

FLEXIBLE AND TRANSPARENT BENZENE SENSOR USING FUNCTIONALIZED FEW-LAYER MoS₂

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ABSTRACT

We demonstrated a flexible and transparent benzene sensor using cobalt-metalloporphyrin (Co-MPP)-functionalized few-layer MoS₂ as sensing material for the first time. The sensor detected benzene down to 10 ppm at room temperature. The functionalization with Co-MPP catalysts enhanced sensitivity ($\Delta R/R_0$) over 250% compared to pristine MoS₂. The fabricated sensor showed good mechanical flexibility and optical transparency, which is advantageous for a wide variety of chemical sensing applications.

KEYWORDS

MoS₂, functionalization, benzene, gas sensor, flexible, transparent

INTRODUCTION

VOCs generally refer to organic chemicals existing as vapor at room temperature, which may significantly degrade indoor air quality and threaten human health. One of the popular symptoms caused by VOCs is sick building syndrome (SBS), which occurs as a result of exposure to harmful chemical toxins in indoor place. Benzene is one of the most well-known VOCs, which is carcinogenic and can also increase the risk of other illnesses such as aplastic anemia, acute leukemia and bone marrow abnormalities.

Recently, two-dimensional (2D) layered nanomaterials have been actively studied for sensors [1], solar cells [2], supercapacitors [3], batteries [4], and electrocatalysis applications [5] because of their unique structure and properties. Among them, Molybdenum disulfide (MoS₂), which is a transition metal dichalcogenide, has attracted a lot of interest because of its large surface-to-volume ratio, direct band gap from 1.2 eV for bulk to 1.9 eV for monolayer, and outstanding field-effect transistor (FET) behavior [6, 7]. The unique properties of few-layered MoS₂ nanosheets make them as a promising sensing element for highly sensitive gas detection at room temperature. Several gas sensors based on MoS₂ nanosheets to detect NO [8], NO₂ [9-11], NH₃ [10, 11, 12], and triethylamine [13] were developed previously. On the other hand, metalloporphyrin (MPP) is well known as a binding material for VOCs and also as adsorption sites to promote sensitive and selective detection of VOCs. For example, MPP-functionalized ZnO [14], SnO₂ [14, 15], and CNT [16] showed enhanced sensitivity toward VOCs.

In this work, we utilized few-layer MoS₂ as sensing material to detect benzene, and it was functionalized with Co-MPP catalysts for the first time to achieve enhanced sensitivity. We also demonstrated flexible and transparent

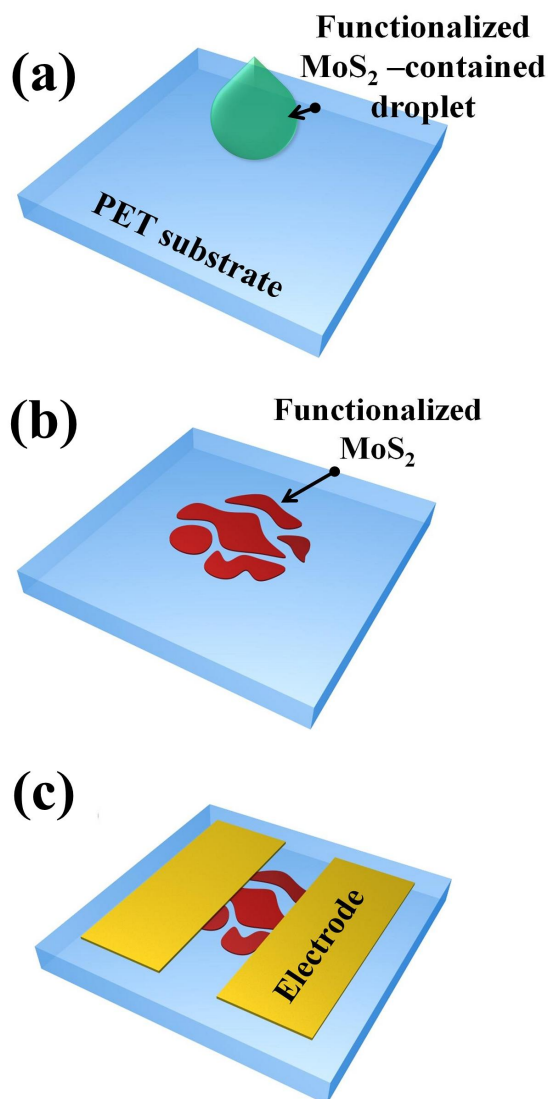


Figure 1: Fabrication steps of MoS₂-based sensor. (a) The functionalized MoS₂-contained solution is dropped on PET substrate and (b) dried at the temperature of 100°C. (c) Metal (Cr/Au) electrodes are patterned with 5 μ m-gap and two-terminal devices are formed.

sensor using polyethylene terephthalate (PET) substrate by utilizing the outstanding optical and mechanical properties of MoS₂.

FABRICATION

Figure 1 depicts the fabrication steps of the sensor on PET substrate. Firstly, the MoS₂-contained solution is mixed

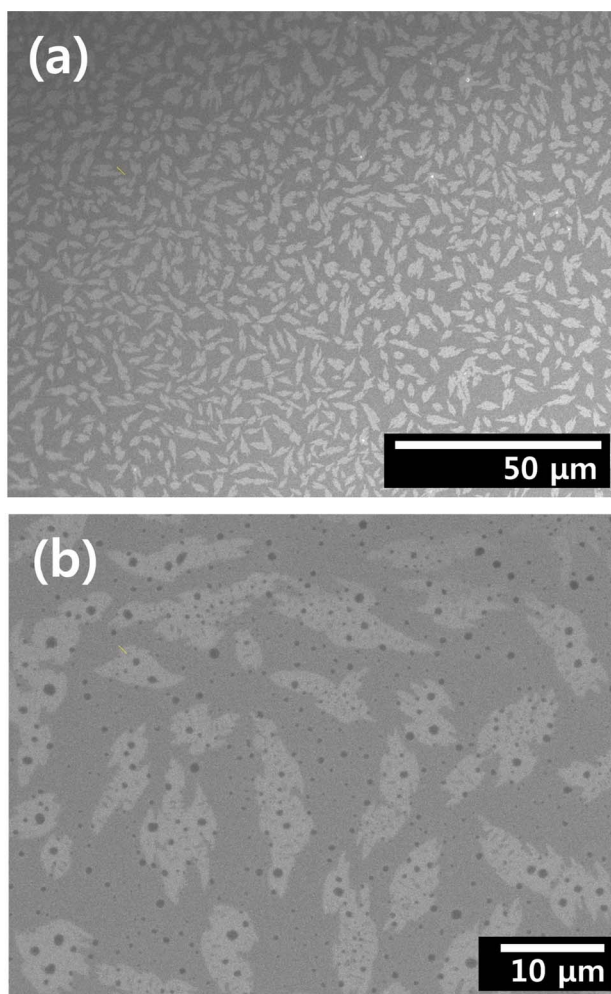


Figure 2: SEM images of (a) the pristine and (b) the Co-MPP-functionalized MoS_2 on Si substrate after the drop casting and drying process. The bright area in the figure is the MoS_2 . Because the length of each MoS_2 piece is around $10\ \mu\text{m}$, two terminal devices could easily be batch-fabricated by patterning the metal electrodes with gap of $5\ \mu\text{m}$ without precise alignments.

with the Co-MPP-contained solution for functionalization of MoS_2 as shown in Figure 1(a). Then the functionalized MoS_2 -contained solution is dropped on PET substrate and dried at the temperature of 100°C (Figure 1(b)). Finally, metal (Cr/Au) was patterned on top of the deposited MoS_2 to form electrodes (Figure 1(c)).

RESULTS AND DISCUSSION

Figure 2 shows the scanning electron microscope (SEM) images of (a) the pristine MoS_2 and (b) the Co-MPP-functionalized MoS_2 dispersed on Si substrate. It is clearly shown that the MoS_2 pieces were uniformly distributed on the substrate after the drop casting and drying. Because the length of single piece of MoS_2 is around $10\ \mu\text{m}$, two terminal devices were easily obtained by patterning the

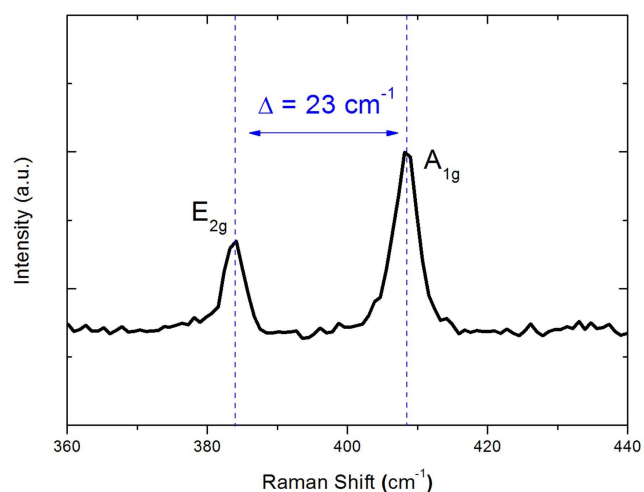


Figure 3: Raman spectrum of MoS_2 . The Δ represents the distance between in-plane E_{2g} mode and out-of-plane A_{1g} mode, which allows the determination of the number of MoS_2 layers. In this study, the number of layers is estimated to be three. The Raman measurement was performed using a $521\ \text{nm}$ laser.

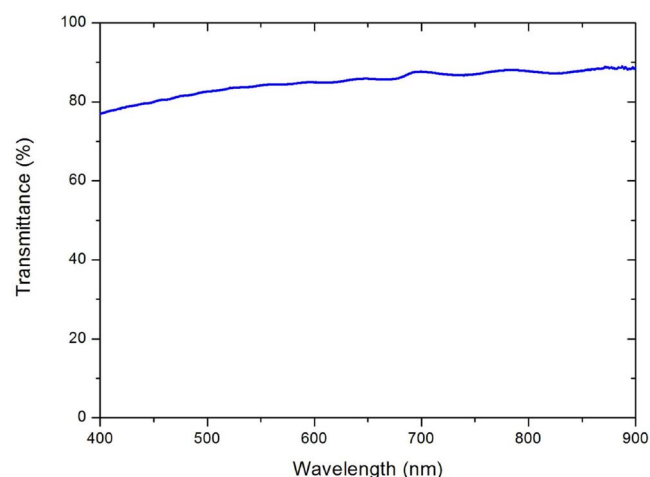


Figure 4: Optical transmittance of the functionalized MoS_2 on PET substrate. Figure exhibits the good mechanical flexibility and optical transparency of the fabricated sensor.

metal electrodes with a gap of $5\ \mu\text{m}$ without precise alignment to MoS_2 pieces. The Raman spectrum of the MoS_2 is shown in Figure 3. This was obtained using a 521-nm Ar-ion laser irradiated on the MoS_2 nanosheets with power of $0.5\ \text{mW}$ and a spot diameter of $1\ \mu\text{m}$. The Raman shift Δ represents the distance between the in-plane E_{2g} mode and out-of-plane A_{1g} mode, which allows the determination of the number of MoS_2 layers. In this work, the average number of layers is estimated to be three. The optical transmittance for different wavelength of light of the functionalized MoS_2 on

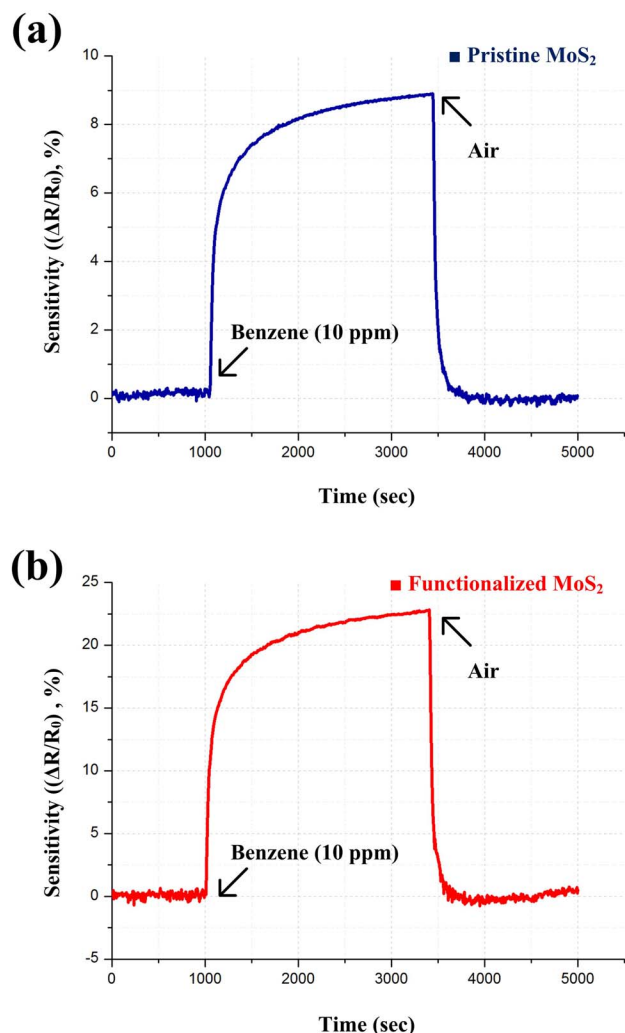


Figure 5: Sensing performance of the functionalized MoS₂ and the pristine one at room temperature. Real time response of (a) the pristine and (b) the functionalized MoS₂ sensors at the exposure to benzene of 10 ppm. The functionalization with Co-MPP catalysts enhanced sensitivity by 250% at an identical concentration of benzene.

the PET substrate is shown in Figure 4. The MoS₂-based sensors were exposed to benzene of 10 ppm as shown in Figure 5. Figure 5(a) shows real time response of the pristine MoS₂ after exposure to benzene. The sensitivity ($\Delta R/R_0$) of the sensor is defined as a relative change of resistance (ΔR) with respect to initial resistance (R_0), and the measured sensitivity of pristine MoS₂ was 8.9%. The total flow rate of air and benzene was remained constant, while the concentration of benzene was changed. Figure 5(b) shows the sensitivity of the functionalized MoS₂ for the same concentration of benzene. The measured sensitivity of the functionalized one was 22.7%. The functionalization with Co-MPP enhanced the sensitivity by 250% compared to the pristine MoS₂. The improvement of sensitivity is attributed to

the increased adsorption sites by MPP.

CONCLUSIONS

In summary, we developed flexible and transparent benzene sensor using few-layer MoS₂ nanosheets with solution process on PET substrate. The MoS₂ nanosheets were functionalized by Co-MPP to improve the response to benzene molecules. The functionalized MoS₂ showed enhanced sensitivity over 250% compared to the pristine one, while the sensor showed good mechanical flexibility and optical transparency. The sensors were batch-fabricated by simple process, without any requirement of precise alignment.

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