

Electrochemical Behavior of SWCNT-TPLF Electrode Compared to SWCNT-coated GCE and GE Electrodes

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Redox reaction $[\text{Fe}(\text{CN})_6]^{3-} / [\text{Fe}(\text{CN})_6]^{4-}$ has been studied with a Single-Walled Carbon Nanotube (SWCNT)-coated Glassy Carbon Electrode (GCE), SWCNT-coated Gold Electrode (GE) and a lab-made SWCNT-TPLF (SWCNT-Thin-Paper-Like-Film) Electrode. The SWCNT-modified electrode has shown a well-defined redox peak compared to bare electrodes. Cyclic voltammetry was used in 50.0×10^{-3} M aqueous solution of KCl containing $\text{K}_4[\text{Fe}(\text{CN})_6]$ to obtain information on both the capacitive background and electron transfer from the faradaic reaction of the redox species. The capacitance gives insight into the effective surface area (including both the exterior and interior surfaces within the coated and TPLF electrodes) as well as the pseudocapacitance due to faradaic reactions of surface bonded oxides. Among the three types of electrodes, the SWCNT-TPLF electrode showed the largest volume specific capacitance, consistent with its highest carbon nanotube packing density and largest effective surface area. This indicates that the carbon nanotube working electrode (whether coated or film electrode) behaves as a three-dimensional electrode. The redox reaction of $[\text{Fe}(\text{CN})_6]^{3-} / [\text{Fe}(\text{CN})_6]^{4-}$ was found to occur not only at the outer surface of the carbon nanotube but also at the interior surface of the thin paper like nanotube electrode.

Keywords

SWCNT-TPLF electrode
SWCNT-coated GCE
SWCNT-coated GE
cyclic voltammetry
charge capacitance
surface area

INTRODUCTION

The principal focus of modern research in electrocatalysis of SWCNT-coated working electrodes is to discover electrode materials that exhibit excellent electrochemical stability and show interesting activity towards typical electrochemical reactions. Gold and GC modified electrodes have been widely used for electrochemical measurements of the effect on the electrochemical responses of various surface states driven by various surface pre-treatments. Our main objective was to study the electrochemical behavior of common electroactive species of $\text{K}_4\text{Fe}(\text{CN})_6$ with SWCNT-coated (physically modified)

Gold and GC electrodes, and SWCNT-TPLF electrode directly immersed in electrochemical solutions.

CNTs consisting of cylindrical graphitic sheets have emerged as a new class of materials with intriguing nanometer scale structures and unique properties, which attract intensive attention in many fields such as nanoelectronic devices, composite materials, field-emission devices, atomic force microscope probes, gas and chemical sensors, lithium ion storage. CNTs are generated by rolling a single or several layers of graphite into a seamless and hollow cylinder, and can be divided into multi-walled carbon nanotubes (MWNTs)¹ and single-walled carbon

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nanotubes (SWNTs)² based on the number of carbon atom layers of the wall of the nanotubes. Since the discovery of CNTs by Iijima in 1991 using transmission electron microscopy, CNTs have been the subject of numerous investigations in chemical, physical and material areas due to their novel structural, mechanical, electronic and chemical properties.³ Depending on their atomic structure, CNTs behave electrically as a metal or as a semiconductor.^{4–6} Their subtle electronic properties have confirmed that CNTs have the ability to promote electron-transfer reactions when used as an electrode in chemical reactions.^{7–10} Recent studies have demonstrated that a CNT modified electrode could impart strong electrocatalytic activity to some important biomolecules, including cytochrome *c*, NADH and hydrogen peroxide, catecholamines such as dopamine, epinephrine, and ascorbic acid.^{11–13}

From the chemical point of view, CNTs are expected to exhibit inherent electrochemical properties similar to other carbon electrodes widely used in various electrochemical applications.¹⁴ It is important to investigate the fundamental electrochemical properties of CNT electrodes regarding the background, capacitance, and electron transfer rate. Unlike other carbon-based nanomaterials such as C₆₀ and C₇₀,¹⁵ CNTs shows very different electrochemical properties. Liu *et al.*¹⁶ compared a single-walled carbon nanotubes film with that of a C₆₀ film cast in the same way from suspensions on a Pt or Au electrode. Cyclic voltammetry of the SWCNT-coated film showed a broad featureless curve with a large effective capacitance in contrast to that of the C₆₀ film showing several pairs of discrete redox waves. Liu *et al.* attributed the featureless CV and the large effective capacitance to two possibilities: (i) an average of many closely spaced peaks corresponding to nanotubes of different length, diameter and helicity, and (ii) CNTs behaving like bulk carbon materials with a large effective surface area rather than individual redox active molecules. Even though the exact mechanism is not clear, the high specific capacitance was proposed for the application as supercapacitors. Barisci *et al.*¹⁷ investigated the capacitance behavior of SWCNT electrodes and suggested that the large surface area and surface-surface bonded oxides are mainly responsible for the capacitance. The [Fe(CN)₆]³⁻ / [Fe(CN)₆]⁴⁻ couple was used as a benchmark to characterize the electron transfer properties of the SWCNT-TPLF and coated electrodes.

CNT's novel structural and electronic properties, high chemical stability, and extremely high mechanical strength, which has become a major subject of many experimental and theoretical investigations, offer its wide potential application from structural materials to nanoelectronic components. Theoretical calculations have shown that, depending on its symmetry and diameter, CNT can behave as either a metal or a semiconductor.^{4,18,19} Furthermore,

it has been proved that CNT has better conductivity than graphite.²⁰ These results suggest that SWCNT can be used as electrode material and has the ability to promote electron transfer in electrochemical reactions. This is a new application of SWCNT and has received increasing attention. SWCNT electrodes, particularly those never used before SWCNT-TPLF as working electrodes directly in electrochemical experiments, are often found to contain a thin paper like film with the other electrode surface when submerged into an aqueous electrolyte solution. We found that the electrode properties differ due to the highly porous three-dimensional nature and the high hydrophobicity of the SWCNT surface.

EXPERIMENTAL

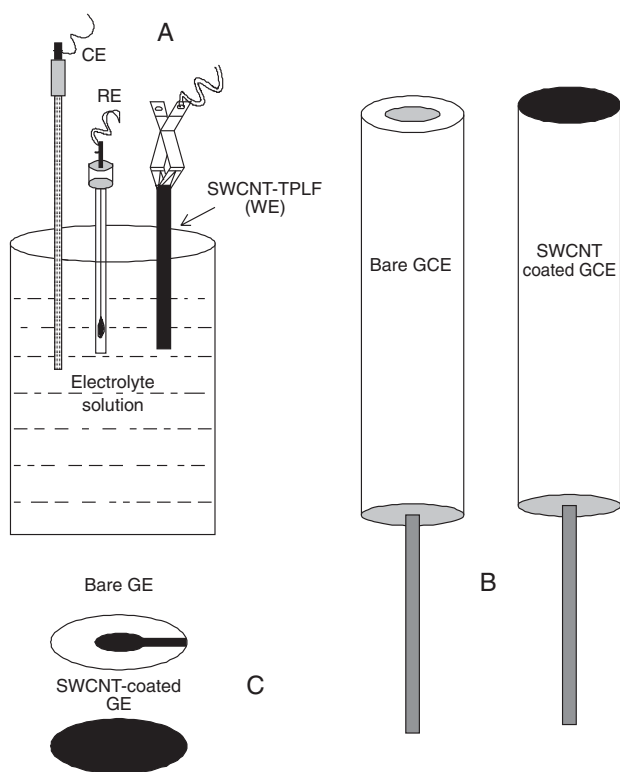
Instruments and Chemicals

All the electrochemical experimental observations are carried out using an electrochemical analyzer BAS100B Potentiostat (USA) and SHIn EQCM (Korea). The active surface areas of SWCNT-coated GC and Gold electrodes are 0.027 cm² and 0.26 cm², respectively. All voltammetric measurements, notably cyclic voltammetry, are performed in a one-compartment cell containing the SWCNT-TPLF or bare or SWCNT-coated Gold (gold coated quartz crystal) or GC as a working electrode, a Pt wire as an auxiliary or counter electrode and a saturated Ag/AgCl as a reference electrode. Cyclic voltammetry is performed at various concentrations of K₄Fe(CN)₆ in 50 × 10⁻³ M aqueous solution of KCl with SWCNT-TPLF or SWCNT-coated gold or GC electrode at various scan rates. The commercial SWCNT dispersed solution, obtained from the Tubes@Rice company, is used in making the SWCNT-TPLF electrode and SWCNT-coated gold or GC working electrode. K₄Fe(CN)₆ and KCl are used as received without further purification. Aqueous solutions are prepared with deionized water and other chemicals used are of reagent grade. A thin SWCNT film is deposited by dropping the commercially dispersed SWCNT solution on the GC and Gold electrode surface and is then heated with hot air.

Preparation of the SWCNT-coated and SWCNT-film Electrodes

Purification of common SWCNTs is of great importance since most carbon nanotube applications require materials of high quality. Nitric acid is a common reagent for purification of carbon nanotubes and constitutes the first step in many different purification schemes. Nitric acid treatment is usually employed to remove metal catalysts, together with some of the amorphous carbon.^{21,22}

The glassy carbon electrode surface is cleaned with high purity alumina powder (particle size, dia. 0.05 μm to obtain a mirror-like, shiny electrode surface, and then washed with water. The gold-coated film electrode (10 MHz quartz crystal, ICM Co., OK, USA) is chemically cleaned in a Piranha solution (98 % H₂SO₄ and 30 % H₂O₂, volume ratio 2:1)



Scheme 1. Settings of all working electrodes: SWCNT-TPLF, bare and SWCNT-coated.

under ultra-sonication. Dropping of the supplied commercial SWCNT dispersed solution makes a thin-coated film. A few drops of SWCNT solutions are placed onto the GC and Gold electrodes surfaces using a dropper and allowed to dry slowly. This is repeated one or two times again. The same coating procedure is repeated two or three times and then air-dried at room temperature overnight to make SWCNT-coated working GCE or Gold electrodes. For the SWCNT-film electrode, the SWCNT solution is separated from dispersed solvent with a vacuum suction pump on PTFE (Polytetrafluoroethylene) filter paper. Then the sample is oven-dried overnight at a temperature of 60 °C. After drying, the SWCNT-TPLF film is automatically separated from PTFE filter paper. This lab-made SWCNT-TPLF is directly used as a working electrode in all experiments. The thickness of SWCNT-TPLF is *ca.* 1 μm . The physical dimension of the SWCNT-TPLF electrode is 47 mm (diameter of round thin paper), which is automatically separated from filter paper. Then SWCNT-TPLF (tetragonal shape, 4 mm \times 30 mm) is taken for electrochemical measurements. The SWCNT-TPLF electrode setting is shown in Scheme 1.

RESULTS AND DISCUSSION

Cyclic voltammetry is a versatile electroanalytical technique for studies of electroactive $\text{K}_4\text{Fe}(\text{CN})_6$ species in a three electrodes system. CV monitors the redox behavior of chemical species within a wide potential range. The

current at the working electrode is monitored as a triangular excitation potential is applied to the SWCNT-TPLF or SWCNT-coated gold or GC electrode. The resulting voltamogram can be analyzed for fundamental information about the redox reaction of electroactive components.

Five different types of electrodes: Bare GC, Bare Gold, SWCNT-coated Gold, SWCNT-coated GC, SWCNT-TPLF electrodes, were used during cyclic voltammetry measurement. The SWCNT-TPLF electrode exhibits the highest activity towards $\text{K}_4[\text{Fe}(\text{CN})_6] / \text{K}_3[\text{Fe}(\text{CN})_6]$ redox reactions as promising electrocatalytic materials.

SWCNT-coated Gold Electrodes

The large effective charge capacitance of SWCNT electrodes has been thoroughly investigated in a simple supporting electrolyte, 50×10^{-3} M KCl. To understand the electron-transfer property of these electrodes, 4×10^{-3} mol dm^{-3} $\text{K}_4\text{Fe}(\text{CN})_6$ was introduced in the electrolyte as the redox benchmark in this study. Figure 1a shows CV obtained with the bare gold (dotted line) and SWCNT-coated gold (solid line) electrodes. The redox potential is measured for the bare gold electrode at about +0.31 and +0.13 V, and at +0.32 and +0.11 V for the SWCNT-coated gold electrode. The peak separation is about 0.21 V for the SWCNT-coated gold electrode, which is greater than 0.18 V of the bare gold electrode for the ideal reversible one-electron-transfer reaction, indicating quasi-reversible processes between the $[\text{Fe}(\text{CN})_6]^{3-} / [\text{Fe}(\text{CN})_6]^{4-}$ couple and the electrodes. This indicates a larger effective surface area compared to the bare electrode. With the SWCNT-coated gold electrode, the peak currents are significantly increased compared to the bare gold systems. The redox peak current is very stable through ten cycles for the SWCNT-coated gold electrode in the same electrolyte solution at a 0.1 V s^{-1} scan rate.

Cyclic voltammetry was also studied thoroughly at a series of scan rates ranging from 0.025 to 0.4 V s^{-1} in Figure 1b. The anodic or cathodic peak current is almost linearly increased with the square root of scan rates from 0.025 to 0.4 V s^{-1} in Figure 1b (inset). The peak separation increases with the scan rate ($\Delta E_p = 0.21 \text{ V}$ at 0.1 V s^{-1} vs. $\Delta E_p = 0.07 \text{ V}$ at 0.025 V s^{-1}) compared to the bare gold electrode, indicating a quasi-reversible process probably as the result of both the slow electron transfer at the SWCNT-surface (due to the graphite basal plane-like structure) and the slow diffusion through the narrow pores.

Clearly, the peak current is almost linearly proportional to the square root of scan rate, indicating that the baseline current corresponds to the capacitive charge current. The current can be simply expressed as:

$$I = C \cdot dE/dt,$$

where,

dE/dt is the linear scan rate in CV measurements.

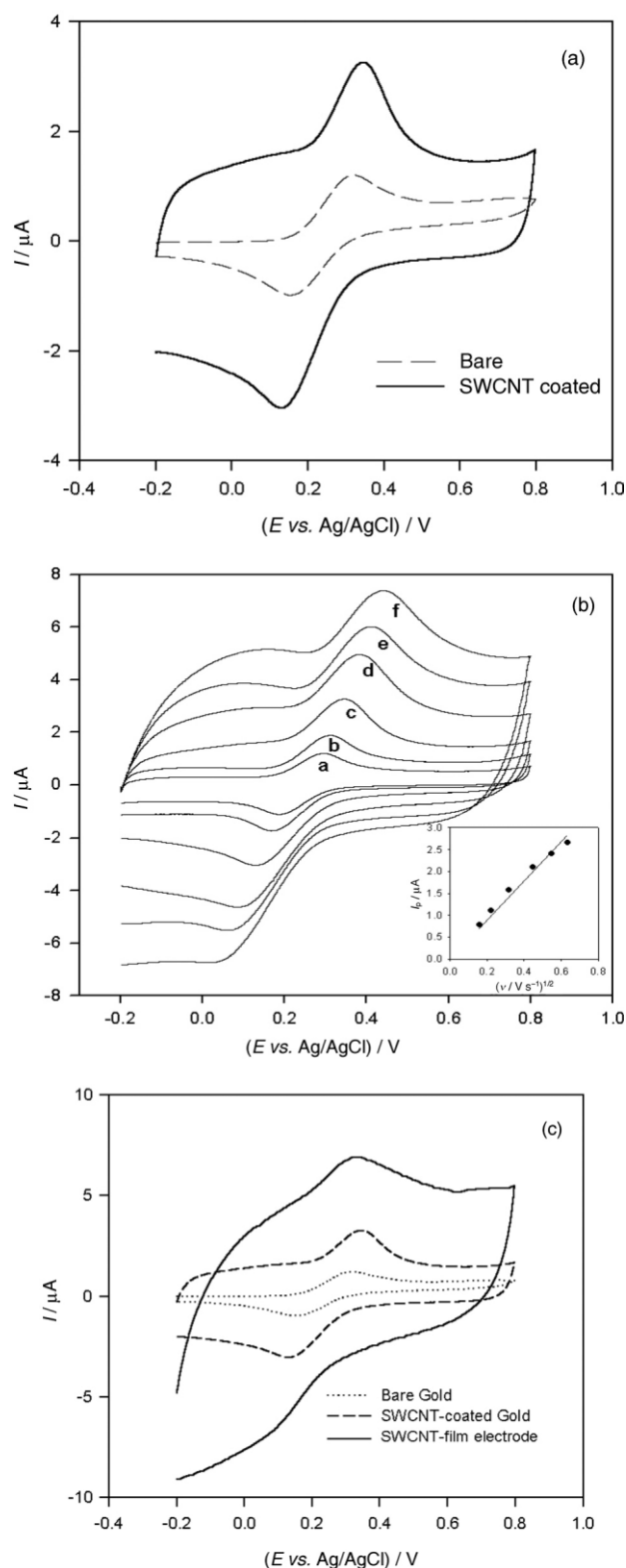


Figure 1. (a) Cyclic voltammety obtained with SWCNT-coated and bare gold electrodes in 5×10^{-3} mol dm^{-3} KCl electrolyte solution containing 4×10^{-3} mol dm^{-3} $\text{K}_4\text{Fe}(\text{CN})_6$ at a scan rate of 0.1 V s^{-1} . (b) CV obtained with SWCNT-coated gold electrode in the same electrolyte solution at different scan rates (a, 0.025 ; b, 0.050 ; c, 0.1 ; d, 0.2 ; e, 0.3 , f, 0.4 V s^{-1}). The peak current vs. the square root of the scan rates plot is drawn in the inset. (c) Comparison of SWCNT-film electrode with the bare and SWCNT-coated gold electrode. Measuring conditions: the same as in (a)

The capacitance could consist of two contributions: (i) the capacitance due to the double-layer at the electrode/electrolyte interface, which is proportional to the effective surface area, and (ii) the »pseudocapacitance« due to the surface faradaic reaction of redox active oxides such as various quinines formed during the acid treatment in the sample preparation.¹⁴ The weak and broad oxidation wave around $+0.32 \text{ V}$ and the reduction wave around $+0.11 \text{ V}$ are likely due to the latter, similar to those observed by Barisci *et al.*²³ This might be the reason why the effective capacitance below $+0.11 \text{ V}$ is larger than that above $+0.32 \text{ V}$. However, the pseudocapacitance only accounts for about one third of the observed value of effective capacitance. The double-layer capacitance is still the major component and can be used as a parameter to characterize the accessible surface area (0.26 cm^2) in porous SWCNT materials. In Figure 1c, the redox current of the SWCNT-TPLF electrode is clearly much bigger than that of the bare gold and SWCNT-coated gold electrodes.

CV measurements with different types of electrodes indicate that the redox current is largely increased for SWCNT-TPLF electrodes. Since both sides of the thin nanotube film are of a highly porous material, electrolytes are likely to access the interior surface. As a result, the volume instead of the outer surface should be considered for charge capacitance, which is much more different from a simple bare gold electrode.

SWCNT-coated Glassy Carbon Electrodes (GCE)

The same electrochemical strategy is used to compare the electrochemical behavior of the GC working electrode in different treatments. The same electrochemical investigations are carried out on $[\text{Fe}(\text{CN})_6]^{4-} / [\text{Fe}(\text{CN})_6]^{3-}$ couples for the SWCNT-coated GC electrode, in order to find out the electrochemical behavior of the coated film and to obtain information about the properties of this material. Dealing with the well-known redox couples $[\text{Fe}(\text{CN})_6]^{4-} / [\text{Fe}(\text{CN})_6]^{3-}$, their electrochemical behavior can be used to characterize a new electrode material, with the aim to elucidate its properties. As compared to the voltammogram obtained at a bare GC electrode, the SWCNT-coated GC electrode showed a shift of the oxidation/reduction peak to more negative/positive potentials, respectively (Figure 2a). However, the observed current response is significantly higher and the shape of the peak is much better defined. The increased current is ascribed to the interaction of the $\text{K}_4\text{Fe}(\text{CN})_6$ complex with the coated SWCNT on the electrode surface.

The CV curves of this compound were studied at various scan rates. It was found that the peak currents increase along with raising the scan rate, while the ΔE_p expands gradually. At a low scan rate, the cathodic peak current increases linearly with the increase of the square root of scan rates in Figure 2b, indicating that the redox reaction is a surface process. The complex/SWCNT-coated GC

electrode has good stability and reproducibility. In the CV experiments, the reductive and oxidative peak currents are very stable through ten cycles in $4 \times 10^{-3} \text{ mol dm}^{-3} \text{ K}_4\text{Fe}(\text{CN})_6$ and $50 \times 10^{-3} \text{ mol dm}^{-3} \text{ KCl}$. The influence of scan rate on the redox peak potential and the current of $\text{K}_4\text{Fe}(\text{CN})_6$ at the SWCNT-coated GC electrode are also studied by CV. The CV results showed that the redox peak current varies linearly with the scan rate, and also the oxidation and reduction potential shift to more negative and positive values, respectively, with increasing scan rates. The plot of peak current (anodic or cathodic) against the square root of scan rate is almost a straight line (inset figure).

The voltamograms obtained with the $[\text{Fe}(\text{CN})_6]^{4-} / [\text{Fe}(\text{CN})_6]^{3-}$ redox couple are shown in Figure 2c. It is important to note that although these redox couples are known to be quasi-reversible, the shape of the profiles depended on the surface conditions. Important observations can be summarized as follows:

– An increase in the current and the peak-to-peak potential compared to the values on the bare GC electrode; it is evident from the figures that these changes not only depend on the redox couple but also on the surface nature.

– The bare GC working electrode has shown a very little redox peak current during redox reactions when compared to the SWCNT-coated electrode, it may be due to the enhancement of the surface area on the coated GC electrode.

SWCNT-TPLF Electrodes

It seems straightforward to repeat the above measurements of the $[\text{Fe}(\text{CN})_6]^{4-} / [\text{Fe}(\text{CN})_6]^{3-}$ couple with SWCNT-TPLF electrodes. However it is too difficult to prepare thin paper like SWCNT-TPLF electrodes. The $[\text{Fe}(\text{CN})_6]^{4-/3-}$ redox system used in this study, one of the most extensively studied redox couples in electrochemistry, exhibits a heterogeneous one electron transfer and is very stable in many repeated cycles (Figure 3a). As the potential is scanned positively (forward scan) and is sufficiently positive to oxidize $[\text{Fe}(\text{CN})_6]^{4-}$, the anodic current is due to electrode processes and the electrode acts as an oxidant and the oxidation current increases to a peak. The concentration of $[\text{Fe}(\text{CN})_6]^{4-}$ at the SWCNT-TPLF film electrode surface decreases and the current then decays. As the scan direction is switched to negative, for the reverse scan the potential is still sufficiently positive to oxidize $[\text{Fe}(\text{CN})_6]^{4-}$, so anodic current continues even though the potential is now scanning in the negative direction. When the electrode becomes a sufficiently strong reductant, $[\text{Fe}(\text{CN})_6]^{3-}$, which has been forming adjacent to the electrode surface, will be reduced by the electrode process.

With increasing scan rates, the anodic peak slightly shifted to the positive potential direction and the cathodic peak moved a little to the negative potential direction

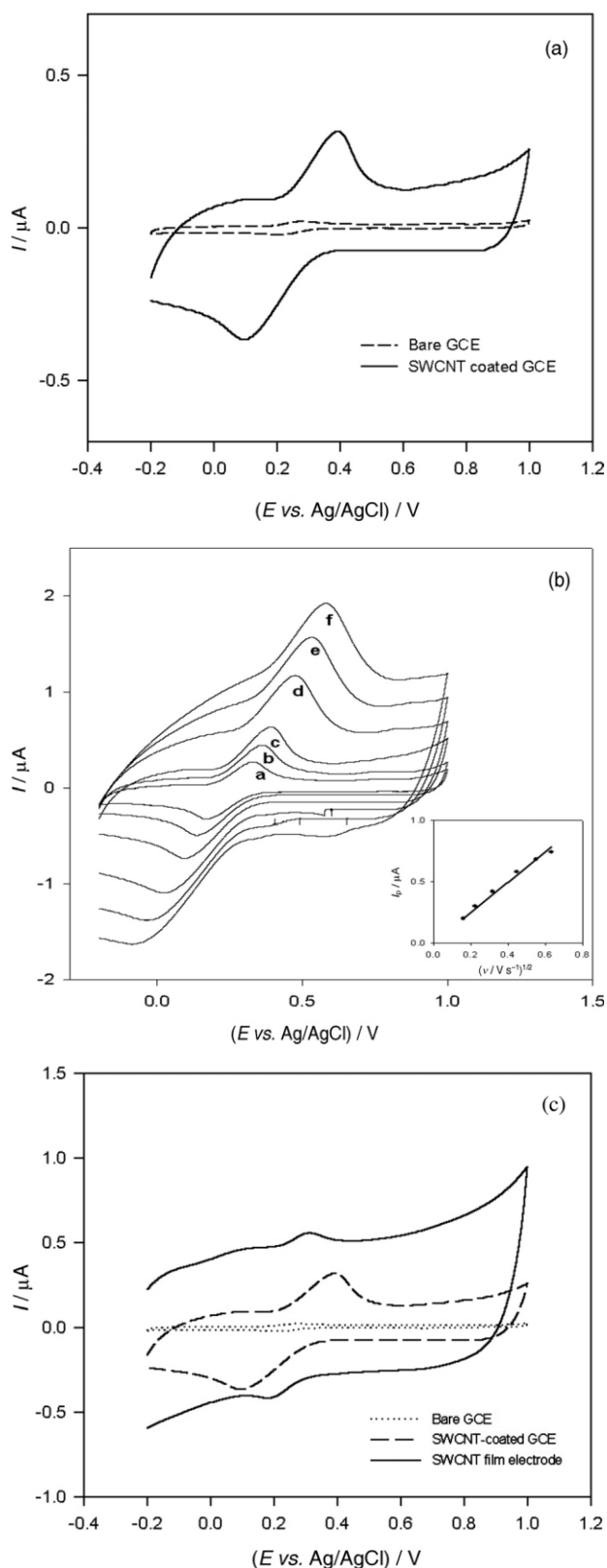


Figure 2. (a) Bare and SWCNT-coated GC electrode at a 0.1 V s^{-1} scan rate for $4 \times 10^{-3} \text{ mol dm}^{-3} \text{ K}_4\text{Fe}(\text{CN})_6$ and $50 \times 10^{-3} \text{ mol dm}^{-3} \text{ KCl}$ electrolyte. (b) SWCNT-coated GCE used as a working electrode at various scan rates (a, 0.025; b, 0.050; c, 0.1; d, 0.2; e, 0.3; f, 0.4 V s^{-1}). Inset figure is drawn for the peak current vs. square root of scan rates. (c) Comparative CV's of the bare, SWCNT-coated GCE and SWCNT-film electrodes.

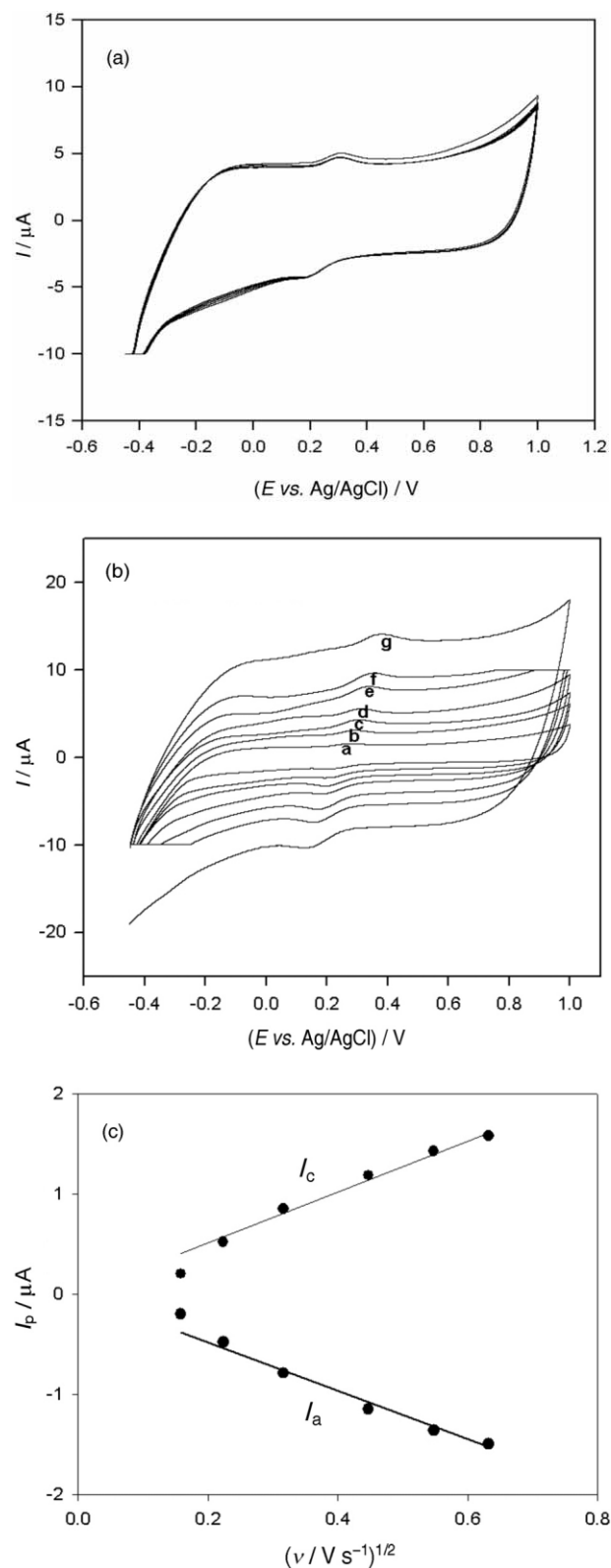


Figure 3. (a) The thin film of SWCNT used as a working electrode (5 cycles) at a 0.1 V s^{-1} scan rate. (Reaction conditions, $4 \times 10^{-3} \text{ mol dm}^{-3} \text{ K}_4\text{Fe}(\text{CN})_6$ and $50 \times 10^{-3} \text{ mol dm}^{-3} \text{ KCl}$ electrolyte). (b) The thin paper like film of SWCNT used as a working electrode at different scan rates (a, 0.025; b, 0.05; c, 0.1; d, 0.2; e, 0.3; f, 4; g, 0.5 V s^{-1}). (c) Plot of peak currents (cathodic, I_c and anodic I_a) vs. the square root of scan rates. The same reaction conditions as in (a).

in Figure 3b. The peak current increased remarkably with increasing scan rates but the ratio of the anodic to cathodic peak currents (I_a / I_c) lies above unity. It indicates that the $\text{Fe}^{\text{II}} = \text{Fe}^{\text{III}}$ oxide transformation process is quasi-reversible. Variations of peak currents with changing scan rates from 0.025 to 0.5 V s^{-1} are shown in Figure 3b. It can be seen that both the anodic and cathodic peak currents (I_a and I_c , respectively) show a linear dependence on the series of square roots of scan rates and pass almost through the origin in Figure 3c. Such behavior of the peak current vs. square root of the scan rates relationship generally appears in a quiescent solution in case of diffusion of an ionic species in the vicinity of the electrode surface, which defines the rate of the reaction. The peak current is increased greatly. The reason for the better performance of the SWCNT-TPLF electrode may be the nanometer dimensions of the CNT, the electronic structure and the topological defects present on the CNT surfaces. Meanwhile, the CNT increases the effective area of the electrode, so the peak current increases significantly.

The cyclic voltammetric experiments of the complex/SWCNT-coated GC electrode at different scan rate showed that the reductive and oxidative peak currents of the complex were both linear with the scan rate v .

The SWCNT-TPLF shows better performance compared to the SWCNT-coated gold and GC electrodes. The SWCNT-TPLF electrode can produce large capacitance; the latter is more suitable for applications in aqueous solutions. For three-dimensional surface areas, the total surface area includes both the surface of SWCNT's interior of the film and that of the outer surface of the film. During SWCNT synthesis, it creates more oxide defects on the sidewalls and makes the SWCNT-TPLF more hydrophilic so that the aqueous solution can better contact the surface. As a result, the electron transfer rate can be improved.

Ajayan and co-workers^{26,27} used the density-functional-theory calculation and molecular dynamics simulations to study the microscopic mechanism of electron transfer on carbon nanotubes. They found that the improved activation behavior of oxygen reduction resulted from the dimensionality presence of topological defects in the lattices, which provided higher local electron density. Concretely, for this experiment, the surfaces of the single wall carbon nanotubes contain numerous defects; the pentagons at the nanotube tips, the pentagon–heptagon defect pairs in the lattice and the curvature contribute to high surface activation, which can benefit the electron transfer between the electrolyte solution and the nanotubes. On the other hand, the special nano-structure of SWCNT maybe acts as a »molecular wire« to lead electrons to the redox centers of the desired complex. Both factors stand a good chance to result in direct electron transfer at the SWCNT surface, not at GC.

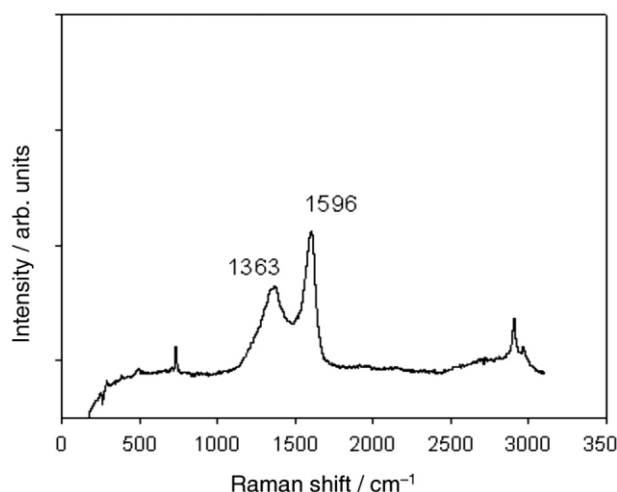


Figure 4. Raman spectrum of purified SWCNT samples (Laser exposure time 30 s).

In summary, we present the electrochemical characterization of three different types of carbon nanotube electrodes: SWCNT-coated Gold, SWCNT-coated Glassy Carbon and SWCNT-TPLF electrodes. The electrochemical results reveal two types of information: the capacitive current and the faradaic current due to the redox reaction of $[\text{Fe}(\text{CN})_6]^{4-} / [\text{Fe}(\text{CN})_6]^{3-}$ pairs present in the solution. Capacitance indicates the change in the total surface area as well as the density of surface oxides. For the three-dimensional structure, the total surface area includes both the surface of the CNT interior of the film and that at the outer surface of the film. The redox reaction of $[\text{Fe}(\text{CN})_6]^{4-} / [\text{Fe}(\text{CN})_6]^{3-}$ is found to occur not only at the outer surface of the SWCNT-TPLF but also in the interior of the film.

The defects are characterized by the D-line in the Raman spectrum in Figure 4. It has been shown the G-line at 1596 cm^{-1} originates from the graphitic sheets, and the peak at 1363 cm^{-1} is related to the defects in SWCNT samples.²⁶

CONCLUSIONS

The electrochemistry of $\text{K}_4[\text{Fe}(\text{CN})_6]$ was studied by cyclic voltammetry at the SWCNT-TPLF, SWCNT-coated Gold and SWCNT-coated GC electrodes. A pair of well-defined redox waves was obtained. The peak currents of cyclic voltammetry increased linearly at different scan rates of $\text{K}_4[\text{Fe}(\text{CN})_6]$ from 0.025 to 0.5 V s^{-1} . The SWCNT-TPLF, SWCNT-coated GC and Gold electrodes exhibited remarkable electrocatalytic effect on the redox reaction of $\text{K}_4\text{Fe}(\text{CN})_6$ and improved the redox peak current. The SWCNT provides many active sites, enhancing the sensitivity of the $\text{K}_4\text{Fe}(\text{CN})_6$ compound. Compared to the bare GC and Gold electrodes, the SWCNT-coated electrodes show high efficacy in detecting $\text{K}_4\text{Fe}(\text{CN})_6$ re-

dox peaks, exhibit excellent stability and reproducibility. We have illustrated that the SWCNT-TPLF electrodes offer a stable and sensitive fixed-potential electrochemical detection of redox couples complexes. Our efforts will be further aimed at a better understanding of the mechanism of redox couples complexes at SWCNT-coated electrodes. Effects of the scan rate and the concentration change of $\text{K}_4\text{Fe}(\text{CN})_6$ on the performance of the SWCNT-TPLF/SWCNT-coated Gold/GC electrode were studied. The analysis of all results indicates that the electrode surface coated with SWCNT or the thin-film one, the presence of holes, defects, charge capacity and their size and the possible interactions between the different species involved are the principal factors that determine the shapes of voltamograms. Additionally, the dependence of the behavior of the couple on the electrode surface composition is of great importance.

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SAŽETAK

Elektrokemijsko ponašanje SWCNT-TPLF elektrode u odnosu na SWCNT-GCE i SWCNT-GE elektrodu

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Proučavana je redoks reakcija $[\text{Fe}(\text{CN})_6]^{3-} / [\text{Fe}(\text{CN})_6]^{4-}$ sa SWCNT-GCE (engl. SWCNT, *Single-Walled Carbon Nanotube*; GCE, *Glassy Carbon Electrode*), SWCNT-GE (GE, *Gold Electrode*) i SWCNT-TPLF (TPLF, *Thin Paper-Like Film*) elektrodom. U usporedbi s nemodificiranom elektrodom, preinačena SWCNT elektroda pokazala je vrlo dobro definirane redoks maksimume. Kako bi se dobili podaci o kapacitetnoj struji i o procesu prijenosa elektrona faradejske reakcije redoks vrsta korištena je ciklička voltametrija u vodenoj otopini KCl ($50,0 \times 10^{-3}$ M) koja je sadržavala $\text{K}_4[\text{Fe}(\text{CN})_6]$. Kapacitet daje uvid u efektivnu veličinu površine (uključujući vanjske i unutarnje površine u sklopu presvučene i TPLF elektrode) kao i pseudokapacitet uslijed faradejskih reakcija površinskih oksida. Između tri tipa elektroda, SWCNT-TPLF elektroda pokazala je najveći specifični kapacitet, što je u skladu s njenom najvećom gustoćom pakiranja nanocjevčica ugljika i najvećom stvarnom površinom. To upućuje na to da se radne elektrode od nanocjevčica ugljika (bilo presvučene ili film elektrode) ponašaju kao trodimenzionalne elektrode. Utvrđeno je da se redoks reakcija $[\text{Fe}(\text{CN})_6]^{3-} / [\text{Fe}(\text{CN})_6]^{4-}$ odvija na vanjskoj površini nanocjevčica ugljika kao i na unutarnjoj površini elektroda s poput papira tankim slojem nanocjevčica.