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Communication

Synthesis of magnetic polyphosphazene-Ag composite particles as surface enhanced Raman spectroscopy substrates for the detection of melamine

Ci Huang[1], Feifei Lu[1], Ke Xu, Guanjun Ding, Lijun You*, Jiabin Wang, Qiqing Zhang

Institute of Biomedical and Pharmaceutical Technology, College of Chemistry, Fuzhou University, Fuzhou 350002, China

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ABSTRACT

Magnetic polyphosphazene (MPZS) particles coated by Ag nanoparticles (MPZS-Ag) have been developed as surface enhanced Raman spectroscopy (SERS) substrates for sensitive detection of melamine in aqueous solutions and milk samples. 5,5′-Dithiobis-(2-nitrobenzoic acid) (DTNB) was used as model analyte to test the SERS activity of the MPZS-Ag particles. The prepared MPZS-Ag particles possess both magnetic responsiveness and excellent SERS properties. SERS detection of different concentrations of melamine aqueous solutions and spiked milk samples were performed by the MPZS-Ag particles. The limit of detection (LOD) of the melamine in aqueous solutions was 10^{-7} mol/L (0.0126 mg/L) and 0.6 mg/L in real milk samples using the MPZS-Ag particles as SERS substrates. The LOD of the melamine are much lower than the safety values of Food and Drug Administration and Codex Alimentarius Commission. These results indicate that the MPZS-Ag particles have promising application prospect for SERS analysis in food safety fields.

Melamine is an important organic chemical material that is used as the raw material for producing melamine-formaldehyde resin, which is widely used in coatings, plastics, leather and textile industries [1]. Due to its low cost and high nitrogen content (66.7% by mass), melamine is illegally added to milk or dairy products by unscrupulous manufacturers to reduce costs and increase protein content measured by the Kjeldahl method in its products [2,3]. Although melamine is a low toxic substance, long-term intake can damage the kidney or even cause death [4,5]. To ensure human health and food safety, many countries and organizations have proposed a limit standard of melamine in food. Both the Codex Alimentarius Commission (CAC) and the US Food and Drug Administration (FDA) have set a maximum melamine level of 1.0 mg/L for infant formula and of 2.5 mg/L for other foods and animal feeds [6,7]. Currently, various methods including enzyme-linked immunosorbent assay (ELISA) [8,9], high performance liquid chromatography (HPLC) [10], gas chromatography-mass spectrometry (GC–MS) [11], electrochemical method [12] and colorimetry [13,14] have been reported for the detection of melamine in food products. However, shortcomings such as complicated separation process, long detection time and high cost exist. Therefore, it is still necessary to develop simple, sensitive and efficient analysis methods for detecting melamine in food.

Surface enhanced Raman spectroscopy (SERS) has attracted great interest in recently years due to its high sensitivity and rapid non-destructive detection [15–17]. The SERS phenomenon can be observed in analytes adsorbed on the surface of crude noble metal particles (such as Ag, Au or Cu) [18,19]. It is considered that the amplified SERS signal originates from long-range electromagnetic enhancement and short-range chemical enhancement [20–22]. Although SERS-based melamine detection has been reported, there still remain problems including unsatisfactory stability and activity of the SERS substrates, and the substrates are difficult to recycle [23,24]. Therefore, it is important to fabricate SERS substrates with high sensitivity, good stability and rapid separation property for the detection of melamine. Recently, magnetic SERS substrates with rapid separation properties have been reported. However, in the coating or growth process of noble metal shells, magnetic attraction may leads to aggregation between particles and makes it difficult to obtain uniformly coated magnetic composite particles [25,26]. The polymer shell, which can stabilize the magnetic particles, effectively avoids uncontrolled aggregation of magnetic particles, and provides nucleation sites for *in-situ* deposition of Ag or Au nanoparticles [27,28]. Polyphosphazene (PZS) is a highly

* Corresponding author.
E-mail address: ibptylj@fzu.edu.cn (L. You).
[1] These authors contributed equally to this work.

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crosslinked polymer with excellent thermal stability and oxidation resistance. In addition, PZS is rich in P, N atoms and phenolic hydroxyl groups, making it easy for transition metal or metal oxide nanoparticles to deposit on the surface [29,30]. Herein, in present work, novel magnetic polyphosphazene (MPZS) particles coated by Ag nanoparticles (MPZS-Ag) have been developed as surface enhanced Raman spectroscopy (SERS) substrates for sensitive detection of melamine in aqueous solutions and milk samples.

Magnetic Fe_3O_4 nanoparticles were prepared using solvothermal method as reported [31]. Fig. 1A shows typical SEM image of the prepared Fe_3O_4 nanoparticles with an average diameter of 350 nm. The MPZS particles were prepared by precipitation polymerization in the presence of Fe_3O_4 nanoparticles. The preparation procedure of the MPZS-Ag particles is shown in Scheme S1 (Supporting information) and the details of experimentation are described in the experimental part of the Supporting information. In the initial stage of polymerization, the condensation polymerization of hexachlorocyclotriphosphazene (HCCP) and 4,4-sulfonyldiphenol (BPS) generated primary nucleus particles. Then these primary nucleus particles coated on the surface of Fe_3O_4 nanoparticles and formed stable aggregates. Afterwards, the aggregates grew into MPZS particles with a core-shell structure by absorbing oligomer species in solution [32]. It can be clearly observed from Fig. 1B that the surface of the prepared particles are smooth, indicating that the magnetic composite particles have been prepared. The clear core-shell structure of MPZS particle observed from the TEM image in Fig. 1G also confirms that PZS was coated on the surface of the Fe_3O_4 nanoparticles and the PZS shell thickness is about 300 nm.

The zeta potential of the MPZS particles is -40 ± 3.99 mV (Fig. S1 in Supporting information), which provides nucleation sites for aggregation of positively charged Ag^+ and is favorable for the *in-situ* deposition of Ag nanoparticles [28,30]. Ag nanoparticles were rapidly deposited on the surface of the MPZS particles by *in-situ* reduction of silver nitrate in the presence of absolute ethanol and *n*-butylamine. In order to prevent the formation of free Ag nanoparticles without loading on the surface of the MPZS particles and make Ag nanoparticles more uniformly coated on the surface of the MPZS particles, multiple deposition strategy of Ag nanoparticles was adopted with low concentration of silver nitrate in ethanol solution. The SEM images in Figs. 1C-F show the MPZS-Ag particles fabricated with different count of Ag nanoparticles deposition. According to the images, the density of the Ag shell and the size of Ag nanoparticles on the surface increased as the number of deposition count increased. Compared with the clear core-shell structure of the MPZS by TEM image in Fig. 1G, the core-shell structure of the MPZS-Ag particles is difficult to be observed in Fig. 1H by TEM image, because the transmission electron microscopy is difficult to penetrate the Ag nanoparticle shell deposited on the surface of the MPZS-Ag particles. However, the rough morphology of Ag nanoparticle shell was obviously observed, verifying that the silver nanoparticles are successfully coated on the surface of the MPZS particles.

The MPZS-Ag particles were also characterized by XRD and TGA (Fig. S2 in Supporting information).The characteristic XRD peaks of Fe_3O_4 and Ag appear in the XRD pattern of the MPZS-Ag particles, which confirmed the existence of Fe_3O_4 core and indicated that Ag nanoparticles were completely coated on the particles. The silver amount in the MPZS-Ag particles was calculated to be about 24% in weight by the TGA results in Fig. S2B. Moreover, as shown in Fig. 1I, the MPZS-Ag particles can be separated by a magnet in 90 s and redispersed after the magnet is removed, suggesting good magnetic responsiveness and dispersibility of the MPZS-Ag particles.

DTNB was used as model analyte to investigate the effect of the amount of Ag deposited on the SERS activity of the MPZS-Ag particles. The SERS spectra of 10^{-5} mol/L DTNB measured on the MPZS-Ag particles fabricated with different deposition count of Ag deposition are shown in Fig. 2A. It is observed that the intensity of the characteristic peak is obviously enhanced with the number of deposition times increased. As the amount and denseness of Ag nanoparticles on the surface of the MPZS particles increased, the distance between the Ag nanoparticles became closer, which promoted the plasma coupling of Ag nanoparticles and the formation of hot spots, thus strongly enhanced the Raman signal. When deposition of Ag nanoparticle

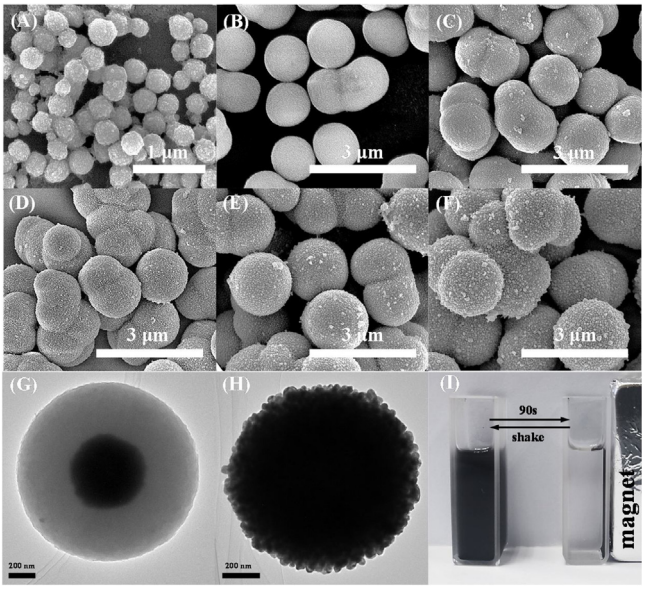

Fig. 1. SEM images of (A) Fe_3O_4 nanoparticles, (B) MPZS and MPZS-Ag particles prepared with different number of times of silver deposition: (C) once, (D) twice, (E) thrice and (F) four times; TEM images of (G) MPZS particles; (H) MPZS-Ag particles; (I) Photograph of the MPZS-Ag particles in ethanol separated by a magnet.

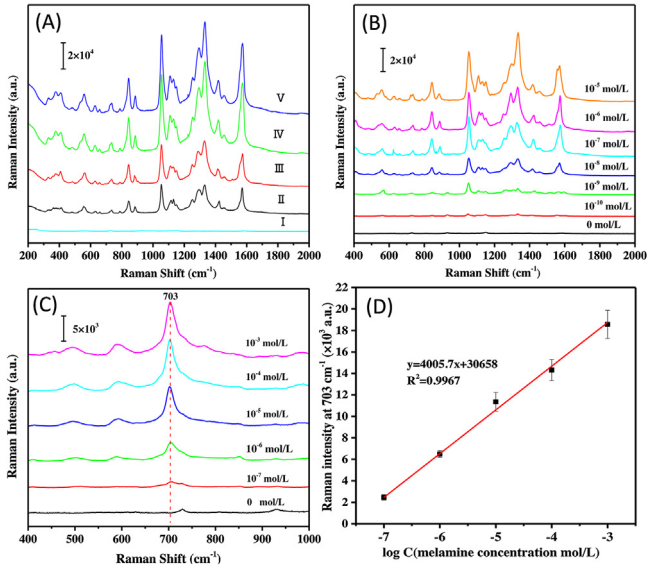

Fig. 2. (A) SERS spectra of 10^{-5} mol/L DTNB by the MPZS-Ag particles with different Ag deposition times: (I) The MPZS particles without Ag deposition, (II) once, (III) twice, (IV) thrice, (V) four times; (B) SERS spectra of DTNB at different concentrations by the MPZS-Ag particles; (C) SERS spectra of different concentration of melamine in aqueous solution by the MPZS-Ag particles; (D) Fitting curve of the dependence of Raman intensities at 703 cm^{-1} on the logarithm concentrations of melamine.

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