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# Development of pH sensor by inkjet printing or layer-by-layer deposition of IrOx nanoparticles

envirobot


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## 1. INTRODUCTION

pH sensor is a common tool used in chemical laboratories since many biological and chemical reaction mechanisms are pH dependent.[1] Glass electrode is mostly used, but for environmental applications it is more advantageous to have small, portable and flexible pH sensors. Metal oxide electrodes satisfy several criteria to be useful as pH transducers. Among them, iridium oxide has more advantages compared to other materials, including response over a wider pH range, low impedance, fast response even in non-aqueous solutions, and excellent biocompatibility.[2] Iridium oxide can be produced by numerous methods, including sol-gel processes, thermal decomposition of iridium salts, sputtering, electrochemical oxidation or growth. Herein, we present two new methods for deposition of iridium oxide nanoparticles for pH sensing purposes: layer-by-layer deposition and inkjet printing of $IrO_x$.

## 2. PREPARATION OF pH SENSORS

### Synthesis of IrOx nanoparticles

**Figure 1.** Synthesis of citrate-stabilized IrOx nanoparticles performed with a method described by Mallouk and co-workers.[3]

### pH sensing characteristics of IrOx

$$Ir_2O_3 + 6H^+ + 6e^- \leftrightarrow 2Ir + 3H_2O$$

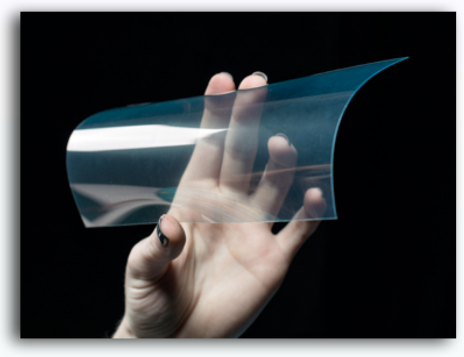
$$IrO_2 + 4H^+ + 4e^- \leftrightarrow Ir + 2H_2O$$

$$2IrO_2 + 2H^+ + 2e^- \leftrightarrow Ir_2O_3 + H_2O$$

and the redox potential is determined by

$$E = E^0 - 2.303\frac{RT}{F}\mathrm{pH} = E^0 - 0.05916 \quad \mathrm{pH}$$

### Substrate for IrOx nanoparticles



ITO/PET foil 60 Ω/sq, 125 μm thickness, *Sigma Aldrich*

FTO electrode 15 Ω/sq, 2.2 mm thickness, *Solaronix*, with 14 bilayers of IrOx/PDDA

### Layer-by-layer deposition of IrOx nanoparticles

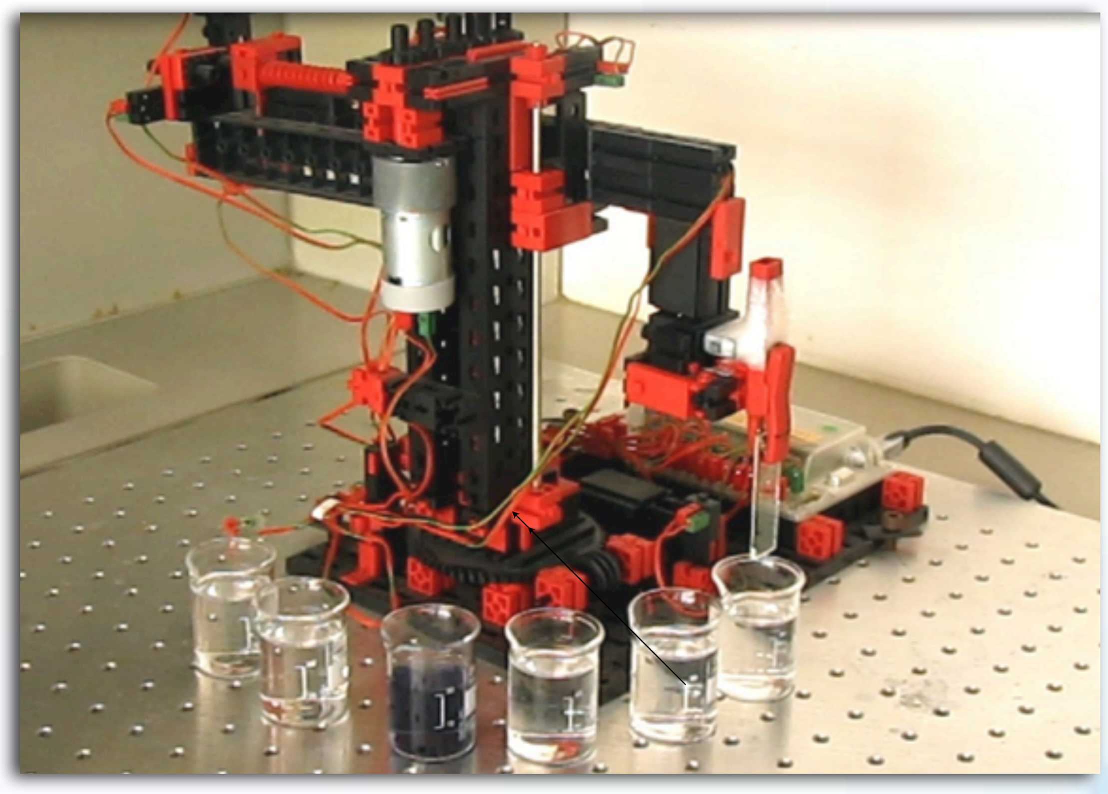


**Figure 2.** Citrate stabilized nanoparticles were deposited on fluorine-doped tin oxide substrate using layer-by-layer methodology, with cationic polymer (poly(diallyldimethylammonium chloride (PDDA)). Layer-by-layer disposition was controlled by a custom made robot. The robot sequence starts by immersing the clean FTO substrate for 15 minutes in a solution containing PDDA (4.76% p/V) in NaCl 0.4 M, then sample is rinsed twice with water. Afterwards, the slide was immersed in a 0.62 mM solution of citrate stabilized $IrO_x$ NPs during 30 minutes, rinsed twice in deionized water and finally dried. By repeating this procedure a multilayer of $IrO_x$ is obtained.

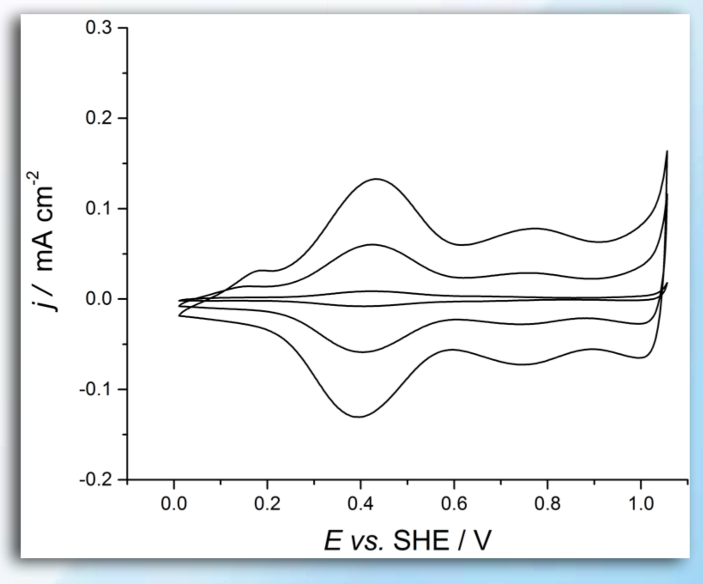



**Figure 3.** Cyclic voltammetry obtained from PDDA/$IrO_x$ films deposited on FTO: 2, 8, and 14 layers from bottom to top. Cyclic voltammograms were recorded in phosphate buffer solution (pH=7) and at a scan rate of 0.01Vs$^{-1}$.

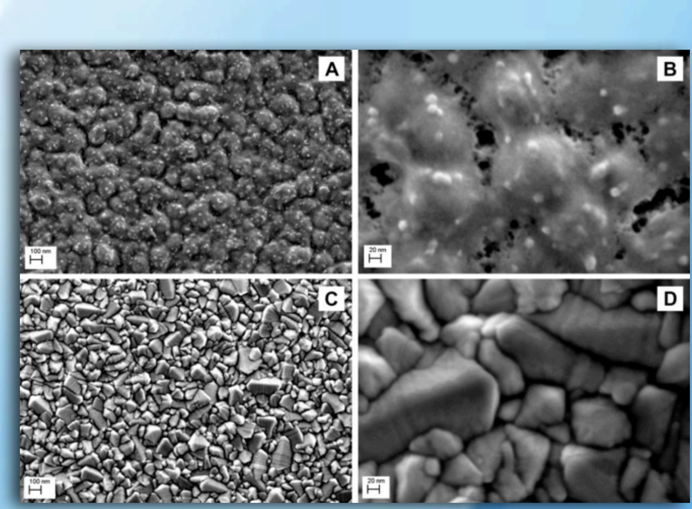



**Figure 4.** SEM images for the PDDA-$IrO_x$ modified FTO electrode prepared by the layer-by-layer methodology at two different magnifications. SEM images for the bare FTO electrode are shown in the figures C and D respectively.

### Inkjet printing of IrOx nanoparticles

**Figure 5.** Printing of IrOx NP was performed using Dimatix inkjet printer DMP-2381.
Ink was prepared by mixing of synthetized IrOx NP with Nafion and isopropanol.

Ink surface tension: 25.20 mN/m[2]

Ink viscosity: 10.37 mm[2]/s

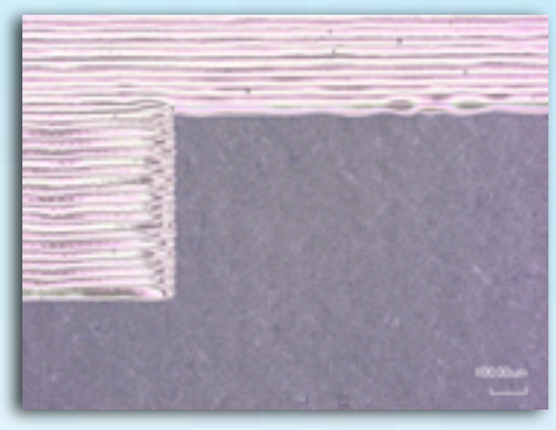


**Figure 6.** Laser-color micrograph with optical characteristics of three layers of IrOx NP on ITO/PET foil.

## 3. pH MEASUREMENTS

pH measurement were performed as chronopotentiometric measurement using the robot sequence synchronized with *Autolab* potentiostat driven by Nova 11.1 software. As a reference electrode an external Ag/AgCl (3 M KCl) was employed.

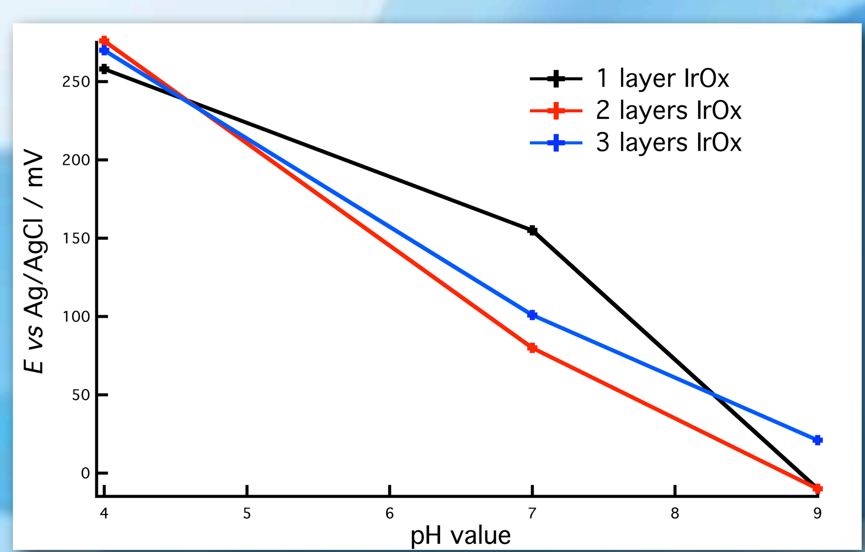



**Figure 7.** pH - potential dependence for the inkjet printed IrOx electrodes with different number of layer: 1, 2 and 3.

**Slope values:**

1 layer IrOx 52 mV/pH

2 layers IrOx 57 mV/pH

3 layers IrOx 50 mV/pH

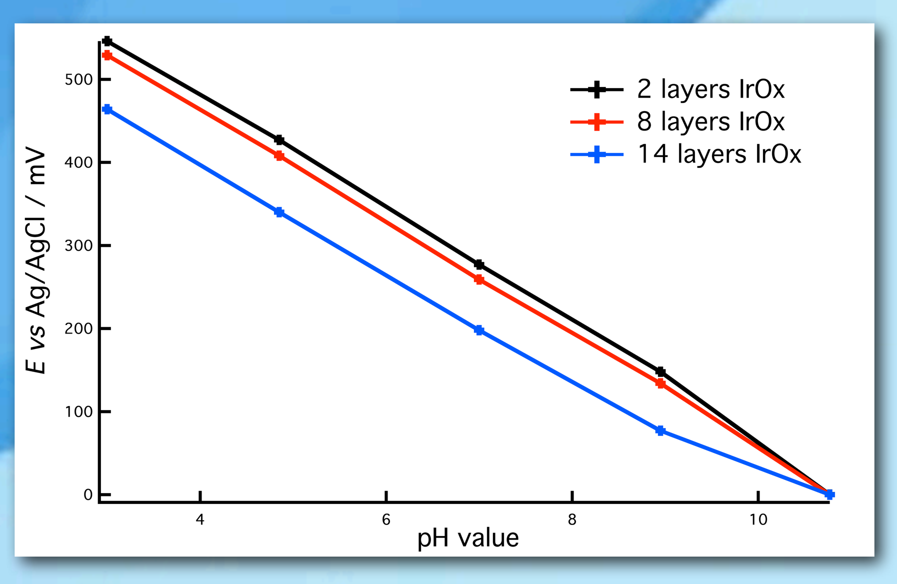



**Figure 8.** pH - potential dependence for the layer-by-layer deposited IrOx electrodes with different number of layer: 2, 8 and 14.

**Slope values:**

2 layers IrOx 69 mV/pH

8 layers IrOx 67 mV/pH

14 layers IrOx 59 mV/pH

**Theoretical value 59 mV/pH**

## 4. CONCLUSIONS AND PERSPECTIVES

Two types of IrOx pH sensitive electrodes, prepared by layer-by-layer deposition and inkjet printing of IrOx nanoparticles, were employed for pH measurement. Both of them give sensitivity equal or close to theoretical value of 59 mV/pH and can be used as portable pH sensor for on-field environmental monitoring. By optimizing the number of IrOx layers better pH sensitivity can be achieved. Future work will be focused on development of internal reference electrode and implementation of present strategy into the Envirobot module.

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### References


**1.** Huang, W. D.; Cao, H.; Deb, S.; Chiao, M.; Chiao, J. C. Sensors and Actuators A: Physical (2011) 169, 1-11.

2. Prats-Alfonso, E; Abad, L.; Casan-Pastor, N.; Gonzalo-Ruiz, J.; Bardlich, E. Biosensor and Bioelectronics (2013) 39, 163-169.

3. Hara, M.; Mallouk, T. E.; Chem Comm. (2000) 1903-1904


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