

Short Communication

A chestnut-like hierarchical architecture of a SWCNT/microsphere composite on an electrode for electroanalysis

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Abstract

A new electrochemical interface of a chestnut-like hierarchical microsphere/SWCNT composite array was constructed. The composite was then characterized by means of scanning electron microscopy and cyclic voltammetry. The voltammetric response of SWCNT/microsphere-array electrodes was demonstrated by applying them to the analytical determination of the three different redox couples of the neutral molecule $\text{Fc}(\text{NH}_2\text{OH})_2$, the multiply charged cation $\text{Ru}(\text{NH}_3)_6^{3+}$, and the multiply charged anion $\text{Fe}(\text{CN})_6^{3-}$. The effects of the CNT loading, the sample concentration, the pH, the sweep rates, and the ionic strength on the electrochemical properties of this new generation of hierarchical structure were studied. The stability of this composite in a solution was also investigated.
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1. Introduction

Carbon nanotubes (CNTs) have been widely investigated in electrochemistry, and a large number of works related to CNTs are published every year. A significant challenge faced in this field involves the construction of new electrochemical interfaces, such as the carbon nanotube forest electrode [1,2]. On the other hand, in material science, multi-walled carbon nanotubes films based on colloidal templates have been successfully synthesized using the well-known layer-by-layer assembly technique [3,4]. Polymeric thin films not only maintain their conductive properties [5,6], they also display considerable adhesion and friction, which indicates a strong interconnectivity and adhesion between CNTs and polymers as well as the resis-

tive role of tangled carbon nanotubes against the tip [5]. However, despite some degree of success in aligning and patterning carbon nanotubes into polymeric sphere structures, assemblies of carbon nanotubes/polymer spheres are usually focused on electrostatic interactions [3–10], and attempts at chemically assembling SWCNT/microsphere composite arrays have been met only with limited success [11]. Moreover, no electrochemical properties have been addressed; only references to electrical properties are readily available [3–11]. Thus, new experimental developments are required in the pursuit of potential applications of CNT polymer composites. In the present study a new hierarchical SWCNT/microsphere composite array is constructed on a 25- μm -diameter Pt electrode surface using a chemical self-assembly technique. This hierarchical structure has a large surface area and allows for the construction of heterostructures; thus, it can be applied in electrochemistry. The electrochemical properties of this new generation of hierarchical structures are shown as a function of the amount of CNT loading, the sample concentration, the pH, and the ionic strength.

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2. Experimental section

2.1. Materials

Hexaamineruthenium(III) chloride, $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ (98%, Aldrich), Potassium ferrocyanide(III), $\text{K}_3\text{Fe}(\text{CN})_6$ (KAN-TO Chemical Co., Inc. Japan), 1,1'-ferrocenedimethanol, $\text{Fc}(\text{NH}_2\text{OH})_2$ (98%, Aldrich), Mercaptoethylamine (95%, Sigma), and potassium chloride, KCl (Junsei Chemical Co., Ltd., Japan) were used as received. Polystyrene spheres (PS) that were 5.0 μm in diameter were purchased from Soken Chemical and Engineering Company (Soken, Chemisnow SX-350H, Japan). *Tris*-(2,2'-bipyridyl) iron(II), $\text{Fe}(\text{bipy})_3^{2+}$, was synthesized according to procedures available in the literature [12]. Double deionized water (DDW) was used in all measurements. The required SWCNTs–COOH/COO[−] acetone suspension was obtained according to a previous report by the authors [2].

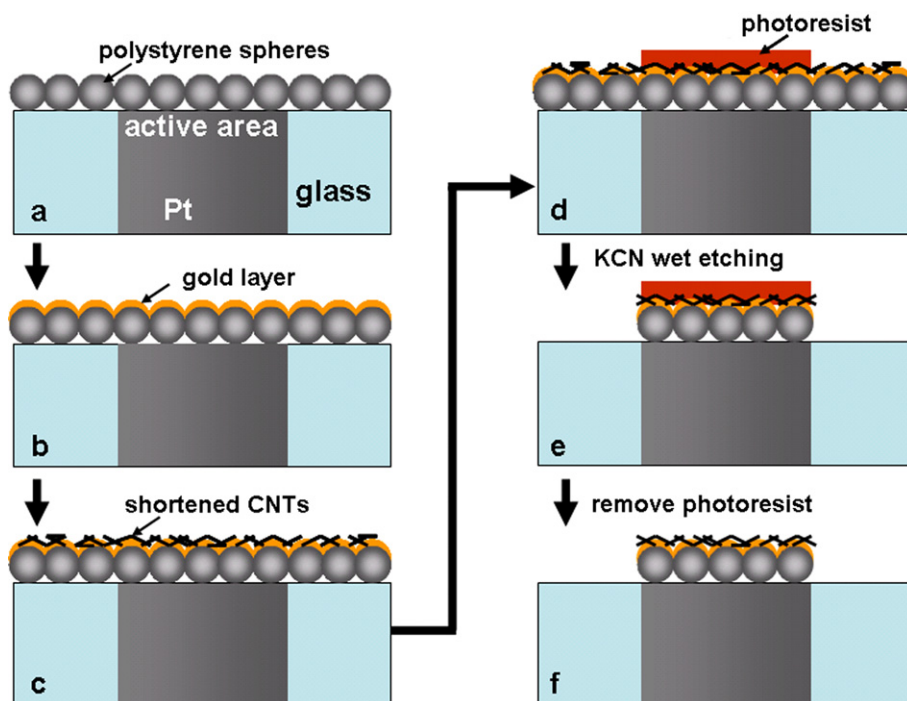
2.2. Chestnut-like hierarchical microsphere/SWCNT composite array

Polystyrene microspheres monolayer films were deposited on Pt microelectrode (25 μm in diameter, CH Instruments Inc., USA) surfaces by placing the electrodes vertically [13,14] in a colloidal solution of spheres in ethanol and evaporating the solution for 2–3 days in a fume hood (Scheme 1a). A gold layer was then coated onto the surface of the colloidal crystal by plasma sputtering deposition (Scheme 1b). This was followed by exhaustive cleaning using a 0.05 M H_2SO_4 solution and DDW. After

introducing an amino group onto the gold surface using a mercaptoethylamine ethanol solution, the SWCNTs–COOH/COO[−] acetone suspension was then dropped onto the surface of the colloidal crystal (Scheme 1c). The SWCNT loading of the final dried film depends on the deposition cycle which is defined as the process performed from the dropping of the first SWCNT solution to the dropping of the second solution. The active region of the microelectrode was protected by an AZ6612KE positive photoresist pattern (Scheme 1d), and the unprotected gold was removed from the substrate by a 100:1 diluted KCN wet etching process (Scheme 1e). The photoresist was then removed using acetone and AZ400T, a photoresist remover, which left the microsphere-array-coated gold layer exposed to the ambient environment (Scheme 1f).

2.3. Characterization and voltammetric measurement

SEM images were obtained with a Philips XL 30 AFEG scanning electron microscope (Eindhoven, The Netherlands). Cyclic voltammetry (CV) measurements were performed on a CHI 600B electrochemical analyzer (CH Instruments Inc., USA). All CV experiments were carried out in a conventional three-electrode cell at room temperature. An Ag/AgCl and a Pt wire were employed as the reference and counter-electrodes (CH Instruments Inc. USA), respectively. Potassium chloride was used as a supporting electrolyte. The pH of the aqueous solutions was adjusted by the addition of acetic acid and sodium hydroxide.



Scheme 1. The construction of a SWCNT/polymer microspheres composite array on a Pt microelectrode.

3. Results and discussion

The SEM images show that microsphere/SWCNT follows the morphology with ordered chestnut-like arrays in microscale after several layer depositions (Fig. 1a and b). A photographic negative image (Fig. 1c) shows that SWCNTs form an interdigitated layer on the microsphere surface. Furthermore, the gaps between the spheres are fully covered, and many shortened carbon nanotubes provide bridge connections between neighboring microspheres (Fig. 1d). The bridge connections lead to the formation of a porous structure with well-defined topography in nanoscale. The diameter of this porous structure ranges from ~ 10 to ~ 100 nm. Clearly, this hierarchical structure differs from the films of a SWCNT deposited on Pt or Au plane electrode surfaces [15,16]. By considering the defect sites on the sidewalls and ends of the shortened tubes, the hierarchical micro/nano structure of the chestnut-like microsphere/SWCNT composite array promises a large amount of active sites when used for electrochemical reaction.

For comparison purposes, the voltammetric responses of bare Pt, PS/Pt and SWCNT/Pt microelectrodes to the redox species were measured. It was observed that the behavior of the bare Pt microelectrode displays the sigmoidal

shape characteristic of near-steady-state radial diffusion of the redox species to a microelectrode [17], a $\sim 56\%$ reduction in the current was observed after PS assembly (Fig. 2a). Following deposition of the SWCNT film, similar sigmoidally shaped voltammetric responses were obtained, but with an increase in the reduction current for each deposition. The increased current is due to: (i) the shortened tubes with more defects on the sidewalls or ends that provide more active sites that are involved in the electrochemical reaction [2], and (ii) geometrical effects, i.e., three-dimensional interdigitated porous structures that formed on the sphere and sphere joints allowing the redox molecules to come into contact fully with the active sites. However, as the SWCNT film thickness increases, the current increases slowly. This case can be explained by considering the relationship between the molecular flux and the thickness of the SWCNT film. Although additional tubes provide additional active sites, they also affect the flux of redox molecules and mass transport. Besides, as shown in Fig. 2a, the electrochemical current of SWCNT/PS/Pt electrode is about twice larger than that of bare Pt electrode. This case is likely due to that the diffusion layer of SWCNT/PS/Pt electrode is wider than that of Pt electrode; the mass transport is therefore hindered. On the other hand, the results in Fig. 2a show that the electrochemical

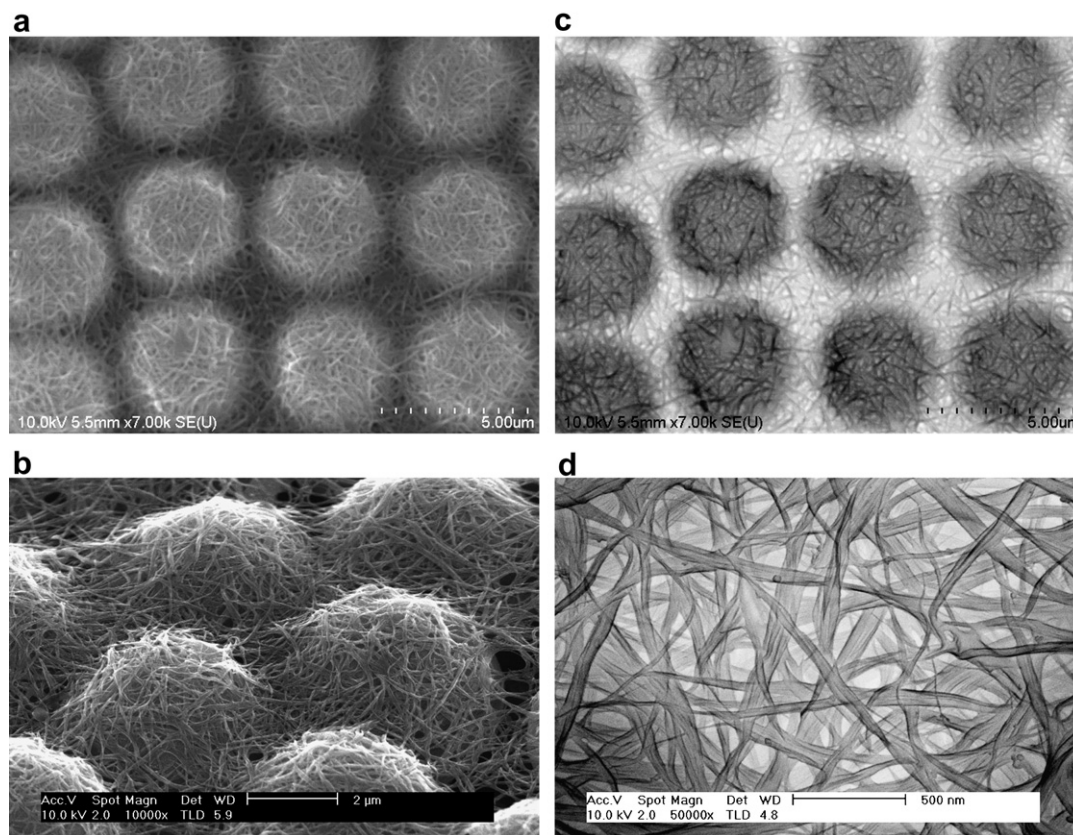


Fig. 1. Topography SEM images of the SWCNT/polymer microspheres array electrode. Image (a) shows a SWCNT multilayer on a PS array corresponding to 20 cycles at the given concentration of 0.2 mg l^{-1} . Image (b) was obtained with a tilting angle of 40° . Image (c) shows a photographic negative picture that corresponds to panel a; image (d) shows a photographic negative picture of the netlike structure on a sphere and sphere joints from the top view.

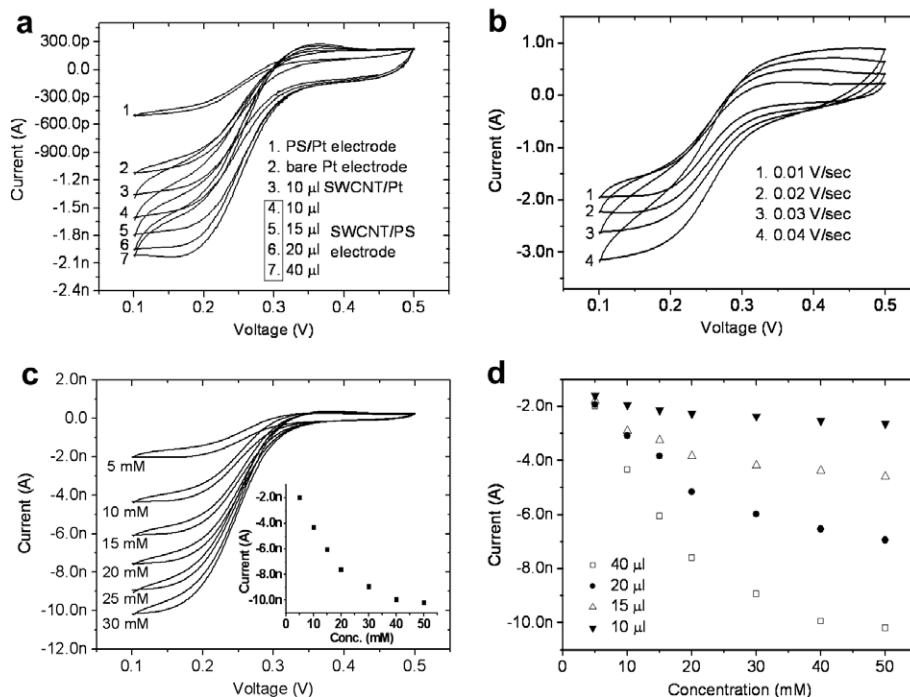


Fig. 2. Voltammetric responses of a chestnut-like hierarchical microsphere/SWCNT composite array electrode in a $\text{Fe}(\text{CN})_6^{3-}/0.1 \text{ M KCl}$ solution at a neutral pH. (a), (b) and (c) show the effect of the SWCNT loading, the sweep rates, and $\text{Fe}(\text{CN})_6^{3-}$ concentration on the electrochemical behavior, respectively. The inset in (c) shows the calibration curve corresponding to the amperometric responses of the microsphere/SWCNT ($40 \mu\text{l}$) electrode (at $E = 0.1 \text{ V}$) in the presence of different concentrations of $\text{Fe}(\text{CN})_6^{3-}$. (d) Calibration curves corresponding to the amperometric responses (at $E = 0.1 \text{ V}$) of microsphere/SWCNT electrodes in the presence of variable concentrations of $\text{Fe}(\text{CN})_6^{3-}$ and different CNT loadings.

capacitance of the chestnut-like hierarchical microsphere/SWCNT composite array electrodes has increased substantially due to the addition of the SWCNT layer. The capacitance is calculated from the CV curves, with $C = i/v$, where i is the current and v is the sweep rates (V/s). At a potential of 0.15 V , for example, the effective capacitance of the chestnut-like hierarchical structure electrode is nearly eight times higher than that of conventional Pt microelectrodes. This high capacitance is consistent with the large surface area of the shortened carbon nanotubes [16]. Moreover, electrolytes can penetrate through the film of the tubes and gain access to the interior surface due to the fact that SWCNTs form not only an interdigitated multilayer on the microsphere surface in microscale but also a three-dimensional interdigitated porous structure in nanoscale on the sphere and sphere joints. The effect of the sweep rate on the electrochemical reaction was also studied in a $\text{Fe}(\text{CN})_6^{3-}/0.1 \text{ M KCl}$ solution over the range of $0.01\text{--}0.04 \text{ V/s}$. Results show that an increase in the capacitance is produced by increasing the sweep rates (Fig. 2b). Fig. 2c shows the voltammetric responses corresponding to the chestnut-like hierarchical microsphere/SWCNT composite array electrode in the presence of different concentrations of $\text{Fe}(\text{CN})_6^{3-}$. The reduction current becomes higher as the concentration of $\text{Fe}(\text{CN})_6^{3-}$ increases. The calibration curve, depicted in the inset in Fig. 2c, shows a well-defined trend and saturation current that corresponds to $\sim 10 \text{ nA}$. Fig. 2d shows the respective calibration curves

corresponding to the reduction currents generated by chestnut-like hierarchical microsphere/SWCNT composite array electrodes that differ in terms of their SWCNT coverage in the presence of variable $\text{Fe}(\text{CN})_6^{3-}$ concentrations. A clear dependence on the coverage of the shortened tubes is observed. Therefore, these results suggest that additional defect sites on the tubes and the hierarchical micro/nano structure promise much better electrochemical behavior.

An investigation of the effect of pH on the electrochemical behavior was conducted by choosing three different redox couples: the neutral molecule $\text{Fc}(\text{NH}_2\text{OH})_2$, the multiply charged cation $\text{Ru}(\text{NH}_3)_6^{3+}$, and the multiply charged anion $\text{Fe}(\text{CN})_6^{3-}$. It was observed that the electrochemical reactions for three different types' molecules occur at pH 3 and with neutral solutions (Fig. 3). In addition, the investigated electrode has responses on $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fc}(\text{NH}_2\text{OH})_2$ for a wide range of pH values (Fig. 3b and c). This demonstrated that neutral, positively, and negatively charged species freely enter the SWCNT porous film under these conditions. However, the voltammetric response on the positively charged species $\text{Ru}(\text{NH}_3)_6^{3+}$ is nearly reduced to a background level at $\text{pH} \sim 9$ (Fig. 3a). It appears that the flux of $\text{Ru}(\text{NH}_3)_6^{3+}$ through SWCNT porous 3D structure film is hindered. For a more thorough understanding of this phenomenon, the experiments were performed again using $\text{Fe}(\text{bipy})_3^{2+}$ under the same conditions, and similar results ensued. This was odd: for amine-modified opal films, the permselectivity is ascribed

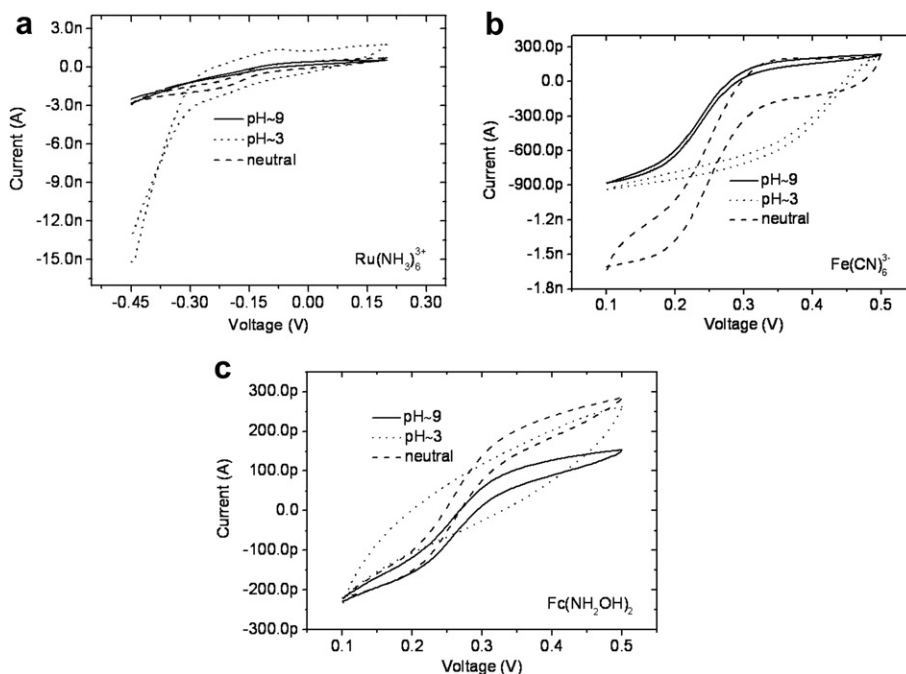


Fig. 3. Voltammetric responses of $\text{Ru}(\text{NH}_3)_6^{3+}$ (a), $\text{Fe}(\text{CN})_6^{3-}$ (b), $\text{Fc}(\text{NH}_2\text{OH})_2$ (c) with a chestnut-like hierarchical microsphere/SWCNT composite array electrode at pH 3 (dot line), pH 9 (solid line) and neutral (dash line) in a 0.1 M KCl solution.

as electrostatic in nature, and no permselective behavior is shown for a chemically treated bare Pt electrode [13]. The electrostatic effect should not be a repulsive force. As the $-\text{COOH}$ group changes to a $-\text{COO}^-$ group in an alkali solution, positively charged molecules can be attracted to the electrode surface. However, the chemical and electrochemical properties of the SWCNT are strongly dependent on the postgrowth processing procedures and on acid treatment procedures [18]. Moreover, the hierarchical micro-

nano structure has an effect on the flux of the redox species. It is therefore, believed that the permselectivity at high pH values as shown here results from the shortened tubes and from the chestnut-like hierarchical structure, although the mechanism is, at present, not fully understood.

Measurements were also made as a function of the solution ionic strength in the $\text{Fc}(\text{NH}_2\text{OH})_2$ and $\text{Fe}(\text{CN})_6^{3-}$ neutral solution. The resulting data are shown in Fig. 4. By increasing the KCl concentration, the current increases

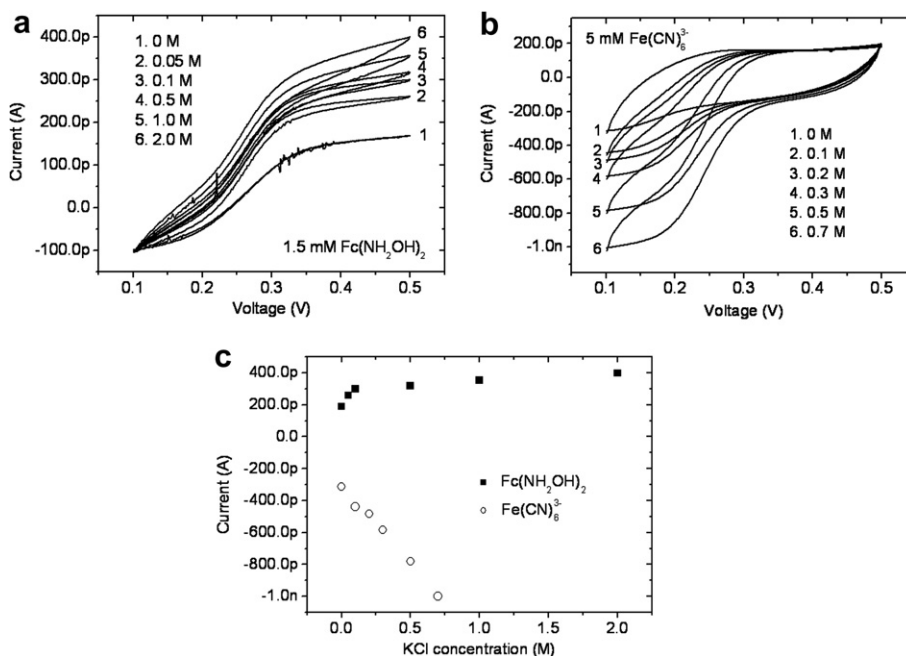


Fig. 4. Voltammetric responses of the chestnut-like hierarchical microsphere/SWCNT composite array electrode for $\text{Fc}(\text{NH}_2\text{OH})_2$ oxidation (a) and $\text{Fe}(\text{CN})_6^{3-}$ reduction (b) in water as a function of the KCl concentration and (c) shows the effect of the KCl concentration on the electrochemical current.

for both species (Fig. 4a and b). The current change in the $\text{Fe}(\text{CN})_6^{3-}$ solution is, however, more apparent compared to that in the $\text{Fc}(\text{NH}_2\text{OH})_2$ solution (Fig. 4c). Moreover, the differences in the ΔE_p values between the peak potential of the anodic and cathodic peaks that increase for $\text{Fc}(\text{NH}_2\text{OH})_2$ and decrease for $\text{Fe}(\text{CN})_6^{3-}$ were observed as the ionic strength increased. The following equation was used to describe the effect of the ionic strength [19]:

$$E = \sum_i V_{i \neq d} + \Delta\phi_d$$

Here, $\Delta\phi_d$ is the potential drop of the diffusing layer, and $\sum_i V_{i \neq d}$ is the potential drop related to the monolayer. If the electrolyte solution is highly diluted, $\Delta\phi_d \gg \sum_i V_{i \neq d}$ and the change of potential of potential drop E , with electrolyte solution c is then given by $\partial E/\partial c = \partial\Delta\phi_d/\partial c$. Clearly, a change in the ionic strength will affect the kinetics of the electrode process. When the solution is highly concentrated, $\sum_i V_{i \neq d} \gg \Delta\phi_d$ and $\partial E/\partial c \approx 0$. No effect of the ionic strength on the kinetics should then be observed. Extracting the current (Fig. 4c), a moderate oxidation current and a sharp reduction current increasing are observed for $\text{Fc}(\text{NH}_2\text{OH})_2$ and $\text{Fe}(\text{CN})_6^{3-}$, respectively, indicating that the ionic strength has no obvious effect on the kinetics of the electrode process for the neutral molecules in this study.

For this chestnut-like hierarchical microsphere/SWCNT composite array electrode, an important parameter is stability. The voltammetric responses of the studied electrode were investigated after 1000 cycles, and no significant difference was observed (Fig. 5). At approximately 330 mV, for example, the current change is less than 22.7% (marked by an arrow) 1000 cycles later, demonstrating that the microsphere/SWCNT film could not peel off from the substrate in an aqueous solution, or that the SWCNT could not dissociate from the microsphere surface.

4. Conclusions

A chestnut-like hierarchical microsphere/SWCNT composite array was constructed by using a chemical assembly technique. The electrochemical behavior demonstrated that

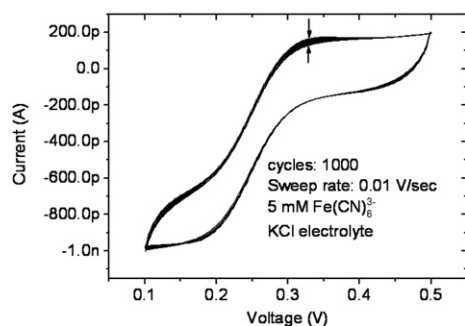


Fig. 5. The stability of the chestnut-like hierarchical microsphere/SWCNT composite array electrode in a $\text{Fe}(\text{CN})_6^{3-}/\text{KCl}$ solution at a neutral pH.

it can be used as a new electrochemical interface. The composite exhibits improved electrochemical sensitivity and a greater electrochemical capacitance due to the unique hierarchical surface. At a high pH, the new composite film has permselectivity to positively charged redox species. The ionic strength has no obvious effect on the kinetics of the electrode process in a neutral molecule solution. These results show that chestnut-like systems of SWCNTs with a microspherical array have several interesting new electrochemical properties. Research regarding the pH-dependent permselectivity of the hierarchical structure is currently underway.

Acknowledgements

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