Danish Offshore Technology Centre
Technology Conference 2024

Metal-organic framework functionalized glass surfaces as surface enhanced Raman spectroscopy substrates

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Produced water contains both inorganic and organic pollutants, and innovations in reuse, recovery and discharge are needed to minimize the environmental impact [1],[2]. The most abundantly present aromatic hydrocarbons benzene, toluene, ethylbenzene, and xylene isomers (BTEX). The BTEX class are present at concentrations exceeding the limits for safe environmental discharge, posing risks to both the surrounding ecosystem and human health [2]. To support both monitoring and removal technologies, there is a need to develop rapid, inexpensive, accurate, sensitive and effective sensors. Currently, BTEX is primarily quantified using gas chromatography coupled with mass spectrometry, which are labour and cost intensive, or in-line monitoring using fluorescence spectroscopy which lacks selectivity and sensitivity [3],[4].

Raman spectrometry is an attractive alternative due to its capability to resolve compounds with weak scattering response for water, allowing in-line measurements [5]. The main disadvantage is that the scattering effect typically is weak, leading to low sensitivity. This can be addressed by surface-enhanced Raman spectrometry (SERS), which utilizes metallic nanoparticles to enhance the scattering effect by a factor of 10^6 to 10^{14}. This occurs due to the excitation of localized surface plasmons (LSPR) or charge-transfer mechanisms facilitated by the interaction between the analyte and metallic nanoparticles, typically gold or silver [6]. When LSPR metals are irradiated by light, the oscillating electric field causes their electron cloud to oscillate at frequencies corresponding to the excitation light, thereby amplifying the weak Raman signal of materials in their vicinity [5],[6].

A fundamental challenge of SERS is the low binding affinity of the target analytes towards unfunctionalized metal nanoparticles. Metal–organic frameworks (MOFs) represent a highly porous class of hybrid organic-inorganic supramolecular materials characterized by high specific surface areas and periodic networks of metallic nodes interconnected by organic linkers. The structural flexibility of these frameworks can be tuned to selectively extract target molecules and locate them in near vicinity of the metallic nanoparticles to enhance the SERS effect [6].

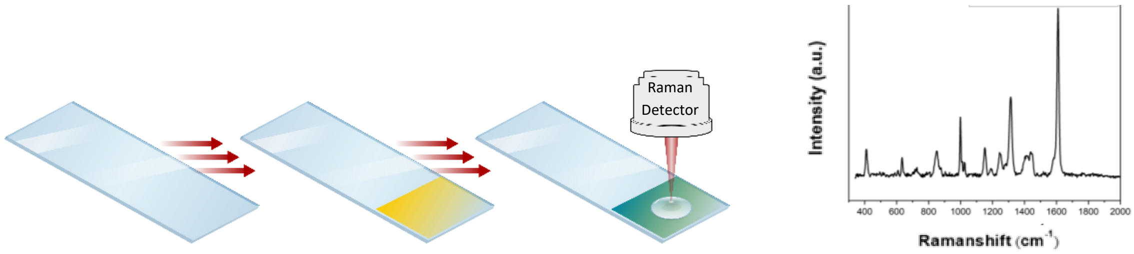

Figure 1: Schematics representing functionalization of glass slides for SERS-based detection of targeted pollutants in water (Left) and Raman spectrum of selected MOF powder (Right)

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In this project, we present the functionalization of MOF thin films on plasmon-active optical glass slides as potential substrates for detecting BTEX impurities using Raman spectroscopy [Figure 1 (Left)]. We fabricate SERS substrates using the chemical interactions between surface-anchored chemical groups through self-assembly. The activation of the surface of an oxide substrate with anchors results in the formation of a monolayer when the substrate is immersed in a solution of organic molecules [7]. This process self-terminates, leading to the creation of a self-assembled monolayer (SAM) on the substrate. In our case, we first fabricated the substrates by activating the hydroxyl groups (-OH) on the glass surface using oxygen plasma. The -OH rich glass surfaces were treated with an ethanolic (3-aminopropyl) trimethoxy silane (APTES) solution which is a well-known coupling agent for the surface modification for Au NPs, via−NH_2 groups. After silanization, the amine-modified silica surface was immersed into a gold colloidal solution with series of reaction times. In the last step, the carboxyl group was created in the surface of gold nanoparticles with a thiol monolayer of 16-mercaptohexadecanoic acid as nucleation site for the layer-by-layer (LbL) growth of MOF thin-film carried out in the next step. The layer-by-layer MOF growth technique involves the repetitive sequential introduction of metal ions and linkers to candidate support, such as glass, alumina, gold, conductive glass, or silicon. This approach offers advantages such as user-defined thickness and orientation of crystallite growth for specific applications [7]. For this purpose, metal precursor was dissolved in dimethyl formamide (DMF) was introduced to glass substrates then followed by rinsing with DMF. After the nucleation process, the two components, metal precursor and the linker, were separately dissolved DMF and the solutions were introduced to glass substates in a cyclic way, while each step was followed by rinsing with DMF. Different functionalization introduced to glass surface were confirmed after each modification step using scanning electron microscopy (SEM), atomic force microscopy (AFM), Raman and X-ray photoelectron spectroscopy (XPS). We finally also showcase the adsorption capability of the selected MOF for BTEX compounds in water using Raman spectroscopy [Figure 1 (Right)].

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