

***In situ* imaging and control of layer-by-layer femtosecond laser thinning of graphene**

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IN SITU IMAGING AND CONTROL OF LAYER-BY-LAYER FEMTOSECOND LASER THINNING OF GRAPHENE

Paper (#N203)

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Abstract

Although existing methods (chemical vapor deposition, mechanical exfoliation, etc.) are available to produce graphene, the lack of thickness control limits further graphene applications. Laser-thinning is a new technique for modifying graphene and other related two-dimensional (2D) layered nanomaterials. In this study, we demonstrate an approach to precise thinning of graphene films to a specific thickness using a femtosecond (fs) laser raster scanning. By controlling laser fluence and scanning duration, graphene thinning with an atomic layer precision, namely layer-by-layer graphene removal, has been realized. Graphene with smooth surface and controlled thickness is produced. An fs-laser-based four-wave mixing (FWM) system is developed that is capable of distinguishing graphene of different thicknesses and counting the number of layers using the linear relationship between the FWM signal intensity and the graphene thickness, which is more accurate and much faster than Raman microscopy. Furthermore, FWM imaging has been successfully applied to achieve *in situ*, real-time monitoring of the fs laser graphene thinning process based on the large optical nonlinearity of graphene. This method can not only realize large-scale thinning of various 2D nanomaterials with atomic layer precision, but also provide *in situ*, rapid imaging capability of 2D nanomaterials for accurate assessment of the number of layers.

Introduction

Graphene as a archetypical 2D nanomaterial, which was first discovered experimentally in 2004 by Geim and Novoselov,[1] exhibits unique and fascinating physical properties, such as high carrier mobility and optical transparency,[2-3] remarkable magnetotransport,[4-5] and fascinating mechanical property.[6-7] These excellent properties make

graphene suitable to use in a wide variety of applications, such as transistors,[8] transparent conducting electrodes,[9-10] optoelectronics,[2] and Hall effect sensors.[11] To realize the use of graphene in these applications, the most important challenge is controlled fabrication. Despite recent advances in the synthesis of graphene using various methods, such as mechanical exfoliation of large crystals using adhesive tape,[1] chemical exfoliation by dispersing in a solvent,[12] solution-phase growth,[13] chemical vapor deposition (CVD) growth,[14-15] the precise control of graphene layer thickness is still a challenge. It is known that different layer thicknesses of graphene have different physical properties. Therefore, new procedures for fabricating “on-demand” graphene are urgently needed for future applications.

Laser-thinning is a relatively new technique for modifying graphene. Previously, Zhou *et al.* reported laser thinning of graphene oxide (GO) film from a multi-layer (> five layers) to a tri-layer film.[16] The laser thinning arose from the oxidative burning of the GO films in air. Recently, Han *et al.* utilized a laser with Raman spectroscopy to attenuate multi-layer to monolayer graphene.[17] The accumulation of heat induced by a laser leads to the oxidative burning of upper graphene. In general, laser thinning can only produce tri-layer or monolayer graphene samples; no other layers can be controlled in this way. This is mainly because the laser sources described above are all continuous-wave (CW) lasers. Due to their heat transfer and dissipation mechanism, they are not suitable for layer-by-layer thinning of graphene. Recently, layer-by-layer thinning of graphene was achieved by sputter coating graphene with zinc and dissolving the latter with dilute acid; however, this is a complex and time consuming process that is likely to cause damage or contamination due to acid corrosion.[18] Unlike CW laser irradiation, femtosecond (fs) laser pulse excitation induces a very different response in

Experimental Section

Material preparation

Two kinds of graphene samples were used in this study: a commercial CVD graphene product and micromechanically cleaved, few-layer graphene. (1) **Commercial CVD graphene:** The commercial few-layer CVD graphene on a quartz substrate with six to eight layers was purchased from ACS MATERIAL. (2) **Micromechanically cleaved few-layer graphene:** Few-layer graphene samples were fabricated by tapping and shearing highly oriented pyrolytic graphite (HOPG) onto the surface of a transparent fused silica substrate. To make it easier to find the few-layer (less than ten layers) graphene, we located the prepared graphene substrate under an optical microscope and initially estimated the number of layers through their different optical contrast.

Characterization of graphene samples

Atomic force microscopy (AFM, Agilent 5500, CA, U.S.A) and Raman spectroscopy (Renishaw InVia Plus, Renishaw, Gloucestershire, U.K.) were used to determine the number of graphene layers. A Raman spectrometer with an excitation wavelength of 514 nm and a lateral resolution of approximately 1 μm was used to evaluate the quality of graphene and to check the number of graphene layers.

In addition, an FWM system was used to investigate the nonlinear optical properties of graphene and to determine the number of graphene layers. The schematic and photography of the FWM system used in this study are shown in Figs. 2(a) and (b), respectively. A Ti:Sapphire fs laser (MaiTai DeepSee HP, SpectraPhysics), in conjunction with a supercontinuum generator (SCG-800, Newport), provides two incident pump laser beams. The Ti:Sapphire fs laser provides a laser beam with a wavelength of 800 nm, whose power, pulse duration, and repetition rate were 2.95 W, 100 fs, and 80 MHz, respectively. The laser power of the two pump laser beams divided by a beam splitter was controlled independently. One pump laser beam was formed using a 500 mW laser beam to generate the supercontinuum using the supercontinuum generator, and then the laser beam was filtered through a long-pass filter (10CGA-830, Newport); the other pump laser beam was formed by introducing an 800 nm laser beam through an attenuator and a delay line. Then the two pump lasers were focused collinearly onto the sample surfaces using a water-immersion objective with a numerical aperture of 1.05 and a working distance of 2 mm. The signal was collected in the forward direction by a sensitive photomultiplier (PMT)

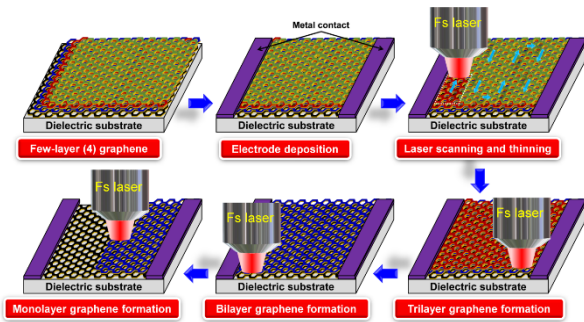


Figure 1. Schematic of controlled fs laser thinning of few-layer graphene on a dielectric substrate with single atomic layer precision.

graphene.[19] By optimizing the pulse energy, duration, and number of exposures, we believe that fs laser-thinning of graphene layer-by-layer can be realized. Since the physical properties of graphene are determined by the number of layers, it is of great importance to be able to experimentally determine the number of graphene layers. Optical microscopy, atomic force microscopy (AFM), and Raman spectroscopy are currently the three most important tools to identify and characterize graphene samples. While it is possible to observe even monolayer graphene using optical microscopy, it is extremely difficult due to very low contrasts. Although AFM is powerful in determining the layer thickness, its imaging speed is slow, and discrepancies arise from differences in the interactions of the tip with the sample and substrate. With Raman spectroscopy, the Raman spectra of graphene are only sensitive to monolayers, bilayers, and tri-layers. To address these issues, we introduced a new approach to distinguishing the number of graphene layers based on the large optical nonlinearity of graphene.

In this study, we demonstrated a new approach to obtaining graphene with a controlled number of layers based on fs laser thinning of few-layer graphene with single atomic layer precision, as shown in Fig. 1. The fs laser used is configured in a four-wave mixing (FWM) system, the use of which enables *in situ*, real-time monitoring of the laser thinning process based on the large optical nonlinearity of graphene. It was determined that there is a linear relationship between the FWM signal intensity and the graphene layer thickness, which can be used as a new and efficient method for identifying the number of graphene layers. We also found that fs laser-thinning of few-layer graphene with single atomic layer precision is a novel, effective, and fast strategy for fabricating graphene with a specific layer thickness.

tube. Imaging was obtained by raster scanning of the excitation laser beam. Figure 2c shows a diagram of

energy conservation in the FWM process, which involves the generation of mixed optical frequency

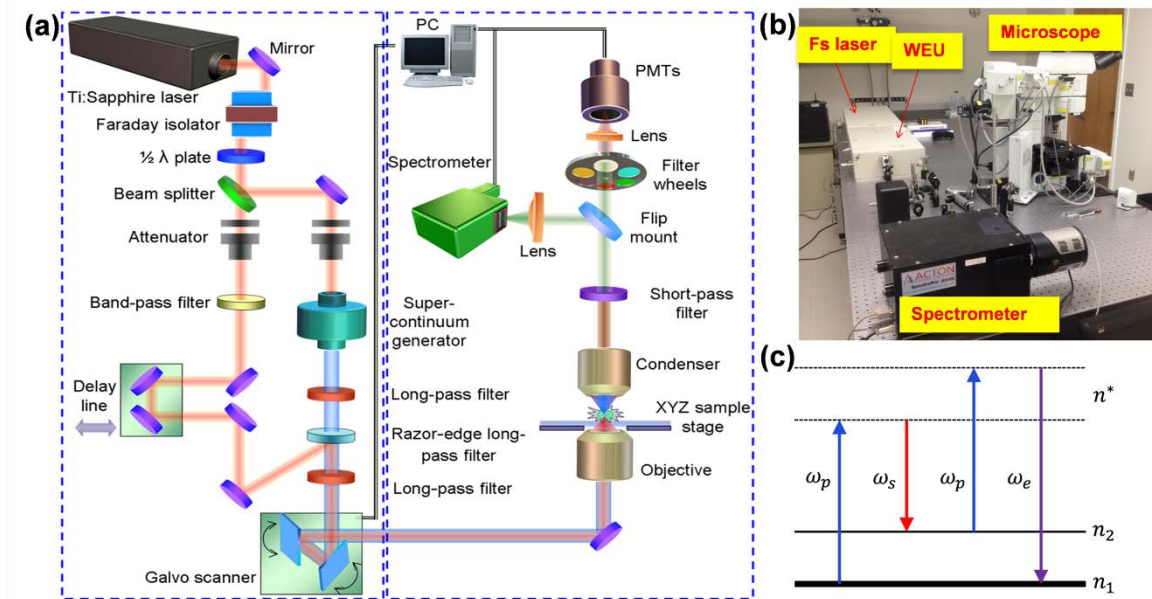


Figure 2. (a) Schematic setup of the graphene thinning and FWM imaging system; (b) photo of FWM imaging system; (c) diagram of energy conservation in FWM process.

harmonics $2\omega_p - \omega_s$ under irradiation by two monochromatic waves with two frequencies of ω_p and ω_s . [20-22]

Fs laser thinning of few-layer graphene

For thinning, few-layer graphene samples were raster scanned and thinned by the same fs laser in the FWM system in the process of imaging, which means that FWM imaging of thinned graphene can be immediately obtained after each cycle of the laser scanning process. The fs laser fluence and scanning rate were adjusted to realize laser thinning of graphene layer by layer. Our FWM system is superior in scan speed, which can realize the maximum areas of $500 \mu\text{m} \times 500 \mu\text{m}$ scanning in 1 second. Therefore, FWM imaging and graphene thinning processes are expected to be completed in a few seconds, depending on the scanning area and rate.

Results and Discussion

Characterization and imaging of graphene samples

First, we demonstrated and characterized the nonlinear optical property of few-layer graphene using a nonlinear, coherent FWM technique. FWM, as a kind of coherent anti-Stokes form, is enhanced by on-photon resonances and is very sensitive to the nonlinear electronic response. Strong FWM signals are expected when the excitation energies overlap with the

electronic excitation energies of graphene, which is carbon nanotubes. [21, 23] Figure 3 shows the FWM images for two different types of few-layer graphene samples prepared by (a) CVD method (six to eight layers) after transfer onto a quartz substrate and (b) mechanical exfoliation. Although the physical appearances of CVD and exfoliated graphene are different, the FWM images are all clearly observed, indicating their similar nonlinear optical properties. The successful detection of nonlinear optical signals from graphene opens up opportunities for optical investigations on an atomic level resolution. In addition, the optical nonlinearity of graphene can be used for high-contrast imaging to distinguish different types of graphene.

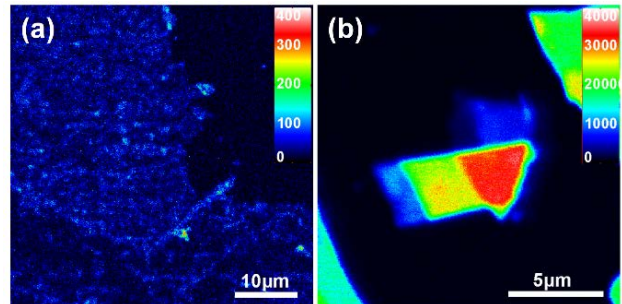


Figure 3. FWM images of two types of few-layer graphene prepared by: (a) CVD method (six to eight layers) after transfer onto a quartz substrate and (b) mechanical exfoliation.

For comparison, a few-layer graphene flake with different number of layers prepared by mechanical

exfoliation was characterized by optical microscopy, Raman spectroscopy, AFM, and FWM, respectively.

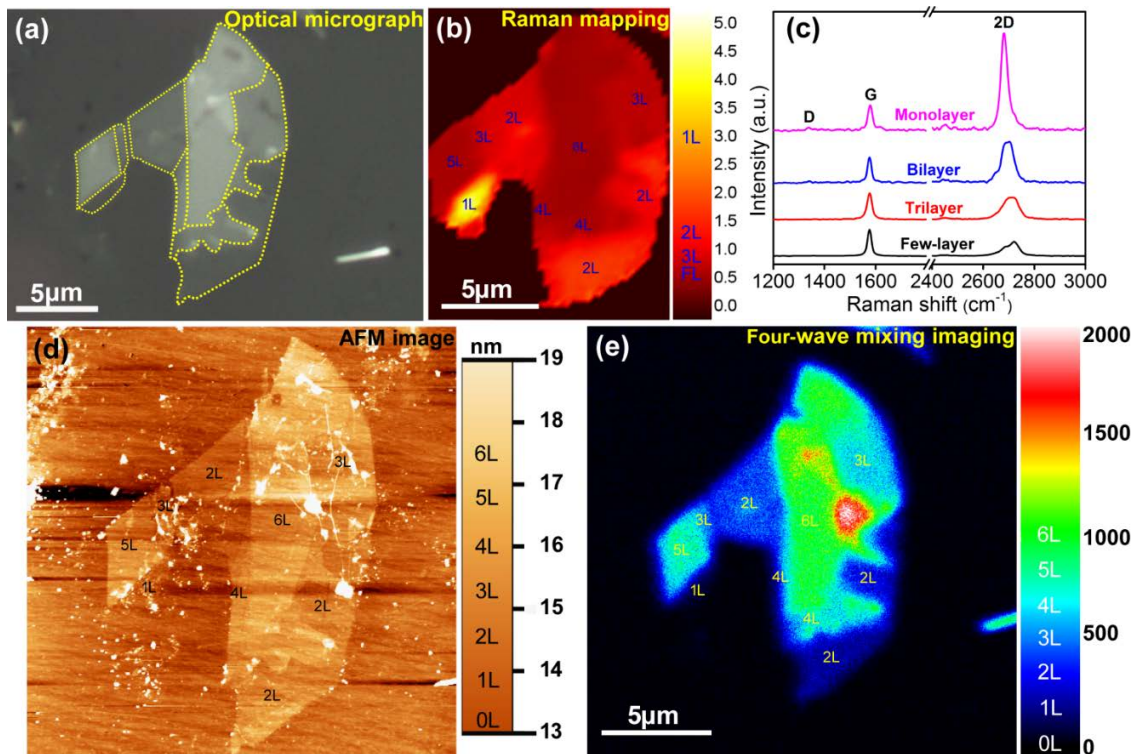


Figure 4. (a) Optical micrograph of few-layer graphene transferred onto a fused silica substrate after mechanical exfoliation; (b) Raman mapping of the I_{2D}/I_G ratio of the graphene in the area of (a); (c) Raman spectra of monolayer, bilayer, trilayer and few-layer graphene corresponding to the regions in (b); (d) AFM image of the few-layer graphene in (a); and (e) FWM image of the few-layer graphene in (a).

Figure 4a shows a typical optical micrograph of a few-layer graphene transferred onto a fused silica substrate. It is possible, but difficult, for us to observe the monolayer graphene and distinguish different layer thicknesses due to the low contrast. Distinguishing the number of graphene layers was further carried out using Raman spectroscopy by mapping the I_{2D}/I_G ratio (Fig. 4b). The I_{2D}/I_G ratio decreases as the number of graphene layers increases (Fig. 4c). Through Raman characterization, it is easy to identify monolayer graphene from bilayer and multilayer graphene; however, multilayer graphene with different layers of thickness is difficult to distinguish. An AFM was used to measure the morphology of the sample (Fig. 4d). The number of graphene layers at different positions can easily be measured, as shown in Fig. 4d. Figure 4e shows the FWM imaging for the few-layer graphene as shown in Fig. 4a. Similar to the morphological information shown in Fig. 4d, it is extremely easy to distinguish and quantify graphene with different thicknesses from one to five layers, due to the high contrast in the FWM images, which allows us to count the number of graphene layers in each region.

To more quantitatively investigate the relationship between Raman scattering/FWM signal and graphene layer thickness (or numbers), the dependences of the Raman I_{2D}/I_G ratio and

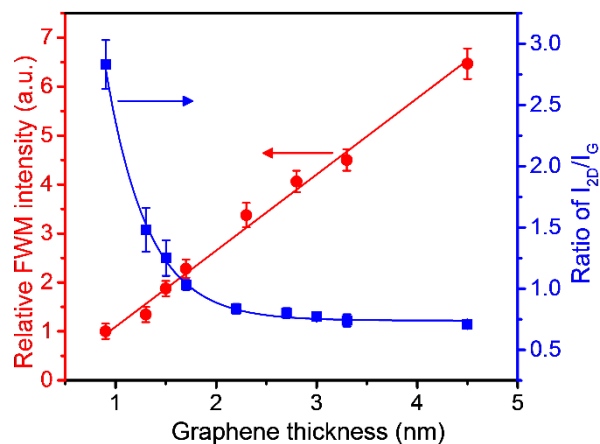


Figure 5. I_{2D}/I_G Raman peak ratio (blue curve) and FWM intensity (red curve) as a function of graphene layer thickness.

FWM signal intensity on graphene thickness are plotted in Fig. 5. It can be seen (blue curve) that

monolayer/bilayer graphene is sensitive to the Raman I_{2D}/I_G ratio; however, there is not much

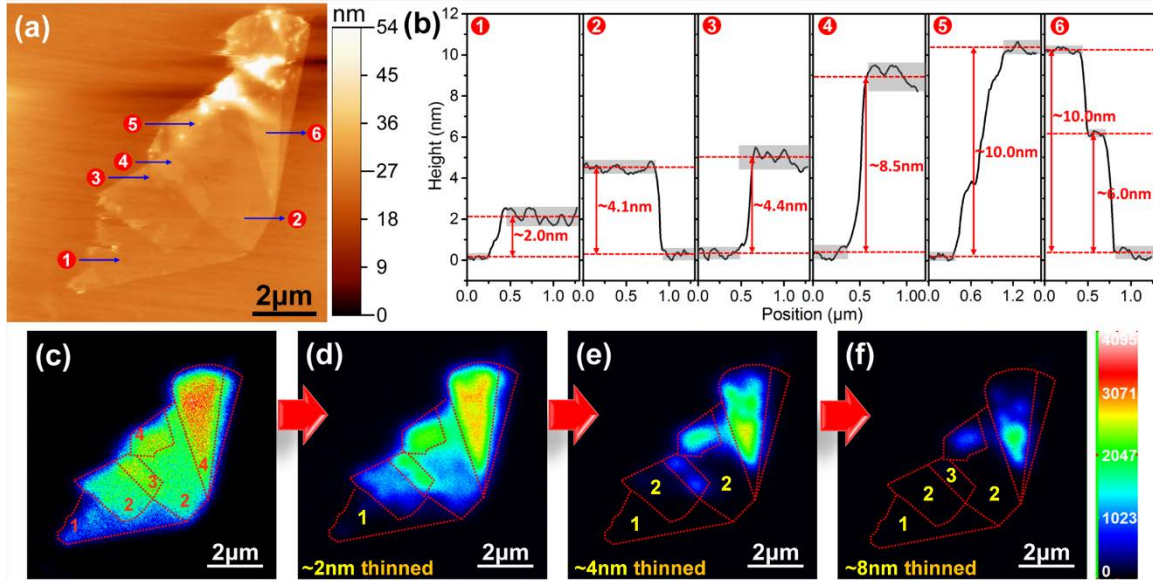


Figure 6. (a) AFM image of a few-layer graphene with different layer thicknesses; (b) the thickness profiles along the lines drawn in (a); (c) FWM image of the same graphene before fs laser thinning; (d)-(f) FWM images of the same graphene after fs laser scanning for (d) 10, (e) 20, and (f) 40 times of laser scanning, respectively.

difference in the Raman I_{2D}/I_G ratio for few-layer or multi-layer graphene. The ratio decreases slightly as the graphene layer thickness increases. In general, the I_{2D}/I_G ratio of graphene decreases exponentially as the graphene layer thickness increases, which fits well the equation of $I_{2D}/I_G = a \cdot (1 - \exp(-b \cdot H))^c$, where H is graphene layer thickness, a , b , and c are 0.016, 0.275 and -0.746, respectively. Although Raman spectroscopy has been proven to be a valuable tool for distinguishing monolayer graphene from the graphene of bilayers and few-layers, it is not an efficient, accurate, or quantitative method for characterizing, or distinguishing few-layer graphene nor accurately judging the layer number of few-layer graphene. It can be seen from the red curve that the FWM signal intensity varied among graphene of different thicknesses. In fact, the FWM signal scales linearly with the number of graphene layers, which is much different from Raman scattering. The linear relationship between the few-layer graphene thickness and the FWM signal can be briefly explained as follows: First, few-layer graphene exhibits a very strong nonlinear optical response in the near-infrared region used in the FWM technique, which enables high-contrast imaging of few-layer graphene compared to dielectric substrate with weak nonlinearity (fused silica). Second, the linear relation is caused by the different constructive

interferences of the radiated fields from different layers, as the thickness of few-layer graphene is significantly smaller than the wavelength of the light (800 nm for pump pulses).[21] Based on the results of Fig. 5, we can conclude that after calibration, an FWM signal can be used to distinguish graphene layer thickness and count the number of layers, which is more accurate than Raman spectroscopy, especially for few-layer graphene. In addition, FWM measurement is much faster (in seconds) compared to Raman and AFM measurements. Therefore, FWM imaging can be used to rapidly realize real time to monitor graphene layer control by fs laser thinning.

FWM imaging to monitor fs laser thinning of few-layer graphene

Few-layer graphene flakes, prepared by mechanical exfoliation from HOPG, were used for fs laser thinning in this study. An fs laser configured in the FWM system with a wavelength of 800 nm was used to scan few-layer graphene to a specific number of layers. The FWM system (Fig. 2) was used to perform both laser-thinning and real-time monitoring through *in situ* imaging.

First, we investigated the laser-thinning threshold of the exfoliated graphene. The thinning threshold of graphene was defined as the laser fluence at which ten times of fs laser scanning causes the FWM signal intensity to weaken. The thinning threshold for the 800

nm fs laser with a pulse duration of 100 fs was obtained, around 0.125 J/cm^2 .

We investigated the fs laser thinning of graphene with different layer thicknesses. Figure 6 shows an AFM image of a typical few-layer graphene with different

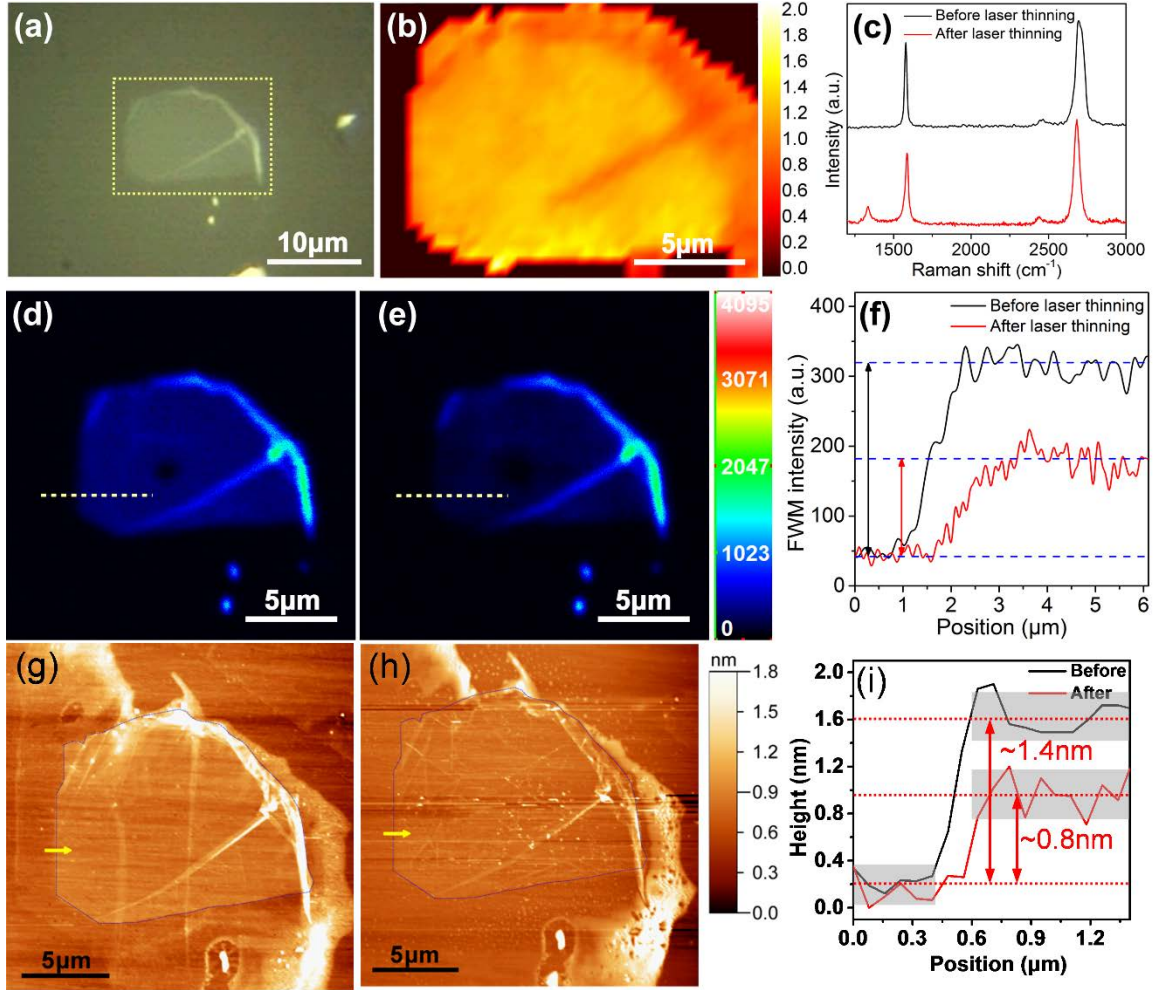


Figure 7. (a) Optical micrograph of few-layer graphene deposited on a fused silica substrate; (b) Raman mapping of the I_{2D}/I_G ratio of the graphene in the area marked by a dashed rectangle in (a); (c) Raman spectra of the graphene shown in (a) before (black line) and after (red line) fs laser scanning with a fluence around 0.263 J/cm^2 ; (d) FWM image of the graphene in (a); (e) FWM image of the graphene after fs laser scanning with a fluence around 0.263 J/cm^2 ; (f) FWM intensity profiles along the lines drawn in (d) and (e). (g, h) Corresponding AFM images of the graphene sample shown in (d) and (e), respectively. (i) The thickness profiles of the graphene along the lines in (g) and (h).

layer thicknesses before laser thinning. The average layer thicknesses for Regions 1 to 6 were approximately 2.0, 4.1, 4.4, 8.5, 10.0, and 10.0 nm, respectively (Fig. 6b). The FWM image of the same sample before laser thinning is shown in Fig. 6c. To distinguish different thickness of the graphene, dotted lines were drawn on the FWM images to indicate four different regions with the numbers. The fs laser with a fluence of about 0.475 J/cm^2 was used to scan and thin the same area with different scanning times, as shown in Figs. 6d-f. Figure 6d shows the FWM image of the sample for ten times of laser scanning. The FWM

signal in the whole graphene area decreased, and the signal from Region 1 almost disappeared, which indicates that the graphene layer thickness has been reduced by approximately 2 nm with ten times of the fs laser scanning. Continuing with 20 and 40 more times of laser scanning, the FWM signal from Regions 2 and 3 disappeared successively, as shown in Figs. 6e and 6f, indicating that the graphene was thinned for about 4 and 8 nm, respectively. The thickness of graphene can be effectively thinned by fs laser scanning with precise control of thickness. The graphene lattice survived without much modification up to a certain laser fluence.

Beyond that value, it began to be thinned. By choosing fs laser fluence and scanning times appropriately, graphene thinning with single atomic layer precision,

namely layer-by-layer graphene thinning can be realized.

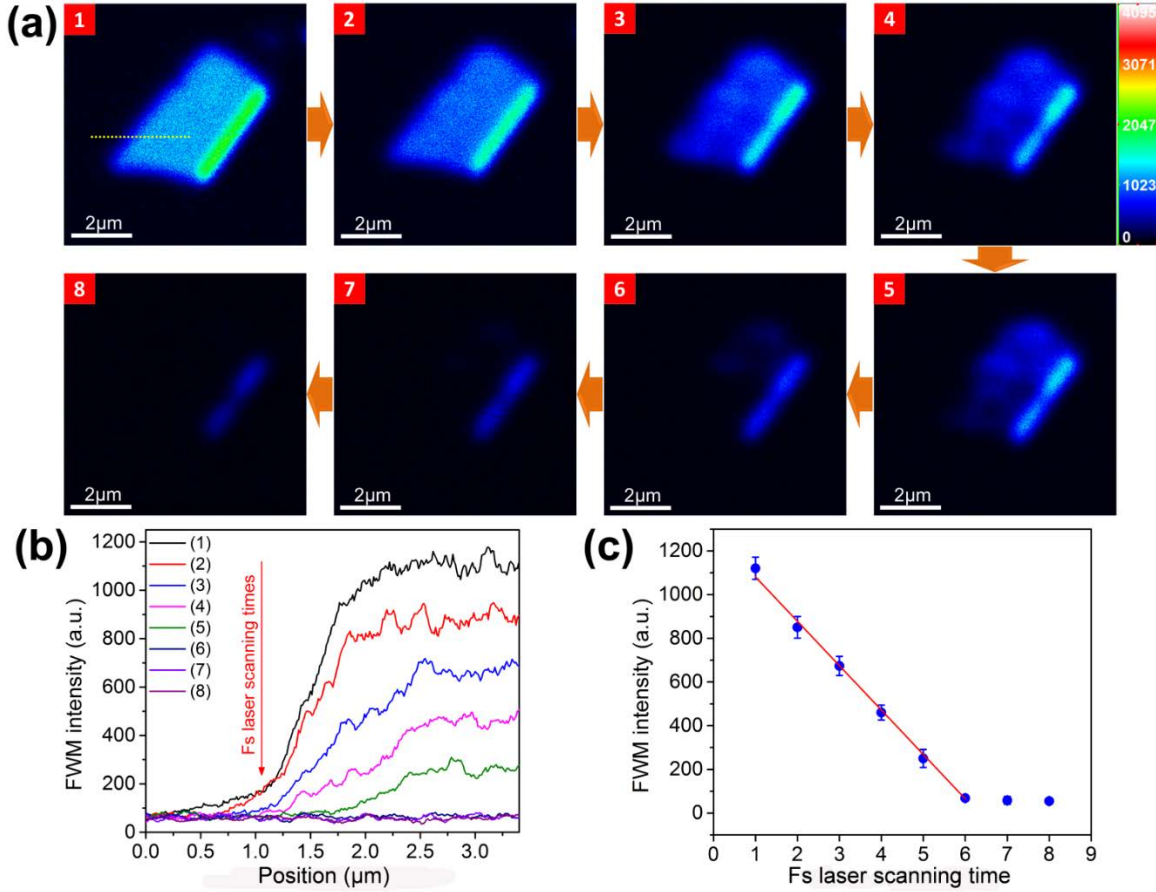


Figure 8. (a) In situ real-time laser thinning of six-layer graphene. Numbers in (a) indicate cumulative laser scanning times; (b) Changes of FWM intensity of graphene along the dotted yellow line in (a) with an increase in laser scanning time; (c) Dependence of FWM intensity of the graphene on laser scanning time.

Figure 7a shows an optical micrograph of a few-layer graphene flake deposited on a fused silica substrate. The Raman mapping of the I_{2D}/I_G ratio is shown in Fig. 7b, and the FWM image is shown in Fig. 7d. The nonlinear signal intensities for the whole graphene area are almost the same due to the uniform layer thickness, which is consistent with the Raman results (Fig. 7b). Fig. 7e shows the FWM image of the graphene flake after scanning by a fs laser with a fluence around 0.263 J/cm^2 for ten times. The FWM imaging of the thinned graphene area is uniform with a weaker signal intensity as compared to the imaging of the sample before laser thinning. Fig. 7f compares the FWM signal intensity profiles of the graphene before (d) and after (e) the laser thinning, where the FWM signal intensity of the graphene is reduced by approximately 50%. According to the linear relationship between the FWM signal intensity and the graphene layer thickness described above, we can quantitatively judge how many graphene layers were removed or remained if we

know the initial graphene layer thickness. From FWM imaging, we can obtain the expression for the number of graphene layers after laser thinning as follows:

$$N_{thinned} = \frac{I_{initial} - I_{thinned}}{I_{initial} - I_{background}} \times N_{initial}, \quad (1)$$

where $N_{thinned}$ is the number of graphene layers that have been removed, and $N_{initial}$ is the number of graphene layers before laser thinning. $I_{initial}$, $I_{thinned}$, and $I_{background}$ are FWM intensities of initial graphene, thinned graphene, and background signal, respectively. To determine the initial graphene layer thickness (number of layers), an AFM image of the same graphene sample before laser thinning was measured (Fig. 7g). The initial thickness of the graphene was approximately 1.4 nm, therefore, using equation (1), the thickness of the thinned graphene was calculated to be approximately 0.7 nm. This suggests that approximately one atomic layer of the graphene was removed during this laser thinning process. To

further confirm this conclusion, AFM imaging of the same graphene after laser thinning was performed, as shown in Figs. 7(h) and (i). It can be seen from Fig. 7(i) that approximately a thickness of 0.8 nm of the graphene remained after laser thinning. Namely, a thickness of approximately 0.6 nm thick was removed, which is consistent with the calculation results. Therefore, fs laser thinning of graphene with precision of a single atomic layer has been successfully realized.

Finally, we carried out an experiment to realize *in situ*, real-time optical monitoring of uniform graphene during the laser-thinning process using the FWM system. The sample we used was exfoliated graphene with a layer thickness of approximately 4.2 nm, corresponding to a six-layer sample. To ensure that each time of the fs laser scanning corresponded to the reduction of one single layer of graphene, the laser fluence and the scanning speed were adjusted. We found that the laser fluence around 2.5 J/cm^2 is ideal to realize this thinning requirement. Fig. 9a shows the *in situ*, real-time monitoring of fs laser thinning of the six-layer graphene using FWM imaging. Numbers in (a) indicate cumulative laser scanning times. It took only a few seconds ($\sim 2\text{-}3 \text{ s}$) to complete one time of FWM imaging and laser scanning, with a scanning rate of approximately $25 \text{ }\mu\text{m}^2/\text{s}$, which is much faster than Raman spectroscopy. After each time of laser scanning, a homogenous reduction of FWM intensity was observed on the graphene surface, indicating that the whole graphene area was uniformly getting thinned. Fig. 9b shows the changes in FWM intensity of the graphene, along the dotted yellow line shown in (a), as the laser scanning time increased. It was clearly observed that the graphene was completely removed by six to seven fs laser scans. To further prove the layer-by-layer thinning of graphene, the dependence of the FWM intensity from the graphene on the laser scanning time was plotted in Fig. 8c. A linear relationship between the FWM intensity and the scanning time (< 7 times) was observed, which can be expressed as:

$$I_{FWM} = a \times N_{scan} + b, \quad (2)$$

where I_{FWM} and N_{scan} represent the FWM intensity arising from the graphene and laser scanning times, respectively. Equation (2) includes two constants of a (< 0) and b . With more than six scans, the FWM intensity did not change further due to the complete removal of graphene. The linear relationship between the FWM intensity and the graphene layer number can be simply described by:

$$I_{FWM} = a' \times H_{graphene} + b', \quad (3)$$

where I_{FWM} and $H_{graphene}$ represent the FWM intensity and graphene layer number, respectively, with two constants of a' (> 0) and b' . Substituting equation (3) into equation (2), we obtain

$$H_{graphene} = \frac{a}{a'} \times N_{scan} + \frac{b-b'}{b'}. \quad (4)$$

According to Fig. 8c, when $H_{graphene} = 6$, $N_{scan} = 0$ and when $H_{graphene} = 0$, $N_{scan} \approx 6$. Then equation (4) can be transformed to

$$H_{graphene} \approx -N_{scan} \text{ or } \Delta H_{graphene} \approx -\Delta N_{scan}. \quad (5)$$

This means that layer-by-layer thinning of graphene has been realized by fs laser scanning. In addition, the successful realization of fs laser thinning of graphene with such a fast scanning rate ($25 \text{ }\mu\text{m}^2/\text{s}$) provides the capability to scale up the modification of graphene.

Laser thinning of graphene involves either thermal or non-thermal effects. In general, CW laser-thinning of graphene arises from a heat transfer by absorption of photons and subsequent energy dissipation through phonons (thermal effect).[17] Unlike CW laser irradiation, an fs laser produces a different response in graphene during the thinning process. The energy from the fs laser pulse is transferred at rates much faster than the phonon relaxation time. Thus, the hot electrons are created and cool by transferring their energy to phonons at a time much shorter than thermal diffusion.[24] This ultrafast absorption will create a unique energy transfer mechanism within the graphene which depends on the amount of energy absorbed. In this study, the fs laser irradiation energy levels are much lower than those of aforementioned CW laser thinning processes. Therefore, the thermal effect is minimized, and non-thermal effects play an important role in the layer-by-layer thinning of graphene *via* fs laser scanning. This laser thinning process can be used as a new laser-based lithography for modifying graphene with atomic layer precision.

Conclusions

In summary, we have developed a rapid layer-by-layer graphene controlled thinning and imaging method *via* fs laser raster scanning. *In situ* and real time monitoring of the fs laser thinning process was achieved using the FWM imaging technique. The laser fluence and scanning repetition time play crucial roles in the controlled laser thinning process. Smooth surfaces of graphene after laser thinning can be achieved. In addition, the *in situ* FWM imaging can be utilized to quantify the number of graphene layers, which is more accurate and much faster than the Raman microscopy. Due to the high speed (in seconds) and simplicity of this method, it is a promising method

to achieve large-scale fabrication of graphene with accurate thickness control with atomic layer precision.

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References

- [1] Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V., Grigorieva, I. V. & Firsov, A. A. (2004) Electric Field Effect in Atomically Thin Carbon Films. *Science* 306, 666-669.
- [2] Bonaccorso, F., Sun, Z., Hasan, T. & Ferrari, A. C. (2010) Graphene photonics and optoelectronics. *Nat Photon* 4, 611-622.
- [3] Pallecchi, E., Lafont, F., Cavaliere, V., Schopfer, F., Maily, D., Poirier, W. & Ouerghi, A. (2014) High Electron Mobility in Epitaxial Graphene on 4H-SiC(0001) via post-growth annealing under hydrogen. *Sci. Rep.* 4.
- [4] Woszczyzna, M., Friedemann, M., Pierz, K., Weimann, T. & Ahlers, F. J. (2011) Magneto-transport properties of exfoliated graphene on GaAs. *Journal of Applied Physics* 110, -.
- [5] Lee, K., Kim, S., Points, M. S., Beechem, T. E., Ohta, T. & Tutuc, E. (2011) Magnetotransport Properties of Quasi-Free-Standing Epitaxial Graphene Bilayer on SiC: Evidence for Bernal Stacking. *Nano Letters* 11, 3624-3628.
- [6] Lee, C., Wei, X., Kysar, J. W. & Hone, J. (2008) Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene. *Science* 321, 385-388.
- [7] Ovid'ko, I. (2013) MECHANICAL PROPERTIES OF GRAPHENE. *REVIEWS ON ADVANCED MATERIALS SCIENCE* 34, 1-11.
- [8] Schwierz, F. (2010) Graphene transistors. *Nat Nano* 5, 487-496.
- [9] Wang, X., Zhi, L. & Müllen, K. (2007) Transparent, Conductive Graphene Electrodes for Dye-Sensitized Solar Cells. *Nano Letters* 8, 323-327.
- [10] Park, H., Brown, P. R., Bulović, V. & Kong, J. (2011) Graphene As Transparent Conducting Electrodes in Organic Photovoltaics: Studies in Graphene Morphology, Hole Transporting Layers, and Counter Electrodes. *Nano Letters* 12, 133-140.
- [11] Bolotin, K. I., Ghahari, F., Shulman, M. D., Stormer, H. L. & Kim, P. (2009) Observation of the fractional quantum Hall effect in graphene. *Nature* 462, 196-199.
- [12] Liu, W. W. & Wang, J. N. (2011) Direct exfoliation of graphene in organic solvents with addition of NaOH. *Chemical Communications* 47, 6888-6890.
- [13] Green, A. A. & Hersam, M. C. (2009) Solution Phase Production of Graphene with Controlled Thickness via Density Differentiation. *Nano Letters* 9, 4031-4036.
- [14] Mattevi, C., Kim, H. & Chhowalla, M. (2011) A review of chemical vapour deposition of graphene on copper. *Journal of Materials Chemistry* 21, 3324-3334.
- [15] Zhang, Y., Zhang, L. & Zhou, C. (2013) Review of Chemical Vapor Deposition of Graphene and Related Applications. *Accounts of Chemical Research* 46, 2329-2339.
- [16] Zhou, Y., Bao, Q., Varghese, B., Tang, L. A. L., Tan, C. K., Sow, C.-H. & Loh, K. P. (2010) Microstructuring of Graphene Oxide Nanosheets Using Direct Laser Writing. *Advanced Materials* 22, 67-71.
- [17] Han, G. H., Chae, S. J., Kim, E. S., Güneş, F., Lee, I. H., Lee, S. W., Lee, S. Y., Lim, S. C., Jeong, H. K., Jeong, M. S. & Lee, Y. H. (2010) Laser Thinning for Monolayer Graphene Formation: Heat Sink and Interference Effect. *ACS Nano* 5, 263-268.
- [18] Dimiev, A., Kosynkin, D. V., Sinitskii, A., Slesarev, A., Sun, Z. & Tour, J. M. (2011) Layer-by-Layer Removal of Graphene for Device Patterning. *Science* 331, 1168-1172.
- [19] Roberts, A., Cormode, D., Reynolds, C., Newhouse-Illige, T., LeRoy, B. J. & Sandhu, A. S. (2011) Response of graphene to femtosecond high-intensity laser irradiation. *Appl. Phys. Lett.* 99, -.
- [20] Kim, H., Sheps, T., Collins, P. G. & Potma, E. O. (2009) Nonlinear Optical Imaging of Individual Carbon Nanotubes with Four-Wave-Mixing Microscopy. *Nano Letters* 9, 2991-2995.
- [21] Hendry, E., Hale, P. J., Moger, J., Savchenko, A. K. & Mikhailov, S. A. (2010) Coherent Nonlinear Optical Response of Graphene. *Physical Review Letters* 105, 097401.
- [22] Wang, Y., Lin, C.-Y., Nikolaenko, A., Raghunathan, V. & Potma, E. O. (2011) Four-wave mixing microscopy of nanostructures. *Adv. Opt. Photon.* 3, 1-52.
- [23] Sheps, T., Brocious, J., Corso, B. L., Gül, O. T., Whitmore, D., Durkaya, G., Potma, E. O. & Collins, P. G. (2012) Four-wave mixing microscopy with electronic contrast of individual carbon nanotubes. *Physical Review B* 86, 235412.
- [24] Currie, M., Caldwell, J. D., Bezares, F. J., Robinson, J., Anderson, T., Chun, H. & Tadjer, M. (2011) Quantifying pulsed laser induced damage to graphene. *Appl. Phys. Lett.* 99, 211909.

Biography

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