JOURNAL OF ENVIRONMENTAL SCIENCES 39 (2016) 134–143

Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jes

JES JOURNAL OF ENVIRONMENTAL SCIENCES

www.jesc.ac.cn

Review article

Recent progress in detection of mercury using surface enhanced Raman spectroscopy — A review

*Zhenli Sun, Jingjing Du, Chuanyong Jing**

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China. E-mail: sunzhenli1988@163.com

ARTICLE INFO

Article history:
Received 31 July 2015
Revised 30 November 2015
Accepted 1 December 2015
Available online 28 December 2015

Keywords:
Mercury
SERS
Detection
Substrate
Nanoparticles

ABSTRACT

Concerns over exposure to mercury have motivated the exploration of cost-effective, rapid, and reliable method for monitoring Hg^{2+} in the environment. Recently, surface-enhanced Raman scattering (SERS) has become a promising alternative method for Hg^{2+} analysis. SERS is a spectroscopic technique which combines modern laser spectroscopy with the optical properties of nano-sized noble metal structures, resulting in substantially increased Raman signals. When Hg^{2+} is in a close contact with metallic nanostructures, the SERS effect provides unique structural information together with ultrasensitive detection limits. This review introduces the principles and contemporary approaches of SERS-based Hg^{2+} detection. In addition, the perspective and challenges are briefly discussed.

Introduction

Mercury is one of the most dangerous pollutants in the environment (Cai et al., 2015; Qi et al., 2015a, 2015b). Mercury is toxic to the cardiovascular, urinary, gastrointestinal, and neurological systems. In particular, the water-soluble mercuric ion (Hg^{2+}) has long been a concern due to its gravest damage to human health (Du et al., 2015). The U.S. Environmental Protection Agency (EPA) has mandated a limit of 2 μg/L (10 nmol/L) for Hg^{2+} in drinking water. Such a low mandatory level would surely challenge the sensitivity of its detection system. Up to now, several traditional Hg^{2+} detection methods have been developed including atomic fluorescence spectrometry (AFS), cold vapor atomic absorption spectroscopy (CVAAS), inductively coupled plasma-mass spectrometry (ICP-MS) and enzyme linked immune sorbent assay (ELISA). Most of these detection systems require highly precise sample preparation, expensive experimental equipment, and long turnaround times, which make them unsuitable for remote or on-site applications. Therefore, it is an urgent need to develop simple and reliable methods for rapid and sensitive determination of Hg^{2+} on-site.

Surface enhanced Raman scattering (SERS) spectroscopy provides an alternative tool for fast screening of Hg^{2+}. SERS can be applied to detect target molecules without any tagging or sample pre-treatment, which makes SERS particularly well suited for field analysis (Li et al., 2010, 2014; Halvorson and Vikesland, 2010; Alvarez-Puebla and Liz-Marzan, 2010; Hao et al., 2015). However, direct SERS detection of monoatomic metal ions, such as Hg^{2+}, is challenging due to their small scattering cross section (Li et al., 2014; Alvarez-Puebla and Liz-Marzan, 2012). This is why the SERS sensing of Hg^{2+} was

* *Corresponding author*. E-mail: cyjing@rcees.ac.cn (Chuanyong Jing).

http://dx.doi.org/10.1016/j.jes.2015.11.009
1001-0742/

first reported in 2008, about 35 years since the discovery of the SERS effect (Zamarion et al., 2008). Recently, the number of publications and citations of SERS in Hg^{2+} detection has increased significantly (Fig. 1). Instead of using bare Au/Ag nanoparticles (NPs) as SERS substrates, numerous methods for SERS detection of Hg^{2+} have been reported based on the "reporter approach" and "T–Hg^{2+}–T approach" (Fig. 2). The first well-known Raman reporter approach was based on the specific interaction between Hg^{2+} and Raman reporters (Raman active molecules). The T–Hg^{2+}–T approach relies on the thymidine–Hg^{2+}–thymidine coordination chemistry.

The recent research effervescence paves the way for future development of Hg^{2+} sensors. This paper reviews the recent application of SERS in Hg^{2+} analysis. The potential of SERS technique for fast screening and field test of Hg^{2+}-contaminated environmental samples is evaluated. Finally, the challenges are briefly discussed and an outlook is featured.

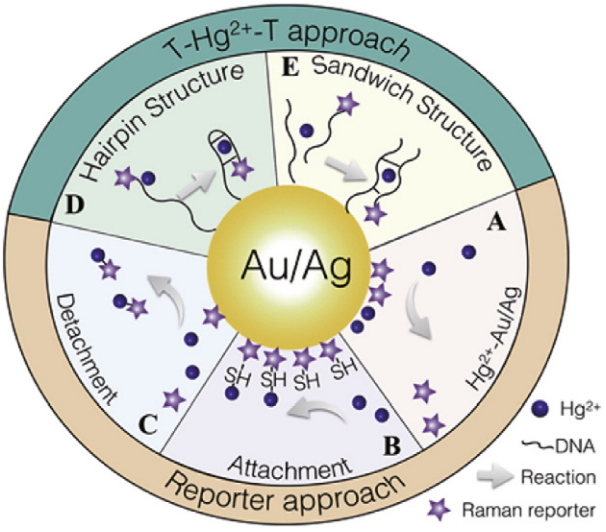

Fig. 2 – Principles and approaches for Hg^{2+} detection using SERS.

1. Reporter approach

Detection of Hg^{2+} can be achieved by "turning on" or "turning off" the SERS signals of Raman reporters. In general, molecules exhibiting a strong and specific SERS spectrum are suitable to serve as reporters. The Raman reporter molecules could adsorb on the SERS substrate via chemisorption or physisorption. Recognition of Hg^{2+} by reporters is based on three mechanisms: Hg^{2+}–Au/Ag incorporation, reporter attachment, and reporter detachment (Fig. 2). Table 1 summarizes the recent reporter-based SERS approaches and the corresponding detection limits.

1.1. *Hg^{2+}–Au/Ag incorporation*

The Hg^{2+}–Au/Ag incorporation mechanism shows that the Raman reporter is first adsorbed on Au/Ag SERS substrate, and then replaced by Hg^{2+} (Fig. 2A). The citrate-reduced colloidal Au NP has been used as a single entity for rapid scanning and sequestration of Hg^{2+} from multicomponent aqueous solutions (Ojea-Jimenez et al., 2012). Wang et al. (2009) performed SERS analysis of Hg^{2+} using the rhodamine B (RB) as a reporter. In their work, an initial SERS signal was recorded for RB which was adsorbed on Au NPs via electrostatic interactions. The presence of Hg^{2+} induces the desorption of RB from Au surfaces, resulting in a decreased SERS signal (Fig. 3A). Further study of Senapati et al. (2011) speculated that the decreased SERS signals may be attributed to the formation of the Hg–Au amalgam (Fig. 3B). Ren et al. (2012) further demonstrated that Hg^{2+} could readily react with citrate-reduced Ag NPs by the formation of complexes with citrate and then amalgam due to the reduction of Hg^{2+}. Accordingly, Hg^{2+} was detected with a limit of 18.2 ng/L (Fig. 3C).

The quantitative trace analysis of Hg^{2+} might be hindered using colloidal Au or Ag NPs due to the difficulty in controlling the degree of NP aggregation. To solve this problem, Kandjani et al. (2015) synthesized ZnO/Ag nanoarrays for Hg^{2+} sensing. The

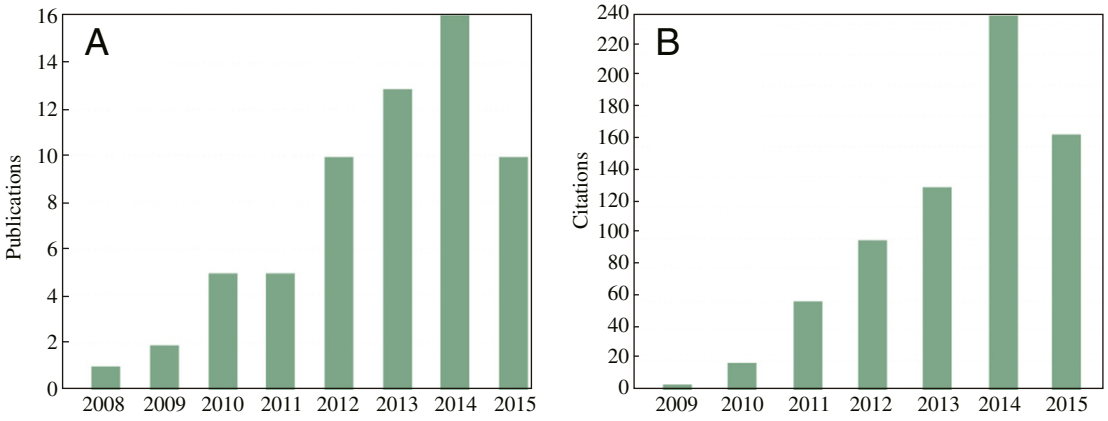

Fig. 1 – The number of publications (A) and citations (B) on Hg^{2+} surface-enhanced Raman scattering (SERS) detection through the Web of Science™ Core Collection.