Inkjet Printable Organic-Inorganic Hybrids Based On Polyaniline

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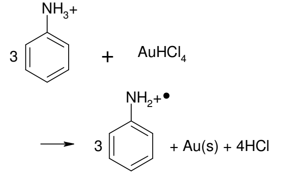
Introduction

Polyaniline (PANI) is an organic polymer that has generated significant interest as an electrically conductive material component, and is used in applications such as sensors and flexible displays. A significant number of PANI-based devices have been prepared using inkjet printing; a fabrication technique favoured for its additive patterning ability and its efficient use of material.

Combining precious metals and conducting organic polymers through compositing provides combinatorial materials, potentially possessing both the properties of the metallic component and the conducting polymer, as well as unique ensuing properties due to the compositing itself. The type of research is critical for driving innovation in materials research. Exploiting an established oxidative polymerisation protocol for producing stable nanodispersions of PANI was used where the standard oxidant was replaced with $HAuCl_4$ or $AgNO_3$ at a range of monomer:oxidant ratios to produce a range of composite dispersions. The morphology and populations of the metallic structures (including spherical nanoparticles and nano-whiskers), as well as the quality of the PANI were shown to be influenced by the concentration and type of oxidant used.

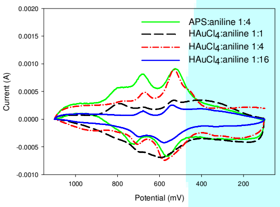
This area of research is currently in its infancy where the research is focusing on demonstrating composite synthesis rather than the application of these materials for device fabrication. However, anticipated applications of these composite materials include noble metal deposition, electro-catalysis, neural tissue engineering, sensors, photovoltaic cells and memory devices.

PANI-Au Hybrids

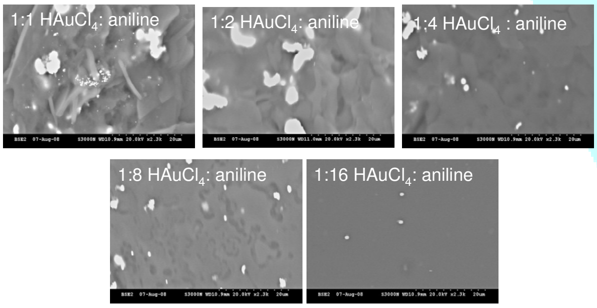


Inkjet printable polyaniline-gold (PANI-Au) dispersions were synthesised according to the reaction scheme (left). The synthesis was carried out in the presence of dodecylbenzene sulphonic acid (DBSA) in order to produce a spherical nanoparticulate form of PANI, as well as stabilising the metallic Au particles that were produced on reduction of $HAuCl_4$.

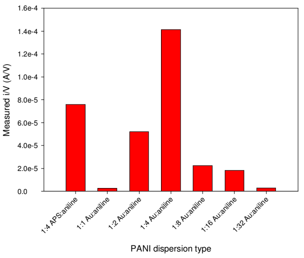
By varying the amount of $HAuCl_4$ used, the size, morphology and population of the gold within the polymer was controllable. It was shown however, that the metallic gold particles contained within the resulting dispersions did not seem to affect the conductivity of the PANI, but that by varying the amount of $HAuCl_4$ used, the quality of the PANI produced could be affected. The polymer synthesised using a ratio of 1:0.25 aniline:HAuCl4 was shown to be optimum as it resulted in a PANI dispersion with high conjugation lengths and doping levels (UV-Vis data not shown), as well as high conductivity and well-defined electrochemistry.



CVs of electrodes modified with the materials synthesised using different HAuCl4:aniline dispersions. Voltammograms performed in 1 M HCl vs. Ag/AgCl (scan rate: 500 mVs^{-1})

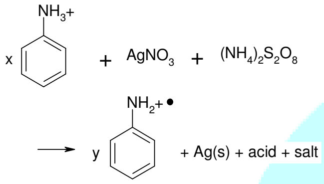


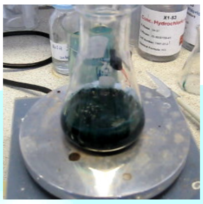
SEM images of cast PANI-Au films. The ratio of $HAuCl_4$:aniline was varied for the syntheses of each of the dispersions All images taken in backscattered electron (BSE) mode.



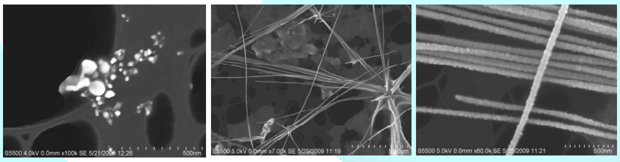
Histogram showing the measured slopes of the current-to-voltage plots for inkjet printed films of the different PANI-Au composites inkjet printed to inter-digitated electrodes. Measurements based on the slope of the current-to-voltage curves (see inset) obtained when sweeping the potential between ±1 V.

PANI-Ag Hybrids



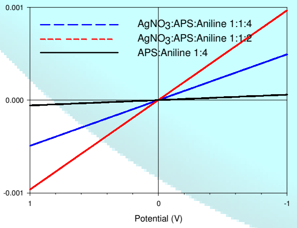


PANI-Ag was synthesised according to the reaction scheme (above). APS was added as Ag(I) could not polymerise the aniline alone. It was found that the polymerisation reaction in the presence of APS and Ag(I) was at least 30 times faster than the reaction where no silver salt was present. Transition metals are known to greatly facilitate the decomposition of persulphate allowing the production of Ag(II) which is capable of performing the oxidation of the aniline. The exact mechanism is not yet fully elucidated, but it is hypothesised that the persulphate ion is not only responsible for the oxidation but also the Ag(II) that is generated in situ.



FE-SEM images of cast PANI-Ag films. Silver particles aswell as silver wires were observed in the resulting films.

PANI nanoparticle-based formulation – starting material ratios	Film resistance/ kΩ
APS:Aniline 1:4	12.1
$AgNO_3$:APS:Aniline 1:1:2	0.98
$AgNO_3$:APS:Aniline 1:1:4	2.31



Presence of metallic silver resulted in dramatically increased conductivity compared to pure PANI. It may be that the percolation threshold of silver was reached within the material which contributed to the enhanced conductivity. Alternatively, it could be that the novel route to oxidation of the PANI resulted in a more conductive material. Experiments are ongoing to elucidate the reasons for the increase in conductivity

Conclusion Developing hybrid systems comprising of PANI and noble metals has to date produced some interesting materials. It is clear that the morphology of the metallic components and the properties of the hybrid material can be varied depending on the metal and the reaction conditions used. For the PANI-Au hybrid, the population and morphology of the metallic gold was controlled by the initial concentration of $HAuCl_4$. The presence of the metallic gold did not affect the conductivity of the resulting polymer films as the percolation threshold of the gold was not reached. On the otherhand, the presence of silver had a direct, dramatic effect on the conductivity of the hybrid.