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## Novel Liquid Precursor-Based Facile Synthesis of Large-Area Continuous, Single, and Few-Layer Graphene Films

Anchal Srivastava,<sup>\*,†,‡</sup> Charudatta Galande,<sup>†</sup> Lijie Ci,<sup>†</sup> Li Song,<sup>†</sup> Chaitra Rai,<sup>§</sup>  
Deep Jariwala,<sup>†,⊥</sup> Kevin F. Kelly,<sup>§</sup> and Pulickel M. Ajayan<sup>\*,†</sup>

<sup>†</sup>Department of Mechanical Engineering and Materials Science, and <sup>§</sup>Department of Electrical and Computer Engineering and the Rice Quantum Institute, Rice University, Houston, Texas 77005, and

<sup>‡</sup>Department of Physics, Banaras Hindu University, Varanasi, 221005, India. <sup>⊥</sup>Present Address:

Department of Metallurgical Engineering, Institute of Technology, Banaras Hindu University, Varanasi 221005, U.P., India

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Graphene has attracted a great deal of attention because of its unique band structure and electronic properties that make it promising for applications in next-generation electronic devices, transparent flexible conducting electrodes, and sensors. Here, we report the substrate selective growth of centimeter size ( $\sim 3.5\text{ cm} \times 1.5\text{ cm}$ ), uniform, and continuous single and few-layer graphene films employing chemical vapor deposition technique on polycrystalline Cu foils using liquid precursor hexane. Structural characterizations suggest that as-grown graphene films are mostly single and few layers over large areas. We have demonstrated that these graphene films can be easily transferred to any desired substrate without damage. A liquid-precursor-based synthesis route opens up a new window for simple and inexpensive growth of pristine as well as doped graphene films using various organic liquids containing the dopant atoms.

### Introduction

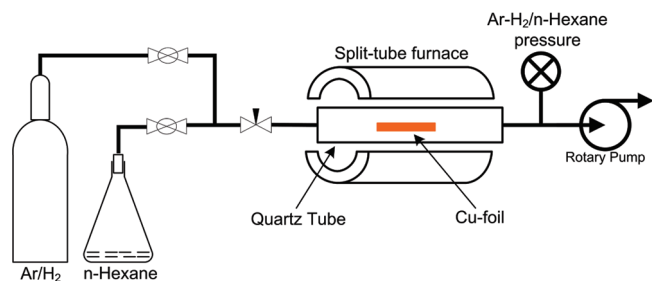
Graphene is a monolayer of  $sp^2$ -bonded carbon atoms packed into a honeycomb crystal structure and can be viewed either as an individual atomic plane extracted from graphite or unrolled single-wall carbon nanotubes. 2D graphene crystals exhibit many exciting properties, like room temperature quantum Hall effect,<sup>1</sup> long-range ballistic transport at room temperature with around ten times higher electron mobility than silicon,<sup>2</sup> availability of charge carriers that behave as massless relativistic quasiparticles like Dirac fermions,<sup>3</sup> quantum confinement resulting in finite band gap and Coulomb blockade effects in graphene nanoribbons,<sup>4</sup> and ultimate sensitivity of adsorption of individual gas molecules.<sup>5</sup> This two-dimensional material, despite its short history, has already established an area of exciting research for new physics and potential applications in electronics. To realize the above properties and applications of graphene,

a consistent, reliable, simple and inexpensive method of growing high-quality, uniform, and continuous, single, and few-layer graphene films is a prerequisite. Graphene flakes produced by exfoliating graphite are limited by its size and scalability.<sup>6</sup> Epitaxial growth of multilayer graphene on SiC single crystal at atmospheric pressure requires high temperatures of around 1650 °C.<sup>7</sup> Recently, graphene growth by a vapor phase deposition of gaseous hydrocarbons on metal substrates such as Ni, Co, Ir, Ru, etc., has been reported.<sup>8–11</sup> Large-scale synthesis of graphene flakes using supported metal catalysts has also been achieved using RF-cCVD.<sup>12</sup> However, the problem of efficiently synthesizing high-quality, single-layer graphene still persists. More recently, large-area, single-layer graphene has been grown on Cu substrates by chemical vapor deposition technique using methane gas as a precursor.<sup>13</sup> This method produces large-area, mostly single-layer graphene; however, the major disadvantage

\*To whom correspondence should be addressed. E-mail: ajayan@rice.edu (P.M.A.); anchalbhu@gmail.com (A.S.).

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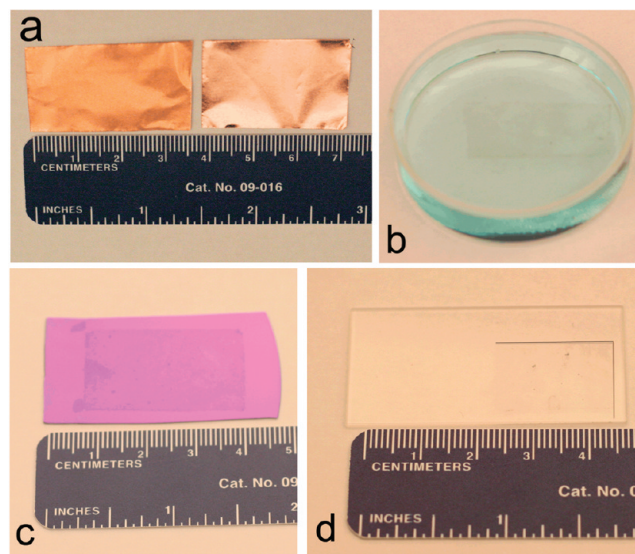


**Figure 1.** Schematic of chemical vapor deposition setup for growing graphene films. In this vacuum-assisted process, the vapors of liquid hexane flow because of pressure difference between the liquid precursor in the flask and the heating zone of the furnace. This zone consists of a rotary-pump-fitted quartz tube mounted in a temperature-controlled cylindrical furnace. The temperature of the furnace was raised to 950 °C. To avoid the oxidation of Cu, we evacuated the quartz tube and backfilled it with Ar/H<sub>2</sub> gas to maintain a pressure of 8–9 Torr until temperature reached 950 °C in 30 min. Before exposing the tube to hexane vapor, the flow of Ar/H<sub>2</sub> was stopped; n-hexane (C<sub>6</sub>H<sub>14</sub>) vapor was introduced for a desired period of time to maintain a pressure of ~500 mTorr. After exposure to n-hexane vapors, the furnace was cooled to room temperature at a rate of 50 °C/min under Ar/H<sub>2</sub>.

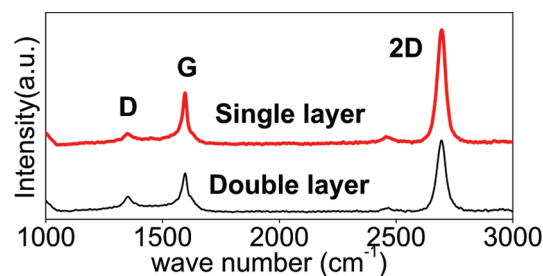
with this is that the process requires high vacuum and because the precursor is gaseous (methane), handling and maintaining pressure is difficult. However, liquid-precursor-based growth of graphene could be a milestone in graphene synthesis since organic solvents are inexpensive and easy to use. Here, we report the substrate selective growth of centimeter long, highly continuous, single, and few-layer graphene films employing vacuum assisted chemical vapor deposition technique on polycrystalline Cu foils using hexane as a novel liquid precursor. Growth based on a liquid precursor will certainly be advantageous over gas phase growth (methane, ethylene), because most of the organic compounds and its derivatives are readily and cheaply found in a liquid phase at room temperatures. Moreover, handling and transportation for gas-based organic precursors is always an issue. Another important issue is opening of the band gap in graphene by chemical doping in the carbon lattice. Liquid precursor based growth can help in realizing graphene doping because nitrogen- and boron-containing organic solvents (pyridine, triethylborane) are inexpensive and easy to use, whereas organic gases containing dopant atoms are rather uncommon. Doping can also be achieved by mixing a gas containing dopant atoms with precursor gas (e.g., CH<sub>4</sub> + NH<sub>3</sub>). However, this will also lead to inhomogeneities in gas pressures, flow rates, and doping over large areas.

### Experimental Details

Continuous graphene films were grown on 25 μm thick Cu foils by the chemical vapor deposition technique using hexane as a liquid precursor. A similar method is used to synthesize, large



**Figure 2.** (a) Photographs of as-received Cu foil (left), and image of graphene film grown on Cu substrate (right). The appearance of Cu foil after graphene growth is brighter and smoother. (b) Photograph of the PMMA-supported graphene film floating on dilute HNO<sub>3</sub> etching solution. Graphene films transferred onto a (c) SiO<sub>2</sub>/Si substrate and (d) ITO slide.



**Figure 3.** Raman spectrum of single-layer (red) and double-layer (black) graphene. It is clearly visible that the intensity of the G peak is much lower than that of the 2D peak, confirming the thickness, and that there is a negligible D peak, suggesting low defect density.

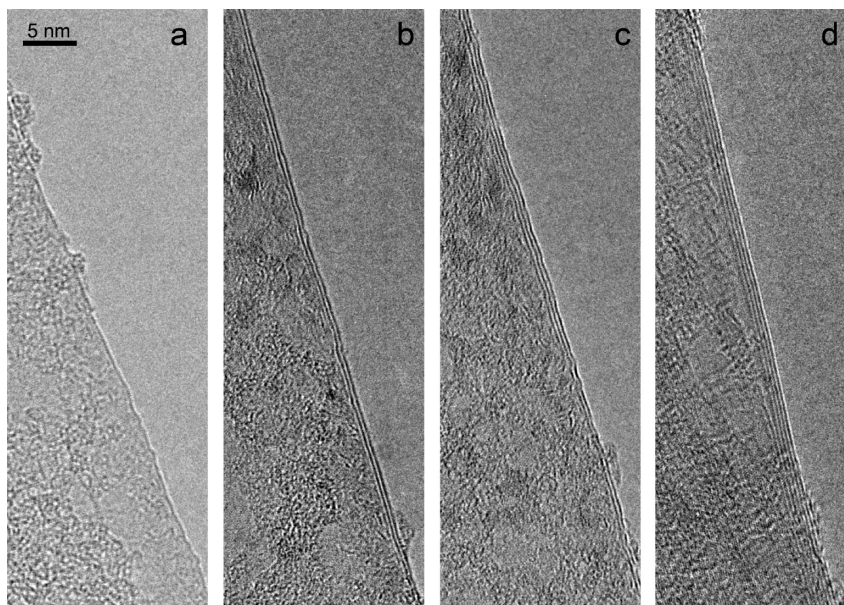
area wafer scale graphene films.<sup>13–16</sup> Cu foil was loaded in a quartz tube and pumped down until 10<sup>−2</sup> Torr before flowing in Ar/H<sub>2</sub> at a pressure of ~8–9 Torr (with flow rate of ~400 sccm). Samples were then heated to 950 °C inside the quartz tube in Ar/H<sub>2</sub> ambient. Maintaining relatively higher pressures of 8–9 Torr during annealing also reduces the chances of substrate getting oxidized. When the desired temperature was achieved, the Ar/H<sub>2</sub> flow was stopped and hexane vapor was passed in the quartz tube to maintain the tube pressure of 500 mTorr for 4 min. The flow rate of hexane was ~4 mL/h. A schematic of the experimental setup for the graphene growth and its parameters has been shown and discussed in Figure (1). Compared to the gaseous precursor (methane) based CVD synthesis reported on copper foils, good quality growth using liquid precursors have been achieved at comparatively lower temperatures (950 °C compared to 1000 °C) and higher pressures of Ar/H<sub>2</sub> (8–9 Torr as compared to 40 mTorr during annealing).

Cu foils with as-grown graphene films were first spin-coated with a thin layer of PMMA (poly methyl methacrylate). These films were separated from the Cu foils by dissolving the foil in dilute nitric acid as shown in Figure 2. After dissolution, the

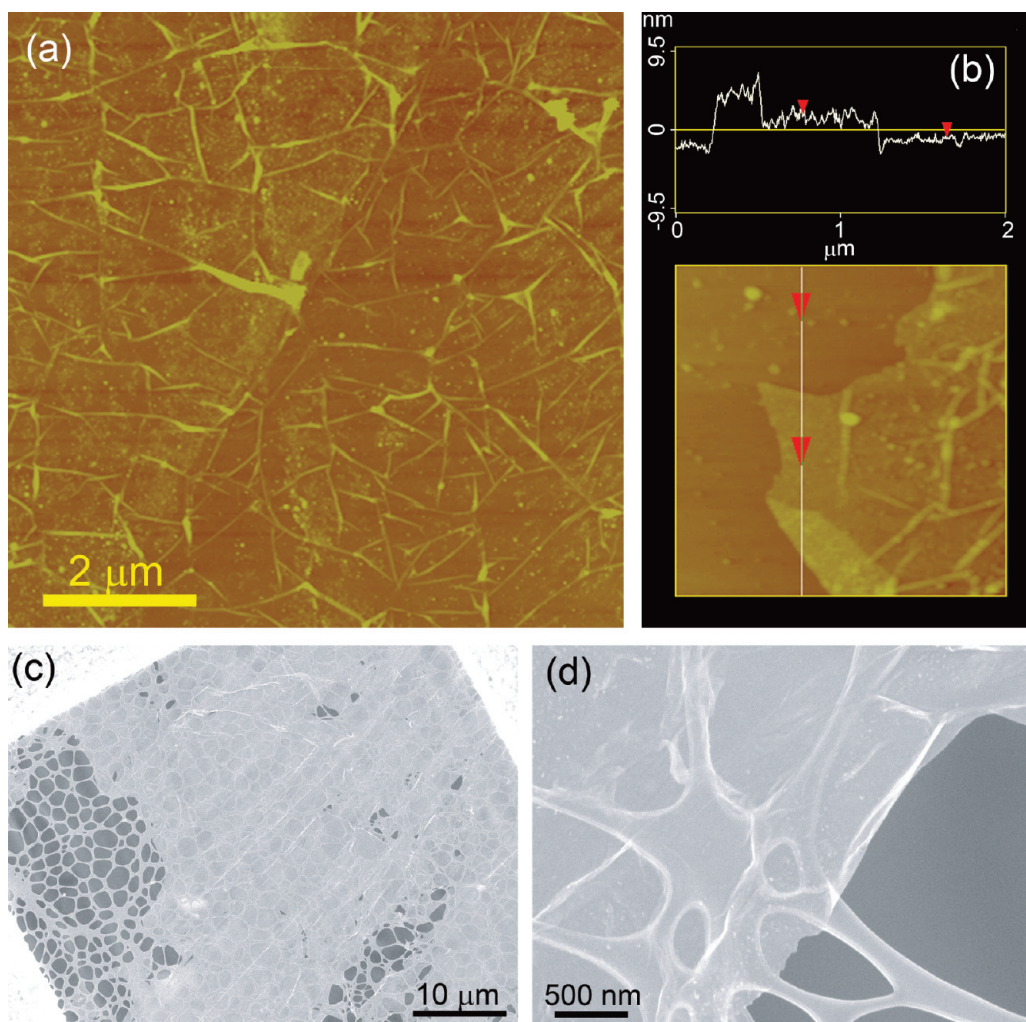
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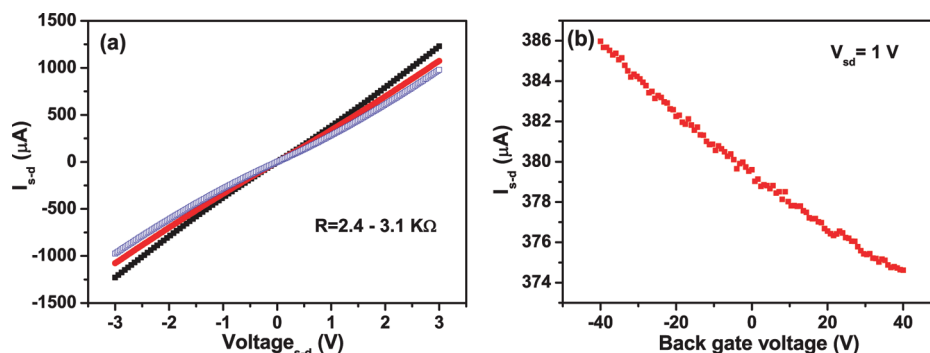




**Figure 4.** TEM images of CVD grown graphene showing (a) one, (b) two, (c) three, and (d) four layers.



**Figure 5.** AFM image of CVD-grown graphene transferred onto a SiO<sub>2</sub> substrate. It is clearly evident that the films are uniform and highly continuous. The wrinkles formed on the films during transfer are also clearly visible. The linear thickness analysis also shows that the films are about 1.5 nm thick. SEM image of as-grown graphene transferred on TEM grid clearly shows that the graphene film is uniform and continuous. The lacey carbon in the background can also be seen through the film.

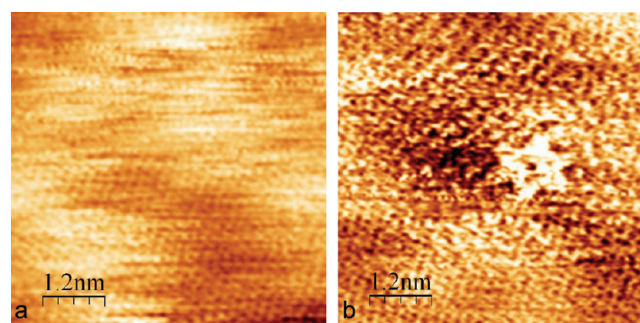


**Figure 6.** Electrical properties of the graphene grown by liquid precursor hexane (a)  $I_{ds}$ – $V_{ds}$  characteristics for three graphene FET devices and (b) its transfer characteristics  $I_{ds}$ – $V_{bg}$  curve.

PMMA-supported graphene, which remains floating on the solution, is carefully washed by placing it in a Petri dish of DI water (Figure 2b), and is then transferred onto SiO<sub>2</sub>/Si or indium tin oxide (ITO) substrates. After transferring, the PMMA film can be easily dissolved using acetone, leaving behind pure graphene on the desired substrate (Figure 2c, d). A detailed schematic of the graphene transfer process has been illustrated in Figure 8. After transfer, the CVD-grown graphene films, various techniques were used to characterize the films. Raman spectroscopy (Renishaw inVia) was used to characterize the thickness of the film at 514.5 nm laser excitation. Transmission electron microscopy was carried out for microstructural characterization using JEOL-2100 field emission HRTEM operated at 200 kV. Scanning Electron Microscopy (JEOL-6500F) was carried out at 15 kV to confirm the uniformity of the films. AFM analysis was carried out on Digital Instruments Nanoscope III A. The as-grown graphene films were also transferred onto an n-type silicon wafer with a 300 nm thick SiO<sub>2</sub> layer for the fabrication of a back-gated field-effect transistor. Electrodes (Au/Ti = 30 nm/3 nm) were patterned onto the graphene films by using optical lithography and e-beam evaporator techniques. A probe station was used to test the electrical properties of graphene at room temperature. All of the reported electrical transport measurements were made in a  $1 \times 10^{-5}$  Torr vacuum chamber. STM analysis was also carried out on a home-built table top apparatus.

## Results and Discussion

Raman spectroscopy was used to characterize the thickness and quality of these films. The Raman spectra shown in Figure 3 confirms that these films were of reasonably good quality. The intensity of disorder-induced Raman D-peak at 1350 cm<sup>-1</sup> was very feeble, signifying that the graphene films grown using vacuum-assisted chemical vapor deposition (VA-CVD) are of good quality. These samples, grown using VA-CVD technique, show G and 2D peaks at 1595 and 2695 cm<sup>-1</sup>, respectively, which closely resembles the graphene grown by other techniques. The 2D line consists of a narrow peak (full-width at half-maximum:  $40 \pm 4$  cm<sup>-1</sup>) for monolayer and (full-width at half-maximum:  $43 \pm 4$  cm<sup>-1</sup>) for double layers graphene shown in Figure 3.<sup>17,9</sup> Moreover, the intensity of the 2D peak was found to be more than



**Figure 7.** (a) Typical STM topograph obtained during the scanning of the graphene samples. The hexagonal atomic structure as mapped by STM is clearly visible. Tunneling set point:  $I = 417$  pA,  $V = -19.8$  mV. (b) STM topograph revealing a 6-fold defect of the type previously observed on graphene formed on silicon carbide.<sup>20,21</sup> Tunneling set point:  $I = 417$  pA,  $V = -19.8$  mV.

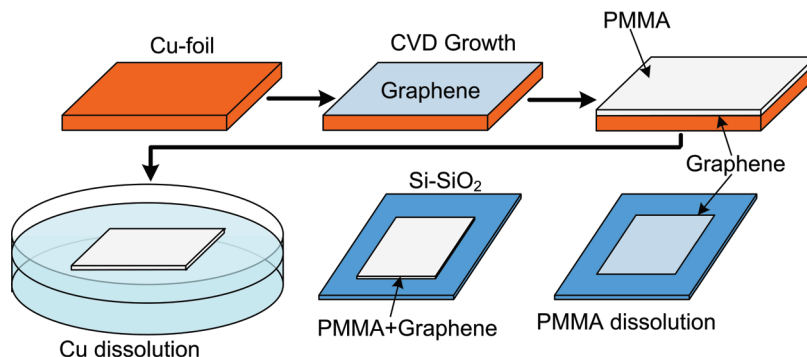
twice as high as the G peak for most areas of the sample indicating a single layer or few layers growth in most parts of the sample (Figure.3). AFM analysis also shows that the films are highly continuous and uniform Figure (5a, b). A large number of wrinkles were also observed on these films. Wrinkle formation occurs because of thermal stresses developed during cooling of the substrate after growth as there is a wide difference in thermal expansion coefficients of Cu and graphene.<sup>18</sup> We also believe that some wrinkle formation occurs during the transfer process. The thickness profile measurement using AFM shows that the typical film is approximately 3 layers thick. The observed thickness using AFM for single layer graphene was found 0.8 nm, which is consistent with that reported for single-layer graphene on SiO<sub>2</sub>.<sup>6</sup>

The VA-CVD grown graphene films are transferred to lacey carbon-coated grids for TEM and SEM investigations (Figures 4 and 5c, d). High-resolution TEM examination confirms that the films have one, two, three and four layers depending on growth conditions (Figure 4a–d). Typically, 1–4 layers are observed depending on the experimental conditions in our samples, which are consistent with our AFM results. Low-magnification SEM image of graphene transferred onto a lacey carbon-coated grid are shown in Figure 5c, d. Micrographs clearly

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**Figure 8.** Schematic illustration of CVD growth of graphene and its transfer process.

suggest that the graphene films are uniform and continuous up to a long-range. The lacey carbon in the background can also be seen through the film.

To measure the electrical properties of these VA-CVD grown graphene films and compare them with the properties of exfoliated graphene, standard lithography techniques were used to fabricate micrometer size bottom-gated field-effect transistors (FETs) with the channel length 10–15  $\mu\text{m}$  and channel width 5  $\mu\text{m}$ . Figure 6a shows the typical source-drain current vs the source-drain voltage curves for several graphene devices. The graphene shows a good conductivity and a linear  $I$ – $V$  behavior. The typical sheet resistance of as-grown graphene film is in the range of 100–300  $\Omega/\text{square-cm}$ . The transfer curve of graphene-based FETs (Figure 6(b)) shows the  $I_{\text{ds}}$  increase, with the back voltage sweep from 40 V to –40 V, indicating a p-type behavior.

In addition, we employed scanning tunneling microscopy (STM) to obtain atomic-scale images to further characterize the quality of the graphene samples. For this analysis, the graphene samples were transferred onto conducting ITO substrates using a PMMA-based lift-off process as mentioned above. The metal oxide substrates were chosen over silicon dioxide for their conductive nature. The scanning was carried out in ambient conditions using a home-built STM that has been described previously.<sup>19</sup> Prior to scanning, the samples were subjected to annealing under UHV conditions of 200 °C for 10 min at a pressure of  $1 \times 10^{-7}$  Torr to remove any possible contamination from the transfer process. Initial imaging by STM obtained clear atomic resolution of the graphitic surface as seen in Figure 7a. Additionally, a few defects on the surface were also imaged as seen in the second image, Figure 7b. However, during scanning, we observed a very low defect density for a CVD grown sample. A conservative, preliminary estimate of the defect density in these samples is around 0.000004 defects/ $\text{nm}^2$ .

This is somewhat higher in comparison to bare HOPG<sup>19</sup> but nowhere near the defect density revealed by the STM imaging of graphene grown on SiC substrates.<sup>20,21</sup> The defect shown is a 6-fold scattering defect that has been previously observed in graphene.<sup>21,19</sup> The presence of a  $\sqrt{3} \times \sqrt{3}$  R30° superlattice structure around the defect is clearly visible.<sup>22,23</sup> It is produced by the perturbation of the electronic structure by steps, point defects, and adsorbates, where the wavelength and anisotropy directly reflect the Fermi surface.<sup>24</sup>

## Conclusions

In summary, we have synthesized large-area, continuous, and uniform graphene films with hexane as the liquid precursor. This novel synthesis route can prove highly advantageous in doping graphene, as it allows for a better process maneuverability by using various organic solvents as liquid precursors containing the dopant atoms. It also allows for cheap and safe synthesis, as compared to gases, because liquid precursors are readily available and easy to handle.

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