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Surface-dopylated carbon nanoparticles sense gas-induced pH changes

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ABSTRACT

Carbon nanoparticles of ca. 9–18 nm diameter (Emperor 2000^{TM}) are surface-modified by covalently linking L-dopa-boc (boc-protected L-3,4-dihydroxyphenylalanine) with a surface coverage of approximately 100 per particle (or 3×10^{13} cm^{-2}). In solution environments these redox-active nanoparticles provide chemically stable and pH-sensitive voltammetirc responses (reversible 2-electron 2-proton oxidation) over a pH range from 2 to 12.

When mixed into Dowex 50 Wx4 cation exchanger or Dowex 50 1x2 anion exchanger and placed in contact with a glassy carbon electrode in a flow of humidified gas, the L-dopa-boc-modified carbon nanoparticles provide pH-sensitive surface probes to monitor the surface conditions. In a two-terminal cell it is demonstrated that gas flow measurements are possible with both modified cation and anion exchanger particles in contact to glassy carbon electrodes. The anion exchanger particles allow pH control after pre-conditioning in phosphate buffer. Loading-dependent sensitivity to ammonia gas is investigated and high sensitivity to ammonia is observed for Dowex 50 1x2 anion exchanger pre-equilibrated in phosphate buffer pH 3 and decorated with L-dopa-boc-modified carbon nanoparticles. Responses are observed with sequential injections of 1 cm^3 ammmonia into a gas flow-through device.

1. Introduction

Many types of pH sensitive redox systems are known and in particular quinone–hydroquinone redox systems with pH dependence are ubiquitous in nature [1]. L-Dopa (3,4-dihydroxyphenylanaline or S-2-amino-3-(3,4-dihydroxyphenyl) propanoic acid) plays a special role as a redox active amino acid derivative with functions ranging from anti-oxidant [2], metal complexant [3], melanin precursor [4], to biological (marine) adhesive [5]. The chiral nature of L-dopa has been exploited recently to probe chiral electrode processes [6]. The effect of pH on the dopa redox reactivity has been studied by Brun and Rosset [7] and a transition from chemically reversible to irreversible oxidation has been observed due to a cyclisation reaction and formation of a leuco-dopachrome intermediate (see Fig. 1) at lower proton activities [8]. Nucleophilic attack of the reactive dopaquinone has also been reported with water [9], nitrite [10], and with thiol derivatives [11]. L-Dopa is an important analytical target [12], but it also has been used to make sensor devices [13] and to detect metals such as aluminium [14,15]. There have been several examples of pH probe designs based on quinone–hydroquinone type redox systems [16,17] in particular based on anthraquinones [18]. A combination of a pH-dependent redox system and a pH-independent redox system has been proposed for reference-free pH measurements [19].

In order to employ quinone–hydroquinone or other pH-dependent redox systems at an electrode surface, immobilisation onto an appropriate substrate is required. Several types of carbon substrates have been used as substrate materials including glassy carbon [20,21], graphite [22], carbon spheres [23], carbon nanotubes [24], and carbon nanoparticles [25]. Carbon nanoparticles (CNPs) combine high surface area (high immobilisation density [26]), versatile surface chemistry, and low cost. For example, industrial pigment materials such as Emperor 2000^{TM} (Cabot Corp.) carbon nanoparticles are readily available as starting materials and readily surface functionalised via sulphonate functional groups [27]. The reaction with thionylchloride followed by amines has been shown to open up a range of functionalisation opportunities [28]. In this report amide coupling chemistry is developed to connect L-dopa-boc units covalently to the surface amine functionalities of these carbon nanoparticles.

Ammonia sensors have been reported for gas media based on for example oxide films [29,30] and for aqueous media based on direct detection [31,32] or based on indirect detection with

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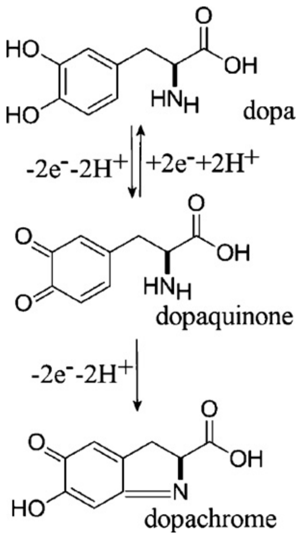

Fig. 1. Reaction scheme for L-dopa oxidation.

immobilised anthraquinones [33]. Here, proof-of-principle experiments are reported for an ammonia gas induced effect on a L-dopa-boc sensed pH change at the electrode | aqueous electrolyte | gas triple phase boundary. In order to investigate the effect of gas pH (e.g. introducing ammonia) on the electrochemical response of dopa-boc functional groups on the surface of carbon nanoparticles, a two-terminal cell is employed. Fig. 2A shows a drawing of the glassy carbon working electrode in contact to the Dowex ion exchanger particles, which carry the aqueous electrolyte phase and provide the electrical connection to the counter-reference electrode. The L-dopa-boc-functionalised carbon nanoparticles are distributed over the Dowex surface and allow direct contact to the working electrode surface (see Fig. 2B).

Flow of gas through this cell is initially limited to argon (humidified with 80% relative humidity by flowing through saturated ammonium sulphate solution [34]) to allow L-dopa-boc electrochemistry to be studied as a function of the pH (imposed by pre-treatment of the ion exchanger in buffer). Finally, injection of small doses of ammonia is shown to change L-dopa-boc reactivity to provide a highly sensitive probe for ammonia exposure.

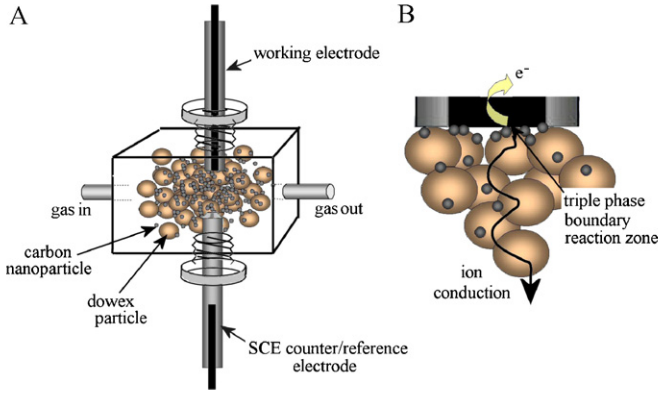

Fig. 2. (A) Schematic drawing of the two-terminal electrochemical cell with carbon nanoparticle decorated Dowex ion exchanger particles acting as electrolyte and support for the redox system. (B) Scheme of the carbon nanoparticles in contact to the glassy carbon electrode surface, the ion conducting particles, and the surrounding gas phase.

2. Experimental

2.1. Chemicals

Dowex 50 Wx4 cation exchanger and Dowex 50 1x2 anion exchanger, phosphoric acid, NaOH, thionylchloride, ethylenediamine, ammonium sulphate, L-dopa, were obtained from Aldrich and used without further purification. Emperor 2000^{TM} carbon nanoparticles were obtained from Cabot Corporation. Argon (Pureshield, BOC) was used for de-aeration of solutions. Demineralised and filtered water was taken from a Thermo Scientific water purification system (Barnstead Nanopure) with 18.2 MΩ cm resistivity.

2.2. Instrumentation

A microAutolab III potentiostat system (EcoChemie, The Netherlands) was employed in electrochemical measurements. A 3 mm diameter glassy carbon disc electrode (BAS, US) or a Dropsense screen printed carbon disc electrode (Dropsense) were the working electrode and a KCl-saturated calomel electrode (SCE, Radiometer) was the counter-reference. In solution experiments a platinum wire served as counter electrode. A custom-made PEEK cell with gas in and outlet (see Fig. 2A) was used with a wash bottle to pre-saturate argon with 80% relative humidity [35]. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were obtained on JEOL JSM6301F field emission scanning electron microscope (FESEM) and JEOL JEM1200EXII TEM systems, respectively.

2.3. Procedures

2.3.1. Boc protection of L-dopa

L-Dopa (4 g, 20.3 mmol) was dissolved in dioxane (40 mL), 1 M sodium hydroxide (28 mL) and water (25 mL). Boc-anhydride (1.1 eq, 4.87 g, 22.3 mmol) was dissolved in 10 mL of dioxane and added to the orange L-dopa solution. This was stirred for 1 h, after which the pH was adjusted to between pH 9 and 10 by adding 1 M sodium hydroxide dropwise and testing with indicator paper. The black solution was stirred for 18 h, overnight. The resulting solution was concentrated by rotary evaporation before being acidified to pH 2 using 1 M hydrochloric acid. This was extracted four times using ethyl acetate. The organic layers were combined and dried using magnesium sulphate. The magnesium sulphate was removed by filtration and the remaining solvent was removed by rotary evaporation. The solid product (see structure 1 in Fig. 3) was placed under high vacuum to ensure product was completely dry. The product was a brown solid (4.28 g, 71%). $[M+Na]^{+} = 320.1110$ and $[M+H]^{+} = 298.1291$. The mass of M ($C_{14}H_{19}NO_6$) expected is 297.1212, mass spectrometry confirmed the expected formula with a mass accuracy of 4.5 ppm for $[M+H]^{+}$ and 1.9 ppm for $[M+Na]^{+}$. δH (300 MHz, DMSO-d_6): 1.31 (9H, s, Boc), 2.72 (2H, m, $\mathrm{ArC\underline{H_2}R}$), 3.95 (1H, m, $\mathrm{ArCH_2C\underline{H}(NHBoc)R}$), 6.44 (2H, d, $\mathrm{Ar\text{-}\underline{H_2}H}$), 6.51 (1H, s, $\mathrm{Ar\text{-}H_2\underline{H}}$), (6.92 (1H, d, $\mathrm{N\underline{H}Boc}$ confirmed by HMQC), 8.68 (1H, broad s, $\mathrm{COO\underline{H}}$). δC (75 MHz, DMSO-$d_6$) confirmed by pendant: 28.52 (Boc $\mathrm{\underline{C}H_3}$ groups), 36.23 ($\mathrm{R\underline{C}H_2R}$), 55.94 ($\mathrm{R\underline{C}HR}$), 78.35 ($\mathrm{RO\underline{C}C_3H_9}$), 115.61–120.13 (3 $\mathrm{Ar\text{-}\underline{C}H}$), 129.06–145.19 (3 $\mathrm{Ar\text{-}\underline{C}}$), 155.80 ($\mathrm{RHN\underline{C}(O)OR}$), 174.16 ($\mathrm{R\underline{C}OOH}$).

2.3.2. Ethylenediamine modified carbon nanoparticles [28]

(a) Emperor 2000^{TM} carbon nanoparticles (5 g) were sonicated in dry dichloromethane for 30 min after which the flask was degassed with nitrogen and placed in an ice bath to reduce the temperature to 0 °C. Thionylchloride (50 mL, 0.69 mol) was added drop-wise to the cooled suspension under continuous stirring. The suspension was left to stir for 18 h, allowing to warm to