

# Polyaniline-Silver Hybrid Materials For Ink-Jet Printing



Hannah Hayes, Karl Crowley, Malcolm R. Smyth, Aoife Morrin\*

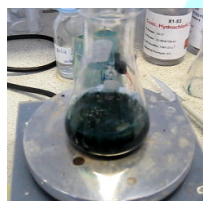
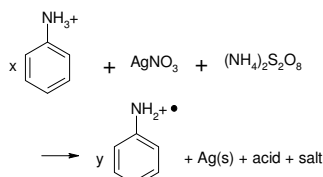
National Centre for Sensor Research, School of Chemical Sciences, Dublin City University, Dublin 9

\*email address: aoife.morrin@dcu.ie

## Introduction

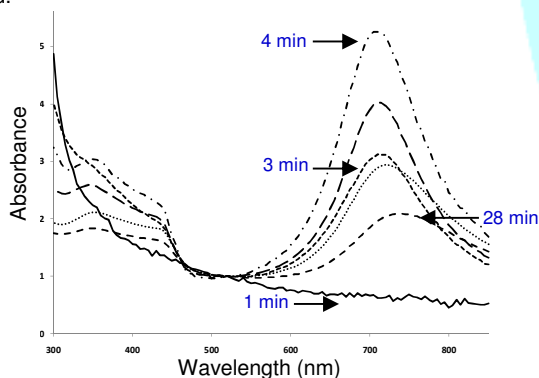
The synthesis of PANI/Ag hybrid materials has been carried out via a rapid chemical oxidative, in-situ polymerisation method, using silver nitrate and ammonium peroxydisulfate as oxidant precursors. These species react together to produce  $Ag_2^+$ , an oxidising intermediate which has greater oxidising power than either persulphate or  $Ag^+$  alone. The reaction thus proceeds at a much accelerated rate than that of pure PANI, approximately 6 times faster. Various characterisation techniques were used to characterise this new hybrid material, PANI-Ag. UV-vis absorption spectroscopy was used to follow the formation of polymer over time and monitor the rate at which the reaction progresses for both PANI and PANI-silver. It is evident from the absorption spectra that the polymer forms via the fully-oxidised pernigraniline state initially, before reducing back into the more stable emeraldine salt form. This process is significantly accelerated using both APS and  $AgNO_3$ , as opposed to when using APS or  $AgNO_3$  alone. These new composites could potentially find use as functional materials for the printed electronics industry where new processable, hybrid materials as required for applications in sensing, memory, logic and photovoltaics.

## Synthesis



PANI-Ag was synthesised according to this reaction scheme. APS was added along with  $AgNO_3$  to aniline. The polymerisation reaction in the presence of APS and  $Ag(I)$  was at least 30 times faster than the reaction where only APS was present.

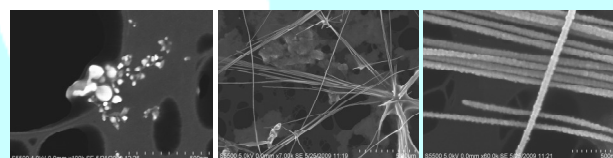
Transition metals can facilitate the decomposition of persulphate allowing the production of  $Ag(II)$  which is capable of performing the oxidation of the aniline. The exact mechanism is not yet fully elucidated, but it is hypothesised that the persulphate ion is not only responsible for the oxidation but also the  $Ag(II)$  that is generated in situ.



The progression of the synthesis of PANI-Ag was monitored by UV-Vis spectroscopy. Figure 2 shows the spectra at different time intervals. Initially, after one minute, no polymerisation has occurred. By 3 minutes, polymerisation is initiated and the typical PANI bands were observed.

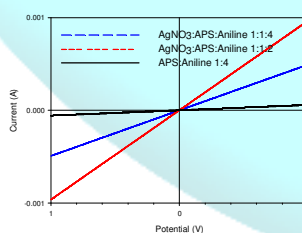
The band at  $\sim 730$  nm increases in absorbance and shifts to shorter wavelengths with increasing time up to 4 min. It has been previously reported that as this peak grows in absorbance and shifts to shorter wavelengths (blue-shift), the PANI becomes more oxidised, and as the absorbance decreases slightly and the peak is shifted to longer wavelengths (red-shift) PANI becomes reduced.

When APS only is used as oxidant, PANI only exhibits a colour change from after a period of approx. 45 minutes, thus indicating the accelerated speed at which polymerisation occurs when  $AgNO_3$  is used in conjunction with APS and the level of oxidation which occurs. PANI-Ag in this system is being oxidised to the pernigraniline state for a number of minutes before being reduced back to the emeraldine state.



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

PANI nanoparticle-based formulation – starting material ratios	Film resistance/ k $\Omega$
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 other hand, the presence of silver had a direct, dramatic effect on the conductivity of the hybrid.