Compact quartz-enhanced photoacoustic sensor for ppb-level ambient NO₂ detection by use of a high-power laser diode and a grooved tuning fork

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ABSTRACT
A compact quartz-enhanced photoacoustic sensor for ppb-level ambient NO₂ detection is demonstrated, in which a high-power blue laser diode module with a small divergence angle was employed to take advantages of the directly proportional relationship between sensitivity and power, hence improving the detection sensitivity. In order to extend the stability time, a custom grooved quartz tuning fork with 800-μm prong spacing is employed to avoid complex signal balance and/or optical spatial filter components. The sensor performance is optimized and assessed in terms of optical coupling, power, gas flow rate, pressure, signal linearity and stability. A minimum detectable concentration (1σ) of 7.3 ppb with an averaging time of 1 s is achieved, which can be further improved to be 0.31 ppb with an averaging time of 590 s. Continuous measurements covering a five-day period are performed to demonstrate the stability and robustness of the reported NO₂ sensor system.

1. Introduction
Nitrogen dioxide (NO₂) is a red-brown, pungent and toxic gas recognized as a primary air pollutant due to its impact on tropospheric ozone formation and destruction. In addition to natural lightning, ambient NO₂ is mainly released from anthropogenic high-temperature combustion processes, such as vehicle exhaust and boiler exhaust emissions. NO₂ is one of the main causes of photochemical smog and acid rain, thus representing one of the key contributors to the determination of air quality in urban environments [1-5]. Besides that, NO₂ is designated as one of the United States Environmental Protection Agency’s (US EPA) “criteria pollutants”, therefore the NO₂ concentration is an important indicator in daily urban air pollution index [6,7]. In the atmosphere, the typical average mixing ratio of NO₂ is about 10–30 ppb by volume, but it may even rise by several orders of magnitude in highly polluted areas. Prolonged exposure to NO₂ gas at even low concentration level can lead to respiratory diseases in humans and animals, hence there is a need to develop a robust, sensitive and cost-effective sensor system for atmospheric NO₂ monitoring [8-12].

Various gas analysis techniques have been developed and widely used for NO₂ detection and they are mainly based on the principles of electrochemistry and optics [13-23]. Electrochemical sensors have relatively slow response time, limited lifetime and poor selectivity for NO and NO₂. Compared with electrochemical methods, optical detection techniques for NO₂ measurement can provide the advantages of sensitivity, selectivity, and real-time monitoring, such as differential optical absorption spectroscopy (DOAS) [24], laser-induced fluorescence (LIF) [25], cavity ring-down spectroscopy (CRDS) [26-29] and photoacoustic spectroscopy (PAS) [30,31]. Among them, PAS is one of the most promising techniques to monitor trace gas level due to its benefits of high sensitivity, selectivity, and fast response [32-35]. Besides, PAS-based gas sensors provide two unique interests: (1) ...
Wavelength independence, meaning that trace gas with different characteristic absorption spectrum can be measured by employing the same spectrophone and the photodetector is not required; (2) The directly proportional relationship between sensitivity and incident laser power, which means that use of a higher laser power could provide better sensing performance.

Quartz-enhanced photoacoustic spectroscopy (QEPAS), a modification of the PAS, was first reported and demonstrated in 2002 [36, 37]. In QEPAS-based sensors, commercially available piezoelectric quartz tuning fork acoustically couples with two acoustic micro resonators (AmRs) acting as sharply resonant acoustic transducer to detect sound signal instead of conventional wideband microphone [38–43]. In 2011, Yi et al. [32] used a 7-mw blue laser diode for the first time to demonstrate a trace NO\textsubscript{2} detection in the laboratory using the QEPAS technique. The detection sensitivity and the stability time are not sufficient for ambient NO\textsubscript{2} detection. In order to take advantage of the linear relationship between sensitivity and power, a high power light source is needed, but usually is characterized by a degraded beam quality. This brings a great...
challenge to couple a high-power beam through a 300-μm prong-spacing QTF since any light hitting the QTF can cause a large background signal. In 2015, Zheng et al. [44] developed a NO$_2$ sensor based on the QEPAS technique by use of a 160-mW wide-stripe LED. An electrical modulation cancellation method (E-MOCAM) was demonstrated capable to reduce the excessive background signal and a detection limit of 1.3 ppb was obtained at 1-s integration time. But this method increase the complexity of the sensing system and hence reduced its robustness. Moreover, the stability time of the system is only tens of seconds so that a routine calibration must be performed at fixed intervals. In 2016, a scattered light modulation cancellation method (SL-MOCAM) was combined with QEPAS technique to detect the NO$_2$ and a $1\sigma$ detection limit of ~ 60 ppb was achieved at 1-s integration time [45]. This method suppressed background signal by exploiting two light sources: excitation and balance light sources, and extended the stability time up to 360 s. But the issue regarding sensor size was still not solved and this detection sensitivity was insufficient for ambient NO$_2$ detection. Therefore, the current QEPAS-based sensors can not be employed for long-term ambient NO$_2$ monitoring, due to the insufficient detection sensitivity or/and the short stability time.

In fact, the MOCAM methods introduce an inverted external signal to balance, rather than eliminate, the background signal which changes slowly over time and external environment. As a result, a passive constant compensation cannot balance the slow drift and hence a long stability time cannot be achieved. To essentially remove this background signal, there are two ways: (1) design and use large-prong-spacing QTF so that the beam can clearly pass through the prong gap of the QTF; (2) employ a light source with an improved beam quality. These two ways should work together to achieve the best results.

In this work, we demonstrate a miniaturized and integrated QEPAS-based NO$_2$ sensor, in which a custom surface-grooved QTF and a high-power small-sized laser diode (LD) module are used. The grooved QTF has a prong spacing of 0.8 mm and a high quality factor of ~ 15,000, avoiding the use of complicated MOCAM and/or spatial beam filter, and thus reducing the background signal as well as extending the stability time of the sensor. Besides, both prong surfaces have rectangular grooves to enhance the piezoelectric effect of the QTF. By means of the linear relationship between sensitivity and power, the performance of the QEPAS sensor in terms of detection sensitivity and long term stability is significantly improved.

2. Sensor design and characterization

2.1. Selection of the exciting diode laser

According to the HITRAN database [46], the NO$_2$ has a broadband absorption from 250 nm to 650 nm and the corresponding absorption cross sections is exhibited in Fig. 1. The absorption cross section of NO$_2$ gas is large within the wavelength range of 400–450 nm, and a
maximum cross-section of 7.4 × 10^{-19} \text{ cm}^2/\text{molecular} is observed at 414 nm. Nevertheless, the wavelength of 414 nm is not the best choice for NO\textsubscript{2} photoacoustic detection due to the photochemical dissociation which can be induced by the excitation laser with \( \lambda < 415 \text{ nm} \) as following [1]:

\[
\begin{align*}
\text{NO}_2 + h\nu (\lambda < 415 \text{ nm}) & \rightarrow \text{NO}_2^* \rightarrow \text{NO} + \text{O} \\
\text{O}_2 + \text{O} + \text{M} & \rightarrow \text{O}_3 + \text{M}
\end{align*}
\]

where NO\textsubscript{2}* represents the NO\textsubscript{2} molecule in the excited state and \( \text{M} \) represents one of N\textsubscript{2}, O\textsubscript{2} and other molecules. Hence the wavelength of the excitation light source should satisfy the condition \( \lambda > 415 \text{ nm} \) to avoid the attenuation of photoacoustic signal due to the photolysis.

Considering the excitation wavelength and miniaturization of the laser source, a custom blue multimode LD module (Changchun New Industries Optoelectronics Technology, China) emitting at 450 nm was selected as excitation source of the NO\textsubscript{2}-QEPAS sensor with a maximum continuous wave (CW) output power of 3.5 W. The LD module operated at room temperature with a power fluctuations (rms, 24 h) of 3%. The LD emission spectrum was measured by employing a spectrometer (Avantes, Netherland, Model AVS-DESKTOP-USB2) and a spectra width (full width at half maximum) of ~ 7 nm was obtained as shown in Fig. 1. The LD has a beam divergence (full angle) of 1.4 × 0.2 mrad, bringing significant improvement in the beam quality compared with the Refs. [44,45].

Furthermore, small size is a noticeable feature of this LD module which has an outside dimension of ~ 800 cm\(^3\) (163 × 77 × 65 mm\(^3\)), allowing the laser source to apply to compact gas sensors. In this work, the laser intensity was modulated by a square-wave signal with a duty cycle of 50%, making the average optical power only half that in CW mode. The relationship between the LD average power and the driving voltage was plotted in Fig. 2, showing a good linearity.

**Fig. 8.** (a) QEPAS signals recorded as a function of time at different NO\textsubscript{2} concentration levels. (b) Same data averaged and plotted as a function of NO\textsubscript{2} concentration. The red line represents the linearity of the sensor response.

**Fig. 9.** Allan deviation analysis from time series measurements in pure N\textsubscript{2} for the QEPAS-based sensor system.

**Fig. 10.** On-line NO\textsubscript{2} monitoring on the campus of Shanxi University from Mar. 30, 2021 to Apr. 3, 2021 (blue). And the corresponding data available from a nearby station of the CNEMC (red).
2.2. Integrated QEPAS-based NO2 sensor design

The experimental setup of the developed NO2 sensor based on the high-power blue LD module and the surface-grafted QTF is schematically depicted in Fig. 3. To miniaturize the QEPAS-based system, all the components were integrated into a two-floor architecture which has an outside dimension of $38 \times 23 \times 20 \text{ cm}^3$. The small-sized blue LD module was used as excitation source to excite QEPAS signal. A laser driver board was employed to control the current and temperature of the LD module. A square-wave signal with a frequency of $f_0$ from a function generator was applied to the LD by means of the intensity modulation photoacoustic detection approach. Then the modulated laser beam pass through an acoustic detection module (ADM) which consists of a spectrophone and a gas enclosure. Due to the high transmissivity efficiency (95%) at 450 nm, two quartz windows ($M_1$, $M_2$) with diameters of 25.4 mm was mounted on the either side of the gas enclosure for optical access. The spectrophone was composed of a custom grooved QTF and two AmRs which were symmetrically positioned on both sides of the QTF. The current signal generated from piezoelectric effect of the QTF was amplified by a low noise trans-impedance pre-amplifier (TA) with a feedback resistor $R_2$ of 10 MΩ and then directed to a lock-in amplifier (LIA) board (FEMTO Inc., Germany, Model LIA-BVD-150-H) for demodulation processing. The filter slope and the time constant of the LIA board were set to a 12 dB/oct and 300 ms, respectively, leading to a detection bandwidth $\Delta f$ of 0.833 Hz. A power meter (PM) was placed behind the ADM to measure the laser power and facilitated the beam alignment. Besides, a gas inlet and outlet were located at the top of the ADM for gas exchange. The gas dilution system (Environics Inc., USA, Model EN4000) diluted a certified 10-ppm NO2:N2 mixture gas with a pure N2 to produce the NO2:N2 mixture gases with different concentration levels for assessing the performance of the NO2 sensor system. A pressure control module (CSensor Inc., China, Model XGZP6847A) was combined with a diaphragm pump to control the gas pressure in the ADM. The gas flow rate was adjusted and monitored via a needle valve and a mass flow sensor (Consenc Inc., Model CAFS3000), respectively.

The custom-made QTF used in the spectrophone is a grooved QTF with a resonance frequency of 15.2 kHz which was acoustically coupled with two identical AmRs with an inner diameter of 1.65 mm and a length of 7 mm, forming an on-beam QEPAS configuration. A signal enhancement factor of ~30 is achieved with such an optimum configuration compared to the bare grooved QTF without AmRs. The two prongs of the grooved QTF are separated by 800 μm, and the QTF has a prong length of 19.4 mm, a width of 2 mm, and a thickness of 0.25 mm. Furthermore, four rectangular grooves with an area of $1.8 \times 7 \text{ mm}^2$ and depth of 0.05 mm were carved on each QTF prong surface in order to provide a reduced electrical resistance $R$ without affecting the quality factor $Q$. Such a modified QTF has a $Q$ value of 107.15 kΩ and Q-factor of 15022, effectively enhancing the piezoelectric effect of the QTF. The details of the QTF design are described in Refs. [47–49]. The QEPAS signal amplitude $S$ can be expressed as [50–52]:

$$S_{\text{QEPAS}} = \alpha P f_0$$

where $\sigma$ is the absorption coefficient, $P$ is the laser power, $Q$ and $f_0$ is the quality factor and the resonance frequency of QTF. The custom grooved QTF having a resonance frequency of 15.2 kHz can provide a higher QEPAS signal than a 32.7-kHz standard QTF under the same condition, according to Eq. (3).

The employed LD is a multimode laser source which has an elliptical beam spot with a divergence of $1.4 \times 0.2 \text{ mrad}$. Hence a convex quartz lens with 100-mm focal length was utilized to focus the elliptical beam so that it can pass through the spectrophone. As shown in Fig. 4(a), the beam propagation through the ADM was detected by a Pyrocam IIIHR Beam Profiling Camera, demonstrating the dimensional change of laser spot along beam propagation path. The detailed size parameters of the laser spot at different distances from the convex lens are depicted in Fig. 4(b) and all measurements were operated at the same height which is defined as the zero point of the y-axis. The minimum lengths of major and minor axis of the elliptical laser spots are 840 μm and 500 μm, respectively, at the focal point of the lens ($x = 10 \text{ cm}$), demonstrating that the converging laser beam can pass through the prong spacing (800 μm) of the grooved QTF without being blocked.

### Table 1

| Detection technique          | Power (mW) | QTF gap (μm) | Stability time (s) | Detection sensitivity (ppb) | Long term on-line monitoring | Refs. |
|-----------------------------|------------|--------------|--------------------|-----------------------------|-----------------------------|-------|
| BB-OB-QEPAS                 | 7          | 300          | 20                 | 18                          | No                          | [27]  |
| E-MOCAM                     | 156        | 300          | 1                  | 1.3                         | No                          | [38]  |
| SL-MOCAM                    | 4.8        | 300          | 360                | 60                          | No                          | [39]  |
| This paper                  | 153        | 800          | 590                | 7.3                         | Yes                         | –     |

### 3. Results and discussion

#### 3.1. Parameter optimization of sensor system

Based on Eq. (3), the QEPAS signal is proportional to the incident optical power since more gas molecules are excited to higher energy levels with power increasing, thereby the NO2 sensor performance can benefit from the high laser power. However, the background signal and noise level induced by the stray light due to the multimode nature of the LD also increase with the laser power rising. Here the background signal refers to the offset of the zero baseline of QEPAS signal, while the noise level is defined as the random disturbance of QEPAS signal when measuring a specific gas concentration. In this work, a certified 10-ppm N2: NO2 gas mixture (Nanjing Special Gas Factory Co., Ltd.) was flushed into the ADM at atmospheric pressure and the gas flow rate was set to 30 sccm (standard-state cubic centimeter per minute). The relationship between QEPAS signal, noise and laser power was investigated as shown in Fig. 5(a). No significant variations in the background signal are observed with the power increasing, while the 1σ noise level significantly increases when the laser power is $>160 \text{ mW}$, as shown in the inset. The signal-noise-ratio (SNR) which is an important performance parameter of sensors is plotted in Fig. 5(b) according to the following equation:

$$\text{SNR} = \frac{S_{\text{QEPAS}} - S_{\text{RS}}}{S_n}$$

where $S_{\text{QEPAS}}$, $S_{\text{RS}}$, $S_n$ are the QEPAS signal amplitude, the background signal and the 1σ noise level, respectively. As described in Fig. 5(b), the SNR value increases gradually with the laser power increasing until a maximum is reached and then decreases. The maximum QEPAS SNR of 2510 was achieved at laser power of 153 mW. The corresponding driving voltage of the LD module is 2 V according to Fig. 3 and hence this optimum voltage value was selected in the following experiments.

When the inner volume of the ADM is defined, a faster response time can be achieved with a faster gas flow rate. However, the noise level grows with the gas flow rate since the gas turbulence disturbs the QTF prongs. The 1σ noise level is depicted in Fig. 6 as a function of the nitrogen flow rate ranging from 5 sccm to 100 sccm. The results show that the 1σ noise value increases by only 6% when the gas flow rate increases from 5 sccm to 40 sccm, while a rapid increase of the noise level occurs when the gas flow rate is $>50 \text{ sccm}$. Thus 40 sccm was selected as the optimum flow rate for the QEPAS-based NO2 sensor operation. A gas
exchange time of 110 s was experimentally measured for the 70-cm⁻³ inner volume of the ADM. In QEPAS, the pressure in ADM has to be taken into account since the quality factor of QTF, the vibration-translation relaxation and the intensity of absorption spectrum are all pressure dependent. Therefore, the gas pressure must be optimized and chosen appropriately for the optimization of the sensor performance. Fig. 7 shows the relationship between the QEPAS signal and the gas pressure from 25 Torr to 700 Torr. Although the Q-factor of the QTF decreases as the pressure increases, the intensity of the absorption spectrum and the V-T relaxation rate of gas molecules increases when the gas pressure rises. Therefore, a linear relationship (R Square ~ 0.999) between the gas pressure and the QEPAS signal is observed. Hence the atmospheric pressure was determined as the optimum operating pressure and thus there was no need for the sensor pressure control, further simplifying the NO₂ sensor.

3.2. Sensor performance assessment

In order to assess the sensor performance for the NO₂ detection, the QEPAS response to the NO₂:N₂ mixtures in the concentration range of 0–10 ppmv were measured and analyzed as shown in Fig. 8(a). These data were acquired at 1-s acquisition time under atmospheric pressure and the parameters (the laser power, the flow rate and the gas pressure) were fixed at the optimum values. The inset shows that a background signal of 120 µV was obtained when pure N₂ was fed into the ADM. The QEPAS signals under different NO₂ concentration were averaged, as shown in Fig. 8(b). The linear relationship with R square of 0.999 confirms the linearity of the NO₂ sensor response to concentration level. With 200-ppb NO₂:N₂ mixture flushed into the system, a minimum detection limit (MDL) of 7.3 ppbv with 0.833-Hz detection bandwidth (300-ms time constant and 12-dB filter slope) was achieved which is ~ 8 times lower than the SL-MOCAM based QEPAS sensor reported previously [45]. Due to the LD module which was used to probe a broadband absorption feature, the average cross-section of the LD emission spectrum must be less than the SL-MOCAM based QEPAS sensor. Furthermore, the reported sensor provides a smaller size, a higher linearity of the NO₂ sensor, due to the fact that the upper limit of the excitation power is usually subject to the saturation power of the photodetector. Nevertheless, in photoacoustic spectroscopy, sound waves rather than light waves are detected. The dynamic range of a sound transducer for sound detecting can be up to 130 dB and especially a QTF in QEPAS can ensure a linear response over four orders of magnitude. In this work, we demonstrated the realization of a compact QEPAS sensor for ppb-level ambient NO₂ detection, exploiting the linearity between QEPAS signal and laser power. A minimum detectable concentration (1σ) of 7.3 ppbv at the averaging time of 1 s and the stability time of 590 s were achieved with an excitation optical power of ~ 150 mW, which is very suitable for continuous ambient monitoring. Although there is a linear relationship between sensitivity and power in QEPAS, how much optical power can be used depends on the coupling quality of the QTF and the laser beam. A poor coupling quality will cause large background signal and noise level in the case of a high power excitation. Hence, when the QTF geometry and the beam quality are determined, there is an optimal excitation optical power maximizing the SNR. Thanks to the new QTF design and the custom LD module, the reported sensor exploits as much optical power as possible to improve the detection sensitivity without degrading stability time. Compared with MOCAM, the reported sensor provided a smaller size, a higher detection sensitivity and a longer stability time. The side-by-side comparison between the QEPAS-based NO₂ sensors demonstrated so far is listed in Table 1. The results show that the reported sensor provides the best performance. Deployment of the sensor system in a vehicle operation test to assess its performance for ambient NO₂ monitoring will be conducted in the future.

Declaration of Competing Interest

The authors declare that there are no conflicts of interest.

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