Sensors & Actuators: B. Chemical 275 (2018) 31–42

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Selective electrochemical polymerization of 1-napthylamine on carbon electrodes and its pH sensing behavior in non-invasive body fluids useful in clinical applications

Nandimalla Vishnu[a,b], Annamalai Senthil Kumar[a,c,d,*], Guan-Ting Pan[e,f], Thomas C.-K. Yang[e,f]

[a] *Nano and Bioelectrochemistry Research Laboratory, Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology, Vellore 632014, Tamil Nadu, India*
[b] *Department of Electrical Engineering, Indian Institute of Technology Hyderabad, Kandi 502285, India*
[c] *Carbon dioxide Research and Green Technology Centre, Vellore Institute of Technology, Vellore, 632014, Tamil Nadu, India*
[d] *Institute of Biochemical and Biomedical Engineering, National Taipei University of Technology, Taipei 10608, Taiwan, ROC*
[e] *Centre for Precision Analysis and Research Center, National Taipei University of Technology, Taipei, 10608, Taiwan, ROC*
[f] *Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taipei, 10608, Taiwan, ROC*

ARTICLE INFO

Keywords:
Poly(1-naphthylamine)-MWCNT hybrid
Conducting redox polymer
pH sensor
Real sample analysis

ABSTRACT

pH value of a non-invasive sample is an important biomarker in diagnosing certain clinical disorders of a human body. Herein, we report, a stable, surface-confined and redox active poly(1-naphthylamine) (PNPA) on multi-walled carbon nanotube modified gold and pencile graphite electrodes (Au/MWCNT@PNPA and PGE@PNPA) prepared via electrochemical polymerization of 1-naphthylamine (1-NPA) in pH 7 phosphate buffer solution for sensitive and selective pH monitoring of non-invasive samples (saliva, tears and urine). Control experiment with 2-NPA isomer failed to show such redox feature, indicating the selective electrochemical polymerization of 1-NPA. Physicochemical characterizations of MWCNT@PNPA by SEM, TEM, XPS, Raman, FTIR, UV–vis (an ethanolic extract) and several control electrochemical experiments revealed that 4th (para) position of 1-NPA isomer is involved in the initiation of electro-polymerization on a carbon surface and followed by a stable redox polymer formation. Interestingly, the redox peak responsible for pH sensing showed negligible to permissible level of alteration with several biochemicals. As as a diverse application, selective monitoring of bacterial (E. coli) growth was demonstrated using this new electrochemical pH sensor system with result comparable to that of conventional pH sensor.

1. Introduction

Non-invasive samples like urine, saliva, sweat and tears are alternate diagnostic fluids to direct blood [1,2]. The pH value of such non-invasive samples is assumed to be a biomarker for direct information about acid-base balance of human body and helpful in assessing certain clinical disorders [1–3]. For instance, urinary crystals formation upon altering the pH of urine [4] Similarly, pH of saliva is an indicator for oral diseases such as dental caries, periodontitis and oral malodor [5]. Meanwhile, tear fluid pH also contributes to the health and function of the anterior ocular tissues [6]. Thus, a simple, sensitive and quick measurement of pH of non-invasive samples is an signifigant esearch interest in clinical analytical chemistry.

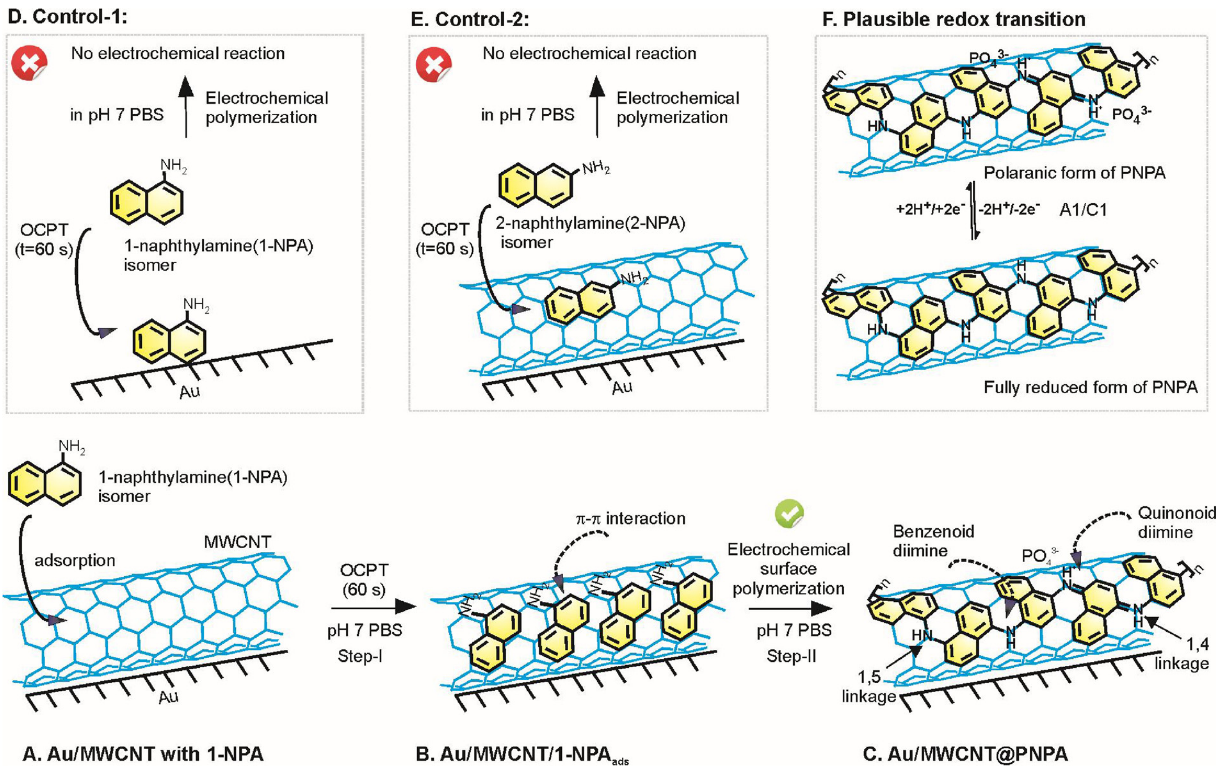
For the measurement of pH, several spectroscopic methods based on UV–vis, fluorescence and Nuclear Magnetic Resonance (NMR) and potentiometric techniques have been reported. For example, monolithic silica doped alizarin red [7], 4-((p-nitrophenyl)azo) phenol and 2-methoxy-4-((4-nitrophenyl)azo)phenol dyes immobilized triacetyl cellulose membrane [8] and a Donor–π–Acceptor heterocyclic azo chromosphere [9] as pH sensitive absorbance systems by UV–vis spectroscopy; 4-(p-*N*,*N*-dimethylamino phenyl methylene)-2-phenyl-5-oxazolone embedded plasticized PVC polymer film [10], 4-trifluoromethylcarbostyril derivative of diethylene triaminepentaacetic acid-europium (III)-complex entrapped sol–gel and ormosil [11] and bromocresol purple sol-gel modified thin film [12] as pH sensitive fluorescence systems for pH sensing were reported. For NMR based pH measurement, a concentrated acidic aqueous solution buffered by fluoride ion in the pH 1.5–4.5 range, wherein, the fluoride ^{19}F chemical

---

[*] Corresponding author. Present address: Carbon dioxide Research and Green Technology Centre, Vellore Institute of Technology, Vellore 632014, Tamil Nadu, India.

E-mail addresses: askumarchem@yahoo.com, askumar@vit.ac.in (A.S. Kumar).

https://doi.org/10.1016/j.snb.2018.08.022
Received 3 December 2017; Received in revised form 23 May 2018; Accepted 6 August 2018



Scheme 1. (A–C) Schematic representation for selective preparation of poly (1-naphthylamine) (PNPA) from 1-naphthylamine (1-NPA) isomer on pristine multi-walled carbon nanotube (MWCNT) modified electrode in neutral pH condition and its control experiments (D&E). (F) Plausible redox transition of PNPA on MWCNT.

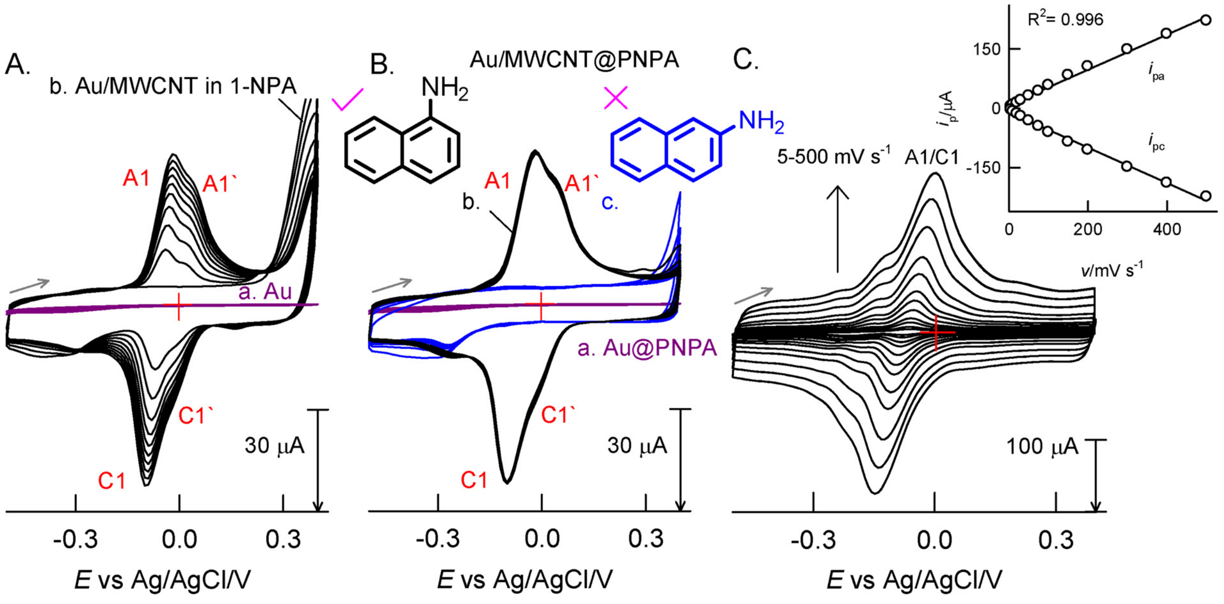


Fig. 1. Continuous CV responses of (A) Au (curve a) and Au/MWCNT (curve b) in 1 mM 1-NPA, (B) Au@PNPA (curve a) and Au/MWCNT@PNPA formed from 1-NPA (curve b) and 2-NPA (curve c) in pH 7 PBS and (C) effect of scan rate (5–500 mV s^{-1}) on CV of Au/MWCNT@PNPA in pH 7 PBS. Inset plot is peak current vs scan rate.

shift with respect to an internal standard, 3-fluoropyridine, was reported [13]. Indeed, with respect to on-line measurement, necessary off-line treatment and rare to realize the real-time monitoring in living systems, these methods restrict for routine sample analysis. On the other hand, electrochemical techniques offer a simple, rapid and efficient route for pH sensing. At present, a glass-membrane based ion-selective electrode, in which, a dilute solution of HCl filled membrane micro-ball coupled with Ag/AgCl reference electrode, has been widely used for pH measurements [7–14]. But, they are fragile and need a large volume of sample (> 2 mL). Alternately, pH sensitive redox probe coupled with voltammetric technique, wherein, the electro-active probe either mounted on working electrode surface (heterogeneous) or dissolved in test solution (homogenous) offers a better alternative for routine and practical analysis.

Electrochemical probes like quinone [15], metal oxide (iridium oxide [16], ruthenium oxide, tin dioxide [17] and zinc oxide [18]), azo dye [19] and conducting polyaniline (PANI) [20] modified on glassy carbon [21], gold [22] screen-printed electrode [23] and pencil lead