# Polyaniline Nanoparticles for Sensing Applications

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## Introduction

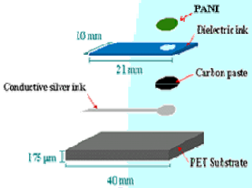
Conducting polymers are being widely employed in the manufacture of nanostructured sensors due to breakthroughs in the development of sophisticated nano-sized forms. One of the most attractive conducting polymers is polyaniline (PANI) due to its interesting electrical, electrochemical and optical properties, such as air stability and simple acid/base doping/dedoping chemistry. However, the fact that aniline is a carcinogenic monomer, its insolubility in common solvents and the acidic conditions required to the most conductive form of PANI are made its commercial application very difficult so far. The synthesis of PANI nanoparticles using dodecylbenzenesulphonic acid (DBSA) as both dopant and surfactant have allowed the use of this polymer in aqueous media, improving its processability. The additional use of ammonium persulphate (APS) as an oxidant together with DBSA during chemical PANI polymerization have led to the creation of a spherical PANI nanoparticle aqueous dispersion. Such dispersion can be deposited onto the electrodes by means of traditional methods, such as drop coating, or using more sophisticated techniques, such as inkjet printing.

The application of PANI nanoparticles inkjet printed onto carbon paste screen-printed electrodes for ascorbic acid sensing is shown in the present work.

## Inkjet printing as a Deposition Tool

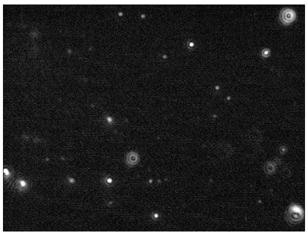
Inkjet printing is a non-contact printing method that allows us to pattern our conducting polymers onto different substrates in a low-cost and high precision way. In this work, a piezoelectric drop-on-demand inkjet printer was used to deposit our PANI nanoparticle ink. In this device, deformation of the piezoceramic material confined in the printhead increase the pressure inside the nozzles, causing the ejection of an ink drop through the orifice, .

Carbon-paste screen-printed electrodes were fabricated in-house and were used as electrode platforms for depositing PANI nanoparticles. PANI was inkjet printed using a Commercial Research Fuji Dimatix printer.



## Characterization of PANI Nanoparticles

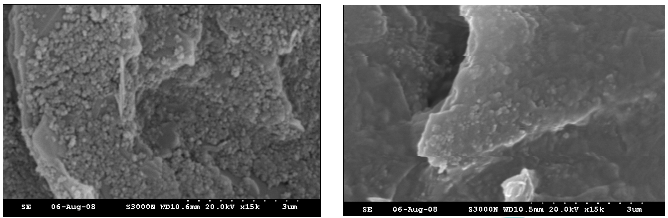
PANI nanoparticles were synthesized by the rapid mixing method. The use of DBSA as dopant during the polymerization induces a spherical nanoparticulate growth, leading to a inkjet printable PANI-DBSA nanodispersion. The size of the resulting nanoparticles is a key factor for its later use as an inkjet printable material. Typical inkjet nozzle size is ~20-30µm, which means that PANI must be a stable nanodispersion to avoid the nozzle orifice blocking.



Visualization of PANI nanoparticles using NANOSIGHT system. This technique allows the real time visualization of nanoscale particles in liquids as well as nanoparticles sizing. The system comprises a metallised optical element illuminated by laser beam at the surface of which nanoscale particles in suspension (500µl) can be directly visualized using only a conventional optical microscope. The program analyses the paths that the particles take under Brownian motion over a suitable period of time (10-20s) in order to calculate nanoparticle size. For PANI aqueous nanodispersion, PANI size is about 75nm.

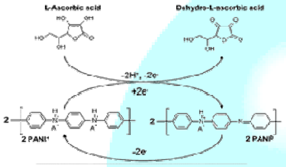
## Characterization of Inkjet Printed PANI Films

Scanning Electron Microscopy images obtained on a bare carbon-paste screen-printed electrode (left) and an PANI film inkjet printed (20 layers) on top of the carbon-paste electrode. A rough, nodular surface can be observed on the bare carbon paste due to the particulate nature of the paste. In contrast, a smooth surface was observed for the PANI-modified carbon paste, due to the infill of the carbon structure by the PANI nanoparticles.

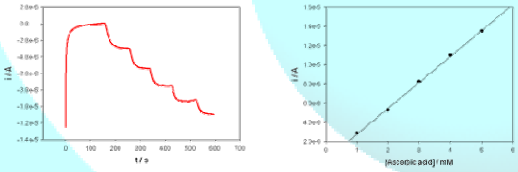


## Inkjet Printed PANI for Ascorbic Acid Sensing

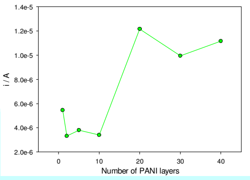
At pH=6.8 (experimental conditions) , ascorbic acid is present as ascorbate. The oxidation of L-ascorbate to dehydro-L-ascorbic acid is a two electron transfer process that is enhanced in the presence of PANI. At neutral pH, polyaniline exists as the emeraldine salt. Two oxidized polyaniline monomers (2PANI$^+$) react with L-ascorbic acid, carrying out the oxidation of the ascorbate to dehydro-L-ascorbic acid whereas reduced PANI (2PANI$^0$) is reoxidized at the electrode



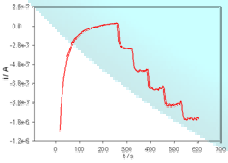
Amperometric curve (left) at 0 V vs Ag/AgCl for 600 s in PBS pH=6.8. Catalytic response of an inkjet printed PANI-modified electrode (20 layers) when ascorbic acid was added to solution (1 - 5 mM). Calibration curve (right) for ascorbic acid sensing. The data corresponds to the previous modified electrode measured in PBS pH=6.8, when ascorbic acid (1 – 5 mM) was added.



Optimization of the number of inkjet printed PANI layers (i.e., film thickness). Standard procedure was carried out using electrodes inkjet printed with a range of PANI layers (0 - 40). The analysis of the catalytic responses when [ascorbic acid] in solution was 5 mM was carried out. The dependence of the response on the number of inkjet printed PANI layers is shown in the graph (right). It can be observed that the catalytic response increased as the number of PANI layers was increased up to an optimum of 20 layers Increasing the number of layers of PANI beyond 20 did not result in higher responses.



## Measurement of ascorbic acid in fresh oranges



Amperometric curve at 0 V vs Ag/AgCl for 600 s in PBS (pH = 6.8). Catalytic response of a inkjet printed PANI film (20 layers) when juice from an orange was added to the solution (100 - 500 µl). Using a standard calibration curve, the concentration of ascorbic acid found in the natural orange juice was 0.32 mM.

Inkjet printing was found to be an ideal deposition tool for the polyaniline dispersions, given its stability and nanoparticulate nature in an aqueous system. The particle size in solution was found to be of about 75 nm using the NANOSIGHT system making it suitable for piezoelectric inkjet printing. Inkjet printed PANI films on carbon-paste electrodes resulted in an excellent platform for ascorbic acid sensing, where 20 printed layers of polymer was found to be optimal. The application of this sensor for measuring ascorbic acid in oranges was demonstrated.