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Original article

Determination of primary aromatic amines using immobilized nanoparticles based surface-enhanced Raman spectroscopy

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ABSTRACT

Primary aromatic amines (PAAs) are substances with toxicity and suspected human carcinogenicity. A facile method for highly sensitive detection of PAAs using surface-enhanced Raman spectroscopy (SERS) is reported. The immobilization of Au nanoparticles (AuNPs) on the glycidyl methacrylate–ethylene dimethacrylate (GMA-EDMA) materials makes the substrate a closely packed but not aggregated Au NP arrays which provides a prominent SERS enhancement. Four PAAs with different substituent groups, namely, *p*-toluidine, *p*-nitroaniline, benzidine and 4,4-methylene-bis-(2-chloroaniline) have been successfully identified and quantified. High sensitivity and good linear relationship between SERS signals and concentrations of PAAs are obtained for all four PAAs.

1. Introduction

Currently, many primary aromatic amines (PAAs) are classified as toxic compounds or suspected human carcinogens [1–3]. They are widely used as starting substances or intermediates in pesticides, polymers, pharmaceuticals, cosmetics, and azo-dyes. However, the reactivity of PAAs has biological implications, with exposure to these compounds being linked to a number of toxicological effects, including carcinogenicity and genotoxicity. Many of them are specified by the National Institute for Occupational Safety and Health (NIOSH) as chemical hazards [4], as well as by the International Agency for Research on Cancer (IARC) [5]. For the proven carcinogenic substances, no detectable exposure levels are allowed for controlling work place exposures.

The published literature shows that a number of different analytical methods have been employed for the detection of PAAs [6–9]. The simplest approach for the analysis of PAAs is the colorimetric method [10,11]. However, this approach lacks selectivity and has high risk of false positive results. Various more confirmatory and sensitive methods for PAAs were developed based on mass spectrometry due to its high accuracy, reliability, and selectivity. Gas chromatography-mass spectrometry (GC–MS) after previous derivatization with isobutyl chloroformate is a sensitive method for PAA detection [9]. Currently the most exploited technique is liquid chromatography coupled with mass spectrometry (LC–MS) or tandem mass spectrometry (LC–MS/MS) [12,13]. Not only do these approaches usually need expensive instruments and sophisticated technicians, but also the process is time-consuming. Therefore, it is urgent and meaningful to develop a simple and sensitive detection method for identification and quantification of PAAs.

Surface-enhanced Raman spectroscopy (SERS) is a rapid and ultrasensitive spectroscopic technique in chemical analysis. Some porous material has been used as SERS substrate because of their high SERS enhanced property. The porous structure might benefit to high SERS enhancement [14–17]. The objective of this study was to develop a rapid and sensitive SERS sensor for PAAs detection and identification using nanoparticles decorated GMA-EDMA organic porous material. The effectiveness of the SERS sensor was validated using a group of PAAs with different substituent groups. This SERS

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sensor provides an easy and reliable method for trace PAAs detection.

2. Experimental

All reagents were of analytical reagent grade and used without further purification. Glycidyl methacrylate (GMA) was obtained from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Ethylene dimethacrylate (EDMA), benzoperoxide (BPO), 1-dodecanol and cyclohexanol were purchased from Acrosorganics (New Jersey, USA). Benzidine, *p*-toluidine, *p*-nitroaniline and 4,4-methylene-bis-(2-chloroaniline) were obtained from J&K Scientific, Ltd. (Beijing, China). The PAAs stock solutions (100 mg/L) were prepared in ethanol. The PAAs working solutions were obtained by diluting the stock solutions.

Glycidyl methacrylate–ethylene dimethacrylate (GMA–EDMA) porous material and AuNPs colloids were synthesized according to literature procedures [18,19]. Gold colloid was synthesized using the method of Freeman [20]. The synthesized polymeric material was ground with a mortar and sieved with a sieve whose size was 60–80 mesh. GMA–EDMA powder material was modified by amino group. Then, the AuNPs were immobilized on the GMA–EDMA material through the interaction between amino groups and AuNPs. Thus, AuNPs decorated GMA–EDMA material was obtained for further use.

PAAs samples (100 μL) with various concentrations were mixed with appropriate amounts of the above materials, and the mixture was shaken for 1 min. Then, the materials were taken out and put on a quartz plate for SERS detection. A portable Raman spectrometer (i-Raman, B&W Tek Inc., USA) with 785 nm excitation source was used for the measurement at an integration time of 10 s. The laser power and laser spot were 200 mW and 150 μm, respectively.

3. Results and discussion

The resultisng Au-immobilized GMA–EDMA substrate was characterized by UV–vis spectrum and SEM (See Supporting information). Fig. S1(a) in Supporting information demonstrates the UV–vis spectrum of AuNPs decorated GMA–EDMA substrate. The maximum plasmon absorption of the Au colloid is located at 548 nm. Fig. S1(b) shows a SEM image of AuNPs decorated GMA-EDMA substrate and the inset is the blank GMA–EDMA materials without NPs. It clearly shows that AuNPs are self-assembled on GMA–EDMA porous materials with high density and homogeneity. Very little stacking of AuNPs is observed on the surface, which ensures the stability and reproducibility of SERS signals in the following measurements.

In order to evaluate SERS performance of the synthesized substrate, the SERS spectra using traditional gold colloid as SERS substrate were collected for comparison. One kind of PAAs-4,4-methylene-bis-(2-chloroaniline) (MOCA) was used as target compound to demonstrate the highly efficient enhancement of SERS signal on synthesized substrate. The spectra in Fig. 1 demonstrated that SERS spectrum of MOCA had some same characteristic peaks as Raman spectra (curve *c vs.* curve d) and synthesized substrate can obtain higher SERS signal intensity of MOCA at 10^{-5} mol/L (curve b *vs.* curve d).

In the present work, four PAAs under investigation and their known carcinogenic risk to humans [5] are listed in Table S1 in Supporting information. They were analyzed by SERS based on immobilized NPs, and their spectra were shown in Fig. S2. For comparison, the Raman spectra of the PAAs standards were also collected. The observed SERS spectra agreed well with the corresponding Raman spectra for PAAs standards. The lack of change in SERS peaks from the Raman spectra implies that the enhancement may be mainly due to the electromagnetic mechanism, which does not require the formation of chemical bonds between the analyte and substrate. To quantify the SERS intensity as a function of the PAAs concentration, the SERS peak which had higher intensity and well-shaped peak was selected for quantification. The Raman shift of quantitative peaks were 730 cm^{-1} for *p*-toluidine, 851 cm^{-1} for *p*-nitroaniline, 1183 cm^{-1} for benzidine, and 1603 cm^{-1} for MOCA. Their possible peak assignments based on literature data were C–C, out of plane vibration of C–H, in-plane bending vibration of C–H, and stretching mode of C=C, respectively [21–23].

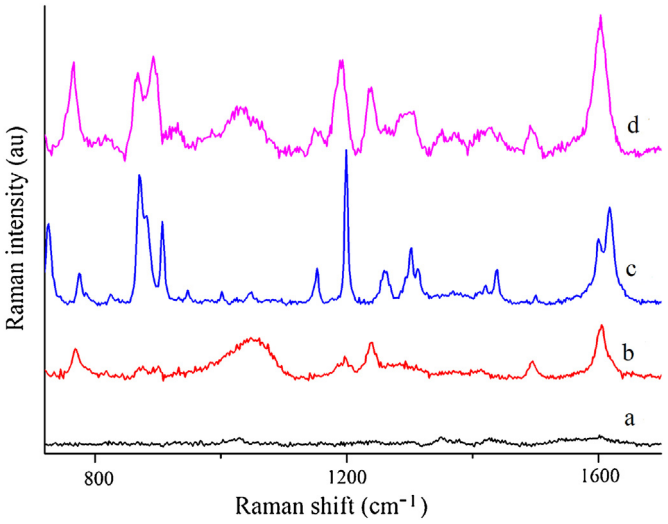

Fig. 1. (a) SERS spectrum of synthesized substrate; (b) MOCA SERS spectrum when Au colloid as substrate; (c) MOCA Raman spectrum; (d) MOCA SERS spectrum on synthesized substrate. The concentrations of MOCA are (a) 0 mol/L; (b) 10^{-5} mol/L; (c) pure MOCA; (d) 10^{-5} mol/L.

The PAAs samples with various concentrations were measured and their spectra were shown in Fig. 2. It was demonstrated that the signal intensity of quantitative peaks increased in response to the increasing PAAs concentration. The calibration curves of four PAA samples were linear within certain concentration ranges (2×10^{-9}–6×10^{-8} mol/L for *p*-toluidine, 5×10^{-9}–8×10^{-8} mol/L for *p*-nitroaniline, 5×10^{-10}–8×10^{-8} mol/L for benzidine, and 1×10^{-9}–5×10^{-8} mol/L for 4,4-methylene-bis-(2-chloroaniline)) and their corresponding correlation coefficients squared were 0.9869, 0.9830, 0.9842, and 0.9852, respectively. The limit of detection was calculated to be 1.9×10^{-10}, 3.7×10^{-10}, 2.1×10^{-11} and 1.5×10^{-10} mol/L for *p*-toluidine, *p*-nitroaniline, benzidine and 4,4-methylene-bis-(2-chloroaniline), respectively.

Compared with other methods for the determination of *p*-toluidine, *p*-nitroaniline, benzidine and 4,4-methylene-bis-(2-chloroaniline), our method has much better LOD than spectrophotometry [24], SPE-CZE [25], LC–MS/MS [26], CFME–HPLC [27], HLLE–IMS [28], *etc.*, comparable LOD to HPLC [29,30], but lower LOD than GC–MS [31]. Also, it should be noted that short analysis time and low cost are the advantages of SERS in comparison with GC–MS. The proposed method was applied for the determination of MOCA in tap water in order to test its feasibility for real samples. After pretreatment of precipitation and filtration, samples were detected directly using our method. Results showed that no MOCA could be detected in tap water. Furthermore, two tap water samples spiked with MOCA solution at concentrations of 1.5×10^{-8}–5×10^{-8} mol/L were analyzed and the recovery results were 84.2% and 112.6%. Detailed results were shown in Table S2 in Supporting information.