**ORIGINAL PAPER**

# Gas phase reaction combined light-regulated electrochemical sensing technique for improved response selectivity and sensitivity to hydrocarbons

Junkan Yu[1] · Shengwei Deng[2] · Han Jin[3] · Minxuan Huang[4,5,6] · Shaopeng Wang[4,5,6] · Xiaowei Zhang[1]

## Abstract

Yttria-stabilized zirconia (YSZ)-based potentiometric gas sensor has been widely utilized for detecting non-methane hydrocarbons (NMHCs) that derived from exhaust gases. Nevertheless, poor selectivity and sensitivity still remained a challenging issue. Herein, we reported an efficient strategy to sense NMHCs (e.g., $C_3H_6$) at high temperature through the gas phase reaction combined light-regulated sensing technique. When the YSZ-based sensor that was attached with ZnO sensing electrode and Mn-based reference electrode was operated without illumination, significant mutual interference that derived from CO was witnessed for sensing $C_3H_6$. On the contrary, enhanced sensitivity and selectivity are observed by simply illuminating the sensor. The low detection limit of the sensor to $C_3H_6$ extends to 0.768 ppm with the response/recovery rate of 27 s/30 s. These pilot results clearly indicate the validity of employing gas phase reaction combined light-regulated sensing technique in tailoring the response selectivity and sensitivity for future exhaust gas sensing.

**Keywords** Non-methane hydrocarbons (NMHCs) · Light-regulated electrochemical reaction · Carbon monoxide (CO) · Yttria-stabilized zirconia (YSZ) · Gas phase reaction

## Introduction

Nowadays, stringent emission regulations are for non-methane hydrocarbons (NMHCs) which are frequently found in exhaust gases, since they are able to react with nitrous oxides in the presence of sunlight leading to the generation of photochemical smog [1, 2]. According to the recently announced China VI vehicle emission standards, total emission amount of NMHCs must be strictly controlled within the value of 68 mg/km for new vehicles. Consequently, high-performance and reliable gas sensors that are capable of in situ monitoring the level of NMHCs directly emitted from vehicle engine are strongly required [3, 4]. Among those reported vehicle NMHC sensors, yttria-stabilized zirconia (YSZ)-based sensors are mainly focused, owing to their reliable performance in harsh conditions (e.g., high temperature and high humidity) [5–7]. However, it should be noted that for part of YSZ-based NMHC sensors, poor selectivity and inadequate detection limit significantly restrain their application in the real environment [8–11].

---

Junkan Yu, Shengwei Deng and Han Jin contributed equally to this work.

✉ Han Jin
jinhan10@sjtu.edu.cn

✉ Shaopeng Wang
wsp@gxu.edu.cn

✉ Xiaowei Zhang
zhangxiaowei@nbu.edu.cn

1 Environmental Monitoring & Sensing Technology Lab, School of Electrical Engineering and Computer Science, Ningbo University, Ningbo 315211, People's Republic of China

2 College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, People's Republic of China

3 Institute of Micro-Nano Science and Technology, Shanghai Jiao Tong University, Shanghai 200240, China

4 School of Marine Sciences, Guangxi University, Nanning 530004, China

5 Guangxi Laboratory on the Study of Coral Reefs in the South China Sea, Nanning 530003, China

6 Guangxi Key Laboratory of Processing for Nonferrous Metallic and Featured Materials, Nanning 530003, China
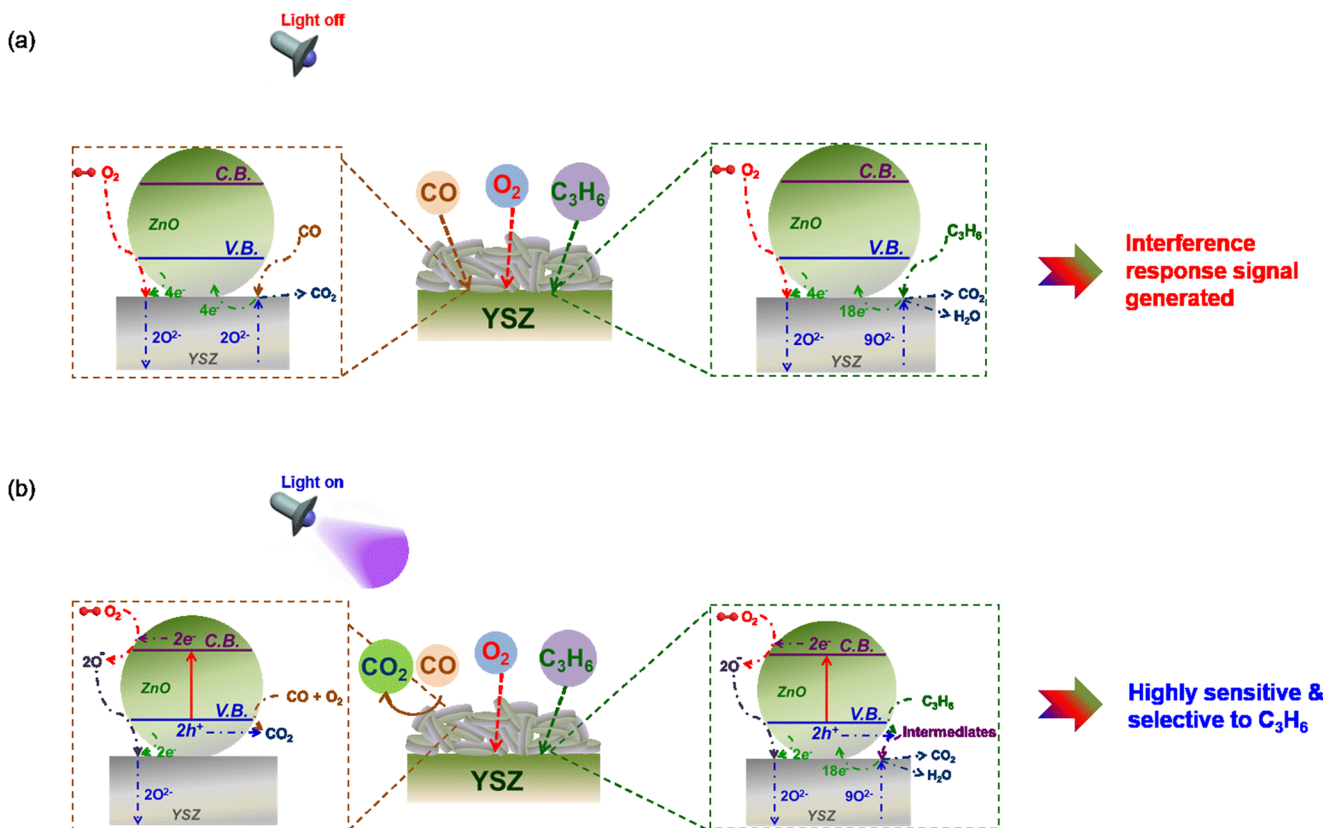
**(a)**



**(b)**

**Fig. 1** Illustration on the mechanism of gas phase reaction combined light-regulated electrochemical sensing technique: reaction process for the YSZ-based sensor operated at (**a**) light off and (**b**) light on

Quite recently, we proposed an alternative strategy, namely, light-regulated sensing technique, for efficiently enhancing sensing response of the YSZ-based gas sensors. For instance, low detection limit (LOD) of the YSZ-based sensor to part of target gases can be even extended to dozens of ppb (parts per billion) which is useful for detecting target gases at ultra-low

concentration [12–14]. Moreover, several examples about the impact of the light-regulated sensing technique on the selectivity have been reported [15, 16]. Among them, YSZ-based sensor operated at light-regulated amperometric mode shown desirable selectivity to NMHCs (e.g., $C_3H_6$) without any assistance of algorithm [14]. However, it must be noted that
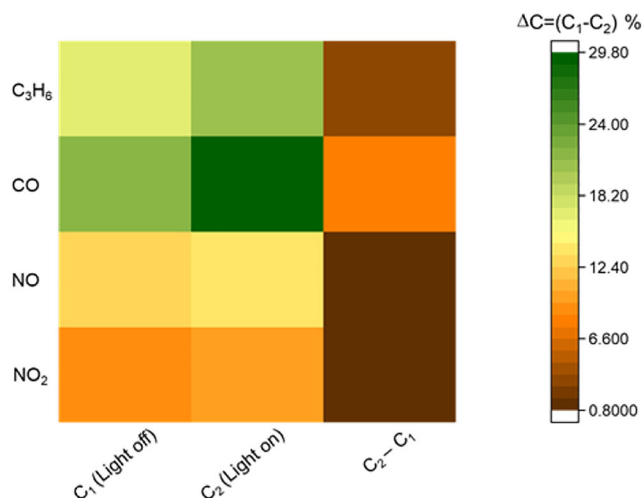


**Fig. 2** Comparison on the photocatalytic activity of the ZnO sensing material to CO, $C_3H_6$, and NOx, where C1 (light off), C1 (light on), and ⊿C represent conversion rate of each gas measured at light off, light on, and difference in conversion rate
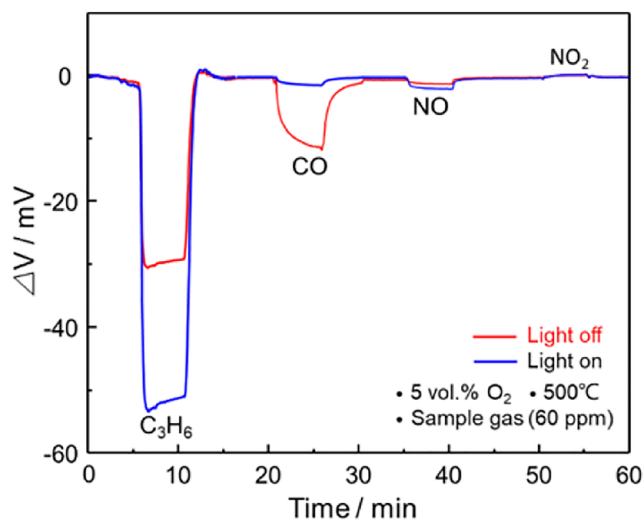
**Fig. 3** Sensing characteristics of the YSZ-based sensor utilizing ZnO-SE (vs. Mn-based RE) to 60 ppm various typically found exhaust gases, operated at light on (or off)
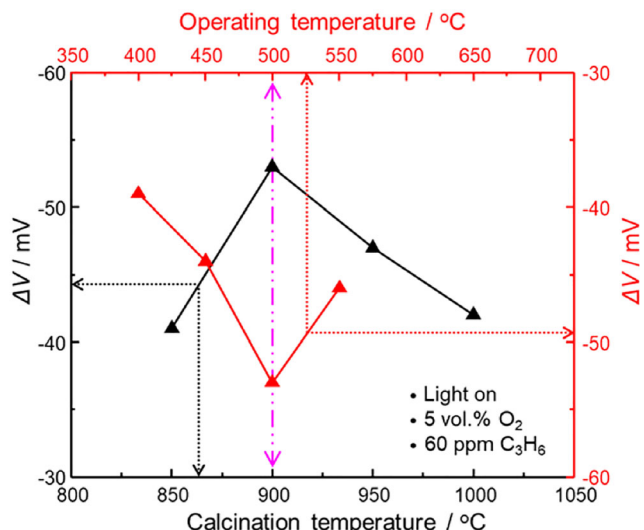
**Fig. 4** Variation of the response signal of the YSZ-based sensor that operated at light on to 60 ppm $C_3H_6$, at different fabricating/operating temperature

specific bias voltage has to be continuously applied on a sensor that operated at amperometric mode; this would decrease the long-term stability due to the inevitable electrode polarization that derived from the continuously applied bias voltage. Consequently, it is highly desirable to find extra alternative strategy to figure out the concerned issue.

Herein, we proposed gas phase reaction combined light-regulated electrochemical sensing technique and confirmed the practicability of adopting the presented sensing technique in tailoring the response selectivity. In addition, sensing behavior of the YSZ-based sensor that operated with the newly proposed sensing technique was systematically studied.

## Experimental section

### Fabrication of the sensors

YSZ-based gas sensor was fabricated with the previously reported procedure [14]. In brevity, commercial $Mn_3O_4$ that was mixed with α-terpineol was screen printed on the surface of YSZ plates to form $Mn_3O_4$-banded electrode. After drying overnight, the YSZ plate was calcined at high temperature to form the Mn-based reference electrode (RE). Then, photoactive ZnO powder that was mixed with α-terpineol was screen printed on the surface of YSZ plate and calcined at high temperature to obtain the ZnO sensing electrode (SE).

### Evaluation of the sensing behavior and characterization of the sensors

Sensing experiments were also performed with the similar procedure that was previously reported [14]. In brevity, the sensor was simultaneously exposed to the base gas (air base) or the sample gas that contains each of the selected hazardous gases ($C_3H_6$, CO, and NOx in the range of 20–500 ppm, total flow rate: 200 mL/min) to evaluate gas-sensing characteristics. A UV lamp (Yonglin, China, 5 W, 385 nm) was used for illumination. The sensing signal of electric potential difference $\Delta V$ ($\Delta V = V_{sample\ gas} - V_{base\ gas}$) was recorded by using an electrochemical analyzer system. Current-voltage (polarization) curves were measured with the electrochemical analyzer system using the linear potential sweep method scanning at 500 °C in air base (or sample gas). The details of measuring of gas phase catalytic activity of ZnO to each examined hazardous gases can be summarized as follows:
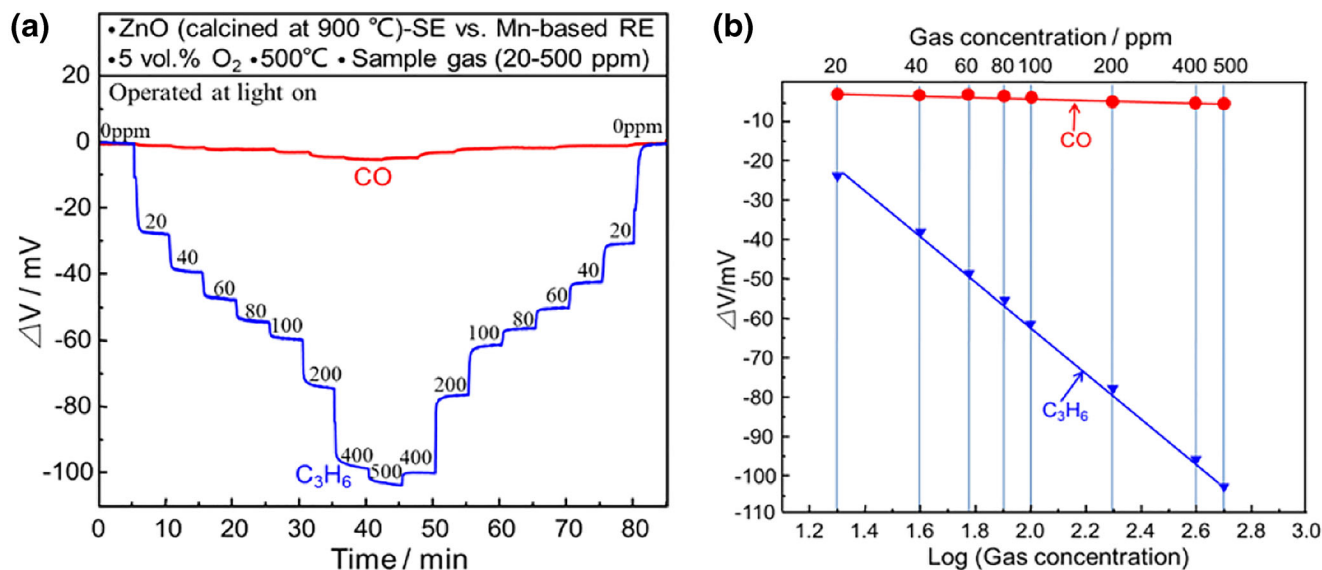


**Fig. 5** (**a**) $\Delta V$-response transients toward different $C_3H_6$ (and CO) concentrations and (**b**) dependence of sensitivity ($\Delta V$) on the logarithm of $C_3H_6$ (and CO) concentration, for the YSZ-based sensors using ZnO-SE and Mn-based RE, operated at 500 °C with illumination
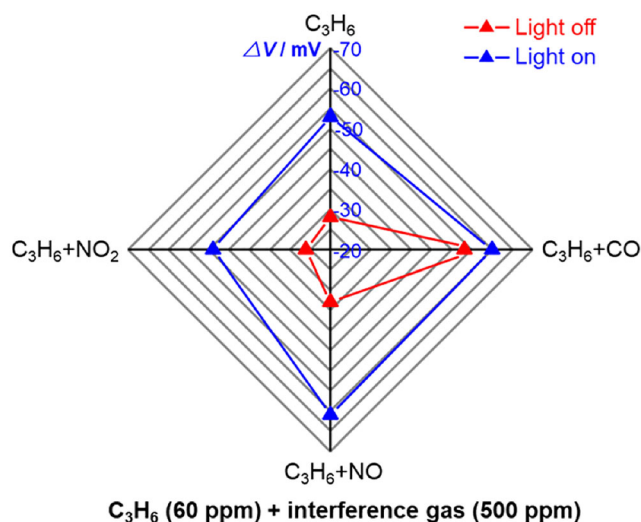
**Fig. 6** Comparison of the sensing behavior to $C_3H_6$ against other interference gases for the YSZ-based sensor, recorded at light off or on

60 ppm sample gas were flowed through 20 mg ZnO powder at 500 °C (with or without illumination), and the changes in gas concentration were measured via gas chromatography (GC) with TCD detector (for NOx) or FID detector (for $C_3H_6$ and CO) to obtain the sample gas convert percentage.

## Results and discussion

Mechanism of the gas phase reaction combined light-regulated electrochemical sensing technique can be summarized as follows: (1) when operating the YSZ-based sensor without the illumination (light off), target NMHCs (e.g., $C_3H_6$) and typical interference gases (e.g., CO) as well as surrounding oxygen (5 vol.%) reach the reaction interface
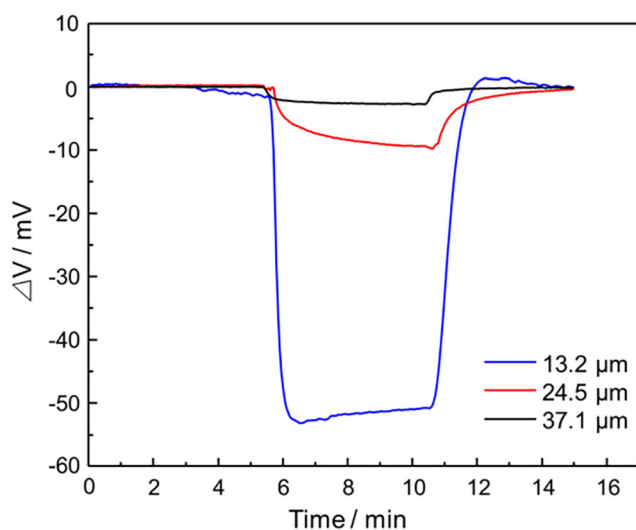


**Fig. 7** Impact of the thickness for the ZnO sensing layer on the response value of 60 ppm $C_3H_6$, for the YSZ-based sensor operated at light on and 500 °C

(triple phase boundary, TPB), generating response signal. Since the total response signal includes part of signal derived from interference gases, mutual interference would be found (Fig. 1a); (2) when illuminating the YSZ-based sensor, light-regulated electrochemical reaction is triggered. In this case, if the sensing material demonstrates high photocatalytic activity to interference gases and modest photocatalytic activity to NMHCs, interference gases will be converted to electrochemically inactive products, while more electrochemically active intermediates are expected for target NMHCs during gas phase reaction. Technically, response signal derived from interference gases can be removed, solely leaving response signal to target NMHCs. Besides, enhanced response signal to target NMHCs is speculated, and thus, the YSZ-based sensor would give high selectivity and sensitivity to NMHCs, as shown in Fig. 1b.

In order to confirm the assumption that was depicted in Fig. 1, photocatalytic activity is implemented. In this study, ZnO (to be the sensing material) is selected as the research example. Figure 2 gives the comparison on the photocatalytic activity of the ZnO sensing material to those gas species that can be typically found in vehicle exhaust gases. In brevity, ZnO demonstrates the highest, modest, and lowest photocatalytic activity to CO, $C_3H_6$, and NOx (NO and $NO_2$). Since the largest difference in conversion rate ($\Delta C = C_2 - C_1$) that measured at light on ($C_2$) and light off ($C_1$) (around 8.1%) is observed for CO. In comparison with CO, difference on conversion rate for $C_3H_6$, NO, and $NO_2$ is about 3.5%, 1.1%, and 0.8%. This important finding indicates the possibility that CO could be directly converted to electrochemical inactive $CO_2$ when illuminating the ZnO. In other words, response signal derived from CO will be removed.

Based on the abovementioned discussion, it is speculated that CO would be chemically removed during gas diffusion process. In light of demonstrating the attractive vision, initially sensing behavior of the YSZ-based sensor utilizing ZnO-SE and Mn-based RE is thoroughly studied with light on (or off). Note that the sensor fabricating temperature of 900 °C and operating temperature of 500 °C are selected for the pilot study, according to our previous research experience. As shown in Fig. 3 that without illumination, response signal of CO significantly is interfered with that of the response signal of $C_3H_6$. Response value to 60 ppm CO and $C_3H_6$ is around − 12.23 mV and − 28.17 mV, respectively. On the contrary, after triggering the gas phase reaction light-regulated electrochemical sensing process by exposing the sensor to illumination, response value of 60 ppm CO decreased down to − 2.66 mV, while response signal to $C_3H_6$ at the same level increased up to − 53.24 mV. It should be additionally mentioned that other interference gases that can be typically found in vehicle exhaust gases, such as NO and $NO_2$, contribute to negligible response. Then, sensor fabricating temperature and operating temperature are further optimized, as shown in

**Table 1** Sensing magnitude at 60 ppm, LOD, and sensitivity for the sensor operated at light on and off for the selected 4 exhaust gases

| VOCs | $-\Delta V$ (at 60 ppm)/mV | | -Sensitivity/(mV/Dec.) | | LOD/ppm | |
|------|-----------|----------|-----------|----------|-----------|----------|
| | Light off | Light on | Light off | Light on | Light off | Light on |
| $C_3H_6$ | 28.17 | 53.24 | 12.5 | 36.4 | 8.97 | 0.768 |
| CO | 12.23 | 2.66 | 8.71 | 4.23 | 28.57 | 64.53 |
| NO | 3.18 | 2.99 | 2.62 | 2.62 | 62.36 | 62.19 |
| $NO_2$ | −1.11 | −1.21 | −1.17 | −1.16 | 70.94 | 70.94 |

Fig. 4. YSZ-based sensor comprised of ZnO-SE (vs. Mn-based RE) gives optimal sensing behavior to $C_3H_6$ when fabricated at 900 °C and operated at 500 °C, with illumination.

Figure 5 exhibits (a) the $\Delta V$-response transients and (b) the dependence of $\Delta V$ on the logarithm of $C_3H_6$ concentration in the range of 20–500 ppm, operated at light on. The $\Delta V$ value changes quickly with a change in gas concentration and reaches a steady-state value in a short while; the 90% response/recovery time is approximately 27 s/30 s. In addition, $\Delta V$ varied linearly with the logarithm of $C_3H_6$ concentration in the examined range. $\Delta V$-response transients and (b) the dependence of $\Delta V$ on the logarithm of CO concentration are also studied to further verify its minor interference on the response behavior of $C_3H_6$. It is easy to see that the sensor exhibits minor response value to CO (− 1.66 to − 5.89 mV) in the examined range, suggesting that a high selectivity is obtained for the sensor when sensing $C_3H_6$.

Figure 6 depicts that the response fluctuation for the wearable electronic that was exposed to various gas mixture (60 ppm $C_3H_6$ + 500 ppm exhaust gases) is recorded and presented in the form of radar map. These typically coexisted exhaust gases heavily influence the response signal to $C_3H_6$ when the sensor is operated at light off, since response signal

to the gas mixture largely deviated from that of the gas species solely containing acetone. On the contrary, minor fluctuated response signal within the acceptable range (response value: − 51.67 to − 60.50 mV) is witnessed for the sensor operated at light on, indicating a desirable selectivity to $C_3H_6$ even mixed with high concentration interference gases. Impact of the thickness for the sensing layer on the response value of the sensor to 60 ppm $C_3H_6$ is examined (Fig. 7). It is clear that the increase in the sensing layer results in the decrease in the response value of $C_3H_6$ which can be attributed to the increased gas diffusion pathway. Since the increase in the gas diffusion pathway indicates more amount of sample gas being consumed, leaving less amount of sample gas participating the electrochemical reaction at TPB, decrease in the response value is expected. Table 1 summarizes the difference in the sensing magnitude at 60 ppm and the detection limit as well as sensitivity for the sensor operated at light on and off in relation to these selected exhaust gases. After applying the illumination on the sensor, the response value of $C_3H_6$ is clearly enhanced regarding LOD and sensitivity; most notably, the detection limit for $C_3H_6$ extended from 8.97 ppm to 768 ppb. On the other hand, significant decline in the response value and sensitivity as well as LOD is found for the sensor when
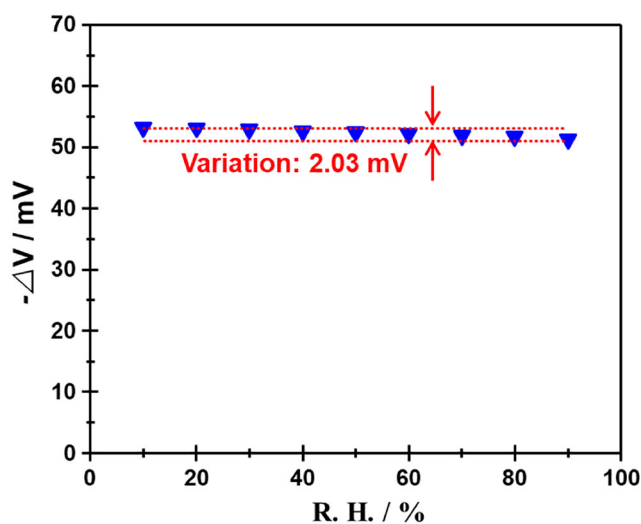


**Fig. 8** Response behavior of the sensor to 60 ppm $C_3H_6$ at different relative humidity (R. H.), recorded at light on
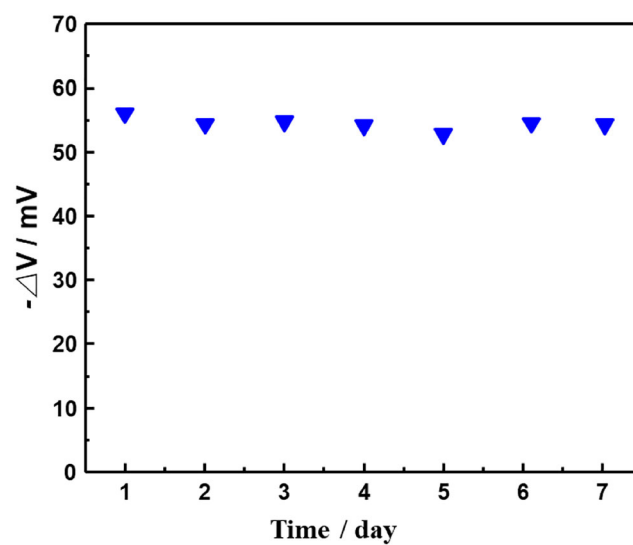


**Fig. 9** Stability of the sensor to 60 ppm $C_3H_6$ within 1 week, recorded at light on
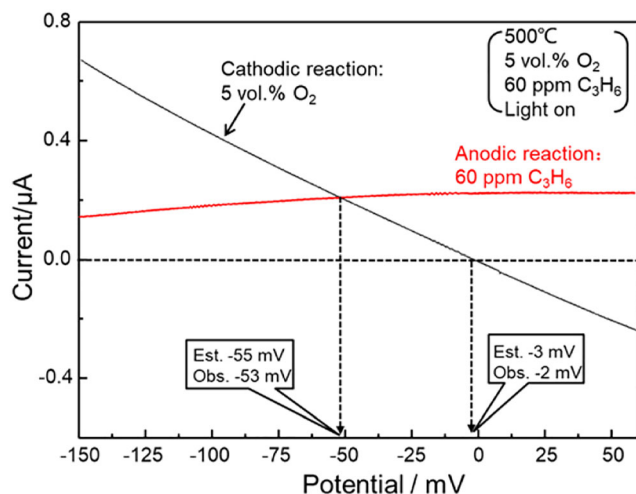
**Fig. 10** Standard modified polarization curves of the sensor coupled with ZnO-SE and Mn-based RE operated at 500 °C (with illumination) for air base and 60 ppm $C_3H_6$

sensing CO. The humidity effect on the sensing performance and stability of the sensor within 1 week are specifically investigated. As shown in Fig. 8, that minor variation of the response value (2.04 mV) is found in the relative humidity (R. H.) range of 0–90% which may be due to the water vapor trends to desorption at such high temperature. Moreover, the sensor gives relative stable performance when sensing of $C_3H_6$ (Fig. 9). In summary, with the assistance of the gas phase reaction combined light-regulated sensing technique, the sensor shows satisfactory sensitivity and selectivity to NMHCs (e.g., $C_3H_6$).

Current-voltage (polarization) curves for the YSZ-based sensor using ZnO-SE calcined at 900 °C are measured with illumination to confirm the sensing behavior of the sensor, being presented in the form of standard modified polarization curves (shown in Fig. 10). It was found that the sensing behavior of the sensor that operated light on perfectly matched with the mixed-potential behavior, the difference between the $V_{sample-gas}$ value observed from experiment (herein after denoted as Obs.) and the $V_{sample-gas}$ value estimated from the standard modified polarization curves (hereinafter denoted as Est.) for the sensors toward 60 ppm $C_3H_6$ was within 2 mV. Based on the results presented in Fig. 10, it can be deduced that mixed-potential behavior governed the sensing behavior.

## Conclusion

For the purpose of achieving high performance in detecting NMHCs, gas phase reaction combined light-regulated sensing technique is proposed for exhaust gas sensing. Based on the comparison on photocatalytic activity, it can be concluded that interference response signal derived from part of interference

gases (e.g., CO) can be removed by simply exposing the sensor to illumination. Interestingly, the experiment results perfectly matched the theoretical speculation. It was found that when the sensor was operated at light off, significant mutual interference that derived from CO was witnessed for sensing NMHCs (e.g., $C_3H_6$). By illuminating the sensor, enhanced sensitivity and selectivity are observed. These preliminary results clearly indicate the validity of employing gas phase reaction combined light-regulated sensing technique in tailoring the response selectivity and sensitivity.

## References

1. Greenberg JP, Zimmerman PR (1984) Nonmethane hydrocarbons in remote tropical, continental, and marine atmospheres. J Geophys Res 89:4767–4778. https://doi.org/10.1029/JD089iD03p04767

2. Hagerman LM, Aneja VP, Lonneman WA (1997) Characterization of non-methane hydrocarbons in the rural southeast United States. Atmos Environ 31:4017–4038. https://doi.org/10.1016/S1352-2310(97)00223-9

3. Sato T, Ikeda H, Miura N (2014) Mixed-potential type zirconia-based $NH_3$ sensor using $SnO_2$-disk sensing-electrode attached with sputtered Au. ECS Electrochem Lett 3:2014–2016. https://doi.org/10.1149/2.004406eel

4. Espid E, Taghipour F (2017) Development of highly sensitive ZnO/$In_2O_3$ composite gas sensor activated by UV-LED. Sensors Actuators B Chem 241:828–839. https://doi.org/10.1016/j.snb.2016.10.129

5. Mori M, Itagaki Y, Sadaoka Y (2012) VOC detection by potentiometric oxygen sensor based on YSZ and modified Pt electrodes. Sensors Actuators B Chem 161:471–479. https://doi.org/10.1016/j.snb.2011.10.063

6. Liang X, Yang S, Li J, Zhang H, Diao Q, Zhao W, Lu G (2011) Mixed-potential-type zirconia-based $NO_2$ sensor with high-performance three-phase boundary. Sensors Actuators B Chem 158:1–8. https://doi.org/10.1016/j.snb.2011.02.051

7. Jin H, Huang Y, Jian J (2015) Sensing mechanism of the zirconia-based highly selective NO sensor by using a plate-like $Cr_2O_3$ sensing electrode. Sensors Actuators B Chem 219:112–118. https://doi.org/10.1016/j.snb.2015.04.123

8. Plashnitsa VV, Elumalai P, Fujio Y, Miura N (2009) Gas sensing characteristics of Au sensing electrode fabricated on YSZ single-crystals. Proc IEEE Sensors:711–714. https://doi.org/10.1109/ICSENS.2009.5398553

9. Wang B, Haick H (2013) Effect of chain length on the sensing of volatile organic compounds by means of silicon nanowires. ACS Appl Mater Interfaces 5:5748–5756. https://doi.org/10.1021/am401265z

10. Brosha EL, Mukundan R, Lujan R, Garzon FH (2006) Mixed potential NOx sensors using thin film electrodes and electrolytes for stationary reciprocating engine type applications. Sensors Actuators B Chem 119:398–408. https://doi.org/10.1016/j.snb.2005.12.044

11. Huynh TP, Haick H (2016) Self-healing, fully functional, and multiparametric flexible sensing platform. Adv Mater 28:138–143. https://doi.org/10.1002/adma.201504104

12. Lu G, Xu J, Sun J, Yu Y, Zhang Y, Liu F (2012) UV-enhanced room temperature $NO_2$ sensor using ZnO nanorods modified with $SnO_2$ nanoparticles. Sensors Actuators B Chem 162:82–88. https://doi.org/10.1016/j.snb.2011.12.039

13. Li H, Jin Q, Zhang X, Bi C, Zhang X, Jin H, Li F, Shen W, Zou J, Deng S, Cheung W, Kam W, Wang J, Jian J (2019) Artificial tailored catalytic activity for identification of 6 kinds of volatile organic compounds via the light-regulated electrochemical reaction. Sensors Actuators B Chem 282:529–534. https://doi.org/10.1016/j.snb.2018.11.090

14. Zou J, Sun H, Zhang X, Zhang X, Jin H, Li F, Zhang S, Hua C, Sheng W, Jin Q, Jian J (2018) Light-regulated electrochemical reaction: can it be able to improve the response behavior of amperometric gas sensors? Sensors Actuators B Chem 267:366–372. https://doi.org/10.1016/j.snb.2018.04.032

15. Gu D, Wang X, Liu W, Li X, Lin S, Wang J, Rumyantseva MN, Gaskov AM, Akbar SA (2020) Visible-light activated room temperature $NO_2$ sensing of $SnS_2$ nanosheets based chemiresistive sensors. Sensors Actuators B Chem 305:127455. https://doi.org/10.1016/j.snb.2019.127455

16. Isaifan RJ, Couillard M, Baranova EA (2017) Low temperature-high selectivity carbon monoxide methanation over yttria-stabilized zirconia-supported Pt nanoparticles. Int J Hydrog Energy 42:13754–13762. https://doi.org/10.1016/j.ijhydene.2017.01.049