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Enhanced Acetone-Sensing Properties of PEI Thin Film by GO-NH_2 Functional Groups Modification at Room Temperature

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The functional groups of organic gas-sensing materials play a crucial role in adsorbing specific gas molecules, which is significant to the sensing performances of gas sensor. In this work, amido-graphene oxide (GO-NH_2) loaded poly(ethyleneimine) (PEI) composite thin film (PEI/GO-NH_2) with abundant amino functional groups -NH_2 was successfully prepared on quartz crystal microbalance (QCM) by a combined spraying and drop coating method for acetone detection at room temperature (25°C). The morphological, spectrographic and acetone-sensing properties of composite film were investigated. The results demonstrated that a wrinkled surface morphology was formed and the ratio of nucleophilic -NH_2 was increased for PEI/GO-NH_2 composite film. Meanwhile, the composite film sensor possessed excellent acetone-sensing performances, and its sensitivity was about 4.2 times higher than that of pure PEI one owing to the increased -NH_2 groups. This study reveals the important role of absorbing favorable functional groups and provides a novel method for the rational design and construction of acetone-sensing materials.

Keywords: amino functional groups, composite materials, poly(ethyleneimine), amido-graphene oxide, acetone sensing performances

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INTRODUCTION

Acetone is a volatile, flammable and deleterious industrial product that widely used in our daily life (Jia et al., 2014). In addition, acetone detection can be applied to painless diabetes diagnosis because the concentration of acetone exhaled by diabetics is much higher than that by healthy people (Righettoni and Tricoli, 2011; Shin et al., 2013; Zhang et al., 2017). Therefore, it is urgent to develop acetone gas sensors with excellent performances through optimizing the sensing materials (Wang et al., 2017). So far, many types of acetone gas sensors have been developed (Xu et al., 2009; Epifani et al., 2015; Kim et al., 2016; Wang et al., 2016), in which most of them were chemiresistive sensor operated at high temperature with metal-oxide sensing-materials. On the other hand, quartz crystal microbalance (QCM, for short) is an excellent and reliable mass gas sensing device that can detect mass change at sub-nanogram level and has attracted attention for its room working

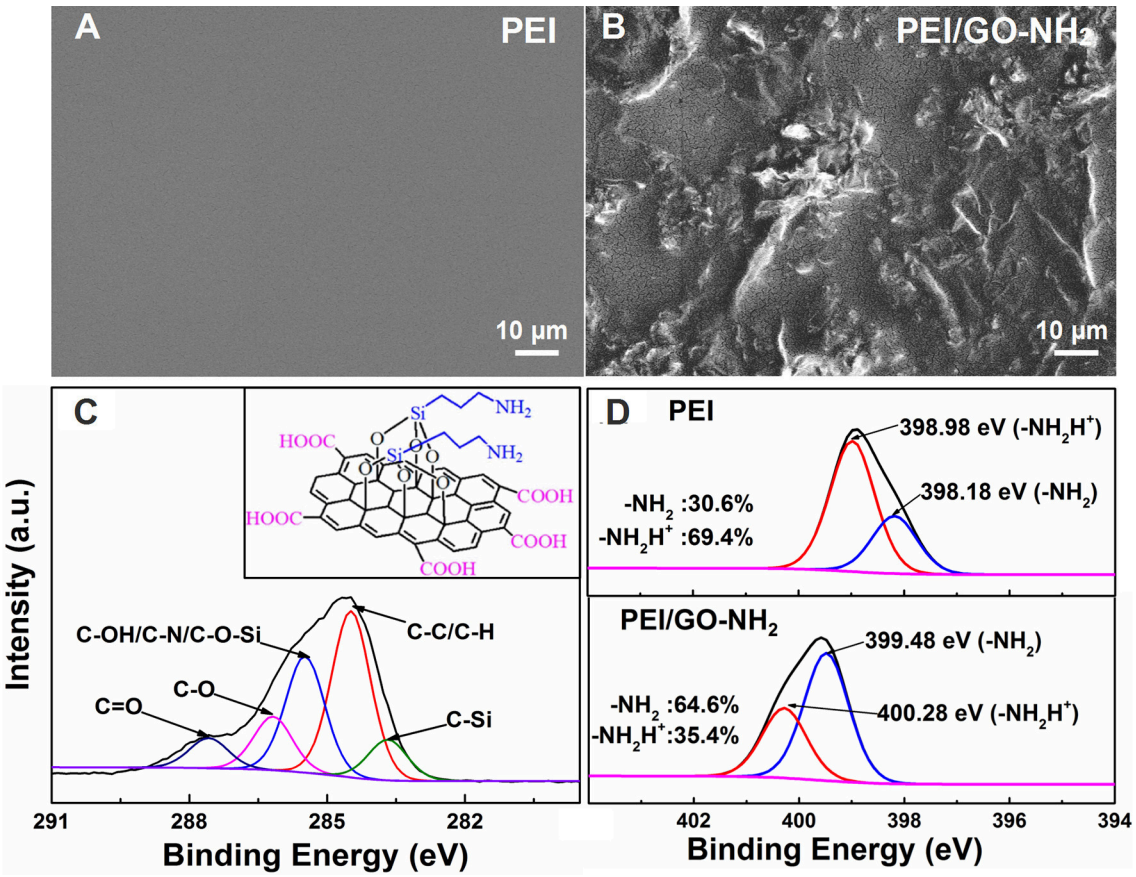

FIGURE 1 | SEM images of **(A)** PEI and **(B)** PEI/GO-NH_2 film. High-resolution XPS of **(C)** C1s spectra of PEI/GO-NH_2 and **(D)** N1s spectra of pure PEI and PEI/GO-NH_2, the inset of **(C)** is GO-NH_2 material structure.

temperature, high sensitivity, good stability, and small physical size (Matsuguchi and Uno, 2006; Lal and Tiwari, 2018). The gas sensing properties of QCM gas sensor are mainly determined by the coated sensing material to the gas molecules (Wang et al., 2017). Conductive polymer materials were widely used as sensing films in QCM gas sensors because they possess specific functional groups for adsorbing target gas molecules. In order to develop high performance gas sensor based on QCM, one of important strategies is to construct gas sensing materials with special functional groups. As a typical organic polymer, poly(ethyleneimine) (PEI) can be used in QCM-based acetone sensors due to the amino functional groups (-NH_2, for short) that can adsorb acetone molecules through nucleophilic addition reaction (Smith and March, 2007). However, the acetone-sensing properties of pure PEI based QCM gas sensors are restricted and still need to be further improved. Inspired by the large specific surface area of graphene oxide (GO, for short) and the importance of functional groups in gas sensing materials, compositing with GO to improve the acetone performance of PEI is a good strategy. In view of the amide reaction between—NH_2 of PEI and hydroxyl groups (-OH, for short) of GO (Tai et al., 2016), the amido-graphene oxide (GO-NH_2, for short) could be chose to prepare composite film, and the acetone-sensing properties would be enhanced by loading more -NH_2 onto the PEI film. In this work, PEI film loaded GO-NH_2 (PEI/GO-NH_2, for short) with abundant -NH_2 was prepared by a combined spraying and drop coating method, and characterized by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), ultraviolet-visible spectroscopy (UV-vis). The QCM acetone sensors based on PEI and PEI/GO-NH_2 films were fabricated and their acetone gas sensing properties including dynamic response, repeatability, selectivity and stability were investigated. Moreover, the mechanisms for the enhanced acetone sensing properties of the PEI/GO-NH_2 gas sensors were discussed.

EXPERIMENTAL

All the chemicals used in the experiment were analytical reagents. PEI aqueous solution [50% (w/v)] was obtained from Sigma-Aldrich and diluted to 1% (w/v) by deionized water. GO-NH_2 aqueous solution (0.5 mg/ml) was prepared by Shenzhen University (-NH_2 was carried by 3-aminopropyltriethoxysilane (APTES), which was modified on GO by a one-pot hydrothermal method described in Liu et al. (2013). QCM devices (Wuhan Hitrusty Electronics Co., Ltd., China) consist of AT-cut quartz

crystal with a fundamental resonance frequency of 10 MHz and the 5 mm diameter sliver electrodes were used on both sides of devices.

PEI/GO-NH_2 composite thin film was deposited on QCM devices by spraying 0.9 ml PEI solution and dropping 20 μl GO-NH_2 solution in sequence. After the deposition, the composite thin film sensors were dried in vacuum drying oven at 80°C for 48 h. For comparison, pure PEI film QCM gas sensor was also fabricated by the same spray method. The SEM, XPS and UV-vis of PEI and PEI/GO-NH_2 composite films were characterized by S4800 (HITACHI, Japan), UV-1700 (Shimadzu, Japan), and ESCALAB 250Xi (Thermo Fisher, American), respectively.

The details for measurement of QCM gas sensors can refer to our previous work (Yuan et al., 2016). The acetone gas was generated by MF-3C (Beijing Ruiyisi Technology Co., Ltd.). QCM-5 Oscillator (ShenyangVacuum Technology Institute, China) drived the QCM gas sensors, and an SS7200 intelligent frequency counter (The Fourth Radio Factory, China) was used to measure the resonance-frequency of QCM gas sensors. All the sensing measurements were executed at room temperature 25°C. The response (Δf) of the sensor is calculated as following equation: $\Delta f = f_{air}\text{-}f_{gas}$, where f_{air} and f_{gas} is the frequency measured in air and target gases, respectively. The slope coefficient of response vs. gas concentrations curve is defined as sensitivity of the gas sensor:

$$\mathbf{S = \Delta f/(\Delta Conc.)}$$

where ΔConc. is the gas range of linear concentration. The response/recovery times (τ_{res}/τ_{rec}) are defined as the time spans to the sensor achieved 90% of total frequency change exposure to gas and air.

RESULTS AND DISCUSSION

The SEM and XPS of pure PEI and PEI/GO-NH_2 composite films are shown in **Figure 1**. As can be seen, the SEM image in **Figure 1A** indicates a smooth and uniform deposition of PEI film. However, **Figure 1B** displays a rough and wrinkled surface morphology caused by GO-NH_2, which should be beneficial to enlarging the specific surface area of sensing film and improving the adsorption capacity of gas molecules (Kuila et al., 2011). As shown in **Figure 1C**, the binding energy of GO-NH_2 at O1s can be assigned to individual peaks at 283.7, 284.5, 285.5, 286.2, and 287.6 eV, corresponding to C-Si,C-C/C-H,C-OH/ C-N/C-O-Si, C-O, and C=O, respectively, which are conformed to the structure diagram (inset of **Figure 1C**) of GO-NH_2 (Liu et al., 2013). N1s spectra of pure PEI and PEI/GO-NH_2 are curve fitted and shown in **Figure 1D**. The N1s peaks are assigned to -NH_2 and protonated amine groups (-NH_2H^+), respectively. The N1s peaks of PEI/GO-NH_2 shifted about 1.3 eV compared with that of pure PEI, implying the existence of hydrogen bonds between PEI and GO-NH_2 (Finšgar et al., 2009). On the other hand, -NH_2 are nucleophilic while -NH_2H^+ are not nucleophilic, so the

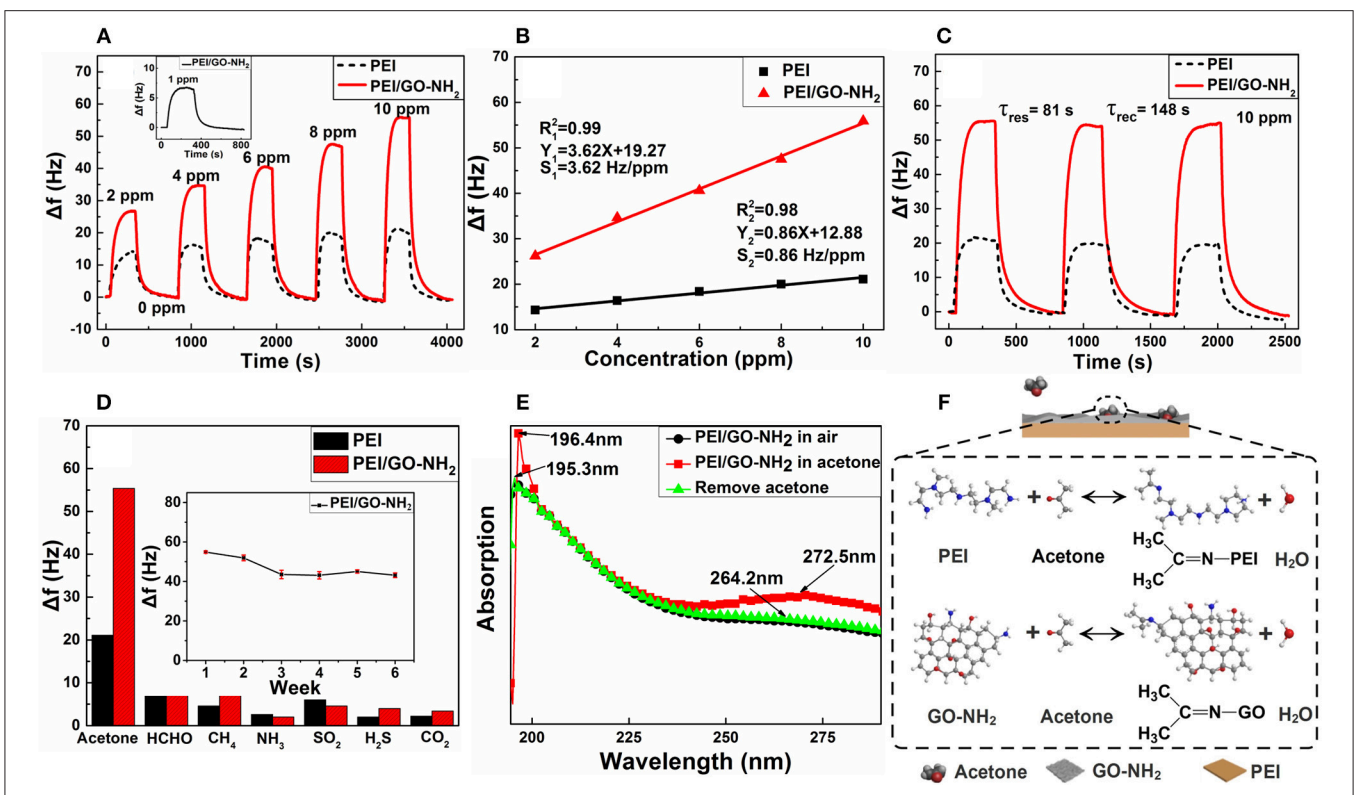

FIGURE 2 | (A) Dynamic response curves. **(B)** Linear fitting curves. **(C)** Repeatability curves and **(D)** selectivity of PEI and PEI/GO-NH_2 QCM sensors to acetone, the inset of **(A)** is the response curve of PEI/GO-NH_2 sensor for 1 ppm acetone, the inset of **(D)** is long-term stability curve. **(E)** UV-Vis spectrum of PEI/GO-NH_2 films. **(F)** Schematic of acetone-sensing mechanism.

increased ratio of nucleophilic -NH_2 in PEI/GO-NH_2 (from 30.6 to 64.6%) can increase the acetone gas molecules adsorption and enhance the acetone-sensing properties of composite thin film (Smith and March, 2007).

Typical dynamic responses of pure PEI and PEI/GO-NH_2 film sensors vs. acetone concentration (2–10 ppm) were measured at room temperature (25°C), as shown in **Figure 2A**. It can be observed that the responses of two gas sensors increase gradually with the increasing acetone concentrations and reach saturation, and the frequency come back to the initial state with insignificant baseline drift after the acetone is replaced by dry air. The response of pure PEI and PEI/GO-NH_2 sensors to 10 ppm acetone is about 21.1 and 55.4 Hz, respectively. **Figure 2B** demonstrates the linear fitting curves of two gas sensors, indicating both pure PEI and PEI/GO-NH_2 film sensors are of good linearity to 2–10 ppm acetone. The sensitivity of pure PEI and PEI/GO-NH_2 QCM gas sensor is 0.86 and 3.62 Hz/ppm, respectively, indicating that the sensitivity of PEI/GO-NH_2 composite thin film sensor shows about 4.2 times higher than that of pure PEI one. It is worth noting that the PEI/GO-NH_2 film sensor could detect 1 ppm acetone with 6.4 Hz response as shown in the inset of **Figure 2A**, whereas PEI film sensor shows no obvious response. **Figure 2C** shows good repeatability for two film sensors on successive exposure to 10 ppm acetone. It can be observed that the responses of two sensors exhibit very little fluctuation in adsorption and desorption process, indicating excellent repeatability and baseline stability. The response and recovery times of the PEI/GO-NH_2 film sensor are 81 s and 148 s. As shown in **Figure 2D**, the selectivity of PEI/GO-NH_2 acetone sensor was investigated in comparison to different kinds of interference gases (10 ppm HCHO, CH_4, NH_3, SO_2, H_2S, and 1,000 ppm CO_2), which demonstrate that the composite film has higher response to acetone gas than other gases. Except for formaldehyde and acetone, other gases have no carbon-heteroatom double bond (C=O) which plays an important role in nucleophilic addition reaction with –NH_2. In addition, the molecular mass of formaldehyde is less than that of acetone at the same concentration. Therefore, PEI/GO-NH_2 composite film shows a comparatively good selectivity to acetone. The insert in **Figure 2D** shows the long-term stability of PEI/GO-NH_2 acetone sensor during a period of 6 weeks. The result shows the response of composite sensor to 10 ppm acetone decreases about 18% in the first 14 days and tends to be stable afterwards.

UV-Vis spectra were carried out to further confirm the recoverability of PEI/GO-NH_2 film. As shown in **Figure 2E**, when exposed to acetone atmosphere, enhancement and redshift of absorption peaks appeared in PEI/GO-NH_2 film, representing the adsorption of acetone molecules. When above films were replaced back to the air atmosphere, the absorption peaks also restored to their positions, indicating the good recovery characteristic of the films. The acetone-sensing mechanism is further proposed. **Figure 2F** indicates the chemical reaction during adsorption/desorption process. Carbon atom of polar carbon-heteroatom double bond (C=O) on acetone molecule carries a partial positive charge, making the carbon atom as electrophilic center. When exposed to acetone gas, negatively charged nucleophilic -NH_2 on PEI/GO-NH_2 film will attack and bond with the electrophilic carbon atom to form an imine and produce a molecule of water. The above adsorption will lead to mass increase of PEI/GO-NH_2 film and the frequency shift of QCM sensor based on Sauerbrey's equation (Sauerbrey, 1959). According to the pattern followed by analogous nucleophiles, the produced compounds are generally unstable. In the process of acetone molecular desorption, carbon atom of polar carbon-nitrogen double bond (C=N) for produced compounds carries a partial positive charge, produced water molecule will bond with the electrophilic carbon atom to form reversible reaction, thus the PEI/GO-NH_2 film coated QCM acetone sensors possess good response and recoverability (Madura and Jorgensen, 1986; Smith and March, 2007).

CONCLUSION

In summary, PEI/GO-NH_2 composite film was fabricated on QCM via a combined spraying and drop coating method. Moreover, the acetone-sensing properties were investigated at room temperature (25°C). Compared with the pure PEI film based QCM acetone sensor, PEI/GO-NH_2 composite film sensor exhibited an improved acetone-sensing performance, and its sensitivity was about 4.2 times higher than that of pure PEI film. The gas sensor based on PEI/GO-NH_2 composite film showed nearly linear response at acetone gas concentrations ranges of 2–10 ppm, and its sensitivity was about 3.62 Hz/ppm. In addition, the PEI/GO-NH_2 composite film sensor possessed good repeatability and selectivity. The enhanced acetone-sensing performances could be attributed to the rich -NH_2 and enlarged surface area introduced by GO-NH_2. This work demonstrated a promising PEI/GO-NH_2 composite film for high-performance acetone-sensing materials construction.

AUTHOR CONTRIBUTIONS

QZ and ZH co-wrote the submitted perspective and performed the experiments. HW and CS prepared GO-NH_2 aqueous solution. YJ, ZY, and HT designed and guided the entire experimental process.

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REFERENCES

Epifani, M., Comini, E., Siciliano, P., Faglia, G., and Morante, J. R. (2015). Evidence of catalytic activation of anatase nanocrystals by vanadium oxide surface layer: acetone and ethanol sensing properties. *Sensors Actuat. B Chem.* 217, 193–197. doi: 10.1016/j.snb.2014.07.118

Finšgar, M., Fassbender, S., Hirth, S., and Milošev, I. (2009). Electrochemical and XPS study of polyethyleneimines of different molecular sizes as corrosion

inhibitors for AISI 430 stainless steel in near-neutral chloride media. *Mater. Chem. Phys*. 116, 198–206. doi: 10.1016/j.matchemphys.2009.03.010

Jia, Q., Ji, H., Zhang, Y., Chen, Y., Sun, X., and Jin, Z. (2014). Rapid and selective detection of acetone using hierarchical ZnO gas sensor for hazardous odor markers application. *J. Hazard. Mater*. 276, 262–270. doi: 10.1016/j.jhazmat.2014.05.044

Kim, N. H., Choi, S. J., Kim, S. J., Cho, H. J., Jang, J. S., Koo, W. T., et al. (2016). Highly sensitive and selective acetone sensing performance of WO_3 nanofibers functionalized by Rh_2O_3 nanoparticles. *Sensors Actuators B Chem*. 224, 185–192. doi: 10.1016/j.snb.2015.10.021

Kuila, T., Bose, S., Khanra, P., Mishra, A. K., Kim, N. H., and Lee, J. H. (2011). Recent advances in graphene-based biosensors. *Biosens. Bioelectron*. 26, 4637–4648. doi: 10.1016/j.bios.2011.05.039

Lal, G., and Tiwari, D. C. (2018). Investigation of nanoclay doped polymeric composites on piezoelectric Quartz Crystal Microbalance (QCM) sensor. *Sensors Actuat. B Chem*. 262, 64–69. doi: 10.1016/j.snb.2018.01.200

Liu, Z., Duan, X., Qian, G., Zhou, X., and Yuan, W. (2013). Eco-friendly one-pot synthesis of highly dispersible functionalized graphene nanosheets with free amino groups. *Nanotechnology* 24:045609. doi: 10.1088/0957-4484/24/4/045609

Madura, J. D., and Jorgensen, W. L. (1986). *Ab initio* and Monte Carlo calculations for a nucleophilic addition reaction in the gas phase and in aqueous solution. *J. Am. Chem. Soc*. 108, 2517–2527. doi: 10.1021/ja00270a005

Matsuguchi, M., and Uno, T. (2006). Molecular imprinting strategy for solvent molecules and its application for QCM-based VOC vapor sensing. *Sensors Actuat. B Chem*. 113, 94–99. doi: 10.1016/j.snb.2005.02.028

Righettoni, M., and Tricoli, A. (2011). Toward portable breath acetone analysis for diabetes detection. *J. Breath Res*. 5:037109. doi: 10.1088/1752-7155/5/3/037109

Sauerbrey, G. (1959). Verwendung von schwingquarzen zur wägung dünner schichten und zur mikrowägung. *Zeitschrift Für Phys*. 155, 206–222. doi: 10.1007/BF01337937

Shin, J., Choi, S. J., Lee, I., Youn, D. Y., Park, C. O., Lee, J. H., et al. (2013). Thin-wall assembled SnO_2 fibers functionalized by catalytic Pt nanoparticles and their superior exhaled-breath-sensing properties for the diagnosis of diabetes. *Adv. Funct. Mater*. 23, 2357–2367. doi: 10.1002/adfm.201202729

Smith, M. B., and March, J. (2007). *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, Sixth Edition.* Hoboken, NJ: John Wiley and Sons.

Tai, H., Yuan, Z., Liu, C., Ye, Z., Xie, G., Du, X., et al. (2016). Facile development of high performance QCM humidity sensor based on protonated polyethylenimine-graphene oxide nanocomposite thin film. *Sensors Actuat. B Chem*. 230, 501–509. doi: 10.1016/j.snb.2016.01.105

Wang, L., Wang, Z., Xiang, Q., Chen, Y., Duan, Z., and Xu, J. (2017). High performance formaldehyde detection based on a novel copper (II) complex functionalized QCM gas sensor. *Sensors Actuat. B Chem*. 248, 820–828. doi: 10.1016/j.snb.2016.12.015

Wang, P., Wang, D., Zhang, M., Zhu, Y., Xu, Y., Ma, X., et al. (2016). ZnO nanosheets/graphene oxide nanocomposites for highly effective acetone vapor detection. *Sensors Actuat. B Chem*. 230, 477–484. doi: 10.1016/j.snb.2016.02.056

Xu, X., Cang, H., Li, C., Zhao, Z. K., and Li, H. (2009). Quartz crystal microbalance sensor array for the detection of volatile organic compounds. *Talanta* 78, 711–716. doi: 10.1016/j.talanta.2008.12.031

Yuan, Z., Tai, H., Ye, Z., Liu, C., Xie, G., Du, X., et al. (2016). Novel highly sensitive QCM humidity sensor with low hysteresis based on graphene oxide (GO)/poly (ethyleneimine) layered film. *Sensors Actuat. B Chem*. 234, 145–154. doi: 10.1016/j.snb.2016.04.070

Zhang, Z., Zhu, L., Wen, Z., and Ye, Z. (2017). Controllable synthesis of Co_3O_4 crossed nano sheet arrays toward an acetone gas sensor. *Sensors Actuat. B Chem*. 238, 1052–1059. doi: 10.1016/j.snb.2016.07.154

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