



## Enrichment-enhanced photoacoustic spectroscopy based on vertical graphene

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### ABSTRACT

This manuscript proposes a method to improve the gas detection sensitivity of the photoacoustic spectroscopy (PAS) by the enrichment of the concentration of a gas species based on vertical graphene (VG). This is accomplished by exploiting the characteristics of vertical graphene grown on Ni foam to adsorb gas molecules and subsequently desorb them at high temperatures. After the adsorption by the VG material, the enrichment cell is heated to 150 °C; then the enriched gas is collected and passed into the PAS cell. A DFB-QCL laser tuned at 5263 nm was used as the excitation light source of the PAS sensor for NO detection. The experimental results showed that at a gas pressure of 760 torr and with a signal integration time of 1 s, the ultimate detection limit of traditional photoacoustic spectroscopy for NO gas is 14 ppb, while that of enrichment-enhanced photoacoustic spectroscopy is 1.3 ppb, proving that this method can increase the sensitivity of one order of magnitude.

### 1. Introduction

With the improvement of population living standards, people have paid more and more attention to health issues in recent years. The factors that affect human health include many aspects and require different actions, from the air quality control to the prevention of human diseases. Due to the rapid development of industry, fossil fuels are used in large quantities, and a large amount of harmful nitrogen oxides are released in atmosphere after combustion, of which 90 % is nitric oxide gas [1–3]. Nitric oxide can react with water vapor to form acid rain and fog, which seriously affects people's lives [4,5]. At the same time, the increased content of nitric oxide in the human body could also lead to the generation of human diseases. It is reported that a large amount of NO gas can promote the occurrence of inflammation in the human body, leading to the formation of osteoarthritis. For this reason, NO is also used as an early diagnostic marker for osteoarthritis [6–9]. Therefore, the monitoring of nitric oxide is of great significance for air pollution monitoring

as well as for non-invasive medical diagnosis.

There are several methods for gas detection, including electrochemical sensors [10], semiconductor sensors [11], gas chromatography [12], and optical techniques. Optical detection methods have received increasing attention in recent years due to their unique high sensitivity, fast response, and real-time online measurement [13,14]. The optical detection methods can be mainly divided into two categories, the direct absorption spectroscopy and the indirect absorption spectroscopy techniques. Direct absorption techniques compare the spectral dependence of the light transmitted through the gas medium with that of the incident light, according to the Lambert-Beer law. Their sensitivity can be enhanced by increasing the optical path length with a multi-pass cell. For example, in 2019, Ruyue Cui et al. designed a dense spot pattern multi-pass cell based on a spherical mirror aberration, with a great improvement of the optical pathlength by using two spherical mirrors to fold the optical path [15]. Indirect absorption spectroscopy measures light absorption-induced, local changes in a related property of a gas

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sample. The excited molecules relax the excess of energy in non-radiative pathways, generating a local thermal diffusion (photo-thermal spectroscopy) and a sound wave propagation (photoacoustic spectroscopy, PAS). The more representative PAS techniques are quartz-enhanced photoacoustic spectroscopy (QEPAS) and cantilever-enhanced photoacoustic spectroscopy (CEPAS). They are significant improvements to the standard PAS obtained by replacing the traditional microphone with a quartz tuning fork (QEPAS) and a cantilever (CEPAS) for sound wave detection. In 2019, Shangzhi Li et al. realized a QEPAS sensor for carbon monoxide detection by employing a surface grooved tuning fork, achieving a CO minimum detection limit of 7 ppb for a 300 ms averaging time [16]. In 2022, a miniature dual-resonance CEPAS sensor based on silicon cantilever beam was developed by Guojie Wu et al. A minimum detection limit of 35.6 ppb was reached for methane detection, with a signal averaging time of 100 s [17]. The PAS signal is proportional to the exciting optical power and very high sensitivity levels were reached implementing cavity-enhanced based configurations [18–20] taking advantage of the power buildup occurring inside the resonator, although they required complex and bulky sensor configuration. Since the PAS signal is also proportional to the gas concentration [21], the detection sensitivity can also be improved by increasing the concentration of the gas to be measured. Sample enrichment methods can be adopted for this scope.

In this paper, we proposed a gas samples enrichment method by first exploiting adsorption processes of nitric oxide on the vertical graphene (VG) material, and then desorption processes triggered by heating to 150 °C, leading to an increase of the concentration of nitric oxide in the gas sample. VG material, often referred to as vertically aligned graphene nanosheets, consists of graphene layers oriented perpendicularly to a substrate. These sheets are typically arranged in a dense, forest-like structure. The vertical arrangement significantly increases the surface area compared to planar graphene, making it highly advantageous for applications requiring high surface interactions. The edges of graphene sheets are more exposed in a vertical arrangement, enhancing the material's chemical reactivity. This feature is beneficial for catalysis, sensing, and environmental applications. The enriched samples were sent to a PAS sensor, composed by a DFB-QCL laser emitting at 5263 nm as the excitation light source and a standard PAS cell. The feasibility of the enrichment method was verified by three runs of repeated measurements under the same operating conditions.

## 2. Experimental system

The growth process of the vertical graphene (VG) was carried out on the nickel foam. During the growth process, commercially available

high-purity nickel (99.99 %), with a porosity of approximately 98 %, was used as the deposition matrix. After cleaning the copper substrate with acetone, ethanol and deionized water, VG was grown in a plasma-enhanced chemical vapor deposition (PECVD) system [22–24]. The nickel foam substrate was placed in the center of the PECVD and heated to 900 °C under vacuum conditions (below 0.05 mbar). With a plasma power of 500 W, 2 standard cubic centimeter per minute (sccm) of H<sub>2</sub> and 6 sccm of C<sub>2</sub>H<sub>2</sub> were introduced as precursors. The entire growth process lasted for one hour, and then was naturally cooled to room temperature. Fig. 1 shows the SEM images of the VG grown on Ni foam.

The vertical graphene grown by PECVD has a special coral-like three-dimensional structure, a large specific surface area, and a large number of dangling bonds at the edge of the material. These properties will ensure an efficient gas molecule capturing effect: the gas molecules will easily combine with the dangling bonds on VG material by van der Waals force. Being unstable, the bonds will break, and the gas molecules will be released when exposed to high temperatures [25,26]. The enrichment of a gas mixture can be obtained in three steps: first, by forcing the gas flow to pass through VG to trigger the adsorption of the target gas species; subsequently, the VG is heated at high temperature to facilitate the trapped molecules desorption; then, the collected enriched mixture can pass to a PAS sensor for the measurement of the target species.

Thus, to combine the enrichment process with the PAS system, an enrichment cell containing the VG was fabricated. A sketch and a picture of the enrichment cell are shown in Figs. 2(a) and 2(b), respectively. The enrichment cell is surrounded by a high-temperature heating system; furthermore, it is provided by a gas inlet and outlet with two valves to regulate the gas flow: the mixture will pass through the enrichment cell to be adsorbed by the VG in it.

To demonstrate the feasibility of the process as well as the improvement in the sensitivity of detection, nitric oxide was selected as target gas. Since nitric oxide has the strongest bands in the mid-infrared region, the absorbance of a mixture of 200 ppb of NO was simulated by using the HITRAN database in the range 1899.3 cm<sup>-1</sup>-1901 cm<sup>-1</sup> at 760 Torr, together with the main component of the air, namely nitrogen dioxide, carbon monoxide, carbon dioxide, methane and water, at their typical atmospheric concentrations. The NO line at 1900.08 cm<sup>-1</sup> was selected because it was spectrally-free from the selected interferents, as shown in Fig. 3.

The outlet of the enrichment cell is connected to the inlet of the PAS cell to realize the enrichment-enhanced photoacoustic spectroscopy system for NO detection, shown in Fig. 4.

A DFB-QCL laser (Institute of Semiconductors, China) with a central wavelength of 5263 nm was selected as the laser source. A temperature

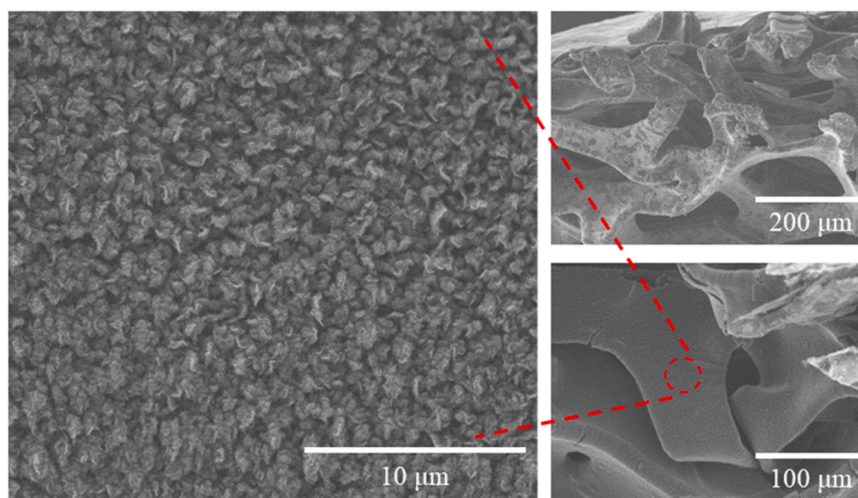


Fig. 1. SEM images of the vertical graphene grown on Ni foam.

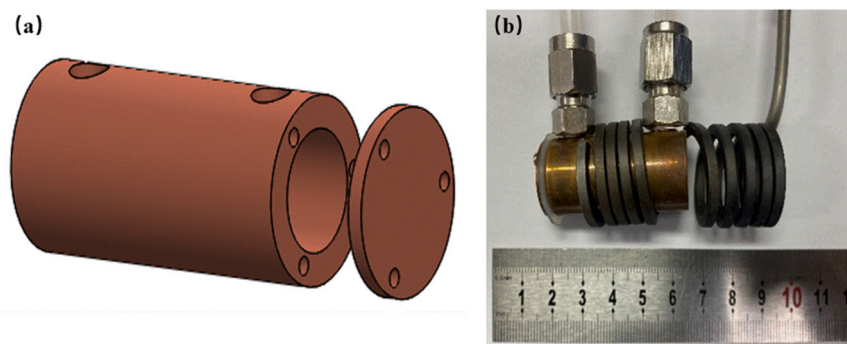


Fig. 2. (a) Schematic diagram of the enrichment cell. (b) The actual picture of the enrichment cell, the black ring outside of the cell is a high-temperature heater.

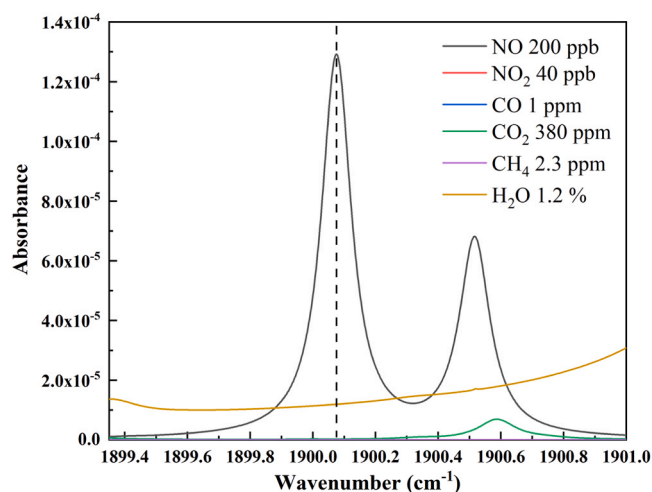


Fig. 3. Absorption line of nitric oxide, nitrogen dioxide, carbon monoxide, carbon dioxide, methane and water based on the HITRAN database at 760 torr.

controller (Thorlabs, Model TED 200 C) and a current driver (ILX Lightwave, Model LDX-3232) were used to fix the temperature of the DFB-QCL at 52 °C and its current at 283 mA, in order to tune the laser wavelength at the NO absorption line. The 2f WMS was implemented by a function generator (Tektronix, Model AFG 3022) which provides a fast sine and a slow

triangle wave to the current driver in order to simultaneously modulate and slowly scan the laser current to reconstruct the NO absorption line, respectively. The frequency of the sine wave was set to 897.5 Hz, which is half the resonance frequency of the photoacoustic cell, and the triangle wave was scanned from 0 to 150 mV to obtain a complete second harmonic scan of the NO absorption line. At the same time, the function generator triggers the lock-in amplifier (Stanford Research Systems, Model SR830) to demodulate the photoacoustic signal at twice the modulation frequency of the sine wave. All the data was subsequently acquired and analyzed on a laptop to derive the information of NO concentration.

A differential photoacoustic cell was used to measure the PAS signal. The photoacoustic cell had two identical cylindrical acoustic resonators, with a length of 90 mm and a diameter of 8 mm. Two electret condenser microphones (Primo Microphones Inc., Japan, model EM258) were placed at the center of the acoustic resonators to detect the sound wave. The enrichment cell with two valves 1 was placed upstream the PAS cell, together with an additional gas line with valve 2 that bypass the enrichment cell and allow the input gas mixture to flow directly to the PAS cell; downstream, a vacuum pump (Oerlikon Leybold Vacuum Inc. Model D16C) and a flow meter (Alicat Scientific, Model M-2SLPM-D/5 M) were used to handling the gas flow within the PAS cell.

### 3. Results and discussion

In 2f-WMS technique, the PAS signal is related to the modulation depth of the sine wave added to the current driver. Several studies showed that the PAS signal is strongest when the modulation depth of

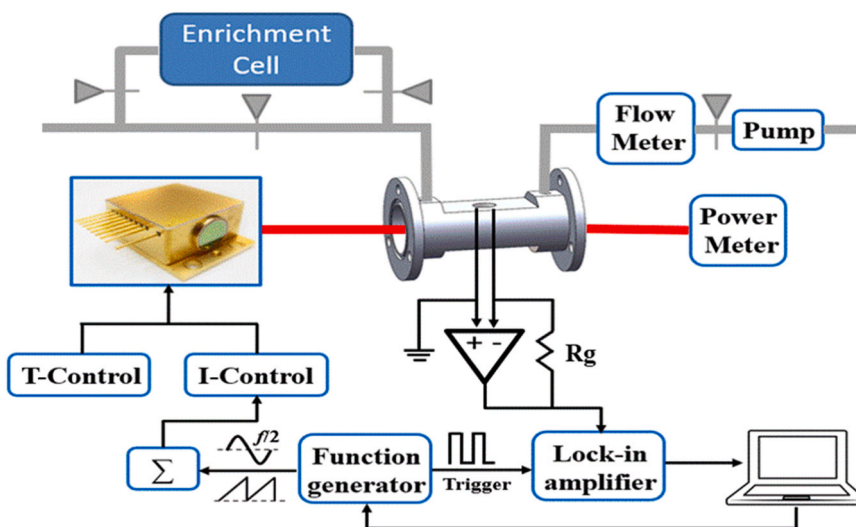


Fig. 4. Schematic diagram of the enrichment enhanced photoacoustic spectroscopy system. Rg: preamplifier feed-back resistor; 1,2: needle valve; T-control: temperature controller; I-control: current controller.

the laser current matches the full linewidth of the absorption feature to be reconstructed [27]. Therefore, the modulation depth needs to be optimized in the experiment. Keeping both needle valves 1 closed and valve 2 open (see Fig. 4), a mixture of 500 ppb of NO in N<sub>2</sub> was injected into the PAS cell, while the laser current and temperature were fixed to 283 mA and 52 °C, respectively, to lock the laser wavelength at the NO absorption peak. The flow rate was set to 150 sccm. Fig. 5 shows the PAS signal at different modulation depths.

The PAS signal monotonically increases with the modulation depth until it reaches a maximum value at 14 mA, then it starts to decrease slowly. Therefore, hereafter the experiments will be carried out at a modulation depth of 14 mA, a pressure of 760 torr, and a flow rate of 150 sccm.

After the optimization, the enrichment enhanced photoacoustic spectroscopy experiments were carried out. The entire process is divided into three phases. In the first phase that we can call refresh time, the graphene is enriched with NO. The vertical graphene material was placed in the enrichment cell with all three needle valves open and the heating system turned off. A certified concentration of 500 ppb NO: N<sub>2</sub> gas was injected both into the enrichment cell and photoacoustic cell. During this time, the NO gas molecules were absorbed by the vertical graphene material in the enrichment cell. In the second phase that we can call enrichment time, a NO enrichment of the gas sample is achieved. Both needle valves 1 were closed and the heating system surrounding the enrichment cell was turned on. The temperature inside the enrichment cell quickly reaches 150 °C, causing the desorption processes from the vertical graphene material, and, consequently, the increase of NO gas concentration within the enrichment cell. In the last phase that we can call measuring time, the NO concentration is measured. All three valves were opened, the enriched NO gas mixture flows to the PAS cell to be measured. It can be seen from Fig. 6 that the measurement was repeated by three times. The entire measurement process duration was about 200 s, and it takes about 15 s for the signal to pass from its highest value to its lowest value.

During phases I and II, only the certified concentration of 500 ppb NO: N<sub>2</sub> flows in the PAS cell, resulting in a PAS signal of ~46 μV referred to the NO concentration of 500 ppb. During phase III, the certified mixture is mixed with the enriched one, and the PAS signal increases to ~500 μV, more than 10 times higher than phases I and II. The results of the three measurements maintained a good consistency, verifying the

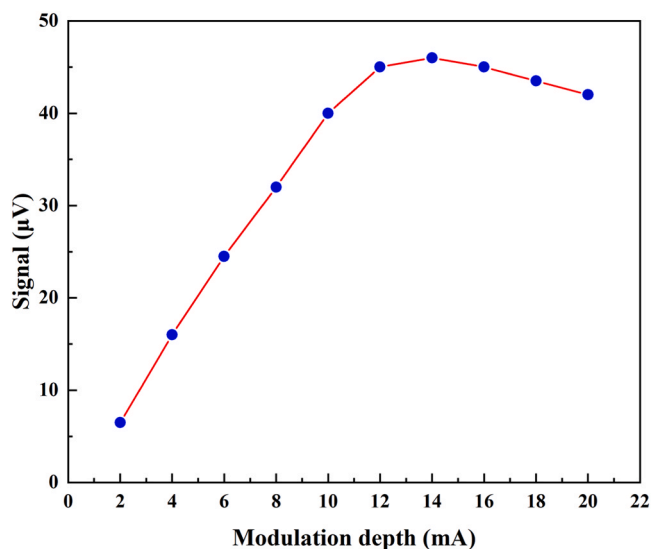


Fig. 5. The relationship between peak photoacoustic signal of NO gas with different laser current modulation depths. All data were acquired at a NO gas concentration of 500 ppb and under the pressure of 760 torr. The flow rate was 150 sccm.

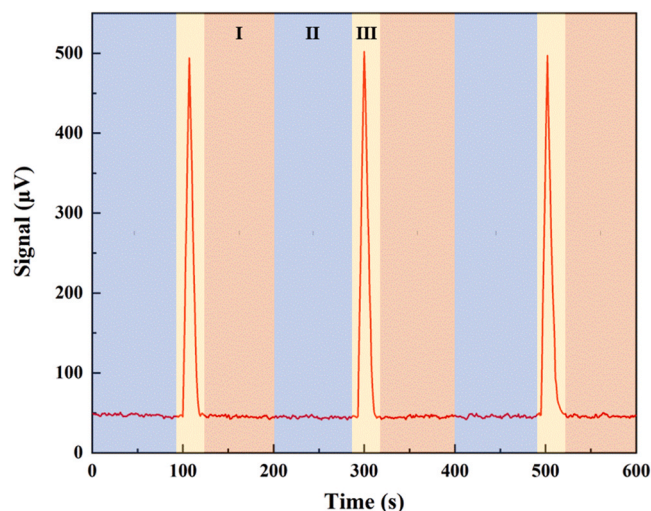


Fig. 6. Measurements for three repeated processes were conducted using a 500 ppb NO: N<sub>2</sub> gas mixture by using enrichment enhanced photoacoustic spectroscopy technology. Each process is divided into three phases: Phase I: refresh time; Phase II: enrichment time; Phase III: measuring time.

feasibility and robustness of the enrichment enhanced photoacoustic spectroscopy technology.

The linearity of the enrichment-enhanced photoacoustic spectroscopy was obtained by measuring the NO photoacoustic peak signal in phase III at different injected gas sample NO concentrations. The laser current was set to 283 mA to match the peak of the NO gas absorption line, and the integration time of the lock-in amplifier was set to 1 s. Different NO concentrations, from 0 to 1000 ppb, were obtained by using a gas dilution system starting from a certified concentration of 1000 ppb NO: N<sub>2</sub> cylinder and pure nitrogen. The PAS signal was measured as a function of time in Fig. 7(a): peak values are related to phase III and represents the NO PAS signal of the enriched mixtures (see Fig. 6); small steps identify the beginning of Phase I and correspond to the time instants when the concentration of NO is varied upstream by the dilution system, therefore this signals can be referred to the NO concentration in the not-enriched mixture.

The average values of PAS signal as a function of NO concentrations were recorded and plotted in Fig. 7(b), both for the enriched and not-enriched mixtures. For each point we performed several measurements and variations < 2 % were observed with respect to the calculated average value. With a 1σ noise level of 1.3 μV and a sensitivity of 0.093 μV/ppb, a minimum detection limit of 14 ppb can be estimated when the not-enriched mixtures flow in the PAS sensor. For the enriched mixtures, the sensitivity increases to 1.007 μV/ppb, corresponding to a one order of magnitude improvement of the minimum detection limit, which resulted in 1.3 ppb, a record value for NO detection using PAS-based technique, including QEPAS [28].

#### 4. Conclusion

In this work, an enrichment-enhanced photoacoustic spectroscopy approach exploiting vertical graphene was proposed. The VG material grown on Ni foam was used to enrich NO gas mixtures. An enrichment cell was coupled to a PAS sensor for NO detection. The PAS sensor exploited a DFB-QCL laser with a central wavelength of 5263 nm as excitation source. The sensing system was tested both with enriched and not-enriched gas mixtures, starting from the injection of different gas mixtures with NO concentrations ranging from 0 to 1000 ppb. The linearity of the sensor response was verified, and results showed that an improvement of more than 10 times can be achieved by using enrichment enhanced photoacoustic spectroscopy. The proposed research represents an innovative way to improve the sensitivity of gas detection

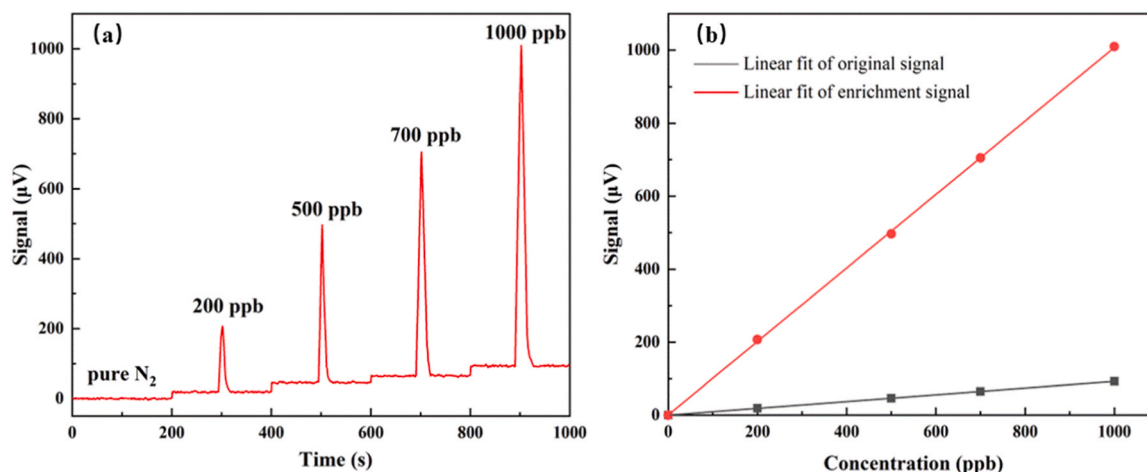


Fig. 7. (a) NO photoacoustic signal and the enhanced signal were acquired at different concentration of NO gases ranging from 0 to 1000 ppb. (b) Linear response of the photoacoustic peak signal versus the concentration of NO in the gas samples. Red line represents the enrichment signal while the gray line represents the not-enriched signal.

systems.

#### CRediT authorship contribution statement

**Pietro Patimisco:** Writing – review & editing, Methodology, Conceptualization. **Jiapeng Wang:** Investigation, Data curation. **Hongpeng Wu:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization. **Lei Dong:** Writing – review & editing, Project administration, Funding acquisition, Conceptualization. **Angelo Sampaolo:** Writing – review & editing, Methodology, Conceptualization. **Biao Li:** Writing – original draft, Methodology, Conceptualization. **Chaofan Feng:** Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Vincenzo Spagnolo:** Writing – review & editing, Methodology, Funding acquisition. **Yujing Jing:** Writing – original draft, Methodology, Investigation.

#### Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Vincenzo Spagnolo reports financial support was provided by Shanxi University. Lei Dong reports financial support was provided by National Natural Science Foundation of China. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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joint research laboratory.

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