Flexible, Transparent and Ultrathin Single-Layer Graphene Earphone

He Tian,[1,2] Yi Yang,[1,2] Cheng Li,[1,2] Wen-Tian Mi,[1,2] Mohammad Ali Mohammad,[1,2] Tian-Ling Ren[1,2,*]

[1]Institute of Microelectronics, Tsinghua University, Beijing 100084, China

[2]Tsinghua National Laboratory for Information Science and Technology (TNList), Tsinghua University, Beijing 100084, China

*Corresponding Author E-mail:

RenTL@tsinghua.edu.cn

Abstract

Graphene is flexible and transparent with one-atom layer thickness, which is novel building block with potential applications in future portable devices. Here a flexible, transparent and ultrathin earphone based on single-layer graphene (SLG) is reported. The SLG earphone operates in the frequency range of 20 Hz to 200 kHz and has a highest sound pressure level (SPL) of 70 dB in 1 cm distance. The SPL emitted from one to six layers of stacked SLG are compared. It is observed that the SPL decreases with an increasing number of stacked layers. The SLG earphone, which is packaged with a commercial earphone casing, can play music clearly. Compared with a conventional earphone, the SLG earphone has a broader frequency response and a lower fluctuation. Testing results in both time and frequency domains show a frequency doubling effect, which indicates that the working principle is based on the electro-thermoacoustic (ETA) effect. As the SLG earphone operates in both the audible and ultrasonic frequency range, it can be used for a wide variety of applications.

Introduction

Flexible and transparent devices are of great importance for next generation electrical systems.[1] Flexible and transparent transistors,[2-5] solar cells,[6-8] photodetectors,[9, 10] light emitting diodes[11] have been developed. To date, the commercial earphone is based on magnetic coil,[12] which could not achieve the flexibility and transparency. But recently, various nanomaterials, including nanowires,[13-15] carbon nanotubes,[16-20] and graphene[21, 22] have been used for the development of novel sound sources based on electro-thermoacoustic (ETA) effect. The main advantage of using nanomaterials is their low heat capacity per unit area (HCPUA), which could convert joule heating to sound waves more efficiently. Single-layer graphene (SLG) has the lowest HCPUA,[23] which could be more efficient than other materials. Despite the promise, to date, there is no reported on SLG earphone.

Here a SLG earphone, which operates according to the ETA effect, is demonstrated. Exploiting such a working principle, the SLG earphone is fundamentally different from conventional ones. A systematic study of the sound generation from one to six stacked layers of SLG is made here. The sound spectrum of the SLG earphone is significantly wider than a commercial earphone, covering both the audio and ultrasound frequencies up to 200 kHz. The earphone core is flexible, transparent and ultrathin. As a demonstration, the SLG earphone is packaged into a commercial earphone casing and tested successfully.

Experiment

Fabrication of SLG Earphone: The schematic of graphene earphone is shown in Figure 1a. The fabrication process of the SLG earphone has eight steps (Figure 1b). Briefly, the SLG is grown on copper by CVD at 1000 °C. The domain size is ~20 μm. Wet transfer is used to transfer the SLG on a polyethylene terephthalate (PET) or polyimides substrate. Subsequently, silver electrodes are applied to the SLG and wired out (Figure 1c). Finally, the device is packaged into a commercial earphone casing (Figure 1d). A drive circuit is also made to supply a DC bias so that the SLG earphone can directly connect to laptop for playing music (Figure 1e). Real images of the fabrication process is shown in Figure S1.

Stacked SLG Fabrication and Characterization: Large area of SLG (5×10 cm^2) can be transferred on PET substrates with high transparency and flexibility (Figure 2a). Stacked SLG (from one to six layers) were made and tested to understand the layer-dependence on sound performance. Furthermore n (2~6) such layers can be transferred to the same PET substrate (Figure S2). This can be done by repeated Poly(methyl methacrylate) wet transfer of SLG grown on copper by CVD. Sheet resistance was measured by the automatic four point probe meter (model 280SI, Four Dimensions, Inc.). The sheet resistance of the SLG is ~90 Ω/□ (Figure 2b), showing a higher quality as compared to roll-to-roll SLG, whose resistance is reported to be 125 Ω/□.[24] Stacking SLG layers decreases the sheet resistance down to 26 Ω/□ in a six-layer stack. It is observed that the transparency of the stacked layers decreases with an increasing number of layers (Figure S3). The stacked SLGs were also transferred to SiO_2/Si substrates for optical (Figure S4) and Raman analysis. 2D images of SLGs surface were captured by white light interference microscope microXAM-1200 (MapVue AE Inc.). As the stacked SLGs were not perfectly aligned, the layer number could be identified through the edges of the films (Figure 2c). The Raman spectroscopy was obtained using a laser with a wavelength of 532 nm (HORIBA Inc.). Raman spectra show that the SLG yield stronger 2D peaks as compared with G peaks (Figure 2d). There are almost no D-peaks indicating a C-C lattice structure with very little defects. Due to the random stacking of SLG layers, unlike graphite, the intensities of the G and 2D peaks increase together. Statistical results show that 2D/G ratios are larger than 1 for stacked SLG layers (Figure 2e).

Sound Testing: The acoustic platform for testing the SLG earphones consisted of a standard microphone and a dynamic signal analyzer. A 1/4 inch standard microphone (Earthworks M50) was used to measure the sound pressure level of the loudspeakers. This microphone has a very flat frequency response reaching up to 50 kHz and a 31 mV/Pa high sensitivity. A signal analyzer (Agilent 35670A) was used to generate sine signals to drive the earphones, perform fast Fourier transform analysis and record the value of the sound pressure level. Our testing was performed in a soundproof box measuring $1.0\times0.5\times0.5\ m^3$. In order to avoid echo, the box was filled with sound-absorbing sponges.

Results and discussion

Layer Dependence on Sound Performance: The sound performance of the stacked SLGs are tested by applying 5 V AC and 5 V DC signals. The frequency is swept from 20 Hz to 50 kHz. The original results of SPL vs. frequency is shown in Figure S5. From layers 1 to 5, the sound pressure level (SPL) decreased (Figure 3a) which could be explained by an increased heat capacity per unit area (HCPUA). It is concluded that the SLG has the highest SPL due to its lowest HCPUA (Figure 3b). It is also noticed that there is an anomaly for a six-layer SLG stack. Since six layers have a larger HCPUA, it is expected that the SPL would be lower. However, another SPL influencing factor is the thermal leakage from the substrate. As six layers have a larger total gap, the thermal coupling with the substrate is weaker, which in-turn could enhance the sound performance. The six-layer device has much lower thermal coupling with substrate than other sample. A direct evidence is that during the wet transfer, the six-layer graphene is much easier to peel off from the substrate, which indicates the six-layer graphene has weaker interaction with the substrate compared to other samples. Based on this observation, it is hard to stack more than six layers. And it also confirmed that the effect thermal coupling of the six-layer graphene is much weaker than other samples.

Sound Performance of the SLG Earphone: The time domain response of the SLG earphone is investigated and compared to a commercial earphone. An input sine signal is swept from 0 Hz to 20 kHz in 20 s. It is observed that the SLG earphone reaches 20 kHz in 10 s (Figure 4a), indicating that the output frequency has been doubled. In order to reproduce the same frequency as the input signal, a DC bias is added and both single-frequency and double-frequency tones are generated (Figure 4b). There is no obvious differences from one layer to six layers graphene both in time and frequency domain (Figure S6). It is also noted that the conventional earphone only has a single-frequency tone (Figure 4c).

The SLG earphone also has a wider frequency response than a commercial earphone, especially in the ultrasound range (Figure 5a). The sound spectrums of the SLG earphone under different input power levels are also tested (Figure 5b) and a linear relationship is observed (Figure 5c). The frequency-doubling effect in the SLG earphone is also found in time-domain (Figure 5d). A sine-pulse response testing shows that the delay time is 20 μs (Figure 5e), which is similar to a commercial earphone. As shown in Figure 5f, this is the first experimental demonstration that the graphene earphone can emit sounds up to 200 kHz. In Table 1, the performance of our SLG earphone is compared with previous efforts[20,22,23]. The SPL of SLG earphone is 10 dB higher than CNT earphone and 35 dB higher than rGO earphone due to the lower HCPUA of graphene. The SPL of SLG earphone is also 24 dB higher than previous graphene speaker due to the better quality of graphene film. Our SLG has the even lower sheet resistance than well-known roll-to-roll graphene.[24] The higher conductivity of SLG could convert electrical power to Joule heating more efficiency. The SLG earphone reported in this work represents the state-of-art earphone, which could open wide applications in consumer electronics such as phone, pad, computer *et*.

Theoretical analysis of SLG Earphone: The schematic shows the sound generation process in SLG earphone (Figure 6a), which is different from conventional mechanical damping. Simulation results show a good agreement with the experimental results (Figure 6b). The minor discrepancy in low frequency is due to the environment noise.

Potential application for transparent SLG earphone: The concept of "transparent electronics" was proposed by John. F. Wager[25] and attracted a lot of attention. The transparent earphone is very useful for consumer and military applications. For example, the transparent earphone could be used as hearing aid. The person who wear hearing aid would not like people know this. The visible transparent hearing aid could make them feel comfortable since other people do not notice the hearing aid. The transparent earphone could also be used for secure communication since other people could not aware it.

Conclusion

A transparent, flexible SLG earphone has been demonstrated for the first time operating based on the ETA effect. The earphone operates in the range of 20 Hz to 200 kHz, with a highest SPL of 70 dB. These metrics indicate that the SLG earphone has a performance exceeding other recent state-of-the-art sound generation devices. Furthermore, the SLG earphone has a broader frequency response and a lower fluctuation as compared to a commercial earphone. A systematic study of the sound generation performance of one to six stacked SLG layers was conducted. Further performance enhancement can be achieved by driving the SLG earphone using pulse density modulation. The SLG earphone technology is expected to bring transparent flexible earphone in the field of acoustics.

Acknowledgements

This work was supported by National Natural Science Foundation (61434001), 973 Program (2015CB352100), National Key Project of Science and Technology (2011ZX02403-002), and Special Fund for Agroscientic Research in the Public Interest (201303107) of China. H.T is thankful for receiving support through the Ministry of Education Scholarship of China. M.A.M is thankful for receiving support from the postdoctoral fellowship (PDF) program of the Natural Sciences and Engineering Research Council of Canada (NSERC).

Supporting Information Available: Testing results of graphene earphones.

Notes: The authors declare no competing financial interest.

References

1. J. A. Rogers, T. Someya and Y. Huang, *Science*, 2010, **327**, 1603-1607.
2. K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano and H. Hosono, *Nature*, 2004, **432**, 488-492.
3. E. Artukovic, M. Kaempgen, D. S. Hecht, S. Roth and G. GrUner, *Nano Letters*, 2005, **5**, 757-760.
4. T. Georgiou, R. Jalil, B. D. Belle, L. Britnell, R. V. Gorbachev, S. V. Morozov, Y.-J. Kim, A. Gholinia, S. J. Haigh, O. Makarovsky, L. Eaves, L. A. Ponomarenko, A. K. Geim, K. S. Novoselov and A. Mishchenko, *Nature Nanotechnology*, 2013, **8**, 100-103.
5. S. Ju, A. Facchetti, Y. Xuan, J. Liu, F. Ishikawa, P. Ye, C. Zhou, T. J. Marks and D. B. Janes, *Nature Nanotechnology*, 2007, **2**, 378-384.
6. C.-C. Chen, L. Dou, R. Zhu, C.-H. Chung, T.-B. Song, Y. B. Zheng, S. Hawks, G. Li, P. S. Weiss and Y. Yang, *Acs Nano*, 2012, **6**, 7185-7190.
7. M. W. Rowell, M. A. Topinka, M. D. McGehee, H.-J. Prall, G. Dennler, N. S. Sariciftci, L. Hu and G. Gruner, *Applied Physics Letters*, 2006, **88**, 233506.
8. L. G. De Arco, Y. Zhang, C. W. Schlenker, K. Ryu, M. E. Thompson and C. Zhou, *ACS Nano*, 2010, **4**, 2865-2873.
9. N. Liu, H. Tian, G. Schwartz, J. B. H. Tok, T.-L. Ren and Z. Bao, *Nano Letters*, 2014, **14**, 3702-3708.

10. Z. Gao, W. Jin, Y. Zhou, Y. Dai, B. Yu, C. Liu, W. Xu, Y. Li, H. Peng, Z. Liu and L. Dai, *Nanoscale*, 2013, **5**, 5576-5581.
11. D. Zhang, K. Ryu, X. Liu, E. Polikarpov, J. Ly, M. E. Tompson and C. Zhou, *Nano Letters*, 2006, **6**, 1880-1886.
12. M. R. Gander, *J. Audio Eng. Soc.*, 1981, **29**, 10-26.
13. A. O. Niskanen, J. Hassel, M. Tikander, P. Maijala, L. Gronberg and P. Helisto, *Applied Physics Letters*, 2009, **95**, 163102.
14. V. Vesterinen, A. O. Niskanen, J. Hassel and P. Helisto, *Nano Letters*, 2010, **10**, 5020-5024.
15. H. Tian, D. Xie, Y. Yang, T.-L. Ren, Y.-X. Lin, Y. Chen, Y.-F. Wang, C.-J. Zhou, P.-G. Peng, L.-G. Wang and L.-T. Liu, *Applied Physics Letters*, 2011, **99**, 253507.
16. L. Xiao, Z. Chen, C. Feng, L. Liu, Z.-Q. Bai, Y. Wang, L. Qian, Y. Zhang, Q. Li, K. Jiang and S. Fan, *Nano Letters*, 2012, **12**, 2652-2652.
17. K. Suzuki, S. Sakakibara, M. Okada, Y. Neo, H. Mimura, Y. Inoue and T. Murata, *Japanese Journal of Applied Physics*, 2011, **50**, 01BJ10.
18. A. E. Aliev, M. D. Lima, S. Fang and R. H. Baughman, *Nano Letters*, 2010, **10**, 2374-2380.
19. L. Xiao, P. Liu, L. Liu, Q. Li, Z. Feng, S. Fan and K. Jiang, *Journal of Applied Physics*, 2011, **110**, 084311.
20. Y. Wei, X. Lin, K. Jiang, P. Liu, Q. Li and S. Fan, *Nano Letters*, 2013, **13**, 4795-4801.
21. H. Tian, T.-L. Ren, D. Xie, Y.-F. Wang, C.-J. Zhou, T.-T. Feng, D. Fu, Y. Yang, P.-G. Peng, L.-G. Wang and L.-T. Liu, *ACS Nano*, 2011, **5**, 4878-4885.
22. H. Tian, C. Li, M. A. Mohammad, Y. L. Cui, W. T. Mi, Y. Yang, D. Xie and T. L. Ren, *Acs Nano*, 2014, **8**, 5883-5890.
23. J. W. Suk, K. Kirk, Y. Hao, N. A. Hall and R. S. Ruoff, *Advanced Materials*, 2012, **24**, 6342-6347.
24. S. Bae, H. Kim, Y. Lee, X. Xu, J.-S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. Ri Kim, Y. I. Song, Y.-J. Kim, K. S. Kim, B. Ozyilmaz, J.-H. Ahn, B. H. Hong and S. Iijima, *Nature Nanotechnology*, 2010, **5**, 574-578.
25. J. F. Wager, *Science*, 2003, **300**, 1245-1246.

Figures and Captions

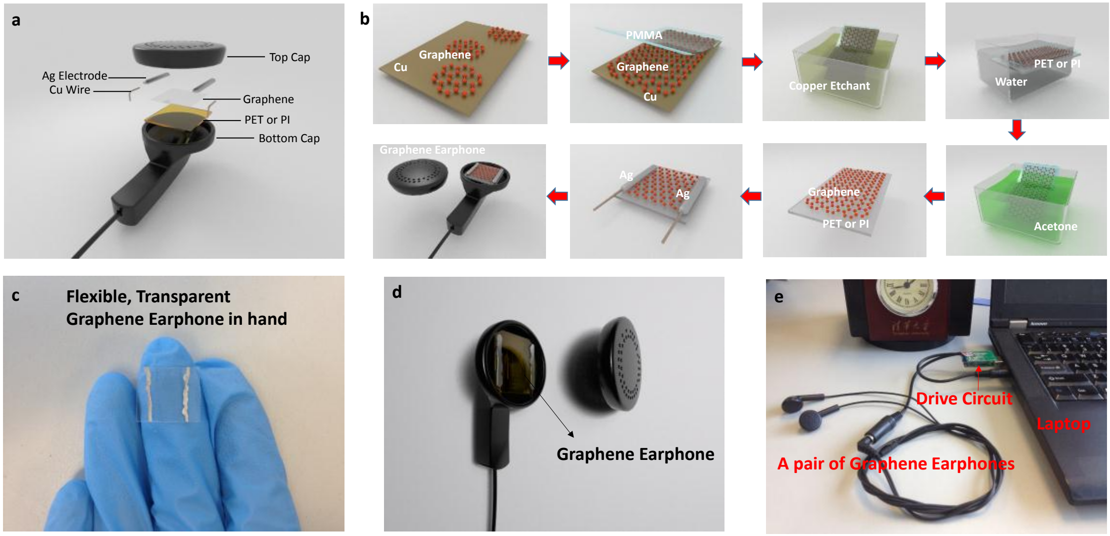


Figure 1. a, Schematic of the graphene earphone. **b,** Fabrication process of the graphene earphone. **c,** A single-layer graphene (SLG) earphone in hand. **d,** View of the SLG earphone in a commercial earphone casing. **e,** A Pair of SLG earphones connected to a laptop through a drive circuit. The music in laptop could be played through SLG earphone.

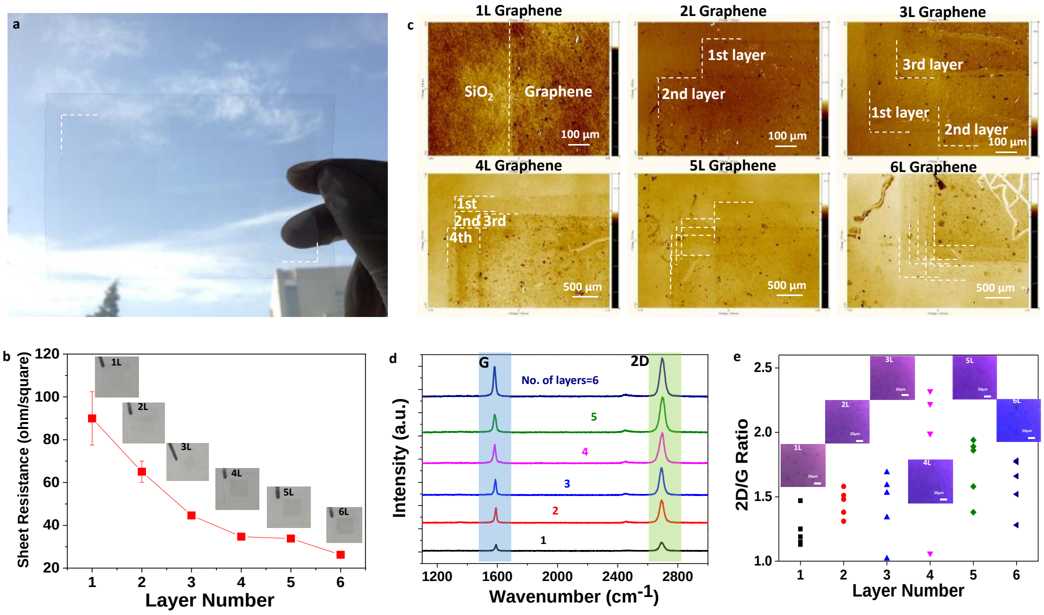


Figure 2. a, A highly transparent 5 cm × 10 cm SLG on PET. The dashed lines show the edges of the graphene film. **b,** Images of graphene films with 1 to 6 stacked layers on a SiO2/Si substrate captured by a white light interference microscope. Each graphene layer can be identified by the color contrast and corner shape. **c,** Sheet resistance vs. layer number of SLG films. The quality of SLG (<100 Ω/☐) is even better than well-known roll-to-roll SLG [2]. **d,** Raman spectra of graphene films with different numbers of stacked layers. Due to the random stack of graphene layers, unlike graphite, the intensities of the G and 2D peaks increase together. **e,** 2D/G ratio of graphene films with different numbers of stacked layers. The 2D/G ratios are larger than unity, indicating the presence of SLG.

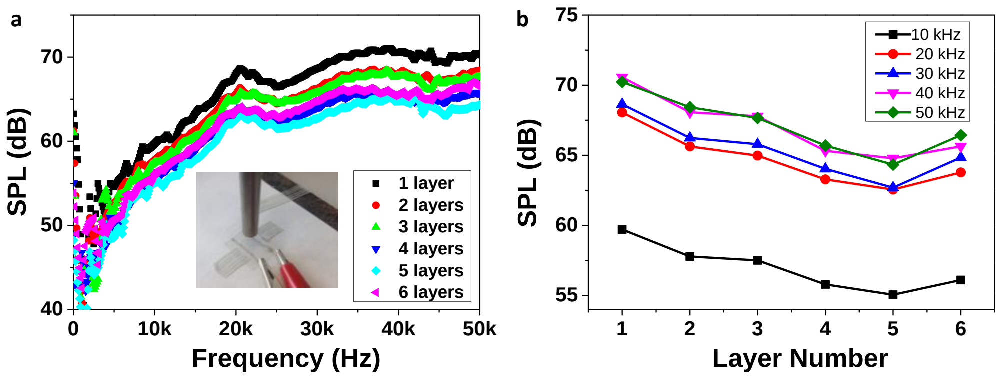


Figure 3. a, The SPL vs. frequency for different graphene layers. The single-layer graphene has the highest SPL value. The measure distance is fixed at 1 cm. **b,** The SPL vs. layer number for different acoustic frequencies. The thinner graphene has higher sound pressure due to lower HCPUA.

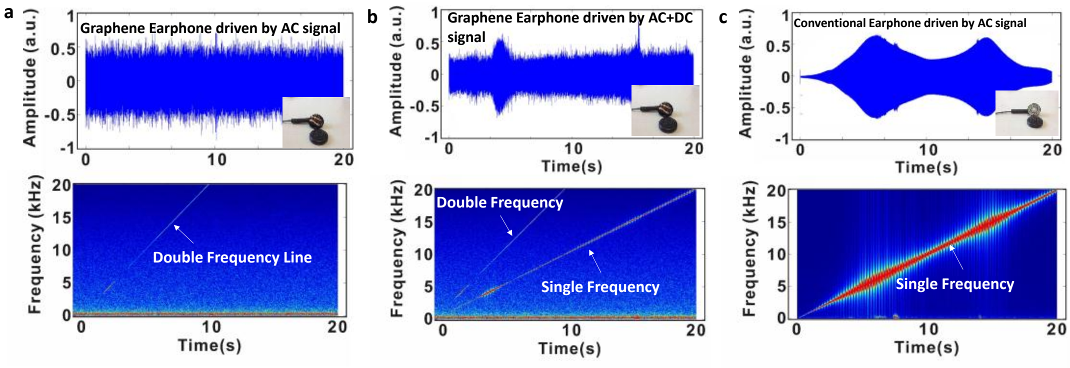


Figure 4. a, The amplitude spectrum and its Fourier transform of the sound generated by the SLG earphone driven by an AC signal. **b,** The amplitude spectrum and its Fourier transform of the sound generated by the SLG earphone driven by an AC+DC signal. **c,** The amplitude spectrum and its Fourier transform of the sound generated by a conventional magnetic coil earphone.

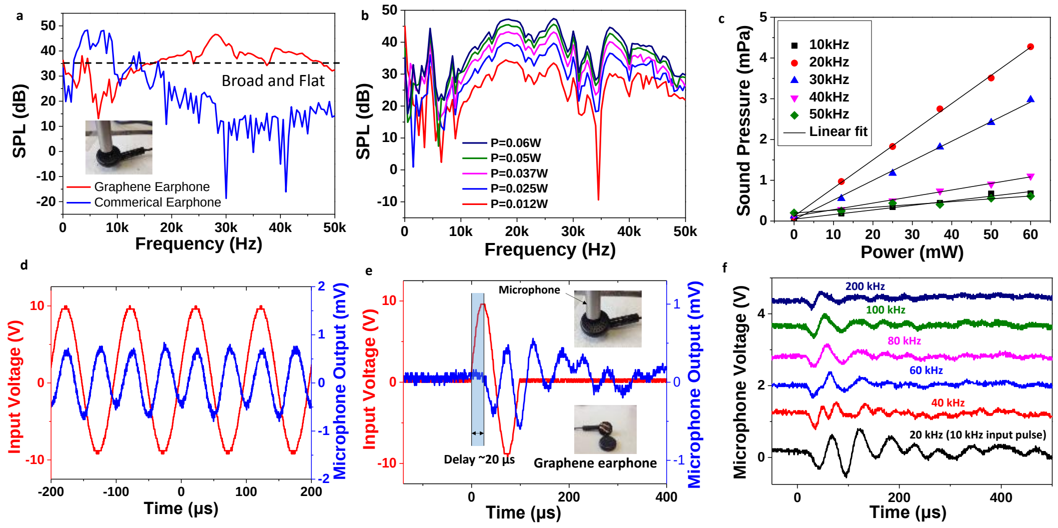


Figure 5. a, SPL cures of a SLG graphene earphone compared with a commercial earphone. **b,** The SPL of the graphene earphone under different powers. **c,** Power-dependent sound pressure under different frequencies. **d,** A 10 kHz input signal fed to the SLG earphone and the corresponding sound signal collected by the microphone, showing the frequency-doubling effect. **e,** The measured acoustic response for electrical a single 10 kHz sine-pulse input, showing a time delay of 20 μs. **f,** The measured acoustic response driven by different frequencies of sine-pulse. There is output signal under 100 kHz, corresponding to 200 kHz sound frequency.

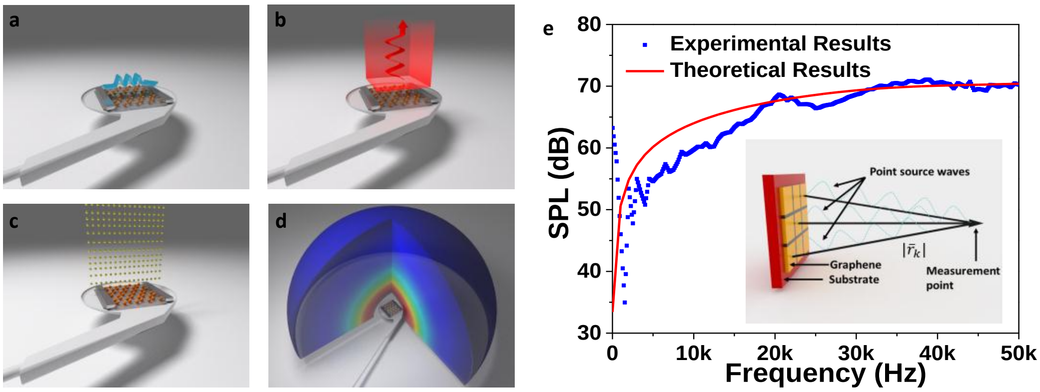
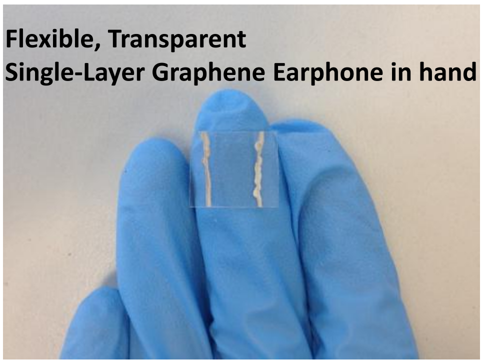


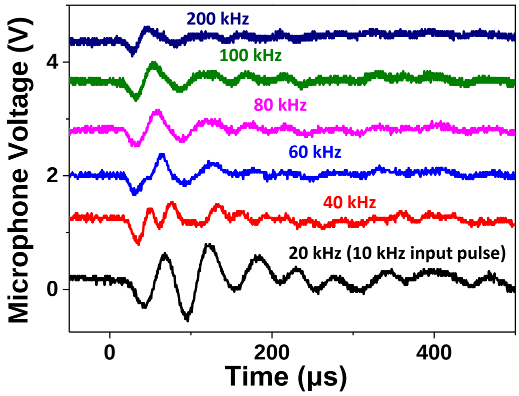
Figure 6. Sound generation in a SLG graphene earphone. An applied **a,** signal causes **b,** Joule heating, inducing **c,** longitudinal, and **d,** spherical sound waves in the near- and far-fields respectively. **e,** SPL vs. frequency showing that the model agrees well with the experiment. The inset illustrates the model of sound generation in a SLG earphone.

Table 1. A performance comparison of recent acoustic devices. SLG earphone has the highest SPL and widest frequency range. Note the input power are normalized to 1 W.

Materials	SPL (dB)	f Limit (kHz)	References
CNT	60	20	*Nano Letters* 2013 [Ref. 20]
rGO	35	50	*ACS Nano* 2014 [Ref. 22]
SLG	46	20	*Advanced Materials* 2012 [Ref. 23]
SLG	70	200	This Work

Table of content





A flexible and transparent single-layer graphene earphone is demonstrated to operate in the frequency range of 20 Hz to 200 kHz with high performance.