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Effect of forced convection on the collision and interaction between nanoparticles and ultramicroelectrode

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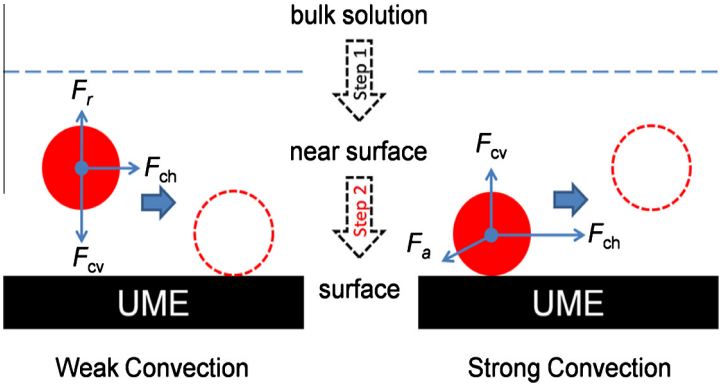
GRAPHICAL ABSTRACT



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ABSTRACT

Detection of nanoparticle (NP) collision events at ultramicroelectrode (UME) has emerged as a new methodology for the investigation of single NP in recent years. Although the method was widely employed, some fundamental knowledge such as how the NP moves to and interacts with the UME remain less understood. It was generally recognized that the recorded rate of collision was determined by diffusion that should follow Fick's first law. However, significant lower collision frequency compared with that of predicted by theory were frequently reported. Experiments carried out by us suggest that the collision frequency will increase dramatically if forced convection (stir or flow injection) is applied during detection. Furthermore, the collision frequency gradually increases to a maximum and then decreases, along with the increase of the convection intensity. This phenomenon is interpreted as follows: (a) there are two steps for a freely moving NP to generate a detectable collision signal. The first step is the move of NP from bulk solution to the surface of the UME which is mass transfer limited; the second step is the landing of NP on the surface of UME which is affected by many factors and is the critical step; (b) there is a barrier that must be overcame before the contact between freely moving NP and UME. Forced convection with moderate intensity can not only increase the mass transfer rate but also help to overcome this barrier and thus enhance the collision frequency; (c) the landing of NP on the surface of UME can be suppressed by stronger convections, because NP will be swept away by hydrodynamic force.

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1. Introduction

Recently, a new electrochemical method was developed to study single metal nanoparticle (NP) by means of detecting NP collision event at an ultramicroelectrode (UME). This approach enables us to detect NP at the individual particle level and to evaluate the size distribution, concentration of NPs in a fast and convenient manner [1–7]. The basis of detection is the current transient that is induced when a single nanoparticle collides with an UME. According to the origin of the current transient, the detection of single NP as well as the collision can be classified into three categories. The most extensively studied current transients are called electrocatalytic amplification (ECA), which means when a catalytic nanoparticle collides with a catalytically inactive electrode in the presence of an appropriate redox couple, current transient will appear due to the catalytic current induced by the nanoparticle. Bard and his coworkers have accomplished a considerable amount of work in this area [8–10]. The second type of current transient signal is caused by the direct electrochemical redox reaction of the NPs themselves. This type of detection has been widely studied by Compton's group [11–13]. The last kind of signal is opposite to ECA and is known as a blocking signal. In this case, the individual collision event of NP is detected by monitoring the blocking of the diffusion of redox mediator to UME substrates [14]. In addition to current transient induced by NP collision, researchers found that collision can also result in changes of the open circuit potential (OCP) [15,16]. In recent years, the method of detection of current transient caused by NP collision has been extending to many other applications. For instance, the method was adopted for ultrasensitive detection of single DNA molecular [17,18], analysis of NPs with the combination of electrically induced chemiluminescence [19,20], and the evaluation of the electron transfer kinetics for single nanoparticle [21,22].

Although the method was widely employed, some fundamental knowledge remain less understood. A distinct example is how the NP moves to and interacts with the UME and what factors determine whether a NP can generate a detectable current transient or not. Theoretically, in addition to the three types of basic chemical environment as described in the above paragraph, there are at least two requirements for the NP to generate a detectable current transient: (a) the NP must move close to the surface of the UME at least within the maximum tuning distance; (b) this state must be kept for a long enough period of time. Nevertheless, it was simply but generally recognized that the recorded rate of collision was determined by diffusion that should follow Fick's first law. However, significant lower collision frequency compared with that of predicted by theory were frequently reported [5,23,24].

In order to account for the much lower observed frequency of transient signal appearance, several explanations were proposed. Bard and co-workers attributed this contradiction to the low stay rate of NP and a parameter termed "stay coefficient" was introduced [5]. Investigation carried out by Koper suggested that agglomeration resulted from the reaction of electroactive species should account for this contradiction [23]. Compton et al. suggested that there is a shield effect because of the insulation glass that was widely used to seal the UME [24].

According to the classical theory of mass transfer, there exist three approaches: diffusion, electromigration and convection. David's study indicated that electromigration also had a great influence on NPs collisions [25]. In certain circumstances, contribution of electromigration may be even greater than diffusion. Nevertheless, most of the existing researches were carried out with common electrochemical cells under stationary conditions. Recently, Stevenson and Crooks explored the impact of forced convection on NPs collisions with a microfluidic microband electrode under laminar flow. Their researches indicated that the transfer of Pt NPs to the electrode surface can be enhanced and thus the limit of detection of the NPs can be improved under forced convection [26].

In order to further investigate the effect of forced convection on the interaction between NPs and UME, two approaches were employed to generate convection by us. The first approach is simply stirring the detection solution with a magnetic stirrer; the second approach is placing the UME under wall-jet flow with the combination of an injection pump and a specially designed electrochemical flow injection cell. The flow near the surface of the UME is believed to be turbulent rather than laminar for both approaches. However, the intensity of convection is adjustable within a wide dynamic range for the second approach. Experiments were carried out with the classic Pt NPs and Hg/Pt UME collision system [6]. Some new insights on the manner of interaction between nanoparticle and UME are revealed thereafter.

2. Experimental section

2.1. Chemicals and materials

Ferrocene (99.0%), potassium ferricyanide (99.5%), potassium phosphate monobasic (99.5%), potassium hydrogen phosphate anhydrous (99.5%), potassium nitrate (99.0%), sodium citrate (99.0%), citric acid (99.8%), sodium borohydride (96.0%), and $N_2H_4{\cdot}H_2O$ (95%) were all purchased from Guangzhou Tianjin trading Co., Ltd. Chloroplatinic acid hydrate, $Hg(NO_3)_2{\cdot}H_2O$ (97.0%) were acquired from J&K Scientific Ltd (Shanghai, China), and sulfuric acid and nitric acid from Shanghai Chemical Corp. All other reagents were of analytical grade and used without further purification. Doubly distilled water was used throughout all the experiments. All UMEs were purchased from Shanghai Xian Ren instrument Co., Ltd (Shanghai, China). The radius of the Pt, Au and carbon fiber UME is 10 μm, 12.5 μm and 7 μm, respectively.

2.2. Synthesis of Pt NPs

Pt NPs of an average diameter of about 6 nm were prepared by reducing H_2PtCl_6 aqueous solution with sodium citrate [27]. Briefly, 0.5 mL of 1% H_2PtCl_6 aqueous solution was added into 50 mL of water and then the solution was heated to boiling. Aging of the H_2PtCl_6 solution was not necessary in this synthetic procedure. Then, 1.5 mL of 1% sodium citrate aqueous solution was added rapidly, and the mixture was kept at a boiling temperature for certain times. Pt NPs of an average diameter of about 25 nm were synthesized by following procedures from the literature [6]. First, 3.88 mL of 0.2% chloroplatinic acid hydrate aqueous solution was added into 50 mL of boiling distilled water for a minute under boiling temperature. Second, 1.185 mL of a freshly prepared solution containing 1% sodium citrate and 0.05% citric acid was injected and allowed to boil for 30 s. Third, 0.59 mL of the freshly prepared solution containing 0.08% sodium borohydride, 1% sodium citrate and 0.05% citric acid was added and then boiled for additional 10 min. Forth, 1 mL of the solution synthesized above was taken into 29 mL of distilled water at room temperature, and 0.045 mL of a 0.4 M chloroplatinic acid solution and 0.5 mL of a solution containing 1% sodium citrate and 1.25% of L-ascorbic acid were injected to the mixture while it was stirred. Temperature was then slowly increased to boiling point (~at the rate of 10 °C/min). Finally, the forth step was repeated, and the only difference was the amount of chloroplatinic acid solution, which was 0.023 mL instead. Transmission electron microscopy (TEM) was used to determine the size of Pt NPs, and the NP concentration was usually calculated from the concentration of Pt precursor divided by the average number of Pt atoms contained in each particle. The