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Preparation of a tetrahydroxyphenazine-modified carbon as cathode material for supercapacitor in aqueous acid electrolyte

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ABSTRACT

A procedure for the grafting of oxocarbon compounds is proposed by condensation reaction with a benzenediamine to obtain an attached-phenazine moieties. A technical proof of concept is given by the covalent capture of rhodizonic acid on the Norit activated carbon and potentiality for supercapacitors is evidenced. The composite material obtained was tested as positive electrode for aqueous supercapacitors in 1 M H_2SO_4. The redox activity covering a wide range of potential gives an unprecedented increase in specific charge of 350% and a specific energy at the discharge 3.4 times higher than the unmodified carbon.

1. Introduction

Grafting of electroactive molecules on the high specific surface of a porous carbon has found a widespread use for improving the performances of energy storage devices by adding a Faradaic contribution into the electrical double layer of a polarizable electrode [1]. Nevertheless, the major drawback of the grafting is the weak concentration of molecules attached to the surface. Here, we propose to focus our attention on a specific redox group exchanging several electrons per molecule. While redox-active molecules with a reversible one or two-electron process are widely illustrated in literature [2–4], mention of three or four-electron systems is rare [5,6]. In the case of oxocarbon derivatives, such as rhodizonic acid, the main difficulty consists in attaching the molecule to a surface without sacrificing the carbonyl groups which are essential in the redox activity. For addressing this complex issue, we propose to use the facile condensation reaction of primary aromatic amines with oxocarbon compounds for the covalent capture of rhodizonic acid at carbon surface. A phenazine compound designed for grafting was obtained from rhodizonic acid and 4-nitro-*o*-phenylenediamine.

2. Experimental section

2.1. General methods

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance III 300 (^{1}H: 300 MHz; ^{13}C: 75 MHz) Spectrometer using DMSO-d_6 as solvent. The chemical shift of DMSO-d_6 was calibrated at 2.50 ppm in ^{1}H NMR spectra and 39.52 ppm in ^{13}C NMR. High resolution mass spectroscopy was obtained by using a Jeol-JMS-700 double-focusing mass spectrometer using the electron impact (EI) method. X-ray photoelectron spectroscopy (XPS) data have been collected in the CEA (constant analyser energy) mode with analyser pass energy of 20 eV, using a Kratos Nova spectrometer with a monochromatized Al anode X-ray source ($h\nu = 1486.6$ eV). Data treatment was performed with CasaXPS software and all spectra were calibrated taking 284.4 eV (graphite like carbon) as a reference binding energy. Electrochemical measurements were performed in a three-electrode configuration with an aqueous 1 M sulfuric acid electrolyte and a potentiostat/galvanostat model VMP3 (from Bio-Logic) monitored by ECLab software was used. Working electrodes were glassy carbon (from Bioanalytical Systems, model MF-2012) or modified and unmodified activated Norit carbon electrodes prepared according to a previously published procedure [7]. All the potential values were reported versus an Ag|AgCl reference electrode, except for galvanostatic charge/discharge experiments performed in a three electrode Swagelok cell with a silver wire as a quasi-reference electrode.

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Thermogravimetric analyses (TGA) were performed with a TA Instruments by heating carbon products in N_2 atmosphere to 1000 °C at a rate of 10 °C·min^{-1}.

2.2. Synthesis of the 2,3-dihydroxy-7-nitrophenazine-1,4-quinone

Synthesis of 2,3-dihydroxy-7-nitrophenazine-1,4-quinone was performed by condensation between rhodizonic acid and 4-nitro-o-phenylenediamine, according to a previously published procedure [8]. 4-nitrobenzene-1,2-diamine (367.5 mg, 2.42 mmol) dissolved in warm H_2SO_4 (10 mL, 25% *w/v*) was added at 100 °C to a rhodizonic acid dihydrate (500 mg, 2.42 mmol) solution in water (10 mL). After 10 min stirring at 100 °C, the heating was stopped and the mixture returns at room temperature for 2 h. The precipitate was recovered by filtration and washed with water, ethanol, acetone and ether to give the 2,3-dihydroxy-7-nitrophenazine-1,4-quinone as a red solid (416 mg, 60%).

^{1}H NMR (DMSO-d_6) δ: 9.06 (d, 1H, Hc, $J = 2.2$ Hz), 8.66 (dd, 1H, Hb, $J = 9.2$, 2.2 Hz), 8.52 (d, 1H, Ha, $J = 9.2$ Hz). ^{13}C NMR (DMSO-d_6) δ: 177.11 (C═O), 148.98, 145.56, 145.20, 145.10, 144.46, 141.06, 132.06, 125.86, 125.64. HRMS for $C_{12}H_5N_3O_6$: calcd 287.0178; found 287.0174.

2.3. Chemical modification of the activated carbon

2,3-Dihydroxy-7-nitrophenazine-1,4-quinone (28 mg) was first sonicated for 30 min in 80 mL of 0.5 M HCl before to be electrochemically converted into the amino compound under controlled potentiostatic conditions at 0 V on a glassy carbon plate. When the cathodic charge consumed corresponded to 6 F·mol^{-1}, the electrolysis was stopped and $NaNO_2$ (20 mg; 3 equiv.) was added under stirring at room temperature for producing in situ the 2,3-dihydroxy-7-diazoniumphenazine-1,4-quinone salt and then the carbon powder (64 mg) was added. After stirring at room temperature for 24 h, the carbon product was vacuum filtered and thoroughly washed before to be dried over night at 80 °C. The carbon product containing the molecule just adsorbed was prepared by dispersing the carbon powder in acetonitrile with 0.02 equiv. of nitro compound for 24 h.

3. Results and discussion

Condensation of rhodizonic acid with 4-nitrobenzene-1,2-diamine yields the 2,3-dihydroxy-7-nitrophenazine-1,4-quinone (7-nitro DHPhQ) in situ diazotized through a sequential approach already published by our group [9]. In this procedure, the nitro group was first completely reduced into the amine under controlled potentiostatic conditions at 0 V vs. Ag/AgCl in 0.5 M HCl on a glassy carbon plate, which is subsequently in situ diazotized (Fig. 1a). Fig. 1b shows two cyclic voltammograms (CVs) recorded on a glassy carbon electrode (GCE) before (solid line) and after electrolysis (dotted line). At the end of the electrolysis, CV shows two reversible systems centered at 0.005 and 0.300 V. Following the nitro consumption, an excess of $NaNO_2$ was added and after 15 min stirring, a series of CVs was recorded showing an irreversible cathodic wave at 0.1 V assigned to the reduction of the diazonium salt in situ produced, which decreases until complete passivation of the GCE (inset in Fig. 1b). CV recorded in 1 M H_2SO_4 with the modified

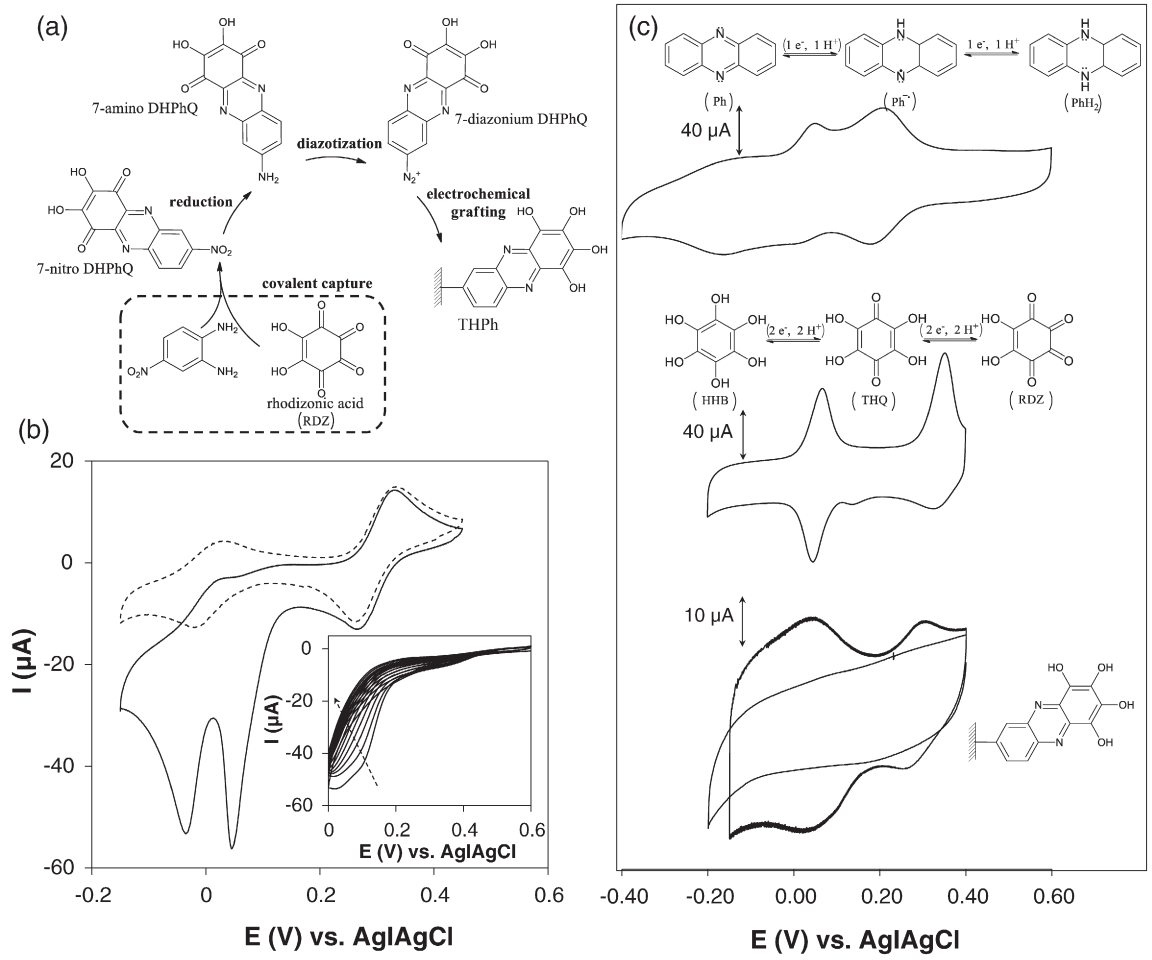

Fig. 1. (a) Schematic illustration for the grafting of an oxocarbon compound. (b) CVs on GCE at 100 mV·s^{-1} of 1 mM 7-nitro derivative in 0.5 M HCl before (solid line) and after electrolysis (dotted line) at 0 V. Inset in Fig. 2b shows CVs on GCE at 50 mV·s^{-1} of the 7-diazonium derivative generated in situ. (c) CVs in 1 M H_2SO_4 at 100 mV·s^{-1} of the THPh-modified GCE, 2 mM rhodizonic acid and 0.3 mM phenazine.