Growth and characterization of partially oxidized platinum polymers in nanoscale templates

B. M. ANDERSON
Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235, USA

S. K. HURST*, L. SPANGLER, E. H. ABBOTT, P. MARTELLARO
Department of Chemistry and Biochemistry, Montana State University, Bozeman, Montana 59717, USA
E-mail: shurst@montana.edu

P. J. PINHERO, E. S. PETERSON
Idaho National Laboratory, Idaho Falls, Idaho 83401, USA

The polymerization capabilities and characteristics of the electrochemically prepared partially oxidized (PO) salts of the bis(oxalato)platinate(II) (Pt-Ox) and tetra(cyano)platinate(II) (Pt-CN) complexes were investigated via optical microscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The polymers were synthesized in glass capillary templates at lengths of 900 mm, as well as through porous anodic alumina oxide (AAO) templates with pore diameters of 200 nm and 20 nm respectively. The average diameter of the unconstricted polymeric structures of PO Pt-Ox and PO potassium Pt-CN salts were found to be approximately 200 nm and 700 nm respectively. The PO Pt-Ox polymers, which are brittle in macroscale form when dehydrated, were found to possess significant flexibility on the nanoscale even after exposure to air for 2 months. During the electrochemical syntheses, the formation of the PO polymers could be directed by varying the positions and the number of electrodes. Growth of the polymers through AAO templates, caused further reduction in the diameter of the nanoscopic polymers. TEM analysis observed polymeric strands having diameters ranging from 3 nm to 5 nm and containing approximately 30 individual anionic chains. A new PO guanidinium (Guan) containing Pt-Ox complex, $(Guan)_{1.61}Pt(C_2O_4)_2 \cdot H_2O$, was synthesized and characterized.
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1. Introduction

The field of nanomaterials and particularly nanowire research has been the subject of significant recent interest [1–4]. Two materials which form nanowire structures that we have recently reinvestigated are the square planar, anionic platinum(II) salts of bis(oxalato)platinate(II) (Pt-Ox) and tetra(cyano)platinate(II) (Pt-CN) [5, 6]. These materials are of interest because of their one-dimensional electrical conductivity and optical anisotropy, however, despite the significant current interest in nanowire research these materials have received little attention in the past decade. The chemical composition of numerous Pt-Ox salts were studied and reported over 100 years ago by Söderbaum [7, 8] and many of these salts

were reinvestigated by Krogmann in the mid-1960's [9, 10] and later by other researchers [11–15]. It was observed that when certain salts of Pt-Ox were oxidized, long gold-bronze colored crystals formed. Analysis showed that these crystals were stacks of partially oxidized (PO) Pt-Ox complexes, oxidized with respect to the average charge on the platinum atoms. It was determined that upon oxidation, the platinum atoms within the complexes were bonding via the now partially filled $d_z{}^2$ orbitals which allowed metallic conduction properties to arise.

Recently, attempts to exert greater control over self-assembling structures have resulted in the use of templates in order to control the length, shape and diameter of many one-dimensional nanomaterials [16–18]. One attractive

template material is porous anodic alumina oxide (AAO), due to it's uniform pore density and diameter, and it's columnar pore structure. AAO templates are commercially available in many different sizes with varying pore diameters that are ideal for creating small arrays of nanoscale structures [19–22].

The majority of reports on these partially oxidized platinum complexes have simply involved investigation of their conductivity [15, 23]. It was our intention to examine the growth characteristics on the macro-, micro- and nanoscopic scales, and to investigate any unique growth properties which would allow us to further exploit the interesting features exclusive to these conductive inorganic nanowire structures. In the present work, we report on the physical growth characteristics from electrochemical synthesis of partially oxidized salts of Pt-Ox and Pt-CN conductive polymers within microscopic and nanoscopic templates.

2. Experimental section
2.1. General conditions, reagents and instruments
Potassium tetrachloroplatinate(II) was purchased from Pressure Chemical and used without further preparation. All other chemicals were purchased from Fisher Scientific and used without further preparation. Water was deionized and subsequently distilled to remove any metal and organic impurities. Capillary tubes were purchased from Fisher Scientific. Ultra thin capillary tubes and distorted capillary tubes were made by pulling 5 mm^3 capillary tubes over a Bunsen burner. Whatman 200 nm and 20 nm alumina oxide Anodisc^{TM} porous filters were purchased from Fisher Scientific.

2.2. Synthesis of potassium tetra(cyano)platinate(II) [K$_2$Pt(CN)$_4$·1.5H$_2$O]
To 1×10^{-4} m^3 of H$_2$O was added 1.0 g (2.4 mmol) of potassium tetrachloroplatinate(II) [24]. To the stirred solution was added 0.576 g (8.8 mmol) of KCN. The solution was allowed to stir for 1 h and the solvent was removed via rotary evaporation. The resulting yellow-green solid was redissolved in 1×10^{-6} m^3 of 50°C H$_2$O and placed in a sodium chloride ice bath whereupon a yellow-green solid precipitated. The solid was then filtered and washed with a minimal amount of cold water. The yield of K$_2$Pt(CN)$_4$·1.5H$_2$O can be increased if the solvent removal and precipitation steps are repeated. The reaction results in a 96% yield of K$_2$Pt(CN)$_4$·1.5H$_2$O.

2.3. Synthesis of the bis(oxalato)platinate(II) salts [M$_x$Pt(C$_2$O$_4$)$_2$·yH$_2$O]
Potassium bis(oxalato)platinate(II) was synthesized by following Krogmann's method [25]. To 3.0×10^{-5} m^3 of distilled water was added 0.996 g (6 mmol) of potassium oxalate. To the solution was added 0.6735 g (1.5 mmol)
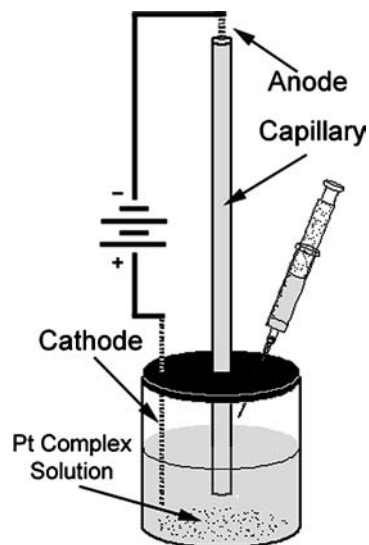

Figure 1 Illustration of the apparatus used for the polymerization of the Pt-CN and Pt-Ox salts within glass capillary templates.

of potassium tetrachloroplatinate. The reaction was allowed to stir for three days at room temperature. At the end of three days, the light green precipitate of potassium bis(oxalato)platinate(II) was clearly visible. The solution was filtered using a medium porosity glass fritted filter. The filtrate was returned to the reaction vessel and allowed to stir for another three days whereupon the solution was refiltered. The yellow-green solid was allowed to dry in a desiccator in the dark overnight. The cobalt, manganese, nickel, sodium and guanidinium [C(NH$_2$)$_3$]$^+$ salts were synthesized by using known methods [26, 27] which involved reacting the appropriate nitrate salt with the acid salt of bis(oxalato)platinate(II).

2.4. Growth of PO Pt-Ox and Pt-CN polymers in macroscopic and nanoscopic templates
The bulk synthesis of the PO Pt-CN potassium salt (K$^+$Pt-CN) and various Pt-Ox salts was performed using Miller's method [28]. A saturated solution of the appropriate Pt-Ox salt (approximately 22 kg/m^3) was electrolyzed at 1.5 V in a small Pyrex dish using a constant voltage source. After the polymerization was completed, the solvent was removed and the dark brown colored polymers were twice washed with distilled water. The polymers were allowed to dry in air.

The polymerization of the various Pt-Ox salts within capillary tubes was also performed using a variation on Miller's method [28] in conjunction with the reaction vessel shown in Fig. 1.

A small piece of platinum wire was soldered to iron wire and placed on the bottom of a 5 mL round flask. The top of the flask was sealed off with a rubber septum that had been previously perforated to allow the entry of a capillary tube. A 0.05 M solution of potassium Pt-Ox (2.0×10^{-6} m^3) was pumped into the flask and the solution was forced up the capillary tube and the top
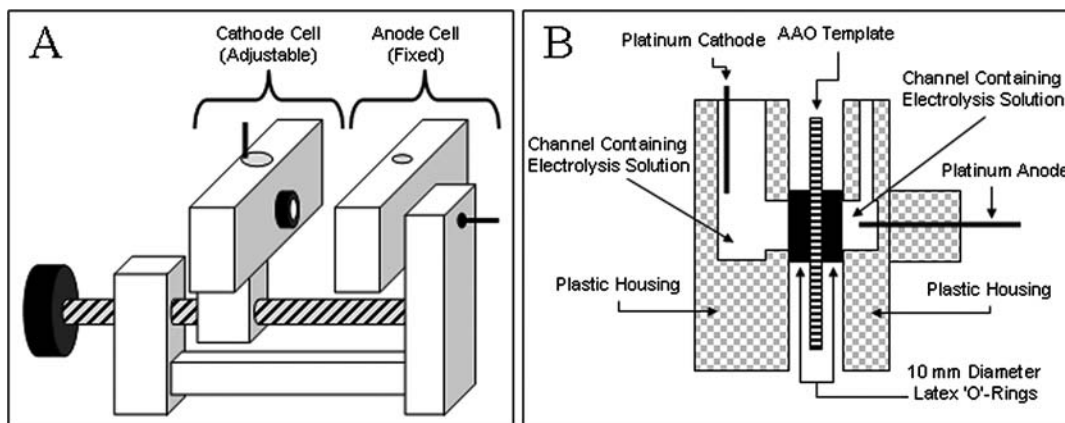
Figure 2 Block diagrams of (A) the mount used to secure the AAO templates during polymerization and (B) an expansion of the electrolysis cell portion of the mount.

of the tube was capped with a piece of platinum wire. A 1.5 V dry cell battery was connected to the two pieces of platinum wire so that the Pt wire cap was the anode. The electrolysis was allowed to continue from 1 h to 2 days depending on the inner diameter of the capillary tube.

Another reaction vessel was designed and built to allow polymerization through the AAO templates using a variation on Miller's method (Fig. 2A). This plastic electrolysis vessel consisted of an anode cell and cathode cell connected to a clamp. The anode cell was made stationary whereas the cathode cell was attached to a moveable stage.

An expansion of the electrolysis vessel used in the AAO template experiments is shown in Fig. 2B. Within each cell was made a channel to hold the solution to be electrolyzed and, to the channel opening, was attached a 10 mm wide latex 'O'-ring. The use of the stage and the flexible 'O'-rings allowed for the AAO templates to be tightly secured between the two cells using a uniform horizontal force which reduced the probability of fracturing the AAO template prior to electrolysis. The platinum wire anode was placed inline with the anode cell/cathode cell junction to reduce any disordered polymerization.

A 0.05 M solution of potassium Pt-Ox (1×10^{-6} m³) was added to the reaction vessel whereupon a dry cell battery in conjunction with a constant voltage circuit was used in order to supply a constant voltage source of approximately 1.5 V. The applied voltage was allowed to continue for 10 h whereupon the AAO template was removed, lightly rinsed with distilled water to remove any unreacted potassium Pt-Ox and allowed to air dry at room temperature for 24 h.

2.5. Fabrication of potassium Pt-CN in various templates

The synthesis of the PO K⁺Pt-CN polymers in bulk, within capillary tubes and AAO templates was performed following the same method as for the Pt-Ox salts. A 0.73 M solution of K⁺Pt-CN was used for all experiments.

2.6. Characterization of the partially oxidized bis(oxalato)platinate(II) polymers

The structural and morphological properties of the macroscopic and nanoscopic PO Pt-Ox polymers were obtained using a variety of techniques. Optical investigation was performed using a standard 10X optical microscope. Scanning Electron Microscopy (SEM) was carried out using a JEOL Model 6100 microscope. Small sections of the AAO templates were fractured and attached to the SEM sample holder using conductive carbon sticky tape. The samples were sputter coated with 1.67 nm of Au/Pd in order to increase the conductivity of the alumina surface. Transmission Electron Microscopy (TEM) was performed on a Zeiss 912 microscope using 300 mesh Formvar/carbon reinforced copper grids. Atomic Force Microscopy (AFM) was carried out on a Digital Instruments MultiMode scanning probe microscope.

3. Results and discussion
3.1. Elemental analyses of the partially oxidized Pt-Ox salts

In order to confirm that our electrochemical methodology was producing PO platinum polymers possessing the same chemical composition as those synthesized via chemical oxidation, elemental analyses were performed on the PO Pt-Ox salts of potassium, nickel, sodium, barium and the newly prepared guanidinium salt. The found and calculated molecular compositions for the five salts are listed in Table I and confirmed that that the samples were analogous to the chemically prepared complexes.

Although partially oxidized guanidinium containing Pt-CN polymers have been reported previously [29], the analogous Pt-Ox salt $(Guan)_{1.61}Pt(C_2O_4)_2 \cdot H_2O$ is reported here for the first time. The polymers of $(Guan)_{1.61}Pt(C_2O_4)_2 \cdot H_2O$ formed electrochemically, em-

TABLE I

Polymer subunit	Element	Experimentally determined percentage	Calculated percentage
$Ni_{0.8}Pt(C_2O_4)_2 \cdot 6H_2O$	Ni	8.68%	8.92%
	Pt	35.96%	37.08%
	C	9.06%	9.13%
$Na_{1.62}Pt(C_2O_4)_2 \cdot 4H_2O$	Na	7.89%	7.75%
	Pt	41.35%	40.61%
	C	10.77%	10.00%
$Ba_{0.83}Pt(C_2O_4)_2 \cdot 4H_2O$	Ba	20.43%	20.46%
	Pt	34.98%	35.01%
	C	8.81%	8.62%
$K_{1.6}Pt(C_2O_4)_2 \cdot 2H_2O$	K	12.90%	13.32%
	Pt	40.10%	41.53%
	C	9.72%	10.23%
	H	0.79%	0.86%
$Guan_{1.61}Pt(C_2O_4)_2 \cdot H_2O$	Pt	40.20%	40.15%
	C	13.94%	13.87%
	H	1.68%	2.42%
	N	14.07%	13.92%

anating from the anode as thin brown fibers and were isolated by filtration. The unoxidized parent complex $(Guan)_2Pt(C_2O_4)_2 \cdot H_2O$ has been previously reported by Sakai and coworkers [30], and although the platinum atoms stack in a one-dimensional pattern, the intermolecular Pt-Pt bond distance is 3.5876(7) Å, too large for any direct platinum bond overlap. The determination of the Degree of Partial Oxidation (DPO) for $(Guan)_{1.61}Pt(C_2O_4)_2 \cdot H_2O$ was based upon elemental analysis. Single crystals of sufficient size and quality for crystallographic examination were never isolated so it was not possible to estimate the DPO by examination of diffuse X-ray scattering.

3.2. Optical analysis and bulk experiments with the partially oxidized platinum polymers

From visual observations as well as SEM and AFM imaging of the electrochemically prepared Pt-Ox and Pt-CN crystals, it was observed that the linear chain polymer crystals were often highly flawed; possessing many branching points and structural imperfections. It was found that many flaws were visible in the PO crystals when K^+Pt-Ox or K^+Pt-CN salts were electrolytically oxidized at the maximum electrolysis voltage of 1.5 V. Since the polymerization potential is directly related to the polymerization rate, when an electrolysis voltage lower than
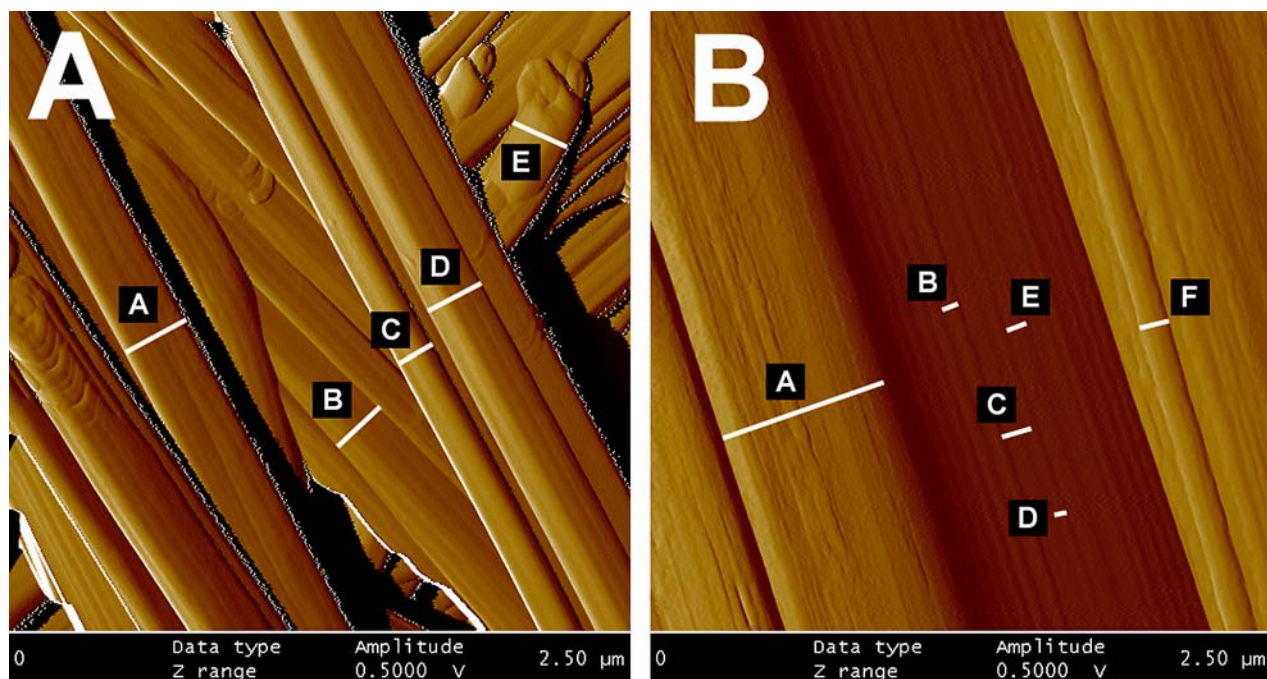

Figure 3 AFM images of (A) PO K^+Pt-Ox, A-284.6 nm, B-228.3 nm, C-157.5 nm, D-236.4 nm, E-251.9 nm. (B) PO Zn^+Pt-Ox, A-702.4 nm, B-62.0 nm, C-113.1 nm, D-41.9 nm, E-67.0 nm, F-121.2 nm.
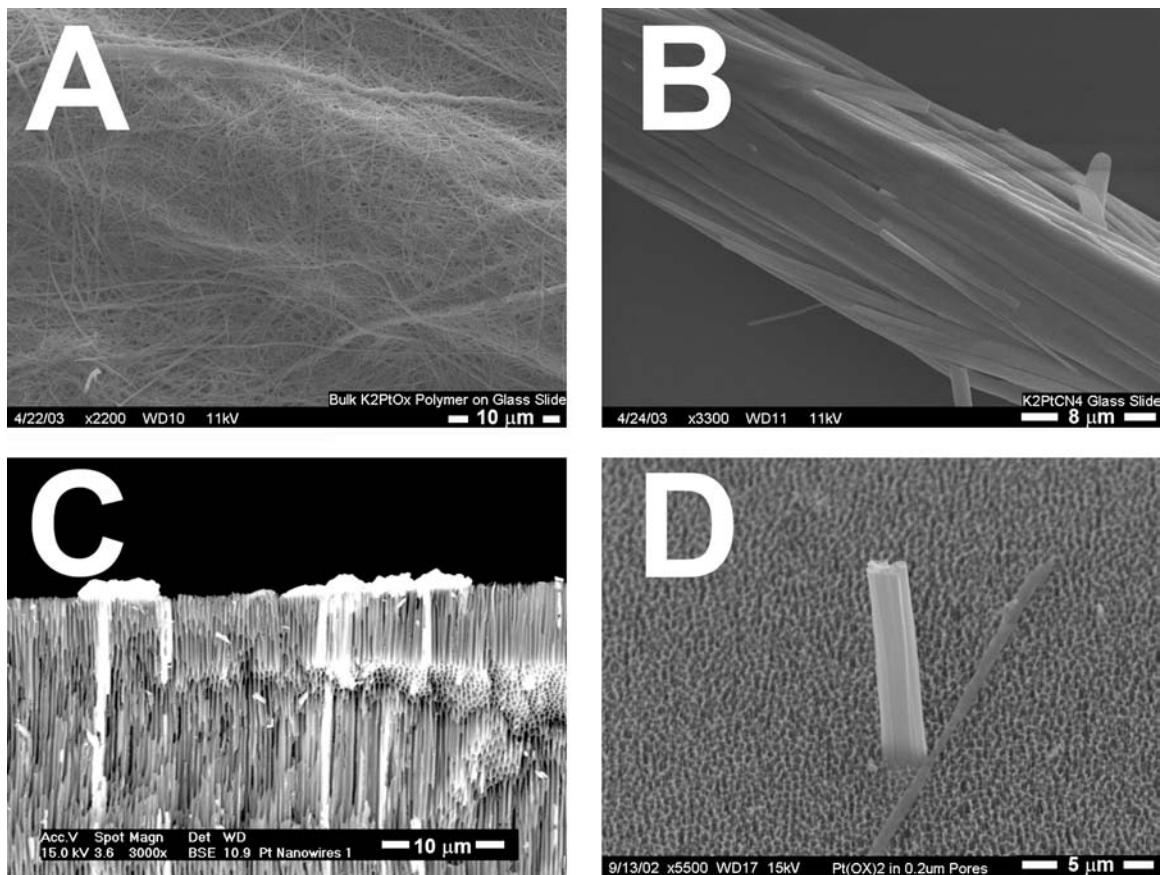
Figure 4 (A) Bulk electrolyzed PO K$^+$Pt-Ox. (B) Bulk electrolyzed PO K$^+$Pt-CN. (C) PO K$^+$Pt-CN polymers inside an AAO template (Side View). (D) An array of 200 nm PO K$^+$Pt-Ox strands.

1.5 V was used, the polymerization rate was decreased and the number of polymeric flaws was subsequently reduced.

In a set of experiments to examine the ability of the polymers to grow in highly constricted environments, capillary templates were drawn at high temperature to various lengths ranging from 130 mm to 940 mm. The inner diameter of the capillaries was thereby reduced on average from 25 μm to 1–3 μm. Previous macroscale electrolyses yielded polymers on the order of a few centimeters long,

with the use of the drawn capillaries, polymers ranging from 100 mm to 900 mm in length were formed. The rate of polymerization in these experiments was altered by the diameter of the capillary templates. The amount of time needed to begin nucleation of the PO K$^+$Pt-CN polymers within a thin capillary greatly increased as the diameter of the capillary decreased. Nucleation in unmodified capillaries normally began within 1 to 5 min, however in narrow capillaries polymerization could be delayed for up to 72 h.
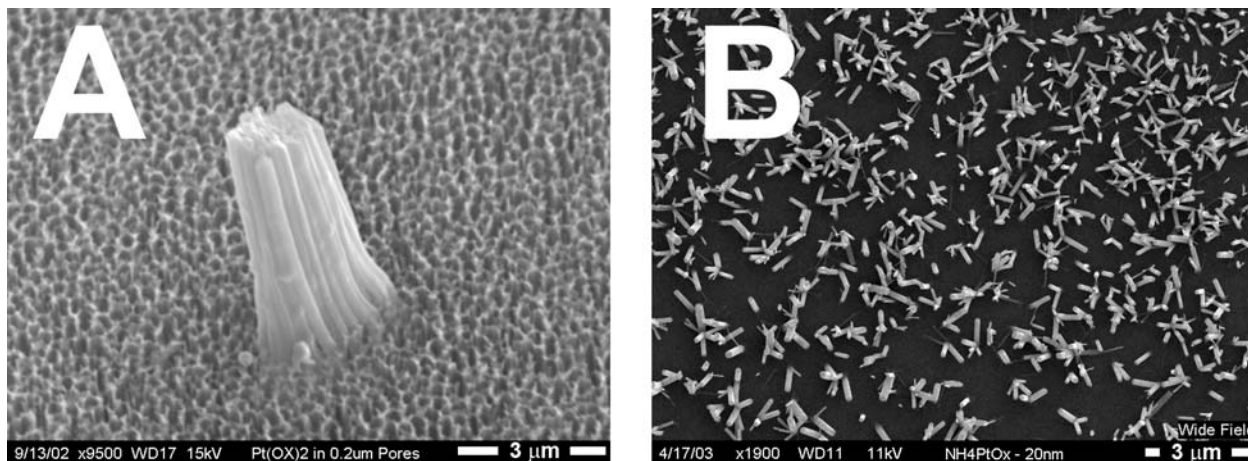

Figure 5 (A) A "tower" structure of 200 nm PO K$^+$Pt-Ox. (B) Large field of 250 nm diameter PO NH$_4$$^+$Pt-Ox columns.

The "linear chain" platinum polymers were highly flexible during the growth period and were able to navigate distortions within the capillary channels during the entire formation interval. Additionally, the use of multiple anodes caused the formation of polymers from multiple points, whereas the use of multiple cathodes caused the polymeric strands to polymerize towards the cathode in closest proximity.

3.3. AFM analysis of the partially oxidized bulk polymers

AFM analysis was performed on the macroscale PO polymers of the zinc and potassium Pt-Ox salts. As seen in Fig. 3A, the PO K^+Pt-Ox salt had a bundled substructure which runs parallel with the long, growth axis of the macroscale crystals. The microscale PO K^+Pt-Ox polymeric chains bind together to form larger, bronze colored macroscale chains. All of the polymer substructural bundles were 200 nm to 300 nm in diameter. Significant polymer branching was commonly observed when polymerization occurred at a fast rate. Fig. 3A, label E shows a flaw in a polymer bundle where polymer branching had occurred. It was observed that the PO K^+Pt-Ox polymer bundles grew with diameters of approximately 200 nm even upon branching. Fig. 3A, labels A through E all measure approximately 200 nm.

For the PO Pt-Ox zinc salt (Zn^{2+}Pt-Ox), the substructure of the macroscale polymer is less visible. Fig. 3B shows a 2.5 μm $\times$ 2.5 μm area of bulk PO Zn^{2+}Pt-Ox polymer. The bulk polymer chains for this salt polymerize with a greater diameter than that of the PO K^+Pt-Ox salt. The polymer bundle measured in Fig. 3B, label A has a diameter of approximately 700 nm which is 2.5 times larger than those polymers observed for the PO K^+Pt-Ox salt. The PO Zn^{2+}Pt-Ox macroscopic polymer bundles are more tightly packed and possess fewer defect sites. The center structure in Fig. 3B has a repeating pattern of surface features that range in size from 62 nm to 121 nm.

3.4. SEM analysis of the bulk partially oxidized polymers

Upon inspection of the SEM images of the bulk-polymerized complexes (Fig. 4), it was observed that the diameter of the PO K^+Pt-Ox polymer bundles varied between 200 nm to 450 nm when electrolyzed in bulk, yielding a superstructure consisting of intertwining, microscopic strands (Fig. 4A). In contrast, the PO K^+Pt-CN salt polymerizes with an average diameter of approximately 700 nm (Fig. 4B). The uniform, parallel growth of PO K^+Pt-CN accounts for the large single crystals that are normally formed during bulk polymerization. The SEM images of the PO K^+Pt-Ox showed significantly different features, specifically the absence of the macroscopic ordering observed in the superstructure of the PO K^+Pt-Ox polymers and the increased uniformity of the indi-
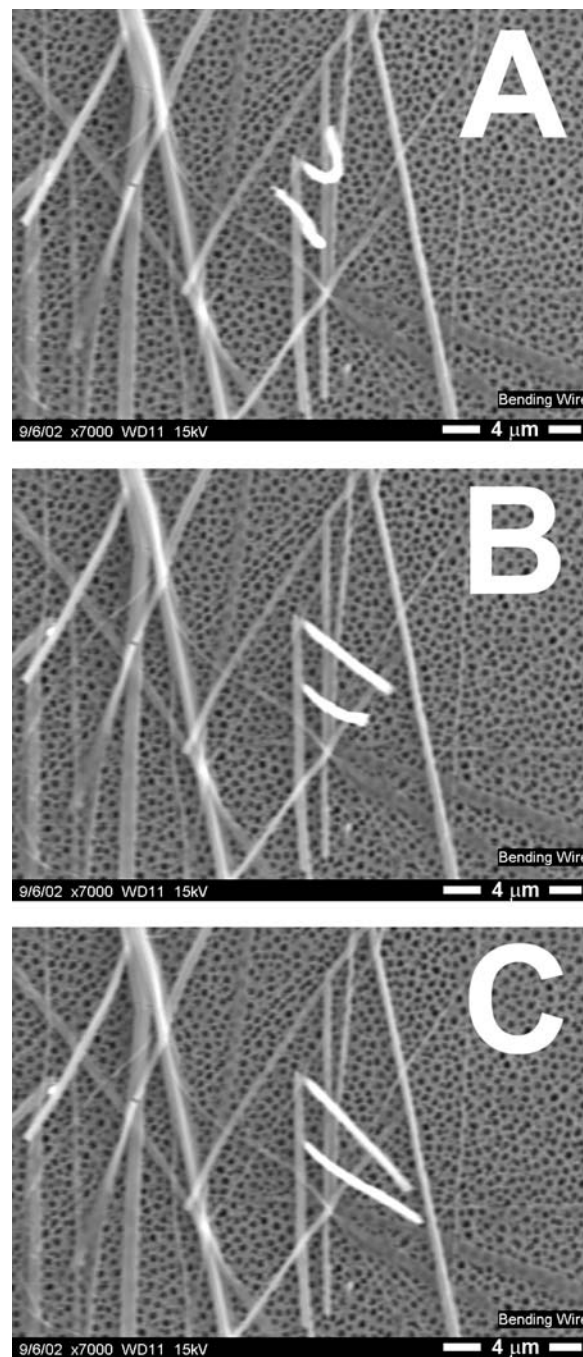

Figure 6 Two single 200 nm PO K^+Pt-Ox strands that had polymerized through an AAO filter. Each image was taken at 40 s intervals.

vidual polymer bundles. Based on the degree of bending and intertwining observed in the PO K^+Pt-Ox polymeric strands, these polymers possessed significant flexiblity on the nanoscale, which is in contrast to the brittle nature of the macroscale polymer. Conversely, bending was rarely observed in the PO K^+Pt-CN polymers.

3.5. SEM imaging of nanoscopic structures in AAO templates

Observation of microstructures grown within the pores of AAO templates by SEM has been previously reported

[22]. In the present work, Fig. 4C is a side view of a template that had been fractured and imaged along the fracture edge. The PO K⁺Pt-CN polymers appear white in the SEM images due to their higher average Z, thus increased electron backscatter, versus the surrounding template material. In order to penetrate the template channels, a number of polymeric structures had reduced in size from the average diameter of 700 nm to the channel diameter of 200 nm. In some channels the polymeric strands reached over 20 μm in length. The total length of the polymers that had penetrated the template was not explored due to instrumental limitations. The self-regulating nature of the PO K⁺Pt-CN polymer caused the polymeric chains to dynamically reduce in diameter to fit through the 200 nm channels within the AAO template.

The behavior observed in Fig. 4C for the PO K⁺Pt-CN complexes is the same for the PO Pt-Ox salts. Fig. 4D shows an array of eight polymeric PO K⁺Pt-Ox bundles that had all grown through the 200 nm porous template and that had recombined to form a larger structure. The cylindrical structure of the individual 200 nm strands was still visible even though the strands had exited the template and polymerized over 4 μm. The recombination of polymeric strands after emerging from the template was commonly observed. Linear arrays containing three, four and sixteen strands having diameters of 200 nm were observed exiting the AAO templates. Fig. 4D is a combined group of strands having a footprint of 1.6 μm × 0.7 μm and measuring 4.5 μm long. We believe that these particular bundled structures were formed when a growing polymer bundle approached the AAO template, divided in order to polymerize through the nanoscale channels and subsequently recombined after exiting the other side. The anionic nature of the platinum chains may predispose these polymers to form the bundles that we observed emerging from the AAO template.

Fig. 5A shows a close up of a single "tower-like" structure consisting of PO K⁺Pt-Ox strands which had emerged from a 200 nm AAO template. This structure possesses finer structural features which were analogous in size to the diameter of the AAO pores. One interesting feature visible in Fig. 5A is that the smaller polymers contained within the larger "tower" all have similar lengths and diameters. Fig. 5B shows a field of columnar structures of PO Ammonium Pt-Ox (NH₄⁺Pt-Ox) polymers which had emerged from a 20 nm AAO template. Although the polymers grew successfully through the 20 nm AAO template, upon emerging, they expanded to approximately 250 nm in diameter, analogous to the size of the material prepared by bulk electrolysis. No fine surface patterns were visible on the PO NH₄⁺Pt-Ox columns and it appears that they consist of a single crystalline structure.

We have noted previously that the PO Pt-Ox salts are highly flexible during the growth phase based on the synthesis of bulk materials in contorted capillaries. Figs. 6A through C show two, 200 nm PO K⁺Pt-Ox strands that had exited 200 nm wide AAO channels. These images, taken at 40 s intervals, show the two polymer strands bending approximately 90°. Bending was observed in real-time where, after approximately 2 min, the polymers ceased their "wagging" movement, finally resting in the position seen in Fig. 6C. Previous work observed that the macroscale polymers became increasingly brittle if allowed to dry in air, which was attributed to the loss of waters of crystallization. The samples observed in Figs. 6A to C were allowed to dry in air for over 1.5 months and still showed excellent flexibility. In the larger structures seen in Figs. 4D and 5, bending was also visible although to a lesser extent. Bending was also observed for templated single strands of the PO cobalt Pt-Ox salt (Co²⁺Pt-Ox). The bending observed in both samples was attributed to charging effects caused by interactions of the sample with the SEM's electron beam. The polymers on the nanoscale were therefore significantly more pliable than the same polymers on the macroscale.
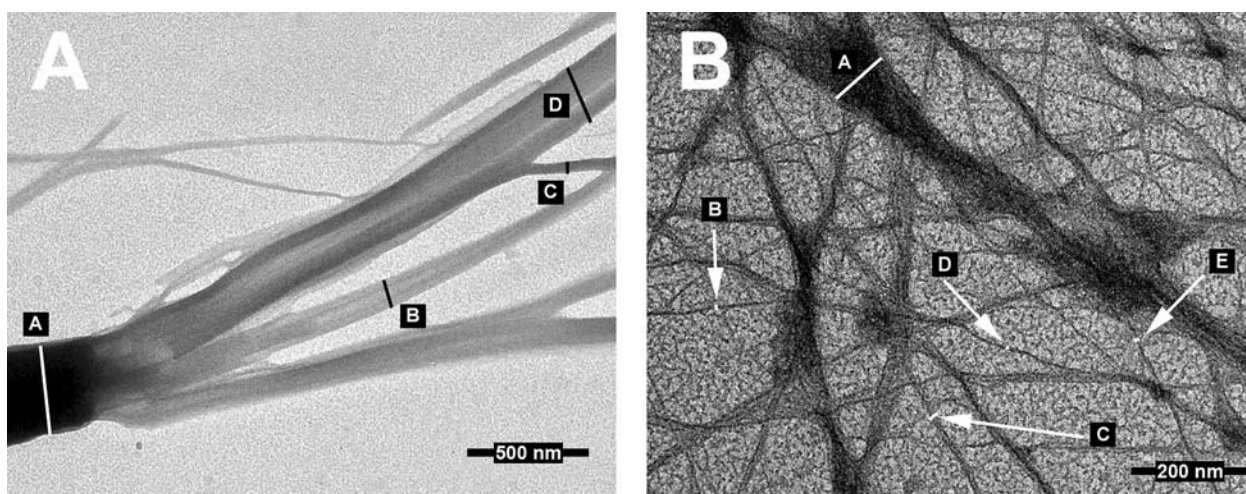

Figure 7 (A) PO Mn⁺Pt-Ox strand with multiple, smaller strands. A-308.55 nm, B-95.73 nm, C-31.04 nm, D-204.85 nm. (B) PO Mn⁺Pt-Ox nano-polymers. A-104.11 nm, B-6.71 nm, C-10.82 nm, D-5.87 nm.

3.6. TEM images of the partially oxidized Pt-Ox polymer

Fig. 7A shows a TEM image of a single, 300 nm PO Manganese Pt-Ox (Mn^{2+}Pt-Ox) bundle splitting into smaller fragments. In the upper right corner, an even smaller fragment is observed (the C labeled branch) peeling away from the larger D branch. In both the B and D branches, it was noticeable that the branches were made up of smaller bundles similar in size to that of the C branch. Fig. 7B is a high-resolution view of the PO Mn^{2+}Pt-Ox salt in which many nanoscopic strands ranging in thickness from 105 nm down to 5 nm were visible. Using the previously published unit cell dimensions for the PO Mn^{2+}Pt-Ox salt [26], it was estimated that the polymers within the 'A' and 'D' labeled strands contained approximately 9000 and 30 individual anionic chains respectively. Individual, molecular-level polymeric chains were not observed in these experiments, but may exist below the resolution of the TEM.

4. Conclusions

In the present work, we have demonstrated that the PO Pt-Ox salts and K^+Pt-CN salt form macroscopic polymeric chains consisting of smaller 200 nm and 700 nm bundles respectively. It has been demonstrated that the electrochemical polymerization of the Pt-Ox and Pt-CN linear chain polymers can be utilized to control and guide the self-assembly of the PO linear chain polymers. Conductive polymers of up to 900 mm in length were synthesized with control over their size and length. These inorganic polymers were significantly pliant during their formation and possessed high flexibility on the nanoscale, even after dehydration. During the electrochemical synthesis, the PO polymers were found to have the ability to self-regulate their diameter in order to polymerize through pores within AAO templates. PO salts of Pt-Ox with diameters below 10 nm were observed. We are currently examining the formation of complex 2-dimensional structures via synthesis of these PO polymers in multichannel arrays utilizing multiple cathodes and anodes for the construction of microscale and nanoscale electrical devices.

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