Efficient Excitation of Multiple Plasmonic Modes on Three-Dimensional Graphene: An Unexplored Dimension

Jingchao Song,† Lei Zhang,‡ Yunzhou Xue,†,⊥ Qing Yang Steve Wu,§ Fang Xia,¶ Chao Zhang,‖ Yu-Lin Zhong,⊥ Yupeng Zhang,† Jinghua Teng,§ Malin Premaratne,‖ Cheng-Wei Qiu,*‡ and Qiaoliang Bao*†⊥†

†Department of Materials Science and Engineering and ‡Department of Electrical and Computer Systems Engineering, Monash University, Wellington Road, Clayton, Victoria 3800, Australia
‡Department of Electrical and Computer Engineering, National University of Singapore, Singapore 117583, Singapore
⊥Institute of Functional Nano and Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials and Devices, Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou 215123, People’s Republic of China
§Institute of Materials Research and Engineering, Agency for Science, Technology and Research (A*STAR), Singapore 138634, Singapore
‖School of Engineering and Information Technology, Murdoch University, Murdoch, Western Australia 6150, Australia
¶School of Physics, University of Wollongong, Wollongong, New South Wales 2552, Australia
*

Supporting Information

ABSTRACT: Graphene is a typical two-dimensional (2D) allotrope form of carbon. Excellent optical and electric properties of graphene, such as broadband absorption and high mobility of carriers, promise prosperous applications in optic and optoelectronic devices. However, flat graphene structures (either graphene film on a structural substrate or structural graphene) hardly support efficient excitation of high-order plasmonic modes, which results in a serious deficiency in realizing efficient light–matter interaction in graphene-based devices. Here, by configuring the flat graphene into complex three-dimensional (3D) pillars, strong high-order plasmonic modes were observed and verified numerically and experimentally. It is found that, despite the influence of geometry and material parameters on resonance, the excitation efficiency of high-order modes is highly dependent on the graphene on the sidewall of pillars. Therefore, the proposed 3D graphene structures not only retain the merits of 2D materials but also introduce a new dimension to control the light–matter interaction. In addition, the fabrication technique in this work can be readily applied to other 2D materials with various geometric shapes. It is believed that the proposed 3D form of 2D materials will ignite a plethora of unprecedented designs and applications in THz communication such as THz pulse generators, modulators, detectors, and spectrometers.

KEYWORDS: graphene pillars, sidewall thickness, high-order modes, plasmon, THz

Graphene, a two-dimensional (2D) form of carbon allotrope, has shown excellent electrical and optoelectronic properties,1–3 which resulted in many practical applications such as optical modulators,4 plasmonic devices,5 saturable absorbers,6 and broadband photodetectors.7–10 Due to its zero-band-gap nature, graphene has obtained relatively high Dirac charge conductivity,10 large mode confinement,11–13 and chemical/electrical tunability.14,15 As a consequence, graphene is able to support highly localized plasmon resonance (LPR) modes, which makes it possible to observe stronger light–matter interactions in graphene-based structures. Specifically, graphene has boosted plasmon research in the terahertz (THz) range15,16 and led to a variety of practical applications in THz pulse generators,17–19 modulators,20–22 photodetectors,23 spectroscopy,24 imaging,24,25 and telecommunications.26,27

To obtain excellent optical and electrical properties based on graphene plasmonic resonances, various flat graphene structures have been proposed and studied, as shown in Figure 1a–c, such as graphene films,26 graphene hole arrays,28 graphene patches,29 and graphene photonic crystal structures.30 However, only the fundamental mode is strongly supported by the
structural graphene, as shown in Figure 1f. In order to further enhance the light–matter interaction, multilayer stacking of graphene and an insulator has been employed. Nevertheless, most flat graphene structures (either graphene film on a structural substrate, structural graphene, or multilayer graphene stacking) hardly support efficient excitation of higher order plasmonic modes, which results in a limited light–matter interaction process in graphene-based devices.

In this work, a new dimension is proposed and studied based on a three-dimensional (3D) form of 2D graphene structures, which is fabricated by growing controllable graphene films on prefabricated silicon (Si) pillars. High-order plasmonic modes can thus be efficiently excited by a normally incident plane wave, which helps to surmount the obstacles occurring in flat graphene structures. The underlying mechanism was investigated both numerically and experimentally. Significantly, it is found that the resonance features of high-order modes are highly dependent on the thickness and materials properties of graphene at the sidewall of pillars, despite the geometric dimensions. The proposed 3D graphene pillar structures not only retain the merits of 2D periodic structures but also introduce a new freedom (vertical sidewall of the structures) to control the light–matter interaction of 2D materials based devices, and the fabrication process can be readily extended to structures with various geometries based on other 2D materials. We believe that our work will definitely shine new light on the practical applications of 2D materials based optoelectronic devices.

RESULTS AND DISCUSSION

As shown in Figure 1f, the jejune response of flat graphene structures can only lead to strong excitation of the fundamental plasmonic mode. Similar mode properties also exist for a two-layer graphene structure consisting of a graphene patch and its complementary hole, as shown in Figure 1d. However, by introducing a graphene film at the sidewall of a Si pillar (Figure 1e), obvious multiple modes can be efficiently excited, which are barely achieved with other structures. Therefore, this indicates that the graphene at the sidewall plays a significant role in determining the resonance properties and provides a novel dimension to engineer light–graphene interactions.

Figure 2a shows the schematic of a 3D graphene pillar network wrapped on a Si pillar studied in this work. The graphene film was grown on Si pillar arrays predefined by photolithography, which affords a great flexibility to fabricate structures with arbitrary shapes. The thickness of the graphene layer can be well-controlled by a chemical vapor deposition (CVD) process. To confirm the graphene coverage on the real samples, scanning electron microscopy (SEM) and Raman characterizations were carried out. Figure 2b and c show the smooth silicon pillar surface before and after graphene growth.
respectively. Micrometer-sized grains of graphene crystal flakes can be clearly identified in Figure 2c, which suggest a grain-merging mechanism during the graphene growth stage. Raman mapping of the graphene G peak of the sample has confirmed that all the horizontal surfaces of the silicon pillar have been covered with graphene (Figure 2d). To examine the sidewall of the graphene pillar, an SEM image of the pillar sidewall was taken from a tilted angle (Figure 2e), and a cross-section sample was prepared by cleaving the graphene-wrapped silicon chip in dry ice (Figure 2f) for Raman characterization (Figure 2h). Furthermore, the graphene sample is continuous and uniform in a larger scale (Figure 2g). Raman spectra collected from five representative positions (top, bottom (I–IV) and sidewall (V)) are presented in Figure 2h. Three characteristic peaks of the graphene Raman spectra can be clearly identified, i.e., the D peak at 1352.2 cm\(^{-1}\), the G peak at 1598.6 cm\(^{-1}\), and the 2D peak at 2712 cm\(^{-1}\). The intensity ratio between the G peak and the 2D peak from different positions suggested that the thickness of as-grown graphene is greater on the horizontal surfaces (the top surface and the bottom surface have about the same thickness), while thinner on the vertical surface (Figure 2h inset). The nonuniformity of the graphene layer is mainly caused by the nonhomogenous chemical vapor distribution, specifically the carbon source, along the substrate surface (the top and bottom surfaces are more likely to be exposed to the carbon source in comparison with the vertical surfaces).\(^{36}\) Furthermore, by connecting the graphene at the top surface and the bottom surface of pillars with a multimeter, it is found that they are electrically shorted with each other via the graphene at the vertical sidewalls, which indicates a good conductivity and continuity of the graphene film. The mobility of thus grown graphene is measured to be 500 cm\(^2\) V\(^{-1}\) s\(^{-1}\), which agrees with the result measured in similar graphene materials.\(^{37}\) Therefore, high-quality graphene film in a large scale is employed in our work.

To verify the abundant resonance modes on the graphene pillars, numerical transmission spectra and charge distributions are plotted in Figure 3. As shown in Figure 3a and b, multiple resonance dips can be readily observed from the transmission spectra. As the graphene layer number increases, the dips shift into the larger wavenumber region (Figure 3a). A similar trend can also be observed in the nonuniform graphene (Figure 3b), in which case a thicker graphene sidewall causes a blue-shift of the transmission dip. Furthermore, it is also noticed that the shape of the spectrum varies greatly for graphene at the sidewall with different thicknesses. For instance, for the case of 2/10 layers of the vertical/horizontal graphene, the third and the fourth resonance modes disappear into the background in comparison with the counterparts with a thicker sidewall graphene. To better identify and understand the origin of these modes, the charge distributions of the first four modes at the cross-section plane are plotted in Figure 3c–f. It is obvious that the number of charge nodes increases for higher orders. Although the charge distributions of the first and the second modes have some similarities, their dependence on the thickness of graphene differs greatly. The first and the third modes are highly dependent on the top surface of the graphene pillar, while the second mode is majorly supported by the sidewalls, and the fourth mode is supported by the complete pillar structure as a whole. Since higher order modes have more nodes on the sidewall of the graphene pillar than the lower order modes, they, especially the fourth mode, have shown distinct height-dependent resonance features in the transmission spectra shown in Figure S1. Our graphene pillar resonance model is similar to that of the hollow silver pillars in previous research,\(^{38}\) in which a hexagonal mode on the sidewall of the silver pillar was attributed to the resonant absorption. Here, specifically, the power flow penetrates through the graphene sidewall at the position of zero net charge and then exits at the bottom, encircling the charge like a vortex. The mode energy will gradually dissipate through the graphene absorption and radiative scattering of the pillars.

However, due to the practical imperfections, resonant properties of plasmonic modes become complex in the experiment. Although the first mode is still robust (blue line in Figure 4a), the position of higher order modes deviates from the simulated result (red line calculated with a uniform graphene film in Figure 4a). In order to match the dip positions of the first mode between experiment and simulation, by retaining the horizontal surface at 10 layers while reducing the thickness of graphene at the sidewall at 4 layers, the simulated transmission (green line) tends to approach the experimental spectrum. Importantly, it is observed that some modes become invisible in the experiment. This could be attributed to the unintentional decay channels introduced during the growth process, such as point defects and residue impurity. Due to the increased decay rate, the spectrum becomes shallower and broader, which is well verified in our simulations (Figure S2). Therefore, the scattering rate has been further increased to 2 meV for better matching of the first two modes with experimental counterparts (black and blue lines in Figure 4a). These results indicate that the excitation efficiency of higher
order modes is very sensitive to the thickness of graphene at the sidewall and, especially, the decay rate, which should be carefully reduced by improving the quality of the graphene samples.

To further study the spectrum dip shift caused by the graphene thickness on the sidewall, samples with the same geometry parameters and horizontal graphene thickness but with differentiated vertical graphene thickness were prepared utilizing the chemical vapor dynamics in the CVD furnace. In practice, the chemical vapor environment varies spatially. It is found that the graphene growth on the sidewalls relies more on the chemical vapor environment than the horizontal surfaces. Therefore, a series of graphene films with the same horizontal graphene thickness but varied thickness at the sidewall were grown by manipulating the sample placement location in the furnace (Figure S3). The pillars covered by nonuniform graphene are further discussed by comparing the measured and simulated transmission spectra. By calculating the intensity ratio of Raman peaks, the thickness of graphene at a horizontal surface is around 10 layers ($I_{2D}/I_G \approx 3.0$), while the counterpart at the vertical surface increases from 2 layers, to 4 layers, to 7 layers (close assumption made from Raman $I_{2D}/I_G$ ratio: $I_{2D}/I_G = 1.01, 1.31, 1.60$, respectively) (Figure S4). Accordingly, the measured transmission dip shows a prominent shift to the larger wavenumbers from 30.8 cm$^{-1}$ to 38.5 and 43.0 cm$^{-1}$, respectively (Figure 4b). A similar shift trend is observed in simulations. However, the dip positions of the three different samples are at 38.4, 63.9, and 75.7 cm$^{-1}$, respectively. The trend of blue-shift for both experiment and simulation matches well with each other, while more flat features at larger wavenumbers in the experiment could be attributed to a larger decay rate of real graphene sample, as discussed above.

Another key factor that can cause a large shift in the spectrum dip is the lateral pillar width. In order to verify the influence of the width, we first excluded the influence from the periodicity. As the working wavelength of interest is 25–100 μm, which is much larger than the periodicity in our sample ($P = 12 \mu m$), no diffraction effect exists in our samples according to the diffraction equation $\sin \theta_i = \sin \theta + m \lambda / P$, where $\theta_i$ and $\theta_f$ are diffraction and incidence angles, respectively, and $\lambda$ is the wavelength. Also there is no pronounced resonant frequency shift observed when periodicity increases from 8.0 μm to 12.0 μm, especially for the first three modes (Figure S5), where the variation in transmission magnitude could be attributed to the pillar density change. As the graphene pillar width increases from 6.0 μm to 7.5 and 9.5 μm, the transmission dip shows a significant red shift from 69.4 cm$^{-1}$ to 53.9 and 38.5 cm$^{-1}$, respectively, which shows the same trend as graphene nanoribbons. The same shift trend is also observed in the simulation (Figure 4c). However, the dip positions of the three different samples are at 70.3, 67.38, and 60.0 cm$^{-1}$, respectively. The small discrepancy in dip positions may result from either nonuniformity of graphene thickness or Fermi energy, or other defects in the used samples. In the frequency range of interest, the optical conductance can be described in a Drude form. Therefore, the resonance wavenumber of the graphene surface plasmon in an isolated pillar can be estimated with the formula $\frac{1}{\theta} \approx \sqrt{\frac{\mu e G}{2\pi \hbar W}},$ where $n$ is the mode number, $\alpha$ is the fine-structure constant, $\epsilon$ is the light speed in a vacuum, and $\hbar$ is the reduced Planck constant. The frequencies of the plasmon modes are subject to the scaling laws. It has also been proved that the wavenumber of the first mode matches perfectly in the theoretical linear relation with $E_{1/2}^{3/2}$ and $1/W^{1/2}$ (Figure S6). In addition, as an excellent active material, the optical response of graphene can be well tuned by varying the Fermi energy level (Figure S7) in addition to the decay rate.

**CONCLUSION**

In conclusion, we have fabricated a novel graphene pillar structure with controllable geometry parameters and thickness of graphene at both horizontal surfaces and the vertical sidewall. To the best of our knowledge, this is the first time that high-order plasmonic mode excitation can be efficiently excited on the graphene network. The underlying mechanism and parameter dependence of these modes have been discussed in detail. Besides the well-known width-dependence, it is...
interesting to see that the graphene thickness at the pillar sidewalls plays an important role in determining the resonance modes. As the sidewall graphene thickness increases, an obvious blue-shift in dip position has been observed. In addition, the Fermi energy, decay rate, etc., also show a strong influence on resonance modes, which provides a feasible way to achieve a dynamic device based on graphene. Our approach to access higher order resonance modes is not limited to graphene but can also be applied to other highly doped 2D materials.\textsuperscript{45,46} In sum, this work contributes to the designing of more sophisticated plasmonic devices and metamaterials based on 2D materials and enables new ways of controlling terahertz, far-infrared, and visible radiation.

### Experimental Section

To fabricate the complex graphene pillar structure, a standard silicon-based fabrication process accompanied by the CVD method was employed. First, the photolithography technique was used to transfer the arrayed patterns from a photolithographic mask (Figure S8a) onto the photoresist on the substrate (Figure S8b,c). With the hard mask protected substrate (Figure S8d), the reactive ion etching process was carried out under a chilled environment (\(-110^\circ\text{C}\)) (Figure S8e). The cryogenic etching process effectively slows the isotropic chemical etching process and finally leads to a much better controlled etching process over the Bosch process.\textsuperscript{47} After mask removal, the intrinsic silicon substrates were cleaned by sonication with acetone and 2-propanol. Subsequently, the substrate can be placed into a high-vacuum furnace chamber for graphene seed implantation and growth (Figure S8f). The chemical environment in the furnace finally ensures full coverage of the graphene layer on the silicon pillars. Specifically, in the CVD process for direct graphene growth, oxygen was used as an aid to activate the growth substrate in a temperature-elevated atmosphere.\textsuperscript{37} Thus, high-quality graphene can be grown on the nucleation spots created in the activation stage. In this way, the direct graphene growth mechanism avoids the complex graphene transfer process.

**Photolithography.** The fabrication of silicon pillars began with transferring the designed array patterns to the intrinsic silicon wafers with direct write photolithography techniques. The photoresist solution (AZ1512) was applied to the wafer with an optimized two-step spin-coating program (500 rpm for 20 s, 3500 rpm for 2:30 min), resulting in a \(\sim 1.5\ \mu\text{m}\) thick photoresist layer. The wafers were subsequently baked at 110 °C for 3 min, followed by exposure using an Intelligent Micro Patterning device (IMP SF-100 XPRESS) for 2.5 s. Then the photoresist was immersed in AZ726 solution for about 50 s and rinsed with DI water for developing.

**Hard Mask Deposition.** After developing the photoresist, the photoresist-covered silicon wafers were deposited with 5 nm Cr and 50 nm Al with an e-beam evaporator. The reason to use a hard mask instead of the photoresist is that the AZ series photoresist can be easily cracked at low temperatures, which would cause failure in transferring the patterns to create the 3D structured silicon.

**Cryogenic Etching.** The cryogenic-DRIE technique was selected to manufacture these silicon pillars, as it can provide much better sidewall profiles than the standard Bosch process in the designed dimensions.\textsuperscript{47} In the cryogenic-DRIE step, the wafers were cooled to \(-110\ ^\circ\text{C}\) by liquid nitrogen to slow the chemical reaction during the etching process, thus approaching isotropic etching with a high aspect ratio and smoother sidewalls. The DRIE system employed is an Oxford PlasmaLab 100 ICP system. The overall processing pressure was set to 10 mTorr with a SF\(_6\) flow rate of 60 sccm and O\(_2\) flow rate of 8 sccm. The lower bias power (13.56 MHz) and upper source power (13.56 MHz) were set to 4 and 800 W, respectively. The depth of etching was controlled by the etching time, which varied from 3 to 5 min.

**Direct Graphene Growth.** The graphene-wrapped surfaces were fabricated by directly growing polycrystalline graphene on the patterned 3D intrinsic silicon substrate. To directly grow graphene on the silicon wafers, the patterned intrinsic silicon chips were directly placed in a quartz tube mounted in a high-temperature furnace (1100 °C). First, the cleaned silicon chip was annealed at 800 °C in an atmosphere environment to activate the nucleation spots. Then, the nucleate allocated surface was exposed to the mixed reaction gas flow (CH\(_4\):H\(_2\):Ar = 14:50:65 sccm) for 3 h. The graphene nanosheets were first formed as separated islands and subsequently connected with the neighboring graphene sheets to form a large-area covered graphene surface. As the back side of the silicon chip was treated with acid, there was no graphene signal being collected.

**Raman Characterization.** Raman spectra and mapping measurements were performed using a confocal microscope system (WITec, alpha 300R) with a 100x objective (NA = 0.9) in ambient conditions. A 532 nm laser was used to illuminate the graphene samples that were placed on a piezo crystal-controlled scanning stage. The spectra were collected using 600 line/mm grating with an integration time of up to 1 min.

**SEM and AFM Characterization.** The morphology of the silicon pillars and the topography of the covered graphene flakes were characterized by a dual-beam FIB-SEM (FEI Helios Nanolab 600) and atomic force microscopy (Bruker, Dimension Icon SPM) in the tapping mode, respectively.

**FTIR Measurements.** The Fourier transform infrared (FTIR) spectroscopy measurement was carried out with a vacuum Bruker 80v FTIR instrument with a deuterated triglycine sulfate detector. The samples were mounted on the sample holder in a vacuum environment. The spectra in the range of 30−700 cm\(^{-1}\) and 300−7000 cm\(^{-1}\) were collected. All the measurements were carried out at room temperature. All the background signals resulting from intrinsic silicon were subtracted before data analysis.

### Associated Content

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsphotonics.6b00566.

Simulations results of dependence of transmission of the graphene-wrapped pillar array on the height, scattering rate, periodicity, and Fermi energy of graphene pillars;
schematic of simultaneous CVD growth of graphene pillar samples; Raman spectra for horizontal and vertical graphene films; relationship fitting between wavenumber of first mode with $E^{1/2}$ and $1/W^{1/2}$; schematic of the fabrication process (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**

*E-mail (C.-W. Qiu): eleqc@nus.edu.sg.*

*E-mail (Q. L. Bao): qlbao@suda.edu.cn.

**Author Contributions**

*J. Song, L. Zhang, and Y. Xue contributed equally to this work.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors acknowledge support from the Youth 973 Program (2015CB932700), the National Natural Science Foundation of China (Grant Nos. 91433107, 51222208, and 51290273), ARC (DE120101569, DP140101501, and FT150100450), the Collaborative Innovation Center of Suzhou Nano Science & Technology, and the Priority Academic Program Development of Jiangsu Higher Education Institutions. Y.X. acknowledges support from China Postdoctoral Science Foundation (2014MS50303). L.Z. and C.-W.Q. acknowledge the financial support from the A*STAR Pharos Programme (Grant No. 152 70 00014, with Project No. R-263-000-B91-305). C.-W.Q. acknowledges support from the National Research Foundation, Prime Minister’s Office, Singapore, under its Competitive Research Programme (CRP Award No. NRF-CRP15-2015-03). J. S. acknowledges the technical support from Dr. Saksiran Kandasamy, Dr. Ricky Tjeung, and Mr. Dan Smith. This work was performed in part at the Melbourne Centre for Nanofabrication (MCN) in the Victorian Node of the Australian National Fabrication Facility (ANFF).

**REFERENCES**


