Regulating the Stable Lithium and Polysulfide Deposition in Batteries by a Gold Nanoparticle Modified Vertical Graphene Host

Zhiyuan Han, Zhijia Huang, Tong Li, Yunbo Zhang, Guangmin Zhou,* Chen Zhang, Jiabin Ma, Feiyu Kang, and Wei Lv*

3D hosts have been widely investigated to stabilize the lithium (Li) metal anode (LMA) for next-generation high-energy-density batteries. However, the complicated porous structure and the lithiophobic framework always lead to nonuniform Li deposition and low host utilization. Herein, Au nanoparticle (NP)–modified vertical graphenes, which are grown on flexible graphite paper, are prepared as the 3D host (denoted Au-VG-GP) to guide Li nucleation and deposition. It is shown that the vertical graphene structure with the low tortuosity effectively decreases the ion diffusion resistance and avoids the formation of a concentration gradient, ensuring uniform ion distribution in the 3D host. At the same time, the uniformly distributed Au NPs act as heterogeneous seeds guiding fast and uniform Li nucleation and growth. As a result, the Au-VG-GP host effectively stabilizes the LMA and achieves a high Coulombic efficiency in the half-cells. A small overpotential and long cycling stability are also achieved for the LMA in the symmetrical cells and full batteries with such a host. In addition, such a host can also guide uniform and high-capacity deposition of Li$_2$S in the cathode of lithium–sulfur batteries, showing its potential uses in energy storage devices based on a dissolution–deposition mechanism.

1. Introduction

The lithium (Li) metal anode (LMA) is an attractive anode for next-generation batteries with high energy density because of its high specific capacity (3860 mA h g$^{-1}$) and low electrochemical potential ($-3.04$ V vs standard hydrogen electrode). However, uncontrollable interfacial reactions and lithium dendrite growth during cycling lead to poor cycling stability and severe safety concerns, hindering their practical applications. The reaction of the LMA relies on a dissolution–precipitation process, and the dendrite growth is mainly derived from the uneven Li$^+$ ion and electric field distribution on the electrode surface and the large nucleation overpotential. 3D hosts have been widely investigated to homogenize the Li$^+$ ion distribution and decrease the local current density to regulate the Li deposition. However, preferential Li accumulation on the upper conductive electrode surface always occurs due to the high Li$^+$ ion concentration at the interface between the bulk electrolyte and the complicated porous structure, which blocks the Li$^+$ ion diffusion inside the 3D host, decreasing the pore utilization, and even worse, leading to anode failure in long cycling.

Decreasing the tortuosity is an effective way to homogenize the ion distribution and guide uniform Li deposition in the 3D host. Recently, vertical graphene (VG) structures have been investigated to achieve homogeneous deposition. However, most of them are grown on a 3D framework, such as 3D carbon nanofibers/carbon cloth-metallic mesh, and have a lithiophobic surface with a large nucleation energy barrier. Although many researches have shown that surface coating or modification with lithiophilic materials or functional groups can solve the lithiophobic problem, the understanding of mediated Li deposition is still limited. A similar problem also troubles the sulfur cathode of lithium–sulfur (Li–S) batteries as uncontrollable lithium sulfide (Li$_2$S) deposition from the dissolved lithium polysulfide (LiPS) intermediates in the electrolyte always occurs due to the poor sulﬁphility of the carbon hosts, leading to cathode passivation.
Herein, we prepared VG grown on a flexible graphite paper (GP) substrate by a plasma-enhanced chemical vapor deposition (PECVD) method as a low-tortuosity 3D host. During lithium deposition, Au forms the alloy phase of Li$_2$Au above 0 V,\textsuperscript{[10]} which can effectively reduce the nucleation barriers. Therefore, Au nanoparticles (NPs) with precisely controlled size were then decorated on graphene surface by an ion sputter, and the obtained sample was denoted as “Au-VG-GP.” The low-tortuosity VG structure effectively decreases the ion concentration gradient, and the uniform Au NPs with the small size guide homogeneous Li nucleation and deposition on the graphene surface, as shown in Figure 1. The half-cell with the Au-VG-GP electrode exhibits improved cycling performance with high Coulombic efficiency (CE) of 93% for more than 90 cycles at 3 mA cm$^{-2}$ with a capacity of 1 mAh cm$^{-2}$. Moreover, the full cell with LiFeO$_2$ (LFP) also shows a high CE of 99.1% after 100 cycles, indicating its excellent long-term cycling stability. Moreover, the Au NPs also show good sulfphilicity, and thus, such a structure can also regulate the Li$_2$S precipitation with a large capacity (Figure 1), improving the sulfur utilization. This work shows the importance of electrode structure and the heterogeneous seed designs for energy storage devices based on the dissolution–precipitation mechanism.

2. Results and Discussion

The GP substrate shows a smooth surface (Figure S1, Supporting Information), and as shown in Figure S2, Supporting Information, the VGs grown on the GP substrate through a PECVD method are interconnected with each other and have a corrugated sheet morphology. The cross-sectional view shows that they are uniformly and vertically grown on the GP with a width of $\approx$5 μm (Figure 2b). The vertical structure remains after a press for the coin cell assembly, indicating its high structural stability (Figure S3, Supporting Information). Au NPs were then introduced onto the graphene surface by ion sputtering to obtain the Au-VG-GP and the size of Au NPs can be precisely controlled by the sputtering time. Figure 2a shows the preparation of Au-VG-GP, and Figure 2c,d,f shows the morphologies of Au-VG-GP with different sputtering times. As shown in Figure 2c, only a few unevenly distributed Au NPs with a size of $\approx$8 nm can be observed after a 2 s sputtering deposition (the obtained sample is denoted as “Au-VG-GP-2”), and when the sputtering time increased to 5 s (denoted as “Au-VG-GP-5”), uniformly distributed Au NPs with size of $\approx$10 nm on the graphene surface could be observed (Figure 2d). The uniform Au distribution on Au-VG-GP-5 was further confirmed by energy-dispersive X-ray spectroscopy (EDS) mapping (Figure 2e). However, when the sputtering time further increased to 15 s (denoted as “Au-VG-GP-15”), the Au NPs were grown together to form large particles ($\approx$20–30 nm) with irregular shapes (Figure 2f). The Raman spectra of the aforementioned samples show the typical D band (1331 cm$^{-1}$) and G band (1581 cm$^{-1}$),\textsuperscript{[34–36]} (Figure 2g), and the $I_D/I_G$ ratios of VG-GP, Au-VG-GP-2, Au-VG-GP-5, and Au-VG-GP-15 are 1.05, 0.97, 0.93, and 0.31, respectively. The decrease of $I_D/I_G$ may be derived from the coverage of defects by the deposited Au NPs, which is beneficial to suppress the side reactions. The Au $4f$ X-ray photoelectron spectroscopy (XPS) spectra (Figure S4, Supporting Information) deconvolute into two main peaks at 84.7 and 88.4 eV, corresponding to Au 4$\Delta$f$_{7/2}$ and 4$\Delta$f$_{5/2}$, indicating successful decoration of Au on the VG surface. Figure S5, Supporting Information, shows the wetting ability of VG-GP, Au-VG-GP-2, Au-VG-GP-5, and Au-VG-GP-15 by the electrolyte. It is shown that they have a similar contact angle, suggesting the good wetting ability of the VG structure.

The Li deposition behaviors on the aforementioned samples were then investigated through half-cell tests using Li metal as the counter electrode. Figure S6, Supporting Information, shows the cycling performance of cells at 1 mA cm$^{-2}$ with a capacity of 1 mAh cm$^{-2}$. The CE of the GP electrode fluctuates after 24 cycles (87% for CE), which should be ascribed to the nonuniform Li deposition according to our previous report,\textsuperscript{[37]} whereas the cell with the VG-GP electrode shows better cycling stability (86.4% for CE) as the vertical structure decreases the local current density and homogenizes the Li$^+$ ion distribution on the electrode surface. The cycling performance was further improved after decorating the lithiophilic Au NPs. The Au-VG-GP-5 with uniform Au distribution shows the highest CE of 97.8% for 300 cycles because the lithiophilic Au NPs reduce the nucleation barrier (Figure S7, Supporting Information) and act as heteroseeds guiding the Li deposition. Moreover, the decorated Au NPs with a large surface area will increase the reaction area of the electrodes, which

![Figure 1. Schematic diagram of the Li and Li$_2$S deposition on Au-VG-GP.](image)
reduces the local current density and regulates the \( \text{Li}^+ \) ion flux significantly. In addition, Au-VG-GP-2 (98.1% for 160 cycles) and Au-VG-GP-15 (97.1% for 190 cycles) show inferior CEs, suggesting the morphology of Au NPs plays an important role in guiding the uniform Li deposition. When the current density increases to 3 mA cm\(^{-2}\), the CEs of the cells with Au-VG-GP-2 and Au-VG-GP-15 electrodes fluctuate after 60 and 75 cycles, but the cell with Au-VG-GP-5 can keep 93% after 90 cycles (Figure 3a), further proving the earlier conclusion. With a higher capacity of 3 mAh cm\(^{-2}\), the CEs of these cells show a similar phenomenon and the cell with Au-VG-GP-5 displays the best cycling stability (Figure 3b). The galvanostatic discharge–charge profiles at 1 mA cm\(^{-2}\) with a capacity of 3 mAh cm\(^{-2}\) show that the voltage hysteresis of Au-VG-GP-5 remains stable after long cycling, indicating the stable Li plating/stripping behavior (Figure 3c).

Electrochemical impedance spectroscopy (EIS) test was further used to prove the stabilized Li deposition with Au NPs as the heteroseeds (Figure 3d). The cell with Au-VG-GP-5 shows the smallest semicircle (9.33 \( \Omega \)) after five cycles compared to the cells with Au-VG-GP-2 (32.87 \( \Omega \)) and Au-VG-GP-15 (17.64 \( \Omega \)) (Table S1, Supporting Information). Even after 50 cycles at a high current density, the Au-VG-GP-5 electrode remains the smallest charge transfer resistance compared with Au-VG-GP-2 and Au-VG-GP-15 electrodes (Figure S8, Supporting Information), indicating stable interfacial properties and suppressed side reactions were achieved by the stabilized Li deposition with the help of uniform and small Au seeds and their defect-shielding effect mentioned earlier.\(^{38}\) The symmetrical cells were assembled with predeposited 3 mAh cm\(^{-2}\) Li onto Au-VG-GP as the electrode. As shown in Figure 3e,f, the symmetrical cell with the Li/Au-VG-GP-2 electrode exhibits a stable Li stripping/plating overpotential at the initial 280 h and then sharply increases to 120 mV after 300 h cycling, indicating an unstable plating/stripping behavior. Although the cell with Li/Au-VG-GP-15 shows better stability, the overpotential also becomes very large after 400 h cycling. In contrast, the cell with Li/Au-VG-GP-5 shows the best cycling stability with low overpotential over 450 h, further suggesting that the Au seeds with uniform distribution and particle size play significant roles in guiding uniform Li deposition.

The guided Li nucleation and deposition by VG-GP and Au-VG-GP-5 were further proved by the SEM images with different deposition capacities. As shown in Figure 4a,b, the Li deposition on the VG-GP mainly occurred on the top surface and blocked the vertical channel even with the low deposition capacity of 0.1 mAh cm\(^{-2}\). This should be ascribed to the largest electric field and highest ion concentration at the top
surface of the thick VG structure, and moreover, the large nucleation barrier of lithiophobic VG, which induced the large polarization and made the deposited Li mainly aggregate on the surface. In contrast, the vertical structure of Au-VG-GP-5 was well kept, and the Li deposition mainly occurred on the graphene surface. When the Li deposition capacity increased to 1 mAh cm\(^{-2}\), the vertical structure could still be observed (Figure 4c). These results show the introduction of lithiophilic Au NPs as the seeds ensures fast and uniform Li deposition on the graphene surface around the Au seeds. After the stripping in the first cycle, the Au NPs remain on the VG-GP surface, which indicates their continuous stability for guiding the Li deposition in the cycling (Figure S9, Supporting Information). The Li deposition morphology was further investigated after 50 cycles at 3 mA cm\(^{-2}\) with a capacity of 1 mAh cm\(^{-2}\) (Figure 4d, f). As shown in Figure 4d, severe accumulation of the Li deposit can be observed on Au-VG-GP-2 and only some vertical channels remain after long cycling, suggesting the nonuniform distribution of Au NPs cannot well guide the following Li nucleation and deposition. In contrast, Li can be uniformly deposited into the vertical channels of Au-VG-GP-5 with the help of uniform Au seeds with small size. However, further increasing the sputtering time will lead to aggregation of Au NPs, which also cannot effectively regulate the following Li deposition during cycling. The aforementioned results clearly indicate the roles of lithiophilic Au NPs with small size in guiding uniform Li nucleation and growth. As shown in Figure S10, Supporting Information, the binding energy of the Au 4f peak in Au-VG-GP-5 obviously shifts to a lower value after Li deposition, suggesting the formation of Li–Au alloy in the SEI film.\(^{[32]}\) The surface morphologies of electrodes with 3 mAh cm\(^{-2}\) predeposited Li were also investigated (Figure 4g–i and S11, Supporting Information). It shows that the Li deposited on the Au-VG-GP-5 electrode has a highly ordered structure compared to that of the VG-GP electrode. The uniform Au NPs increase the nucleation density of lithium metal as heterogeneous seeds. Meanwhile, the vertical structure homogenizes the electronic and ionic flux, allowing Li\(^+\) ions to move across the electrode surface easily. Therefore, uniform and lateral growth of the lithium metal deposits is

Figure 3. Cycling performance of half-cells with Au-VG-GP-2, Au-VG-GP-5, and Au-VG-GP-15 at a) 3 mA cm\(^{-2}\) with the capacity of 1 mAh cm\(^{-2}\) and b) 1 mA cm\(^{-2}\) with the capacity of 3 mAh cm\(^{-2}\). c) Voltage–capacity curve of Au-VG-GP-5 at 1 mA cm\(^{-2}\) with the capacity of 3 mAh cm\(^{-2}\). d) EIS of Au-VG-GP-2, Au-VG-GP-5, and Au-VG-GP-15 after five cycles at 3 mA cm\(^{-2}\) with the capacity of 1 mAh cm\(^{-2}\). e) The voltage–time curve of symmetrical cells with composite Li/Au-VG-GP-2, Li/Au-VG-GP-5, and Li/Au-VG-GP-15 electrodes, and f) the enlarged voltage profiles.

Adv. Energy Sustainability Res. 2021, 2100044 2100044 (4 of 9) © 2021 The Authors. Advanced Energy and Sustainability Research published by Wiley-VCH GmbH
realized until they bump into one another, after which the deposits are restricted to growing vertically. The resulting highly ordered columnar structure with low tortuosity can further regulate the following Li plating/stripping processes during cycling and maintain the bulk Li with a continuous electron conducting pathway.

Full cells were assembled with LFP cathodes and VG-GP or Au-VG-GP-5 plated with 5 mAh cm$^{-2}$ as the anodes. Figure 5a shows the voltage profiles of the full cell with Li/Au-VG-GP-5 at 1 C, which displays a lower polarization compared to the cell with Li/VG-GP after cycling (Figure 5b,c). The full cell with Li/Au-VG-GP-5 also delivers a much higher specific capacity (Figure 5d). The cycling performance of both full cells at 1 C is shown in Figure 5e. The Au-VG-GP-5 electrode exhibits a higher specific capacity of 120 mAh g$^{-1}$ with a higher CE of 99.1% after 100 cycles. The full cells with a low N/P of 3 (LFP loading of 6 mg cm$^{-2}$ on the cathode and 3 mAh cm$^{-2}$ on the anode) were also tested (Figure S12, Supporting Information). The cells with Au-VG-GP-5 electrodes still show better cycling performance than those with VG-GP electrodes, indicating excellent long-term cycling stability.

The sulfur cathode in Li-S batteries also relies on a dissolution–precipitation process, and the nonuniform precipitation of insoluble Li$_2$S from the dissolved LiPSs leads to a high energy barrier for the charging process and blocks the pores in the electrode. Therefore, we further explored the effects of such a vertical structure with homogeneous Au seeds on the regulation of Li$_2$S deposition. The deposition of Li$_2$S was investigated by potentiostatic discharge of Li$_2$S$_8$ in tetraglyme solution. The nucleation capacity of Li$_2$S can be calculated by the integral area of the plotted curve through Faraday's law. It is shown that the capacity of precipitated Li$_2$S on Au-VG-GP-5 (121.7 mAh g$^{-1}$) is higher than those on VG-GP (92.25 mAh g$^{-1}$), Au-VG-GP-2 (100.65 mAh g$^{-1}$), and Au-VG-GP-15 (98.26 mAh g$^{-1}$) (Figure 6a–c and S13, Supporting Information). The deposited morphology of Li$_2$S was then characterized by SEM (Figure 6d–f). The thickness of Li$_2$S nanosheets formed on Au-VG-GP-2 varies from 30 to 70 nm. In contrast, the Li$_2$S formed on Au-VG-GP-5 is more uniform vertical nanosheet with thickness of around 60 nm. The Au-VG-GP-15 electrode shows lower deposition capacity with thinner nanosheets, possibly due to the decrease of nucleation sites with the large Au NPs.

The full cells were also assembled with the Li metal as the anodes and the VG-GP or Au-VG-GP-5 loaded with sulfur as the cathodes (denoted S/VG-GP and S/Au-VG-GP-5). Sulfur powder was first dissolved in carbon disulfide and then dipped in the aforementioned samples to allow infiltration of sulfur into the vertical structure. As shown in Figure 6g, S/Au-VG-GP-5 exhibits much better rate performance than S/VG-GP, and when the current density shifts back to 0.5 C, the discharge capacity recovers to 840 mAh g$^{-1}$, indicating the high reversibility and fast reaction kinetics with the introduction of Au NPs. Figure 6h compares the charge/discharge curves of the batteries with S/VG-GP and S/Au-VG-GP-5 electrodes at the first cycle, and the battery with S/Au-VG-GP-5 exhibits smaller polarization (0.140 V), further suggesting the enhanced redox reactions. Moreover, Au-VG-GP-5 shows a higher conductivity of 1.463 S cm$^{-1}$ than VG-GP (1.299 S cm$^{-1}$). Considering the conversion reaction from solid S$_8$ to liquid LiPS is an electroconductivity-dominated process, Au-VG-GP-5 as sulfur host with higher conductivity enables a fast kinetics for conversion reactions.
as confirmed by the higher capacity of S₈-Li₂S₄. For Li–S cells, the total theoretical capacity ($T_{DCAP}$)/high-plateau discharge capacity ($HP_{dcp}$) can reflect the redox accessibility or kinetics of converting LiPS to Li₂S₂. The calculated $T_{DCAP}/HP_{dcp}$ ratios of VG-GP (3.38) and Au-VG-GP-5 (3.37) are almost identical, indicating a similar conversion rate from liquid LiPS to solid Li₂S₂/Li₂S. However, with higher capacity of S₈-Li₂S₄, Au-VG-GP-5 still shows an increased capacity of precipitated Li₂S, which is consistent with the potentiostatic discharge test. In addition, as the GP substrate has good flexibility (Figure S14, Supporting Information) and the vertical structure can remain stable during repetitive bending, we prepared a rectangle-shaped flexible Li–S cell with Li/Au-VG-GP-5||S/Au-VG-GP-5 to verify the stability of the Au-VG-GP-5 in flexible devices. The flexible Li–S battery can lighten up a light emitting diode (LED) in various folding angles from 0° to 45°, 180°, and then back to 0° (Figure 6i), and the EIS results show no apparent changes under different folding angles, suggesting the potential for practical use (Figure S15 and Table S2, Supporting Information).

3. Conclusion

In summary, we prepared an Au NP–modified VG structure for the stable deposition of LMA and showed the synergistic effect between the low-tortuosity VG and the Au NPs as the hetero-seeds. The vertical structure decreases the ion diffusion resistance and avoids the formation of a concentration gradient, ensuring uniform ion distribution in the 3D host. At the same time, the uniformly distributed lithiophilic Au NPs decrease the nucleation barrier and guide fast and uniform Li deposition. These two factors effectively enhance the stability of the LMA, and thus, the half-cell with Au-VG-GP-5 shows a stable cycle performance with a high CE of 93% for 90 cycles at 3 mA cm⁻² of 1 mAh cm⁻². The full batteries with LFP as cathodes also show good cycling stability. Moreover, such a structure can also guide the controllable Li₂S deposition in the cathode of Li–S batteries, suggesting its potential uses in energy storage devices based on the dissolution–precipitation mechanism.

Figure 5. Voltage profiles of a) Li/Au-VG-GP-5||LFP and b) Li/VG-GP||LFP full cells at 1 C. Comparison of VG-GP and Au-VG-GP-5 from c) plateau potential difference and d) specific capacity. e) Cycling performance of Li/VG-GP||LFP and Li/Au-VG-GP-5||LFP full cells at 1 C.
4. Experimental Section

Preparation of VG-GP and Au-VG-GP: The VG was grown on the GP by a PECVD method in Yick Xin Technology Development Ltd. Co (Shenzhen, China). GP as a substrate was cleaned in ethanol through sonication for 5 min and then dried in air. Methane was used as the carbon source. The radio frequency power, total gas flow rate, and gas pressure were set at 900 W, 10 cm$^3$ min$^{-1}$, and 12 Pa, respectively. The deposition continued for 20 min. The obtained VG was 25 μm in height and was cut into a square of 1 cm$^2$. Then, the samples were modified by Au NPs through ion sputtering. The vacuum degree, sputtering current, and correction factors were set at 10 Pa, 50 mA, and 1.4, respectively. The samples sputtered for 2, 5, and 15 s were denoted as “Au-VG-GP-2,” “Au-VG-GP-5,” and “Au-VG-GP-15,” respectively.

Material Characterizations: SEM and EDS measurements were conducted on a field emission scanning electron microscope (SU 8010) at 5 kV. The Raman spectra were obtained by a HORIBA Jobin Yvon LabRAM HR800 with a 532 nm laser. XPS spectrums were used on ESCALAB 250Xi with a DSA30 (Kruss) instrument to measure the components of samples.

Electrochemical Measurements: The CR2032 coin cells were assembled in an Ar-filled glove box with oxygen and water content lower than 0.1 ppm. For the half-cell assembly, VG-GP or Au-VG-GP was used as the working electrode, Li foil was used as counter electrode, and Celgard 2500 was used as the separator. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (1 M) in 1,3-dioxolane (DOL):1,2-dimethoxyethane (DME) (1:1 vol%) with 1 wt% lithium nitrate (LiNO$_3$) was used as the electrolyte, and 60 μL electrolyte was added in each cell. All batteries were tested on a LAND multichannel battery testing system.

The CE was tested by depositing a fixed amount of Li (1 and 3 mAh cm$^{-2}$) at different current densities (1 and 3 mA cm$^{-2}$) and then stripped away to 1.0 V. EIS measurement was tested by a BioLogic.

Figure 6. Potentiostatic discharge profiles of cells with a) Au-VG-GP-2, b) Au-VG-GP-5, and c) Au-VG-GP-15. The light and dark colors indicate the reduction of Li$_2$S$_6$/Li$_2$S$_8$ and the precipitation of Li$_2$S, respectively. d–f) Top-view SEM images at precipitation termination of cells with Au-VG-GP-2, Au-VG-GP-5, and Au-VG-GP-15. g) Rate capabilities at various current densities and h) galvanostatic charge/discharge profiles of the batteries with S/VG-GP and S/Au-VG-GP-5 electrodes. i) The photograph of a flexible Li–S cell lighting up an LED under different folding angles.
VMP3 electrochemical workstation with a frequency range from 100 kHz to 10 mHz and an amplitude of 5 mV. For the symmetrical cell test, 3 mAh cm$^{-2}$ Li was predeposited onto Au-VG-GP and assembled as symmetrical cells. The cells were then cycled at 1 mA cm$^{-2}$ with a capacity of 1 mAh cm$^{-2}$.

To observe the morphology of the deposited Li, the half-cells were assembled and tested under the current density of 1 and 3 mA cm$^{-2}$, with the capacity of 0.1, 1, and 3 mA h cm$^{-2}$. After deposition, the batteries were disassembled in the Ar-filled glove box and the obtained electrode was washed with DME to remove the residual electrolyte and salt.

For Li–LFP cell assembly, LFP was used as the cathode material with the mass loading of ≈1 and 6 mg cm$^{-2}$. VG-GP or Au-VG-GP host with predeposited a certain amount of Li (3 or 5 mAh cm$^{-2}$) was used as the anode. The negative/positive capacity ratio was 36 and 3, respectively. The electrolyte was the same as that in the half-cells and the added amount to the cell was 50 μL. The cycle performance of full cells was tested by galvanostatically cycling between 3.0 and 3.8 V at 1 C.

For Li–S cell assembly, VG-GP and Au-VG-GP-S loaded with sulfur were used as the cathodes (denoted S/VG-GP and S/Au-VG-GP-S) and Li metal was used as anodes. Sulfur powder was first dissolved in carbon disulfide and then dipped on the aforementioned samples to allow infiltration of sulfur into the vertical structure. The electrolyte was the same as that in the half-cells and the added amount to the cell was 50 μL. The cells were galvanostatically tested between 1.7 and 2.8 V.

To test for the nucleation of Li$_2$S, nanosulfur and Li$_2$S powder were combined at a molar ratio of 7:1 in tetraglyme and stirred vigorously for 24 h to prepare the Li$_2$S$_8$ solution. 10 μL Li$_2$S$_8$ (0.5 mol L$^{-1}$) catholyte was dropped on the cathode side and 15 μL electrolyte was dropped on the anode side. During electrochemical measurements, the batteries were first galvanostatically discharged to 2.08 V at a current of 0.113 mA, and then discharged galvanostatically at the voltage of 2.05 V until the current was less than 0.01 mA, which led to the nucleation of Li$_2$S. The obtained samples were dropped on the cathode side and 15 μL electrolyte was dropped on the anode side. The batteries were discharged galvanostatically at the voltage of 2.05 V until the current was less than 0.01 mA, which led to the nucleation of Li$_2$S. The nucleation capacity of Li$_2$S$_8$ can be calculated by the integral area of the plotted curve through Faraday’s law.

Assembling of the Flexible Li–S Cell: The flexible Li–S cell with the encapsulation of PDMS was assembled in an Ar-filled glove box. Sulfur powder was first dissolved in carbon disulfide and then dipped on the aforementioned samples to allow infiltration of sulfur into the vertical structure. Molten Li was absorbed into Au-VG-GP-5 and the obtained samples were used as anodes. Celgard 2500 was used as the separator and the electrolyte was the same as that in the half-cells.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
Z.H. and Z.H. contributed equally to this work. This work was supported by the National Natural Science Foundation of China (Nos. 51972190, 52072205), the National Key Research and Development Program of China (2019YFA07050700), Guangdong Natural Science Funds for Distinguished Young Scholars (2017B030306006), Guangdong Special Support Program (2017TQ04C664), the Local Innovative and Research Teams Project of Guangdong Pearl River Talents Program (2017T101111), and the Shenzhen Basic Research Project (Grant Nos. JCYJ2018050152037520). The authors would like to thank testing technology center of materials and devices, Tsinghua Shenzhen International Graduate School for the SEM, EDS, Raman, and XPS analysis.

Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords
dual-functional hosts, gold nanoparticles, lithium–sulfur batteries, nucleation control, vertical graphene

Received: February 6, 2021
Revised: March 29, 2021
Published online:

[1] D. Lin, Y. Liu, Y. Cui, Nat. Nanotechnol. 2017, 12, 194.
[2] J. Liu, Z. Bao, Y. Cui, E. J. Dufek, J. B. Goodenough, P. Khalifah, Q. Li, B. Y. Liaw, P. Liu, A. Manthiram, Y. S. Meng, Y. R. Subramanian, M. F. Toney, V. V. Viswanathan, M. S. Whittingham, J. Xiao, W. Xu, J. Yang, X.-Q. Yang, J.-G. Zhang, Nat. Energy 2019, 4, 180.
[3] X.-B. Cheng, R. Zhang, C.-Z. Zhao, Q. Zhang, Chem. Rev. 2017, 117, 10403.
[4] W. Xu, J. Wang, F. Ding, X. Chen, E. Nasybutin, Y. Zhang, J.-G. Zhang, Energy Environ. Sci. 2014, 7, 513.
[5] P. Albertus, S. Babinec, S. Litzelman, A. Newman, Nat. Energy 2018, 3, 16.
[6] Y.-Y. Yao, X.-Q. Zhang, B.-Q. Li, C. Yan, P.-Y. Chen, J.-Q. Huang, Q. Zhang, InfoMat 2020, 2, 379.
[7] B. J. Goodenough, Y. Kim, Chem. Mater. 2010, 22, 587.
[8] M. D. Tikekar, S. Choudhury, Z. T., L. A. Archer, Nat. Energy 2016, 1, 16114.
[9] C.-P. Yang, Y.-X. Yin, S.-F. Zhang, N.-W. Li, Y.-G. Guo, Nat. Commun. 2015, 6, 8058.
[10] Q. Li, S. Zhu, Y. Lu, Adv. Funct. Mater. 2017, 27, 1606422.
[11] H. Zhao, D. Lei, Y.-B. He, Y. Yuan, Q. Yun, B. Ni, W. Lv, B. Li, Q.-H. Yang, F. Kang, J. Lu, Adv. Energy Mater. 2018, 8, 1800266.
[12] S. Jin, Y. Jiang, H. Ji, Y. Yu, Adv. Mater. 2018, 30, 1802014.
[13] L. Liu, Y.-X. Yin, J.-Y. Li, S.-H. Wang, Y.-G. Guo, L.-J. Wan, Adv. Mater. 2018, 30, 1706216.
[14] C. Yang, Y. Yao, S. He, H. Xie, E. Hitz, L. Hu, Adv. Mater. 2017, 29, 1702714.
[15] C. Zhang, R. Lyu, W. Lv, H. Li, W. Jiang, J. Li, S. Gu, G. Zhou, Z. Huang, Y. Zhang, J. Wu, Q.-H. Yang, F. Kang, Adv. Mater. 2019, 31, 1904991.
[16] X. Chen, X.-R. Chen, T.-Z. Hou, B.-Q. Li, X.-B. Cheng, R. Zhang, Q. Zhang, Sci. Adv. 2019, 5, eaa7728.
[17] M. Wan, S. Kang, L. Wang, H.-W. Lee, G. W. Zheng, Y. Cui, Y. Sun, Nat. Commun. 2020, 11, 829.
[18] L. Fu, M. Wan, B. Zhang, Y. Yuan, Y. Jin, W. Wang, X. Wang, Y. Li, L. Wang, J. Jiang, J. Lu, Y. Sun, Adv. Mater. 2020, 32, 2070218.
[19] Y. Liu, D. Lin, Z. Liang, J. Zhao, K. Yan, Y. Cui, Nat. Commun. 2016, 7, 10992.
[20] X. Ji, D.-Y. Liu, D. G. Prendiville, Y. Zhang, X. Liu, G. D. Stucky, Nano Today 2012, 7, 10.
[21] H. Chen, A. Pei, J. Wan, D. Lin, R. Villa, H. Wang, D. Mackanick, H.-G. Steinhäuser, W. Huang, Y. Li, A. Yang, J. Xie, Y. Wu, H. Wang, Y. Cui, Joule 2020, 4, 938.
[22] S. H. Wang, Y. X. Yin, T. T. Zuo, W. Dong, J. Y. Li, J. L. Shi, C. H. Zhang, N. W. Li, C. J. Li, Y. G. Guo, Adv. Mater. 2017, 29, 1703729.
[23] C. Zhang, W. Lv, G. Zhou, Z. Huang, Y. Zhang, R. Lyu, H. Wu, Q. Yun, F. Kang, Q.-H. Yang, Adv. Energy Mater. 2018, 8, 1701404.
[24] X. Li, J. Wang, *InfoMat* **2020**, *2*, 3.
[25] Q. Song, H. Yan, K. Liu, K. Xie, W. Li, W. Gai, G. Chen, H. Li, C. Shen, Q. Fu, S. Zhang, L. Zhang, B. Wei, *Adv. Energy Mater.* **2018**, *8*, 1800564.
[26] S. Huang, H. Yang, J. Hu, Y. Liu, K. Wang, H. Peng, H. Zhang, L.-Z. Fan, *Small* **2019**, *15*, 1904216.
[27] F. Ren, Z. Lu, H. Zhang, L. Huai, X. Chen, S. Wu, Z. Peng, D. Wang, J. Ye, *Adv. Funct. Mater.* **2018**, *28*, 1805638.
[28] Y. J. Zhang, S. F. Liu, X. L. Wang, Y. Zhong, X. H. Xia, J. B. Wu, J. P. Tu, *J. Power Sources* **2018**, 374, 205.
[29] Z. Liang, D. Lin, J. Zhao, Z. Lu, Y. Liu, C. Liu, Y. Lu, H. Wang, K. Yan, X. Tao, Y. Cui, *Proc. Natl. Acad. Sci. USA* **2016**, *113*, 2862.
[30] K. Yan, Z. Lu, H.-W. Lee, F. Xiong, P.-C. Hsu, Y. Li, J. Zhao, S. Chu, Y. Cui, *Nat. Energy* **2016**, *1*, 16010.
[31] R. Zhang, X.-R. Chen, X. Chen, X.-B. Cheng, X.-Q. Zhang, C. Yan, Q. Zhang, *Angew. Chem., Int. Ed.* **2017**, *56*, 7764.
[32] J. Xiang, L. Yuan, Y. Shen, Z. Cheng, K. Yuan, Z. Guo, Y. Zhang, X. Chen, Y. Huang, *Adv. Energy Mater.* **2018**, *8*, 1802352.
[33] B.-Q. Li, L. Kong, C.-X. Zhao, Q. Jin, X. Chen, H.-J. Peng, J.-L. Qin, J.-X. Chen, H. Yuan, Q. Zhang, J.-Q. Huang, *InfoMat* **2019**, *1*, 533.
[34] F. Tuinstra, *J. Chem. Phys.* **1970**, *53*, 1126.
[35] R. J. Nemanich, S. A. Solin, *Phys. Rev. B: Condens. Matter Mater. Phys.* **1979**, *20*, 392.
[36] A. Ferrari, J. Robertson, *Phys. Rev. B* **2000**, *61*, 14095.
[37] Z. Huang, D. Kong, Y. Zhang, Y. Deng, G. Zhou, C. Zhang, F. Kang, W. Lv, Q.-H. Yang, *Research* **2020**, *2020*, 7163948.
[38] Q. Lin, J. Zhang, D. Kong, T. Cao, S.-W. Zhang, X. Chen, Y. Tao, W. Lv, F. Kang, Q.-H. Yang, *Adv. Energy Mater.* **2019**, *9*, 1803078.
[39] R. M. Kasse, N. R. Geise, J. S. Ko, J. Nelson Weker, H.-G. Steinrück, M. F. Toney, *J. Mater. Chem. A* **2020**, *8*, 16960.
[40] W. Zhang, Q. Wu, J. Huang, L. Fan, Z. Shen, Y. He, Q. Feng, G. Zhu, Y. Lu, *Adv. Mater.* **2020**, *32*, 2001740.
[41] L. Borchardt, M. Oschatz, S. Kaskel, *Chem. Eur. J.* **2016**, *22*, 7324.
[42] F. Y. Fan, Y.-M. Chiang, *J. Electrochem. Soc.* **2017**, *164*, A917.
[43] M. J. Klein, K. Goossens, C. W. Bielawski, A. Manthiram, *J. Electrochem. Soc.* **2016**, *163*, A2109.
[44] H. Wu, L. Wang, J. Bi, Y. Li, X. Pang, Z. Li, Q. Meng, H. Liu, L. Wang, *ACS Appl. Mater. Interfaces* **2020**, *12*, 15228.