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Review

Surface enhanced Raman spectroscopy (SERS): A novel reliable technique for rapid detection of common harmful chemical residues

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ABSTRACT

Background: The irrational usage of chemical substances including pesticides and drugs in agricultural and food production is a significant food safety issue due to its residues. Therefore, the detection of harmful residues in foods is an indispensable step for guaranteeing the consumer's health. Conventional methods, such as HPLC, GC-MS and LC-MS are accurate enough, but they fail to meet the requirements of the modern industry for rapid and on-line detection. Novel reliable techniques should thus be developed as alternatives.

Scope and approach: In this review, fundamentals of surface-enhanced Raman spectroscopy (SERS) is introduced. Recent advances in its usage for detecting harmful chemical residues in agricultural products including pesticides, antibiotics and β_2-adrenergic agonists are discussed by two typical ways of detection improvement, and the advantages of SERS are addressed. Finally, future trends to routine use of SERS applications in harmful residues are presented.

Key findings and conclusions: SERS is a promising detection technique for the detection of common harmful chemical residues with merits of simple sampling, rapid data collection and non-destructiveness. Despite rapid developments in the technology, there is much studies should be done before SERS could be used as a daily tool for the industry.

1. Introduction

Chemical substances including pesticides and drugs are needed in modern agricultural and food production, however irrational or excessive usages of these chemical substances also cause severe concern for environmental and food safety reason. The resistance in organism and ecological cycle created due to the irrational use of these chemical substances in foods are ensuing persistent problems. Food safety issues, like harmful residues in foods are fetching people's attention all over the world and supervision is being reinforced in these areas. In 2017, China Agricultural Quality and Safety of Special Rectification Program held by the Agriculture Ministry of China indicated that it would start seven special rectification actions in foods. Among them, pesticides, antibiotics and β-agonists are the three most commonly added harmful residue for any living beings. Pesticides for keeping pest away can be a pure substance or a mixture of various substances. The pivotal role of pesticides in increasing the productivity cannot be denied, as one-third of the total agriculture and food production would be destroyed at any stage of growth to storage, if pesticides were not used (Malvano, Albanese, Pilloton, Di Matteo, & Crescitelli, 2017). However, it is evident that most of the pesticides are toxic in nature and their residues can affect the environment and the health of any living creature. The uses of antibiotics and β-agonists are no different from the pesticides (Mungroo & Neethirajan, 2014). Antibiotics are naturally occurring, semi-synthetic or synthetic compounds with antibacterial activity for the treatment and prevention of diseases, and many antibacterial agents are used in livestock production (Gaskins, Collier, & Anderson, 2002; Stokstad & Jukes, 1949). However, the abuse of antibiotics has led to the spread of resistance genes in large areas of other animals and humans. Many countries, including China, the USA and the EU have declared the illegality in using some antibiotics, such as macrolides and nitrofurans in animal feed and treatment (Aerts, Beek, & Brinkman,

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1990; Leitner, Zã¶Llner, & Lindner, 2001; Pengov, Flajs, Zadnik, Marinšek, & Pogačnik, 2005). In spite of this, antibiotics still pass into the human body indirectly through the daily diet, which contains seafood, fish or edible tissues that are already given antibiotic infested animal fodder or veterinary medicines (Davis et al., 2009). On the other hand, β_2-adrenergic agonist is a group of synthetic phenylethanolamine compounds, which contains a typical aromatic group, β-hydroxy and aliphatic nitrogen. It is a growth regulator in animals breeding to reduce fat tissue precipitation and promote protein synthesis. However, its residues were proved to be harmful for human and strict regulations have been adopted internationally in its uses in cultivation (Vanoosthuyze, Arts, & Peteghem, 1997). However, β_2-adrenergic agonist is still used illegally in livestock breeding, such as sheep, swine and cattle (Shao et al., 2009). All these chemical hazards are detrimental to the environment and living beings. Therefore, besides the need for preservation techniques such as drying (Delgado & Sun, 2002; Ma, Sun, Qu, & Pu, 2017; Pu & Sun, 2016; Pu & Sun, 2017; Qu, Sun, Cheng, & Pu, 2017; Sun, 1999; Sun & Woods, 1993; Yang, Sun, & Cheng, 2017), cooling (Desmond, Kenny, Ward, & Sun, 2000; McDonald, Sun, & Kenny, 2001; Sun & Eames, 1996; Sun & Zheng, 2006; Sun, 1997; Wang & Sun, 2001; Wang & Sun, 2004) and freezing (Cheng, Sun, & Pu, 2016; Cheng, Sun, Zhu, & Zhang, 2017; Kiani, Zhang, Delgado, & Sun, 2011; Kiani, Sun, Delgado, & Zhang, 2012; Ma et al., 2015; Pu, Sun, Ma, & Cheng, 2015; Xie, Sun, Xu, & Zhu, 2015; Xie, Sun, Zhu, & Pu, 2016) to enhance food safety, it is also essential to seek reliable techniques for the detection of harmful residues in foods.

Traditional methods, including high performance liquid chromatography (HPLC), gas chromatography-mass spectrometer (GC-MS), and liquid chromatography-mass spectrometer (LC-MS), are well established. Although these chromatography-based methods are sensitive, accurate and reliable, they require complicated pretreatments and hours even days for complete the analysis (Craig, Franca, & Irudayaraj, 2013). Therefore, reliable, non-contact and rapid detection methods such as hyperspectral imaging (Cheng & Sun, 2015; Cheng & Sun, 2017; Cheng, Sun, Pu, Wang, & Chen, 2015; Cheng, Sun, Pu, & Zhu, 2015; Cheng et al., 2016; Cheng, Sun, & Cheng, 2016; Dai, Cheng, Sun, Zhu, & Pu, 2016; ElMasry, Sun, & Allen, 2013; Ma, Sun, & Pu, 2016; Pu, Kamruzzaman, & Sun, 2015; Pu, Xie, Sun, Kamruzzaman, & Ma, 2015; Pu, Liu, Wang, & Sun, 2016; Xiong et al., 2015; Xu, Riccioli, & Sun, 2016), Raman chemical imaging (Li, Sun, Pu, & Jayas, 2017; Pan et al., 2017; Pan, Pu, & Sun, 2017; Yaseen, Sun, & Cheng, 2017), etc are highly needed. Surface-enhanced Raman spectroscopy (SERS) is a powerful and effective detection technique, which has grown dramatically with the development of nanotechnology and material surface science. There are several areas in which SERS has gained excellent achievements, such as in environmental chemistry (Truong et al., 2007), explosive detection (Demeritte et al., 2012), food safety (Craig et al., 2013; Lee & Herrman, 2016) and biomolecules (Cho, Lee, Liu, Agarwal, & Lee, 2009) as well as forensic science (Muehlethaler, Leona, & Lombardi, 2016). So far, a large number of scientific publications have been published on SERS detection of harmful residues (Fig. 1) and a few relevant reviews have been published in the past. Petrović, Hernando, Díaz-Cruz, and Barceló (2005) reviewed the analytical methods based on liquid chromatography–tandem mass spectrometry (LC–MS/MS) for the detection of several pharmaceutical residues, covering antibiotics, non-steroidal anti-inflammatory drugs, β-blockers, lipid regulating agents and psychiatric drugs. Pang, Yang, and He (2016) only focused on the applications of SERS for the detection of synthetic chemical pesticides in both simple and complex matrices. Recently, Xu, Gao, Han, and Zhao (2017a) described a general process for SERS-based pesticide detection. However, no review is available on advanced SERS techniques for the detection of most common harmful chemical residues including pesticides, antibiotics and β-agonists. Therefore, in the current review, the principles of SERS are discussed first. Then the state-of-the-art applications of SERS in the detection of artificially added harmful residues, mainly on pesticide, antibiotic and β_2-adrenergic agonist are summarized by the ways of Raman signal improvement. Future perspectives are also offered in the current review.

2. Principles of SERS

2.1. Theoretical basis of SERS

The principles of Raman spectroscopy are based on scattering spectrum that can be used to analyze molecular vibrations, rotations, or other low-frequency modes. Raman spectroscopy mainly refers to the non-elastic scattering between the monochromatic light and the sample molecules. Non-elastic scattering (Raman scattering) involves only a very small percentage of the energy changes. The decrease in energy is called Stokes Raman scattering, while the increase is called anti-Stokes Raman scattering. Normally, Stokes scattering and anti-Stokes scattering are symmetric. Ordinary Raman scattering signal is weak (usually one millionth of the intensity of incident light), which cannot be applied to analysis and detection of trace substances since the cross-section of the inelastic scattering event is too small (McCreery, 2000). Therefore, it is such a challenge to detecting harmful molecular compounds by spontaneous Raman scattering without enhancement (Lu, Al-Qadiri, Lin, & Rasco, 2011).

The enhancement phenomenon of Raman signal was first observed by Fleischmann, Hendra, and Mcquillan (1974), who found that when pyridine was adsorbed on an electrochemically coarse silver electrode, the Raman signal of pyridine could be significantly enhanced. Since then, the technology of surface enhanced Raman spectroscopy (SERS) has progressed rapidly with the developments of nanotechnology and material surface science. The ability of amplification of Raman signal (almost coming entirely from the molecules) by several orders of magnitude is mainly a phenomenon related to the enhancement of electromagnetic field around a small metal (or other) object that is excited by intensive and sharp (high Q) dipole resonance (eg, surface plasmon). Electromagnetic enhancement and chemical enhancement are the basis of the SERS signal enhancements, which are two different classic mechanisms. Electromagnetic enhancement is decided by the localized surface plasmon excitation, which is the core of SERS, on the surface of the metal substrate with extended characteristics. On the other hand, the principle of chemical enhancement is the charge transfer between the substrate and the analyte (Haynes, Mcfarland, & Duyne, 2012). In common, both of the analytes must be absorbed on substrates, which are illuminated by the laser, and the resulting scattered light is analyzed. It is generally believed that electromagnetic enhancement is stronger than chemical enhancement. When the laser is irradiated on the metal surface, it is absorbed by the molecules on the metal surface, and the charge is transferred between the metal and the molecule, changing the polarization of the system, as a result, the SERS signal is significantly increased (Yang et al., 2008).

Nowadays, it is widely accepted that the average enhancement factor of SERS signals is about 10^6, but the peak of 10^{10} may appear in local enhancement of some efficient subwavelength regions of the surface (Le Ru, Blackie, Meyer, & Etchegoin, 2007). The chemical bonds of the components and the vibrational properties of the functional groups in the sample are represented by spectral bands, providing a fingerprint for a specific substance.

In addition to the advantages of simple sample preparation and rapid analysis procedure, there are other prominent characteristics in SERS, which includes good compatibility with water systems and linear relationship between spectral intensity and analytical concentration (Sowoidnich, Schmidt, Maiwald, Sumpf, & Kronfeldt, 2010). Hence, the resultant Raman spectra can be used for quantitative detection. Raman intensity can be calculated by the following equation (Jancke, Malz, & Haesselbarth, 2005):

$$I_v = I_0 K_v C \tag{1}$$