Direct Synthesis of MoS$_2$ Nanosheets in Reduced Graphene Oxide Nanoscroll for Enhanced Photodetection

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Abstract: Due to their unique tubular and spiral structure, graphene and graphene oxide nanoscrolls (GONS) have shown extensive applications in various fields. However, it is still a challenge to improve the optoelectronic application of graphene and GONS because of the zero bandgap of graphene. Herein, ammonium tetrathiomolybdate ((NH$_4$)$_2$MoS$_4$) was firstly wrapped into the ((NH$_4$)$_2$MoS$_4$@GONS) by molecular combing the mixture of (NH$_4$)$_2$MoS$_4$ and GO solution on hydrophobic substrate. After thermal annealing, the (NH$_4$)$_2$MoS$_4$ and GO were converted to MoS$_2$ nanosheets and reduced GO (RGO) simultaneously, and, thus, the MoS$_2$@RGONS was obtained. Raman spectroscopy and high-resolution transmission electron microscopy were used to confirm the formation of MoS$_2$ nanosheets among the RGONS. The amount of MoS$_2$ wrapped in RGONS increased with the increasing height of GONS, which is confirmed by the atomic force microscopy and Raman spectroscopy. The as-prepared MoS$_2$@RGONS showed much better photoresponse than the RGONS under visible light. The photocurrent-to-dark current ratios of photodetectors based on MoS$_2$@RGONS are ~570, 360 and 140 under blue, red and green lasers, respectively, which are 81, 144 and 35 times of the photodetectors based on RGONS. Moreover, the MoS$_2$@RGONS-based photodetector exhibited good power-dependent photoresponse. Our work indicates that the MoS$_2$@RGONS is expected to be a promising material in the fields of optoelectronic devices and flexible electronics.

Keywords: ammonium tetrathiomolybdate; thermal annealing; MoS$_2$@reduced graphene oxide nanoscroll; photosensitivity; photodetection

1. Introduction

By scrolling two-dimensional graphene nanosheet into a one-dimensional structure, a graphene nanoscroll (GNS) is formed with a tubular, spiral structure and open ends [1]. Due to the excellent properties resulting from its unique structure, graphene nanoscroll has attracted great attention in the fields of energy storage, sensors and flexible electronics [2–5]. In recent years, graphene oxide nanoscrolls (GONS) have been widely investigated instead of GNS because of the facile mass production of graphene oxide [2,6–15]. In order to further improve the performance of GONS, various functional nanomaterials were wrapped into GONS to extend their applications in supercapacitors, batteries and photocatalysts [16–20]. By encapsulating sulfur into GONS during the freeze-casting process, the as-prepared S/GONS was used as a good cathode material for a lithium-sulfur battery [21,22]. After Fe$_2$O$_3$ nanoparticles were wrapped into GONS as electrode materials by ultrasonication, a high volumetric energy density supercapacitor with quite good cycling stability was obtained [23]. Fe$_{1-x}$S/Fe$_3$O$_4$ nanoparticles were also confined into GONSs and GO nanosheets by cold quenching and freeze drying, and the as-obtained composites were used as promising electrodes for a flexible lithium-ion battery [3].

It is well known that the application of graphene in high-performance photodetectors has been seriously hindered due to its low optical absorption ability [24]. To improve...
the photoresponse of graphene-based devices, a large number of functional nanomaterials have been integrated with graphene, including quantum dots [24], transition metal dichalcogenides [25–27], metallic nanostructures with plasmonic effects [28,29] and so on. Although the GONS has shown promising applications in the fields of energy storage, sensing and photocatalysis, it is still a challenge to apply the GONS as a high-performance photodetector. Previously, we have embedded chemical vapor deposition (CVD)-grown MoS\(_2\) nanoflakes into RGO nanoscrolls to improve the photodetection performance [25]. The photosensitivity of MoS\(_2\)@RGO nanoscrolls increased by 20 times compared to the RGO nanosheet. However, it is difficult to further increase the amount of MoS\(_2\) grown on an RGO nanosheet by using the CVD method. Therefore, it is highly desirable to develop an alternative method to wrap a large amount of MoS\(_2\) into GONS and thus further enhance its photodetection performance.

In this work, a large amount of a precursor, ammonium tetrathiomolybdate ((NH\(_4\)\(_4\)MoS\(_4\)), was successfully wrapped into GONSs with length up to hundreds of micrometers by using the molecular combing method. After high temperature annealing, the (NH\(_4\)\(_4\))\(_2\)MoS\(_4\) was in situ decomposed to MoS\(_2\) nanosheets, which were well encapsulated into the GONS. Meanwhile, the GONSs were simultaneously converted to reduced GONSs (RGONS). By optimizing precursor concentration and annealing temperature, high-quality MoS\(_2\)@RGONS was facilely obtained with mass production. The optical microscopy (OM), atomic force microscopy (AFM), high-resolution transmission electron microscopy (HRTEM) and Raman spectroscopy were employed to demonstrate the uniform distribution of MoS\(_2\) nanosheets in RGONSs. The photodetectors based on MoS\(_2\)@RGONSs showed photosensitivity two orders of magnitude higher than that of the RGONS under visible light. The MoS\(_2\)@RGONS-based photodetectors also exhibited good power dependent behavior. The improved performance could be attributed to the formation of multiple graphene/MoS\(_2\) interfaces in the scrolled structure of MoS\(_2\)@RGONS, which increases the light absorption efficiency and enables the ultrafast charge transfer, resulting in a much higher photocurrent and photosensitivity.

2. Experimental Section

2.1. Preparation of (NH\(_4\)\(_4\))\(_2\)MoS\(_4\) Solution and Hydrophobic Substrate

Graphene oxide (GO) was synthesized by the modified Hummers method. A total of 0.038 g of (NH\(_4\)\(_4\))\(_2\)MoS\(_4\) was ground to fine powder and dissolved in water to form aqueous solutions with concentration of 5, 10, 20, 30 and 50 mM. Thereafter, the (NH\(_4\)\(_4\))\(_2\)MoS\(_4\) solution was treated by ultrasonication to ensure complete dissolution. Finally, the (NH\(_4\)\(_4\))\(_2\)MoS\(_4\)@GO solution was prepared by mixing 0.2 mg/mL GO and (NH\(_4\)\(_4\))\(_2\)MoS\(_4\) solution with a volume ratio of 1:1.

The preparation of hydrophobic substrate is a key step to form GO nanoscrolls by the molecular combing method [6,7,10,11]. Firstly, the cleaned 300 nm SiO\(_2\)/Si substrate was immersed into a glass bottle containing a mixture of 8 mL toluene and 200 \(\mu\)L OTS (Octadecyltrimethoxysilane, purchased from Aladdin). Then, the glass bottle was sealed and heated at 60 °C for 24 h. After that, the SiO\(_2\)/Si substrate was washed with ethanol and DI water three times. Therefore, the hydrophobic OTS-modified SiO\(_2\)/Si substrate (OTS-SiO\(_2\)/Si) was obtained.

2.2. Preparation of (NH\(_4\)\(_4\))\(_2\)MoS\(_4\)@GONS and MoS\(_2\)@RGONS

The (NH\(_4\)\(_4\))\(_2\)MoS\(_4\)@GO nanoscrolls ((NH\(_4\)\(_4\))\(_2\)MoS\(_4\)@GONSs) were prepared by the molecular combing method [6], as shown in Scheme 1a,b. Firstly, 30 \(\mu\)L of the (NH\(_4\)\(_4\))\(_2\)MoS\(_4\)@GO solution was dropped onto the hydrophobic OTS-SiO\(_2\)/Si substrate. A glass coverslip was then used to slowly drag the droplet from one end to the other end of the substrate. In this way, the (NH\(_4\)\(_4\))\(_2\)MoS\(_4\)@GONSs were formed on the OTS-SiO\(_2\)/Si substrate. The MoS\(_2\)@RGON nanoscrolls (MoS\(_2\)@RGONSs) were prepared as shown in Scheme 1c,d. After the (NH\(_4\)\(_4\))\(_2\)MoS\(_4\)@GONSs were put into a tube furnace, a mixture gas of N\(_2\)/H\(_2\) (80/40 sccm) was introduced as a protective gas. Then, the temperature of the furnace increased to 400 °C gradually, with a speed of 10 °C/min, and was kept for 60 min. During
this period, (NH₄)₂MoS₄ was decomposed to MoS₂, while GO was reduced to RGO at the same time. Therefore, the MoS₂@RGONSs were successfully obtained.

![Diagram](image)

**Scheme 1.** Schematic diagram of the preparation of (NH₄)₂MoS₄@GO and MoS₂@RGO nanoscrolls. (a) A drop of (NH₄)₂MoS₄ and GO solution is dragged by the cover slip on the hydrophobic substrate. (b) The (NH₄)₂MoS₄@GO nanoscroll is formed by molecular combing. (c) After the as-prepared (NH₄)₂MoS₄@GO nanoscroll is treated at 400 °C in the N₂/H₂ environment, (NH₄)₂MoS₄ is decomposed to MoS₂ nanosheets and GO is reduced to RGO. (d) The as-obtained MoS₂@RGO nanoscroll after high temperature annealing. The inset in the top right shows the cross-section structure of the MoS₂@RGO nanoscroll.

### 2.3. Characterizations

An optical microscope (ECLIPSE LV100ND, Nikon, Tokyo, Japan), AFM (Dimension ICON with Nanoscope V controller, Bruker, Billerica, MA, USA) and TEM (JEM-2100F JEOL, Tokyo, Japan) were used to characterize the as-prepared (NH₄)₂MoS₄@GONS and MoS₂@RGONS. In addition, Raman spectroscopy and Raman mapping of the as-prepared (NH₄)₂MoS₄@GONS and MoS₂@RGONS were tested on a LabRAM HR Evolution Raman spectrometer (Horiba Jobin Yvon, Palaiseau, France) with a 532 nm laser focused through a 100 × objective lens.

### 2.4. Device Fabrication and Photodetection

First, 30 nm thick gold and 5 nm thick chromium films were deposited on RGO and MoS₂@RGO nanoscrolls, respectively, by thermal evaporation with a TEM grid (200 mesh) as a mask.

A probe station (model TTPX, Lake Shore Inc., Rhinelander, WI, USA) and Keithley 4200 semiconductor characterization system (Advanced Test Equipment Corp., San Diego, CA, USA) were used to monitor the real-time current change of the as-prepared devices. The photocurrent was collected from individual ROG and MoS₂@RGO nanoscrolls with Au pads as the source and drain electrodes, respectively, as shown in Figure S1. The photo-detection test was recorded under blue (405 nm), green (532 nm) and red (633 nm)
lasers. The power of the laser was measured with a laser power meter (Laser power meter LP1, SanWa, Okayama, Japan).

3. Result and Discussion

Scheme 1 shows the preparation of MoS$_2$@RGONSs by molecular combing and thermal annealing. After the (NH$_4$)$_2$MoS$_4$ was wrapped into GO nanoscrolls by molecular combing, the (NH$_4$)$_2$MoS$_4$ was decomposed to MoS$_2$ at a high temperature under the atmosphere of N$_2$/H$_2$ [30]. It was found that the (NH$_4$)$_2$MoS$_4$ was decomposed to MoS$_2$ as the temperature increased from 120 to 260 °C under an inert atmosphere. The MoS$_2$ was further reduced to MoS$_2$ as the temperature was higher than 230 °C under N$_2$/H$_2$ [30]. The process can be described as the following chemical reactions,

\[
\begin{align*}
\text{(NH}_4\text{)}_2\text{MoS}_4 & \rightarrow 2\text{NH}_3 + \text{H}_2\text{S} + \text{MoS}_3 \quad (120-260 \degree \text{C}) \\
\text{MoS}_3 + \text{H}_2 & \rightarrow \text{MoS}_2 + \text{H}_2\text{S} \quad (230-450 \degree \text{C})
\end{align*}
\]

We heated the (NH$_4$)$_2$MoS$_4$@GONSs in the temperature range of 300 to 500 °C. The Raman spectroscopy was used to characterize the amount of MoS$_2$ in GONSs by measuring the peak intensity of A$_{1g}$. As shown in Figure S2a, the peak intensity of A$_{1g}$ increased as the temperature increased from 300 to 400 °C, while it decreased as the temperature further increased to 500 °C. The flow ratio of N$_2$ to H$_2$ also affects the formation of MoS$_2$ during the thermal annealing process. As shown in Figure S2b, the A$_{1g}$ peak of the (NH$_4$)$_2$MoS$_4$@GONS annealed with a gas stream of 80 sccm N$_2$ and 40 sccm H$_2$ showed the highest intensity. Therefore, a mixture gas of N$_2$/H$_2$ (80/40 sccm) was introduced as a protective gas during the experiment. The concentration of the (NH$_4$)$_2$MoS$_4$ solution also has an important effect on the formation of MoS$_2$@GONSs and MoS$_2$@RGONSs. The peak intensity of A$_{1g}$ increased as the concentration of (NH$_4$)$_2$MoS$_4$ solution increased from 5 mM to 30 mM, while it decreased when 50 mM (NH$_4$)$_2$MoS$_4$ solution was used (Figure S2c). In addition, the diameter of the (NH$_4$)$_2$MoS$_4$@GONSs increased as the concentration of (NH$_4$)$_2$MoS$_4$ increased from 5 mM to 50 mM (Figure S3). Meanwhile, the long and straight nanoscrolls were changed to irregular and thick aggregations. In order to wrap more MoS$_2$ and maintain the good scroll structure, (NH$_4$)$_2$MoS$_4$ solution with a concentration of 30 mM was used as the optimal concentration and annealed at 400 °C.

Figure 1a,b show the OM images of an (NH$_4$)$_2$MoS$_4$@GO nanoscroll before and after thermal annealing, respectively. It can be seen that the color of the nanoscroll changed from cyan to gray blue after thermal annealing. In addition, the height of the MoS$_2$@GONS is quite smaller than that of the (NH$_4$)$_2$MoS$_4$@GO nanoscrolls. As shown in Figure S4, the height of the (NH$_4$)$_2$MoS$_4$@GO is 201.4 nm, while it decreases largely to 3.52 nm after high temperature annealing, which could be attributed to the evaporation of water molecules trapped in the nanoscroll and the decomposition of (NH$_4$)$_2$MoS$_4$. In order to confirm the formation of the MoS$_2$@GONS nanoscroll, Raman spectroscopy was conducted at the same position of the nanoscroll before and after annealing. As shown in Figure 1c, there are only two Raman peaks located at 1359 and 1587 cm$^{-1}$ for the (NH$_4$)$_2$MoS$_4$@GO nanoscroll, which are assigned to the D and G peaks of GO. After thermal annealing, there are two more peaks located at 384.4 and 404.2 cm$^{-1}$ besides the D and G peaks, which are characteristics of MoS$_2$ nanosheets [31,32]. In addition, the intensity ratio of the D to G peak decreased from 1.24 to 0.72 for the (NH$_4$)$_2$MoS$_4$@GO nanoscroll after thermal annealing, indicating the formation of reduced GO (RGO). The D band originates from the lattice destruction of sp$^2$-hybridized carbon, and the G band arises from the first-order scattering of the E$_{2g}$ mode. The intensity ratio (I$_D$/I$_G$) reflects the disorder of the carbon structure, and the higher intensity ratio of I$_D$/I$_G$ means more defective graphitic structures. Therefore, the Raman characterization confirms the successful conversion of the (NH$_4$)$_2$MoS$_4$@GO nanoscroll to the MoS$_2$@RGO nanoscroll after thermal annealing at 400 °C for 60 min. In order to investigate whether the MoS$_2$ was uniformly wrapped into the RGO nanoscroll, the as-obtained MoS$_2$@RGO nanoscroll was characterized by Raman mapping. As shown in Figure 1d,e, the G peak of GO nanoscroll was unchanged after
thermal annealing. Meanwhile, the Raman mapping of the $A_{1g}$ peak of MoS$_2$ showed a homogeneous signal (Figure 1f), indicating that the MoS$_2$ was uniformly distributed in the RGO nanoscroll.

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**Figure 1.** The OM images of the (NH$_4$)$_2$MoS$_4$@GO nanoscroll (a) before and (b) after thermal annealing. (c) Raman spectra of the (NH$_4$)$_2$MoS$_4$@GO and MoS$_2$@RGO nanoscrolls. The Raman mapping images of (d) the (NH$_4$)$_2$MoS$_4$@GO nanoscroll and (e) the RGO at peak G (1587 cm$^{-1}$), and the MoS$_2$@RGO nanoscroll at peak (f) $A_{1g}$ (404.2 cm$^{-1}$) of MoS$_2$.

We found that the Raman peak intensity of MoS$_2$ in the MoS$_2$@RGO nanoscrolls varied with the height of the nanoscrolls. To investigate the relationship between the height of the MoS$_2$@RGO nanoscroll and the amount of trapped MoS$_2$ in it, the MoS$_2$@RGO nanoscrolls with various heights were characterized using AFM and Raman spectroscopy, respectively. Figure 2a shows the OM image of the MoS$_2$@RGO nanoscroll, where the boxes marked by d, e and f are three nanoscrolls with different heights. Figure 2d-f show the corresponding AFM images, and the measured heights of the three nanoscrolls are 137.4 nm, 83.5 nm and 35.4 nm, respectively. As shown in Figure 2b, the nanoscroll with a height of 137.4 nm presents a stronger Raman signal (box d), while the nanoscroll with a height of 35.4 nm has a weaker Raman signal. To further reveal the influence of the height of the MoS$_2$@RGO nanoscrolls on the Raman peak intensity of MoS$_2$, a lot of nanoscrolls were measured to plot the Raman peak intensity as a function of the height of the nanoscrolls. As shown in Figure 2c, with the increasing height of the MoS$_2$@RGO nanoscrolls, the Raman peak intensity of MoS$_2$ gradually increases, indicating that more MoS$_2$ was trapped in a higher nanoscroll.

In order to clearly observe the detailed structure and confirm the formation of MoS$_2$ in the as-prepared MoS$_2$@RGO nanoscroll, high-resolution transmission electron microscopy (HRTEM) was used for characterization. Figure 3a shows the low-resolution TEM image of the MoS$_2$@RGO nanoscroll. We can see that the MoS$_2$@RGO nanoscroll exhibits a multilayer scrolled structure with a dark, dense inner layer. Figure 3b shows the HRTEM characterization result of the red dashed box shown in Figure 3a. The well resolved lattice stripes with spacing of 0.63 nm are clearly presented, which is consistent with the interlayer spacing of layered MoS$_2$ [33]. Moreover, the energy dispersive X-ray (EDX) elemental mapping analysis of the MoS$_2$@RGO nanoscroll shown in Figure 3c provides strong evidence for the homogeneous distribution of C, O, Mo and S elements in the
MoS$_2$@RGO nanoscroll. The HRTEM and EDX results confirm the uniform existence of the MoS$_2$ nanosheet in the RGO nanoscroll.

Graphene and its derivatives are severely limited in optoelectronic applications due to their zero band gap and poor absorption of visible light. In order to improve the optoelectronic performance of graphene, MoS$_2$, as a typical transition metal dichalcogenides (TMDCs) material, has been widely used to combine graphene for photodetection [34]. By wrapping MoS$_2$ into the RGO nanoscrolls, we found that the MoS$_2$@RGO nanoscroll also showed promising photodetection performance. Photodetectors based on RGO nanoscrolls and MoS$_2$@RGO nanoscrolls were fabricated to investigate the effect of wrapped MoS$_2$. It is well known that photosensitivity is an important parameter to evaluate the performance of photodetectors [35–37], which is usually defined by the ratio of photocurrent to dark current (PDR), as follows:

$$\text{PDR} = \frac{I_{\text{photo}}}{I_{\text{dark}}} \quad (2)$$

The photocurrent and dark current of the RGO nanoscrolls and MoS$_2$@RGO nanoscrolls-based photodetectors were firstly measured under the dark and the illumination of blue, red and green lasers with different laser power densities, respectively. Because of the low light absorption of RGO, we found that the RGO-based photodetectors exhibited photosensitivity of ~7, ~2.4 and ~4 under blue, red and green lasers (Figure S5). Figure 4a–c show the PDRs of photodetectors based on RGO nanoscrolls and MoS$_2$@RGO nanoscrolls under blue (405 nm), red (633 nm) and green (532 nm) lasers. The PDRs of photodetectors based on the MoS$_2$@RGO nanoscrolls were 570, 360 and 140 under blue, red and green lasers, which are almost 81, 144 and 35 times those of the photodetectors based on the RGO nanoscrolls measured under the same conditions. In addition, the photocurrent of the MoS$_2$@RGO nanoscroll is highly dependent on the power density of the incident light. As shown in Figure 4d–f, the PDRs increased as the incident laser power density increased. The different photoresponse of MoS$_2$@RGO nanoscrolls to blue, green and red light could be explained as follows. In our experiment, the power intensity of green light is the lowest.
However, the PDR of MoS$_2$@RGONS is around 140 at a power density of 0.56 mW/mm$^2$ (Figure 4f), while the PDRs of MoS$_2$@RGONS are around 100 and 70 for blue and red lasers at power densities of 1.05 mW/mm$^2$ and 1.41 mW/mm$^2$ (Figure 4d,e), respectively. The MoS$_2$ nanosheets synthesized in GONS could be multilayer, which can be confirmed by the HRTEM images shown in Figure 3b. Therefore, the multilayer MoS$_2$ trapped into RGONS should be more suitable for detecting green lasers than blue and red lasers given that they are at the same power intensity. A similar phenomenon has also been reported in a multilayer MoS$_2$@glassy-graphene heterostructure [38]. In addition, the MoS$_2$@RGONS shows higher PDR under the blue laser than under the red laser at similar power intensities. This could be attributed the higher photon energy of the blue laser compared to the red laser, which can generate more photoinduced carriers at the same power [39].

The excellent photodetection performance of the MoS$_2$@RGO nanoscroll could be attributed to the formation of multiple heterojunction interfaces between the RGO and MoS$_2$ nanosheets. It is known that the ultrafast separation and transfer of photogenerated carriers can be achieved at the heterojunction interface of graphene and MoS$_2$, resulting in a substantial increase in photocurrent and photoresponse. Due to the roll-up structure of the MoS$_2$@RGO nanoscroll, the MoS$_2$ nanosheets are wrapped between adjacent RGO layers spirally, forming multiple heterojunction interfaces. When light was shined on the MoS$_2$@RGO nanoscroll, the MoS$_2$ nanosheets in each heterojunction interface could absorb light, and charge carriers were generated simultaneously. Meanwhile, the photogenerated charge carriers can be separated and transferred in an ultrafast way. Therefore, the photocurrent of the MoS$_2$@RGO nanoscroll can be greatly enhanced due to the syn-

![Figure 3](image-url)
ergetic enhancement of photocurrent at each heterojunction interface. As a consequence, the photosensitivity of the MoS\(_2@\)RGO nanoscroll is much higher than that of the RGO nanoscroll.

Figure 4. (a–c) The PDRs of photodetectors based on RGO and MoS\(_2@\)RGO nanoscrolls under (a) blue, (b) red and (c) green lasers. (d–f) Plots of PDR values of photodetectors based on MoS\(_2@\)RGO nanoscrolls under (d) blue, (e) red and (f) green lasers as a function of power density.

4. Conclusions

In summary, (NH\(_4\))\(_2\)MoS\(_4\) was encapsulated into the GO nanoscrolls by the molecular combing method on hydrophobic substrate. By optimizing the precursor concentration and annealing temperature, the (NH\(_4\))\(_2\)MoS\(_4\) and GO nanoscrolls were successfully converted to MoS\(_2\) and RGO nanoscrolls, forming the MoS\(_2@\)RGO nanoscroll. The OM and AFM characterization results showed that the high-density MoS\(_2@\)RGO nanoscrolls were successfully prepared. The uniform distribution of the MoS\(_2\) nanosheets in the RGO nanoscrolls was confirmed by the Raman spectroscopy and HRTEM characterization. Compared to the RGO nanoscroll, the MoS\(_2@\)RGO nanoscroll showed much better photodetection performance. The PDRs of photodetectors based on the MoS\(_2@\)RGO nanoscrolls were about two orders of magnitude higher than those of photodetectors based on the RGO nanoscrolls under blue, red and green lasers. The formation of multiple graphene/MoS\(_2\) heterojunction interfaces in a scrolled structure can not only enhance the light absorption of MoS\(_2\) but also accelerate the electron-hole separation. Our work indicates that the MoS\(_2@\)RGO nanoscrolls could be promising materials for high-performance graphene-based photodetectors.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/nano12091581/s1: Figure S1. The optical images of photodetectors based on individual (a) RGO nanoscroll and (b) MoS\(_2@\)RGO nanoscroll with Au pads as source and drain electrodes. Figure S2. Plots of Raman peak intensity of 6\(_{\text{lg}}\) as function of (a) annealing temperature, (b) the flow ratio of N\(_2\) to H\(_2\), and (c) concentration of (NH\(_4\))\(_2\)MoS\(_4\). Figure S3. OM images of (NH\(_4\))\(_2\)MoS\(_4@\)GONS prepared by molecular combing (NH\(_4\))\(_2\)MoS\(_4\) solution with concentration of (a,e) 0.005 M, (b,f) 0.01 M, (c,g) 0.03 M, and (d,h) 0.05 M before and after thermal annealing. Figure S4. AFM height images of the same (NH\(_4\))\(_2\)MoS\(_4@\)GONS (a) before and (b) after thermal annealing. Figure S5. PDR plots of RGO nanoscrolls measured under (a) blue, (b) red, and (c) green lasers.
Author Contributions: Conceptualization, H.L.; supervision and project administration, X.H. and H.L.; methodology, H.L. and X.L.; formal analysis, Z.W., F.L.; X.L. and Y.Y.; investigation, Z.W. and X.L.; writing—original draft preparation, H.L., Z.W. and X.L.; revision of the manuscript, H.L. and Z.W. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Natural Science Foundation of China (Grant No. 51832001, 21571101 and 5132202), the Natural Science Foundation of Jiangsu Province in China (Grant No. BK20161543), and the Natural Science Foundation of the Jiangsu Higher Education Institutions of China (Grant No. 15KJB430016).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data can be available upon request from the authors.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Berman, D.; Deshmuk, S.A.; Sankaranarayanan, S.K.R.S.; Erdemir, A.; Sumant, A.V. Macroscale Superlubricity Enabled by Graphene Nanoscroll Formation. Science 2015, 348, 1118–1122. [CrossRef] [PubMed]
2. Chen, Z.; Wang, J.R.; Pan, D.X.; Wang, Y.; Noetzel, R.; Li, H.; Xie, P.; Pei, W.L.; Umar, A.; Jiang, L.; et al. Mimicking a Dog’s Nose: Scrolling Graphene Nanosheets. ACS Nano 2018, 12, 2521–2530. [CrossRef] [PubMed]
3. Zhao, Y.; Wang, J.J.; Ma, C.L.; Cao, L.J.; Shao, Z.P. A Self-Adhesive Graphene Nanoscroll/Nanosheet Paper with Confined Fe_{x−y}S/Fe_3O_4 Hetero-Nanoparticles for High-Performance Anode Material of Flexible Li-Ion Batteries. Chem. Eng. J. 2019, 370, 536–546. [CrossRef]
4. Liu, P.W.; Jin, Z.; Katsukis, G.; Drahushuk, L.W.; Shimizu, S.; Shih, C.J.; Taggart-Scarff, J.K.; Qin, B.; Van Vliet, K.J.; et al. Layered and Scrolled Nanocomposites with Aligned Semi-Infinite Graphene Inclusions at the Platelet Limit. Science 2016, 353, 364–367. [CrossRef] [PubMed]
5. Lai, Z.C.; Chen, Y.; Tan, C.L.; Zhang, X.; Zhang, H. Self-Assembly of Two-Dimensional Nanosheets into One-Dimensional Nanostructures. Chem 2016, 1, 59–77. [CrossRef]
6. Li, H.; Wu, J.; Qi, X.Y.; He, Q.Y.; Liu, C.; Lu, G.; Zhou, X.Z.; Zhang, H. Graphene Oxide Scrolls on Hydrophobic Substrates Fabricated by Molecular Combing and Their Application in Gas Sensing. Small 2013, 9, 382–386. [CrossRef]
7. Wu, J.M.T.; Li, H.; Qi, X.Y.; He, Q.Y.; Xu, B.X.; Zhang, H. Graphene Oxide Architectures Prepared by Molecular Combing on Hydrophilic–Hydrophobic Micropatterns. Small 2014, 10, 2239–2244. [CrossRef]
8. Wu, Y.; Pan, X.; Huang, Y.; Li, H.; Fan, Z.X.; Liu, J.Q.; Cao, X.H.; Huang, X.; Huang, W.; Zhang, H. Graphene Oxide Scroll Mesophases Prepared by Molecular Combing for Transparent and Flexible Electrodes. Adv. Mater. Technol. 2017, 2, 1600231. [CrossRef]
9. Wang, L.; Yang, P.; Liu, Y.; Fang, X.R.; Shi, X.T.; Wu, S.Y.; Huang, L.; Li, H.; Huang, X.; Huang, W. Scrolling up Graphene Oxide Nanosheets Assisted by Self-Assembled Monolayers of Alkanethiols. Nanoscale 2017, 9, 9997–10001. [CrossRef]
10. Liu, Y.; Wang, L.; Zhang, H.; Ran, F.R.; Yang, P.; Li, H. Graphene Oxide Scroll Mesophases Encapsulated Ag Nanoparticles for Humidity Sensing. RSC Adv. 2017, 7, 40119–40123. [CrossRef]
11. Zhao, W.H.; Wang, L.; Pei, C.J.; Wei, C.; You, H.; Zhang, J.D.; Li, H. Impact of pH on Regulating Ion Encapsulation of Graphene Oxide Nanoscrolls for Pressure Sensing. Nanomaterials 2019, 9, 548. [CrossRef] [PubMed]
12. Tang, B.; Gao, E.L.; Xiong, Z.Y.; Dang, B.; Xu, Z.P.; Wang, X.G. Transition of Graphene Oxide from Nanomembrane to Nanoscroll Mediated by Organic Solvent in Dispersion. Chem. Mater. 2018, 30, 5951–5960. [CrossRef]
13. Fang, Q.L.; Zhou, X.F.; Deng, W.; Liu, Y.W.; Zheng, Z.; Liu, Z.P. Nitrogen-Doped Graphene Nanoscroll Foam with High Diffusion Rate and Binding Affinity for Removal of Organic Pollutants. Small 2017, 13, 20160379. [CrossRef] [PubMed]
14. Zheng, B.N.; Gao, C. Preparation of Graphene Nanoscroll/Polyaniline Composites and Their Use in High Performance Supercapacitors. New Carbon Mater. 2016, 31, 315–320. [CrossRef]
15. Rani, J.R.; Thangavel, R.; Oh, S.I.; Lee, Y.S.; Jang, J.H. An Ultra-High-Energy Density Supercapacitor: Fabrication Based on Thiol-functionalized Graphene Oxide Scrolls. Nanomaterials 2019, 9, 148. [CrossRef] [PubMed]
16. Li, X.J.; Natsuki, J.; Natsuki, T. A Recyclable Silver Nanoparticles/Graphene Oxide Nanoscroll Composite Photocatalyst. Environ. Technol. Innov. 2021, 21, 101210. [CrossRef]
17. Zhang, Y.F.; Zhao, C.Y.; Zeng, Z.H.; Ang, J.M.; Che, B.Y.; Wang, Z.; Lu, X.H. Graphene Nanoscroll/Nanosheet Aerogels with Confined SnS_2 Nanosheets: Simultaneous Wrapping and Bridging for High-Performance Lithium-Ion Battery Anodes. Electrochim. Acta 2018, 278, 156–164. [CrossRef]
18. Yang, B.J.; Chen, J.T.; Liu, B.; Ding, Y.X.; Tang, Y.; Yan, X.B. One Dimensional Graphene Nanoscroll-Wrapped MnO Nanoparticles for High-Performance Lithium Ion Hybrid Capacitors. J. Mater. Chem. A 2021, 9, 6352–6360. [CrossRef]
19. Lin, Y.T.; Zhou, F.S.; Chen, M.; Zhang, S.; Deng, C. Building Defect-Rich Oxide Nanowires@Graphene Coaxial Scrolls to Boost High-Rate Capability, Cycling Durability and Energy Density for Flexible Zn-Ion Batteries. Chem. Eng. J. 2020, 396, 125259. [CrossRef]
20. Cho, S.H.; Kim, J.H.; Kim, I.G.; Park, J.H.; Jung, J.W.; Kim, H.S.; Kim, I.D. Reduced Graphene-Oxide-Encapsulated MoS2/Carbon
Nanofiber Composite Electrode for High-Performance Na-Ion Batteries. *Nanomaterials* **2021**, *11*, 2691. [CrossRef]

21. Yoo, S.; Lee, J.; Kim, J.M.; Seong, C.Y.; Seong, K.D.; Piao, Y. Well-Dispersed Sulfur Wrapped in Reduced Graphene Oxide
Nanoscroll as Cathode Material for Lithium-Sulfur Battery. *J. Electroanal. Chem.* **2016**, *780*, 19–25. [CrossRef]

22. Guo, Y.; Zhao, G.; Wu, N.T.; Zhang, Y.; Xiang, M.W.; Wang, B.; Liu, H.; Wu, H. Efficient Synthesis of Graphene Nanoscrolls for
Fabricating Sulfur-Loaded Cathode and Flexible Hybrid Interlayer toward High-Performance Li-S Batteries. *ACS Appl. Mater. Inter.*
**2016**, *8*, 34185–34193. [CrossRef] [PubMed]

23. Rani, J.R.; Thangavel, R.; Oh, S.I.; Woo, J.M.; Das, N.C.; Kim, S.Y.; Lee, Y.S.; Jang, J.H. High Volumetric Energy Density Hybrid
Supercapacitors Based on Reduced Graphene Oxide Nanoscrolls. *ACS Appl. Mater. Inter.* **2017**, *9*, 22398–22407. [CrossRef] [PubMed]

24. Liu, C.H.; Chang, Y.C.; Norris, T.B.; Zhong, Z.H. Graphene Photodetectors with Ultra-Broadband and High Responsivity at Room
Temperature. *Nat. Nanotechnol.* **2014**, *9*, 273–278. [CrossRef] [PubMed]

25. Fang, H.C.; Wang, J.; Li, X.Y.; You, H.; Li, X.Z.; Pei, C.J.; Huang, X.; Li, H. Direct CVD Growth of MoS2 on Chemically and
Thermally Reduced Graphene Oxide Nanosheets for Improved Photosensivity. *APL Mater.* **2021**, *9*, 051105. [CrossRef]

26. Zhang, W.J.; Chuu, C.P.; Huang, J.K.; Chen, C.H.; Tsai, M.L.; Chang, Y.H.; Liang, C.T.; Chen, Y.Z.; Chuhe, Y.L.; He, J.H.; et al.
Ultrahigh-Gain Photodetectors Based on Atomically Thin Graphene-MoS2 Heterostructures. *Sci. Rep.* **2014**, *4*, 3826. [CrossRef]

27. Gao, S.; Wang, Z.Q.; Wang, H.D.; Meng, F.X.; Wang, P.F.; Chen, S.; Zeng, Y.H.; Zhao, J.L.; Hu, H.G.; Cao, R.; et al. Graphene/MoS2/MoS2/Graphene Vertical Heterostructure-Based Broadband Photodetector with High Performance. *Adv. Mater. Interfaces* **2021**, *8*, 2001730. [CrossRef]

28. Rohizat, N.S.; Ripain, A.H.A.; Lim, C.S.; Tan, C.L.; Zakaria, R. Plasmon-Enhanced Reduced Graphene Oxide Photodetector with
Monometallic of Au and Ag Nanoparticles at VIS-NIR Region. *Sci. Rep.* **2021**, *11*, 19688. [CrossRef]

29. Liu, Y.; Cheng, R.; Liao, L.; Zhou, H.L.; Bai, J.W.; Liu, G.; Liu, L.X.; Huang, Y.; Duan, X.F. Plasmon Resonance Enhanced
Multicolour Photodetection by Graphene. *Nat. Commun.* **2011**, *2*, 579. [CrossRef]

30. Brito, J.L.; Ilija, M.; Hernandez, P. Thermal and Reductive Decomposition of Ammonium Thiomolybdates. *Thermochim. Acta*
**1995**, *256*, 325–338. [CrossRef]

31. Mao, Y.; Dong, N.N.; Wang, L.; Chen, X.; Wang, H.Q.; Wang, Z.X.; Kislyakov, I.M.; Wang, J. Machine Learning Analysis of Raman
Spectra of MoS2. *Nanomaterials* **2020**, *10*, 2223. [CrossRef]

32. Lai, Y.Y.; Yeh, Y.W.; Tsou, A.J.; Chen, Y.Y.; Wu, Y.S.; Cheng, Y.J.; Kuo, H.C. Dependence of Photosensivity and On/Off Ratio on
Quantum Dot Density in Quantum Dot Sensitized MoS2 Photodetector. *Nanomaterials* **2020**, *10*, 1828. [CrossRef]

33. Fang, X.R.; Wei, P.; Wang, L.; Wang, X.S.; Chen, B.; He, Q.Y.; Yue, Q.Y.; Zhang, J.D.; Zhao, W.; Wang, J.L.; et al. Transforming
Monolayer Transition-Metal Dichalcogenide Nanosheets into One-Dimensional Nanoscrolls with High Photosensivity. *ACS Appl. Mater. Inter.*
**2018**, *10*, 13011–13018. [CrossRef]

34. Seo, D.B.; Trung, T.N.; Bae, S.S.; Kim, E.T. Improved Photo electrochemical Performance of MoS2 through Morphology-Controlled
Chemical Vapor Deposition Growth on Graphene. *Nanomaterials* **2021**, *11*, 1585. [CrossRef]

35. Wang, L.; Yue, Q.Y.; Pei, C.J.; Fan, H.C.; Dai, J.; Huang, X.; Li, H.; Huang, W. Scrolling Bilayer WS2/MoS2 Heterostructures for
High-Performance Photo-Detection. *Nano Res.* **2020**, *13*, 959–966. [CrossRef]

36. Yue, Q.Y.; Wang, L.; Fan, H.C.; Zhao, Y.; Wei, C.; Pei, C.J.; Song, Q.S.; Huang, X.; Li, H. Wrapping Plasmonic Silver Nanoparticles
inside One-Dimensional Nanoscrolls of Transition-Metal Dichalcogenides for Enhanced Photosensivity. *Inorg. Chem.* **2021**, *60*,
4226–4235. [CrossRef]

37. Zhao, Y.; You, H.; Li, X.Z.; Pei, C.J.; Huang, X.; Li, H. Solvent-Free Preparation of Closely Packed MoS2 Nanoscrolls for Improved
Photosensivity. *ACS Appl. Mater. Inter.* **2012**, *14*, 9515–9524. [CrossRef]

38. Xu, H.; Han, X.Y.; Dai, X.; Liu, W.; Wu, J.; Zhu, J.T.; Kim, D.Y.; Zou, G.F.; Sablon, K.A.; Sergeev, A.; et al. High Detectivity and
Transparent Few-Layer MoS2/Graphene Heterostructure Photodetectors. *Adv. Mater.* **2018**, *30*, 1706561. [CrossRef]

39. Naqi, M.; Kaniselvan, M.; Choo, S.; Han, G.; Kang, S.; Kim, E.; Yoon, Y.; Kim, S. Ultrahigh Sensitivity Multilayer MoS2-Based
Photodetector with Permanently Grounded Gate Effect. *Adv. Electron. Mater.* **2020**, *6*, 1901256. [CrossRef]