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## Metal Decoration Effects on the Gas-Sensing Properties of 2D Hybrid-Structures on Flexible Substrates

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**Abstract:** We have investigated the effects of metal decoration on the gas-sensing properties of a device with two-dimensional (2D) molybdenum disulfide (MoS<sub>2</sub>) flake channels and graphene electrodes. The 2D hybrid-structure device sensitively detected NO<sub>2</sub> gas molecules (>1.2 ppm) as well as NH<sub>3</sub> (>10 ppm). Metal nanoparticles (NPs) could tune the electronic properties of the 2D graphene/MoS<sub>2</sub> device, increasing sensitivity to a specific gas molecule. For instance, palladium NPs accumulate hole carriers of graphene/MoS<sub>2</sub>, electronically sensitizing NH<sub>3</sub> gas molecules. Contrarily, aluminum NPs deplete hole carriers, enhancing NO<sub>2</sub> sensitivity. The synergistic combination of metal NPs and 2D hybrid layers could be also applied to a flexible gas sensor. There was no serious degradation in the sensing

performance of metal-decorated MoS<sub>2</sub> flexible devices before/after 5000 bending cycles. Thus, highly sensitive and durable gas sensor could be achieved through the metal-decorated 2D hybrid-structure, offering a useful route to wearable electronic sensing platforms.

**Keywords:** MoS<sub>2</sub>; graphene; 2D hybrid-structure; metal decoration; flexible gas sensor

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## 1. Introduction

Two-dimensional (2D) graphene has evoked considerable interest in diverse potential applications [1–5]. 2D graphene has been developed for a long time and primarily employed as a transparent conductor for electronic applications [6] and indeed, it is in the middle of vital advances toward practical applications [7]. In recent years, 2D layered transition metal dichalcogenides (TMDs) have been also attracting much attention since they possess extremely large surface-to-volume ratios, low power consumption, high process compatibility, and inherent flexibility [8–16]. The successful demonstration of 2D MoS<sub>2</sub> for based field-effect transistors [17–19], photodetectors [20,21], and gas sensors [22–26] have proved its outstanding physical properties.

The ultimate goal of the 2D nanomaterial research field is to atomically build 2D architectures with various van der Waals (vdW) interactions, which is referred to as the vdW heterostructure [27–29]. Strong covalent bonds in-plane and relatively weak vdW interactions out-of-plane provide the structural stability for these atomic-scale heterostructures [27]. Thus, various types of the heterostructures have been intensively investigated recently [28,29]. In particular, intense studies have been concentrated on 2D TMD-graphene hybrid-system for field-effect transistor [30] and photonic applications [31]. There are few studies about sensing platforms consisting of all 2D materials, which must be one of breakthrough pathways toward next-generation electronic sensors. Also, functionalization on the 2D materials is essentially required for tuning and optimizing gas-sensing performance. Furthermore, reliable gas-sensing capability of the 2D materials for a futuristic wearable sensing component should be established on a flexible substrate. In this context, gas-sensing tunability and mechanical flexibility can be achieved concurrently utilizing metal-decoration method and all 2D material platforms

In this work, we report on the effect of metal-decoration on the gas-sensing properties of 2D hybrid-structures consisting of molybdenum disulfide (MoS<sub>2</sub>) flakes and graphene electrodes. The device showed an obviously higher response to NO<sub>2</sub> gas molecules (>1.2 ppm) as well as NH<sub>3</sub> (>10 ppm). It was found that metal nanoparticles (NPs) increase the selectivity for a certain gas molecule. Palladium NPs enhanced the response to NH<sub>3</sub> gas molecule with respect to NO<sub>2</sub>. However, aluminum NPs improved NO<sub>2</sub> sensitivity. The synergistic combination of metal NPs and the 2D hybrid layers could be also employed to form Pd:MoS<sub>2</sub> flexible devices, showing no serious change in sensing performance even after 5000 bending cycles. Thus, metal-decorated 2D hybrid-structures could enable highly sensitive and durable gas sensors for wearable electronic sensing platforms.

## 2. Experimental Section

### 2.1. CVD Synthesis of Graphene

A Ni/Ti film with thickness of 300/30 nm was deposited on a SiO<sub>2</sub>/Si wafer using an e-beam evaporator. In order to remove the oxide layer formed on the Ni film, the wafer was annealed at 300 °C under gas condition with Ar (2000 sccm)/H<sub>2</sub> (80 sccm). Finally, the graphene film was synthesized at 900 °C under Ar (2000 sccm)/H<sub>2</sub>(80 sccm)/CH<sub>4</sub> (20 sccm) for 5 min, and then the quartz tube was cooled.

### 2.2. Fabrication of Gas-Sensing Devices Consisting of MoS<sub>2</sub> Channels and Graphene Electrodes

We exfoliated multilayer MoS<sub>2</sub> flakes for the active channel using a conventional Scotch tape method [32] and then transferred them onto a SiO<sub>2</sub>/Si substrate. A multilayer graphene film for electrodes, synthesized on another Si substrate with Ni film using CVD, was patterned using conventional photolithography and reactive ion etching (RIE; O<sub>2</sub>, 20 sccm; pressure, 200 mTorr; and power, 50 W). After spin-coating a poly(methyl methacrylate) (PMMA, 495k, A2, MicroChem, Westborough, MA, USA) supporting layer and then etching Ni film, the patterned graphene electrode was then delivered onto the SiO<sub>2</sub>/Si substrate with MoS<sub>2</sub> flakes. The flexible device needed an additional transfer process as follows: After spin-coating PMMA again onto the SiO<sub>2</sub>/Si substrate, the entire device region including MoS<sub>2</sub> and graphene was transferred onto a polyimide flexible substrate by etching the SiO<sub>2</sub> sacrificial layer using buffered oxide etchant. Finally, the PMMA layer was removed with acetone.

### 2.3. Metal-Decoration on MoS<sub>2</sub>-Based Devices

Metal NPs were deposited on transferred MoS<sub>2</sub> flakes using a thermal evaporator. Specifically, Pd or Al metal with very thin thickness of 1 nm, monitored by a quartz crystal thickness monitor, was deposited on the MoS<sub>2</sub> at deposition rate of ~0.3 Å/s under pressure of ~10<sup>-6</sup> torr. Metal (Pd or Al) atoms nucleate on the atomically flat surface of MoS<sub>2</sub> and then coalescence happens *via* a movement of the atoms, forming NPs. No post treatment was required for the formation of such NPs.

### 2.4. Gas-Sensing Measurement

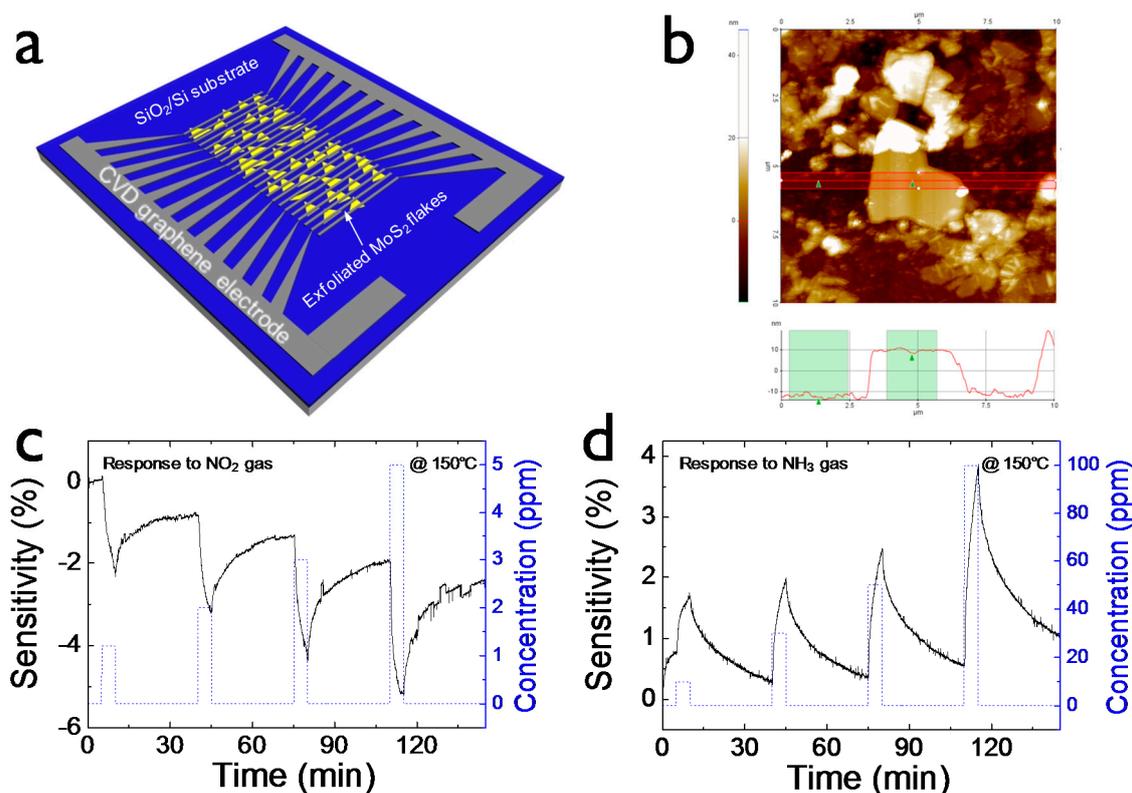
Gas-sensing measurements were carried out under analyte gas (NO<sub>2</sub> or NH<sub>3</sub>) diluted with dry air in a closed chamber. Concentrations of analyte gases were modulated by changing the flow ratio of analyte to air gas. Recovery of sensing test was done by supplying dry air and heating the device. Using a 2401 source meter (Keithley, Cleveland, OH, USA) a resistance signal of the gas-sensing devices kept monitored. An operation temperature of 150 °C was selected for optimizing the gas-sensing characteristics [24].

## 3. Results and Discussion

### 3.1. Gas-Sensing Characteristics of MoS<sub>2</sub> with Graphene Electrode

Figure 1a shows a schematic drawing of the gas-sensing device (referred to as graphene/MoS<sub>2</sub> device) comprised of mechanically exfoliated MoS<sub>2</sub> flakes and CVD-synthesized graphene which function as an

active channel for gas molecule detection and electrode for charge collection, respectively. Interdigitated electrode array structure was selected for higher device yield by increasing a probability that MoS<sub>2</sub> flakes bridge two graphene electrode lines. The height of the MoS<sub>2</sub> flakes connecting two graphene electrode lines was measured to be approximately 20 nm (Figure 1b). Flakes randomly distributed on the substrate have some thickness variation in the range of a few tens of nanometer scale.



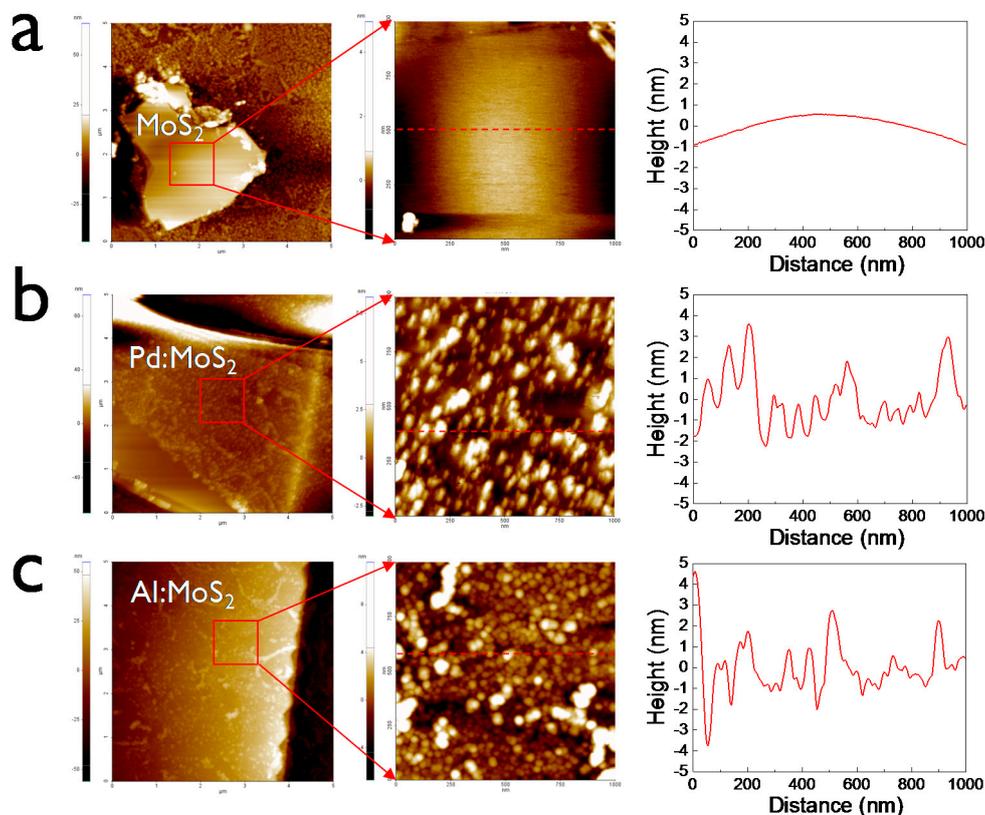
**Figure 1.** (a) Schematic image of the gas-sensing device consisting of mechanically exfoliated MoS<sub>2</sub> flake channels and CVD-synthesized graphene electrodes; (b) AFM morphology of MoS<sub>2</sub> flake connecting patterned graphene lines; Bottom indicates a height profile of MoS<sub>2</sub>. Transient response to (c) NO<sub>2</sub> concentration of 1.2 to 5 ppm and (d) NH<sub>3</sub> concentration of 10 to 100 ppm, respectively. All gas-sensing tests were carried out at an operating temperature of 150 °C.

We monitored the resistance change of the graphene/MoS<sub>2</sub> device when exposed to analyte gas (NO<sub>2</sub> or NH<sub>3</sub>). Sensitivity was defined as  $\Delta R/R_a = (R_g - R_a)/R_a$ , where  $R_a$  and  $R_g$  indicates the resistance of the sensor under air and analyte gas, respectively. Figure 1c shows the sensitivity of the graphene/MoS<sub>2</sub> sensing device under exposure to NO<sub>2</sub> gas concentrations of 1.2, 2, 3, and 5 ppm. All gas-sensing tests were carried out at 150 °C operating temperature since its gas-sensing performance was optimized under this condition. Gas molecules can be strongly adsorbed onto the surface of 2D materials [33]. For desorption of the adsorbed molecules, a thermal or light energy source is necessary, enabling reversible sensing characteristics. Specifically, NO<sub>2</sub> gas molecules resulted in negative sensitivity (*i.e.*, resistance decrease). With the increase of NO<sub>2</sub> concentration, the absolute sensitivity value also increased. On the contrary, NH<sub>3</sub> gas molecules caused positive sensitivity (*i.e.*, resistance increase), as seen in Figure 1d. As the NH<sub>3</sub> concentration increased from 10 to 100 ppm, the sensitivity also increased. At the same

concentration, the response to  $\text{NO}_2$  was much more sensitive responded than to  $\text{NH}_3$ . It is responsible for relatively high adsorption energy of  $\text{NO}_2$  molecules [34,35]. The resistance change of the gas-sensing device is based on charge-transfer phenomena between gas molecules and 2D materials [26]. It is well-known that  $\text{NO}_2$  and  $\text{NH}_3$  analyte gas molecules commonly behave as electron acceptors and electron donors, respectively [5]. Interestingly, the graphene/ $\text{MoS}_2$  gas sensor worked as if it is a p-type device. We propose that the high work function of graphene (4.7 eV) makes it easily hole transport toward the valence band edge of  $\text{MoS}_2$  [36]. It is unlike the n-type behavior commonly found in low work function metal- $\text{MoS}_2$  junction devices where electrons are a major carriers governing the charge transport. Thus, hole carriers involved in charge transfer of graphene/ $\text{MoS}_2$  device are modulated by gas molecules.

### 3.2. Metal Decoration Effect on Graphene/ $\text{MoS}_2$ Gas-Sensing Properties

In order to investigate the influence of metal NPs on the gas-sensing properties of  $\text{MoS}_2$ , various metal NPs were deposited on the  $\text{MoS}_2$ . We made three kinds of sensing devices with bare  $\text{MoS}_2$  and  $\text{MoS}_2$  decorated with Pd or Al NPs (denoted as  $\text{MoS}_2$ , Pd: $\text{MoS}_2$ , and Al: $\text{MoS}_2$  device, respectively). Before the electrical tests, we examined the surface morphology and height profiles of the metal-decorated  $\text{MoS}_2$ . Basically, the morphology of  $\text{MoS}_2$  without metal NPs was ultra-smooth and flat (Figure 2a), indicating the layered structure of van der Waals materials.



**Figure 2.** AFM morphology images and height profiles of (a)  $\text{MoS}_2$ , (b) Pd: $\text{MoS}_2$ , and (c) Al: $\text{MoS}_2$  on Si/ $\text{SiO}_2$  substrate.

As shown in Figure 2b, Pd NPs were randomly distributed on the MoS<sub>2</sub> surface and they aggregated in part. On the other hand, in the case of Al:MoS<sub>2</sub>, Al formed relatively dense and more fine particles. The morphology properties might strongly depend on physical interaction between MoS<sub>2</sub> and metals. The relatively weak interaction between Al metal and MoS<sub>2</sub> forms fine NPs. To investigate the effect of metal NPs on the gas-sensing properties, we checked the gas-sensing characteristics before/after the formation of metal NPs. After the deposition of Pd NPs on MoS<sub>2</sub>, NH<sub>3</sub> sensitivity (@ 100 ppm) increased by 70% while NO<sub>2</sub> sensitivity (@ 5 ppm) decreased significantly (Figure 3a). However, the opposite trend was observed for the case of Al:MoS<sub>2</sub> (Figure 3b). Specifically, the NO<sub>2</sub> sensitivity of the Al:MoS<sub>2</sub> device was enhanced by around 40%. On the contrary, Al NPs decreased the response to NH<sub>3</sub> slightly. Also, we tested the gas response characteristics under different concentrations. From the gas-sensing test results under various gas concentrations (Figure 3c), it was found that Al NPs on MoS<sub>2</sub> film is most effective to detect NO<sub>2</sub> gas. Pd NPs was more helpful for detecting NH<sub>3</sub> gas on MoS<sub>2</sub>. Consequently, Pd NPs improved NH<sub>3</sub> selectivity to NO<sub>2</sub> while Al NPs increased the selectivity of NO<sub>2</sub> to NH<sub>3</sub>. In particular, the sensor with a continuous metal network film shows negligible gas responses since the charge transport of the device is dominated by the metal conductive path rather than the MoS<sub>2</sub> semiconducting channel.

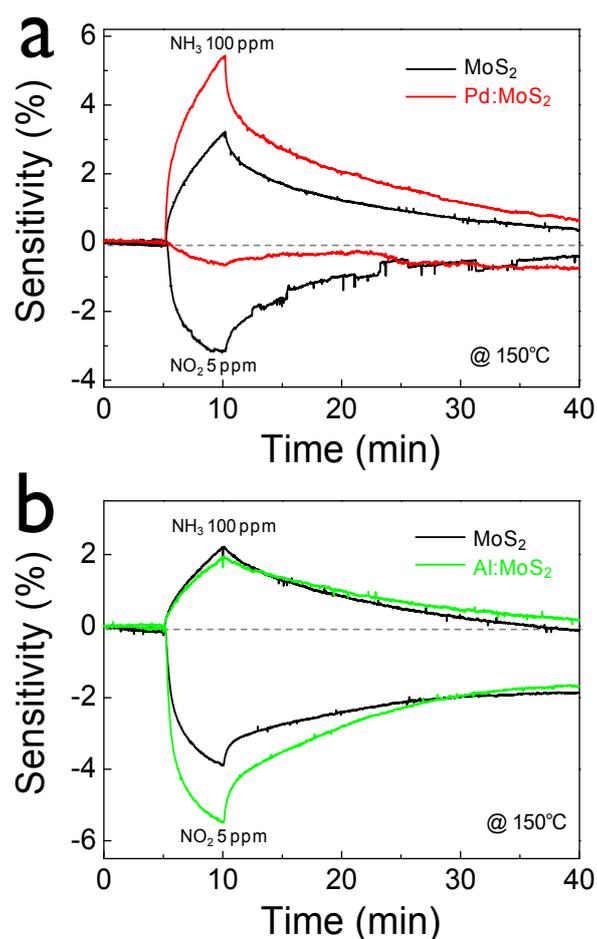
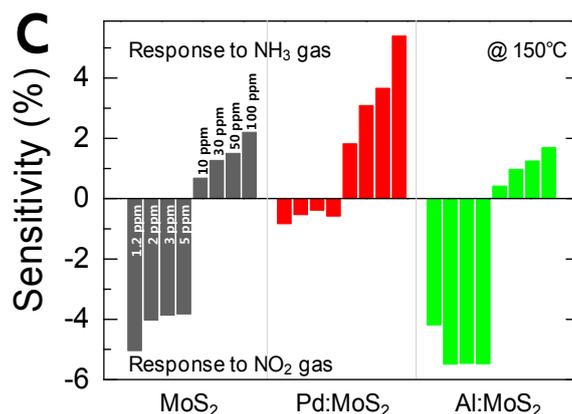


Figure 3. Cont.

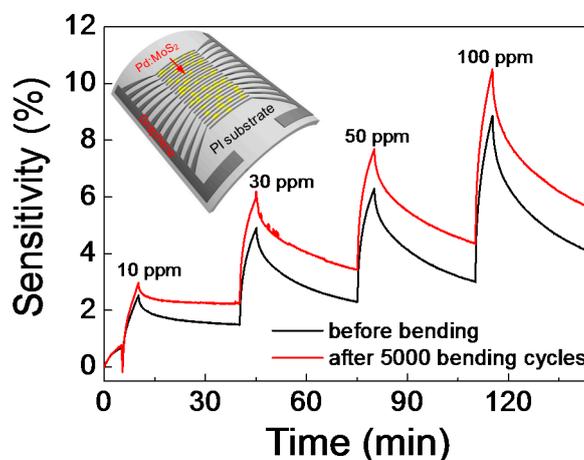


**Figure 3.** Transient gas responses under NH<sub>3</sub> 100 ppm and NO<sub>2</sub> 5 ppm before/after (a) Pd decoration on MoS<sub>2</sub> and (b) Al decoration on MoS<sub>2</sub>; (c) Sensitivity summary of MoS<sub>2</sub>, Pd:MoS<sub>2</sub>, and Al:MoS<sub>2</sub>.

The effects of metal decoration on sensing properties have been explained by chemical sensitization or electronic sensitization [37]. A chemical sensitization effect indicates that metal NPs on a sensing film increase the overall active sensing surface area and thereby the adsorption sites of gas molecules. Electronic sensitization can be also considered as a potential mechanism of the sensitivity tuning for each different metal [37]. Thus, it would be potentially agreeable that changes in the sensitivity in our devices are dominated by the latter model rather than the former. For more clarity, the band-bending attributed to the charge transfer between metal (Pd or Al) and semiconductor MoS<sub>2</sub> was proposed (Figure S1 of Supplementary Information). Pd metal with high work function increases the hole concentration of the graphene/MoS<sub>2</sub> device [38]. Such a p-doping effect of Pd on MoS<sub>2</sub> enhances the gas response to NH<sub>3</sub> (an electron donor molecule). This is similar to the previous study in which SnO<sub>2</sub> nanocrystals act as strong p-type dopants for MoS<sub>2</sub> nanosheets [39]. However, low work function Al metal depletes the hole carriers of the device and thereby increases the sensitivity of NO<sub>2</sub> (an electron withdrawing molecule). Metal decoration on graphene/MoS<sub>2</sub> hybrid structures modifies the electronic properties, which in turn modulates the gas-sensing characteristics. Thus, it would be a useful and simple strategy for achieving a highly selective sensor to a certain analyte gas molecule.

Next, we turned our focus to potential uses of the flexible gas sensor. The whole device region of Pd:MoS<sub>2</sub> including graphene electrodes was transferred from a SiO<sub>2</sub>/Si wafer to a polyimide (PI) substrate (see Experimental Section for the detailed method). The NH<sub>3</sub> gas-sensing characteristics of the device were obtained at 150 °C, which is necessary for reversible sensing tests (Figure 4). The glass transition temperature of the PI film is high over 250 °C so that the device can endure the heating conditions. Bent condition with a bending radius of 1.9 mm was applied to the flexibility test. The inset of Figure 4 shows a schematic image of Pd:MoS<sub>2</sub> with graphene electrodes on PI substrate. Even if there is an upward shift in sensitivity with increasing gas concentration, the device did not experience any serious change in terms of sensing performance of the Pd:MoS<sub>2</sub> flexible device before/after 5000 bending cycles. The cyclic gas-sensing performance was also tested for feasibility, showing a highly reproducible sensing behavior over repetitive sensing cycles (Figure S2 of Supplementary Information). Thus, highly sensitive and reliable gas-sensing performance was achieved in the flexible

2D hybrid structure with metal NPs, indicating a promising route toward the development of wearable electronic sensors.



**Figure 4.**  $\text{NH}_3$  gas response characteristics of flexible Pd:MoS<sub>2</sub> gas-sensing device before/after the bending cycle test. The inset shows a 3D schematic image of the bent device.

#### 4. Conclusions

Herein, we demonstrated metal-decorated gas-sensing devices based on a 2D graphene/MoS<sub>2</sub> hybrid structure. Metal NPs could modulate the electronic properties of the 2D device, thereby modulating the selectivity towards a certain gas molecule. Specifically, Pd NPs electronically sensitized  $\text{NH}_3$  gas molecules while Al NPs enhanced  $\text{NO}_2$  sensitivity. The hybridization process of metal NPs and 2D materials could enable highly sensitive flexible gas sensors along with high bending endurance and stability. Ultimately, the strategy could open an avenue toward wearable sensing platforms.

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#### Author Contributions

B.C. and M.G.H. designed and supervised the experiments; B.C., J.Y., S.K.L., A.R.K., and S.-Y.C. did the experiments; B.C., J.Y., D.-H.K., K.-H.L., B.H.L., and H.C.K. analyzed the data; B.C., J.Y., and M.G.H. wrote the paper.

#### Conflicts of Interest

The authors declare no conflict of interest.

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