



Polyethylenimine-carbon nanotubes composite as an electrochemical sensing platform for silver nanoparticles



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ABSTRACT

For the first time, polyethylenimine (PEI) and carbon nanotubes (CNT) composites (PEI-CNTs) were employed for investigation of electrochemical response of silver nanoparticles (AgNPs) in this work. The PEI-CNTs were easily prepared by sonicating the mixture of PEI and CNTs solution and characterized by SEM, Raman and electrochemical impedance spectroscopy (EIS). The PEI-CNTs/GCE enhanced the electrochemical response for three AgNPs with different capping agents, including citrate-AgNPs (Cit-AgNPs), humic acid-AgNPs (HA-AgNPs) and gum acacia-AgNPs (GA-AgNPs), by cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronocoulometry (CC). On these findings, a new electrochemical method based on LSV was developed for the detection of AgNPs. Under the optimum conditions, the proposed method showed a good linear range from 5 to 200 ng/L, and the limits of detection (LODs) were 4.77 ng/L for Cit-AgNPs, 2.48 ng/L for HA-AgNPs and 1.01 ng/L for GA-AgNPs, respectively. The potential of using the PEI-CNTs modified GCE for determining AgNPs in water samples has been successfully demonstrated.

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1. Introduction

Due to the unique optical, electronic, antibacterial and catalytic properties, silver nanoparticles (AgNPs) have been widely used in a broad range of fields, such as medical industry, water treatment, catalytic and analytical areas [1–7]. As one of the most common nanotechnology-based consumer products, AgNPs has triggered the concern over their potential risks to both environmental and human health [8–10]. Previous studies showed that the potential toxicity of AgNPs cannot be underestimated in their transformation progress in natural environment, including aggregation, sedimentation, adsorption, dissolution and reduction [6,11]. In addition, AgNPs could be formed naturally and exist in the natural environment [12]. For these critical reasons, there is an imperative to develop analytical methods for AgNPs detection [13].

Various analytical techniques have been developed for detection and characterization of AgNPs, including ICP-MS [14,15], UV-Vis spectra [16] and electrochemical methods [17,18]. Among these techniques, electrochemical methods have attracted a great attention due to their advantages of quick response, inexpensive instrument and low energy consumption, and various NPs including AuNPs [19,20], MoNPs [21], PtNPs [22], Cd-based QDs [23], fullerene [24] and AgNPs [25–31] have been measured or

investigated by electrochemical methods [32]. In particular, since anodic particle coulometry (APC) was firstly reported for the electrochemical detection of AgNPs by Compton's group [32], a series of electrochemical methods [25–29] and related coupling techniques [30–32] have been utilized in the detection of AgNPs. For instance, Cheng et al. fabricated a disposable poly(L-cysteine) modified electrode for the detection and quantification of commercial AgNPs [26]. Also, the commercial gold recordable CDs could be fabricated as a disposable gold electrode for AgNPs detection [27]. Cepriá et al. proposed a quick and simple method for the detection of AgNPs using screen printed electrodes [28]. In another work, Goda et al. reported an electrochemical method for simultaneous detection of AgNPs and MoNPs at a commercial glassy carbon electrode [29].

On the other hand, previous work has demonstrated that the capping agents could affect the catalytic properties of the resulting metal NPs [33]. However, the investigation on the effect of capping agents on the electrochemical response of AgNPs is rare. To our knowledge, there is only one paper dealing with such an effect reported by Compton's group, who investigated the influence of capping agents on the oxidation of silver nanoparticles by using anodic particle coulometry on an unmodified GCE [34]. Herein, we reported the electrochemical measurement of AgNPs by PEI-CNTs modified GCE for the first time. PEI-CNTs composite was used because there was a possible synergic effect between CNTs (electron-transfer promotion and electrochemical signal enhancement) and PEI (dispersion for CNTs and enrichment for AgNPs). In

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addition, PEI is an important type of nitrogen-rich polymers and contains primary and secondary amine groups [35], which possess good metal chelation properties. Thus, it is anticipated that AgNPs may achieve satisfactory responses at the PEI-CNTs composite modified electrode. To this end, the electrochemical response of the Cit-AgNPs (widely used AgNPs in a lab), GA-AgNPs (a kind of commercial engineering AgNPs) and HA-AgNPs (a kind of natural AgNPs [12]) were investigated at PEI-CNTs/GCE by cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronocoulometry (CC). The effect of capping agent on electrochemical behaviors of three AgNPs was also discussed. Under the optimization conditions, the linear relationships and detection limits of Cit-AgNPs, HA-AgNPs and GA-AgNPs were obtained. The potential of using the PEI-CNTs modified GCE for determining AgNPs in water samples has been successfully demonstrated.

2. Experimental

2.1. Reagents and instruments

Single-walled carbon nanotubes (SWCNTs) (with diameter of 1–2 nm and length of 30 μm) were purchased from XFNANO Materials Tech Co., Ltd. PEI (with average MW of 25000), humic acid and gum acacia were purchased from Aladdin. Trisodium citrate and other chemicals were purchased from Sinopharm-Group chemical reagent corporation. They were used without further purification. All the solutions were prepared and diluted by ultrapure water.

Electrochemical measurements were carried on a CHI660E electrochemical workstation (Chenhua, Shanghai) or an IM6ex electrochemical workstation (Zahner, Germany). The zeta potential determination was carried on a Zetasizer Nano-ZS90 instrument (Malvern, UK). Scanning electron microscopy (SEM) images were taken on Hitachi S-4800 field emission scanning electron microscope (Hitachi, Japan). Transmission electron microscopy (TEM) images were obtained on Philips Tecnai G2 20 electron microscopy (FEI, USA).

2.2. Preparation of AgNPs with different capping agents

Cit-AgNPs, HA-AgNPs and GA-AgNPs were synthesized following the procedures reported [36–38] with modifications. For synthesis of Cit-AgNPs, 320 mg trisodium citrate was added to a flask containing 800 mL ultrapure water with vigorous stirring for about 10 min, and then 10 mL AgNO_3 aqueous solutions (0.02 M) were added dropwise with constant stirring. Finally, 10 mL NaBH_4 aqueous solutions (8 mg/mL) were quickly added with vigorous stirring for 12 h. For synthesis of HA-AgNPs or GA-AgNPs, 0.5 mL AgNO_3 aqueous solutions (0.02 M) were added dropwise into 50 mL HA or GA aqueous solutions (6 mg/L) with the 5 min stirring. Then 2 mL NaBH_4 aqueous solutions (2 mg/mL) were quickly added with vigorous stirring for another 30 min. Three AgNPs were diluted with ultrapure water to achieve standard solution with different concentrations. TEM images showed that three AgNPs exhibited similar particle sizes and morphologies (Fig. S1).

2.3. Preparation of PEI-CNTs composite

PEI-CNTs composite was prepared based on previous works by ultrasonic method [39,40] with a minor modification. Briefly, 100 mg CNTs and 10 mg PEI were mixed and sonicated in 200 mL ultrapure water for 1 h. Then the mixed solution was transferred into a flask and stirred overnight. After completion of the reaction, the resulting suspension was centrifuged and the obtained product was washed by ethanol and ultrapure water in turn.

2.4. Preparation of PEI-CNTs modified electrodes

Prior to modification, the GCE ($\Phi=3$ mm) was polished carefully on a polishing cloth with 0.05 mm alumina powder and rinsed with ultrapure water. Then the GCE was treated by sonication in ethanol and ultrapure water prior to use. For preparation of PEI-CNTs modified electrode, 1 mg PEI-CNTs was dispersed in 1 mL ultrapure water by ultrasonic to form PEI-CNTs dispersion (1 mg/mL). Then an aliquot of 2 μL of PEI-CNTs dispersion was droplet coating on the GCE surface and then the solvent was evaporated at room temperature to obtain the PEI-CNTs/GCE. For comparison, PEI/GCE and CNTs/GCE were prepared by a similar process, namely, 2 μL PEI solution (1 mg/mL) or 2 μL CNTs dispersion (1 mg/mL) was droplet coating on the GCE surface and then dried in air, respectively.

2.5. Electrochemical measurements

The employed three-electrode system consisted of a modified glass carbon electrode (GCE) as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl (3.0 M KCl) electrode as the reference electrode. All the electrochemical measurements were performed at room temperature. Electrochemical tests, including cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronocoulometry (CC), were performed on a CHI660E electrochemical workstation. The above measurements were performed in pH 5.6 PBS solutions containing a certain amount of analytes. Before LSV or CV measurement, electrode was immersed in electrolyte for a certain preconcentration time. Electrochemical impedance spectroscopy (EIS) was carried out by an IM6ex electrochemical workstation. EIS measurement was performed in 0.1 M KCl solution containing 1.0×10^{-3} M $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$.

3. Results and discussion

3.1. Characterization of PEI-CNTs composite

The morphologies of the CNTs and PEI-CNTs were characterized by SEM. Fig. 1A and B show the SEM images of CNTs before and after PEI treatment. It can be seen that CNTs exhibit uniform tubular structure. After PEI treatment, CNTs were wrapped by PEI and the obtained PEI-CNTs exhibit thicker and smooth tube wall, suggesting successful synthesis of PEI-CNTs composite.

Fig. S2 displays the Raman spectra of raw CNTs and PEI-CNTs composite. Two characteristic peaks were recorded for the CNTs and PEI-CNTs. The band in 1300–1340 cm^{-1} is common in disordered sp^2 carbon material and has been considered as the D-band. The band in 1580–1600 cm^{-1} attributes to the G-band and is corresponding to well-ordered graphite. The calculated I_D/I_G value for CNTs and PEI-CNTs are 0.93 and 0.75, respectively. This demonstrates that the wrapping of PEI on CNTs reduces the number of defects on the surface of CNTs, resulting in a decrease of disordered sp^2 carbon material [39,40]. From the above result, it is clear that CNTs have been wrapped well by PEI, which was consistent with the previous reports [39,40]. In addition, PEI wrapping increased the hydrophilic property of CNTs surface due to the presence of amino group in PEI, thus the formed PEI-CNTs composite could be well dispersed in aqueous solution. Hence, PEI was not only the wrapping reagent but also the dispersant of CNTs.

3.2. Electrochemical characterization of electrodes

EIS was a powerful tool to study the electrode interface properties and could provide information about the electrode surface.

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