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REVIEW

Printing polyaniline for sensor applications

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In recent years, much research has focused on the development of low-cost, printed electrochemical sensor platforms for environmental monitoring and clinical diagnostics. Much effort in this area has been based on utilising the redox properties of conducting polymers, particularly polyaniline (PANI). In tackling the inherent lack of processability exhibited by these materials, several groups have examined various mass-amenable fabrication approaches to obtain suitable thin films of PANI for sensing applications. Specifically, the approaches investigated over the years include the in situ chemical synthesis of PANI, the use of sulphonated derivatives of PANI and the synthesis of aqueous-based nano-dispersions of PANI. Nano-dispersions have shown a great deal of promise for sensing applications, given that they are inkjet-printable, facilitating the patterning of conducting polymer directly to the substrate. We have shown that inkjet-printed films of PANI can be finely controlled in terms of their two-dimensional pattern, thickness, and conductivity, highlighting the level of precision achievable by inkjet printing. Utilising these nanomaterials as inkjet-printable inks opens novel, facile, and economical possibilities for conducting polymer-printed electronic applications in areas of sensing, but also many other application areas such as energy storage, displays, organic light-emitting diodes. Given that inkjet-printing is a scalable manufacturing technique, it renders possible the large-scale production of devices such as sensors for a range of applications. Several successes have emerged from our work and from the work of others in the area of applying PANI in low-cost sensor applications, which is the focus of this review.
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Electrochemical polymerisation of PANI for sensor applications

Electrochemical polymerisation, as a means of modifying electrode surfaces with conducting polymers, has been reported since the early 1980s (Ohsaka et al., 1984; Wang et al., 1986). It has long since been considered the method of choice for the purpose of electrode modification for sensor fabrication. The generally accepted mechanism for the electropolymerisation of aniline (Zotti et al., 1988) is presented in Fig. 1. Formation of the radical cation of aniline by oxidation on the electrode surface is considered the rate-determining step. Radical cation formation is followed by coupling of the radicals and elimination of protons. The dimer thus formed then undergoes oxidation on the electrode surface along with aniline. The radical cation of the oligomer couples with an aniline radical cation, resulting in propagation of the chain. The polymer thus formed is doped by acid present in the solution (Wallace et al., 2003).

In recent decades, this electrochemical polymerisation approach has been widely used in chemical- and bio-sensor fabrication, given the reproducible control over film thickness and the film stability that it imparts (Casella & Guascito, 1997; Grennan et al., 2003; Mu & Kan, 2002; Myler et al., 2005; Oliveira et al., 2012; Trojanowicz et al., 1995). Electropolymerised PANI and other conducting polymers have been used successfully in many electrochemical sen-

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