Gas Sensing



3D MoS₂ Aerogel for Ultrasensitive NO₂ Detection and Its Tunable Sensing Behavior

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A high-performance NO₂ sensor based on the 3D MoS₂ aerogel is presented. Compared to single- or few-layer MoS₂, 3D assemblies of 2D MoS₂ provide more surface area per footprint with a simple and scalable synthesis. Integration of the 3D MoS₂ aerogel on a low-power microheater platform is demonstrated, and the sensing behavior of the 3D MoS₂ aerogel is investigated. A two-step sulfurization treatment is developed to obtain a high-quality MoS₂ aerogel with strong sensing performance. The aerogel exhibits low detection limit (50 ppb) toward NO₂ at room temperature, while after the two-step sulfurization treatment, it also exhibits fast response and recovery at low heater temperature of 200 °C, with no decrease in sensitivity. The observed p-type sensing behavior of MoS₂ aerogel is investigated and identified as being controlled by the defect state (as probed by the S:Mo ratio). It is demonstrated that annealing in a hydrogen environment changes the defect state of the MoS₂ aerogel by creating more sulfur vacancies; concomitantly, a transition from p-type sensing behavior to n-type sensing is observed.

1. Introduction

2D layered materials with unique electronic and mechanical properties hold great potential for many applications such as solar cells, energy storage, electronics, and sensing.^[1-10] In gas sensing, one of the most favorable properties offered by 2D materials is their high surface area to volume ratio.^[9,10] For example, graphene, a 2D carbon material, possesses large specific surface area and high conductivity in the monolayer state and can provide ultimate sensitivity down to the single

molecule level.^[9,10] Recently, 2D MoS₂, one of the emerging layered transition metal dichalcogenides, has been explored as an active channel material in field-effect transistors (FETs) with high performance comparable to graphene-based FETs.^[10] Unlike graphene, which lacks a bandgap, MoS₂ monolayer has a bandgap of 1.9 eV and can be directly used for many applications, such as sensors and transistors.^[10–12]

Despite the excellent semiconducting properties of atomically thin layered MoS₂, few efforts have been made to develop MoS₂-based gas sensors, and almost all of them are FET-based sensors.^[12–22] These sensors mainly use single- or few-layer MoS₂ and have revealed to be extremely sensitive to NO_x and NH₃.^[12–19] However, single- or few-layered MoS₂ sensors are difficult to fabricate, thereby substantially limiting the throughput of sensor produc-

tion.^[20,21] A scalable, low-cost, high-yield production of sensing materials that is compatible with sensor fabrication processes is essential. In addition, most of previous studies of MoS_2 -based FET sensors have reported slow response rates and little to no recovery, greatly hindering the practical applications.^[12–21] Furthermore, the mechanism for the sensing behavior of MoS_2 is not well understood, impeding attempts at optimization. Since MoS_2 is typically an n-type semiconductor, interaction with NO_2 gas molecules, which act as electron acceptors, should decrease the sensor resistance.^[12,15–17] However, there have also

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Figure 1. Schematic of the synthesis process for the MoS₂ aerogel.

been reports of p-type sensing behavior of MoS_2 FET-based sensors.^[13,18,20]

In this communication, we integrate a 3D MoS₂ aerogel on a low-power microheater platform for highly sensitive NO₂ detection. Compared to single- or few-layer MoS₂, 3D assemblies of 2D MoS₂ provide more surface area per footprint with a simple and scalable synthesis. A two-step sulfur treatment process is developed to obtain a high-quality MoS₂ aerogel with strong sensing performance. By integrating the 3D MoS₂ aerogel on a low-power microheater platform, the sensing behavior of the MoS₂ aerogel before and after a two-step treatment at different temperatures is investigated and compared. The aerogel shows high sensitivity toward NO2 at room temperature, while after a two-step sulfurization treatment, it also exhibits fast response and recovery at low heater temperature, with no decrease in sensitivity. The observed p-type sensing behavior of MoS₂ aerogel is investigated and identified as being controlled by the defect state (as probed by the S:Mo ratio). We demonstrate that annealing in a hydrogen environment changes the defect state of the MoS₂ aerogel by creating more sulfur vacancies; concomitantly, a transition from p-type sensing behavior to n-type sensing is observed. To the best of our knowledge, this is the first study directed at identifying the cause of the p- or n-type sensing mechanism as well as controlling the sensing behavior of the MoS₂.

2. Results and Discussion

The 3D MoS₂ aerogel with ultralow density is prepared by thermal decomposition of ammonium thiomolybdate (ATM), according to a previous method with modifications.^[23] Figure 1 shows a schematic of the MoS₂ aerogel synthesis. Briefly, the aqueous solution of the ATM is prepared, freeze dried, and annealed at 400 °C under 2% H₂/Ar to create a 3D MoS₂ aerogel. A two-step sulfurization process is developed to obtain the high-performance MoS₂ aerogel. The aerogel sample is first treated at 500 °C for 1 h in a 10% H₂/Ar environment to reduce any possible MoO₃ into MoO_{3-x}.^[23-27] The sample is then annealed at 750 °C for 1 h in a sulfur-rich environment to allow sulfur vapor reacts with the entire aerogel.

Figure 2 shows the X-ray diffraction (XRD) patterns of the MoS_2 aerogel before and after the two-step treatment. The dominant peaks in the XRD patterns show the characteristic peaks for MoS_2 (JCPDS 37-1492). The peaks at 14.4°, 32.7°, 33.5°, and 58.3° correspond to the (002), (101), (103), and (110) planes of 2H-MoS₂, respectively. In the sample before a two-step treatment, a weak peak at 25.8° corresponding to the (210) plane of MoO_3 (JCPDS 21-0569) is observed, which suggests the presence of a small amount of MoO_3 in the aerogel.^[25,26] After the two-step treatment, the peak at 25.8° is essentially gone, demonstrating that the MoO_3 content is significantly reduced by the treatment. After the two-step treatment, the peak intensities are higher, indicating better crystallinity. This spectrum also indicates the dominant presence of well-stacked, highly crystalline 2H-MoS₂ in the MoS_2 aerogel.^[23]

X-ray photoelectron spectroscopy (XPS) is carried out to determine the surface electronic state and composition in the aerogels. Figure 3a,b shows the high-resolution scans of



Figure 2. XRD patterns of the MoS_2 aerogels before and after the twostep sulfurization treatment.







Figure 3. High-resolution XPS spectra of the MoS_2 aerogels before (top) and after (bottom) the two-step sulfurization treatment: a) Mo 3d and S 2s; b) O 1s regions.

molybdenum 3d and oxygen 1s peaks, respectively. As seen in Figure 3a, before a two-step treatment, the Mo 3d spectrum clearly shows two Mo oxidation states where the peaks around 229.2 and 232.4 eV are related to the Mo $3d_{5/2}$ and Mo $3d_{3/2}$ of Mo⁴⁺ (typical of the Mo-S bond), and the peaks around 232.7 and 236.0 eV are related to the Mo $3d_{5/2}$ and Mo $3d_{3/2}$ of Mo⁶⁺ (typical of the Mo–O bond).^[24] After the two-step treatment, the Mo 3d spectrum only shows the characteristic peaks of Mo⁴⁺, and no obvious peak for the Mo-O bonding is observed. This is consistent with the characteristic peaks in the O 1s region, as shown in Figure 3b. After the two-step treatment, the O 1s region only shows a weak peak at 533.5 eV that is commonly observed in ex situ analyzed samples, while a relatively strong peak at 531.6 eV (which can be assigned to the Mo-O bond) is observed before the two-step treatment.^[24] Furthermore, after the treatment, the atomic ratio of S:Mo increases from 2.4 to 2.7. The extra S in the aerogel may offer more active defect sites as well as unusual electronic properties.

Figure 4 shows the morphology of the MoS₂ aerogel. Figure 4a,b presents representative field-emission scanning electron microscopy (FESEM) images of the MoS₂ aerogel before the two-step treatment with different magnifications, showing that the MoS₂ aerogels are composed of sheet-like structures. The width of the MoS₂ sheets is around 1 μ m, and the thickness is around 20–50 nm. Figure 4c,d shows the FESEM image of the MoS₂ aerogel after the two-step treatment, exhibiting a similar sheet-like morphology as before the treatment. As shown in the high-magnification FESEM image in Figure 4d, the sheet-like structures become more porous compared to before the sulfur treatment, which may be due to the etching effect of hydrogen on MoS₂ at high temperatures.^[28,29]

Further insight regarding structural features of the aerogel is revealed through transmission electron microscopy (TEM). Figure 4e shows a low-resolution TEM image of the MoS₂ aerogel after the two-step treatment, exhibiting the sheet-like morphology with transparent features, indicating the thin nature of the sheet. The sheets are $\approx 1 \ \mu m$ in width, which is consistent with FESEM observation. From the atomic resolution TEM image in Figure 4f, lattice spacing of 0.63 nm is found and can be indexed to the (002) plane of 2H-MoS₂.

The sensing performance of as-synthesized ${\sf MoS}_2$ aerogel is evaluated by integrating it onto a low-power microheater

platform. The MoS₂ aerogel is placed in a solution of deionized water and isopropyl alcohol and sonicated into a suspension. A 0.2 μ L drop of 0.5 mg mL⁻¹ solution is placed on the microheater chip while the microheater is powered to 2 mW (≈100 °C) for the localized deposition. Figure 5a illustrates a cross-sectional schematic of the microheater sensor, which consists of a polycrystalline silicon (polysilicon) microheater embedded in a low-stress silicon nitride (LSN) membrane with the MoS₂ aerogel deposited on top. The LSN membrane thermally isolates the heated sensing area and minimizes the heat loss through conduction to the silicon substrate. Full fabrication details and heater characterization can be found elsewhere.^[24,29,30] By using this design, the microheater sensor requires only ≈4.4 mW to reach 200 °C. Figure 5b exhibits a real color image of the microheater showing the polysilicon heater (green), Pt/Ti sensing leads (yellow), and the silicon nitride membrane (dark red). Figure S1 (Supporting Information) shows the optical image of a microheater chip with MoS₂ aerogel deposited, in which the two sensing electrodes are connected by the MoS₂ aerogel.

After aerogel deposition, the microheater sensor is placed into a gas sensing setup for testing. Figure S2 (Supporting Information) shows a typical IV curve of the MoS₂ aerogelbased sensor. The near linear IV curve indicates that a good contact is formed between the aerogel and Pt/Ti electrodes. Figure 6 shows the dynamic resistance change of the MoS₂ aerogel (before two-step treatment) sensor at various temperatures toward different NO2 concentrations, from 50 ppb to 5 ppm with a bias voltage of 0.5 V. At room temperature (25 $^{\circ}$ C), the sensor exhibits response to all NO2 concentrations (Figure 6a). When the sensor is exposed to NO_2 , the sensor resistance decreases. Since nitrogen dioxide is a known electron acceptor due to the unpaired electron on the nitrogen atom, the decrease in the sensor resistance is consistent with a p-type MoS₂ sensing behavior. During subsequent exposure to clean air, the sensor resistance slowly recovers as NO2 molecules desorb from the surface. This behavior is consistent with the adsorption and charge transfer mechanism of previously reported single- or few-layer MoS₂,^[12-22] graphene,^[31,32] and carbon nanotube gas sensors.^[33,34] The slow response and recovery might be due to the strong bonding between NO_2 and $MoS_2^{[12,35]}$ or the stochastic lag times for an analyte to find an empty site on a mostly







Figure 4. Morphology of the MoS_2 aerogel: a,b) FESEM images of the MoS_2 aerogel before the two-step sulfurization treatment with different magnifications. c,d) FESEM images of the MoS_2 aerogel after the two-step sulfurization treatment with different magnifications. e) Low-resolution TEM images of the MoS_2 aerogel after the two-step sulfurization treatment. f) High-resolution TEM image showing lattice space of 0.63 nm.

saturated surface.^[22] However, understanding the complete mechanism is a complex subject in gas sensing studies because of the combined effects of physisorption, chemisorption, the



Figure 5. Microheater structure: a) Cross-sectional schematic of the microheater sensor. b) Optical image of one microheater showing the Pt/Ti sensing electrodes above the polysilicon heater.

role of defect sites, and the transduction mechanism. The full recovery time of the sensor at room temperature is observed to take several hours. Figure 6b shows the dynamic resistance

change of the sensor at 200 °C. It exhibits a faster response and recovery time compared to room temperature, but it is still slow.

Figure 7 shows the NO₂ sensing performance of the MoS₂ aerogel-based sensor after the two-step sulfurization treatment. At room temperature (Figure 7a), the sensor exhibits response to all NO₂ concentrations, which is similar to the MoS₂ aerogel before the two-step treatment. Figure 7b shows the response of the sensor to 0.5 ppm NO₂ at various temperatures. With the increasing temperature, the sensor shows improved response and recovery rates. At 200 °C with a power consumption of 3.5 mW, the sensor

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Figure 6. Real-time resistance change of the MoS_2 aerogel (before the two-step sulfurization treatment)-based sensor to different NO_2 concentrations from 50 ppb to 5 ppm at a) 25 °C and b) 200 °C.

shows a fast response rate and complete recovery (within 40 s) with a smaller response magnitude. The observed behavior can be understood as follows. At low temperatures, the adsorption of NO₂ continues during the exposure time, while desorption is negligible due to the strong bonding between NO₂ and MoS₂. When the sensor operating temperature is increased, desorption of NO₂ is enhanced. A steady state between adsorption and desorption is reached at a lower concentration of adsorbed NO₂, leading to a smaller response magnitude but a faster response rate at 200 °C.

Figure 7c shows the sensor response at 200 $^{\circ}$ C to various NO₂ concentrations, ranging from 50 ppb to 1 ppm. The sensor exhibits fast and complete response and recovery to all NO₂

concentrations. The average response and recovery times are 33 and 107 s, respectively. Figure 7d shows the sensor response versus NO₂ concentrations with an increased response magnitude with increasing NO₂ concentration. The lack of plateau suggests that the sensor can detect higher NO₂ concentrations than delivered. At low concentrations, the sensor shows a linear response, suggesting the sensor is suitable for detecting low NO₂ concentrations. The sensor shows a clear response to 50 ppb NO₂ with a signal-to-noise ratio of 5.4. Due to the limitations of the gas delivery system, 50 ppb is the lowest concentration that can be reliably delivered to the sensor. The calculated detection limit is around 28 ppb by using a signal-to-noise threshold value of 3, which is a lower detection limit than most



Figure 7. Sensing performance of the MoS_2 aerogel (after the two-step sulfurization)-based sensor: a) dynamical resistance change of the sensor at room temperature to different NO_2 concentration from 50 ppb to 5 ppm; b) sensor response to 0.5 ppm NO_2 at various temperatures, showing the improvement in response and recovery times; c) dynamic resistance change of the sensor with microheater temperature at 200 °C; d) normalized sensor response at 200 °C versus NO_2 concentration.





of the reported MoS_2 -based sensors. This is a very useful detection limit given that the U.S. Environmental Protection Agency has placed a 53 ppb environmental limit for NO_2 .^[24]

NO₂ is an oxidizing gas that acts as an electron acceptor. Upon NO₂ adsorption, the MoS₂ aerogel-based sensor resistance decreases, exhibiting a p-type sensing behavior. Both n-type and p-type MoS₂ sensors have been reported in the literature,^[12–20] but the underlying reason for the differences in performance is not yet clear. Possible reasons for the different doping behavior of MoS₂ include intrinsic defects or vacancies, and extrinsic defects, which may be charged impurities at the interface between the MoS₂ and substrate. It has been reported that the electronic behavior of ultrathin MoS₂ can be modulated by the dangling bonds at the semiconductor/substrate interface, especially when the thickness of MoS₂ is at the level of single or few layers.^[16,36] Typically, oxygen dangling bonds from the SiO₂ surface can result in a p-type MoS₂ system.^[16,36] Due to the bulk form of the MoS2 aerogels and Si3N4 membrane substrate used in this work, the defects from substrate cannot explain the p-type behavior. Another possible form of defect in the MoS_2 system is the presence of MoO_x . A recent study has shown that a MoO_x layer between a metal contact and MoS_2 can yield a p-type MoS₂ transistor characteristic.^[37–39] However, the two-step sulfurization treatment used on the MoS₂ aerogel eliminates the MoO_{x} as shown in the XPS spectra in Figure 3; thus, it is unlikely that this is the reason for the p-type sensing behavior.

Intrinsic defects in the MoS₂ aerogel are the most likely reason for the observed p-type sensing behavior. Here, we demonstrate control over these defects with hydrogen annealing treatment and the subsequent effect on sensing behavior. Hinkle and co-workers reported that surface defects as well as defect chemistry-related variations in the local stoichiometry of the MoS₂ may be correlated with the n- and p-type behaviors of the material.^[40] As determined by XPS, the stoichiometry of the MoS₂ aerogel after the two-step treatment is S:Mo ratio of 2.7:1, which indicates the presence of Mo vacancies or S-rich areas. In order to alter the S:Mo ratio, H₂ annealing is explored as a method for defect engineering. The process is conducted in a quartz furnace tube set to high temperature with 10% hydrogen in argon gas. High temperatures are necessary to create S vacancies, but annealing temperatures higher than 600 °C lead to severe material decomposition and loss; thus, 500 °C is selected as the suitable anneal temperature. Figure S3 (Supporting Information) shows the XPS results of samples annealed at 500 °C for 2 h. After H₂ annealing, both Mo and S peaks shift to higher binding energies. Because the binding energy of the core levels detected in XPS are calculated in reference to the Fermi level of the material, p-type materials appear at a lower binding energy than n-type materials due to the lower Fermi level. Shift in the H2-annealed material to higher binding energy indicates a shift toward n-type behavior rather than the existence of a new chemical state. Table S1 (Supporting Information) shows the detailed binding energies as well as the S:Mo ratios calculated from XPS. After 2 h of H₂ annealing, the ratio further decreases to 1.7 such that the MoS₂ aerogel is now Mo-rich.

Figure S4 (Supporting Information) shows the NO_2 sensing behavior of the Mo-rich MoS_2 aerogel after 2-h H₂ annealing.

The sensor shows a positive response to 20 ppm NO₂, which is consistent with n-type sensing behavior. The alteration of the S:Mo ratio with hydrogen annealing allows for tuning of the sensing behavior, indicating that intrinsic defects must play a role in the way that MOS_2 responds to NO₂ adsorption. A more complete understanding of the effect of H₂ annealing on sensing behavior is needed and studies are ongoing.

3. Conclusion

In summary, we have synthesized the 3D MoS₂ aerogel and integrated it onto a low-power microheater platform to investigate its sensing behavior toward NO2 under different conditions. The sensor is highly sensitive to NO2, with a low detection limit of 28 ppb, which is comparable to or better than most reported single- or few-layer MoS2 sensors, while retaining a scalable fabrication method. A two-step sulfur treatment improves the quality of the MoS₂ aerogel such that the high sensitivity is paired with fast response and recovery, which further demonstrates the potential of this nanomaterial for practical applications. The p-type sensing behavior of the MoS₂ aerogel is investigated and the intrinsic defect state (reflected in a S-rich material) is identified as the reason for the unexpected p-type behavior. Hydrogen annealing is used to alter the defect state from S rich to Mo rich, and n-type sensing behavior is obtained with negative impact on the sensing performance.

4. Experimental Section

 MoS_2 Aerogel Synthesis: The MoS_2 aerogel was initially synthesized according to the literature method.^[22] Briefly, 1 mol L⁻¹ ATM solution was treated with liquid nitrogen freezing and freeze-drying, followed by a thermal annealing at 450 °C under 2% H₂/98% Ar for 4 h to yield the MoS₂ aerogel.^[22] To prepare a high-quality MoS₂ aerogel, a two-step sulfurization process was conducted. The aerogel in a quartz boat was placed in the middle of a tube furnace (hot zone) while the sulfur powder was placed in the upstream low-temperature zone. In the first step, the tube furnace was heated to 500 °C with a 10% H₂/Ar flow. After 1-h annealing at 500 °C, the furnace temperature increased to 750 °C, at which point the temperature of the low-temperature zone reached 120 °C and sulfur was introduced by the flow to react with the aerogel. The second step took 1 h and then the sample was cooled down naturally to room temperature under continued H₂/Ar flow.

Material Characterization: The morphology and structure of the MoS₂ aerogel were characterized using a Zeiss Gemini Ultra-55 Analytical Field Emission Scanning Electron Microscope and a JEOL 2100-F 200 kV Field-Emission Analytical Transmission Electron Microscope (FETEM). Crystal structures of the aerogels were characterized with an X-Ray Diffractometer (Bruker AXS D8 Discover GADDS) with a Vantec-500 area detector and were operated at 35 kV and 40 mA at a wavelength of Co, K α , 1.79Å. XPS measurements were carried out on an Omicron Dar400 system with an achromatic Al K α X-ray source.

Microheater Sensor Fabrication: The low-power microheaters were fabricated using microelectromechanical system (MEMS) technology to create a suspended polysilicon microheater (100 nm thickness) encapsulated in 200 nm LSN film as detailed in our previous reports.^[26,27] The as-synthesized MoS₂ aerogel was suspended in a mixture solution of water and isopropyl alcohol by sonication. The solution was then drop-casted onto the microheater to connect the sensing electrodes.

Sensor Testing: The microheater sensor was wire-bonded to a cer-dip package and placed within a 1 cm³ gas flow chamber. A computercontrolled gas delivery system was used to control NO₂ concentrations **ADVANCED** SCIENCE NEWS _



by diluting the NO₂ gas cylinder (Praxair, 20 ppm in N₂) with clean house air and delivering these gases to the sensor chamber. Flow stream temperatures were recorded and were within a few degrees of room temperature. Sensor testing was conducted with a Keithley 2602 source-meter, which applied a voltage through both sensor and heater channels to monitor the sensor resistance and to control heater temperature. Zephyr, an open-source Java-based software, was used to control the source-meter and acquire data from the source-meter and the gas delivery system. The response and recovery times are defined as the average time taken to reach 90% of the final sensing or baseline signals, respectively.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

low power, microheaters, MOS_2 aerogel, NO_2 detection, p-type sensing behavior

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- K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, A. K. Geim, *Proc. Natl. Acad. Sci. USA* 2005, 102, 10451.
- [2] A. K. Geim, K. S. Novoselov, Nat. Mater. 2007, 6, 183.
- [3] S. Z. Butler, S. M. Hollen, L. Cao, Y. Cui, J. A. Gupta, H. R. Gutiérrez, T. F. Heinz, S. S. Hong, J. Huang, A. F. Ismach, E. Johnston-Halperin, M. Kuno, V. V. Plashnitsa, R. D. Robinson, R. S. Ruoff, S. Salahuddin, J. Shan, L. Shi, M. G. Spencer, M. Terrones, W. Windl, J. E. Goldberger, ACS Nano 2013, 7, 2898.



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- [4] Y. Q. Sun, Q. Wu, G. Q. Shi, Energy Environ. Sci. 2011, 4, 1113.
- [5] N. Yang, J. Zhai, D. Wang, Y. Chen, L. Jiang, ACS Nano 2010, 4, 887.
- [6] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, M. S. Strano, Nat. Nanotechnol. 2012, 7, 699.
- [7] D. Jariwala, V. K. Sangwan, L. J. Lauhon, T. J. Marks, M. C. Hersam, ACS Nano 2014, 8, 1102.
- [8] F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson, K. S. Novoselov, *Nat. Mater.* 2007, *6*, 652.
- [9] T. O. Wehling, K. S. Novoselov, S. V. Morozov, E. E. Vdovin, M. I. Katsnelson, A. K. Geim, A. I. Lichtenstein, *Nano Lett.* 2008, *8*, 173.
- [10] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, Nat. Nanotechnol. 2011, 6, 147.
- [11] T. Doll, J. Lechner, I. Eisele, K. Schierbaum, W. Gopel, Sens. Actuators, B 1996, 34, 506.
- [12] D. J. Late, Y.-K. Huang, B. Liu, J. Acharya, S. N. Shirodkar, J. Luo, A. Yan, D. Charles, U. V. Waghmare, V. P. Dravid, C. N. R. Rao, ACS Nano 2013, 7, 4879.
- [13] H. Li, Z. Yin, Q. He, H. Li, X. Huang, G. Lu, D. W. H. Fam, A. I. Y. Tok, Q. Zhang, H. Zhang, *Small* **2012**, *8*, 63.
- [14] F. K. Perkins, A. L. Friedman, E. Cobas, P. M. Campbell, G. G. Jernigan, B. T. Jonker, *Nano Lett.* 2013, 13, 668.
- [15] J.-S. Kim, H.-W. Yoo, H. O. Choi, H.-T. Jung, Nano Lett. 2014, 14, 5941.
- [16] B. Cho, M. G. Hahm, M. Choi, J. Yoon, A. R. Kim, Y.-J. Lee, S.-G. Park, J.-D. Kwon, C. S. Kim, M. Song, Y. Jeong, K.-S. Nam, S. Lee, T. J. Yoo, C. G. Kang, B. H. Lee, H. C. Ko, P. M. Ajayan, D.-H. Kim, *Sci. Rep.* **2015**, *5*, 08052.
- [17] B. Cho, A. R. Kim, Y. Park, J. Yoon, Y.-J. Lee, S. Lee, T. J. Yoo, C. G. Kang, B. H. Lee, H. C. Ko, D.-H. Kim, M. G. Hahm, ACS Appl. Mater. Interfaces 2015, 7, 2952.
- [18] M. Donarelli, S. Prezioso, F. Perrozzi, F. Bisti, M. Nardone, L. Giancaterini, C. Cantalini, L. Ottaviano, Sens. Actuators, B 2015, 207, 602.
- [19] R. Samnakay, C. Jiang, S. L. Rumyantsev, M. S. Shur, A. A. Balandin, *Appl. Phys. Lett.* **2015**, *106*, 023115.
- [20] Q. He, Z. Zeng, Z. Yin, H. Li, S. Wu, X. Huang, H. Zhang, Small 2012, 8, 2994.
- [21] K. Lee, R. Gatensby, N. McEvoy, T. Hallam, G. S. Duesberg, Adv. Mater. 2013, 25, 6699.
- [22] A. L. Friedman, F. K. Perkins, A. T. Hanbicki, J. C. Culbertson, P. M. Campbell, *Nanoscale* 2016, 8, 11445.
- [23] M. A. Worsley, S. J. Shin, M. D. Merrill, J. Lenhardt, A. J. Nelson, L. Y. Woo, A. E. Gash, T. F. Baumann, C. A. Orme, ACS Nano 2015, 9, 4698.
- [24] H. Long, A. Harley-Trochimczyk, T. Pham, Z.R. Tang, T. L. Shi, A. Zettl, C. Carraro, M. A. Worsley, R. Maboudian, *Adv. Funct. Mater.* 2016, *26*, 5158.
- [25] X. L. Li, Y. D. Li, Chem. Eur. J. 2003, 9, 2726.
- [26] Y. C. Lin, W. J. Zhang, J. K. Huang, K. K. Liu, Y. H. Lee, C. T. Liang, C. W. Chu, L. J. Li, *Nanoscale* **2012**, *4*, 6637.
- [27] Y. H. Lee, X. Q. Zhang, W. J. Zhang, M. T. Chang, C. T. Lin, K. D. Chang, Y. C. Yu, J. T. Wang, C. S. Chang, L. J. Li, T. W. Lin, *Adv. Mater.* **2012**, *24*, 2320.
- [28] D. Kiriya, P. Lobaccaro, H. Y. Y. Nyein, P. Taheri, M. Hettick, H. Shiraki, C. M. Sutter-Fella, P. Zhao, W. Gao, R. Maboudian, J. W. Ager, A. Javey, *Nano Lett.* **2016**, *16*, 4047.
- [29] A. Harley-Trochimczyk, J. Chang, Q. Zhou, J. Dong, T. Pham, M. Worsley, R. Maboudian, A. Zettl, W. Mickelson, *Sens. Actuators, B* 2015, 206, 399.
- [30] H. Long, A. Harley-Trochimczyk, T. Y. He, T. Pham, Z. R. Tang, T. L. Shi, A. Zettl, W. Mickelson, C. Carraro, R. Maboudian, ACS Sens. 2016, 1, 339.
- [31] W. Li, X. Geng, Y. Guo, J. Rong, Y. Gong, L. Wu, X. Zhang, P. Li, J. Xu, G. Cheng, M. Sun, L. Liu, ACS Nano 2011, 5, 6955.

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- [32] J. D. Fowler, M. J. Allen, V. C. Tung, Y. Yang, R. B. Kaner, B. H. Weiller, ACS Nano 2009, 3, 301.
- [33] J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, H. J. Dai, *Science* **2000**, 287, 622.
- [34] P. G. Collins, K. Bradley, M. Ishigami, A. Zettl, Science 2000, 287, 1801.
- [35] J. T. Robinson, F. K. Perkins, E. S. Snow, Z. Wei, P. E. Sheehan, Nano Lett. 2008, 8, 3137.
- [36] K. Dolui, I. Rungger, S. Sanvito, Phys. Rev. B 2013, 87, 165402.
- [37] D. S. Sim, M. Kim, S. Yim, M. J. Choi, J. Choi, S. Yoo, Y. S. Jung, ACS Nano 2015, 9, 12115.
- [38] S. Chuang, C. Battaglia, A. Azcatl, S. McDonnell, J. S. Kang, X. T. Yin, M. Tosun, R. Kapadia, H. Fang, R. M. Wallace, A. Javey, *Nano Lett.* **2014**, *14*, 1337.
- [39] S. McDonnell, A. Azcatl, R. Addou, C. Gong, C. Battaglia, S. Chuang, K. Cho, A. Javey, R. M. Wallace, ACS Nano 2014, 8, 6265.
- [40] S. McDonnell, R. Addou, C. Buie, R. M. Wallace, C. L. Hinkle, ACS Nano 2014, 8, 2880.