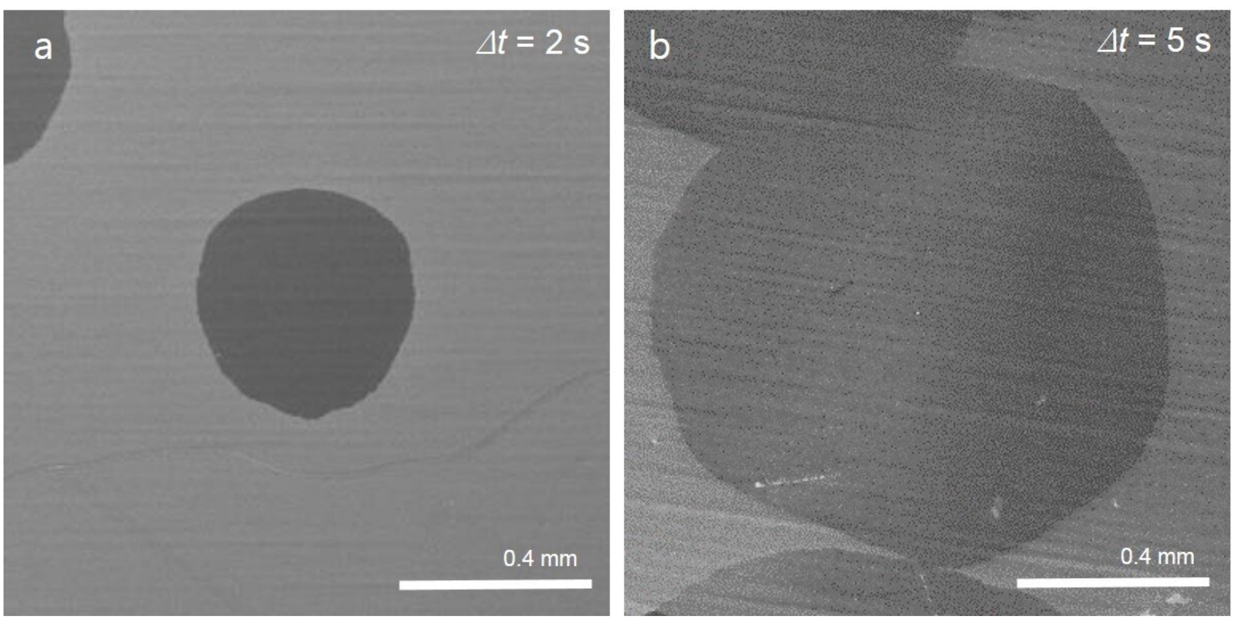


Schematic illustration of local fluorine-modulated graphene growth. Credit: IBS

In fact, active gases such as hydrogen or oxygen are broadly used to tune the growth of graphene and other 2-D materials. "Why not then the most active element, fluorine? The highest electronegativity allows fluorine to form bonds with nearly all the atoms in the periodic table, so it is expected to change the reaction routes of many chemical processes," said Professor Feng Ding, the corresponding author of this study.

Experimentally, it is not preferable to introduce fluorine during a material's growth, as fluorine gets highly toxic in the reactor. To resolve the problem, instead of using fluorine gas directly, the scientists spatially confined the fluorine supply so that only the minimum amount of fluorine is consumed. They placed a metal fluoride substrate (MF_2) below a Cu foil with a very narrow gap in between. At a high temperature, fluorine radicals are released from the fluoride surface and spatially trapped in the narrow gap between the Cu foil and the metal fluoride substrate. Surprisingly, such a simple change leads to a record growth rate of graphene at 12 mm per minute. To put this rate in perspective, this new approach reduces the time of growing a 10 cm^2 graphene from 10 minutes with previous methods, now down to only three minutes.

The introduction of local fluorine entirely changes the methane decomposition route. As the fluorine released from the metal fluoride surface easily reacts with methane gas, there will be a sufficient amount of CH^3F or CH^2F^2 molecules in the gap between Cu and BaF^2 substrates. These molecules could decompose on a Cu surface much more easily than CH4 does. In other words, they feed the graphene growth better by supplying more active carbon radicals (i.e. CH^3, CH^2, CH and C).



SEM images of graphene domains growing. They showed that 2 seconds was enough for a domain to grow to ~400 μm and that ~1 mm domains were formed after 5 seconds. The statistical growth rate is more than three orders of magnitude faster than typical graphene growth and three times faster than the previous record realized with a continuous oxygen supply. Credit: IBS

Further experimental studies showed that the local fluorine supply strategy could greatly accelerate the growth of other 2-D materials such as h-BN and WS2, as well. The scientists investigated how spatially confined fluorine is able to accelerate the growth of 2-D materials. Theoretical studies revealed that fluorine, being highly reactive, readily interacts with methane molecules. The existence of fluorine leads to the formation of CH^3F or CH^2F^2 molecules. These highly active molecules can then be more easily decomposed on the Cu foil surface, which greatly accelerates the carbon supply for fast graphene growth.

Although the detailed mechanism of fluorine boosting the growth of h-BN and WS2 is not clear, the authors are confident that the presence of fluorine could significantly modify the reactions of 2-D materials' growth. "We envision that this local fluorine supply will readily facilitate fast growth of broad 2-D materials or enable the growth of new 2-D materials, which is very difficult to realize by other methods," said Professor Feng Ding. In addition to the fluoride, there are abundant kinds of substrates like sulphides, selenides, chlorides or bromides that might be used as local supply sources of different active materials, which provides wide enough platform to modulate the growth of broad 2-D materials.

More information: Kinetic modulation of graphene growth by fluorine through spatially confined decomposition of metal fluorides. *Nature Chemistry* (2019). DOI: 10.1038/s41557-019-0290-1

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