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Metal organic framework materials enable highly sensitive fiber sensor for real-time detection of water contaminants

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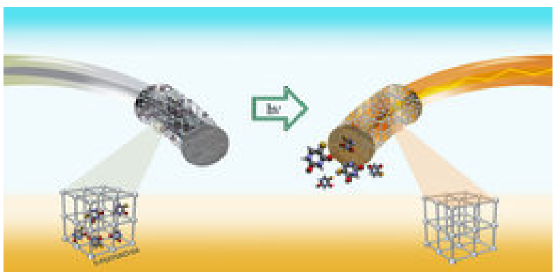

Figure 1: A schematic illustration describing the encapsulation of 5-FU into the UiO-66 MOF thin film optical fiber and its release upon switching on the light at the other end of the optical fiber

Trace contaminants in water are often measured by taking samples from the environment to a lab for analysis, which can lead to inaccurate results due to delayed and irregular sample collection or long-transportation and handling times. Thus, techniques enabling in-situ or real-time measurements of water contaminants are no doubt one of the major steps towards effective control of water quality.

Optical fiber chemical sensors based on optical absorption feature high specificity, fast response, and a much longer lifetime compared to other chemical sensors, qualities that offer significant potential for application in pollution monitoring, environmental protection, and hazardous-material detection. Now by integrating metal organic framework (MOF) materials—a new class of highly porous crystalline material—with optical fibers, researchers from Victoria University and Monash University, Australia, have co-developed a novel, highly sensitive chemical sensor based on an optical fiber coated with a thin film of a specific MOF (namely, UiO-66), which could be potentially used for real-time detection of heavy organic contaminants such as herbicides or pesticides in water. In a paper published this week in the journal *Optics Letters*, from The Optical Society (OSA), the researchers described their work.

"Metal organic frameworks (MOFs) are networks of metal atoms linked and separated by carbon-based (organic) compounds. The UiO-66 MOF we used in the experiment is made from Zirconium and is well known for the stability in water," said Stephen Collins, professor of engineering, Victoria University, Australia. "We have demonstrated for the first time that the advanced porous material MOFs can be coated onto the end-face of optical fibers to create a novel, faster and more sensitive chemical sensor potentially used for measuring heavy organic contaminants on site and in real-time."

Collins said various porous adsorbents such as pyrene-labeled monomer, silica sol-gel and zeolites have been studied recently by scientists for detecting hazardous compounds. However, the low porosity and small pores of the above adsorbents limit their use in the sensing area to small molecules. That is, they cannot detect larger or heavy organic molecules (e.g. herbicides or pesticides) in water.

Metal organic frameworks are about 10 times more porous than any material previously known, so they can absorb larger molecules. MOFs form as crystals and careful selection of MOF constituents can yield crystals of ultrahigh porosity and high thermal and chemical stability.

To fabricate the MOF-fiber sensor, the researchers removed the polymer coating of a conventional single mode fiber several centimeters from the end and activated the fiber surface using plasma. Then, the fiber was placed in MOF liquid solution and heated at 120 degrees Celsius for 24 hours, which allowed the activated fiber surface to attract the MOF to grow on the end-face of the fiber, resulting in a MOF thin film of 17- to 22-micrometer thickness.

Collins explained that the MOF-fiber sensor can be used as an in-fiber Fabry-Perot interferometer, which is a well-established method for detecting the "optical thickness" of a thin film by studying the interference signals generated by the film interfaces. As the MOF-fiber sensor absorbs more and more contaminants, the optical thickness of the MOF thin film increases accordingly, leading to a change in the interference spectra. By using the established optical model and mathematical procedure, the researchers can calculate the optical thickness of the MOF thin film from the experimentally measured interference spectra, and hence infer the concentration of contaminants in water.

In the experiment, Collin's team used the MOF-fiber sensor to detect a specific contaminant in water called Rhodamine-B (RhB) dye, a bright pink dye known as Opera Rose, which is used in the textile industry and is known to be potentially carcinogenic if ingested.

"Our experimental results showed a positive detection response of the MOF-fiber sensor to RhB in water down to 48 parts per million or 0.1 millimolar, which is a very promising result, demonstrating the sensor's ability to detect pollutants at a low concentration before the pollution goes worse," said Collins.

He explained the high sensitivity and fast response of the MOF-fiber sensor are attributed to the MOF's ability to pre-concentrate molecules, which can be imaged as a sponge "soaking" up molecules into its pores. Additionally, the MOF sponge selectively absorbs molecules to fit into its pores and rejects unfit ones, which enhance the sensor's sensitivity and reliability.

The researchers also found the sensor's absorption process of RhB dye is non-reversible, which is ideal for long-term monitoring where RhB concentrations are minimal and a marked increase in the dye's concentration would be recognized easily, said Collins.

"While the non-reversible mode suits many applications, we have also developed methods of releasing absorbed molecules by shining light down the fiber, which would make the sensor re-usable," Collin said.

The researchers' next step is to further explore the MOF-fiber sensor's responses to other heavy organic contaminants such as pesticides and herbicides in water.

More information: M. Nazari, M. Forouzandeh, C. Divarathne, F. Sidiroglou, M. Martinez, K. Konstas, B. Muir, A. Hill, M. Duke, M. Hill and S. Collins. "UiO-66 MOF End-Face-Coated Optical Fiber in Aqueous Contaminant Detection" *Optics Letters* 41, 1696 – 1699. DOI: 10.1364/OL.41.001696

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