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Chemical attachment of functionalized multiwalled carbon nanotubes on glassy carbon electrode for electrocatalytic application

K. Rajalakshmi, S. Abraham John *

Centre for Nanoscience and Nanotechnology, Department of Chemistry, Gandhigram Rural Institute, Gandhigram, 624302 Dindigul, India

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ABSTRACT

The covalent attachment of acid functionalized multiwalled carbon nanotubes (FMWCNTs) on glassy carbon (GC) electrode using 1,8-octanediamine (OD) as a linker via carbodiimide chemistry was described. The attachment of FMWCNTs on GC electrode were confirmed by attenuated total reflectance Fourier transform infra-red (ATR-FT-IR) spectroscopy, Raman, scanning electron microscopy (SEM) and electrochemical impedance studies. Raman spectrum of FMWCNTs modified surface shows the characteristic G and D bands at 1563 cm^{-1} and 1340 cm^{-1}, respectively. This confirmed the successful attachment of FMWCNTs on the OD modified GC surface. Further, the attachment of FMWCNTs on OD modified surface via amide linkage was confirmed from the observed characteristic peak at 1681 cm^{-1} in the ATR-FT-IR spectrum. The SEM images showed that the covalently attached FMWCNTs retained their morphology similar to powder and the average diameter of them was found to be 58 nm. Unlike modification of FMWCNTs on gold substrates with the aid of conventional thiol linkers (Au—S bond), modification of them by the present method was stable for a wide positive potential window due to the robust C—N bond. To demonstrate the electrochemical stability of the MWCNTs modified electrode at more positive potential, guanosine 5′-monophosphate (GMP) was selected as a representative probe because its oxidation occurs at more than 1 V. It was found that the FMWCNTs modified electrode not only showed a stable signal for GMP but also enhanced its oxidation current when compared to bare GC electrode. Further, the present strategy of modifying FMWCNTs was extended to prepare a composite electrode by electrochemically depositing 5-amino-2-mercapto-1,3,4-thiadiazole (AMT) film. The FMWCNTs-polymer composite electrode dramatically enhanced the GMP oxidation current when compared to polymerization of AMT (p-AMT) and FMWCNTs alone. The polymer composite electrode was successfully employed for the sensitive determination of GMP. Using amperometry, a limit of detection of 0.27 μM (S/N = 3) was achieved for GMP at a composite modified electrode.

1. Introduction

Owing to their favourable electronic, electrochemical and mechanical properties research on carbon nanotubes (CNTs) has received much attention in recent years [1]. They found wide range of applications in the fields of supercapacitors [2], biosensors [3], photoelectric conversion [4], optical [5] and electrochemical sensors [6] and coaxial cables instead of copper [7]. Their ends and sidewall defect sites are acting like a pyrolytic graphite edge planes and have a great electrochemical activity similar to that of graphite powder [8]. Besides, the CNTs are highly stable for a wide potential window [9]. Hence, they are well suited for the fabrication of electrochemical sensors. Generally, CNTs modified electrodes were prepared by drop casting a known quantity of CNTs dispersed in mineral oil [10,11], Teflon [12], Nafion [13] and polymer matrixes [14,15]. However, uniform coverage and reproducible films cannot be achieved by this method.

Few reports are available in the literature for the attachment of CNTs using carbodiimide chemistry [16–18]. For example, the acid functionalized single walled carbon nanotubes (SWCNTs) were covalently attached on alkanethiol self-assembled monolayer (SAM) modified Au surface [16,17]. Oyama and his co-workers studied the self-assembly of acid functionalized SWCNTs and ferrocene mono and dicarboxylic acid derivatives on amine terminated SAMs modified on Au surfaces [18]. Further, the CNTs were also attached via Au—S bond formation using thiol functionalized SWCNTs on Au surface [19–21]. Although CNTs were successfully attached on Au electrode surface in the reported papers, they cannot be stable for wide potential window. This is mainly due to the cleavage of Au—S bond both at more positive and

* Corresponding author. Tel.: +91 451 245 2371; fax: + 91 451 245 3031.
E-mail address: abrajohn@yahoo.co.in (S. Abraham John).

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negative potentials. Hence, an alternative method must be developed to prepare the CNTs modified electrode, which would be stable for a wide potential window. Keeping this objective in mind, the present study aims to attach FMWCNTs on the SAM of octanediamine (OD) modified GC electrode via carbodiimide chemistry. The GC was initially attached with OD and subsequently FMWCNTs are attached through amide bond using dicyclohexylcarbodiimide (DCC) as a coupling agent. The attached FMWCNTs were confirmed by ATR-FT-IR, Raman, SEM and electrochemical impedance studies. The SEM studies show that the FMWCNTs retain their morphology after attached with OD. Further, the present strategy of modification was extended to prepare a polymer composite electrode by electropolymerizing 5-amino-2-mercapto-1,3,4-thiadiazole (AMT) on FMWCNTs.

The main intention of the present work is to demonstrate the application of FMWCNTs modified by the present strategy for the determination of analytes whose oxidation occurs at more positive potential. For this purpose, the electrochemical oxidation of guanosine 5′-monophosphate (GMP) is selected because its oxidation at bare GC electrode occurs at more than 1 V. The GMP has several biological impacts. The concentration level of GMP is associated with the action of estrogens on the rat uterus [22], human platelet aggregation [23], biological activity of cis-platin [24], hydrolysis of adenosine monophosphate [25] and vascular smooth muscle relaxation induced by nitrates, nitrites and nitroso compounds [26]. Therefore, the sensitive determination of GMP is essential in the clinical point of view. GMP is an electrochemically active molecule and therefore its electrochemical determination is possible [27]. In the present study, we have successfully used the FMWCNTs/p-AMT modified electrode for the determination of GMP with a limit of detection of 0.27 μM (S/N = 3).

2. Experimental section

2.1. Chemicals

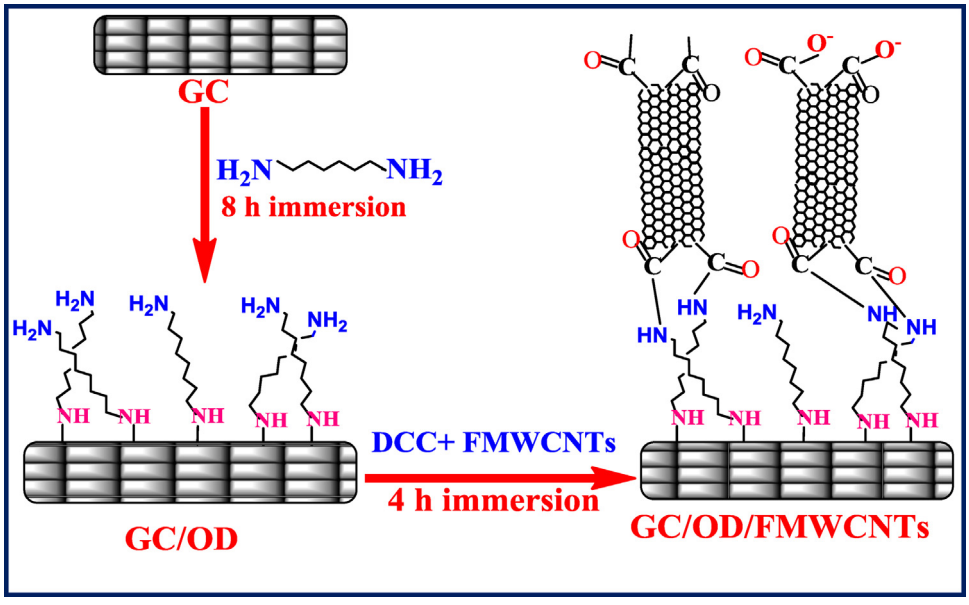
Acid functionalized multiwalled carbon nanotubes (FMWCNTs), dicyclohexylcarbodiimide (DCC), 1,8-octanediamine (OD), guanosine 5′-monophosphate (GMP) and 5-amino-2-mercapto-1,3,4-thiadiazole (AMT) were purchased from Aldrich and were used as received. All other chemicals used in this investigation were of analytical grade. 0.2 M phosphate buffer solution (PBS, pH 7.2) was prepared using Na_2HPO_4 and NaH_2PO_4 and pH 3 PBS solution was prepared by adjusting with orthophosphoric acid. Double distilled water was used to prepare the solutions used in this investigation. GC plates were purchased from Alfa Aesar.

2.2. Instrumentation

FT-IR measurements were taken using a JASCO 460 plus FT-IR spectrophotometer. ATR measurements were carried out on JASCO FT-IR 460 plus model equipped with an ATR attachment with a horizontal ZnSe crystal (Pike Technologies). The resolution of the spectra was 4 cm^{-1} and the scans were repeated 50 times. Raman spectrum was recorded using Lab Ram HR instrument (Ar-ion laser 514 nm, Jobin–Yvon). SEM measurements were carried out by using VEGA3 TESCAN. Electrochemical measurements were performed in a conventional two-compartment three electrode cell with a mirror polished 3 mm GC electrode as a working electrode, Pt wire as a counter electrode and NaCl saturated Ag/AgCl as a reference electrode. All the electrochemical measurements were carried out with a CHI model 634B electrochemical workstation (CH Instruments, Austin, TX, USA). Impedance datas were fitted using ZView software. For differential pulse voltammetry (DPV) measurements, a pulse width of 0.06 s, amplitude of 0.05 V, a sample period of 0.02 s and a pulse period of 0.20 s were used. All the electrochemical measurements were carried out under a nitrogen atmosphere at room temperature. For Raman, SEM and ATR-FT-IR measurements, GC plates were used as a substrate.

2.3. Fabrication of FMWCNTs modified GC electrode

GC electrode was polished with 0.05 μm alumina slurry and rinsed thoroughly with water. Then, the electrode was sonicated in water for 5 min to remove the adsorbed alumina particles. The cleaned GC electrode was immersed in 1 mM OD dissolved in ethanol for 8 h. The electrode was then washed with ethanol and subsequently with water to remove the loosely bound OD molecules from the electrode surface. By this procedure, distal end of the amine SAM was obtained. It has been already



Scheme 1. Schematic representation of the preparation of FMWCNTs modified electrode (not up to the scale).