Study on the electrical properties of polypyrrole nanowires/silica composites

Z J Weng\(^1\), Z W Zhao\(^1,3\), Y Fang\(^4\), J D Wu\(^1\) and H L Jiang\(^2\)

\(^1\)School of Electronic Science and Engineering, Southeast University, Nanjing 210096, P. R. China
\(^2\)State Key Laboratory of Lake Science and Environment, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, 73 East Beijing Road, Nanjing 210008, P. R. China

E-mail: Zhao_zw@seu.edu.cn

Abstract. In recent years, conductive composites have been attracted more attentions, but their applications and developments are restricted by the deficiency of the research on conductive mechanism. The electrical conductivity and percolation threshold of silica (SiO\(_2\)) matrix with different particle sizes using polypyrrole nanowires (PPy-NWs) as fillers are experimentally investigated. The results show that the electrical properties of PPy-NWs/SiO\(_2\) composites typically exhibit a non-linear percolation behavior. PPy-NWs/SiO\(_2\) (30 nm) nanocomposites need more filler content to achieve percolation threshold compared to that of PPy-NWs/SiO\(_2\) composites with 2 \(\mu\)m SiO\(_2\) particles as matrix. The conductive behavior of these composites is the result of the interaction and competition of various conductive mechanisms. The difference in electrical properties of PPy-NWs/SiO\(_2\) composites with different particle size SiO\(_2\) as matrix is attributed to the effect of matrix size on tunnelling conduction and the establishment of conductive pathways. Moreover, a two-dimensional conductive network model filled with PPy-NWs and an effective electrical resistivity model of PPy-NWs/SiO\(_2\) composites were established. The simulation models can reflect the electrical properties of conductive composites, and are well agreement with the experimental data.

1. Introduction
Conductive polymers, with superior properties that are suited to a broad range of applications, have gained considerable attentions [1-3]. The advantageous properties of conductive polymers can be combined with those of inorganic materials, and these materials are referred to as “conductive polymer/inorganic composites” [4-6]. Conductive polymer/inorganic composites are highly functional materials that enabled a plethora of new applications ranging from electronics to bioengineering [7, 8]. It has long been pursued to optimize the relationship between the properties of conductive polymer and inorganic materials to satisfy specific applications.

There is an increasing interest in the development of conductive polymer/inorganic composites due to the presence of functionalities, such as their excellent electrical properties [8-11]. However, the conductive mechanism of conductive polymer/inorganic composites is not well understood, and the challenge to optimize the proportion of conductive polymer for achieving better efficiencies still remains. In previous work, typical conductive theories of polymer composites such as percolation theory [12] and quantum tunneling theory [13], were used to study the insulator-to-conductor transition and percolation network formation using randomly-orientated anisotropic fillers in
disordered mixtures [14-16]. Moreover, several researchers have attempted to extend the application of percolation theory to predict the critical volume fraction of fillers required to achieve electrical conduction [17, 18].

In this work, the matrix size-dependency of the electrical resistivity of polypyrrole nanowires/SiO$_2$ (PPy-NWs/SiO$_2$) composites and the proportion of PPy-NWs that participate in electrical conduction are studied over a wide range of PPy-NWs content, accompanied by analysis of the conductive behavior combined with previous typical conductive theory of polymer composites. Moreover, an extension of this work was also carried out by establishing a two-dimensional (2D) percolation-based model and an effective electrical resistivity model to help study the conductive behavior of PPy-NWs/SiO$_2$ composites.

2. Experimental

2.1 Materials

All chemicals were of analytical grade and used without further treatment except additional description. The composites matrix used in this study was pure SiO$_2$ particles specified with micro-size (2 µm) and nano-size (30 nm) and obtained from Nanjing Hongde Company (China) and Shandong Xiya Reagent Company (China), respectively. Pyrrole (Py) with 98% purity and LiClO$_4$ were both purchased from Sinopharm Chemical Reagent Co., Ltd. Na$_2$HPO$_4$ was purchased from Nanjing Ningshi Chemical Reagent Co., Ltd. Deionized water was used for all aqueous solutions.

2.2 Preparation of PPy-NWs/SiO$_2$ composites

PPy-NWs were fabricated by template-free electrochemical polymerization using LiClO$_4$ as dopant as described in the reference [19]. Briefly, 0.2 M Na$_2$HPO$_4$, and 0.05 M LiClO$_4$ was added in deionized water. Py (0.15 M) was then added to the above solution and subjected to vigorous magnetic stirring at room temperature for 30 min. The room-temperature electropolymerization was performed in a three-electrode electrochemical cell including a working electrode (Ni sheet), a reference electrode (saturated calomel electrode, SCE) and a counter electrode (Pt sheet). A CHI600D electrochemical working station system (Shanghai Chenhua Instrument Co., Ltd. China) was used for controlling the current applied on the working electrode. Upon a constant potential of 0.8 V applied, the PPy-NWs were formed. The PPy-NWs sample was then carefully rinsed by deionized water to remove the absorbed species and air-dried at room temperature.

PPy-NWs/SiO$_2$ composites were prepared by simple mechanical mixing with different PPy-NWs loading and different SiO$_2$ size. At first, pure SiO$_2$ with average diameter of 2 µm and PPy-NWs were air dried at 100°C for 1 h to remove the moisture. After that, PPy-NWs/SiO$_2$ (2 µm) composites with different PPy-NWs loading (≈ 5, 10, 15, 20, 25, 30, 35, 40, 45 wt%) were prepared by simple mechanical mixing using constant speed solid mixer for 15 min and compression molded at 10 MPa pressure. PPy-NWs/SiO$_2$ (30 nm) nanocomposites with PPy-NWs loading (≈ 5, 10, 15, 20, 25, 30, 35, 40, 45, 50 wt%) series as above but respective different SiO$_2$ size were also prepared using the same method.

2.3 Characterizations

Surface morphologies of the composites were examined using scanning electron microscope (SEM) (Quanta 200, FEI Ltd, US). The elemental analysis was conducted by energy dispersive X-ray (EDX). Fourier transform-infrared (FT-IR) measurement was employed to characterize the structure of the composites. Electrical resistivity measurements were carried out by 4-probe method using high resistance meter (ST2254) and powder meter (ST2722) (Suzhou Jingge Electronic Co., Ltd, China).

3. Simulation method

To understand the electrical behavior and investigate how different parameters (e.g., intrinsic resistance and concentration) affect electrical properties of the composite system, a two-dimensional
(2D) percolation-based model and an effective electrical resistivity model were created.

Firstly, a 2D straight PPy-NWs network was generated in the x-y plane by considering each PPy-NW to be a line segment with a length $l$ randomly distributed in the region of $20 \mu m \times 20 \mu m$. The line segments are identified by three parameters: central point coordinates $(x_0, y_0)$, predefined length $l$, and direction angle $\theta$ (defined as the angle from the x-axis to the line segment counterclockwise). Then the occurring of electrical percolation behavior as a result of the formation of a continuous conductive network [17, 18] was evaluated as a function of PPy-NW concentration. Besides, the composite system was set up with random state of the components (e.g., PPy-NWs, SiO$_2$) by mathematical description. Then an equivalent electrical circuit of the composite system was obtained based on the idea that the resistance through the composite system is the result of a series of a large number of resistors combined in series and parallel [20]. The conductive behavior of the circuit of the composite system could be simulated using HSPICE software and the model-predicted results on the effective electrical resistivity of composites were thus obtained.

4. Results and discussion

4.1 Microstructure of the composites

Figure 1. SEM images of PPy-NWs (30 wt%)/SiO$_2$ composites with micron-sized SiO$_2$ particles as matrix (left) and nano-sized SiO$_2$ particles as matrix (right).

Figure 2. EDX results of the PPy-NWs (30 wt%)/SiO$_2$ (nano-sized) composites.

Figure 1 shows the SEM images of the PPy-NWs (30 wt%)/SiO$_2$ composites with micron-sized SiO$_2$ particles (left) and nano-sized SiO$_2$ particles (right). The length of the separate nanowires without any branching was on the order of microns and the diameter varied in the range from dozens of nanometers to two hundred nanometers, which is similar to Chen’s work [19]. As can be seen in figure 1, the micron-sized SiO$_2$ particles and nano-sized SiO$_2$ particles exhibited distinctly different distribution states. Micron-sized SiO$_2$ exhibited much denser agglomerate with less compressible space and nano-sized SiO$_2$ was more evenly distributed around the PPy-NWs. The formation of the
4.2 Electrical resistivity

Figure 4(a) shows the electrical resistivity of PPy-NWs/SiO\(_2\) (2 \(\mu\)m) composites. There is a general trend of decrease in the electrical resistivity with increasing PPy-NWs. The electrical resistivity decreases much more dramatically from 7.62\(\times10^7\) \(\Omega\)-cm at 10 wt% PPy-NWs loading to 8.65\(\times10^3\) \(\Omega\)-cm at 30 wt% PPy-NWs loading. The electrical resistivity is stable up to 40 wt% PPy-NWs loading and the \(\rho\) value of 2.08\(\times10^3\) \(\Omega\)-cm was achieved. This trend is consistent with the non-linear percolation theory. The effect of filler content on PPy-NWs/SiO\(_2\) (30 nm) nanocomposites electrical
resistivity is shown in figure 4(b). The resistivity variation of the PPy-NWs/SiO$_2$ (30 nm) nanocomposites is similar to that of PPy-NWs/SiO$_2$ (2 μm) composites, but an abrupt decrease occurs when much more PPy-NWs are introduced into the PPy-NWs/SiO$_2$ (30 nm) nanocomposites. The increase of PPy-NWs content in the PPy-NWs/SiO$_2$ (30 nm) nanocomposites from 15 wt% to 50 wt% led to a dramatic decrease in the electrical resistivity from 6.98×10$^5$ Ω·cm to 8.62×10$^3$ Ω·cm.

The percolation model [12] predicts that, near a metal-insulator (or conductor-perfect conductor) phase transition, the conductivity (or resistivity) will be given by the percolation equation:

$$\sigma_m = \sigma_h (\phi - \phi_c)^t$$  \hspace{1cm} (1)

Where $\sigma_m$ is composite conductivity (S/cm), $\sigma_h$ is filler conductivity, $\phi$ is filler volume fraction ($\phi$> $\phi_c$), $\phi_c$ is percolation threshold and $t$ is critical exponent.

The values of $\phi_c$ and $t$ were determined by fitting the experimental data to equation (1). The estimated values of $\phi_c$ and $t$ for PPy-NWs/SiO$_2$ (2 μm) composites are ≈ 24.69 wt% and 1.33. For PPy-NWs/SiO$_2$ (30 nm) nanocomposites, the estimated values of $\phi_c$ and $t$ are ≈ 26.38 wt% and 3.21, respectively. The difference in $\phi_c$ and $t$ of PPy-NWs/SiO$_2$ (2 μm) composites and PPy-NWs/SiO$_2$ (30 nm) nanocomposites can be attributed to the particle size of matrix SiO$_2$ and its interaction with PPy-NWs.

Basically, the change in electrical resistivity of PPy-NWs/SiO$_2$ composites with different PPy-NWs loadings could be explained by typical conductive theory. Initially, the electrical resistivity of the pure SiO$_2$ particles was not affected with small amount of PPy-NWs in the composites. The electrical resistivity in the composites might be decreased with further increasing of PPy-NWs loading because of tunneling mechanism effect [13, 14]. Electrically conductive PPy-NWs are randomly dispersed into the SiO$_2$ matrix in a margin of nm apart. Here, tunneling of the electrons happened among the adjacent PPy-NWs through SiO$_2$ matrix with high resistivity or even they are separated by insulating gaps [13]. During this process, tunneling is sensitive to the distance between the PPy-NWs [14], thus highly affected by the SiO$_2$ matrix size. From SEM images in figure 1, PPy-NWs were partly covered by nano-SiO$_2$ matrix with high resistivity and more difficult to contact with each other exactly compared with PPy-NWs/SiO$_2$ (2 μm) composites. The electrical contact between PPy-NWs will be less and contact resistance among them will be high for composites consisting of PPy-NWs and nano-size SiO$_2$. Thus, It was observed that by using SiO$_2$ nanoparticles as matrix, the percolation threshold of PPy-NWs/SiO$_2$ (30 nm) nanocomposites would move towards an increased filler content and exhibit higher resistivity. With PPy-NWs loading at critical concentration, known as percolation threshold [12], the rapid change in electrical resistivity by several orders of magnitude was coincided with the formation of continuous interconnected conductive network chains of PPy-NWs throughout the composites [12, 17, 18]. At this time PPy-NWs are supposed to be connected and PPy-NWs/SiO$_2$ composites show lower electrical resistivity.

Figure 5 shows the simulation results of PPy-NWs/SiO$_2$ composites. The percolation probability simulation results are shown in figure 5(a). State 1 consists of very few PPy-NWs randomly dispersed into the SiO$_2$ matrix. State 2 is the indication for the formation of continuous interconnected conductive network chains of PPy-NWs throughout the composite system. The 2D percolation-based model predicted that the percolation probability increase with increasing number of PPy-NWs. As shown in figure 5(b), the simulated resistivity value of PPy-NWs/SiO$_2$ (2 μm) composites decreased proportionally with the amount of PPy-NWs. It was noteworthy that the increase of PPy-NWs content from 20 wt% to 40 wt% led to a dramatic decrease in the simulated resistivity from 1.58×10$^8$ Ω·cm to 9.68×10$^5$ Ω·cm. The resistivity variation of the composites obtained by simulation is generally consistent with that obtained by experimental measurement, but the percolation threshold value by the simulation is higher than that obtained by experiment due to the super length-diameter ratio of PPy-NWs which is conducive to the formation of conductive network.
5. Conclusions

The electrical resistivity and percolation threshold of PPy-NWs/SiO$_2$ (2 µm) composites and PPy-NWs/SiO$_2$ (30 nm) nanocomposites were studied. The corresponding percolation threshold of PPy-NWs/SiO$_2$ (2 µm) composites and PPy-NWs/SiO$_2$ (30 nm) nanocomposites were determined according to experimental results using a percolation model. The electrical resistivity of PPy-NWs/SiO$_2$ composites strongly depends on the concentration of PPy-NWs. Compared with PPy-NWs/SiO$_2$ (2 µm) composites, PPy-NWs/SiO$_2$ (30 nm) nanocomposites have higher resistivity and higher percolation threshold. This difference can be attributed to the effect of SiO$_2$ matrix size, which is evidenced by SEM measurement. In addition, the 2D conductive network simulation model filled with PPy-NWs can reflect the effects of the number of PPy-NWs on the structure of conductive network and predict the percolation probability of composites well. The electrical resistivity predicted by the effective electrical resistivity model shows the similar trend as experimental results and the effective electrical resistivity model gives an estimation of percolation threshold.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (No.: 51879042, 51839011).

References

[1] Kumar G M, Ilanchezhiyan P, Jin K, Park J and Jayavel R 2013 Sensor Actuat A-Phys. 199 283-8
[2] Zhao J X, Wang J, Deng H M, Tang S, Lan Q, Liang J Y, Liu C, Cao Y C and Cheng S J 2019 J Nanosci. Nanotechno. 19 5656-60
[3] Ramirez A M R, Gacitua M A, Ortega E, Diaz F R and del Valle M A 2019 Electrochem. Commun. 102 94-8
[4] Zhitomirsky I 2007 J. Alloy Compd. 434 823-5
[5] Xiaofeng L U, Chao D, Chen J, Zhang W and Wei Y 2006 MatL. 60 2851-4
[6] Anakli D, Cetinkaya S and Karakisia M 2018 Materials Focus. 7 515-8
[7] Chen P P, Hao L, Wu W J, Li Y F and Wang J T 2016 Electrochim. Acta. 212 426-39
[8] Ju H and Kim J 2016 Chem. Eng. J. 297 66-73
[9] Granström M and Inganäs O 1995 Poly. 36 2867-72
[10] Cai Z and Martin C R 1989 J. Am. Chem. Soc. 111 4138-9
[11] Maiti S, Suin S, Shrivastava N K and Khatua B B 2014 Rsc Advances. 4 7979
[12] Kirkpatrick S 1973 RvMP. 45 574-88
[13] Balberg I 1987 PhRvL. 59 1305-8
[14] Maiti S, Shrivastava N K, Suin S and Khatua B B 2013 Express Polym. Lett. 7 505-18
[15] Jagota M and Tansu N 2015 Sci. Rep. 5 10219
[16] Langley D P, Lagrange M, Giusti G, Jimenez C, Brechet Y, Nguyen N D and Bellet D 2014 Nanoscale. 6 13535-43
[17] Han F, Maloth T, Lubineau G, Yaldiz R and Tevtia A 2018 Sci. Rep. 8 17494
[18] Lee B M and Loh K J 2015 JMatS. 50 2973-83
[19] Chen Y Q, Zhao Z W and Wang C 2013 Nanosci. Nanotech. Let. 5 186-90
[20] Ruschau G R, Yoshikawa S and Newnham R E 1992 JAP. 72 953-9
[21] Wan X B, Zhang W, Jin S, Xue G, You Q D and Che B 1999 J. Electroanal. Chem. 470 23-30
[22] Sankir N D and Dogan B 2010 J. Mat. S. 45 6424-32
[23] Chen H S, Sun Z Y and Shao J C 2011 B. Chin. Ceram. Soc. 04 934-7