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Electrochemical detection of nanomolar dopamine in the presence of neurophysiological concentration of ascorbic acid and uric acid using charge-coated carbon nanotubes via facile and green preparation



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ABSTRACT

Negatively charged multi-walled carbon nanotubes (MWCNTs) were prepared using simple sonication technique with non-toxic citric acid (CA) for the electrochemical detection of dopamine (DA). CA/MWCNTs were placed on glassy carbon (GC) electrodes by drop-casting method and then electrochemical determinations of DA were performed in the presence of highly concentrated ascorbic acid (AA). For the comparison of the charge effect on MWCNTs surface, positively charged polyethyleneimine (PEI)/MWCNT/GC electrode and pristine MWCNT/GC electrode were also prepared. Contrary to conventional GC electrode, all three types of MWCNT modified electrodes (CA/MWCNT/GC, PEI/MWCNT/GC, and pristine MWCNT/GC) can discriminate $\sim\mu\text{M}$ of DA from 1 mM AA using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) due to the inherent electrocatalytic effect of MWCNTs. Compared to positively charged PEI/MWCNT/GC and pristine MWCNT/GC electrodes, negatively charged CA/MWCNT/GC electrode remarkably enhanced the electrochemical sensitivity and selectivity of DA, showing the linear relationship between DPV signal and DA concentration in the range of 10–1000 nM even in the presence of $\sim 10^5$ times concentrated AA, which is attributed to the synergistic effect of the electrostatic interaction between cationic DA molecules and negatively charged MWCNTs and the inherent electrocatalytic property of MWCNT. As a result, the limit of detection (LOD) of DA for CA/MWCNT/GC electrode was 4.2 nM, which is 5.2 and 16.5 times better than those for MWCNT/GC electrode and PEI/MWCNT/GC electrode even in the presence of 1 mM AA. This LOD value for DA at CA/MWCNT/GC electrode is one of the lowest values compared to the previous reports and is low enough for the early diagnosis of neurological disorder in the presence of physiological AA concentration (~ 0.5 mM). In addition, the high selectivity and sensitivity of DA at CA/MWCNT/GC electrode were well kept even in the presence of both 1 mM AA and 10 μM uric acid (UA) as similar as neurophysiological concentration.

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1. Introduction

In neuroscience, dopamine (DA) is a key neurotransmitter, which is responsible for transmitting electrical signals between the substantia nigra and multiple brain tissues. The highly sensitive determination of DA level in extracellular space is needed for the early diagnosis of various neurological disorders and the deep understanding of dopaminergic pathway in the brain for the development of pharmaceutical drugs [1–3]. For example, the release

of high level of DA is related with schizophrenia but that of low level of DA is related with Parkinson's disease, then a DA antagonist can be used as a drug for schizophrenia and a DA releasing agent can be used as a drug for Parkinson's disease. There are many methods to determine DA concentration such as fluorescence, surface enhanced Raman scattering [4], chromatography [5], microdialysis [6,7], and electrochemical method [8–10]. Among the various methods, electrochemical method is very promising for the detection of DA due to its simplicity, cost-effectiveness, and availability to *in-situ* monitoring of DA. However, many neurotransmitters (e.g. uric acid (UA)) can interfere with the electrochemical detection of DA, moreover, high level (0.2–0.5 mM) of ascorbic acid (AA) in our body [11] can overwhelm the electrochemical signal of $\sim\text{nM}$ level of DA. This interfering

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problem can be overcome by utilizing the unique catalytic property of nanomaterials.

Carbon nanotube (CNT) is one of the attractive electrode nanomaterials with high electrical conductivity, good mechanical strength, and catalytic property [12]. Then, both single-walled CNT (SWCNT) and multi-walled CNT (MWCNT) have been utilized as the electrode materials to enhance the selectivity and the sensitivity of various analytes [13]. The surface modification of CNT is one of the most important issues for the application of CNTs [14] because the surface functionality can give synergetic effects in company with inherent excellent properties of pristine CNT. For example, various functional groups on CNT surface can be acted as chemical anchors for further derivatization [14], hydrophilic or hydrophobic functional groups can change wettability for the application to biocompatible or anti-wetting materials [15], and charge moieties of functional groups can affect optoelectronic property, bio-functionality and even toxicity [16–18]. Therefore, various modification methods for the surface of CNT have been developed such as acid treatment, UV/ozone treatment, and wrapping with polymer, and however, most synthetic methodologies are accompanied with complex and time-consuming processes or require harsh reaction conditions or toxic chemicals such as strong acids or aromatic compounds for π - π stacking.

MWCNT modified electrodes have already been used for the electrochemical detection of DA with other neurotransmitters and AA [19–21] thanks to the inherent electrocatalytic property of MWCNTs to promote the sluggish oxidation reaction of AA with overlapping the voltammetric signal of DA oxidation. However, the detection limit of DA is not enough for the early diagnosis of neurological disorder, and even if extremely low detection limit is obtained, most experiments were performed in the presence of low concentration of the interfering AA, which is far from the physiological concentration level (~ 0.5 mM). Negatively charged MWCNTs surface can endow synergistic effect to inherent MWCNT catalytic property because the negatively charged MWCNTs attract cationic DA molecules and repel anionic AA molecules; most DA molecules ($pK_b=8.9$) exists as the cationic form and most AA molecules ($pK_a=4.2$) exists the anionic form at physiological condition (pH 7.4).

Here, we have changed the surface charges of MWCNTs by simple ultrasonication method with negatively charged citric acid (CA) molecules, and have investigated the surface charge effect of MWCNT modified electrodes for the DA determination in the presence of high concentrated AA, comparing with positively charged MWCNT modified electrode using PEI and pristine MWCNT modified electrode. CA is widely used as a stabilizer in the synthesis of metal nanoparticle, and moreover, it is very suitable for the bio-application due to non-toxicity and biocompatibility. Thus, our method should be useful for the development of simple nanosensors for the detection of various biological materials. In addition, electrochemical detection of DA was performed at the CA/MWCNT/GC electrode even in the presence of the neurophysiological concentration of AA and UA.

2. Experimental

2.1. Materials

MWCNTs were purchased from Hanhwa Nanotech Co. Ltd. (10–15 nm in diameter, >90% of purity), which were synthesized by CVD method. Dopamine (DA) hydrochloride, L-(+)-ascorbic acid (AA), citric acid (CA), uric acid (UA), potassium hexacyanoferrate ($K_4[Fe(CN)_6]$) and polyethylenimine (PEI) were purchased from Sigma-Aldrich. All the reagents were analytical grade and used as received.

2.2. Instrumentation

The working electrode was obtained by drop-casting of MWCNT suspension on a conventional glassy carbon (GC) disk electrode. While the pristine MWCNTs were dispersed in ethanol, CA/MWCNTs and PEI/MWCNTs were dispersed in water. A Pt wire and an Ag/AgCl electrode were used as a counter electrode and reference electrode, respectively. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments were performed with a CHI 660D (CH Instruments, Inc., Austin, TX, USA). Contact angle images were taken on a PHOENIX-MINI (SEO Co. Ltd., Korea) and P-1 Glassy Carbon plate (BAS Inc., Japan) was used to substrate for contact angle images. Fourier transform infrared (FT-IR) spectra were performed with a NICOLET iS10 (Thermo scientific Korea Ltd.). FE-SEM images were taken on a JSM-6701F (JEOL, Ltd., Japan).

2.3. Preparation of charged MWCNT modified electrode

In order to obtain charged MWCNT modified electrodes (i.e. CA/MWCNTs or PEI/MWCNTs), pristine CNTs of 1 mg were immersed into 400 μ L of PEI or CA aqueous solution (0.5 mg/mL) with ultrasonication for 30 min. CA/MWCNTs and PEI/MWCNTs were dispersed in de-ionized (DI) water to form a black suspension after ultrasonic agitation. The glassy carbon (GC) electrode was polished with 0.05 μ m alumina slurry and washed in an ultrasonic bath for 10 min, and then, rinsed with DI water several times. 5 μ L of the black suspension containing CA (or PEI) coated MWCNT was dropped on the GC electrode. The electrode was dried with IR lamp for a few minutes and then rinsed with de-ionized water several times (Scheme 1).

3. Results and discussion

3.1. Contact angle experiments

Pristine CNTs are rarely dispersed in water due to their strong van der Waals interactions, which cause them to hold together, forming large bundles and revealing nonpolar and hydrophobic surface [14]. After negative or positive charges were generated by the adsorption of CA or PEI on the surface of MWCNTs, their surface properties were changed to more hydrophilic. In Fig. 1, the surface properties of charged MWCNT/GC substrates were analyzed by the contact angle experiment. While the graphite surface is slightly hydrophilic (i.e. water contact angle $\theta \approx 86^\circ$) due to the high surface energy of sp^2 carbons [15,22], bare GC surface was shown as somewhat hydrophobic ($\theta=100^\circ$), which might be attributed to the difference of manufacturing process. When pristine MWCNTs were modified on the GC substrate, the contact angle was increased to 138° , which is attributed to rough surface formed by the entangled structure of MWCNT bundles on GC surface [23–25], as shown in Fig. 2a. However, the contact angles of CA/MWCNT/GC and PEI/MWCNT/GC surfaces ($\theta=70^\circ$ and 27°) were significantly decreased compared to that of MWCNT/GC surface due to the negative charge of carboxylate and the positive charge of protonated amine group even if the surface morphologies of those charged MWCNT films were almost same as that of pristine MWCNT/GC surface, as shown in Fig. 2a-c. The contact angle of CA/MWCNT/GC was quite higher than that of COOH-functionalized MWCNTs oxidized by strong acid [26], which means the efficiency of COOH functionalization by the adsorption of CA is lower than that by oxidation with strong acid. Many small organic molecules and polymers can be adsorbed on the pristine MWCNT surface by hydrophobic interaction or π - π interaction. CA or PEI might be also adsorbed due to the hydrophobic interaction between the

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