Electrochemistry

DISPOSABLE MULTIWALLED CARBON NANOTUBE PRINTED FILM ELECTROCHEMICAL DETERMINATION OF ACETAMINOPHEN, DOPAMINE, AND URIC ACID

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A novel printed film consisting of multiwalled carbon nanotubes was fabricated on a polyethylene terephthalate substrate by means of a mass flexographic printing process. Potential applications of this film for electrochemical biosensing were examined through the oxidation of acetaminophen, dopamine, and uric acid in phosphate buffer (pH 7.0). The results demonstrate that the printed carbon nanotube film exhibits an enhanced electrochemical response toward these molecules. Dopamine and uric acid did not interfere with each other and, thus, their simultaneous determination may be performed. The results suggest the mass flexographic printing technique has potential application for the construction of low-cost, precise, and disposable multiwalled carbon nanotube films.

Keywords: Acetaminophen; Dopamine; Electrochemical sensor; Mass flexographic printing; Multiwalled carbon nanotubes; Uric acid

INTRODUCTION

Mass printing techniques, such as offset printing, gravure printing, and flexographic printing, are simple and effective methods that can be applied for the fabrication of disposable single-use thin films for electrochemical sensing in broad areas of nanotechnology (Fischer et al. 2011). The printing techniques are preferred over other conventional methods for producing sensors, since they are inexpensive and rapid. Films consisting of multiwalled carbon nanotubes and conducting polymer materials fabricated by means of the mass flexographic printing process provide new electrodes that combine the excellent mechanical and electrical properties of carbon nanotubes with the good flexibility, high transparency, high capacitance, easy
processing, and low cost of polymers (Lazarenko et al. 2008; Li et al. 2011; Matzui et al. 2005; Ritter et al. 2010).

Our research interest is currently focused on the production of multiwalled carbon nanotube films by chemical vapor deposition and their application in electrochemical sensing. Specifically, novel, rapid-response sensors based on carbon nanotubes arrays, which are able to detect selectively down to micromolar concentrations of redox systems, were successfully fabricated (Tsierkezos and Ritter 2012a; 2012b). An additional subject was the production of carbon nanotube-based sensors by means of a mass flexographic printing process using polymer substrates (Fischer et al. 2011).

The goal of the present research is the combination of the excellent electrocatalytic properties of multiwalled carbon nanotubes and the fine electrical properties and great flexibility of polymers for the production of simple, stable, sensitive, and low-priced sensors. It is expected that the printed carbon nanotubes films would be suitable as disposable sensors for routine electrochemical analysis. For this purpose, a novel multiwalled carbon nanotube film was fabricated on a polyethylene terephthalate substrate. The film was characterized electrochemically using the standard ferrocyanide/ferricyanide, $[\text{Fe(CN)}_6]^{3-/4-}$ redox system in aqueous potassium chloride solution (1.0 M) by cyclic voltammetry and electrochemical impedance spectroscopy. Furthermore, the electrochemical response of the film toward the oxidation of acetaminophen, dopamine, and uric acid in phosphate buffer solution (pH 7.0) was examined.

**EXPERIMENTAL**

**Chemicals and Solutions**

Potassium hexacyanoferrate(III) (99.0%), potassium hexacyanoferrate(II) trihydrate (>98.5%), dopamine (>99.0%), acetaminophen (>98.5%), and potassium chloride (>99.0%) were purchased from Sigma-Aldrich, while uric acid (>98%) was purchased from Merck. All chemicals were used as received without any further purification. The measurements were performed in phosphate buffer (Sigma-Aldrich) prepared immediately prior the electrochemical experiments in double-distilled water.

**Apparatus and Procedures**

The cyclic voltammograms and the electrochemical impedance spectra were recorded using a computer controlled system Zahner (model IM6/6EX, Germany). The measurements were performed using a three-electrode cell configuration. The working electrode was the printed carbon nanotube-based film, while the counter electrode and the reference electrode were a platinum plate and Ag/AgCl (sat. KCl), respectively. Impedance spectra were recorded in the frequency range from 0.1 Hz to 50 kHz at the half-wave potential of a standard redox system $[\text{Fe(CN)}_6]^{3-/4-}$ (+0.275 V vs. Ag/AgCl) and analyzed with an equivalent electrical circuit ($R_s + (C_{dl}/R_{ct} + Z_w)$) (software Thales, version 4.15) (Supplementary Material; Figure S1). To simulate the experimental impedance data, the capacitor
was replaced by a constant phase element. The most widely accepted explanation for
the presence of constant phase element is that the microscopic roughness of the car-on nanotube-based film causes an inhomogeneous distribution in solution resist-
ance and double-layer capacitance.

Production of Printed Multiwalled Carbon Nanotubes-Based Film

The fabrication of the printed multiwalled carbon nanotube film was per-
formed by a mass flexographic printing process involving the transfer of water-
dispersed nanotubes on a polyethylene terephthalate substrate. The material
CarboDis TN, used for these experiments, was purchased from Future Carbon
GmbH and consists of an aqueous dispersion of multiwalled carbon nanotubes
(2 wt.%) and an electrically neutral surfactant. Printing tests were performed on a
flexographic test printing press FlexiProof 100-630 (Erichsen, Germany). The
dispersed carbon nanotubes were transferred on the polyethylene terephthalate
substrate (thickness ~ 1.7 mm) using printing plate nyloflex ACE (Flint Group,
Germany). More details concerning the production of printed carbon nanotubes-
based films have been reported previously (Tsierkezos, Wetzold, and Ritter 2013).
The surface of the film was characterized by scanning electrode microscopy images
that demonstrate the surface morphology is rough and porous (Supplementary
Material; Figure S2). In order to connect the printed carbon nanotube working elect-
rode for the electrochemistry experiments, the printed film was attached to a copper
wire by using silver-conductive coating. Once the silver coating was dried (after
about 24 h), the silver-conducting part of the film was fully covered with a
varnish-protective coating.

RESULTS AND DISCUSSION

Oxidation of Ferrocyanide

The printed carbon nanotubes film was initially electrochemically characterized
by using the standard redox system ferrocyanide/ferricyanide, [Fe(CN)₆]³⁻/⁴⁻. Cyclic
voltammograms for [Fe(CN)₆]³⁻/⁴⁻ in the concentration range from 0.099
to 0.990 mM were recorded in aqueous potassium chloride (1.0 M) (Figure 1a) and
illustrate that the redox couple [Fe(CN)₆]³⁻/⁴⁻ is completely reversible over this con-
centration range because the ratio of cathodic (i_p^red) and anodic (i_p^ox) peak currents
reaches unity (i_p^red/i_p^ox ≈ 1). This finding demonstrates that the concentrations of
oxidized and reduced forms of the system are equal and are not consumed in the
coupled chemical reaction, confirming that the charge-transfer process occurring
on surface of carbon nanotube film is Nernstian. In addition, the variation of
peak current with the square root of scan rate was linear over the concentration
range demonstrating that the electrochemical process was diffusion-controlled and
verifying once more the Nernstian response of investigated redox couple
[Fe(CN)₆]³⁻/⁴⁻ on the printed film.

A similar conclusion can be extracted from the anodic and cathodic peak
potential separation (ΔE_p = E_p^ox - E_p^red), which is directly related to the heterogeneous
electron transfer rate constant (k_a) of the redox system through the electrochemical
absolute rate relation (Nicholson 1965). Specifically, the anodic and cathodic peak
potential separation of approximately $\Delta E_p \approx 0.066$ V obtained for all studied concentrations of $[\text{Fe(CN)}_6]^{3-/4-}$ on printed carbon nanotubes film is similar (within experimental error) with the value of $\Delta E_p = 0.064$ V, which is the ideal $\Delta E_p$ for reversible one-electron redox process. From the obtained $\Delta E_p$, the heterogeneous electron transfer rate constant of $k_s = 9.9 \times 10^{-2}$ cm$^2$ s$^{-1}$ was estimated for $[\text{Fe(CN)}_6]^{3-/4-}$ on the printed film by the electrochemical rate relationship. The estimated $k_s$ values for $[\text{Fe(CN)}_6]^{3-/4-}$ on the carbon nanotube film is between the $k_s$ values over the range of $8.5 \times 10^{-2}$–$19.0 \times 10^{-2}$ cm$^2$ s$^{-1}$ reported by Winkler (1995) for the same redox system on platinum electrode. These findings exhibit an enhanced charge transfer kinetics of the redox system $[\text{Fe(CN)}_6]^{3-/4-}$ on the film.

In order to estimate the detection limit and sensitivity of the printed film toward $[\text{Fe(CN)}_6]^{3-/4-}$, the relationship between the oxidation peak current and concentration of $[\text{Fe(CN)}_6]^{3-/4-}$ was investigated over the concentration range of 0.099 to 0.990 mM. The anodic peak current response of the printed carbon nanotube film was proportional to the concentration of analyte over the studied concentration range with a correlation coefficient of 0.9980 (Figure 1b). The detection limit and the sensitivity of the printed film toward $[\text{Fe(CN)}_6]^{3-/4-}$ were estimated graphically as 3.1 $\mu$M and 0.129 A·M$^{-1}$·cm$^{-2}$, respectively. The limit of detection was estimated to be the concentration of $[\text{Fe(CN)}_6]^{3-/4-}$ that provides three times the signal-to-noise ratio. Furthermore, $[\text{Fe(CN)}_6]^{3-/4-}$ was determined several times on different films in order to investigate the precision. The relative standard deviation values were less than 3%, which is quite acceptable.

The detection limit obtained for the printed multiwalled carbon nanotube film toward $[\text{Fe(CN)}_6]^{3-/4-}$ is presented along with literature values in Table 1 for comparison. The detection limit of the printed film toward $[\text{Fe(CN)}_6]^{3-/4-}$ was twice as high compared to the value for a multiwalled carbon nanotube film printed on a polycarbonate substrate (1.36 $\mu$M) (Tsierkezos, Wetzold, Hübler, et al. 2013).
This finding shows the influence of the polymer on the electrode response. However, the printed carbon nanotube film appears to be significantly more sensitive compared to other electrodes reported in literature. For instance, Pandurangachar et al. (2010) reported a detection limit of 100 μM for a carbon paste electrode modified with 1-butyl-4-methylpyridinium tetrafluoro-borate toward \( \text{[Fe(CN)₆]}^{3-}/C₄O^{4-} \). A detection limit of 100 μM was also reported by Niranjana et al. (2009) for a carbon paste electrode modified with sodium dodecyl sulfate, and Hirano et al. (2001) reported a detection limit of 30 μM for a glass capillary ultra-microelectrode. This comparison shows that the detection ability of printed carbon nanotube film is significantly improved compared to electrodes reported in the literature.

The effect of the concentration of \( \text{[Fe(CN)₆]}^{3-}/C₄O^{4-} \) on the kinetics of electron transfer on the surface of the film was further investigated by electrochemical impedance spectroscopy. Representative impedance spectra recorded for various concentrations of \( \text{[Fe(CN)₆]}^{3-}/C₄O^{4-} \) on printed film are displayed in Figure 2. In these plots, the complex impedance is presented as the sum of the real and imaginary impedance components. The recorded impedance spectra reveal a trend for formation...
of a semicircle at higher frequencies that corresponds to the electron-transfer process, and a linear part that appears at lower frequencies attributed to diffusion-limited mass transfer (Warburg impedance). The linear portion prevails over the semicircle part (in fact, only a part of semicircle can be seen) indicating that the barrier for electron transfer process is relatively low on the printed film (Rodriguez Nieto, Tucceri, and Posadas 1996), and confirming the Nernstian response toward the studied redox system.

The findings demonstrate that the charge transfer resistance \( (R_{ct}) \) increases slightly with the concentration of \([Fe(CN)_{6}]^{3-/4-}\). Specifically, the charge transfer resistance varies from 83 to 89\( \Omega \) over the concentration range from 0.196 to 0.990 mM, suggesting interruption of the electron transfer process caused by the uncompensated resistance effect, which becomes more significant with high concentrations of the electroactive substance. From the charge transfer resistance, the \( k_s \) value of \([Fe(CN)_{6}]^{3-/4-}\) on the printed multiwalled carbon nanotube film was estimated \( (k_s \approx 9.0 \times 10^{-2} \text{ cm} \cdot \text{s}^{-1}) \). The determined \( k_s \) value appears to be slightly smaller compared to \( k_s \) estimated using the electrochemical absolute rate relationship \( (k_s \approx 9.9 \times 10^{-2} \text{ cm} \cdot \text{s}^{-1}) \).

**Oxidation of Acetaminophen**

The electrochemical response of the printed film toward oxidation of acetaminophen, dopamine, and uric acid, was investigated in phosphate buffer (pH 7.0). Representative cyclic voltammograms recorded for various concentrations of acetaminophen on the printed film at the scan rate of 0.01 V \cdot s\(^{-1}\) are shown in Figure 3a. The effect of the concentration of acetaminophen on its oxidation peak
current is presented in Figure 3b. The electrochemical measurements were performed at pH 7.0, which is close to physiological pH (pH 7.365). Furthermore, it was verified that at pH 7.0 the sensor’s response toward oxidation of investigated molecules was enhanced.

As it can be seen in recorded cyclic voltammograms, the printed film exhibits a quasi-reversible response toward oxidation of acetaminophen over the concentration range of 0.096 to 0.750 mM. According to literature reports, acetaminophen is electrochemically oxidized via a two-electron transfer process to $N$-acetyl-$p$-quinone imine (Miner et al. 1981). The cyclic voltammograms recorded for the acetaminophen/$N$-acetyl-$p$-quinone imine redox couple are quite symmetric, but nevertheless, some slight current differences between the forward and reverse scans are observed (the peak current ratio is greater than unity, $i_{\text{ox}}/i_{\text{red}} > 1$). These findings indicate that the amount of oxidized and reduced current is not equal, confirming that the charge-transfer process involving acetaminophen/$N$-acetyl-$p$-quinone imine is quasi-reversible on the printed multiwalled carbon nanotube film. The slow kinetics of acetaminophen/$N$-acetyl-$p$-quinone imine may be also somewhat characterized by the large $\Delta E_p$ values obtained for this redox couple. Namely, the estimated $\Delta E_p$ values varying from 162 mV to 461 mV in the concentration range of 0.096 to 0.750 mM, resulting in $k_s$ values in between $3.2 \times 10^{-5}$ and $2.6 \times 10^{-6}$ cm$^{-1}$ s$^{-1}$, which are significantly smaller compared to $k_s$ estimated for the standard reversible redox system $[\text{Fe(CN)}_6]^{3-/4-}$ ($k_s \approx 9.9 \times 10^{-2}$ cm$^{-1}$ s$^{-1}$). The observed concentration dependence of $\Delta E_p$ may be attributed to uncompensated resistance (Feeney and Kounaves 1999; Bond, Oldham, and Snook 2000). In the present work, only 85% of the resistance was compensated in order to avoid circuit oscillation. Thus, some residual uncompensated solution resistance is probably responsible for the $\Delta E_p$ values. However, it is obvious that even at the lowest studied concentration, where the uncompensated resistance effect tends to be negligible, greater $\Delta E_p$, and

![Figure 3. (a) Cyclic voltammograms recorded for various concentrations of acetaminophen (from inner to outer: 0.096, 0.142, 0.272, 0.352, and 0.500 mM) on the printed multiwalled carbon nanotube film at a scan rate of 0.01 V/s (phosphate buffer, pH 7.0); (b) Variation of the oxidation peak current of acetaminophen with concentrations between 0.096 and 0.750 mM.](image-url)
thus, smaller $k_s$ were obtained for acetaminophen/$N$-acetyl-$p$-quinone imine compared to that of standard redox system. This result shows the low electron-transfer kinetics of acetaminophen/$N$-acetyl-$p$-quinone imine redox system on the printed film.

The oxidation potential of acetaminophen/$N$-acetyl-$p$-quinone imine on the printed carbon nanotube film at approximately $+0.480$ V (vs. Ag/AgCl) was more positive ($\sim 40$ mV) compared to that measured for the same redox system on a film based on nitrogen-doped carbon nanotubes ($+0.440$ V vs. Ag/AgCl) (Tsierkezos, Haj Othman, and Ritter 2013). This finding demonstrates the strong influence of nitrogen-doping on carbon nanotubes on their electrocatalytic properties and appears to be in accordance with the literature reports (Szroeder et al. 2010; Szroeder, Górska, et al. 2013). The doping of nanotubes with nitrogen and phosphorus leads to an improvement of the electrocatalytic properties (Yu, Xue, and Dai 2012). In addition, the oxidation potential of acetaminophen/$N$-acetyl-$p$-quinone imine on a printed carbon nanotube film ($+0.480$ V vs. Ag/AgCl) appears to be slightly less positive compared to that on an unmodified bare glassy carbon electrode ($+0.500$ V vs. Ag/AgCl) (Tungkananuruk, Tungkananuruk, and Burns 2005), and significantly less positive compared to values obtained on a glassy carbon electrode modified with copper ions on a terthiophene carboxylic acid polymer ($+0.650$ V vs. Ag/AgCl) (Boopathi, Won, and Shim 2004) or using bismuth oxide nanoparticles ($+0.610$ V vs. Ag/AgCl) (Zidan et al. 2011). This observation demonstrates the electrocatalytic activity of carbon nanotubes that causes a decrease of the overpotential of redox systems and that the electrochemical response of the fabricated printed carbon nanotube film toward acetaminophen/$N$-acetyl-$p$-quinone imine is acceptable.

In order to estimate the detection limit and the sensitivity of printed film toward acetaminophen/$N$-acetyl-$p$-quinone imine, the relationship between the oxidation peak current and the concentration of studied redox system was investigated over a wide concentration range. As it can be seen in Figure 3b, the oxidation peak current of acetaminophen was proportional to concentration between 0.096 and 0.750 mM (with correlation coefficient of 0.9987). The detection limit and the sensitivity of the film toward acetaminophen/$N$-acetyl-$p$-quinone imine were estimated to be $3.9 \mu$M and $0.111$ A·M$^{-1}$·cm$^{-2}$, respectively. The limit of detection of the novel printed film toward acetaminophen/$N$-acetyl-$p$-quinone imine appears to be significantly better compared to that reported by either Goyal and Singh (2006) for glassy carbon electrode modified with fullerene $C_{60}$ ($50 \mu$M) or Fatibello-Filho, Lupetti, and Vieira (2001) for a Vaseline carbon paste electrode modified with avocado tissue ($88 \mu$M) (Table 1). In addition, the limit of detection of the printed film toward acetaminophen/$N$-acetyl-$p$-quinone imine obtained in the present work is lower compared to the value reported by Tungkananuruk et al. (2005) for a conventional glassy carbon electrode ($19.85 \mu$M). These findings confirm the excellent electrochemical quality of the printed multiwalled carbon nanotube film.

**Oxidation of Dopamine and Uric Acid**

Cyclic voltammograms for different concentrations of dopamine over the concentration range of 0.163 to 0.881 mM were recorded on the printed multiwalled carbon nanotube film in phosphate buffer (pH 7.0) (Figure 4a). The film exhibited a
well-defined, reproducible, quasi-reversible response for the oxidation of dopamine. As reported in the literature (Zen and Chen 1997b; Z. Wang et al. 2002), the oxidation of dopamine is characterized as a two-electron transfer that leads to the formation of dopamine-o-quinone (Zhu et al. 1997).

The cathodic peak current was much smaller than the anodic peak current (therefore, \( i_{p}^{ox} / i_{p}^{red} > 1 \)), showing that only a part of the initial dopamine that converted to dopamine-o-quinone can be regenerated, whereas the rest is consumed owing to a competing chemical reaction. Specifically, the kinetics of dopamine/dopamine-o-quinone redox couple on the printed film is somehow slow, and, consequently, a coupled chemical reaction for the conversion of dopamine-o-quinone to another product prevails over its reduction to dopamine. Only at high scan rates does the redox process compete with the chemical reaction. Thus, the peak current ratio for dopamine/dopamine-o-quinone is unity at enhanced scan rates (\( i_{p}^{ox} / i_{p}^{red} \approx 1 \)). The peak potential separation for the dopamine/dopamine-o-quinone redox couple on the printed film between 92 and 152 mV (\( \Delta E_{p} \) varies with the concentration, and, thus, uncompensated resistance effect can be also considered in this case) appears to be greater than the expected \( \Delta E_{p} \) for a two-electron transfer process (even at the lowest studied concentration), confirming the slow kinetics. The obtained \( \Delta E_{p} \) for dopamine/dopamine-o-quinone is between those estimated for the [Fe(CN)₆]³⁻/⁴⁻ and acetaminophen/N-acetyl-p-quinone imine redox couples. As \( \Delta E_{p} \) is related to the heterogeneous electron transfer rate constant (great \( \Delta E_{p} \) reflects slow kinetic of electron transfer reaction), it is concluded that the kinetic parameter \( k_s \) of investigated redox systems varies in the same order. Consequently, \( k_s \) values in the range of \( 1.02 \times 10^{-3} \sim 3.59 \times 10^{-3} \text{ cm} \cdot \text{s}^{-1} \) determined by rate relationships for dopamine/dopamine-o-quinone on the film are smaller than the value for [Fe(CN)₆]³⁻/⁴⁻ (\( 9.9 \times 10^{-2} \text{ cm} \cdot \text{s}^{-1} \)), and greater compared to those estimated for acetaminophen/N-acetyl-p-quinone imine (\( 3.2 \times 10^{-5} \sim 2.6 \times 10^{-6} \text{ cm} \cdot \text{s}^{-1} \)).

![Figure 4.](a) Cyclic voltammograms recorded for various concentrations of dopamine (from inner to outer: 0.291, 0.415, 0.595, 0.712, and 0.881 mM) on the printed multiwalled carbon nanotube film at a scan rate of 0.01 V·s⁻¹ (phosphate buffer, pH 7.0); (b) Variation of oxidation peak current of dopamine with concentrations between 0.163 and 0.881 mM.](b)
It was observed that the oxidation of dopamine to dopamine-o-quinone on the printed carbon nanotube film (+0.240 V vs. Ag/AgCl) is shifted by approximately 55 mV to a more positive potential compared to the value measured on a film consisting of nitrogen-doped carbon nanotubes (+0.185 V vs. Ag/AgCl) (Tsierkezos and Ritter 2012b). This result shows that the ability of the printed carbon nanotube film to decrease the overpotential of dopamine/dopamine-o-quinone is weaker compared to that of nitrogen-doped carbon nanotube film (similar behavior was observed for the oxidation of acetaminophen), confirming once more the greater electrocatalytic activity of nanotubes with nitrogen in their structure (Szroeder, Tsierkezos, et al. 2013). However, it is interesting that the oxidation potential of dopamine/dopamine-o-quinone on the printed carbon nanotubes film was less positive (about 140 mV less anodic) compared to that measured on the unmodified carbon paste electrode (+0.380 V vs. Ag/AgCl) (Huang et al. 2008), and comparable to that measured on a carbon paste electrode modified with palladium nanoparticle-loaded carbon nanofibers (+0.221 V vs. Ag/AgCl) (Huang et al. 2008).

The cyclic voltammograms recorded for various concentrations of dopamine on the printed carbon nanotube film demonstrate that the anodic peak current for oxidation of dopamine was proportional to its concentration over the investigated concentration range with a correlation coefficient of 0.9948 (Figure 4b). The detection limit and sensitivity of the printed carbon nanotube film toward dopamine/dopamine-o-quinone were graphically estimated as 5.0 μM (signal-to-noise ratio of 3) and 0.122 A·M⁻¹·cm⁻², respectively. The detection ability of novel carbon nanotube film printed on the polyethylene terephthalate substrate toward dopamine/dopamine-o-quinone appears to be slightly poorer compared to that obtained on the carbon nanotube film printed on a polycarbonate substrate (Table 1) (Tsierkezos, Wetzold, Ritter, and Hübler 2013). However, the limit of detection of the novel printed film toward dopamine/dopamine-o-quinone is improved compared to literature values for other novel electrode materials. For example, the detection limits reported for dopamine/dopamine-o-quinone on either a platinum electrode modified with polypyrrole (20 μM) (Doyle, Breslin, and Rooney 2009) or a carbon nanotube-based film modified with polyaniline (38 μM) (Sabzi, Rezapour, and Samadi 2010) were significantly poorer (about 4 and 8 times poorer, respectively) compared to the result reported herein. In addition, the detection limit for a glassy carbon electrode modified with nafion/cobalt hexacyanoferrate toward dopamine/dopamine-o-quinone (8.90 μM) (Castro et al. 2008) was approximately two times poorer compared to that obtained on the novel printed film. Consequently, the electrochemical response of the printed multiwalled carbon nanotube film toward dopamine/dopamine-o-quinone is quite acceptable.

Interference studies were also performed in binary mixtures of dopamine and uric acid to investigate the selectivity of the printed film. It is well known that uric acid disturbs the determination of dopamine since the oxidation peaks are adjacent (Zen and Chen 1997a). As shown in Figure 5a, uric acid provides an oxidation wave at about \( E_{p}^{ox} = +0.388 \) V (vs. Ag/AgCl), the current of which is strongly dependent on the concentration. The voltammograms were not symmetrical and the oxidation current of uric acid appears to be greater than the reduction current (therefore, \( i_{p}^{ox} / i_{p}^{red} > 1 \)) demonstrating the irreversible oxidation of uric acid on the printed film.
Previous published studies suggested that the oxidation peak may be attributed to the two electron oxidation of uric acid to uric acid diimine (Owens, Marsh, and Dryhurst 1978). According to literature reports, the oxidation of uric acid is followed by the chemical reaction of uric acid diimine with water to form imine alcohol, which is reduced at a more negative potential than uric acid diimine (Dryhurst 1972). Consequently, as the hydration of uric acid diimine occurs simultaneously with the electron transfer process, the cathodic peak current corresponding to the reduction of uric acid diimine to uric acid is lower than the oxidation peak current. The appearance of a weak reduction peak at about +0.278 V (vs. Ag/AgCl) corresponding to the reduction of uric acid diimine to uric acid, suggests that uric acid diimine is adsorbed at the surface of printed carbon nanotubes-based film and is stabilized to some extent in the adsorbed state. The addition of dopamine in the electrochemical cell leads to an additional oxidation peak (+0.240 V vs. Ag/AgCl) that corresponds to the oxidation of dopamine (the same oxidation potential was identified by measuring dopamine in the absence of uric acid). The separation between the oxidation waves of dopamine-uric acid (140 mV) is sufficiently large in order to permit the determination of dopamine and uric acid in a single measurement.

Cyclic voltammograms recorded at various concentrations of uric acid demonstrate that increasing the concentration of uric acid between 0.166 and 0.681 mM (by keeping the concentration of dopamine constant) increases the oxidation peak current (with a correlation coefficient of 0.9999) (Figure 5b). The detection limit and sensitivity of the printed multiwalled carbon nanotube film toward uric acid/uric acid diimine were estimated to be 4.1 μM and 0.0899 A · M⁻¹ · cm⁻², respectively. Analysis of concentrations of dopamine by keeping the concentration of uric acid constant was also performed and the limit of detection toward dopamine was analogous (within experimental errors) to that estimated for dopamine in the absence of uric acid.
The findings reveal that the sensitivity of the printed multiwalled carbon nanotube film toward uric acid/uric acid diimine was greater compared to values measured for other novel electrodes reported in literature (Table 1). For instance, the detection limit obtained in present work for printed carbon nanotubes film toward uric acid/uric acid diimine appears to be 2 times better compared to the value reported for a carbon nanotube paste electrode modified with 2,2'-[1,2-ethanediyl-bis(nitroloethyldyne)]-bis-hydroquinone (8.8 μM) (Beitollahi et al. 2008). These results demonstrate that the printed film is quite sensitive and may be applied to the determination of uric acid in the presence of dopamine (similarly the film can be used for detection of dopamine in the presence of uric acid). Considering the other advantages of printed film such as the simple, low cost, and productive fabrication process, one can recognize their potential importance in electrochemical sensing.

The precision of the printed films was evaluated by cyclic voltammetry. The reproducibility of the method was studied by measuring the response of five films toward acetaminophen, dopamine, and uric acid. In all cases, a reproducibility of less than 2.5% was estimated. Furthermore, the repeatability of the method was studied by monitoring the current response of the same film toward the studied biomolecules for ten different successive measurements. The repeatability of less than 3.5% estimated for carbon nanotube film was quite acceptable. The findings demonstrate that the novel printed multiwalled carbon nanotubes films have quite good repeatability and reproducibility toward the investigated redox systems.

Urine (six human samples) was analyzed for dopamine and uric acid using the novel printed carbon nanotube film by dilution with phosphate buffer (pH 7.0) using differential pulse voltammetry with no additional sample pretreatment. All analyses were performed using the method of standard addition. The recovery experiments (95–101%) indicated that no matrix effects were observed.

CONCLUSIONS

The fabrication, electrochemical characterization, and application of printed multiwalled carbon nanotubes films in sensing has been reported. The printed film was prepared by the transfer of water dispersed multiwalled carbon nanotubes on a polyethylene terephthalate substrate using the flexographic printing process. The films were successfully employed for the electrochemical determination of acetaminophen, dopamine, and uric acid in phosphate buffer (pH 7.0). The limits of detection obtained for acetaminophen (3.9 μM), dopamine (5.0 μM), and uric acid (4.1 μM) are enhanced compared to the detection limits reported in literature for other novel composite materials. Interference studies reveal that dopamine and uric acid may be determined simultaneously. The results suggest that the multiwalled carbon nanotube film may have application as a disposable electrode for routine electrochemical sensing.

SUPPLEMENTAL MATERIAL

Supplemental data for this article can be accessed on the publisher’s website.
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