Naturally Grown Ag Nanoparticle SERS Substrate As Chemical Sensor in Fresh Water Applying 488 nm Microsystem Laser Diode

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For in-situ monitoring of polycyclic aromatic hydrocarbons (PAHs) in fresh water that flows from rivers into the oceans, a chemical sensor based on surface enhanced Raman spectroscopy (SERS) is well suited for a rapid identification and quantification of these substances. The laboratory set-up contains a microsystem light source at 488 nm suited for shifted excitation Raman difference spectroscopy (SERDS) and also a SERS substrate with a Ag nanoparticle ensemble with a plasmon resonance wavelength around 488 nm. SERS applying SERDS (SERS/SERDS) measurements of water samples containing 2 PAHs (pyrene and fluoranthene) showed Raman signals at 2 nmol/l and 1 nmol/l of concentration.

INTRODUCTION

Raman spectroscopy as a noninvasive method can be applied for the identification and quantification of substances. It is considered to be an efficient analytical tool to trace hydrophobic organic pollutants in a water body. Polycyclic aromatic hydrocarbons (PAHs) are important environmental pollutants formed during the incomplete combustion of coal, oil and gas (Lohmann et al., 2009; Witt, 2002). During the last decades, much attention has been paid to PAHs, because not only they are known to be toxic to biota, but also because they have a tendency to adsorb to the sediment and bioaccumulate in aquatic organisms (Carls et al., 1999). However, because of their high octanol/water coefficient, PAHs dissolve in a water body with extremely low concentration. In addition, the application of Raman spectroscopy is limited because of the low Raman scattering cross-section of analytes which it is necessary to detect.

To overcome this drawback, metal nanostructures have been used as a powerful Raman signal amplifier since the discovery of Raman intensity enhancement of pyridine adsorbed to the electrochemically roughened silver electrode surface (Fleischmann et al., 1974). Recently, the development of nanoparticle-based chemical sensors for surface enhanced Raman scattering (SERS) found great interest for the trace detection of PAHs, e.g. silver colloid-based sol-gel films (Schmidt et al., 2004; Murphy et al., 1999), tailor-made gold nanoparticles (Hubenthal et al., 2009), self-assembled gold colloid film (Péron et al., 2009), synthesized silver nanoparticle aggregates on copper foil (Jiang et al., 2012), partition layer-modified silver film over nanospheres (Jones et al, 2009), polystyrene beads coated with gold nanoparticles (Péron

et al., 2011), gold nanoparticle-modified TiO_2 nanotube arrays (Sheng et al., 2012), silver nanoparticles functionlized with bis-acridinium dication lucigenin (López-Tocón et al., 2011), CD-SH modified gold nanoparticles (Xie et al., 2010), calixarene functionalized silver colloids (Guerrini et al., 2009) and dimercaptoacetic acid calixarene (DMCX) functionalized silver colloid-based sol-gel films (Kwon et al., 2012; Kolomijeca et al., 2011).

The sensitivity of a SERS substrate for trace detection of chemicals in a water body depends on 2 factors, i.e. electromagnetic field enhancement at the metal nanoparticle surface, and the chemical enhancement due to the increased Raman scattering cross-section of an analyte in direct contact with the metal nanoparticle. However, the dominating enhancement mechanism of the analyte Raman signal is electromagnetic, caused by the excitation of plasmon resonances (Hubenthal et al., 2009) and nanoparticle aggregation (Kwon et al., 2011; Kwon et al., 2012). Particularly high Raman enhancement was obtained for plasmon resonances located between the excitation wavelength and the Raman scattering wavelength (Guillot et al., 2010). A tuning of the plasmon resonance of metal nanoparticle ensembles was achieved by varying the morphology of nanoparticles using the natural Volmer-Weber growth and laser-tailoring (Hubenthal et al., 2009; Ossig et al., 2012).

Another drawback of Raman spectroscopy is a broad background due to luminescence such as fluorescence and phosphorescence. Such a background has been a prohibiting factor for the widespread use of Raman spectroscopy, because it often masks the weaker Raman signal and renders the result useless. To obtain fluorescence background free Raman signals by the shifted excitation Raman difference spectroscopy (SERDS) (Zhao et al., 2002), an experimental Raman setup containing a microsystem light source with 2 emission wavelengths (487.61 nm and 487.91 nm) was specially developed by our group and the Ferdinand-Braun-Institut, Leibniz-Institut für Höchstfrequenztechnik in Berlin for SERDS (Maiwald et al., 2009).