Synthesis, characterization, and electrocatalytic properties of a custom-designed conjugated polymer with pyridine side chain

Dorottya Hursán[a,b], Gábor London[c], Balázs Olasz[a,b], Csaba Janáky[a,b,*]

[a] Department of Physical Chemistry and Materials Science, University of Szeged, Aradi sq. 1, 6720 Szeged, Hungary
[b] MTA-SZTE "Lendület" Photoelectrochemistry Research Group, Szeged, Rerrich sq. 1, 6720, Hungary
[c] MTA-SZTE Stereochemistry Research Group, University of Szeged, Dóm Square 8, 6720 Szeged, Hungary

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A newly designed conducting polymer (poly(N(-pyridin-4-ylmethyl)aniline), POB), having a polyaniline backbone and pyridine pendant groups, has been electrosynthesized and studied in this paper. The characterization predominantly focuses on the possible application of the polymer-modified electrode in electrochemical fuel generation (H_2 production and CO_2 reduction). POB can be regarded as a pyridine-based electrocatalyst (mediator) immobilized on an electrode surface as part of a conjugated polymer, as confirmed by the appearance of a redox wave centered at E = −0.53 V (vs. Ag/AgCl) on the cyclic voltammogram of POB. The effects of experimental conditions (pH of the electrolyte, layer thickness, and material of the substrate electrode) on the immobilized pyridine-ring electrochemistry have been carefully analyzed, to understand the underlying factors governing the electrochemical behavior of this new functional material. Finally, the electrocatalytic behavior of POB was tested towards CO_2 reduction and H_2 evolution.

1. Introduction

Electrochemical fuel generation, especially hydrogen evolution from water and the conversion of CO_2 to valuable products is a major research topic nowadays, as it points toward a more sustainable chemical industry. Several electrode materials have been tested in these processes [1], including metals [2–5] metal oxides [6], conductive polymers [7], and carbon materials [8,9], but most of them either require large overpotential, or is very expensive, which hinders their practical application. To overcome the kinetic barriers associated with direct electroreduction, redox mediators can be applied either as freely diffusing species in the electrolyte solution or attached to the electrode surface [10]. Besides the efficiency enhancement, redox mediators are also important to achieve selectivity for a desired product. For example, in aqueous solutions, cobalt phthalocyanine [11] and Ni-cyclame [12] showed selectivity towards the formation of CO, while an Ir-pincer catalyst [13] was developed to assist the selective electro-reduction of CO_2 to formate.

Pyridine (Py) is particularly interesting in this context, because it was shown to be able to catalyze the electroreduction of CO_2, as well as the H_2 evolution reaction [14–20]. The PyH$^+$ catalyzed CO_2 reduction in aqueous medium was first proposed over twenty years ago [14]. It was reported that the reduction can proceed selectively to methanol (with Faradaic efficiency up to 30%) at low overpotential on Pt or Pd electrodes [14,21]. Since then, several groups have studied this system for electrochemical, photochemical, and photoelectrochemical CO_2 reduction [15,20,22,23]. Regarding the mechanism, however, certain discrepancies were revealed [21,24]. In one particular study, not only the mechanism, but even the existence of the Py-catalyzed CO_2 electroreduction itself was questioned, when no carbon-containing products were detected after preparative-scale electrolysis [16]. In this case, the current enhancement in the presence of CO_2 was attributed to enhanced proton reduction, mediated by HCO_3^- (or H_2CO_3) as a weak acid [16]. Besides the above mentioned controversies, there is a widely accepted mechanism applying for the Py-catalyzed CO_2 electroreduction on a Pt electrode which includes the formation of a surface Pt-hydride [17,25]. According to this mechanism, PyH$^+$ is reduced to Py in the first step, while adsorbed H atoms are formed on the Pt surface. Subsequently, the H adsorbates are attacked by the electrophilic CO_2, in a proton coupled hydride transfer (PCHT) step, forming the reduction products.

* Corresponding author at: Department of Physical Chemistry and Materials Science, University of Szeged, Aradi sq. 1, 6720 Szeged, Hungary.
E-mail address: janaky@chem.u-szeged.hu (C. Janáky).

Overall, two experimental conditions are generally accepted to play a key role in the reduction process: (i) the pH of the solution has to be close to the pK_a of PyH^+ [16,24]; and (ii) PyH^+ functions as a low-overpotential catalyst only in conjunction with certain electrode materials such as Pt, Pd or Ir [19,26,27], having low overpotential towards H_2 evolution. Electrodes, which have higher overpotential for H_2 formation (e.g., Au or glassy carbon) showed only an irreversible redox wave at more negative potentials (-1.0 V vs. Ag/AgCl for Au) [26,27]. In these cases, the suggested reduction mechanism did not include the surface metal-hydride formation, instead the one-electron reduction of PyH^+ to pyridinyl radical was suggested. It is also important that no CO_2 reduction products were detected in these works. PyH^+ homogenous electrocatalyst was also applied for CO_2 electroreduction in conjunction with some p-type semiconductor photoelectrodes ($CuInS_2$, GaP, and FeS_2)[15,20,23,28]. Methanol and formic acid were formed, but these works did not elaborate on the mechanism in detail.

In most CO_2 electroreduction studies focusing on Py as a redox mediator, Py is used as a freely diffusing molecule (also called homogenous catalyst), either alone or as a ligand of a metal complex [29,30]. On the other hand, only a few studies have been reported in which a Py-based redox mediator was attached to an electrode surface [31]. Different strategies were described in the literature for Py immobilization: (i) direct grafting by electrochemical reduction of organic compounds containing Py moiety [32,33]; (ii) anchoring of a complex with Py-containing ligands [34,35], and (iii) immobilized as part of a polymer backbone [36]. This last approach is indeed attractive, as it introduces the Py-group as a part of a surface polymer coating through a facile polymerization step. Conducting polymers (CPs) are particularly promising materials for this purpose, because of their electrical conductivity and facile synthesis. Moreover, CPs themselves (such as polyaniline (PANI) and polypyrrole) can be used in electrocatalysis [37], such as in proton [38]-, and CO_2 reduction [7,36,39]. Most recently, we have shown that PANI, as the very first example of a CP, is a promising photocathode material for the photoelectrochemical conversion of CO_2 to alcohol fuels [40].

To the best of our knowledge, however, there is only one precedence of immobilizing Py as a side chain of a CP [41]. It can be an attractive strategy to extend this concept to N-containing polymers, especially because of the excellent CO_2 adsorption properties of these materials [42]. Furthermore, as a side chain, Py can be protonated/deprotonated while this process is hampered when it is part of a conjugated electron system. Since the protonation of Py is a key step in the CO_2 electroreduction [24,43], immobilizing Py as a side chain can be a more promising way in electrocatalytic applications.

Based on these considerations, we designed and synthetized (Scheme 1) a new molecule: N(-pyridin-4-ylmethyl)aniline), further referred as OB, which was electropolymerized to form an N-substituted polyaniline (POB) with pyridine side chains (Scheme 2). For the first time, a pyridine electrocatalyst was immobilized on a N-containing CP electrode. In this study we report on its structural, electrochemical, and electrocatalytic properties.
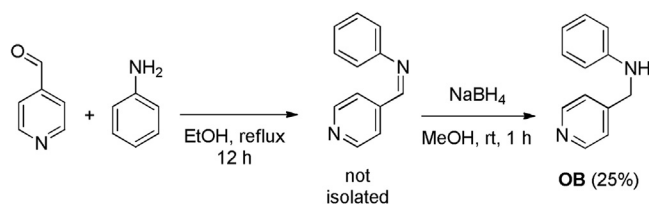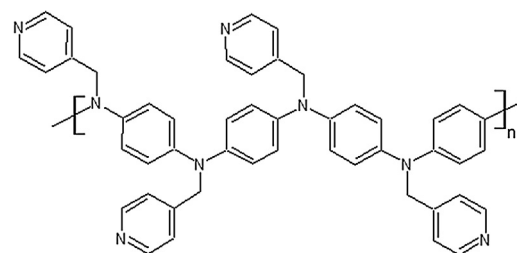
Scheme 2. Structure of POB.

2. Experimental

2.1. General remarks for the synthesis of OB

Commercial reagents (Aldrich, AlfaAesar, Acros, Fluka) were purchased as reagent grade and used without further purification. Solvents for extraction or column chromatography were of technical quality. Organic solutions were concentrated by rotary evaporation at 40 °C. Thin layer chromatography was carried out on SiO_2–layered aluminum plates (60 F254, Merck). Flash column chromatography was performed using SiO_2–60(230–400 mesh ASTM, 0.040–0.063 mm from Fluka) at 25 °C.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX 400 spectrometer at 25 °C. The residual solvent peak was used as the internal reference ($CDCl_3$: $\delta_H = 7.26$ ppm, $\delta_C = 77.16$ ppm). The ^{1}H NMR spectra are reported as follows: chemical shift δ in ppm relative to TMS ($\delta = 0$ ppm), multiplicity, coupling constant (J in Hz), number of protons. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), combinations thereof, or m (multiplet). Broad signals are described with br. (broad). ^{13}C NMR spectra are reported as follows: chemical shift δ in ppm relative to TMS ($\delta = 0$ ppm) (number of carbons if greater than 1). Mass spectra (MS) were registered using an Agilent 5973 GC-MSD. The most important signals are reported in m/z units.

Aniline (1.02 mL, 11.17 mmol) and 4-pyridinecarboxaldehyde (0.88 mL, 9.35 mmol) were dissolved in 10 mL ethanol (EtOH) and 1 g $MgSO_4$ was added to the solution. The mixture was heated at reflux for 12 h while stirring. Subsequently, the solids were filtered, washed with EtOH and the filtrate was concentrated under reduced pressure. The residue was re-dissolved in 10 mL methanol and $NaBH_4$ (0.35 g, 9.25 mmol) was added to the stirred solution in portions at room temperature. The reaction mixture was stirred for 1 h at room temperature followed by the addition of 50 mL water. The aqueous mixture was extracted with EtOAc, the organic phase was washed with water and brine, dried over Na_2SO_4 and filtered. After the removal of the solvent under reduced pressure, purification by column chromatography (SiO_2, EtOAc) gave OB as pale yellow crystals (1.01 g, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 4.29 (br s, 1 H), 4.37 (s, 2 H), 6.58 (d, $J = 8.0$ Hz, 2 H), 6.74 (t, $J = 7.3$ Hz, 1 H), 7.17 (t, $J = 7.9$ Hz, 2 H), 7.28 (d, $J = 5.5$ Hz, 2 H), 8.54 (d, $J = 5.9$ Hz, 2 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 46.99, 112.81 (2), 117.97, 122.00 (2), 129.27 (2), 147.42, 148.93, 149.89 (2) ppm; EI-MS: m/z (%) 184 (100) $[C_{12}H_{12}N_2]^+$, 106 (95) $[C_7H_8N]^+$, 92 (13) $[C_6H_6N]^+$, 77 (26) $[C^6H^5]^+$.

2.2. Polymer electrosynthesis and electrochemical measurements

Potassium dihydrogen phosphate (KH_2PO_4, Reanal), potassium hydrogen phosphate (K_2HPO_4, Reanal), sodium acetate (CH_3COONa, Reanal), sulfuric acid (H_2SO_4, Sigma-Aldrich), and acetic acid (CH_3COOH (VWR)) were of analytical grade and used without further purification. Aniline (Sigma-Aldrich) was vacuum-distilled before polymerization.

Scheme 1. Reaction scheme of the synthesis of OB monomer.