

Electronic Conductivity of Films of Electroflocculated 2 nm Iridium Oxide Nanoparticles

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ABSTRACT: The electronic conductivity of films of iridium oxide (IrO_x) composed of ca. 2 nm nanoparticles (NPs) is strongly dependent on the film oxidation state. The $\text{Ir}^{\text{IV}}\text{O}_x$ NPs can be electrochemically converted to several oxidation states, ranging from Ir^{III} to Ir^{V} oxides. The NP films exhibit a very high apparent conductivity, e.g., $10^{-2} \text{ S cm}^{-1}$, when the NPs are in the oxidized +4/+5 state. When the film is fully reduced to its Ir^{III} state, the apparent conductivity falls to $10^{-6} \text{ S cm}^{-1}$.

There is substantial literature on the potential-dependent conductivity of so-called “conducting polymers”, such as polypyrroles and polyanilines.^{1–9} In contrast, the potential dependence of the conductivity of films of very small nanoparticles (NPs) has not been widely explored. Nanoscale materials often have different electrochemical properties than their parent bulk materials. Gold nanoparticles are an excellent example; their electrochemical properties, optical properties, and conductivity differ dramatically from those bulk gold.^{10,11}

$\text{Ir}^{\text{IV}}\text{O}_x$ NPs are an interesting material, in part because of their high activity as electrocatalysts for water oxidation. The nanoparticles, with weakly ligating counterions (e.g., phosphate), can be deposited by electroflocculation (without concurrent aggregation) as very thin films from the basic medium in which they are hydrolytically prepared. Electrodes coated with their films exhibit overpotentials¹² for the water oxidation reaction that are among the lowest known. Another interesting aspect of IrO_x NPs is that all of the Ir^{IV} sites in an oxide nanoparticle, whether in a film or in solution,^{12,13} can be oxidized to Ir^{V} or reduced to Ir^{III} while exhibiting variations of formal potential signaling concurrent proton transfers.¹³ We have also reported previously on voltammetry of IrO_x NPs anchored atop self-assembled monolayers.¹⁴

The current study describes how the electronic conductivity of IrO_x films composed of 2 nm diameter IrO_x NPs changes upon oxidation of the film to the $\text{Ir}^{\text{IV/V}}\text{O}_x$ state and reduction to the $\text{Ir}^{\text{III/IV}}\text{O}_x$ state.

Figure 1a shows an image of the dual Pt working electrode used in this experiment. The electrode was fabricated by sealing two 300 μm diameter Pt wires in a two-compartment glass capillary such that the distance between the edges of the two electrodes was ca. 300 μm . An electroflocculated film of IrO_x nanoparticles was formed on the dual electrode by applying a potential of 1.2 V vs Ag/AgCl for 90 min in an IrO_x NP solution. As the film grew thicker, the two electrodes became covered and were connected to each other by the film. The electrode assembly was then transferred to an electrolyte

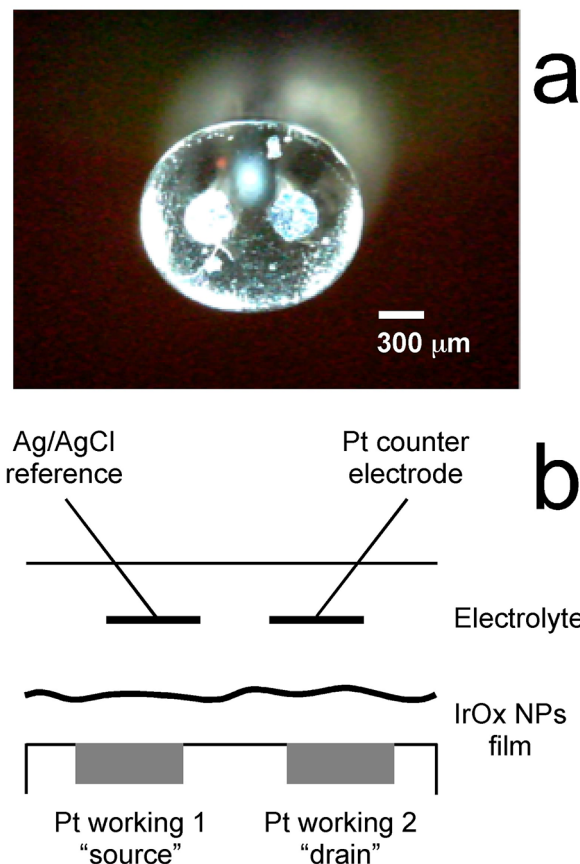


Figure 1. Image of a dual Pt working electrode and schematic of the four-electrode configuration used for conductivity measurements of an IrO_x NP film.

solution composed of 0.1 M NaOH and 2.0 M NaNO_3 for conductivity measurements using the four-electrode configuration¹⁵ shown in Figure 1b. The two IrO_x -NP-coated Pt working electrodes were biased versus one another at a constant potential difference of 20 mV. The potential of one of them was controlled with respect to a Ag/AgCl reference electrode.

Expressing the film conductivity by approximating the electrode configuration as a parallel-plate cell is highly approximate but does facilitate expressing changes in *apparent* conductivity induced by redox-state or pH changes. We express the apparent conductivity as

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$$\sigma_{\text{APP}} = \frac{di}{AV} \quad (1)$$

where d is the distance between the neighboring edges of the two exposed disks in Figure 1, i is the current flowing between them, A is the area of each disk electrode, and V is the imposed potential difference between them (here 20 mV). The two disk electrodes are labeled “source” and “drain”.

Cyclic voltammetry was performed on an IrO_x film electroflocculated onto a 2 mm diameter Pt disk electrode (Figure 2a). The film had a dark-purple-blue color. The cyclic voltammogram (CV) covers three film oxidation states: the film is Ir^{III} from -0.6 to -0.4 V, $\text{Ir}^{\text{III/IV}}$ from -0.4 to -0.1 V, and $\text{Ir}^{\text{IV/V}}$ from -0.1 to 0.4 V vs Ag/AgCl.

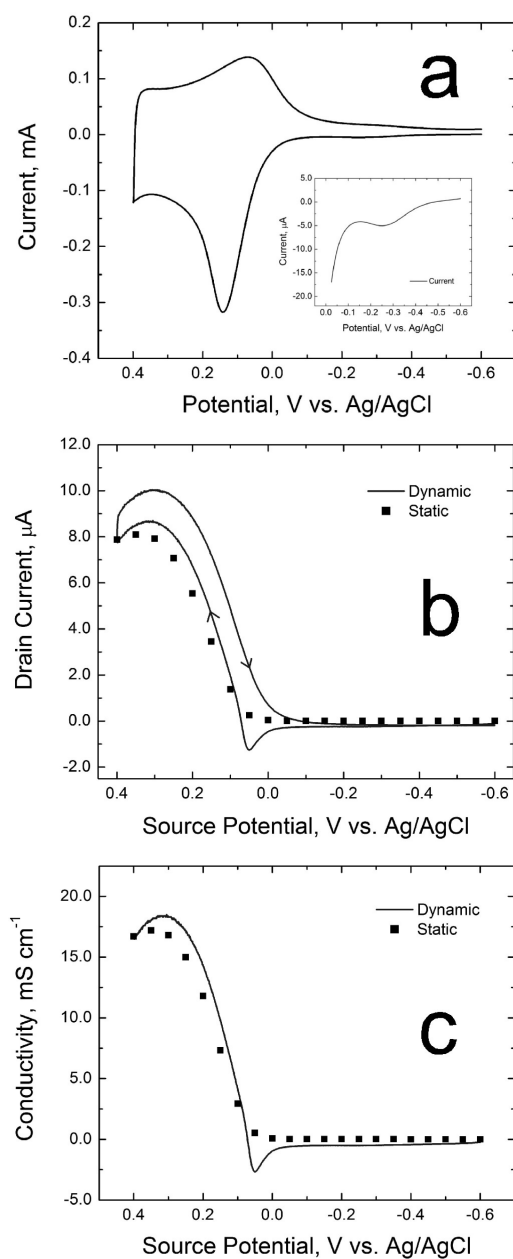


Figure 2. (a) CV of an IrO_x NP film on a Pt electrode surface. (b) Current at electrode 1 (“drain”) vs potential of electrode 2 (“source”). (c) Potential-dependent apparent conductivity of the IrO_x film.

In static measurements of the conductivity of the solvent-wetted IrO_x film at different potentials, the source electrode was held at a constant potential with respect to a Ag/AgCl reference electrode, and a 20 mV bias was applied to the drain electrode. The current between the two electrodes (Figure 2b, points) was measured after it reached a steady-state value (ca. 5 min.). The apparent conductivities of the solvent-wetted IrO_x film at different potentials (black points) are shown in Figure 2c. The conductivity of the film was ca. $5 \times 10^{-6} \text{ S cm}^{-1}$ in the Ir^{III} state and increased to ca. $1.5 \times 10^{-5} \text{ S cm}^{-1}$ in the $\text{Ir}^{\text{III/IV}}$ state. When the film was oxidized to the $\text{Ir}^{\text{IV/V}}$ state, the apparent conductivity of the film increased dramatically to ca. $1.5 \times 10^{-2} \text{ S cm}^{-1}$. There is a 4 orders of magnitude increase in the conductivity in going from the oxidized form to the reduced form of the film; the two redox potentials cross the band-edge energy.¹⁶ The film changes to its highly conductive state over the potential interval from 0.1 to 0.4 V vs Ag/AgCl.

The solid lines in Figure 2b,c show the results of a dynamic conductivity measurement on the solvent-wetted IrO_x film in which the electrode potentials were swept at 0.1 mV/s between -0.6 and 0.4 V vs Ag/AgCl (again with a 20.0 mV bias between the electrodes). Figure 2b shows the recorded drain current and Figure 2c shows the corresponding conductivity values. These two experiments together show a clear transition between the resistive and conductive regions of the IrO_x NP film. The IrO_x NP film was stable at potentials near 0.4 V vs Ag/AgCl but tended to dislodge from the electrode upon scanning to more positive potentials.

The electronic conductivity of an IrO_x film was also measured in the dry state. In this experiment, the oxidation state of the film was first set in the electrolyte solution by applying the same potential to both the source and drain electrodes. The electrode was then removed from the solution and dried under a gentle flow of Ar. The bias between the two electrodes was scanned from 0.1 to -0.1 V at 10 V/s, producing a steady-state linear i - V plot, where the slope expresses the film conductivity. When the film oxidation state was set in the reduced state (at -0.6 V vs Ag/AgCl), the measured dry film conductivity was $1.5 \times 10^{-6} \text{ S cm}^{-1}$, and when the film oxidation state was set at 0.3 V vs Ag/AgCl, the conductivity was $1.1 \times 10^{-2} \text{ S cm}^{-1}$. These values are close to the conductivity values obtained in the above solvent-wetted measurements.

The distance between the two working electrodes in the above experiment was much larger than the micrometer-scale spacings used in interdigitated array (IDA) electrodes. We found that IDA electrodes were not readily suited to the IrO_x film measurements. The positive potentials used for the IrO_x electroflocculation (and possibly the presence of chloride ions in the IrO_x NP solutions) tended to cause detachment of the IDA electrode fingers from the substrate surface. The dual Pt electrode shown in Figure 1, while less elegant than an IDA electrode, withstands the abusive experimental conditions, is easily fabricated, and can be cleaned and used repetitively.

We note that the chosen scan rate used in the dynamic solvent-wetted film conductivity measurements was very low (0.1 mV/s) relative to other film conductivity experiments^{7,8} (e.g., 20 mV/s). This choice was made because of the long distance between the source and drain electrodes and was the impetus for seeking steady-state conductivities.

The overall shape of the CV in Figure 2a differs substantially from that of an ideally behaved redox film; the reduction peak is flattened relative to the oxidation peak, and the capacitive

current in the oxidized region is quite large. These observations are analogous to CVs of conducting polymers such as polypyrrole and polythiophene.⁵ These materials are conductors in the oxidized form and poor conductors in the reduced form. While chemically quite different, the IrO_x films share these features with those traditional materials. The oxidized IrO_x NP film is quite conductive from 0.1 to 0.4 V vs Ag/AgCl, whereas its conductivity is diminished by a factor of ca. 10⁴ when the film is reduced. To our knowledge, this report is the first experimental demonstration of <2 nm IrO_x NPs having such potential-dependent electronic conductivity.

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Notes

The authors declare no competing financial interest.

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