An indoor light-activated 3D cone-shaped MoS2 bilayer-based NO gas sensor with PPb-level detection at room-temperature†

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Utilization of light to boost the performance of gas sensors allows us to operate sensor devices at room temperature. Here, we, for the first time, demonstrated an indoor light-activated 3D cone-shaped MoS2 bilayer-based NO gas sensor with ppb-level detection operated at room-temperature. Large-area cone-shaped (CS)-MoS2 bilayers were grown by depositing 2 nm-thick MoO3 layers on a 2'' three-dimensional (3D) cone-patterned sapphire substrate (CPSS) followed by a sulfurization process via chemical vapor deposition. Because the exposed area of MoS2 bilayers is increased by 30%, the CS-MoS2 gas sensor (GS) demonstrated excellent performance with a response of ∼470% and a fast response time of ∼25 s after exposure to 1 ppm of NO gas illuminated by ultraviolet (UV) light with a wavelength of 365 nm. Such extraordinary performance at room temperature is attributed to the enhanced light absorption because of the light scattering effect caused by the 3D configuration and photo-desorption induced by UV illumination. For NO concentrations ranging from 2 ppm down to 0.06 ppm, the CS-MoS2 GS demonstrated a stable sensing behavior with a high response and fast response time (470% and 25 s at 2 ppm NO) because of the light absorption enhanced by the 3D structure and photo-desorption under constant UV illumination. The CS-MoS2 GS exhibits a high sensitivity (∼189.2 R% ppm⁻¹), allowing the detection of NO gas at 0.06 ppm in 130 s. In addition, the 3D cone-shaped structure prolonged the presence of sulfur vapor around MoO3, allowing MoO3 to react with sulfur completely. Furthermore, the CS-MoS2 GS using an indoor lighting to detect NO gas at room temperature was demonstrated for the first time where the CS-MoS2 GS exhibits a stable cycling behavior with a high response (165% at 1 ppm NO) in 50 s; for concentration as low as ∼0.06 ppm, the response of ∼75% in 150 s can be achieved.

Introduction

The rapid development of heavy industry induces severe air pollution. These pollutants need to be monitored and detected promptly because they are often harmful. Of those air pollutants generated on a daily basis, nitrogen oxides (NOx) are critical pollutants that are associated with acid rain and surface ozone pollution.1–3 In the past, metal oxide-based gas sensors, such as ZnO, TiO2, and SnO2/ZnO4–6-based gas sensors, had been intensively studied and extensively employed in safety, environmental and medical applications, for detecting a variety of air pollutants.7 However, these metal oxide-based gas sensors require a high working temperature for device activation. Recently, through material engineering such as decoration of precious metal particles and device design, metal oxide-based gas sensors have been able to operate at room temperature, whereas, in terms of the gas response, there is still space to be improved.8,9 For example, the working temperature of a ZnO-based gas sensor has to be set to 300–500 °C to record the distinct variation in its resistance and desorb the targeted gas owing to the large activation energy of the associated surface redox reaction.10,11 Although the performance of metal oxide-based gas sensors can be significantly improved at high temperatures, such high working temperatures preclude the detection of some toxic and explosive gases. Most importantly, sensors that require heating are not only less energy-efficient, but also difficult to integrate into...
Al₂O₃ and reduced graphene oxide (r-GO) nanosheets, allowing gas species, such as nitric oxide (NO), to be sensed because of their distinctive properties, such as excellent light-matter interaction, good electronic transport, and exceedingly high surface-to-volume ratio. In particular, the inherent feature of a high surface area makes 2D materials more competitive for gas sensor applications. Chemical vapor deposition (CVD)-grown and mechanically exfoliated MoS₂ has the potential of being an excellent material for sensing specific gas species, such as nitric oxide (NO), nitric dioxide (NO₂), and ammonia (NH₃) owing to its larger adsorption energy and low cost of material manufacturing. In 2013, Late et al. have explored the gas sensing characteristics of a single layer of MoS₂ under green light (wavelength, 532 nm) irradiation. They discovered that both the response and recovery time of sensors improve with an increase in the power density of green light because a larger amount of generated electron–hole pairs can reach a dynamic equilibrium between gas molecules and surface charge more easily. Duy et al. have proposed a three-dimensional (3D) gas sensor that consisted of an atomic-layer-deposited (ALD) ultra-thin layer of Al₂O₃ and reduced graphene oxide (r-GO) nanosheets, allowing them to sense a low gas concentration because of the larger exposed area. However, the recovery time of this 3D gas sensor is longer than that of a 2D planar gas sensor, because of defects, edges and other high-energy binding sites, which resulted in slow gas desorption.

In this regard, we report a reliable and practical approach to fabricate 3D MoS₂-based gas sensors for the detection of NO gas molecules. Large-area (~2”) and highly uniform MoS₂ bilayers were synthesized on a 2” 3D cone-shaped sapphire substrate, leading to the increase in the surface area of MoS₂ bilayers. Furthermore, a CS-MoS₂ GS (cone-shaped MoS₂ gas sensor) was fabricated to detect the NO gas under illumination of UV light with a wavelength of 365 nm where the CS-MoS₂ GS exhibited excellent detection performance with a detection limit of sub-ppb levels at room temperature. The mechanism of NO gas detection by MoS₂ gas sensors upon light irradiation was discussed in detail. Finally, by utilizing the band gap of MoS₂ matching to the visible light range and 3D configuration, we demonstrate, for the first time, the indoor white light-activated CS-MoS₂ GS that can detect sub-ppb NO gas concentrations with a distinct and fast response. We believe that indoor white light-activated CS-MoS₂ GSs can be easily integrated into consumer products, home appliances and other mobile devices to enable real-time gas monitoring.

Results and discussion

It is well known that the surface roughness of a growth substrate dramatically affects the film uniformity of epitaxial 2D materials, which are grown using the vapor phase deposition process. Also, transferring a 2D material onto a non-flat substrate is not suitable to completely cover the entire patterned substrate because it can induce air bubbles, wrinkles and ribbons on the 2D film because of mismatch in the surface area. To address these issues, we proposed a straightforward and reliable approach of directly synthesizing MoS₂ on a 3D architecture substrate through the selenization process. Firstly, a 2 nm-thickness molybdenum oxide (MoO₃) film was deposited onto a 2” cone-patterned sapphire substrate (CPSS) using an electron gun vaporization system (E-gun) as shown in Fig. 1(a1). By reacting with sulfur through the chemical vapor reaction (CVR) process (Fig. 1(a2)), the MoO₃ thin film can be converted into MoS₂ layered structures as shown in Fig. 1(a3).

Note that the thickness of the MoO₃ film plays an important role in determining the number of MoS₂ layers. The detailed growth parameters are shown in the experimental session. As a result, the MoS₂ bilayers can be achieved on the 3D CPSS. Fig. 1(b) shows an image of the 2” CPSS covered by a 2 nm-thick MoO₃ film. After the sulfurization, the color of the
surface turned light yellow as a result of the CVD process, demonstrating the large-area and highly uniform growth of MoS₂ bilayers. Moreover, a confocal Raman microscopy system was used to confirm the properties of MoS₂ bilayers, including quality, numbers of layers and internal strain. Fig. 1(c) shows the Raman spectra of MoS₂ bilayers on the flat (green line) and cone-patterned (red line) substrates, respectively. The two detected peaks correspond to two prominent Raman vibration modes, E₁⁻₂g (385 cm⁻¹, in-plane vibration mode of molybdenum and sulfur) and A₁g (407 cm⁻¹, out of plane vibration mode of sulfur), and the positions of peaks were sensitive to changes in determining the numbers of MoS₂ layers. Hence, by subtracting positions of E₁⁻₂g and A₁g, we can estimate the numbers of layers. Subsequently, the subtracted values calculated for the flat and cone substrates are 22.17 cm⁻¹ and 22.88 cm⁻¹, respectively, corresponding to MoS₂ bilayers. Note that the Raman peak of the sapphire substrate is located at 417 cm⁻¹ (ref. 41) and the A₁g peak detected for the cone substrate exhibits an apparent blue shift from 406.5 cm⁻¹ to 407.21 cm⁻¹ compared with that for the flat substrate. On the basis of previous experimental results, the peak shift is reasonably attributed to the numbers of layers and strain. Fig. 1(d) shows the photoluminescence (PL) spectra of MoS₂ bilayers for the flat and cone cases. Apparently, the PL peak of MoS₂ bilayers on the sapphire is dramatically blue-shifted from 676 to 664 nm, which is in accordance with previous simulation results presented by Lu et al., who pointed out that the band gap of the MoS₂ bilayers is likely to be larger under compressive strain. Since MoS₂ bilayers were confirmed by transmission electron microscopy (TEM) measurements (Fig. 1f1–f3), the effect on the number of layers can be ruled out. As a result, the peak shift is mainly caused by the strain because of the thermal anisotropy expansion on the sapphire during the cooling process. Also, the bonding properties of the resulting MoS₂ bilayers were analyzed using X-ray photoelectron spectroscopy (XPS), and the results are shown in Fig. 1(e). Peaks located at 164.5, 163, 227.5, 230 and 233.5 eV corresponding to S 2p₁/₂, S 2p₃/₂, S 2S, Mo 3d₅/₂ and Mo 3d₃/₂ were found while no Mo⁶⁺, 3d₅/₂ located at ~236 eV was found, confirming the complete conversion from MoO₂ to MoS₂. TEM images of MoS₂ bilayers in different regions of the cone sapphire substrate were obtained to confirm the quality and uniformity of MoS₂ bilayers. Fig. 1(f1) shows the TEM image of a half cone covered by MoS₂ bilayers. The inset in Fig. 1(f1) shows the well-ordered arrangement of the cone. Next, enlarged views of a flat region in between the cone (green square) and the side of the cone (red square) are shown in Fig. 1(f2) and (f3), respectively. Obviously, the continuous MoS₂ bilayers completely cover the entire growth substrate from the cone to the flat. This is why we use MoS₂ bilayers rather than the MoS₂ monolayer as the following sensor application, while it is difficult to achieve the MoS₂ monolayer because of the discontinuous coverage as shown in Fig. S1.† Furthermore, MoS₂ bilayers had been proved to possess superior photoluminescence over the monolayer of MoS₂ as well as tunable bandgaps by applied vertical electrical field. To date, increasing the surface area, such as by creating a 3D architecture, leading to an increase in porosity, has been considered as the most efficient way to boost the sensing performance. In our case, MoS₂ bilayers were successfully synthesized on the CPSS, resulting in a 30% increase (the calculation process is detailed in Fig. S2†) in the sensing area compared with that on the flat sapphire substrate as shown in Table 1. To shed light on the sensing performance of MoS₂ bilayers on the CPSS, cone-shaped MoS₂-based gas sensors were prepared. The fabrication processes of the CS-MoS₂ GS (cone-shaped MoS₂-based gas sensor) are shown in Fig. 2(a). Finger-shaped electrodes were defined by utilizing a hard mask, followed by the deposition of Ti/Au with a thickness of 5/50 nm. Finally, a silver wire was bonded to electrodes to connect the gas sensor and the measurement system. In addition, MoS₂ bilayers grown on the flat sapphire substrate were fabricated as a gas sensor denoted as F-MoS₂ GS for comparison. Fig. 2(b) shows the images of real devices bonded using silver wires. The corresponding optical microscopy (OM) and scanning electron microscopy (SEM) images are shown in Fig. 2(c). In addition, the experimental setup for gas sensing

Table 1: Comparison of the performances of the other Se photodetectors

<table>
<thead>
<tr>
<th>Morphology of the sample</th>
<th>Total sensing area (µm²)</th>
<th>Area ratio of the CPSS/flat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat</td>
<td>5.85</td>
<td>1</td>
</tr>
<tr>
<td>CPSS</td>
<td>7.64</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Fig. 2 (a) Fabrication processes of the gas sensor. (b) Images of the gas sensor devices and (c) an OM image of a finger-shaped electrode bonded to a silver wire and confirmed by SEM. (d) I–V characteristics of (d) F-MoS₂ and (e) CS-MoS₂ illuminated by the UV light with an increased power.
measurements is shown in Fig. S3.† The concentration of NO gas was regulated using a mass flow controller. When the NO gas at the preset concentration was introduced into the system and attached to MoS2 bilayers, a change in the current was recorded in situ by using a Keithley 2400. Note that the gas sensing measurements were performed at room temperature, during which UV light with a wavelength of 365 nm was constantly irradiated on the analyzed samples. After pumping out the NO gas, the photocurrent gradually returned to its original state, which was attributed to a decrease in the resistance. The response to the NO gas was quantified by $R$ vs $t$ plots. Prior to the measurements of $R$ vs $t$ dependence, UV light of 365 nm in wavelength was constantly irradiated on the CS-MoS2 GS to “activate” MoS2 bilayers by generating the photocurrent. The radiant flux spectra of the UV light with a wavelength of 365 nm at different applied powers were confirmed where the maximal peak occurs at 365 nm as shown in Fig. S3.† Furthermore, the photoelectrical properties of devices based on CS- and F-MoS2 bilayers under the UV light of 365 nm in wavelength at different applied powers were examined as shown in Fig. 2(d) and (e). Obviously, the photocurrent measured at the CS-MoS2 bilayers is significantly higher than that measured at the F-MoS2 bilayers, which is attributed to the enhancement of light absorption assisted by the 3D configuration that is in agreement with previous reports.15,30

Fig. 3(a) shows measurements of the F-MoS2 GS with a NO concentration of 1 ppm at different powers of UV light. It is clear that the resistance increases because of the decrease in photocurrent once the device is exposed to the NO gas. For MoS2 bilayers, it shows a naturally n-type semiconducting behavior. The NO gas is considered as a reduction agent, which makes the resistance increase after the MoS2 bilayers are exposed to the NO gas because the electrons transport out of the MoS2 bilayers into NO gas, resulting in depleted n-type semiconduction into intrinsic behaviors of MoS bilayers. Detailed sensing behaviors will be discussed later. For the sensing behavior of the F-MoS2 GS, the sensing behavior quickly responds to NO gas initially while the response is slow and no saturation behavior can be found. After pumping out the NO gas, the resistance starts to decrease but it does not return to its original value after 1500 s. Moreover, the maximal resistance is proportional to the intensity of the applied light. In contrast, the CS-MoS2 GS promptly reacted to the NO gas and saturated in 30 s as shown in Fig. 3(b). Here, “Response” was defined using the following equation: 

$$R\% = \frac{R - R_0}{R_0} \times 100\%.$$ 

where $R$ is the resistance with gas and $R_0$ is the initial material resistance. Therefore, the response of the F-MoS2 GS can be quantified as 150%. However, for the CS-MoS2 GS, a response of 330% was obtained, which is 2.3 times larger than that of the F-MoS2 GS. In general, regardless of the morphology of MoS2, increasing the irradiated light intensity improved both the response and the response time, because a larger number of electrons can reach a dynamic equilibrium faster. 11-13 In addition, it was observed that the F-MoS2 GS exhibited a non-significant response once the intensity of the UV light irradiation $<\sim 20.6$ mW; nevertheless, the CS-MoS2 GS is still able to detect the NO gas under the same intensity of the UV light irradiation. Interestingly, the response time and response of our present F-MoS2 GS are much better compared with those that were reported previously owing to the constant activation by light. 46 However, the significant improvement was observed for the CS-MoS2 GS due to the 3D architecture. In fact, the benefit of creating a 3D structure to boost the device performance, such as in solar cells, has been discovered owing to the enhancement of light absorption. 54-57 Moreover, according to the previous report of utilizing SnO2 for gas sensing, it was found that applying UV light had not only increased the conductance but also increased the photo-desorption by the photochemical reaction.58,59 Herein, to the best of our knowledge, this is the first report of manipulating a 3D structure as well as a photochemical reaction for advancing the performance of a gas sensor. Different from a previous report on manufacturing a 3D platform gas sensor simply by increasing the exposure area, 49 our CS-MoS2 GS combines the advantages of both enhanced light absorption owing to the light scattering induced by the 3D architecture (Fig. S6†) and photo-desorption by a photochemical reaction, demonstrating extraordinary performance at room temperature. The F-MoS2 GS was also characterized for the high operating temperature of 100 °C. Fig. S5† shows the $I$–$V$ characteristics as a function of the operating temperatures. The conductance of MoS2 bilayers increases with the increase in temperature, implying the inherent semiconductor properties. Regarding the sensing ability test, there is no distinct
response under the exposure of NO gas with a concentration of 1 ppm at differently elevated temperatures as shown in Fig. S7(a) and S7(b), suggesting that the response of the device is not significantly determined by the heating process of sensors. Fig. 3(c) shows a single cycle of the sensing process, which can be divided into 5 steps. Each step is schematically illustrated in Fig. 3(d)–(f) to shed light on possible mechanisms of enhanced sensing ability by the 3D structure. First, MoS2 bilayers were constantly irradiated by the UV light with a wavelength of 365 nm where the energy of the UV light is higher than $E_g$ of MoS2 bilayers, resulting in the generation of electron–hole pairs (Fig. 3d). Once the NO gas molecules arrive to the surface of MoS2 bilayers, two photochemical reactions, namely the reduction process of NO and photo-desorption of NO$^-$, occur by the electron transfer process. The reduction process of NO is given by $e^- + NO (gas) \rightarrow NO^-(ads)$, for which NO gases act as the electron acceptor to trigger the transfer of electrons from the MoS2 bilayers to the NO gas molecules (State 1). The reduction of electrons may result in the broadening of the electron-depleted region, leading to an increase in the resistance of MoS2 bilayers since MoS2 has been considered as an n-type semiconductor. In contrast, the photo-desorption of NO$^-$ is given by $h^+ + NO^-(ads) \rightarrow NO (gas)$, for which the electrons are returned from NO$^-$ to MoS2 bilayers, resulting in the desorption of NO. As a result, the narrowing of the electron-depleted region occurs, leading to an increase in the conductance with the decrease in resistance (State 2). Because of the strong chemisorption energy of the NO gas molecules on MoS2,26,60 introducing N2 gas26 or heating sensors at annealing temperatures of 300–500 °C30 to enhance the desorption are imperative steps to maintain the best performance. The former may result in the sluggish desorption while the latter still faces the high operating temperature. On the initial introduction of the NO gas, the reduction process of the NO gas is dominant (State 1), leading to an increase in resistance denoted by the (d1) region in Fig. 3(c) and (e). Subsequently, the competition of the reduction process and photo-desorption occurs, leading to a dynamic balance where a saturation state occurs as denoted by the (d2) region in Fig. 3(c) and (e). After pumping out the NO gas, the reverse reaction takes place, e.g., photo-desorption becomes a dominant process, restoring the photocurrent back to its original value denoted by the (d3) region in Fig. 3(c) and (e). In addition, owing to the higher energy of defects,33 some NO gas molecular residues strongly bonded with the defects of MoS2, such as the residual MoO3, resulting in the sluggish desorption of the NO gas molecules in the (d4) region in Fig. 3(c) and (f).

It is well known that light-assisted gas sensors can exhibit good sensing performance at a low gas concentration.6,51 To shed light on this part, we systematically investigated the performance of gas sensors as we varied the concentrations of NO gases ranging from 0.060 ppm to 2.000 ppm (from low to high concentrations) and vice versa under the irradiation of UV light with a wavelength of 365 nm and a power of 61.5 mW. Fig. 4 (a1) and (a2) show the dynamic responses of the F-MoS2 GS and the CS-MoS2 GS driven by the same voltage of 3 V. For the F-MoS2 GS, the responses of 45% at 0.06 ppm, 60% at 0.125 ppm, 77% at 0.025 ppm, 120% at 0.5 ppm, 150% at 1 ppm and 200% at 2 ppm were measured, respectively (Fig. 4a1). In contrast, for the CS-MoS2 GS, the responses of 95% at 0.06 ppm, 120% at 0.125 ppm, 150% at 0.025 ppm, 250% at 0.5 ppm, 330% at 1 ppm and 470% at 2 ppm were measured, respectively (Fig. 4a2). The response of the CS-MoS2 GS is nearly twofold stronger than that of the flat sensor as shown in Fig. 4(a3). Although the CS-MoS2 can detect diluted NO gas (e.g., 0.06 ppm, the lowest tested concentration ever), the sensor promptly reacted and saturated in 150 s with a response of 95%. In addition, the response time significantly decreases with the increase in the concentration of the NO gas. Most notably for the CS-MoS2 GS, the response time is under 20 s for detecting 2 ppm of NO gas. To the best of our knowledge, this is the shortest response time for the detection of gaseous NO by MoS2-based gas sensors. Next, an equation that is commonly used in metal–oxide based gas sensors was introduced to estimate the sensitivity of the gas sensor.

In general, for gas sensors that are made of metal–oxide semiconductors, the response function depends on the concentration of the tested gas as $R = A[C] + B$ where $R$ is the response, $A$ and $B$ are constants, and $C$ is the concentration of the applied gas.6 Most importantly, the slope, $A$, is regarded as the sensitivity of a gas sensor.61 By fitting the response as a function of concentrations, the equation for the F-MoS2 GS can be obtained as $R = 79.3[C] + 60.8$ and for the CS-MoS2 GS, the obtained equation is $R = 189.2[C] + 114.3$ as plotted in Fig. 4(a3). As a result, the sensitivity of the F-MoS2 GS is 79.3%...
ppm$^{-1}$ and that of the CS-MoS$_2$ GS is 189.2% ppm$^{-1}$, confirming that the CS-MoS$_2$ GS is superior to the F-MoS$_2$ GS as reported elsewhere. To further examine the stability of the proposed gas sensor, the concentration of NO gas is gradually reduced from 2.000 ppm to 0.060 ppm and the corresponding results are shown in Fig. 4(b1) and (b2). Interestingly, the F-MoS$_2$ GS is not able to recover to the initial state when the NO gas is pumped out; even worse, the resistance of the sensor is unstable across measurements. On the other hand, the CS-MoS$_2$ GS displays a regular periodic cycle and can return to the initial state, indicating the high stability and reliability of the CS-MoS$_2$ GS. Meanwhile, even though the gradient of the NO gas concentration was reversed, the sensor detected diluted NO at 0.06 ppm with a response of 200%. Furthermore, by fitting the response as a function of concentrations, the equation for the F-MoS$_2$ GS can be obtained as $R = 1.6[C] + 141.2$ and for the CS-MoS$_2$ GS, the obtained equation is $R = 72.9[C] + 188.1$ as plotted in Fig. 4(b3). As a result, the sensitivity of the F-MoS$_2$ GS is 72.9% ppm$^{-1}$ and that of the CS-MoS$_2$ GS is 1.6% ppm$^{-1}$, confirming that the CS-MoS$_2$ GS is superior to the F-MoS$_2$ GS as the concentrations of NO gas decrease. A plot of response time as a dependence of the NO concentration gradient of CS-MoS$_2$ GS is shown in Fig. S8,† revealing the stable response under concentrations of NO gas increase or decrease. In addition, the reliability test is very critical when it comes to the industry applications. The stability test over 3 weeks is provided as shown in Fig. S9,‡ Clearly, the performance of both F-MoS$_2$ GS and CS-MoS$_2$ GS is degraded and the response of CS-MoS$_2$ GS was still distinct and competitive. Furthermore, the sluggish responses in terms of on/off ratio and time were found as the thickness of layered MoS$_2$ increases (Fig. S10†). To further elucidate the effect of the substrate morphology on the quality of MoS$_2$, XPS was used to analyze the quality of the resulting MoS$_2$ film as shown in Fig. 5. First, the S/Mo ratio was calculated by integrating the enclosed area of the Mo 3d peak and S 2s peak. The S/Mo ratio of CS-MoS$_2$ was nearly twofold higher than that of F-MoS$_2$ (Table 2), implying that the quality of the MoS$_2$ bilayers grown on the CPSS is better than that of MoS$_2$ bilayers grown on the flat substrate. An addition peak can be observed, located at 236 eV, near the Mo 3d peak, which corresponds to residual MoO$_3$ (Fig. 5a). This residual MoO$_3$ results in the longer recovery time for the F-MoS$_2$ GS. However, no MoO$_3$ peak was observed as shown in Fig. S5(b), confirming the high quality of MoS$_2$ bilayers.‡ We believe that periodic patterns allow forming vortices of sulfur around valleys, extending the dwell time of the sulfur vapor and resulting in a complete reaction with MoO$_3$ as shown in Fig. 5(c).

In general, metal oxide gas sensors, such as SnO$_2$ and ZnO sensors, exhibit an unsatisfactory response to the targeted gas at room temperature. Hence, to achieve the best performance of gas sensors, a heating process on sensors at a temperature of 300–500 °C is necessary for ensuring the detection of diluted concentrations. Recently, decorating active materials with metal particles such as Ag, Au, and Cr, or hybridization with graphene and SnO$_2$ have been proposed to promote the sensing ability but the issue of high operating temperature remains unsolved. Another alternative to trigger gas sensors is to apply UV light for generating electron–hole pairs in active materials, leading to enhanced conductance. However, the prolonged exposure to the UV light poses a high-risk factor for skin cancers and induces structural defects in the exposed devices. Therefore, selecting a suitable material system that can be activated using a low thermal budget without incurring harm is imperative. Unlike traditional sensing materials (such as ZnO, TiO$_2$, and SnO), MoS$_2$ bilayers have a smaller band gap <1.8 eV, which matches the visible light range, indicating that MoS$_2$ bilayers can generate electron–hole pairs under illumination by visible light. Therefore, we report for the first time utilization of indoor white-light light-emitting diodes (LEDs), which are commonly used for indoor lighting, to activate the CS-MoS$_2$ GS, following the detection of NO gas molecules. Fig. S11† shows the radiant flux spectrum of the white-light LED and the inset shows the corresponding image of the white-light LED. Fig. 6(a) and 6(b) show the dynamic responses of F-MoS$_2$ and CS-MoS$_2$ GSs at different concentrations of NO gas illuminated by an indoor white-light LED. Remarkably, the F-MoS$_2$ GS still shows a response to NO gas but the response varied with different concentrations. Surprisingly, the CS-MoS$_2$ GS maintains a response of 75% for the detection of diluted NO
gas with a concentration of 0.06 ppm. Although the responses of both devices are somewhat weaker compared with the responses under the UV irradiation, the sensors can be operated under the indoor light and demonstrate significant potential for integration into consumer applications. Note that the CS-MoS2 GS still exhibits a relatively stable performance since its patterned structure can be allowed to collect more photons, resulting in enough photocarriers to adsorb and desorb the targeted gas. The response of the CS-MoS2 GS to NO gas illuminated under the white-light LED can be described by the equation $R = 116.7[C] + 70.6$ as shown in Fig. 6(c). Simulations were performed using a finite difference time domain (FDTD) solver Lumerical solutions to study the electric field intensity and absorption properties of the two types of MoS2/sapphire substrates. The detailed geometric design is based on SEM measurements. Three-dimensional simulations were conducted using a minimum mesh size of 0.1 nm per grid point. Periodic boundary conditions are imposed in the $xy$ and $yz$ planes to reduce the computational demand. Plane-wave light is vertically incident on the simulated MoS2/sapphire substrates with the wavelength ranging from 200 to 1400 nm. A $P_{abs}$ analysis group overlapped with the light source and the MoS2/sapphire substrates. The simulation considers both the refractive indices ($n$) and extinction coefficients ($k$), accounting for the absorption of different materials. For all materials, values of refractive indices are taken from the literature.74 We calculated absorption using the equation, $\text{Abs}(\mathbf{r}, \lambda) = -\pi/\lambda |E(\mathbf{r}, \lambda)|^2 \text{Im}|\varepsilon(\mathbf{r}, \lambda)|$ where $E(\mathbf{r}, \lambda)$ is the electric field and $\text{Im}|\varepsilon(\mathbf{r}, \lambda)|$ is the imaginary part of the permittivity. Note that the white light LED shows the spectral power distribution, consisting of 2 main wavelengths, namely 440 and 550 nm. According to the simulation results, the cone-shaped MoS2 bilayers exhibit periodically localized absorption enhancement at a wavelength of 550 nm owing to the surface scattering effect induced by their 3D architecture, resulting in high sensi-

**Table 3** Comparison of MoS2-based gas sensors

<table>
<thead>
<tr>
<th>Materials</th>
<th>Driven source</th>
<th>Detected gas</th>
<th>Concentration</th>
<th>Response time</th>
<th>Response</th>
<th>Ref.</th>
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</thead>
<tbody>
<tr>
<td>CS-MoS2</td>
<td>365 nm UV</td>
<td>NO</td>
<td>0.06 ppm</td>
<td>130 s</td>
<td>200%</td>
<td>This work</td>
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<tr>
<td>CS-MoS2</td>
<td>White light</td>
<td>NO</td>
<td>0.06 ppm</td>
<td>150 s</td>
<td>75%</td>
<td>This work</td>
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<td>CS-MoS2</td>
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<td>25 s</td>
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<td>This work</td>
</tr>
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<td>&gt;120 s</td>
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<td>This work</td>
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<tr>
<td>F-MoS2</td>
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<tr>
<td>F-MoS2</td>
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<td>200 s</td>
<td>80%</td>
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<tr>
<td>F-MoS2</td>
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<td>&gt;1800 s</td>
<td>12%</td>
<td>26</td>
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<td>F-MoS2</td>
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<td>2 ppm</td>
<td>300 s</td>
<td>0.025%</td>
<td>29</td>
</tr>
<tr>
<td>F-MoS2</td>
<td>Dry air</td>
<td>NH3</td>
<td>4 ppm</td>
<td>N.A</td>
<td>2%</td>
<td>30</td>
</tr>
</tbody>
</table>

**Table 4** Comparison of NOx gas sensors

<table>
<thead>
<tr>
<th>Materials</th>
<th>Driven source</th>
<th>Detected gas</th>
<th>Concentration</th>
<th>Response time</th>
<th>Response</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS-MoS2</td>
<td>365 nm UV</td>
<td>NO</td>
<td>0.06 ppm</td>
<td>130 s</td>
<td>200%</td>
<td>This work</td>
</tr>
<tr>
<td>CS-MoS2</td>
<td>White light</td>
<td>NO</td>
<td>0.06 ppm</td>
<td>150 s</td>
<td>75%</td>
<td>This work</td>
</tr>
<tr>
<td>CS-MoS2</td>
<td>365 nm UV</td>
<td>NO</td>
<td>2 ppm</td>
<td>25 s</td>
<td>470%</td>
<td>This work</td>
</tr>
<tr>
<td>CS-MoS2</td>
<td>White light</td>
<td>NO</td>
<td>1 ppm</td>
<td>&gt;120 s</td>
<td>165%</td>
<td>This work</td>
</tr>
<tr>
<td>F-MoS2</td>
<td>N2 purge</td>
<td>NO</td>
<td>2 ppm</td>
<td>200 s</td>
<td>80%</td>
<td>24</td>
</tr>
<tr>
<td>F-MoS2</td>
<td>N2 purge</td>
<td>NO2</td>
<td>10 ppm</td>
<td>N.A</td>
<td>16%</td>
<td>33</td>
</tr>
<tr>
<td>MoS2/graphene</td>
<td>Heating 100 °C</td>
<td>NO2</td>
<td>0.5 ppm</td>
<td>21.6 s</td>
<td>10%</td>
<td>63</td>
</tr>
<tr>
<td>MoS2/SnO2</td>
<td>Heating 200 °C</td>
<td>NO2</td>
<td>10 ppm</td>
<td>400 s</td>
<td>28%</td>
<td>64</td>
</tr>
<tr>
<td>TiO2</td>
<td>Heating 500 °C</td>
<td>NO2</td>
<td>25 ppm</td>
<td>600 s</td>
<td>100%</td>
<td>5</td>
</tr>
<tr>
<td>ZnO/GrO</td>
<td>N2 purge</td>
<td>NO</td>
<td>5 ppm</td>
<td>360 s</td>
<td>3.5%</td>
<td>4</td>
</tr>
<tr>
<td>SnO2/ZnO</td>
<td>N2 purge</td>
<td>NO2</td>
<td>1 ppm</td>
<td>100</td>
<td>230%</td>
<td>6</td>
</tr>
</tbody>
</table>
tivity to NO gas under the white-light LED illumination. The comparison of our light-assisted MoS2-based gas sensor with other previously reported MoS2-based gas sensors is listed in Table 3. Obviously, our CS-MoS2 GS demonstrates, for the first time, a strong response to the NO gas with a concentration as low as ∼0.06 ppm at room temperature under the illumination of a white-light LED. Furthermore, the comparison of other sensors on detecting NO gases is listed in Table 4. Clearly, the CS-MoS2 GS is a harmless and environmentally friendly sensor that performs satisfactorily in the detection of sub-ppm levels at room temperature for opto-electronic applications.

Conclusion

Large-area MoS2 (~2") was successfully synthesized on both the flat sapphire substrate and the CPSS through the sulfurization of MoO3 films. Confocal Raman measurements and TEM images revealed that MoS2 bilayers grown on the CPSS suffer a significant compressive strain because of a larger thermal expansion coefficient, leading to a remarkable blue shift in Raman and PL spectra. Gas sensors based on flat and cone-shaped MoS2 bilayers were fabricated for detecting NO gas molecules upon illumination with UV light of 365 nm wavelength. Both the response (470% at 2 ppm NO) and the sensitivity (189.2% ppm⁻¹) of the CP-MoS2 GS are much higher than those of the F-MoS2 GS, primarily owing to an increase in the sensing surface area as well as to the light absorption owing to the 3D configuration of MoS2 bilayers. In addition, the CS-MoS2 GS has the potential to detect ultra-diluted (0.06 ppm) NO gas with 200% response under UV light with a wavelength of 365 nm. Interestingly, under the low-power UV light irradiation (20.6 mW), the CS-MoS2 GS still exhibits a clear and fast response, which is attributed to the 3D configuration that enhances the absorption of light. It suggests that the presently described device is a low-power-consumption device. Finally, utilizing an indoor white-light LED to trigger the CS-MoS2 GS for the detection of NO gas was demonstrated for the first time. Under the illumination of the indoor white-light LED, the CS-MoS2 GS can exhibit outstanding performance with the capability to detect sub-ppm NO gas and a remarkable response of ∼75%. We believe that the development of such indoor white-light-assisted gas sensors is a practical way to integrate these devices with furniture for demonstrating the concept of the Internet of Things.

Experimental section

Synthesis of MoS2 bilayers on sapphire substrates

Firstly, a 2 nm-thick layer of molybdenum oxide (MoO3), serving as a precursor layer, was deposited by using an e-gun on sapphire substrates at 0.1 Å s⁻¹ deposition rate. Secondly, both MoO3/sapphire and sulfur powder were put in a furnace tube to conduct the sulfurization process. The sulfur powder with a quartz boat was located upstream where it was wrapped in a heating tape outside a quartz tube and a MoO3/sapphire composite was positioned at 10 cm away from the sulfur powder. During the sulfurization process, the furnace pressure was maintained at ~550 torr, with a H2/N2 gas mixture of 100/50 sccm, and heated up by heating the tape up to 180 °C at a rate of 5 °C min⁻¹, followed by heating up to 1000 °C at a rate of 18 °C min⁻¹. When the temperature increases to 1000 °C, the following reactions took place:

\[
\text{MoO}_3(s) + H_2(g) \rightarrow \text{MoO}_2(s) + H_2O(g)
\]
\[
\text{MoO}_2(s) + 2S(g) \rightarrow \text{MoS}_2(s) + O_2(g).
\]

Measurement of gas sensing

Finger-shaped electrodes were defined by a hard mask, followed by the deposition of Ti/Au with 5/50 nm as electrodes. Next, silver wires were bonded to a sample as bridging to the system. The samples were placed in a hand-made chamber, into which a mixture of NO + N2 at 500 ppm was injected. Once the gas mixture was introduced, the I–t dependence was recorded using a Keithley 2400. A 365 nm-wavelength lamp was used for degassing.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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