Technology Networks

19 Jul 2023

Detecting Air Pollutants To Combat Climate Change

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Photo of the SERS chip developed by the NTU scientists. Credit: NTU Singapore

Researchers led by Prof. Ling Xing Yi of Nanyang Technological University Singapore (NTU Singapore)'s School of Chemistry, Chemical Engineering and Biotechnology have developed a surface-enhanced Raman scattering (SERS) chip that rapidly and accurately detects sulfur dioxide (SO_2) and nitrogen dioxide (NO_2). These gases are emitted by vehicles and industries, contributing to global warming and have also been linked to respiratory problems. The NTU Singapore study was published in *Angewandte Chemie International Edition* in 2022.

A breath of fresh air

Conventional analytical techniques such as gas chromatography are commonly used to detect and quantify SO_2 and NO_2 gases. However, such analyses need to be performed in a laboratory, can struggle to detect gases at low concentrations and are expensive.

In contrast, SERS technology can potentially detect pollutants at much lower concentrations and is more cost effective to operate.

SERS works by amplifying the light-scattering signal of each molecule. When light is shone on a molecule, it scatters the light and generates a signature, called a spectrum. Like a fingerprint, this spectrum is unique to each molecule. With SERS, the molecules in question attach to a substrate, such as metal nanoparticles, and are excited by light from a laser. The metal substrate enhances the light-scattering signature and enables the sensitive detection of molecules at low concentrations.

By analyzing the SERS spectra, individual chemicals in a mixture can be identified. Applications of SERS range from detecting biomarkers in disease diagnosis to monitoring harmful contaminants in the environment.

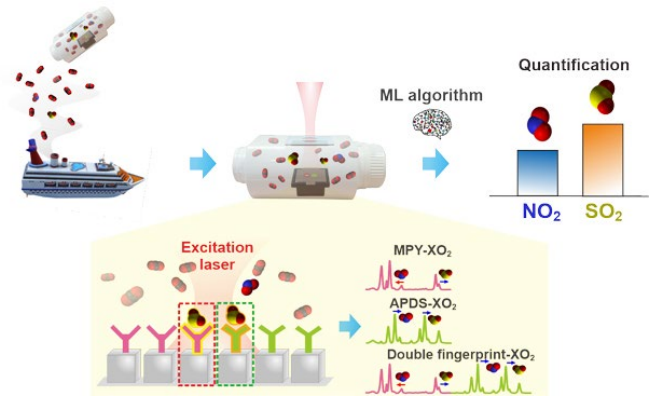
However, capturing low concentrations of gases effectively onto the SERS substrate remains a challenge and the use of the technology to detect gases is a work in progress. This recent study looked to address this with the development of a 1 cm by 1 cm chip that can detect and quantify both gases at the same time.

Detecting gases accurately

To capture low concentrations of SO_2 and NO_2, the scientists tested several probes – compounds that bind to the target molecules to be analyzed – and found that 4-mercaptopyridine (MPY) and 4-aminophenyl disulfide (APDS) bound to the gases most effectively.

The scientists then incorporated MPY and APDS into cube-shaped silver nanoparticles, to create their SERS chip. Silver substantially improves the signal produced by SERS and enables the sensitive detection of gaseous pollutants.

The scientists tested the ability of the chip to detect SO_2 and NO_2 accurately in exhaust gases by exposing the chip to a mixture of SO_2, NO_2 and CO_2, mimicking vehicle exhaust.



An overview of how the SERS chip detects NO2 and SO2 in vehicle exhaust. Credit: NTU Singapore.

The key findings of the study were:

SO_2 and NO_2 bound rapidly to both MPY and APDS and formed stable chemical ring complexes that were detected by SERS, resulting in a shift in the light-scattering spectra.

The binding of SO_2 and NO_2 to the probes formed a "double-fingerprint" spectrum, reducing the impact of background interference from CO_2, a major component of exhaust fumes.

Used together with a machine learning algorithm trained to identify patterns in spectra formed at different concentrations of the gases, the chip enabled SERS to simultaneously quantify SO_2 and NO_2, with 91.7% accuracy and at concentrations 5 to 20 times lower than the amounts typically present in vehicle exhaust.

"Our chip is a step forward in using SERS to detect gases," said PhD student Nguyen Bang Thanh Lam, who was the first author of the paper.

A starting point for on-site environmental monitoring

With climate change and environmental pollution among the biggest threats facing humanity today, the ability to detect gaseous molecules accurately at low concentrations facilitates the enforcement of environmental policies that will mitigate these challenges.

“By improving SERS to detect greenhouse gases reliably, the innovation shows great potential for on-site exhaust and air quality surveillance,” said Prof. Ling.

“In the future, the platform could be expanded to detect other gaseous pollutants.”

The findings also demonstrate how artificial intelligence technologies such as machine learning could be used to enhance the analysis of SERS spectra.

Plans are in the pipeline to develop the prototype chip further. Although the study has shown that CO_2 in the exhaust does not affect the quantification of SO_2 and NO_2, further investigations need to be conducted to determine if other gases interfere with the ability of the chip to detect pollutants.

The cost of Raman spectroscopy and the size of the spectrometer are also major factors that impact the practical applications of the chip for monitoring vehicle and industrial emissions. Handheld or portable Raman spectrometers in the future may hold the key to using the chip as a sensor for on-site surveillance.

The next steps

Building on their study, the researchers are now working to extend the platform to detect other gaseous pollutants such as chlorine, bromine, ammonia and ethylene oxide. In the future, they intend to integrate the chip into a high-throughput data collection system that enables automated collection of the SERS spectra for environmental monitoring.

The scientists are collaborating with a government agency in Singapore to test the chip and a portable Raman spectrometer for environmental surveillance of pollutants in industrial and vehicle exhausts. The team has filed several patents based on the research.

Reference: Nguyen LBT, Leong YX and Koh CSL et al. Inducing ring complexation for efficient capture and detection of small gaseous molecules using SERS for environmental surveillance. *Angew. Chem. Int. Ed.* 2022 (61): e202207447. doi:10.1002/anie.202207447

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