

## Polyindole Nanowires: Synthesis, Characterization and Electrochemical Sensing Property<sup>†</sup>

K. GIRIBABU<sup>a</sup>, R. MANIGANDAN<sup>a</sup>, R. SURESH<sup>a</sup>,  
L. VIJAYALAKSHMI<sup>b</sup>, A. STEPHEN<sup>c</sup> and V. NARAYANAN<sup>a\*</sup>

<sup>a</sup>Department of Inorganic Chemistry, University of Madras, Guindy Campus,  
Chennai-600 025, Tamilnadu, India

<sup>b</sup>Vidhya Sagar Women's College, Chengalpattu, Kancheepuram-603211, India

<sup>c</sup>Department of Nuclear Physics, University of Madras, Guindy Campus,  
Chennai-600 025, Tamilnadu, India

*vnnara@yahoo.co.in*

Received 19 January 2013 / Accepted 15 February 2013

**Abstract:** Polyindole nanowires were synthesized by oxidative polymerization of indole using ammonium persulphate as oxidant. The structure of polyindole nanowires was confirmed by XRD, FT-IR spectroscopy. The FT-IR of polyindole nanowires shows a peak at  $1480\text{ cm}^{-1}$  which corresponds to the C-N stretching of the polymer. The morphology was studied by FESEM, which shows that the synthesized polymer has wire-like morphology. The electrochemical properties of the polyindole nanowires were studied by cyclic voltammetry. The synthesized polyindole nanowires were used to modify the glassy carbon electrode (GCE) and the modified GCE was studied in various background electrolytes in order to understand the oxidation and reduction behaviour of the polyindole nanowire.

**Keywords:** Nanowires, Polyindole, Cyclic voltammetry, Polymerisation

### Introduction

Large-scale interest in conducting polymers is a relatively recent occurrence, although materials that might be considered electrically conducting polymers, such as filled polymers and aniline blacks, were known at the beginning of this century. The current interest in conducting polymers began in the 1970's, when it was found that the electrical conductivity of polyacetylene, a semi-conductor when pristine, could be increased by over fifteen orders of magnitude by treatment with oxidizing agents such as iodine. In heterocyclic polymers, where two non-degenerate regions are separated by a topological defect, the formation of single solitons like polyacetylene is energetically unfavorable<sup>1</sup>, and paired sites are formed<sup>2</sup>. This is the case for polythiophene or polyindole, which can be drawn with either aromatic or quinoid structures, of which the latter possesses a higher energy configuration. Two neutral radicals on a single chain will recombine to eliminate the structural defect<sup>3-7</sup>, although, if one is charged, a polaron is formed, which is delocalized over about four rings. However, when both defects are charged, they are predicted

<sup>†</sup>Presented to the National Conference on Chemistry Solutions at SRM University, India

to pair up to form a 'bipolaron'<sup>8-9</sup>, consisting of a doubly charged defect with no spin and extending over a number of rings to a similar polaron. At higher doping levels, bipolarons may also combine to form 'bipolaron bands' within the gap. In this paper, we have reported the synthesis of polyindole nanowires and its characterization using FT-IR, XRD, FESEM and their electrochemical properties was studied by cyclic voltammetry.

## Experimental

Indole, ammonium persulfate, acetonitrile, sodium hydroxide, sodium sulphate, potassium hydroxide and sulphuric acid were purchased from Qualigens and used without further purification. Doubly distilled water was used as the solvent.

### *Synthesis of polyindole nanowires*

Reaction of indole (0.05 mole) with ammonium persulphate (0.1 mole) yielded polyindole in acetonitrile as solvent and the pH of the reaction mixture was 1. The reaction mixture was allowed to stir for 3 h. After that, the final product was filtered and washed with acetonitrile to remove any unreacted indole and ammonium persulphate.

### *Characterization Methods*

FT-IR spectrum of the polymer was recorded on Shimadzu FT-IR 8300 series instrument by using potassium bromide pellets. The morphology of the polymer was analyzed by FESEM using a HITACHI SU6600 field emission-scanning electron microscopy. The electrochemical experiments were performed on a CHI 600A electrochemical instrument using the as-modified electrode and bare GCE as working electrode, a platinum wire was the counter electrode, and saturated calomel electrode (SCE) was the reference electrode.

### *Preparation of polyindole nanowires modified GCE*

Ultrasonically agitated solution of polyindole nanowires in water for 30 min was used for the coating. 5  $\mu\text{L}$  of the polyindole nanowires suspension was mixed with 10  $\mu\text{L}$  of 5% nafion. The 5  $\mu\text{L}$  of the nafion mixed suspension was coated on the polished GCE and dried at room temperature.

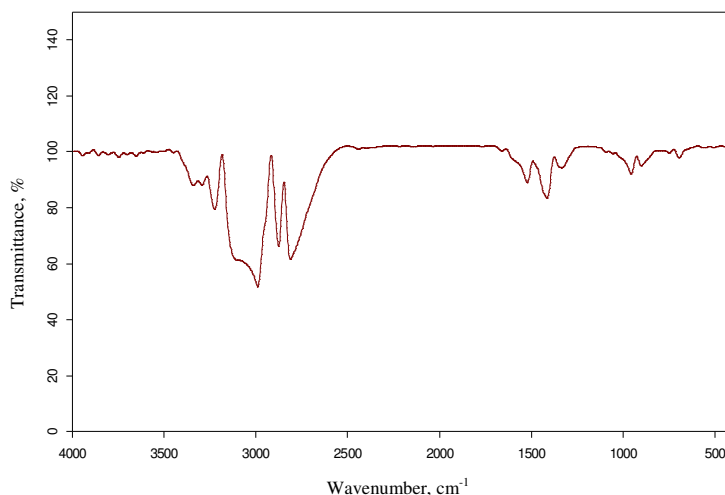
## Results and Discussion

### *Structure and morphology*

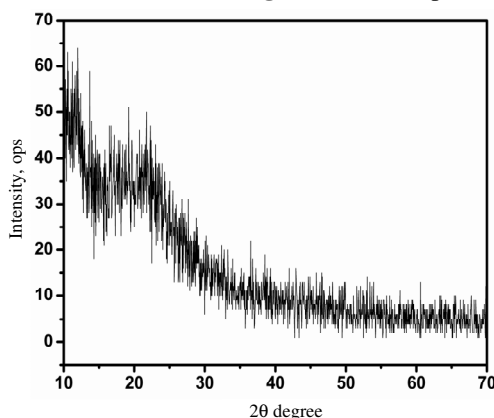
FT-IR spectra of polyindole synthesized by interfacial polymerization (nanowires) are shown in the Figure 1. The peak at  $3400\text{ cm}^{-1}$  is assigned to the N-H stretching indicating nitrogen species are not the polymerization sites, therefore the only possibility of the polymerization is through 2 and 3 positions of the monomers. The peaks at  $2932\text{ cm}^{-1}$  corresponds to the C-H bonds present in the indole moiety. The peak at around  $1100\text{ cm}^{-1}$  corresponds to the stretching mode of C=N. The peak at 1480 and 1550 corresponds to the C-N bonds.

XRD pattern of polyindole nanowires is shown in Figure 2. Various sharp peaks at  $11.3^\circ$ ,  $12.4^\circ$ ,  $17.6^\circ$ ,  $20.06^\circ$ ,  $23.6^\circ$ ,  $26.2^\circ$ ,  $27.3^\circ$  ( $2\theta$ ), support crystalline nature of the nanorods polymer. In particular, one unusual sharp peak around  $2\theta = 7.4^\circ$ , which is common in both can be assigned to the periodic distance between the dopant and the nitrogen atom of the adjacent main chain is observed.

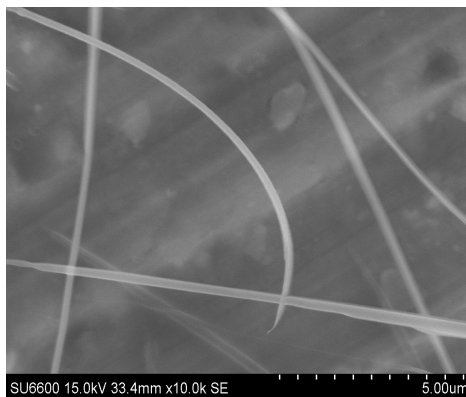
The morphology of the polyindole nanowires was studied by FESEM, which is shown in Figure 3. From the FESEM image (Figure 3), it is clear that the synthesized polyindole are nanowire shaped. The diameter of the nanowires is in the range of 50 to 100 nm with the length of 10  $\mu\text{m}$ .



**Figure 1.** FT-IR spectrum of polyindole nanowires



**Figure 2.** XRD spectrum of polyindole nanowires

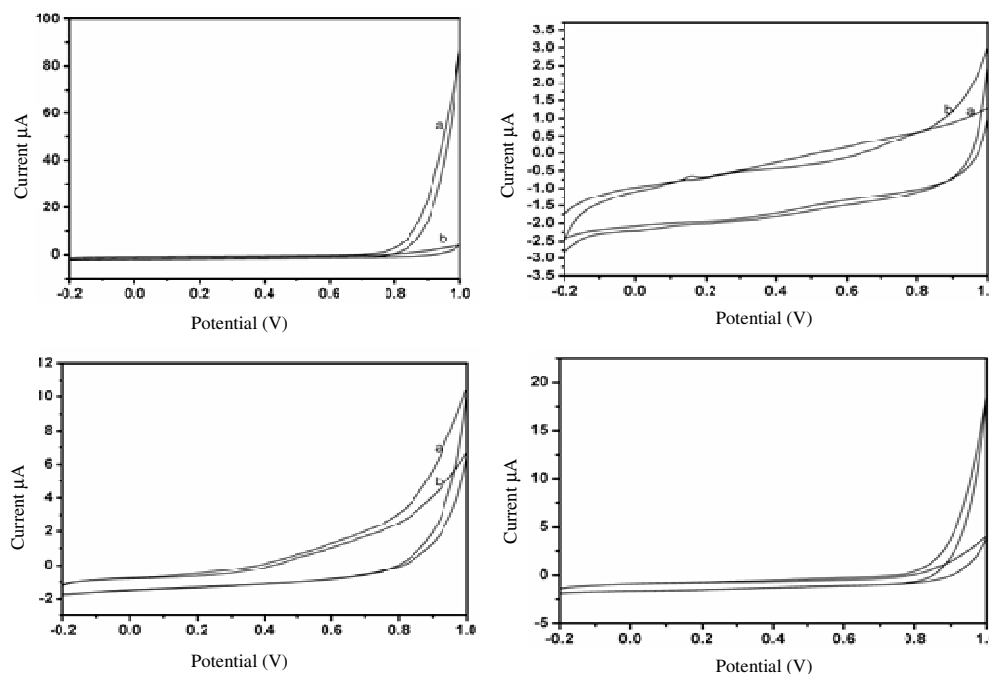


**Figure 3.** FESEM image of polyindole nanowires

### *Electrochemical property*

The electrochemical behaviour of polyindole nanowires on GCE was investigated using cyclic voltammetry in different background electrolyte such as 0.1M background electrolytes (KOH, NaOH, Na<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>). Figure 4 depicts the oxidation/ reduction process of polyindole nanowires on GCE.

From the cyclic voltammetric curves it is clear that the polyindole nanowires modified shows very poor current response when compared to the glassy carbon electrode. This might be due to the absence of charge carriers in the polymer backbone. In all electrolytes except 0.1 M Na<sub>2</sub>SO<sub>4</sub> the modified electrode shows lower current response the reason for the poor response lies on the uncharged nitrogen atoms present in the polymer. Whereas, in case of the 2:1 electrolyte the current response becomes more predominant, due to the mobility of cation. From the cyclic voltammetric measurements it is clear that the addition of dopant is required to utilise the polyindole nanowires for electrochemical sensing.



**Figure 4.** Cyclic voltammogram of polyindole nanowires at different background electrolytes; a) 0.1M KOH; b) 0.1 M NaOH; c) 0.1M Na<sub>2</sub>SO<sub>4</sub>; d) 0.1M H<sub>2</sub>SO<sub>4</sub>

## Conclusion

Polyindole nanowires were synthesised by simple oxidative polymerization method. The synthesised polyindole nanowires were characterised using FT-IR in order to confirm the polymerisation of indole. Further, the XRD spectrum clearly shows the amorphous nature of the polyindole nanowires. The morphology of the polyindole was studied by FESEM, from the study it is observed that the polyindole was found in wire shape. The electrochemical property was studied in various background electrolytes.

## Acknowledgment

One of the authors (KG) acknowledges the DST for the financial assistance in the form of INSPIRE Fellowship. We acknowledge for the FESEM facility provided by the National Centre for Nanoscience and Nanotechnology, University of Madras.

## References

1. Zhijiang C, Xingjuan S and Yanan F, *J Power Sources*, 2013, **227**, 53-59.
2. Syed Abthagir P and Saraswathi R, *Thermochim Acta*, 2004, **424**, 25-35.
3. Ferraris J P, Eissa M M, Brotherston I D, Loveday D C and Moxey A A, *J Electroanal Chem.*, 1998, **459**, 57.
4. Gordon M S, *Chem Phys Lett.*, 1980, **76**, 163.
5. Tourillon G and Garnier F, *J Electrochem Soc.*, 1983, **130**, 2042.
6. Ivory D M, *J Chem Phys.*, 1979, **71**, 1506.
7. Yurtsever M and Yurtsever E, *Polymer*, 2002, **43**, 6019-6025.
8. Walton D J, *Mater Des.*, 1990, **11**, 142.
9. Hillman A R and Mallen E F, *J Electroanal Chem.*, 1987, **220**, 351.