Chinese Chemical Letters Vol. 13, No. 1, pp 79 – 82, 2002
http://www.imm.ac.cn/journal/ccl.html

Modification of Carbon Nanotube Powder Microelectrode and Nitrite Reduction

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Abstract: The properties of the carbon nanotube powder microelectrodes (denoted CNTPME) are remarkably altered by anodic pretreatment and preadsorption of mediators. It seems that anodic pretreatment leads the long and tangled carbon nanotubes to be partially cut shorter, resulting in more openings as shown by TEM. Besides, the anodic pretreatment may adjust the hydrophobicity of nanotubes to match with that of $Os(bpy)_3^{2+}$. As a result, the real surface area and the ability of adsorbing mediator $Os(bpy)_3^{2+}$ of the nanotubes are markedly increased so as to effectively catalyze NO_2^- reduction in acidic solution.

Keyords: Carbon nanotube, powder microelectrode, nitrite reduction, modified electrode.

Introduction

Nitrite is an important species for environment protection and live processes. To develop high quality of nitrite sensors has been paid much attention. It was found in our previous study that nitrite reduction in acidic solution on glassy carbon and Au electrodes is controlled by a preceding chemical process with very thin reaction zone with a thickness close to the double layer. It was further shown that this kind of homogeneous preceding reaction can be speeded up by the method used in heterogeneous reactions, *i.e*. increasing surface area of electrodes. Powder microelectrodes have been proved a very useful technology for this purpose[1]. The powder microelectrode, originated in our laboratory, is a convenient technique for both characterization of powder materials and electroanalytical applications[2]. In fact, the so-called powder microelectrode is a combination of porous electrode and microelectrode. The carbon nanotube powder microelectrode (CNTPME) was formed by filling the cavity at the tip of a microelectrode with carbon nanotubes. Beside the general features of powder microelectrodes, CNTPME is expected to show some peculiar properties associated with the carbon nanotubes. This paper reports the properties of CNTPME without and with modifications (anodic pretreatment, $Os(bpy)_3^{2+}$ preadsorption) and its application to electrochemical reduction and detection of nitrite.

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Experimental

The main experimental methods used in this work were the powder microelectrode and steady state polarization. TEM (Nicong, Japan) was used to observe the morphologic changes of nanotubes brought about by anodic pretreatment.

For preparation of the CNTPME, a Pt micro disk electrode of 100 μm in diameter was chemically etched in aqua regia to form a cavity of hundreds of micrometers deep. Then the cavity was filled with the powder of carbon nanotubes without any binders.

The CNTPME was anodically polarized in 0.05 mol/L H_2SO_4 at 1.1 v (*vs*. SCE) for 80 min and then socked in $Os(bpy)_3^{2+}$ solution for 1 hr for pre-adsorbing $Os(bpy)_3^{2+}$. The CNTPME-$Os(bpy)_3^{2+}$ was rinsed with doubly distilled water and dried in air.

Results and Discussion

Electrochemical Properties of the CNTPMEs without and with modification

Whether the electrode had undergone pretreatment or not, the cyclic voltamogram (CV) of the CNTPME always showed a paired current peaks near 0.35 V *versus* SCE, attributable to surface quinone groups (**Figure 1**). After anodic pretreatment, the double layer current of the CNTPME was about doubled (**Figure 1b**). A pair of stable current peaks for $Os(bpy)_3^{2+/3+}$ redox couple at about 0.6 V appeared and did not appreciably decrease overnight (**Figure 1c**). It indicates that the preadsorbed mediators $Os(bpy)_3^{2+}$ were firmly attached on the anodically treated CNTPME. Without anodic treatment, however, the preadsorbed $Os(bpy)_3^{2+}$ leached out completely in less then one hour in the background solution.

Figure 1 Cyclic voltamograms of the CNTPMEs in 0.05 mol/L H_2SO_4 (a, untreated; b, anodically treated; c, $Os(bpy)_3^{2+}$ preadsorbed after anodic treatment).

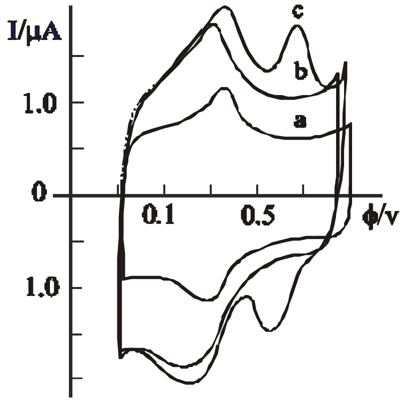
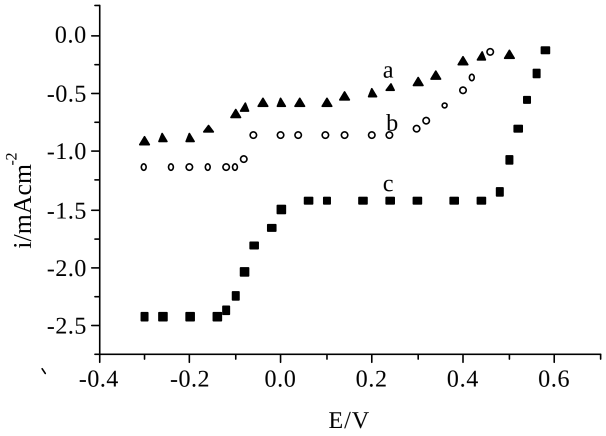
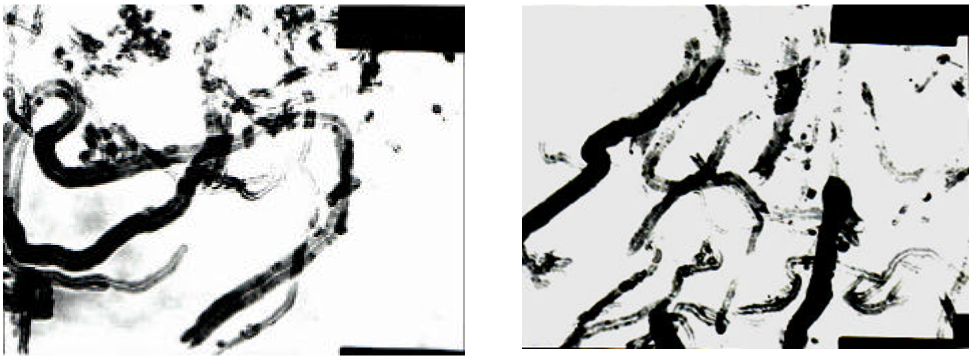


Figure 2 Steady state polarization curves for NO_2^- reduction in 0.05 M H_2SO_4 + 5 mM $NaNO_2$ at CNTPMEs (a, without pretreatment; b, after anodic treatment; c, after anodic treatment and $Os(bpy)_3^{2+}$ preadsorption).



Both the current plateaus of steps 1 and 2 of nitrite reduction can be recognized in the potential region studied on the steady state polarization curve regardless of whether the CNTPMEs were pretreated or not (**Figure 2**). Their plateau current densities (i_{L1}, i_{L2}) increase prominently with pretreatment and $Os(bpy)_3^{2+}$ adsorption. i_{L1} and i_{L2} reached 1.41 and 2.41 mAcm^{-2} on pretreated CNTPME with $Os(bpy)_3^{2+}$(denoted CNTPME-$Os(bpy)_3^{2+}$), respectively (**Figure 2c**). Tafel slopes decreased remarkably with pretreatment and $Os(bpy)_3^{2+}$ adsorption. The Tafel slopes for the step 1 and 2 of nitrite reduction on CNTPME-$Os(bpy)_3^{2+}$ were 59 and 73 mV/decade, respectively, indicating the step 1 being apparently reversible. The half wave potentials for the step 1 and step 2 shifted progressively to positive with anodic treatment and $Os(bpy)_3^{2+}$ preadsorption. Compared with glassy carbon electrode, the half wave potentials for two steps shifted positively about 300 and 430 mV on CNTPME-$Os(bpy)_3^{2}$. Step 2 did not appear on glassy carbon electrode in the potential region studied and the i_{L1} was 10^2 times smaller than that on CNTPME-$Os(bpy)_3^{2}$. The half wave potential for step 1 is close to the CV peak potential of $Os(bpy)_3^{2+/3+}$ redox couple, implying a mediating mechanism of $Os(bpy)_3^{2+}$ for nitrite reduction. In the order of magnitude, there are about 10^{11} pieces of nanotubes in the powder microelectrode as estimated from the charging current of the double layer on cyclic voltammety (**Figure 2c**) and dimensions of the nanotubes (on the average, 20 nm in diameter and 400 nm long) shown in **Figure 3b**. According to the redox charge of $Os(bpy)_3^{2+}$ on CV, the number of the adsorbed $Os(bpy)_3^{2+}$ was found close in the order of magnitude to the number of carbon nanotubes. The result may imply that the $Os(bpy)_3^{2+}$ centers were adsorbed on the openings at the ends of the nanotubes or evenly distributed in every nanotube. Although the causes of the above results remain to be studied further, an apparent reason, as shown in **Figure 3** of TEM, may be the fact that anodic treatment cut carbon nanotubes into shorter pieces and create more openings. Besides, pretreatment may adjust the hydrophobicity of nanotubes to match that of $Os(bpy)_3^{2+}$. Common carbon powders such as activated carbons and acetylene blacks were not affected by anodical treatment and their ability of adsorbing Os(bpy)$_3^{2+}$ and the catalytic activity for nitrite reduction in acidic solution was poorer than that of the CNPMEs.

Figure 3 TEM of nanotubes (a, untreated; b, anodically pretreated. Magnification 72000 (1 mm = 13.9 nm)).


a b

Application of the CNTPME-Os(bpy)$_3^{2+}$ to detection of nitrite in acidic solution

The sensitivity and temperature coefficients for nitrite detection in 0.05 mol/L H_2SO_4 reached 5.7 and 6.8 A cm^{-2}M^{-1} and 0.14 and 0.16%/°C for the two plateau currents, respectively. The lower detection limit was estimated to be 10^{-7} mole/L for the ratio of signal to noise S/N = 4. The evaluated activation energies for the first and second steps are 2.3 and 2.7 kJ mol^{-1} respectively. No interference of Fe^{2+}, Fe^{3+}, Mg^{2+}, Cl^-, NO_3^- and PO_4^{3-} was found except ascorbic acid at the plateau of step 2. Above results and high performance have not been reported in the literature and make the CNPME-Os(bpy)$_3^{2+}$ a promising candidate for high quality of nitrite sensor.

Acknowledgments

The authors are grateful to the National Natural Science Foundation of China for financial support for this work.

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Received 14 May, 2001