Innovative SERS/SERDS Concept for Chemical Trace Detection in Seawater

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A chemical sensor based on Surface-Enhanced Raman Scattering (SERS) is presented for the rapid identification and quantification of polycyclic aromatic hydrocarbons (PAHs) in seawater at trace concentration. The functionalization of Ag colloid-based sol-gel films with calixarene contributes to a significant improvement in SERS sensitivity. Shifted Excitation Raman Difference Spectroscopy (SERDS) effectively reduces the fluorescence-based background in the SERS spectra of PAHs in seawater, resulting in up to three times the lower limits of detection compared to using only SERS. The combined SERS/SERDS concept was demonstrated to be very promising for future in-situ chemical sensor development.

INTRODUCTION

The interest in hydrophobic organic contaminants, including polycyclic aromatic hydrocarbons (PAHs), as toxic chemicals has continuously increased during the last decades. As pollutants, PAHs are of global concern because they have been identified as carcinogenic, mutagenic, and teratogenic (Baussant et al., 2001). The main sources of PAHs in the environment are from the incomplete combustion of fossil fuel and refuse (Patrolecco et al., 2010). They are also introduced into the environment through natural combustion processes such as volcanic eruptions and forest fires as well as through the discharge of crude oil. The temporal and spatial dimensions necessary for monitoring ocean processes can range from the sub-second and sub-millimeter scale of molecular processes up to decades and whole ocean basins (Prien, 2007). For example, the mean concentration of 15 PAHs in the Mecklenburg Bight of the Baltic Sea varied from 2.6 ng/L in August to 8.1 ng/L in November (Witt, 2002). However, many parameters of interest cannot be characterized by infrequent fixed interval sampling. Therefore, special events are missed because no sampling is taking place at the time of their occurrences. To overcome this issue, real-time operative in-situ chemical sensors are required.

Raman spectroscopy as a noninvasive optical method can be applied to the identification and quantification of these substances with fast response times. The technique is considered to be an efficient analytical tool to trace hydrophobic organic pollutants in the water body. Because of the high octanol/water coefficient of PAHs, they are dissolved in seawater with extremely low concentration, e.g., in the case of pyrene, the saturation concentration is 435 nmol/L (Schmidt et al., 2004). In addition, the low Raman scattering cross section of these analytes limits the application of conventional Raman spectroscopy to the trace detection of PAHs in water.

This drawback has been overcome by the application of metal nanostructures acting as a powerful Raman signal amplifier since the discovery of Raman intensity enhancement of pyridine adsorbed onto an electrochemically roughened silver electrode surface (Fleischmann et al., 1974). Recently, the development of nanoparticle-based chemical sensors using Surface-Enhanced Raman Scattering (SERS) is of great interest for the trace analysis of PAHs. These sensors include tailor-made gold nanoparticles (Hubenthal et al., 2009), self-assembled gold colloid films (Peron et al., 2009), calix[4]arene functionalized silver colloids (Guerrini et al., 2009), Ag colloid-based sol-gel films (Pfannkuche et al., 2012), naturally grown silver nanoparticles (Kwon, Ossig, et al., 2012), dimercaptoacetic acid calix[4]arene (DMCX) functionalized silver colloid-based sol-gel films (Kwon, Sowoidnich, et al., 2012), humic acid decorated Ag nanoparticles (Qu et al., 2013), and bare Au nanoparticle coupled film systems (Gu et al., 2016).

For the trace detection of PAHs in seawater, SERS substrates with high sensitivity, signal reproducibility, and long-term chemical stability are needed. For this purpose, the sol-gel process has been adapted to protect Ag colloid films from seawater and to obtain the mechanical and chemical stability of the SERS substrate (Pfannkuche et al., 2012). The SERS activity of the substrate is dependent on the distance between the analyte and the metal nanoparticle surface (Baker and Moore, 2005) as well as the surface coverage of the analyte on the metal surface (Jones et al., 2009). It has also been theoretically proven that the aggregation of metal nanoparticles is one key factor for high electromagnetic enhancement (Garcia-Vidal and Pendry, 1996).