

Substrate Developments for the Chemical Vapor Deposition Synthesis of Graphene

Qitao Shi, Klaudia Tokarska, Huy Quang Ta, Xiaoqin Yang, Yu Liu, Sami Ullah, Lijun Liu, Barbara Trzebicka, Alicja Bachmatiuk, Jingyu Sun, Lei Fu, Zhongfan Liu, and Mark H. Rümmeli*


Since the isolation of graphene and numerous demonstrations of its unique properties, the expectations for this material to be implemented in many future commercial applications have been enormous. However, to date, challenges still remain. One of the key challenges is the fabrication of graphene in a manner that satisfies processing requirements. While transfer of graphene can be used, this tends to damage or contaminate it, which degrades its performance. Hence, there is an important drive to grow graphene directly over a number of technologically important materials, viz., different substrate materials, so as to avoid the need for transfer. One of the more successful approaches to synthesis graphene is chemical vapor deposition (CVD), which is well established. Historically, transition metal substrates are used due to their catalytic properties. However, in recent years this has developed to include many nonmetal substrate systems. Moreover, both solid and molten substrate forms have also been demonstrated. In addition, the current trend to progress flexible devices has spurred interest in graphene growth directly over flexible materials surfaces. All these aspects are presented in this review which presents the developments in available substrates for graphene fabrication by CVD, with a focus primarily on large area graphene.

1. Introduction

There are numerous approaches in which single- and bilayer graphene can be fabricated or isolated. Currently, the most popular synthesis process is chemical vapor deposition (CVD). The CVD method can yield relatively high quality graphene, has the potential to synthesize graphene on a large scale, is well established and is facile.^[1] While the CVD process is for the most part straightforward, some specialist equipment is required and the process parameters and reactor configuration are also important. CVD, in essence, is a process in which gaseous reactants are used to deposit material onto a substrate surface. The use of CVD for the fabrication of graphene rapidly developed once graphene had been demonstrated experimentally. Metal catalysts, in particular transition metals, which had a highly successful history for the growth of carbon nanotubes, where the obvious choice in

Q. Shi, X. Yang, Y. Liu, S. Ullah, Prof. A. Bachmatiuk, Prof. J. Sun, Prof. M. H. Rümmeli
Soochow Institute for Energy and Materials Innovations
College of Energy
Key Laboratory of Advanced Carbon Materials and Wearable Energy Technologies of Jiangsu Province
Soochow University
Suzhou 215006, China
E-mail: mhr1@suda.edu.cn

K. Tokarska, Prof. B. Trzebicka, Prof. A. Bachmatiuk, Prof. M. H. Rümmeli
Centre of Polymer and Carbon Materials
Polish Academy of Sciences
M. Curie-Skłodowskiej 34
Zabrze 41-819, Poland

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/admi.201902024>.

© 2020 The Authors. Published by WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/admi.201902024

Dr. H. Q. Ta, Prof. A. Bachmatiuk, Prof. M. H. Rümmeli
Institute for Complex Materials
IFW Dresden
20 Helmholtz Strasse, Dresden 01069, Germany

Prof. M. H. Rümmeli
Institute of Environmental Technology
VSB-Technical University of Ostrava
17. Listopadu 15, Ostrava 708 33, Czech Republic

X. Yang, Prof. L. Liu
School of Energy and Power Engineering
Xi'an Jiaotong University
No. 28, Xianning West Road, Xi'an, Shaanxi 710049, China

Prof. L. Fu
College of Chemistry and Molecular Science
Wuhan University
Wuhan 430072, China

Prof. Z. Liu
Center for Nanochemistry
Beijing Science and Engineering Centre for Nanocarbons
Beijing National Laboratory for Molecular Sciences
College of Chemistry and Molecular Engineering
Peking University
Beijing 100871, China

early studies for the CVD catalytic growth of graphene. However, in many cases the direct growth of graphene over metal substrates is undesirable and transfer procedures introduce damage and so is for the most part also unwanted. This has led to the development of CVD techniques for the direct fabrication of graphene over different types of substrates. Indeed, the availability of substrates for graphene growth by CVD has matured significantly in recent years and numerous metals and nonmetals can be used. Moreover, these substrates can be used in their solid state and in many cases in a molten state. In addition, progress now includes direct graphene fabrication over flexible substrates. There are numerous reviews on the CVD synthesis of graphene and they, for the most part, tend to connect a broad discussion on the synthesis of graphene, its properties and its application^[2–6] or they remain broad in discussing the synthesis of graphene and focus on a more specific application, for an excellent example, secondary metal ion batteries^[7] or graphene as a smart material.^[8] Other reviews may focus on a specific form of graphene such as N doped graphene^[9] or porous graphene.^[10] However, a review focusing on the substrates for the direct growth of graphene by CVD is lacking. This review addresses the developments in substrate systems for the growth of graphene by CVD, with a focus on large area graphene.

2. The CVD Process in Brief

CVD growth of graphene is a chemical process in which intricately mixed homogeneous gas phase and heterogeneous surface reactions are involved.^[11] In the case of graphene, the gaseous precursor undergoes pyrolysis to form carbon species. These carbon species are then carried and deposited on to the surface of the substrate where nucleation occurs and then forms (grows) into the carbon structure of graphene. To improve the pyrolysis or decomposition of the precursor usually a catalyst is used to reduce the reaction temperature, but this is not a prerequisite. In general, the process for CVD graphene fabrication consists of eight steps: 1) mass transport of the reactant, 2) reaction of the precursor, 3) diffusion of gas molecules, 4) adsorption of the precursor, 5) diffusion of the precursor into the substrate (in many cases this is not true where the solubility is limited), 6) surface reaction, 7) desorption of products and 8) removal of the by-products.^[12,13] Often thermal CVD is used, where, as the name suggests, heating is the driving system for the reaction. However, the use of a plasma (viz., plasma enhanced CVD, PECVD) can help reduce pyrolysis temperatures. In terms of operation pressure, two broad categories exist, namely, atmospheric pressure CVD (APCVD) and low pressure CVD (LPCVD). The reaction pressure, along with flow rates, temperature and growth time can affect the final quality of the as produced graphene. The choice of substrate is also important and different substrates can be used. The most successful are metals, in particular Cu as it serves as a catalyst and also, the low carbon adsorption propensity of Cu allows for easier control to form large area homogeneous mono or bilayer graphene. The main drawback for graphene fabricated over Cu is that, usually, the graphene needs to be transferred off the substrate (e.g., for device fabrication)



Qitao Shi received his bachelor of science degree from the Department of physics and optoelectronic energy at Soochow University, Suzhou, China, in 2016. Currently, he works as doctoral researcher at the Soochow Institute for Energy and Materials Innovations (SIEMIS) and the College of Energy at Soochow University China in Prof. Mark H. Rummeli's group. His current research focuses on solving the pulverization issues of Si particles as anode materials via space engineering or structure optimization.



Klaudia Tokarska is a Ph.D. candidate of the Polish Academy of Sciences (CMPW PAN) in Zabrze, where she works in Laboratory of Carbon and Polymer-Carbon Materials. She received her Bachelor of Science degree at Silesian University of Technology (Zabrze, Poland) in 2016. She joined the Prof. Rummeli's research group in 2017. Her current research focuses on development of graphene coatings on Si nanoparticles and their application as high-performance anode materials in secondary lithium-based batteries.



Mark H. Rummeli heads the electron microscopy and LIN labs at the Soochow Institute for Energy and Materials Innovations (SIEMIS), Soochow University, where he is a full professor. He is also director of the characterization center at the College of Energy and SIEMES. Moreover, he is a full professor of the Polish Academy of Sciences (CMPW PAN) in Zabrze and has full habilitation rights. He obtained his Ph.D. from London Metropolitan University and then worked as a postdoc at the German Aerospace Center. His research focuses on the growth mechanisms of 2D nanostructures and their functionalization.

and this processing step can incur contamination and/or damage, which leads to reduced performance of the graphene. Thus, the potential to directly grow graphene on nonmetallic

substrates by CVD is critical to expand the application potential of graphene.

3. Substrate Systems for Graphene Synthesis by CVD

The activity of transition metals forming graphitic material from heterogeneous catalytic reactions has been known for years from industrial processes. In addition, their successful implementation for carbon nanotubes is also well known and so transition metals were initially used as substrates for graphene growth. The choice of transition metal depends on the end goal (e.g., mono layer, bilayer, few layer graphene films) and consideration of the metals stability at high temperature, and carbon solubility are important along with their catalytic ability, which lowers the activation energy pathways for the reactions in the CVD process. In order to help control issues related to high carbon solubility, various metal alloys have been developed, and these are also discussed in the following subsections.

Metal substrates, although highly successful for graphene growth, when using the graphene for device based applications suffer a significant drawback, namely, the need for transfer which introduces defects and/or contamination which is counterproductive in that this diminishes the performance of the graphene. Hence, considerable efforts have been directed to the growth of continuous and homogeneous growth of graphene directly on dielectric substrates such as hBN, Si/SiO₂, Al₂O₃, GaN, MgO, Si₃N₄, etc. Growth of graphene directly on these substrates is more challenging, none-the-less, great strides have been made, and this is also discussed in the sections below. Moreover, the growth of graphene over molten substrates and flexible substrates is also presented. In addition, it should be noted, that unless explicitly stated, most discussion centers on large area (poly crystalline) graphene. We begin with discussion on metal surfaces.

3.1. CVD over Metal Substrates

While there are a huge number of metal catalysts to choose from in the periodic table of elements (91 of the 118 elements listed in the periodic table), the most successful for the growth of graphene tend to be from the transition metals. Early CVD growth focused on solid metals, in particular Ni and Cu. However, it soon became clear that liquid metals can also be used and that they may have certain advantages. We now briefly look at solid metals first and then molten or liquid metals.

3.1.1. Solid Metal Substrates

Ni was a highly successful metal in the CVD synthesis of carbon nanotubes and, thus, it was no surprise that early research for the CVD synthesis of graphene exploited Ni. Typically, polycrystalline Ni films are used and prior to synthesis they are annealed in an Ar/H₂ atmosphere (≈ 900 – 1000 °C) to reduce the surface oxide and also increase the grain size. For growth,

the Ni film then requires a carbon feedstock, usually this is CH₄. The use of Ar is not necessary, but can be implemented. Ni has a relatively high C solubility, so that as the CH₄ decomposes it produces C species (catalytically aided by the Ni), which then dissolve in the Ni film at the elevated temperatures.^[14] This is followed by a cooling down step during which C atoms diffuse out from the Ni–C solid solution and precipitate on the Ni surface and form graphene films. In other words, graphene films form on Ni through a carbon segregation–precipitation process. Multi- or single-layer graphene can be grown on Ni, and can be controlled by the cooling rate.^[15–17] However, the graphene layer numbers tend not to be homogeneous due to excess C dissolving out at grain boundaries leading to multi-layer nucleation. For this reason, a preannealing treatment is applied to reduce the number of grain boundaries. In addition, the growth time and hydrocarbon concentration can also affect the graphene layer number formation.^[5] One can also use very thin Ni films which then by default can only absorb a certain amount of carbon and this limits C precipitation. None-the-less large area homogeneous single-layer graphene remains difficult to obtain.^[18] A neat tactic to overcome this issue is to use Mo along with Ni, e.g., by depositing Ni on a Mo foil to produce a binary catalytic substrate. The technique yields large area homogeneous monolayer graphene.^[19] Systematic studies show that during the APCVD process, the Ni and Mo films break up, diffuse and mix as independent islands. Graphene nucleation occurs exclusively over the Ni islands while the Mo islands around the Ni soak up excess C (see **Figure 1**).^[20] Thus, C precipitation is controlled in a useful way enabling large area single-layer graphene to form.

Single-crystal Ni (111) can be used for homogeneous single-layer graphene formation,^[21] however, this is difficult to translate to large area single crystalline growth. Aside from Ni, a number of other metal substrates with different carbon solubility and catalytic effect can be used. These include Ru,^[22] Ir,^[23] Pt,^[24] Co,^[25,26] Pd,^[27] and Re.^[28] Varying degrees of success have been obtained with these. A breakthrough came with the use of polycrystalline Cu foils as a substrate since it could relatively easily deliver high-quality homogeneous single-layer graphene at low cost and relatively easy transfer.^[5,29] In the case of Cu as a substrate, while obtaining homogeneous single-layer graphene is easier, growth parameters such as gas flow are crucial. Unrestricted gas flows in APCVD lead to inhomogeneous layer numbers. An alternative configuration in which one end of the inner tube (in which the sample is placed) is closed so as to restrict the gas flow leads to a homogeneous graphene layer number over large areas.^[30] The study showed the graphene layer number to depend on the sample placement, yielding either homogeneous monolayer or bilayer graphene. The data showed that local conditions play a role on layer homogeneity such that under quasistatic equilibrium gas conditions not only is the layer number stabilized, but the quality of the graphene improves. In another systematic study, again using Cu as the substrate in APCVD the flow rates and relative gas ratio of CH₄ to H₂ were explored and two very different growth windows are identified. For relatively high CH₄ to H₂ ratios, graphene growth is relatively rapid with an initial first full layer forming in seconds. Thereafter new graphene flakes nucleate and then grow on top of the first layer.

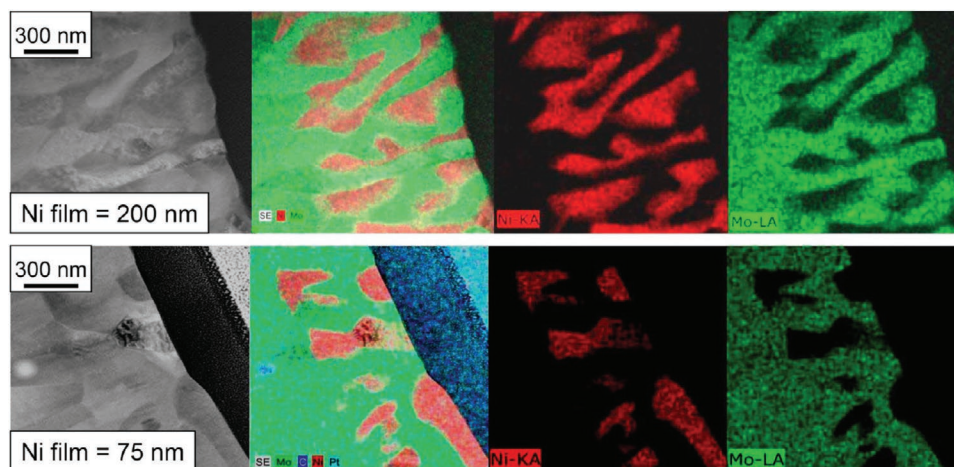


Figure 1. STEM investigations of sample cross-sections (lamellas). Furthermost left: STEM images of sections of lamellas. Next to these are elemental EDS maps (in false color). Reproduced with permission.^[20] Copyright 2013, American Chemical Society.

The stacking of these flakes versus the initial graphene layer is mostly turbostratic. This growth mode can be likened to Stranski–Krastanov growth. While with relatively low CH_4 to H_2 ratios, the growth rates are reduced due to a lower carbon supply rate. In addition, bi-, tri-, and few-layer flakes form directly over the Cu substrate as individual islands. Etching studies were conducted and they showed that in this growth mode subsequent layers form beneath the first layer presumably through carbon radical intercalation. This growth mode is similar to that found with Volmer–Weber growth and produces highly oriented AB-stacked graphene.^[31] **Figure 2** shows examples of the cross parametric studies and the two growth modes.

3.1.2. Liquid Metal Substrates

One of the disadvantages of metal substrates for large area CVD growth of graphene is the presence of microstructure defects such as grain boundaries. Due to differing C solubility at substrate defects (e.g., grain boundaries) during the growth process, uniform large area graphene films are challenging due to excess C precipitation during the cooling down process. In addition, substrate crystal orientation can affect graphene growth too (predominantly through epitaxial considerations). In the case of a liquid metal substrate, these aspects can be significantly reduced. Liquids tend to adopt a random close packed geometry and enable a quasi-atomically smooth surface (with no grain boundaries) through the combined action of surface tension and the thermal motion of atoms.^[32,33] In terms of graphene growth, a liquid surface offers a simpler approach to form high quality uniform graphene.^[34–36] On liquid surfaces the surfaces, the thermal motion of the atoms means the inter-atomic distances fluctuate^[37] and thus weaken the interaction between the liquid (substrate) surface and the adsorbed atoms (C species in the case of graphene growth), thus decreasing the migration barrier energy.^[38] This means the diffusion rate for C atoms is greatly accelerated allowing for the controlled growth of single crystal graphene islands with novel and changeable morphologies.^[39] Moreover, H species also migrate very

efficiently and so results in a unique etching of developing graphene islands during growth leading to interesting fractal etching^[40] and regular etching.^[41]

An early demonstration was the use of liquid p-block elements (e.g., Ga) for the synthesis of monolayer graphene using APCVD.^[42] The electron mobility of single crystal domains grown on liquid Ga surfaces was as high as $7400 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ under ambient conditions indicating high quality single crystal graphene flakes can be obtained from this approach. The technique is relatively simple and does not require film deposition or vacuum systems. A later systematic study with liquid metals showed they are highly suited for strictly single layer graphene. Examples are shown in **Figure 3**.^[43] This is because during cooling from the CVD process, the surface metal solidifies quickly blocking the precipitation of absorbed carbon. As a result, growth is a self-limited catalytic process and moreover, is robust to variations in growth parameters.

The rheological surface of a liquid metal surface allows for the rotation, alignment and movement of growing graphene grains (islands). For example, Fu and co-workers^[44] showed that adjacent graphene islands could merge without grain boundaries via a self-adjusting rotation process and thus assemble the crystals in a superordered and self-aligned manner.^[45] The weak atomic interaction along with the high-vapor pressure of liquid metals allows for intermediary-free graphene fabrication^[46] and results in very clean graphene which is attractive for its practical application.^[36]

3.2. CVD over Nonmetal Substrates

As mentioned earlier, in order to avoid the need to transfer graphene which can damage the graphene as well as leave unwanted surface contamination, the CVD synthesis of graphene over nonmetal substrates is also important, particularly for electronic device fabrication where it is crucial to avoid metallic impurities and transfer contamination which will reduce costs and time.^[47] It is worth noting that graphene/Si and graphene/Ge appear to be promising candidates for

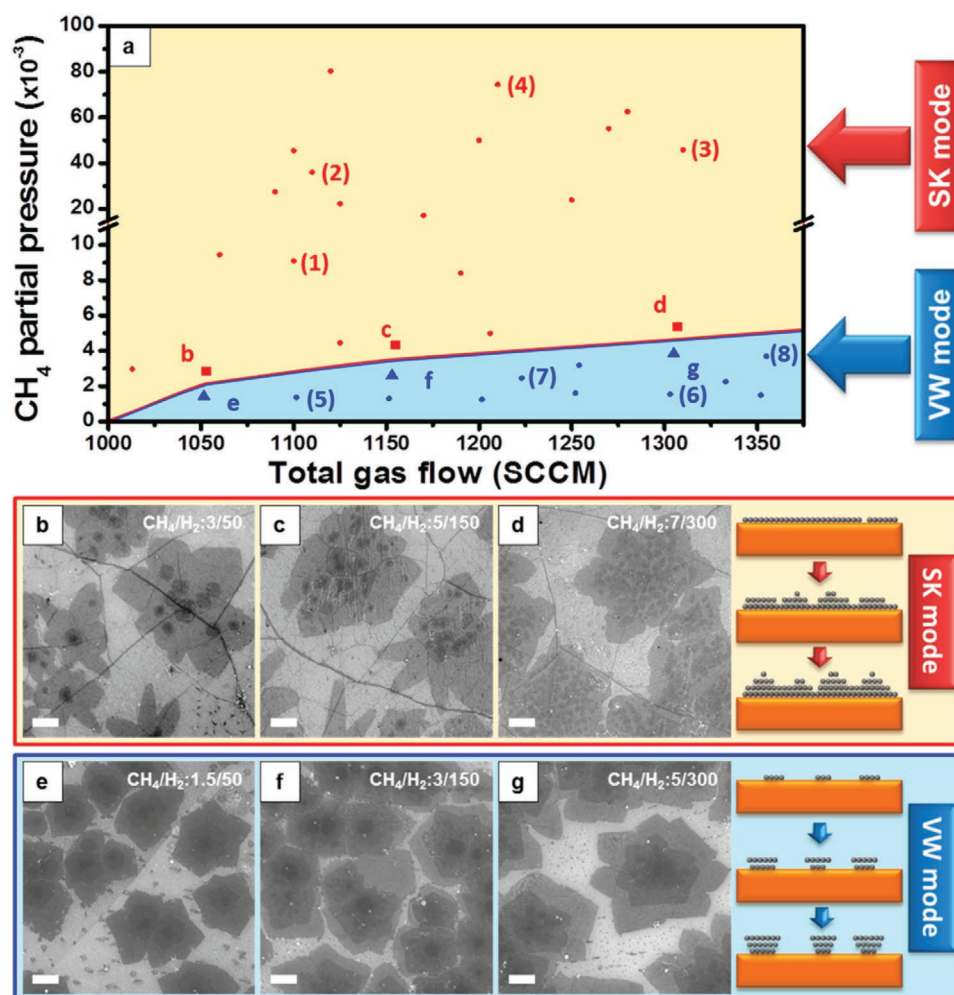


Figure 2. Relative gas flow windows used to investigate the dependence of graphene growth modes with respect to the CH_4 partial pressure (estimated by the flow rate of CH_4 divided by the total flow rate) versus the total gas flow a) (total gas flow includes CH_4 , H_2 , and a constant flow 1000 SCCM of Ar). The small dots indicated all the measured points. b–d) A set of SEM images showing SK-like bilayer graphene growth corresponding to b–d) red square spots in (a). The graphene flakes irregular in shape in the SK-like mode. e–g) A set of SEM images showing VW-like bilayer graphene growth corresponding to e–g) blue triangle spots in (a). The graphene flakes are regular in shape in the VW-like mode. All scale bars are 2 μm . Reproduced with permission.^[31] Copyright 2016, American Chemical Society.

transistors because of the adjustable Schottky barrier, which forms between graphene and semiconductor.^[47]

Early work with nonmetal substrates showed the potential of a number of oxides, namely, SiO_2 , Al_2O_3 , MgO , Ga_2O_3 , and ZrO as substrates for graphene growth.^[48] The study suggested that oxides do have a catalytic role to play, and subsequent studies at the low temperature of 325 °C confirmed that oxide base substrates do provide some catalytic role.^[49]

3.2.1. Solid Nonmetal Substrates

Most CVD approaches with nonmetal substrates use solid substrates. One of the more important substrates is Si wafers (Si/SiO_x). While various studies have been conducted to achieve this directly on the SiO_x surface, to achieve large area homogeneous monolayer graphene is challenging. One approach implemented the use of O_2 to aid an APCVD process

which yielded polycrystalline monolayer graphene.^[50] Another APCVD study (also with CH_4 as the precursor) obtained few-layer graphene.^[51] With near equilibrium CVD, researchers found single crystal graphene flakes with hexagonal and dodecagonal shapes over the SiO_x surface.^[52] However, large area, homogeneous monolayer graphene is particularly difficult to obtain. To overcome this issue, a confinement technique in which two Si/SiO_x wafers with their oxide faces in contact in a sandwich configuration was used to yield homogeneous single-layer large area graphene.^[53] The graphene is polycrystalline and the grain boundaries are faceted (see **Figure 4**) indicating further improvements are needed for single-layer material, but this is still a positive development.

To reduce the CVD synthesis temperature, plasma-enhanced CVD (PECVD) can be used. A low temperature (550–650 °C) PECVD process was demonstrated by a number of investigators.^[54–56] PECVD can also be used for the growth of graphene nanowalls.^[57] One study, showing growth

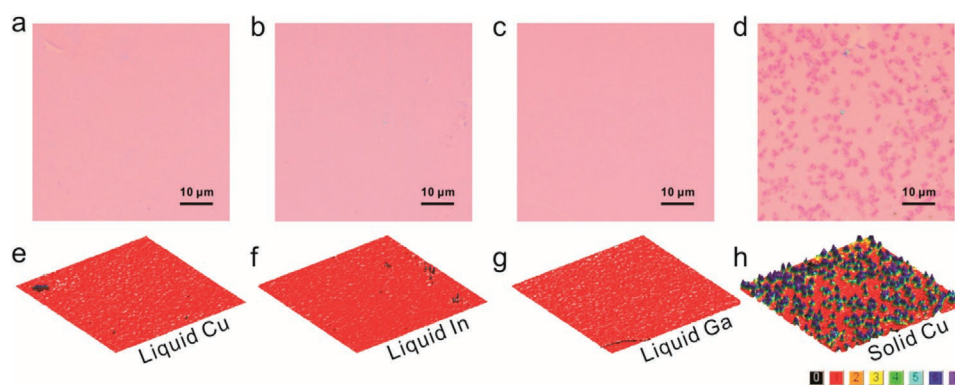


Figure 3. Typical growth results on liquid or solid metal substrates. a–c) Optical microscope images of graphene grown on liquid Cu, In, and Ga, respectively, which demonstrates the excellent uniformity of the single-layer graphene. d) Optical microscope image of graphene grown on solid Cu foil under ambient pressure, which indicates poor uniformity. All the graphene films were transferred onto 300 nm SiO₂/Si substrates for characterization. The scale bars are 10 μ m. e–h) Layer distribution determined by RGB color analysis of the corresponding optical microscope images (a–d), respectively. The layer thickness is represented by different colors as seen from the bottom color codes. Reproduced with permission.^[43] Copyright 2014, American Chemical Society.

temperatures even as low as 400 °C showed micrometer-sized graphene crystals forming the walls.

Graphene can also be directly grown on Al₂O₃ wafers, although this typically requires very high temperatures for good quality (poly-crystalline) graphene.^[58] Al₂O₃ is attractive in that it can serve as a device substrate, viz., a device may be fabricated directly on the synthesized graphene without the need to invoke a transfer process.^[47] The Al sites on γ -Al₂O₃ are highly reactive and act as catalytic sites.^[59,60] Song et al.^[61] presented an APCVD approach using CH₄ as the precursor in which they could obtain mono-layer graphene. Another group employed PECVD and obtained uniform graphene films.^[54]

TiO₂ is another substrate explored for its potential for graphene synthesis by CVD. The direct synthesis of graphene was first demonstrated over r-TiO₂ after wet etching followed by flattening to atomic smoothness over the (001), (110), and (100) faces.^[62] The

graphene quality was found to be superior for the (110) face under the same growth parameters. Another group showed that graphene fabrication of TiO₂ was possible for both APCVD and LPCVD for mono- and few-layer formation.^[63] In the case of SrTiO₃ (STO) graphene film formation by CVD was shown through APCVD.^[64]

The potential for graphene CVD growth at low temperatures on an oxide was demonstrated using MgO crystals at the low temperature of 325 °C using acetylene as the precursor.^[49] Such low temperature approaches are relevant to maintain the mechanical integrity of low-dielectric constant (*K*) intermetal dielectrics in transistor technology. Another, low temperature graphene fabrication, also on a high *K* dielectric material was demonstrated by the same team on ZrO₂, again with acetylene and at a low temperature of 480 °C with acetylene as the precursor.^[65] Another group showed vertically grown graphene sheets could form on ZrO₂ through thermal CVD

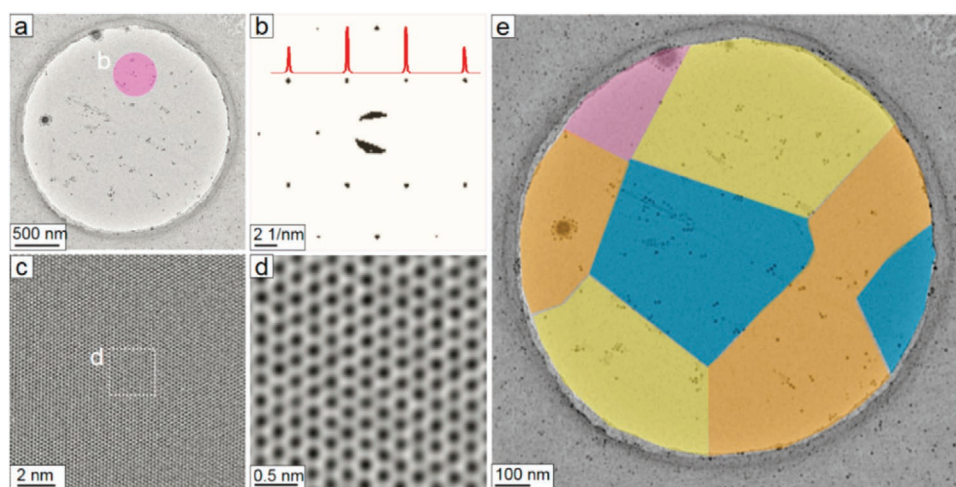


Figure 4. TEM characterizations of the large-area synthetic monolayer graphene (from sandwich configuration). a) Low-magnification micrograph of a graphene film transferred onto a holey carbon TEM grid. b) SAED pattern of the region circled in (a). The inset profile shows the intensity profile of the diffraction spots. c, d) High-resolution TEM images showing the honeycomb atomic configuration of graphene. e) False-color composite micrograph highlighting the different domain (grain) orientations and faceted grain boundaries. Reproduced with permission.^[53] Copyright 2017, American Chemical Society.

using methane or ethanol as the precursor.^[66] This work was also interesting because typically PECVD is required for vertical graphene growth. Another technologically important substrate for graphene growth is silicon nitride (Si_3N_4). This was accomplished with a two-stage CVD process. The graphene sheets are seen to form independently and then later merge to form a polycrystalline film.^[67] Graphene can also form on aluminum nitride. Direct growth of graphene was shown on another nitride, namely, AlN (AlN/Si (111)). In this case, propane served as the precursor and, as found with a number of non-metal catalysts, temperature is relevant in terms of the graphene quality, such that it improves as the temperature increases. In this case, 1350 °C was needed for high quality graphene.^[68]

Graphene can also be grown on a number of traditional glasses and this could be important for a number of daily life applications. An APCVD approach demonstrated for the first time the direct well-controlled growth of high quality graphene on insulating solid glasses was possible. Moreover, the layer thickness could also be tuned.^[69] PECVD can also be employed to grow graphene films directly over quartz (see Figure 5). Nanographene films with good uniformity were grown over 4 in. wafers.^[54] Vertical graphene growth over quartz by CVD has also been shown over quartz substrates^[66] and suggests it is a rather versatile substrate for graphene formation. In the case of vertical graphene, this can also occur over carbon buffer layers.^[70]

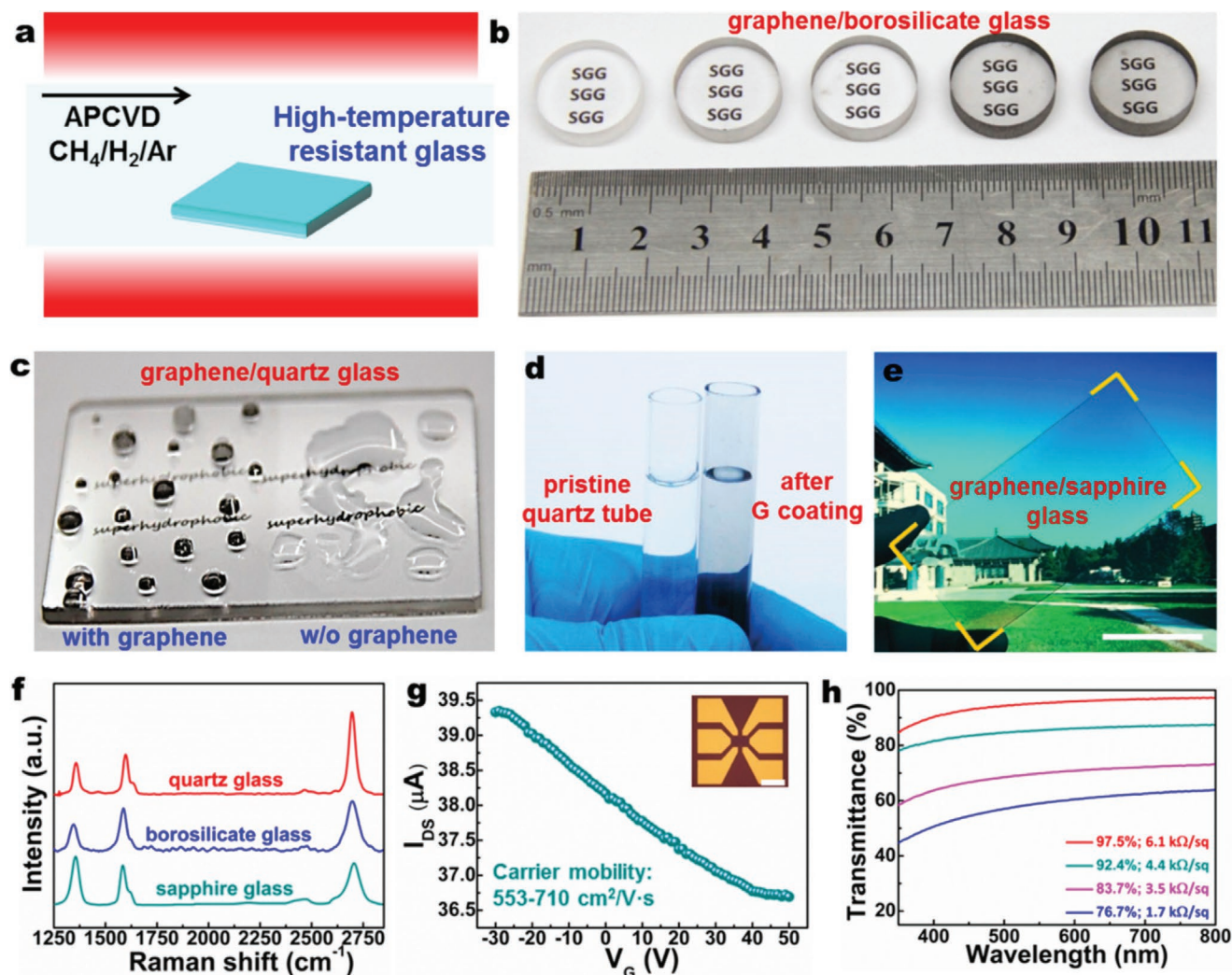


Figure 5. Catalyst-free APCVD growth of uniform graphene on various solid glasses. a) Schematic diagram of the catalyst-free APCVD growth method. b) Photograph of the borosilicate glass substrates before (leftmost) and after graphene growth with different CH_4 flow rates at 2, 5, 7.5, and 10 sccm. c) Demonstration of the hydrophobic and hydrophilic nature of graphene/quartz glass (the left part) and the bare quartz glass, respectively. d) Photograph showing the differences in water containing behaviors between the graphene-coated and pristine quartz test tubes. e) Photograph of graphene/sapphire glass plate displaying a good transparency. Scale bar: 4 cm. f) Representative Raman spectra of directly grown graphene on different types of solid glasses. g) Transfer curve of the graphene FET; the inset shows an optical microscope image of an individual device. The graphene was grown on quartz glass under the following APCVD condition: $\text{Ar}/\text{H}_2/\text{CH}_4$, 100/50/8 sccm at 1020 °C for 3 h. Scale bar: 100 μm . h) Sheet resistance and UV-vis transmittance spectra in the wavelength range of 350–800 nm of the graphene/quartz glass. Reproduced with permission.^[69] Copyright 2015, American Chemical Society.

3.3. Molten Nonmetal Substrates

It is believed that by using a molten liquid insulating substrate, the uniform nucleation and accelerated growth of graphene can occur. This was first shown on soda-lime glass (which has a low softening point of 620 °C). Soda lime glass is cheap and inexpensive and is used in various applications.^[71] In this case an APCVD approach was implemented. The application potential of the as-produced graphene on soda-lime glass was also demonstrated for smart heating-devices such as transparent defoggers and thermochromic displays, and for biocompatible cell culture mediums. The same team extended the growth of uniform graphene (over soda-lime glass) to show large area growth over 12 in. areas.^[72]

3.4. Flexible Nonmetallic Substrates

As for rigid nonmetal substrates, a key advantage of growing graphene directly on flexible substrates is the avoidance of transfer induced damage (e.g., cracks, tears, and wrinkles). Moreover, the direct growth of graphene over flexible substrates has significant promise for flexible and stretchable electronics. Examples include e-skin and health monitoring on humans.^[73–75] However, there are constraints with some of these materials due to low temperatures being a prerequisite to avoid melting, deforming or damaging the substrate (e.g., with polyimide substrates). For some substrates, this is not so, e.g., mica and hBN, which we first look at. Nanographene films were grown on mica using a PECVD approach with CH₄ as the precursor at the relatively low temperature of 525 °C.^[54] There is considerable interest in graphene growth over hBN because its lattice parameter is the same as for graphene.^[8,76] The CVD growth of graphene over hBN as shown for hBN initially grown over a Cu substrate (and the Cu base substrate remained for the CVD growth of graphene, so strictly the substrate was hBN/Cu).^[77] Ding et al.^[78] developed a metal free CVD approach for few-layer graphene.^[77] Similarly, Liu et al.^[79] obtained few-layer graphene over hBN using cyclohexane as the precursor using an APCVD approach. Another approach is to grow graphene directly over hBN using seed-assisted growth. The use of the well-defined poly(methyl methacrylate) seeds enabled effective control over the nucleation densities and locations of the graphene domains on predeposited h-BN monolayers. This allowed the formation of patterned G/h-BN arrays or continuous films.^[80]

For temperature sensitive flexible substrates such polyimide (PI) and polydimethylsiloxane (PDMS) metal capping layers are used to provide a catalyst-assisted CVD system and thus enable low temperatures to be used. Cu deposited on PI allowed a low temperature PECVD route at 300 °C.^[81] While for PDMS Ni was deposited over the base PDMS.^[7]

4. Outlook

For graphene (and other van der Waals 2D materials) to fulfill their promise in applications, it will be crucial that they can be synthesized under appropriate conditions, such as, within certain temperature windows, and that this, in many cases,

can be achieved directly on the surface of the material in question, viz., on any substrate. This is a grand task. CVD is also a well-established technique and is versatile. As has been demonstrated in this review, researchers have been making significant strides to develop the method for graphene synthesis over a broad range of substrates under a variety of conditions and, moreover, have been pushing the boundaries to achieve this on at remarkably low temperatures. Still there are challenges. As was highlighted, the direct synthesis of graphene on polymers, which will be crucial for flexible based devices, is an example where improved CVD approaches are needed. This is likely an area where important developments will be seen in the near future. In addition, directly grown patterned graphene, for example for devices, will become ever more relevant and it is conceivable that CVD merged with another technique could be a key player. One could imagine CVD reactions operating slightly below the nucleation and growth thresholds in combination, with, for example, an electron beam or laser beam that can then overcome the thresholds at specific local regions and in this way yield patterned graphene growth. This same approach could be applied to other 2D materials and pave the way for patterned hetero 2D materials fabrications both in stacked and laterally stitched configurations. Another important aspect of graphene growth likely to be seen in the future is large area and wafer scale single crystal growth of graphene. This remains challenging, but the pace of change in this field suggests breakthroughs will emerge soon, and a key aspect for this is likely to be related to a mix of the right CVD reaction/reactor configurations and clever choice/implementation of substrate. Another aspect one can anticipate in the future is high speed growth of large area single crystal graphene by CVD. Moreover, future developments with substrate use in CVD will minimize or even remove the need for transfer and thus, enable the best graphene performance to be extracted in which ever application it is used.

5. Conclusion

The changes seen in the growth of graphene by CVD have been rapid since the first evidence of single-layer graphene. CVD is a technologically established technique, and is relatively versatile and, is highly successful at producing graphene. Although initially metal substrates were required, in recent years this is no longer true and numerous dielectric substrates can be used for the successful growth of graphene by CVD. Moreover, significant inroads are being made in terms flexible substrates which will be a key technology field in the near future. In addition, it is likely that the patterned direct growth of graphene and large area single crystal graphene will be demonstrated soon. In all these developments (past, present, and future), substrate availability is crucial to the applications success not only of graphene, but also other 2D materials and their combinations to yield hetero 2D systems.

Acknowledgements

Q.S. and K.T. contributed equally to this work. This work was supported by the National Science Foundation China (NSFC, Project 51672181),

the National Science Center, Poland for the financial support within the frame of the Opus program (Grant agreement 2015/19/B/ST5/03399), the Czech Republic from the ERDF "Institute of Environmental Technology - Excellent Research" (No. CZ.02.1.01/0.0/0.0/16_019/00 00853). M.H.R. and L.F. thank the Sino-German Research Institute for support (project: GZ 1400).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

chemical vapor deposition, graphene, substrate, support, synthesis

Received: November 29, 2019

Revised: January 12, 2020

Published online: February 16, 2020

- [1] J. H. Warner, F. Schffell, A. Bachmatiuk, M. H. Rummeli, *Graphene*, Elsevier, UK **2013**.
- [2] R. S. Edwards, K. S. Coleman, *Nanoscale* **2013**, 5, 38.
- [3] P. Avouris, C. Dimitrakopoulos, *Mater. Today* **2012**, 15, 3.
- [4] W. Feng P. Long, Y. Feng, Y. Li, *Adv. Sci.* **2016**, 3, 1500413.
- [5] Y. Zhang, L. Zhang, C. Zhou, *Acc. Chem. Res.* **2013**, 46, 2329.
- [6] M. J. Allen, V. C. Tung, R. B. Kaner, *Chem. Rev.* **2010**, 110, 132.
- [7] G. Li, B. Huang, Z. Pan, X. Su, Z. S. , L. An, *Energy Environ. Sci.* **2019**, 12, 2030.
- [8] B. Aïssa, N. K. Memon, A. Ali, M. K. Khraisheh, *Front. Mater.* **2015**, 2, 58.
- [9] H. Wang, T. Maiyalagan, X. Wang, *ACS Catal.* **2012**, 2, 781.
- [10] P. Russ, A. Hu, G. Compagnini, *Nano-Micro Lett.* **2013**, 5, 260.
- [11] V. P. Pham, *Direct Growth of Graphene on Flexible Substrates toward Flexible Electronics: A Promising Perspective*, IntechOpen **2018**, <https://doi.org/10.5772/intechopen.73171>.
- [12] J. E. Kim, D. H. Lee, T. H. Han, J. W. Hwang, S. Jeon, S.-Y. Choi, S. H. Hong, W. J. Lee, R. S. Ruoff, S. O. Kim, *Adv. Mater.* **2010**, 22, 1247.
- [13] D. W. Hess, K. F. Jensen, T. J. Anderson, *Chemical Vapor Deposition: A Chemical Engineering Perspective*, Vol. 3, Walter de Gruyter GmbH, Germany **2011**.
- [14] T. B. Massalski, H. Okamoto, P. R. Subramanian, L. Kacprzak, *ASM Handbook: Alloy Phase Diagrams*, Vol. 3, ASM International, Materials Park, OH **2002**.
- [15] Q. Yu, J. Lian, S. Siriponglert, H. Li, Y. Chen, S.-S. Pei, *Appl. Phys. Lett.* **2008**, 93, 113103.
- [16] L. G. De Arco, Y. Zhang, A. Kumar, C. Zhou, *IEEE Trans. Nanotechnol.* **2009**, 8, 135.
- [17] A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, M. S. Dresselhaus, J. Kong, *Nano Lett.* **2009**, 9, 30.
- [18] A. J. Pollard, R. R. Nair, S. N. Sabki, C. R. Staddon, L. M. A. Perdigo, C. H. Hsu, J. M. Garfitt, S. Gangopadhyay, H. F. Gleeson, A. K. Geim, P. H. Beton, *J. Phys. Chem. C* **2009**, 113, 16565.
- [19] B. Dai, L. Fu, Z. Zou, M. Wang, H. Xu, S. Wang, Z. Liu, *Nat. Commun.* **2011**, 2, 522.
- [20] M. H. Rummeli, M. Zeng, S. Melkhanova, S. Gorantla, A. Bachmatiuk, L. Fu, C. Yan, S. Oswald, R. G. Mendes, D. Makarov, O. Schmidt, J. Eckert, *Chem. Mater.* **2013**, 25, 3880.
- [21] Y. Zhang, L. Gomez, F. N. Ishikawa, A. Madaria, K. Ryu, C. Wang, A. Badmaev, C. Zhou, *Chem. Lett.* **2010**, 1, 3101.
- [22] P. W. Sutter, J.-I. Flege, E. A. Sutter, *Nat. Mater.* **2008**, 7, 406.
- [23] J. Coraux, A. T. N'Diaye, C. Busse, T. Michely, *Nano Lett.* **2008**, 8, 565.
- [24] P. Sutter, J. T. Sadowski, E. Sutter, *Phys. Rev. B* **2009**, 80, 245411.
- [25] A. Varykhalov, O. Rader, *Phys. Rev. B* **2009**, 80, 035437.
- [26] S. M. Wang, Y. H. Pei, X. Wang, H. Wang, Q. N. Meng, H. W. Tian, X. L. Zheng, W. T. Zheng, Y. C. Liu, *J. Phys. D: Appl. Phys.* **2010**, 43, 455402.
- [27] S.-Y. Kwon, C. V. Ciobanu, V. Petrova, V. B. Shenoy, J. Baren, V. Gambin, I. Petrov, S. Kodambaka, *Nano Lett.* **2009**, 9, 3985.
- [28] E. Miniussi, M. Pozzo, A. Baraldi, E. Vesselli, R. R. Zhan, G. Comelli, T. O. Montes, M. A. Nin, A. Locatelli, S. Lizzit, D. Alfe, *Phys. Rev. Lett.* **2011**, 106, 216101.
- [29] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo, R. S. Ruoff, *Science* **2009**, 324, 1312.
- [30] M. H. Rummeli, S. Gorantla, A. Bachmatiuk, J. Phielers, N. Geißler, I. Ibrahim, J. Pang, J. Eckert, *Chem. Mater.* **2013**, 25, 4861.
- [31] H. Q. Ta, D. J. Perello, D. L. Duong, G. H. Han, S. Gorantla, V. L. Nguyen, A. Bachmatiuk, S. V. Rotkin, Y. H. Lee, M. H. Rummeli, *Nano Lett.* **2016**, 16, 6403.
- [32] G. Kresse, J. Hafner, *Phys. Rev. B* **1993**, 47, 558.
- [33] J. L. Finney, *Proc. R. Soc. A* **1970**, 319, 479.
- [34] H.-B. Li, A. J. Page, C. Hettich, B. Aradi, C. Köhler, T. Frauenheim, S. Irle, K. Morokuma, *Chem. Sci.* **2014**, 5, 3493.
- [35] D. Geng, B. Wu, Y. Guo, L. Huang, Y. Xue, J. Chen, G. Yu, L. Jiang, W. Hu, Y. Liu, *Proc. Natl. Acad. Sci. USA* **2012**, 109, 7992.
- [36] J. Liu, L. Fu, *Adv. Mater.* **2019**, 31, 1800690.
- [37] J. Chen, X. Zhao, S. J. R. Tan, H. Xu, B. Wu, B. Liu, D. Fu, W. Fu, D. Geng, Y. Liu, W. Liu, W. Tang, L. Li, W. Zhou, T. C. Sum, K. P. Loh, *J. Am. Chem. Soc.* **2017**, 139, 1073.
- [38] M. Einax, W. Dieterich, P. Maass, *Rev. Mod. Phys.* **2013**, 85, 921.
- [39] B. Wu, D. Geng, Z. Xu, Y. Guo, L. Huang, Y. Xue, J. Chen, G. Yu, Y. Liu, *NPG Asia Mater.* **2013**, 5, e36.
- [40] D. Geng, B. Wu, Y. Guo, B. Luo, Y. Xue, J. Chen, G. Yu, Y. Liu, *J. Am. Chem. Soc.* **2013**, 135, 6431.
- [41] D. Geng, H. Wang, Y. Wan, Z. Xu, B. Luo, J. Xu, G. Yu, *Adv. Mater.* **2015**, 27, 4195.
- [42] J. Wang, M. Zeng, L. Tan, S. Wang, L. Peng, J. Eckert, B. Dai, Y. Deng, M. H. Rummeli, L. Fu, *Sci. Rep.* **2013**, 3, 2670.
- [43] M. Zeng, L. Tan, J. Wang, L. Chen, M. H. Rummeli, L. Fu, *Chem. Mater.* **2014**, 26, 3637.
- [44] M. Zeng, L. Tan, L. Wang, R. G. Mendes, Z. Qin, Y. Huang, T. Zhang, L. Fang, Y. Zhang, S. Yue, M. H. Rummeli, L. Peng, Z. Liu, S. Chen, L. Fu, *ACS Nano* **2016**, 10, 7189.
- [45] M. Zeng, L. Wang, J. Liu, T. Zhang, H. Xue, Y. Xiao, Z. Qin, L. Fu, *J. Am. Chem. Soc.* **2016**, 138, 7812.
- [46] W. Lu, M. Zeng, X. Li, J. Wang, L. Tan, M. Shao, J. Han, S. Wang, S. Yue, T. Zhang, X. Hu, R. G. Mendes, M. H. Rummeli, L. Peng, Z. Liu, L. Fu, *Adv. Sci.* **2016**, 3, 1600006.
- [47] A. Khan, S. M. Islam, S. Ahmed, R. R. Kumar, M. R. Habib, K. Huang, M. Hu, X. Yu, D. Yang, *Adv. Sci.* **2018**, 5, 1800050.
- [48] M. H. Rummeli, C. Kramberger, A. Grüneis, P. Ayala, T. Gemming, B. Büchner, T. Pichler, *Chem. Mater.* **2007**, 19, 4105.
- [49] M. H. Rummeli, A. Bachmatiuk, A. Scott, V. Hoffman, J.-H. Lin, G. Cuniberti, F. Börrnert, J. H. Warner, B. Büchner, *ACS Nano* **2010**, 4, 4206.
- [50] J. Chen, Y. Wen, Y. Guo, B. Wu, L. Huang, Y. Xue, D. Geng, D. Wang, G. Yu, Y. Liu, *J. Am. Chem. Soc.* **2011**, 133, 17548.
- [51] H. Bi, S. Sun, F. Huang, X. Xie, M. Jiang, *J. Mater. Chem.* **2012**, 22, 411.
- [52] J. Chen, Y. Guo, L. Jiang, Z. Xu, L. Huang, Y. Xue, D. Geng, B. Wu, W. Hu, G. Yu, Y. Liu, *Adv. Mater.* **2014**, 26, 1348.
- [53] J. Pang, R. G. Mendes, P. S. Wrobel, M. D. Włodarski, H. Q. Ta, L. Zhao, L. Giebeler, B. Trzebicka, T. Gemming, L. Fu, Z. Liu, J. Eckert, A. Bachmatiuk, M. H. Rummeli, *ACS Nano* **2017**, 11, 1946.

- [54] L. Zhang, Z. Shi, Y. Wang, R. Yang, D. Shi, G. Zhang, *Nano Res.* **2011**, 4, 315.
- [55] W. Yang, C. He, L. Zhang, Y. Wang, Z. Shi, M. Cheng, G. Xie, D. Wang, R. Yang, D. Shi, G. Zhang, *Small* **2012**, 8, 1429.
- [56] D. Wei, Y. Lu, C. Han, T. Niu, W. Chen, A. T. S. Wee, *Angew. Chem., Int. Ed.* **2013**, 52, 14121.
- [57] I. S. Hosu, M. Sobaszek, M. Ficek, R. Bogdanowicz, H. Drobecq, L. Boussekey, A. Barras, O. Melnyk, R. Boukherroub, Y. Coffinier, *Nanoscale* **2017**, 9, 9701.
- [58] J. Hwang, M. Kim, D. Campbell, H. A. Alsaman, J. Y. Kwak, S. Shivaraman, A. R. Woll, A. K. Singh, R. G. Hennig, S. Gorantla, M. H. Rummeli, M. G. Spencer, *ACS Nano* **2013**, 7, 385.
- [59] R. Wischert, P. Laurent, C. Copéret, F. Delbecq, P. Sautet, *J. Am. Chem. Soc.* **2012**, 134, 14430.
- [60] R. Wischert, C. Copéret, F. Delbecq, P. Sautet, *Angew. Chem., Int. Ed.* **2011**, 50, 3202.
- [61] H. J. Song, M. Son, C. Park, H. Lim, M. P. Levendorf, A. W. Tsen, J. Park, H. C. Choi, *Nanoscale* **2012**, 4, 3050.
- [62] H. Liu, D. Zhu, H. Shi, X. Shao, *ACS Omega* **2016**, 1, 168.
- [63] T. Bansal, C. A. Durcan, N. Jain, R. B. J.-Gedrim, Y. Xu, B. Yu, *Carbon* **2013**, 55, 168.
- [64] J. Sun, T. Gao, X. Song, Y. Zhao, Y. Lin, H. Wang, D. Ma, Y. Chen, W. Xiang, J. Wang, Y. Zhang, Z. Liu, *J. Am. Chem. Soc.* **2014**, 136, 6574.
- [65] A. Scott, A. Dianat, F. Börrnert, A. Bachmatiuk, S. Zhang, J. H. Warner, E. B.-Paleri, M. Knupfer, B. Büchner, G. Cuniberti, M. H. Rummeli, *Appl. Phys. Lett.* **2011**, 98, 073110.
- [66] H. Wang, E. Gao, P. Liu, D. Zhou, D. Geng, X. Xue, L. Wang, K. Jiang, Z. Xu, G. Yu, *Carbon* **2017**, 121, 1.
- [67] J. Chen, Y. Guo, Y. Wen, L. Huang, Y. Xue, D. Geng, B. Wu, B. Luo, G. Yu, Y. Liu, *Adv. Mater.* **2013**, 25, 992.
- [68] A. Michon, A. Tiberj, S. Vezian, E. Roudon, D. Lefebvre, M. Portail, M. Zielinski, T. Chassagne, J. Camassel, Y. Cordier, *Appl. Phys. Lett.* **2014**, 104, 071912.
- [69] J. Sun, Y. Chen, M. K. Priyadarshi, Z. Chen, A. Bachmatiuk, Z. Zou, Z. Chen, X. Song, Y. Gao, M. H. Rummeli, Y. Zhang, Z. Liu, *Nano Lett.* **2015**, 15, 5846.
- [70] Y. Ma, W. Jiang, J. Han, Z. T. , M. Wang, J. Suhr, X. Chen, L. Xiao, S. Jia, H. Chae, *ACS Appl. Mater. Interfaces* **2019**, 11, 10237.
- [71] Y. Chen, J. Sun, J. Gao, F. Du, Q. Han, Y. Nie, Z. Chen, A. Bachmatiuk, M. K. Priyadarshi, D. Ma, X. Song, X. Wu, C. Xiong, M. H. Rummeli, F. Ding, Y. Zhang, Z. Liu, *Adv. Mater.* **2015**, 27, 7839.
- [72] Z. Chen, H. Ci, Z. Tan, Z. Dou, X. Chen, B. Li, R. Liu, L. Lin, L. Cui, P. Gao, H. Peng, Y. Zhang, Z. Liu, *Nano Res.* **2019**, 12, 1888.
- [73] S. Choi, H. Lee, R. Ghaffari, T. Hyeon, D.-H. Kim, *Adv. Mater.* **2016**, 28, 4203.
- [74] M. L. Hammock, A. Chortos, B. C.-K. Tee, J. B.-H. Tok, Z. Bao, *Adv. Mater.* **2013**, 25, 5997.
- [75] H. Kim, J.-H. Ahn, *Carbon* **2017**, 120, 244.
- [76] R. Decker, Y. Wang, V. W. Brar, W. Regan, H.-Z. Tsai, Q. Wu, W. Gannett, A. Zettl, M. F. Crommie, *Nano Lett.* **2011**, 11, 2291.
- [77] M. Yankowitz, J. Xue, D. Cormode, J. D. S.-Yamagishi, K. Watanabe, T. Taniguchi, P. J.-Herrero, P. Jacquod, B. J. LeRoy, *Nat. Phys.* **2012**, 8, 382.
- [78] X. Ding, G. Ding, X. Xie, F. Huang, M. Jiang, *Carbon* **2011**, 49, 2522.
- [79] Z. Liu, L. Song, S. Zhao, J. Huang, P. M. Ajayan, *Nano Lett.* **2011**, 11, 2032.
- [80] X. Song, T. Gao, Y. Nie, J. Zhuang, J. Sun, D. Ma, J. Shi, Y. Lin, F. Ding, Y. Zhang, Z. Liu, *Nano Lett.* **2016**, 16, 6109.
- [81] Y.-J. Kim, S. J. Kim, M. H. Jung, K. Y. Choi, S. Bae, S.-K. Lee, Y. Lee, D. Shin, B. Lee, H. Shin, M. Choi, K. Park, J.-H. Ahn, B. H. Hong, *Nanotechnology* **2012**, 23, 344016.