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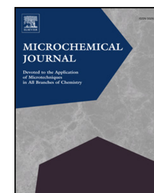

Chemisorbed palladium phthalocyanine for simultaneous determination of biomolecules

Nemakal Manjunatha, Aralekallu Shambhulinga, Mohammed Imadadulla, Keshavananda Prabhu C.P., Koodlur Sannegowda Lokesh*

Department of Chemistry, Vijayanagara Sri Krishnadevaraya University, Ballari 583105, Karnataka, India

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ABSTRACT

In this study, the palladium(II) tetraaminophthalocyanine (PdTAPc) was synthesized and characterized with different analytical techniques to confirm its purity. The synthesized PdTAPc was immobilized on the electrode surface through self-assembled monolayer (SAM) technique. The immobilized PdTAPc on glassy carbon electrode (GCE) was characterized by XPS, Raman spectroscopy and cyclic voltammetry. The Raman spectra and XPS indicated the modification of the electrode surface with the PdTAPc film (GCE/PdTAPc) by chemisorption. The chemisorbed electrode slightly blocked the charge transfer of $K_4Fe(CN)_6$ redox probe. The electroactive species PdTAPc on the electrode surface was used for the sensing of ascorbic acid in the concentration range of 1–25 μmol L^{-1} and the peak current as well as sensitivity of ascorbic acid species was enhanced by using MWCNTs decorated on the PdTAPc modified GCE (GCE/MWCNTs/PdTAPc). The MWCNTs dispersed PdTAPc modified electrode was used for the simultaneous determination of ascorbic acid (AA) in the concentration range 3–24 μmol L^{-1}, dopamine (DA) 2–16 μmol L^{-1} and uric acid (UA) 5–40 μmol L^{-1} respectively and the peaks were clearly separated without any overlapping from one another. The correlation coefficient (r) was found to be 0.9910, 0.9893 and 0.9982 with a limit of detection (LOD) 1.0, 0.60 and 1.50 μmol L^{-1} (S/N = 3) respectively for AA, DA and UA biomolecules. The sensitivity for the simultaneous determination of the biomolecules with MWCNTs modified electrode was high and can be determined without any interference. The sensitivity was found to be 1.0149, 1.9303 and 0.4328 mA μmol^{-1} cm^{-2} respectively for AA, DA and UA compounds. The modified electrode was also successfully applied to the determination of AA, DA and UA in urine samples.

1. Introduction

Biologically important molecules such as dopamine, tyrosine, DNA, amino acids, ascorbic acid, citric acid, L-cysteine and uric acid play vital key roles in the physico-chemical process of the human metabolic system. These biological molecules are present in adequate quantity and coexist in our body matrix. The deficiency of these causes severe diseases; namely, dopamine (DA) known as monoamine neurotransmitter molecule plays a significant role in movement and normal brain function. Deficiency of dopamine causes Parkinson's disease and psychiatric disorders such as schizophrenia; attention deficit hyperactivity disorders (ADHD) [1,2]. Vitamin C or Ascorbic acid (AA) which is a water soluble vitamin significantly absorbs iron from non-heme sources [3]. It shows antioxidant properties, hence, used in healing of wound, common cold and cancer therapy [4,5]. In addition, ascorbic acid also metabolizes proteins, and deficiency causes scurvy. Further, uric acid (UA) is a bicyclic, heterocyclic, diprotic acid and it is the metabolized end product of purine in human. The deficiency of serum uric acid concentration levels in human show different disorders, namely: coronary artery disease, obesity, metabolic syndrome, hypertension, hypouricemia, hyperuricemia and also gout development [6].

These bio-important molecules needs to be monitored continuously in order to overcome the diseases and disorders associated with them. These bio-molecules coexist in the body along with the body fluid and needs to be separated or purified for their detection. Especially, AA, DA and UA co-exists with each other and their separation is a tedious, expensive and time-consuming process and there is an urgency to develop a simple and sensitive method which can determine these biomolecules individually and simultaneously without the interference of each other. Hence, simultaneous determination of AA, DA and UA in the body fluid has received a great deal of attention, in order to detect and prevent the diseases at the early stage. The 'electrochemical sensing' is a promising tool than the other methods [7–9], mainly because

* Corresponding author.
E-mail address: kslokesh@vskub.ac.in (L. Koodlur Sannegowda).

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of the low cost (cheap), good selectivity, sensitivity, stability and simplicity ('ssss'), with very fast electron transport. Simultaneous electrochemical determination of AA, DA and UA has many challenges; because, these bio-molecular species have close oxidation potentials with the overlapping of peaks and in turn, interference of the voltammetric responses from the coexisting molecules [10]. Also, the pronounced poisoning, electrode fouling, poor selectivity and reproducibility during electrochemical sensing make their simultaneous determination highly difficult [10,11]. To overcome these problems, the electrodes were modified by various redox mediators' such as polymer film, nanoparticles, pyrolytic graphite electrode, carbon nanotube modified electrodes and metal complexes [12–16]. It has been reported for other systems that chemisorption of metallophthalocyanine macrocyclic complexes on the GCE surface acts as good electrocatalyst, which lowers the over potentials and there by induces high sensitivity, good mechanical stability, and reproducibility in the detection of important bio-molecular species.

Metallo phthalocyanines (MPc's), which are having structure similar to chlorophyll and hemoglobin and finds numerous potential applications in semiconductors, photovoltaic materials, electrode materials, photodynamic therapy (PDT), drug delivery, dyes, catalysis, electrocatalysis, sensor applications etc. [17–23]. MPc's are known to have rich redox chemistry behavior and the redox peaks can be assigned to phthalocyanine ligand and metal atoms present in the inner core of Pcs [24–26]. By introducing the palladium metal and amine group to the phthalocyanine ring, the properties can be tuned in terms of activity and redox behavior [27,28]. Palladium has been extensively used as a catalyst in homogeneous and heterogeneous reactions [29]. Electrochemical activity of these macrocycles can also be enhanced by doping with MWCNTs, graphite, graphene, reduced-graphene oxide (r-GO) and C_{60}: these provide larger surface area, conductivity and improve the catalytic activity of the doped complexes [29].

The chemisorbed PdTAPc on GCE which was obtained through self-assembled monolayer (SAM) technique was used for the sensing of AA. Further, MWCNTs have been dispersed on PdTAPc electrode and the effect of MWCNTs on sensing has been studied. In addition, the GCE/MWCNTs/PdTAPc modified electrode has been successfully used for the simultaneous determination of AA, DA and UA without any interference from each other at low concentrations.

2. Materials and methods

Palladium chloride ($Pd(II)Cl_2$), 4-nitrophthalonitrile ($C_6H_4(CN)_2NO_2$), Urea ($CO(NH_2)_2$), Ammonium chloride (NH_4Cl), Ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$), Nitrobenzene ($C_6H_5NO_2$), Methanol ($CH_3OH$), Ethanol ($C_2H_5OH$), Sodium hydroxide (NaOH), Sodium chloride (NaCl), Acetone (CH_3COCH_3), Sodium sulfide ($Na_2S\cdot 9H_2O$), Dimethyl sulfoxide (DMSO: ($(CH_3)_2SO$), 98%), Tetrabutyl ammonium perchlorate (TBAP: ($(C_4H_9)_4N(ClO_4)$)), Multiwalled carbon nanotubes (MWCNTs), Hydrochloric acid (HCl), Sulphuric acid (H_2SO_4), Potassium ferrocyanide ($K_4Fe(CN)_6$), Ascorbic acid ($C_6H_8O_6$), Dopamine ($C_8H_{11}NO_2$), Uric acid ($C_5H_4N_4O_3$) were purchased from Sigma-Aldrich. High-purity 99.9% nitrogen was used for deaeration. All solutions were prepared with doubly distilled water.

Inlaid glassy carbon (GC) disks of surface area 0.071 cm^2 (CHI6005E: CH Instruments Inc. USA) were used as working electrodes in the electrochemical characterization and subsequent sensing analyses. The GCE was polished with a polishing cloth (Micro Cloth, Buehler) using sequentially 1.0 and 0.5 μm alumina. It was then repeatedly washed with 1:1 HNO_3, acetone, and water respectively and sonicated for 5 min alternatively in water and ethanol in an ultrasonic bath.

2.1. Synthesis of palladium (II) tetranitrophthalocyanine (PdTNPc)

PdTNPc was synthesized by using the modified procedure reported in the literature [26,30]. In brief, mixture of $PdCl_2$ (10 mmol), 4-nitrophthalonitrile (39 mmol) and NH_4Cl (20 mmol), urea (80 mmol), were mixed along with the catalytic amount of ammonium molybdate. 30 mL nitrobenzene was added to the mixture and heated at 140 °C for 1 h and maintained at 180 ± 5 °C for 5 h with constant stirring to obtain dark blue colored crude compound. The crude product was purified using alkali and acid. Anal. Calc. for PdTNPc; $C_{32}H_{12}N_{12}O_8Pd$: Calc. (%) C, 48.1; H, 1.50; N, 21.04; O, 16.03; Pd, 13.33. Found (%): C, 48.49; H, 1.34; N, 20.79; Pd, 13.56. UV-VIS (DMSO, λ_{max}, nm (log)): 331 (4.51), 412 (4.61), 600 (4.77), 663 (4.82). FT-IR absorption bands (KBr (pellet), cm^{-1}): 3091, 1655, 1529, 1465, 1358, 1278, 1162, 1127, 1054, 948, 809 and 722. Yield: 87%.

2.2. Synthesis of palladium (II) tetraminophthalocyanine (PdTAPc)

The aminophthalocyanine derivative was prepared by modifying the procedure reported in literature [26,30]. 2.0 g PdTNPc was taken in 50 mL distilled water and added 10 g of sodium sulfide nanohydrate ($Na_2S\cdot 9H_2O$). The reaction mixture was stirred at 60 °C for 6 h. The bluish green product was purified and stored in vacuum desiccator. Anal. Calc. for PdTAPc; $C_{32}H_{20}N_{12}Pd$: Calc. (%): C, 56.59; H, 2.95; N, 24.74; Pd, 15.72. Found (%): C, 56.16; H, 3.24; N, 24.79; Pd, 15.84. UV-VIS (DMSO, λ_{max}, nm (log)): 335 (4.52), 421 (4.62), 610 (4.78), 670 (4.82). FT-IR absorption bands (KBr (pellet), cm^{-1}): 3215, 1514, 1423, 1342, 1266, 1117, 1022, 966, 908, 860, 795 and 732. Yield: 83%.

2.3. Fabrication of PdTAPc electrode by self-assembled technique

The chemisorption of PdTAPc on GCE was carried out by self-assembly technique (SAM). 1 mmol solution of PdTAPc in DMSO was prepared and the cleaned GC surface was dipped in it for 6 h. Then the modified electrode was rinsed with DMSO, water and ethanol to remove any physisorbed materials from the electrode surface and dried in vacuum desiccator. The modified electrode is represented as GCE/PdTAPc. The deposition of the PdTAPc on the electrode surface was monitored by CV, XPS and Raman spectroscopy and found a maximum deposition of PdTAPc after 6 h.

2.4. Fabrication of self-assembled PdTAPc on MWCNTs casted GCE surface

10 μL of 1 mg per mL MWCNTs in isopropyl alcohol (IPA) was coated on GCE and dried. Then PdTAPc was chemisorbed on top of the MWCNTs by dipping GCE for 6 h in 1 mmol PdTAPc in DMSO. After the deposition, the electrode was rinsed with DMSO, water and ethanol to remove any physisorbed materials from the electrode surface and dried in vacuum desiccator. The modified electrode is represented as GCE/MWCNTs/PdTAPc.

2.5. Preparation of bio-molecule AA, DA and UA analytical stock solutions

The ascorbic acid (AA) stock solution (1 mmol) was freshly prepared by dissolving 4.4 mg of ascorbic acid in double distilled water and then diluted to the mark in a 25 mL standard volumetric flask. For the detection and determination of AA, different volumes of stock solution were added to 10 mL 0.25 mol L^{-1} H_2SO_4 electrolyte for different concentration studies. Similarly, 4.7 and 4.2 mg of dopamine (DA) and uric acid (UA) respectively were dissolved separately in double distilled water and then diluted in separate 25 mL volumetric flasks to obtain (1 mmol) stock solutions. The stock solutions were stored in refrigerator when not in use at 4 °C in dark. The simultaneous detection and determination of AA, DA and UA biomolecule species was carried out using different volumes of stock solution in experimental cell containing 0.25 mol L^{-1} 10 mL H_2SO_4. The ascorbic acid solution was stored and covered with dark and fresh solution was used to avoid degradation and oxidation of AA.

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