Nano silver diffusion behaviour on conductive polymer during doping process for high voltage application

A Mohammad¹*, A Mahmood¹, K T Chin¹, M K Danquah², S van Stratan¹

¹Department of Mechanical Engineering, Curtin University Sarawak Campus, Faculty of Engineering and Science, Miri 98009, Sarawak, Malaysia
²Department of Chemical Engineering, Curtin University Sarawak Campus, Faculty of Engineering and Science, Miri 98009, Sarawak, Malaysia

*Email: mohammad.asyraf@postgrad.curtin.edu.my

Abstract: Conductive polymer had opened a new era of engineering for microelectronics and semiconductor applications. However, it is still a challenge for high voltage applications due to lower electrical conductivity compare to metals. This results tremendous energy losses during transmission and restricts its usage. In order to address such problem a novel method was investigated using nano silver particle doped iodothiophene since silver is the highest electrical conductive material. The experiments were carried out to study the organometallic diffusion behaviour of nanosilver doped iodothiophene with different concentration of iodothiophene. Five different mixing ratio between nanosilver and the solution of iodothiophene dissolved in diethyl ether were used which are 1:1.25, 1:1.5, 1:2.5, 1:3 and 1:5. It was revealed that there is an effective threshold concentration of which the nano silver evenly distributed and there was no coagulation observed. These parameters laid the foundation of better doping process between the nano silver and the polymer significantly which would contribute developing conductive polymer towards high voltage application for industries that are vulnerable to corrosive environment.

1. Introduction

Conductive polymers are recently discovered polymers that were found to conduct electricity. Some conductive polymers had found the purpose in the semiconductor and microelectronics (Kar, 2013a). Also, the conductive polymer resistance to corrosion are deemed to be good substitutes for metal conductors.

However, the application in the high voltage industries is still a challenge due to limited charge transfer capabilities that only provide lower conductivities (Taherian, 2016). Polythiophene (PT) is one of such conductive polymer. PT has a good solubility in organic solvents like diethyl-ether and good environmental stability properties (Ansari, 2006). Figure 1 below shows the structure of PT.

Figure 1. Polythiophene structure
Intrinsically conductive polymers are highly resistive for electricity flow (Kar, 2013b). In order to make it conductive, they had to undergo doping process (Kar, 2013c). Doping process defined as introducing impurities into a pure substance to enhance its electrical conductivity (Kar, 2013b). PT had been doped with both metallic as well as non-metallic known dopants such as copper (Shanmugapriya and Velraj, 2016) and HClO4 (S Masubuchi et al., 1993), etc. There were also attempts to dope PT with other techniques such as using microwave plasma deposition (Paosawatyanong et al., 2010) and binary organic solvent such as dichloromethane (Jeon et al., 2010) to study the electrical conductivities of that end product.

Among metallic dopant, silver is known as highest electrical conductivity (Fackler, 2011). Multiple attempts had been done before in doping of PT with silver. But these studies had been focused on other area such as photocurrent enhancement (Szeremeta et al., 2014, Bagheri et al., 2016), solar properties enhancement (Liu et al., 2014), and electrode fabrication (Ghanbari, 2014), etc. It is hypothesized that small sizes particle of silver will enhance the charge transfer in the resulted organometallic compound of the PT during doping process in monomer stage (Kong and Jang, 2006). i.e. High electrical conductivity could be achieved through doping nano silver particle with iodothiophene, a monomer of PT.

However, the coagulation and uniform distribution of the nano particle in the iodothiophene monomers are the issues that hamper the effective diffusion during doping process. In order to address such issue, the effect of iodothiophene concentrations to the nano particle is one of the important parameters.

In this paper, the effect of iodothiophene concentrations to the nano particle was investigated. The homogenous nano particles distribution in different iodothiophene concentrations would qualitatively indicate the effective threshold concentration of iodothiophene monomers. It is expected this finding would laid the foundation of better doping process between the nano silver and iodothiophene monomers significantly in order to developed conductive polymer for high voltage application.

2. Experimental

2.1 Materials and preparation

All materials used in this study were supplied by Sigma- Aldrich. The iodothiophene assay is 98% in liquid form. It is stored in temperature around 2-8°C. The nano silver powders are 99% trace metal. 1 mg of nano silver was taken inside the test tube with diethyl ether as a solvent. Then, 1.25mL iodothiophene were added into the test tube. The processes were repeated with 1.50mL, 2.5mL, 3.00mL, and 5.00mL of iodothiophene. The test tubes were then placed in the water bath of ultrasonic cleaner for 15 minutes and left for air drying for 60 minutes. Then, the samples were oven dried for 24 hours.

2.2 Design of experiment

Five different samples concentrations were prepared. The amount of nano silver, diethyl ether and iodothiophene used are displayed in the Table 1 Experiment design for effect of concentration of iodothiophene below.
Table 1. Experiment design for effect of concentration of iodothiophene

| Sample  | Nano Silver (mg) | Diethyl Ether (mL) | Iodothiophene (mL) |
|---------|------------------|--------------------|--------------------|
| KRX1B   | 1                | 0.02               | 1.25               |
| KRX2B   | 1                | 0.02               | 1.50               |
| KRX3B   | 1                | 0.02               | 2.50               |
| KRX4B   | 1                | 0.02               | 3.00               |
| KRX5B   | 1                | 0.02               | 5.00               |

3. Result and Discussion

The diffusion behaviour with distribution and coagulation of nano silver particles are shown in the micrographs Figure 2. It is interesting to note there are distinct distributions of nano silver particles between concentrations of iodothiophene solutions. Several black spots were observed on sample KRX1B (Figure 2) which indicates significant coagulations of the nano silver particles.

![Figure 2(a)](image1)

![Figure 2(b)](image2)

**Figure 2(a)** and **(b)**. KRX2B with (a) 5X magnification and (b) 10X magnification
Similar behaviour was observed for sample KRX2B (Figure 3). It is shown black spots indicating coagulations of nano silver particles (Figure 3). This indicates that the nano silver had not been fully diffused due to the low concentration of iodothiophene.

![Figure 3(a) and (b). KRX2B with (a) 5X magnification and (b) 10X magnification](image)

As per stoichiometry, it can be deduced that the nano silver diffusion had been influenced by iodothiophene concentration. Reaction had stopped when all of the iodothiophene had been saturated with nano silver. The remaining nano silver particles were coagulated and form the black spots. This would indicate that the 1.25mL and 1.5mL of iodothiophene are not sufficient to react completely with 1mg of nano silver. The nano silver is considered to be in excess. However, the sample KRX3B as shown in Figure 4 below shows no black spots visible from the microscopy images. This would indicate that the nano silver had been evenly distributed and there is no coagulation occurred.
It is revealed that this is the concentration which the right concentration of iodothiophene is needed for 1mg of nano silver. Moreover, KRX4B (Figure 5) and KRX5B (Figure 6) shows the similar behaviour of even distribution of the particles as in the KRX3B (Figure 4). However, it can be deduced that all of the nano silver particles had reacted to the iodothiophene. Hence, it is considered as excess reactants, where all of the nano silver had been consumed but the iodothiophene are in excess. However, the two large void spots on both KRX4B (Figure 5) and KRX5B (Figure 6) are not coagulations. They are marks of labelling sticker at the back of the slides and can be ignored.
The following Table 2 were constructed to simplify the results.

| Sample  | Ratio of nano silver to iodothiophene | Observation                        |
|---------|---------------------------------------|------------------------------------|
| KRX1B   | 1.25                                  | Coagulation                        |
| KRX2B   | 1.50                                  | Coagulation                        |
| KRX3B   | 2.50                                  | No coagulation                     |
| KRX4B   | 3.00                                  | No coagulation, excess reactants   |
| KRX5B   | 5.00                                  | No coagulation, excess reactants   |
4. Conclusions

In this study, nano silver particles were added into iodothiophene solution. The effects of iodothiophene concentration on the coagulation and distribution of nano silver were studied. It is revealed that the threshold concentration for 1mg of nano silver is 2.5mL of iodothiophene in 0.02mL. Coagulation will occur in lower concentration of iodothiophene as in 1:1.25 and 1:1.5 ratio of nano silver to iodothiophene. Homogenous distribution was observed at higher concentrations of iodothiophene in 1: 2.5 onwards such as in 1:3.00 and 1:5.00. It is also found that there is an effect of concentration of iodothiophene towards homogenous distribution of nano silver during doping process.

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