

## Synthesis and Characterization of Silver Hexacyanoferrate(II)/ Polyaniline Composites

<sup>1</sup>FARAH KANWAL\*, <sup>1</sup>SAIRA ISHAQ AND <sup>2</sup>TAHIR JAMIL

<sup>1</sup>*Institute of Chemistry, University of the Punjab, Lahore, Pakistan.*

<sup>2</sup>*Faculty of Engineering and Technology, University of the Punjab, Lahore, Pakistan.*

(Received on 10<sup>th</sup> January 2009, accepted in revised form 8<sup>th</sup> October 2009)

**Summary:** Silver hexacyanoferrate(II)/conducting polyaniline composite was synthesized in two steps process; In the first step, silver hexacyanoferrate(III) was synthesized by reaction of  $K_3[Fe(CN)_6]$  and  $AgNO_3$  solutions. In the second step, silver hexacyanoferrate(III) was reacted with aniline/ $HNO_3$  solution. Silver hexacyanoferrate(III) acted as an oxidant to polymerize aniline monomer. Silver hexacyanoferrate(II)/conducting polyaniline composite was prepared at different temperatures (37 °C, 27 °C, 17 °C) and in different concentrations of  $AgNO_3$  (0.4M, 0.8M, 1.2M) and  $HNO_3$  (1M and 2M). Silver hexacyanoferrate(II)/conducting polyaniline composite was characterized by FTIR and DC conductivity was measured by four probe technique. Conductivity of Silver hexacyanoferrate(II)/polyaniline composite was found to be increased with increasing temperature. However, conductivity decreased significantly with increasing concentrations of  $AgNO_3$  but remained unaffected with the change in  $HNO_3$  concentration from 1-2 molar.

### Introduction

Polyaniline (PANI) is one of the most researched organic conducting polymers for technological applications. The choice for PANI stems from the following reasons: fairly good chemical stability in acid electrolytes, high electronic conductivity in the partially oxidized state, good protonic conductivity and easy preparation by chemical, electrochemical and photochemical methods [1, 3].

Metal/polymer composite materials with various properties are synthesized by incorporation of metal and metal oxide particles in conducting polymers. Metal/polymer composites exhibit electrocatalytic activity and gas sensing properties [4, 5]. These materials are also studied as energy storage media and photoactive materials [5].

The use of conducting polymers, as a matrix capable of allowing charge flow through three dimensional redox centers has been proposed in parallel with inorganic redox systems such as Prussian blue and related metal hexacyanoferrates. These composites have been studied due to their some interesting properties as electrochromism [6], membrane and sensing properties [7], ability to mediate redox reactions [8], ionic and electronic (mixed-valence electron hopping) conductivity [9, 10], ability to store charge [11], and molecular magnetism [12]. Composite consisting of Prussian blue impregnated in PANI has shown excellent electrochromic properties [13, 14] and has been used for mediating electro reduction of  $CO_2$  [15].

In this paper, we are reporting synthesis of silver hexacyanoferrate(II)/polyaniline composite *via* two step process. In the first step, silver hexacyanoferrate(III) was synthesized by reaction of  $K_3[Fe(CN)_6]$  and  $AgNO_3$ . In the second step, silver hexacyanoferrate(III) was reacted with aniline/ $HNO_3$  solution in which silver hexacyanoferrate(III) acted as an oxidant to polymerize aniline monomer.

### Results and Discussion

Table-1 shows the experimental conditions for different sample preparation. Figs. 1-3 show the FTIR spectra of all the samples and confirm the formation of silver hexacyanoferrate(II)/polyaniline composite. FTIR spectra of all silver hexacyanoferrate(II)/conducting polyaniline composites were compared with FTIR spectrum of pure PANI prepared at 30 °C [17]. The most important feature in the spectrum (see Table-2, Figs. 1-3) is the band observed at 2040  $cm^{-1}$  which is characteristic of  $[Fe^{II}(CN)_6]^{4-}$  ion. This peak is absent in the spectrum of pure PANI. The absence of higher wave number band at 2130  $cm^{-1}$  is indicative of the reduction of  $[Fe^{III}(CN)_6]^{3-}$  ion in the synthesis of polyaniline [18]. Bands observed at 3510 - 3380  $cm^{-1}$  are indicative of N-H stretch in protonated PANI. The bands located at 1385-1250  $cm^{-1}$  indicate -C=N<sup>+</sup> stretch. Bands at 1509-1472  $cm^{-1}$  indicate -N=B=N- and bands at 1586-1558  $cm^{-1}$  indicate -N=Q=N- where B is benzoid and Q is quinoid [19]. Bands in region of 1140-1100  $cm^{-1}$  are characteristic of conductive PANI and are due to the charge

To whom all correspondence should be addressed.

Table-1: Experimental condition and conductivity of composite samples prepared with different concentration of  $\text{AgNO}_3$  and  $\text{HNO}_3$  at different temperature.

Sample	Concentration		Temperature (°C)	Conductivity ( $\text{S.cm}^{-1}$ )
	$\text{AgNO}_3$ (M)	$\text{HNO}_3$ (M)		
A	0.4	1	37	$1.28 \times 10^{-4}$
B	0.4	1	27	$2.4 \times 10^{-5}$
C	0.4	1	17	$1.11 \times 10^{-6}$
D	0.8	1	37	$1.93 \times 10^{-5}$
E	1.2	1	37	$3.20 \times 10^{-6}$
F	0.4	2	37	$1.2 \times 10^{-4}$

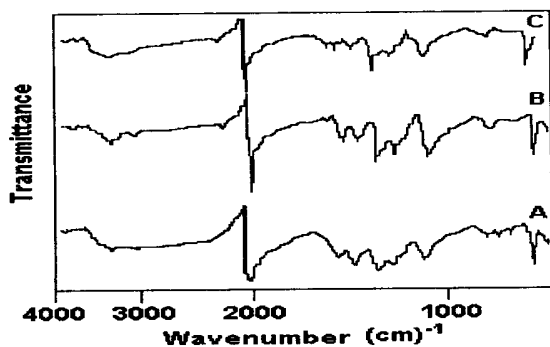


Fig. 1: Comparison of FTIR Spectra of Silver hexacyanoferrate(II)/polyaniline composite prepared at 37 °C (A), 27 °C (B) and 17 °C (C)

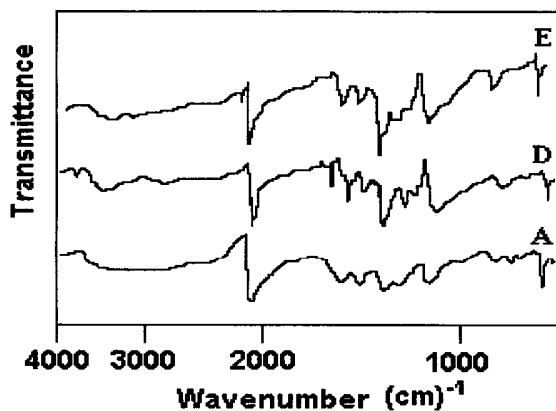


Fig. 2: Comparison of FTIR Spectra of Silver hexacyanoferrate(II)/polyaniline composite prepared with 0.4 M  $\text{AgNO}_3$  (A), 0.8 M  $\text{AgNO}_3$  (D), 1.2 M  $\text{AgNO}_3$  (E).

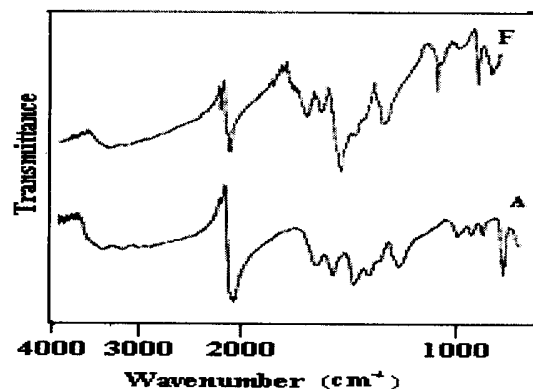


Fig. 3: Comparison of FTIR Spectra of Silver hexacyanoferrate(II)/polyaniline composite prepared with 0.1 M  $\text{HNO}_3$  (A) and 2 M  $\text{HNO}_3$  (F).

delocalization of the electrons on polymer backbone [20]. Intensity of the peak is a measure of the strength of delocalization of the electrons or conductivity [21]. Bands in the range of 1300 - 1000 $\text{cm}^{-1}$  show aromatic C-H stretch in-plane bending mode [22]. Thus all the FTIR bands indicate the presence of silver hexacyanoferrate(II)/polyaniline composite.

Table-1 shows the conductivity of silver hexacyanoferrate(II)/polyaniline composite samples (A, B, C, D, E, and F) determined by the four probe method. Conductivity of pure PANI at 30 °C is reported in the literature as  $5.3 \times 10^{-4} \text{ S cm}^{-1}$  [17]. From Table-1, it is clear that the conductivity of the composite material increases as the reaction temperature is increased. Conductivity was found to rise with increasing temperature showing a direct relationship between conductivity and temperature. At lower temperature, sample has activation energy close to undoped material while at higher temperature the activation energy decreased. At higher temperatures doping has distinct effect on conductivity [23]. With increasing concentration of  $\text{AgNO}_3$  conductivity was found to be decreased as shown in Table-1. In composites D and E the simultaneous decrease in conductivity with increase

Table-2: Infrared absorptions frequencies of composite samples prepared with different concentration of  $\text{AgNO}_3$  and  $\text{HNO}_3$  at different temperature.

Frequency ( $\text{cm}^{-1}$ )	1300-1000	1385-1250	1509-1472	1586-1558	3510-3380	2040
Band	C-H stretch	-C=N <sup>+</sup> stretch	N=B=N	N=Q=N	N-H stretch	$[\text{Fe}^{\text{II}}(\text{CN})_6]^{-1}$
A	1141.6	1382.6	1494	1575	3427.3	2042.1
B	1127.9	1383	1488	1558	3443.3	2039.9
C	1127	1383.7	1489	1575	3382.6	2041.3
D	1125.9	1383.7	1488	1559	3410	2039.5
E	1125.1	1383.7	1488	1574	3398.3	2039.3
F	1137.7	1383.4	1493	1579	3413	2039.3

in concentrations of  $\text{AgNO}_3$  is perhaps due to a decrease in the weight ratio of polyaniline. The decrease in the weight ratio of polyaniline/silver hexacyanoferrate(III) perhaps results in reduced orientation of domains through which ions move, which causes some restricted movements of ions and hence results in decrease in conductivity [17]. By increasing the concentrations of  $\text{HNO}_3$ , conductivity was found to remain unchanged as shown in Table-1.

## Experimental

### Material

Aniline (reagent grade) was distilled at  $178^\circ\text{C}$  prior to use and kept under nitrogen. Reagent grade dimethylformamide (DMF) and acetone was used as purchased. Reagent grade silver nitrate ( $\text{AgNO}_3$ ), nitric acid ( $\text{HNO}_3$ ) and potassium hexacyanoferrate(III) ( $\text{K}_3[\text{Fe}(\text{CN})_6]$ ) was purchased from Merck and used without further treatment.

### Synthesis of Silver Hexacyanoferrate(III)

Solutions of  $0.1\text{M K}_3[\text{Fe}(\text{CN})_6]$  and  $0.4\text{M AgNO}_3$  were mixed in a beaker at  $37^\circ\text{C}$  and an orange colored compound of Silver hexacyanoferrate(III) was formed. Silver hexacyanoferrate(III) was filtered and washed thoroughly with deionized water. The same procedure was repeated with  $0.8\text{M}$ , and  $1.2\text{M AgNO}_3$  while keeping all other chemical concentrations same at  $37^\circ\text{C}$ .

### Synthesis of Silver Hexacyanoferrate(II)/polyaniline Composite

The Silver hexacyanoferrate(II)/conducting polyaniline composite was prepared by reacting silver hexacyanoferrate(III) with a solution of  $0.5\text{M}$  aniline in  $1\text{M HNO}_3$  at  $37^\circ\text{C}$ . As a result of this reaction, a composite was formed and the Orange color, characteristic of silver hexacyanoferrate(III), changed to green which is an indication of polymerization of aniline monomer [16]. The same procedure was repeated to prepare composite at  $27^\circ\text{C}$  and  $17^\circ\text{C}$ . Samples prepared at  $37^\circ\text{C}$ ,  $27^\circ\text{C}$  and  $17^\circ\text{C}$  were labeled as "A", "B", and "C" respectively. Silver hexacyanoferrate(II)/conducting polyaniline composite was also prepared by using  $0.8\text{M}$ , and  $1.2\text{M AgNO}_3$  solutions using the above mentioned procedure. Silver hexacyanoferrate(II)/conducting

polyaniline composite prepared by using  $0.8\text{M}$ , and  $1.2\text{M AgNO}_3$  solutions were labelled as D and E respectively. Sample "F" was prepared from  $0.1\text{M K}_3[\text{Fe}(\text{CN})_6]$  and  $0.4\text{M AgNO}_3$  solution using  $0.5\text{M}$  aniline in  $2\text{M HNO}_3$  at  $37^\circ\text{C}$ .

### Characterization

All composite samples were characterized by FTIR spectroscopy. Infrared spectra of KBr pellet of samples were recorded using Perkin Elmer, A-100 FTIR spectrophotometer. Each sample was prepared thrice at the same conditions.

Conductivities of the silver hexacyanoferrate(II)/polyaniline composite samples (A, B, C, D, E, and F) were measured using four probe apparatus. A Professional Pro's kit multimeter was used as an ammeter and a digital multimeter M 2007 AVO was used as a voltmeter. Four needle-like electrodes of very thin copper (Cu) wires were pasted on the surface of sample parallel to each other with silver paint. Voltage was applied to the sample pellet with a DC power supply and the corresponding voltage and current developed across the sample were noted with a voltmeter and an ammeter respectively. The current was passed in the range of  $0.1\text{A}$  (minimum) to  $5.4\text{A}$  (maximum) and voltage was measured for each of the corresponding value of current. The conductivity ( $\sigma$ ) was determined from the current and voltage using the equation:

$$\sigma = S I / V A$$

where S is mean distance between probes, I is applied current, V is measured voltage, and A is area of the sample.

### Conclusion

Silver hexacyanoferrate(III) can be synthesized by the reaction of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  and  $\text{AgNO}_3$  solutions. The compound thus formed was reacted with aniline/ $\text{HNO}_3$  solution to polymerize aniline monomer and forms silver hexacyanoferrate(II)/conducting polyaniline composite. Composite can be prepared at different temperatures and with different concentrations of  $\text{AgNO}_3$  and  $\text{HNO}_3$ . FTIR spectroscopy confirms the formation of silver hexacyanoferrate(II)/conducting polyaniline composite. DC conductivity study shows that with an increase in reaction temperature results in a

corresponding increase in the conductivity of the composite. Therefore to prepare polyaniline-composites with high conductivity, the reaction temperature should be high with a concurrent lower concentration of AgNO<sub>3</sub>.

#### Acknowledgement

This work was supported by the Institute of Chemistry, University of the Punjab, Lahore. We are also grateful to Dr. S. A. Siddiqi, Centre of Excellence in Solid State Physics, University of the Punjab, Lahore, for conductivity measurements.

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