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High sensitivity gas sensing by Raman spectroscopy in photonic crystal fiber

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ABSTRACT

We report the highly sensitive Raman detection of various gases (ambient nitrogen, oxygen, and carbon dioxide) and vapors (toluene, acetone, and 1,1,1-trichloroethane) using a hollow core photonic crystal fiber probe. With a sensitivity enhancement of around 3 orders of magnitude over direct detection, the minimum instrumentation-limited detectable concentrations for toluene, acetone, 1,1,1-trichloroethane vapors are 0.04%, 0.01%, 1.2%, respectively, with a 30 cm-long fiber probe. Moreover, we demonstrate its multiplexed sensing capability quantitatively using a vapor mixture. This combination of Raman spectroscopy and photonic crystal fiber provides a promising platform for gas sensing in environmental control applications.

1. Introduction

Currently there is an increasing interest in developing compact and reliable sensors for gas detection in applications for environmental control. While global air quality monitoring is usually related to the detection of trace chemicals such as greenhouse gases (e.g., carbon dioxide), local air quality monitoring often includes the detection of toxic gases, explosives, hydrocarbon gases, and malodors. At present, most gas sensing techniques tend to be bulky, expensive, relatively inaccurate, unable to provide real-time data, or non-molecular specific. In particular, highly sensitive multiplexed gas sensing is challenging due to the lack of molecular specificity in most detection techniques.

Raman spectroscopy, in which light is scattered off a molecule following photoexcitation that induces a change in polarization of the molecule, can provide "fingerprint" information about specific molecules since each molecule has its own set of vibrational modes [1]. Raman spectroscopy has been used to analyze the composition of complex gaseous samples [2–4]. However, it is difficult to detect gases at low concentration due to their small Raman scattering cross sections and resultant low signal intensity.

Since its discovery in the 1990s [5,6], photonic crystal fibers (PCFs) have become a promising and powerful platform for various optical sensing techniques, such as absorption [7], fluorescence [8,9], Raman [10–13], and SERS [14–17]. Generally, there are two types of PCF sensors based on Raman spectroscopy: one is the solid core PCF (SCPCF) and the other is the hollow core PCF (HCPCF). In SCPCF, the Raman signal is triggered by the interaction between the evanescent wave and the analyte, and therefore the relatively weak evanescent wave may not generate the Raman signal efficiently while most of the light confined inside the central solid core leads to a large Raman background of fused silica. In contrast, with the microstructures of axially aligned air cladding channels and the air core in the center, HCPCF provides a photonic bandgap for confining light inside the fiber and offers a much stronger overlap between the analyte and mode field, which results in an enhanced sensitivity while minimizing the fused silica Raman background. HCPCF has been utilized for the gas Raman detection; however a systematic and quantitative study has not been given and the target analytes are mainly hydrocarbon gases. More importantly, the multiplexing capability of this technique has not been quantitatively demonstrated [11,12].

In this paper, we report the highly sensitive gas/vapor detections using a HCPCF probe based on Raman spectroscopy. The HCPCF probe has been quantitatively characterized at different lengths choosing ambient nitrogen and oxygen Raman signals as references, and a sensitivity enhancement of ~700 times has been achieved with a 30 cm-long HCPCF segment. With the much enhanced Raman signal, ambient carbon dioxide (~0.04%) is detected. The minimum instrumentation-limited detectable concentrations for toluene, acetone, 1,1,1-trichloroethane vapors are 0.04%, 0.01%, and 1.2%, respectively. Moreover, we demonstrate this technique's multiplexed gas sensing capability quantitatively with the toluene/acetone/1,1,1-trichloroethane mixture.

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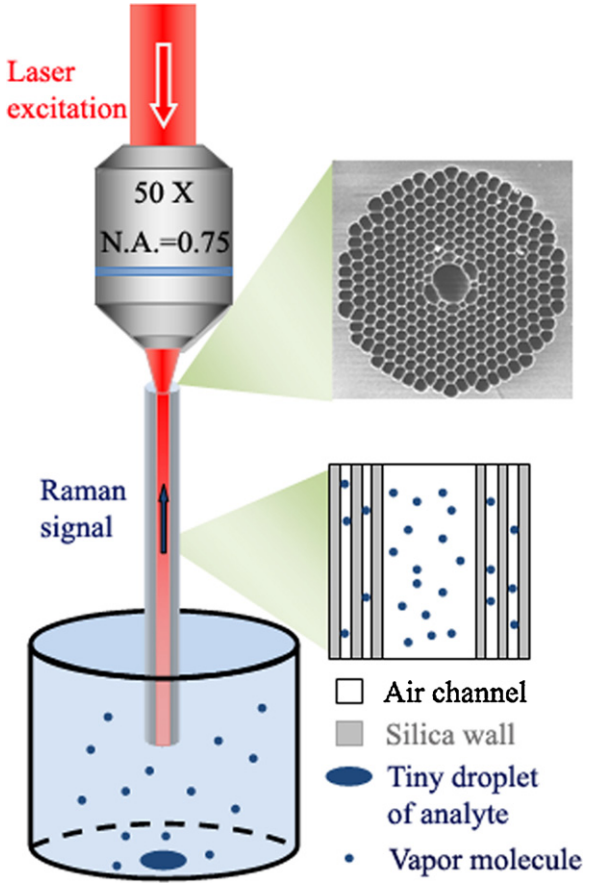

Fig. 1. Schematic of a HCPCF probe for gas/vapor Raman detection. Top right: cross sectional view of the HCPCF probe; bottom right: the air channels of the HCPCF filled with gas/vapor molecules.

2. Experimental

The HCPCF used in our experiment was purchased from Thorlabs Inc. (Model HC-800B) with its cross section shown in Fig. 1. The central core diameter is 7.5 μm and the cladding pitch is 2.3 μm. The fiber has a low transmission loss in the wavelength range of 735–915 nm [18].

A segment of HCPCF probe was cut carefully at both ends with fixed length. One end of the fiber was placed under the microscope for coupling while the distal end was placed in the ambient environment (nitrogen, oxygen, and carbon dioxide) or within a 1.2 L sealed container (toluene, acetone, and 1,1,1-trichloroethane vapors) for remote sensing, as shown in Fig. 1. For the vapor Raman sensing, a controlled amount of the liquid sample was put inside the container to achieve certain concentration. The Raman signal was collected using a Renishaw Invia Raman system with a 785 nm excitation light. The laser power was around 30 mW. In the conventional bulk Raman detection, the laser excitation light was directly focused in the air without using any fibers. All the spectra presented in this study were baseline corrected.

3. Results and discussion

Fig. 2(a) shows the Raman spectra of ambient nitrogen (2331 cm^{-1}) and oxygen (1556 cm^{-1}) collected by both the conventional bulk detection and the 30 cm-long HCPCF probe. Choosing the nitrogen Raman line as a reference, the HCPCF probe achieves a signal intensity of 11,000 (counts) with an integration time of 10 s, while the bulk detection only produces an intensity of 95 (counts) with an integration time of 60 s, which corresponds to a sensitivity enhancement of ~700 times provided by the 30 cm-long HCPCF probe. The length dependence of the gas Raman signals using the HCPCF probe was also characterized quantitatively. Fig. 2(b) shows the Raman spectra of ambient air detected with various fiber

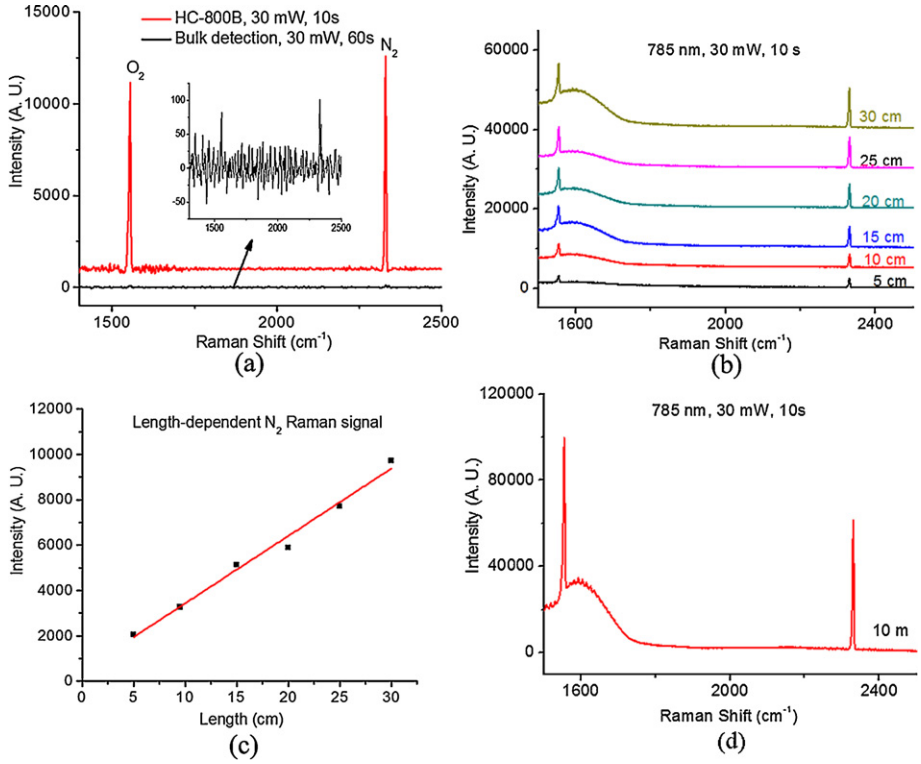

Fig. 2. (a) Comparison of the ambient N_2/O_2 Raman signals collected by the 30 cm-long HCPCF probe (10 s) and the conventional bulk detection (60 s); (b) ambient N_2/O_2 Raman signals obtained by the HCPCF probe at various fiber lengths in the range of 5–30 cm; (c) length-dependence of the N_2 Raman signal detected by the HCPCF probe; (d) ambient N_2/O_2 Raman signals obtained by the 10 m-long HCPCF probe.