Colloids and Surfaces A: Physicochem. Eng. Aspects 504 (2016) 53–61

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

A hydrophobic coenzyme Q10 stabilized functionalized-MWCNT modified electrode as an efficient functional biomimetic system for the electron-transfer study

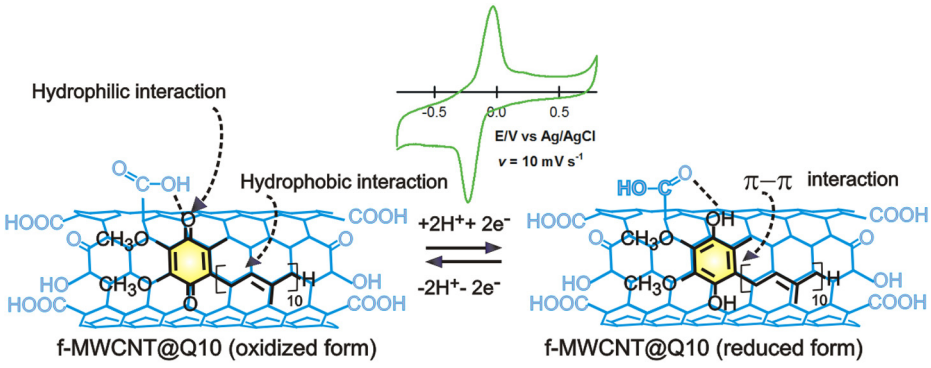
D. Arthisree[a], K.S. Shalini Devi[c], S. Lakshmi Devi[a], K. Meera[a], Girish M. Joshi[b], Annamalai Senthil Kumar[c,*]

[a] Department of Physics, Women's Christian College, College Road, Chennai 600 006, India
[b] Materials Physics Division, School of Advanced Sciences, Vellore Institute of Technology University, Vellore 632 014, India
[c] Nano and Bioelectrochemistry Research Laboratory, Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology University, Vellore 632 014, India

HIGHLIGHTS

- Coenzyme Q10 stabilized functionalized-MWCNT modified electrode was developed.
- A well-defined redox peak with improved electron-transfer activity of Q10 was noticed.
- Redox functional activity of the hybrid system resembles with a cellular Q10 function.
- Obeys Nernstian type potential-pH relation with excellent pH sensing behavior.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 December 2015
Received in revised form 10 May 2016
Accepted 18 May 2016
Available online 19 May 2016

Keywords:
Coenzyme Q10
Functionalized-MWCNT
Functional biomimics
Electron-transfer reaction
pH sensor

ABSTRACT

Coenzyme Q10 (2,3-dimethoxy-5-methyl-6-decaprenyl-1,4-benzoquinone, Q10) is a fat soluble, hydrophobic, vitamin-like quinone present in the cell membranes, regulates metabolic pathways via redox signalling. There have been considerable reports relating to the structural bio-mimics of Q10, wherein, lipid type molecular matrix stabilized Q10 modified micro-porous electrode systems have been used. Most of the reported procedures showed either nil or very poor redox functional activity of the Q10 in cyclic voltammetry (CV) analysis. Here in, we report, a Q10 stabilized functionalized-multiwalled carbon nanotube modified glassy carbon electrode (GCE/f-MWCNT@Q10) as a functional biomimetic system for Q10. CV response of the GCE/f-MWCNT@Q10 showed a well-defined redox active at $E_{1/2} = -138$ mV vs Ag/AgCl with peak-to-peak separation (ΔE_p) and surface excess (Γ_{Q10}) values of 275 mV (at $v = 10$ mV s^{-1}) and 12.57 n mol cm^{-2} respectively. Amongst various carbon nanomaterials investigated, f-MWCNT was found to be the best for the Q10 functional activity. From the physicochemical characterizations it was identified that interactions such as pi-pi, hydrogen-bonding and iron metal impurity-oxygen existing in f-MWCNT@Q10 aided to stabilize molecular structure of the Q10 on f-MWCNT surface. Using CV technique, pro-oxidant activity of Q10 with NADH, ascorbic acid, cysteine, glucose and hydrazine were tested and found that observed interactions were similar to one existing with the real biological system.

* Corresponding author.
E-mail address: askumarchem@yahoo.com (A. Senthil Kumar).

http://dx.doi.org/10.1016/j.colsurfa.2016.05.048

The f-MWCNT@Q10 system showed efficient pH sensing ability with Nernstian type proton-electron transfer mechanism.

1. Introduction

Development of new biochemical composite material that can show biomimetic structure and functional characteristics like natural system is a challenging and rewarding concept in the multidisciplinary areas of material science. Coenzyme Q10 (2,3-dimethoxy-5-methyl-6-decaprenyl-1,4-benzoquinone, Q10; Scheme 1A) is a fat soluble, hydrophobic, vitamin-like quinone present in the cell membranes and is carried in the blood by low density lipoprotein (LDL) [1]. It acts as a pro-oxidant to scavenge certain biochemicals like reduced form of nicotinamide adenine dinucleotide (NADH), H_2O_2, ascorbic acid (AA), cysteine (CySH) in cellular system under controlled redox signalling condition [2,3]. Normal level of Q10 in the blood is $1 \pm 0.2\,\mu g\,mL^{-1}$ with a deficient level in the range of $0.6 \pm 0.2\,\mu g\,mL^{-1}$ [4]. The deficiency is associated with impairment of myocardial function including congestive heart failure (CHF) [5]. In 2012, United States Department of Health and Human Service reported that the CHF is an epidemic in the U.S and approximately 4.8 million Americans are diagnosed for CHF. In addition, each year, there are an estimated 400,000 new cases of CHF are added [6]. Thus, studies relating to the development of biomimetic system that can provide detail about the Q10 functionality are important to understand several Q10 associated diseases. Herein, we report a Q10 molecular unit stabilized functionalized-multiwalled carbon nanotube (f-MWCNT) modified glassy carbon electrode, designated as GCE/f-MWCNT@Q10, as an efficient biomimetic functional system for understanding of the electron-transfer behaviour of the Q10 in cellular system.

Unlike simple quinone (hydroquinone; hydrophilic in nature), which shows well-defined redox behavior in aqueous solution [7], it is highly difficult to study the electron-transfer functionalities of the hydrophobic Q10 in aqueous solutions [8]. Most of the reported papers investigated the Q10 electrochemistry either in organic solvents or in aqueous + non-aqueous solutions, both in absence and presence of protons [9–13]. It is questionable whether the above results obtained from the non-aqueous medium studies can be compared to the natural system [14], where, the Q10 is located in a hydrophobic environment (lipids), water and its ions are able to participate in the redox reactions. For this reason, various methods have been adopted to introduce Q10 at the interface between water and modified solid-electrode, either through direct adsorption or electron-transfer through self-assembled monolayer [15]. or incorporation into an alkanethiol [16] or a phospholipid monolayer deposited on the electrode surface as structural biomimics. Followings are some of the representative examples for the structurally biomicking Q10(or other derivatives)-phopholipid bilayer models: Q8 immobilised octadecyl trichloro silane functionalized porous Al_2O_3 octadecyl mercaptan linked gold nanoparticle modified glass electrode, Q10 functionalized fungal hydrophobin from *Pisolithus tinctorius* modified GCE [17], Q10 stabilized streptavidin - lipid bilayer adsorbed 100 nm pore Al_2O_3 micro-electrode [18], Q10 immobilized Bacillus subtilis tethered gold surfaces modified with cholesterol based thiols [19], ITO supported bilayer lipid system-dipalmitoylphosphatidylcholine (DPPC)-Q10 modified electrode [20] and Q10 stabilized phospholipid layer physisorbed self-assembled monolayer gold electrode [21]. It is noteworthy that to make a non-conducting lipid layer as a conducting system, porous Al_2O_3 and/or its modified microelectrode coupled with gold nanoparticles have been used as an electrochemical systems in their bio-mimicking studies [17,19]. Unfortunately, the above mentioned systems have complex preparation procedures and showed poor electron-transfer functionality, wherein, the peak-to-peak potential difference value observed by cyclic voltammetric (CV) measurement in aqueous system were very high (ΔE_p, $E_{pa} - E_{pc} = 550$ mV, where E_{pa} and E_{pc} are anodic and cathodic peak potentials respectively) (Table 1). Meanwhile, a few non-lipid molecular architectures like quantum dot CdS [22], single walled carbon nature (SWCNT) [23] and multiwalled carbon nanotube (MWCNT)-ionic liquid-gel [24] were also reported as a matrix for Q10 immobilization in the literature. Nevertheless, except Quantum dots CdS-thiol functionalized Q10, all other systems showed poor electron-transfer functions consistently. Interestingly, the f-MWCNT@Q10 modified GCE prepared by a simple adsorption technique within 5 ± 2 min duration showed highly redox active electron-transfer feature with $\Delta E_p \sim 275 \pm 4$ mV ($\upsilon = 10\,mV\,s^{-1}$) in non-deaerated pH 7 phosphate buffer solution, unlike to the previous CNT/Q10 based system reports with high ΔE_p values (Table 1) [23,24].

Oxygen functionalized MWCNTs (f-MWCNT), which contains hydrophobic graphitic core along with hydrophilic oxygen functionalities, are exceptional nanomaterial that have been widely used in several biomedical and biotechnological applications owing to its much reduced cytotoxicity, water solubility and good biocompatibility features [25–27]. Furthermore, f-MWCNT is close similarity with cellular system in respect to nano dimension size, carbonaceous network (in cell, carbon is a major content) and facile adsorption character. Thus, f-MWCNT is chosen as a model functional bio-mimicking matrix to study the electron-transfer characteristic of the Q10 in this work. Present work covers preparation, physico-chemical characterization, electrochemical and electro-analytical (pH sensing) characteristics of f-MWCNT@Q10 modified electrode in aqueous solution.

2. Experimental

2.1. Chemicals and reagents

Q10 (≥98% purity) and multiwalled carbon nanotubes (MWCNTs, >90% carbon basis, outer diameter: 10–15 nm; inner diameter: 2–6 nm; length 0.1–10 μm, metal oxide content = 5.2), single-walled carbon nanotubes (SWCNTs, 50–70 wt.% of carbon basis, outer diameter 1–1.5 nm, metal oxide content = 24.4) and carbon nano fibers (CNF; graphitized, iron free, >99.9 wt.% carbon basis, 100 nm × 20–200 μm) were purchased from Sigma Aldrich (USA). Graphene oxide (GO; >80% carbon basis flake size-0.5–2.0 μm, thickness-0.6–1.2 nm), graphite nano powder (GNP; ~98% purity, 400 nm, metal oxide content = 3.7), H_2O_2 (30%) and hydrazine sulphate (≥99% purity) were purchased from SRL chemicals, India. Q10 as a dietary supplement was obtained from Amway India Ltd. Other chemicals used were all of ACS-certified reagent grade and used without further purification. Aqueous solutions were prepared using deionized and alkaline MnO_4 distilled water (designated as DD water). The supporting electrolyte pH 7 phosphate buffer solution (PBS) of ionic strength = 0.1 mol L^{-1} was used throughout this work.