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Preparation and properties of partially oxidized *N*-methylisoquinolinium bis(oxalato)platinate nanowires

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Abstract

Electrochemical oxidation of $[C_{10}H_{10}N]_2[Pt(ox)_2] \cdot H_2O$ (**1**) ($C_{10}H_{10}N$ = *N*-methylisoquinolinium, ox = oxalate) leads to the synthesis of new partially oxidized platinum nanowires of formula $[C_{10}H_{10}N]_{1.6}[Pt(ox)_2] \cdot 3H_2O$ (**2**). The nanowires were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Wires with diameters of less than 5 nm and lengths of over 1 μm were observed. Energy dispersive spectroscopy (EDS) and microanalysis confirmed the degree of partial oxidation of the nanowires. The bulk electrical properties including phase angle and real and imaginary impedance values were measured and a model of the electrical conduction circuit was proposed. The significance of this work is that the large *N*-methylisoquilolinium cation leads to nanostructures, possibly involving individual molecular wires which has not been previously observed in the bis(oxalato)platinate nanowire system.

Keywords: Platinum; Isoquinolinium; Bis(oxalato)platinate; Nanowire; Partially oxidized

1. Introduction

Electrically conducting inorganic systems with large length to width ratios are of great current interest [1–6]. These inorganic ''nanowires'' represent a novel class of materials with interesting electric [7], magnetic [8], solution [9] and material properties [10,11]. Partially oxidized platinum complexes have been known since the early work of Soderbaum [12,13], although the fact that they are polymeric platinum complexes with extended metal–metal bonds was not appreciated until Krogmann's work in the 1960s [14,15]. The one-dimensional electrical conducting properties were subsequently observed [16] and led to numerous reviews [17–19]. Recent interest in inorganic nanowires has prompted us to reexamine these partially oxidized platinum polymers for potential materials applications. Large numbers of these salts have been prepared using a wide variety of metal counter cations, and the polymer properties can easily be modified by substitution of the cation. Underhill et al. [20,21] demonstrated that organic cations with small structural changes can significantly alter the conductivity and Pt–Pt spacing in the nanowire backbone. A major impediment to the potential use of these polymers as nanomaterials is that they are ionic materials in which many individual wires are strongly held together by the network of small cations to form macroscopic ''bundles'' of wires rather than individual molecular wires. Accordingly, we have begun to investigate organic cations with localized charge surrounded by an extensive non-polar organic framework, ideally to form materials where individual wires are significantly separated from

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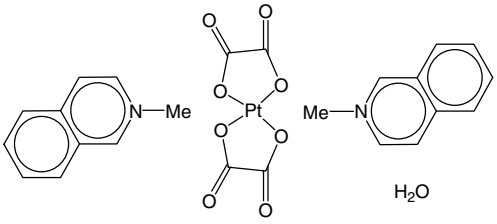
one another by steric hindrance. It may be that introduction of bulkier, non-symmetric cations might force the platinum chains further apart and lead to the production of a true molecular wire consisting of a single platinum chain.

Most of the reports on the electrical conductivity of these partially oxidized platinum polymers has simply involved investigation of their DC conductivity [22–24]. Two reports involving AC measurements appear in the literature, and were performed at 35 GHz to confirm DC measurements [25,26]. By investigating the impedance spectra of these materials over a wide frequency range, it is possible to further understand the electrical conduction processes and better understand the effect of counter ions on the electrical properties. Herein we report the synthesis of platinum nanowires with sub-micron diameters, incorporating a new and novel cation and their corresponding bulk electrical properties.

$[C_{10}H_{10}N]_2[Pt(ox)_2] \cdot H_2O$ (**1**) ($C_{10}H_{10}N$ = *N*-methylisoquinolinium, ox = oxalate) was prepared via reaction of $Ag_2[Pt(ox)_2] \cdot 2H_2O$ with $[C_{10}H_{10}N]I$. The insoluble AgI was coagulated via gentle warming (~40 °C) and filtered off under vacuum. Removal of the solvent gave the yellow product **1** (Scheme 1) in good yield and the composition was confirmed via microanalysis [Found (Calc.): C, 42.93(42.55); H, 2.70(3.27); N, 3.98(4.13)%]. A saturated solution of **1** in H_2O (4 ml) was filtered through a 1 μm-syringe filter and placed in a small electrolytic growth chamber fitted with gold wire electrodes. A 1.25 V voltage was applied and after 24 h, long dark fibers had formed. The fibers were dried in air for several days and did not undergo decomposition. Microanalysis confirmed the product to be $[C_{10}H_{10}N]_{1.6}[Pt(ox)_2] \cdot 3H_2O$ (**2**) [Found (Calc.): C, 36.82(36.63); H, 2.29(3.38); N, 3.26(3.42); Pt, 29.24(29.74)%].

A JEOL Model 6100 Scanning Electron Microscope equipped with energy dispersive spectroscopy (EDS) was used for the scanning electron microscopy (SEM) imaging and EDS analysis. A Zeiss 912 Transmission Electron Microscope was used to obtain the transmission electron microscopy (TEM) and electron diffraction images. Microanalyses were performed by Robertson-Microlit. Impedance measurements between 0.5 MHz and 20 Hz were conducted with a Wayne–Kerr 6430-B impedance analyser. Impedance measurements below 20 Hz were conducted with a Hioki 3522-50 LCR impedance analyser. Interdigitated micro-electrodes (IME 1550 M–Pt–P) were purchased from ABTECH Scientific Inc.

Electrochemical oxidation of $[C_{10}H_{10}N]_2[Pt(ox)_2] \cdot H_2O$ (**1**) leads to the formation of nanowires of $[C_{10}H_{10}N]_{1.6}[Pt(ox)_2] \cdot 3H_2O$ (**2**) of up to 1 cm in length. Imaging of this material via SEM revealed a network of fibers of approximately 2 μm or less in diameter as shown in Fig. 1. Since no wires of diameter greater than 2 μm were observed, this gives a lower bound of the aspect ratio of approximately 500. Our use of a large cation was intended to reduce or prevent molecular



Scheme 1. Chemical structure diagram of **1**.

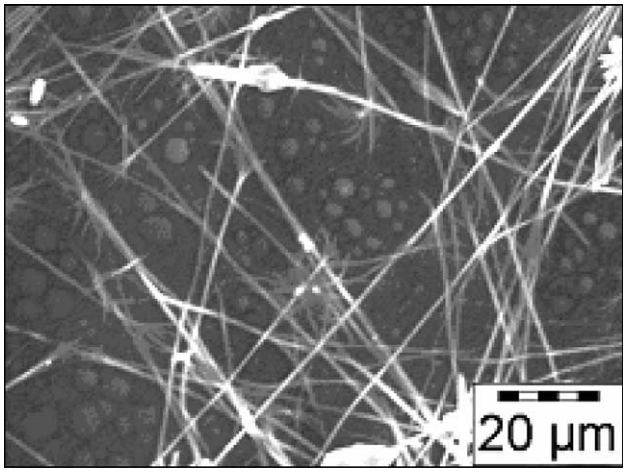


Fig. 1. SEM images of electrochemically grown platinum nanowires.

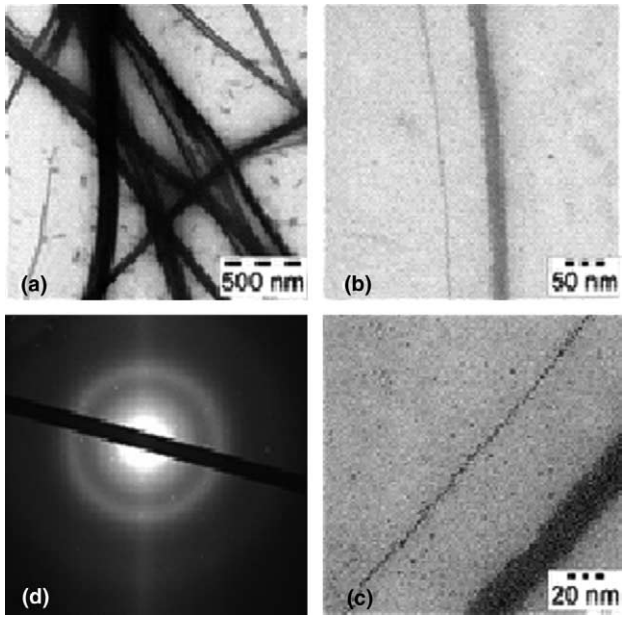


Fig. 2. TEM images and electron diffraction pattern of electrochemically grown platinum nanowires.