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Synthesis of Ag@Polycarbazole Nanocomposite using Ferric Acetate as an Oxidant

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Silver nanowires and Ag@polycarbazole nanocables have been effectively fabricated. Polyol-reduction and ion adsorption process were used to fabricate pure silver nanowires and Ag@polycarbazole nanocomposite by using an oxidant (iron acetate). Ions of oxidant were adsorbed on the surface of pure silver nanowires to oxidize carbazole monomers for efficient polymerization. The morphology of nanowires and Ag@PCz composite were characterized by using SEM, FT-IR and photoluminescence analysis. The SEM shows the presence of a smooth polymeric sheath. FT-IR and photoluminescence analysis shows dominant peaks that indicate the presence of silver nanowires and polycarbazole (PCz) with a smooth polymeric coating. Nanoparticle analyzer was used to determine z-average and actual size of sample. UV-visible spectrum shows two bands that were dominant at 345 and 410 nm. These are π to π^* transitions that indicates the presence of polycarbazole nanocables.

Keywords: Silver nanowires, Polycarbazole nanocable, Oxidant, Ferric acetate.

INTRODUCTION

Metal polymer nanocomposites are efficient and stable materials for different high-tech applications. They have distinctive physical, photo-electrochemical and thermally stable properties [1]. Nanocomposites have potential applications for the fabrication of sensors in food testing and environmental safety monitoring. The metal-based polymer composites can be used to identify metal ions from different aqueous solutions. However, conjugated polymers retain their luminescence, magnetic and electrical characteristics. These properties can be enhanced by using nanocomposites of metal within the polymer matrix [2-4]. Silver is usually used in composites that show conductivity. Silver has high electrical conductivity and better resistance to oxidation. So, silver nanomaterial can be used to enhance properties of conducting polymers effectively. Among conducting and luminescent polymers, polycarbazole plays a significance role due to its electron-hole transporting properties [5] that enhance its application in light emitting diodes and electrochromic displays [6]. In the beginning, polymeric composites were synthesized by using poly(methyl methacrylate) [7], poly(vinyl pyrrolidone), poly (vinyl alcohol) and poly(vinyl acetate) [8]. However, in order to increase the conductivity further, conducting polymers were used to fabricate nanocables like Ag-polythiophene [9], Ag-polyaniline [10] and Ag-polypyrrol [11,12]. The main purpose of this study is to formulate thermal and environmental stable products and protect it from the metal surface oxidations factors. So, polycarbazole (PCz) was used because it produces environmentally balanced and thermally stable products compared to others. Polycarbazole can form a coherent film around the nanoparticles and prevent it from oxidation [13]. Polycarbazole also shows photorefractive properties. It also has non-linear optical properties which are useful in photoluminescence (PL) and surface plasmon resonance (SPR) [14]. The optical properties are used in electro-optic based switches, modulators, and frequency doublers [15]. However, to make a significant sensor with up to trace level detection capability for nitrogen, carbon dioxide and metal ions the polycarbazole must be incorporated with amines, ammonia and nucleotide groups. The polymer beads can be fabricated into fibers [16]. Hence, it was decided to fabricate Ag@PCz nanocomposite for it to have synergistic properties. However, Fe^{3+} ions were adsorbed onto the prepared silver nanowires in order to polymerize monomers of carbazole [17]. The morphology of synthesized polymeric metal nanocomposite was studied by different techniques *i.e.* zeta potential, FTIR, SEM, photoluminescence, UV-Vis, nanoparticle analyzer and EDX. In presnet study, a growth of polycarbazole (PCz) sheath around silver nanowires assisted by iron(III) acetate is reported. The use of polycarbazole (PCz) was to protect the silver nanowires against oxidation and to give a better dispersion of silver.

EXPERIMENTAL

Ethanediol 99 % (Sigma-Aldrich), silver nitrate 99.9% (Sigma-Aldrich), acetone, poly(vinyl pyrrolidone) (PVP, Daejung Reagent Chemicals-Korea), methanol (analytical reagent), ethanol, carbazole 95 % (Merck), acetonitrile 99.9% HPLC grade, iron (III) acetate (Sigma-Aldrich) were procured and used without further purification.

Synthesis of silver nanowires: Polyol reduction method was used to prepare pure silver nanowires. Ethanediol was used as the reducing agent and as solvent [18]. First, 0.5 mL ethanediol was refluxed for 1 h at 160 ºC to eliminate water. Then $AgNO_3$ solution (0.1 M, 0.084 g) and PVP solution (0.1 M, 0.056 g) were added dropwise into the refluxed ethanediol within 10-15 min [19]. The addition process is slow in this method. During the addition process, a solution temperature decreased from 160 to 140 ºC and the ethanediol solution turned bright yellow from colourless. The temperature was adjusted back to 160 ºC. The bright yellow colour gradually turned milky within 15 -20 min. The reaction was maintained for 1 h at 160 ºC. A grey coloured silver nanowire was produced and the product was finally centrifuged at 4000 rpm by using ethanol and acetone. It is to be noted that for the reaction to succeed, pure $AgNO_3$ solution was necessary, together with accurate temperature control and fresh PVP solution to produce pure nanowires.

Synthesis of Ag@polycarbazole nanocomposite: A prepared monodispered solution of silver nanowires were suspended in 5.0 mL of iron(III) acetate (0.001 M , 0.0032 g) and centrifuged for 20 min at 4000 rpm. By using ion adsorption method, Fe^{3+} ions were adsorbed on the surface of pure silver nanowires. This cation containing nanowires were inserted into 0.01 M solution of carbazole. The oxidant ions were used to oxidize carbazole monomers to effect polymerization [20].

The reaction was continued with magnetic stirring for 24 h for polymeric growth over the silver nanowires surface [21]. The final product was centrifuged again at 4000 rpm for 20 min. The reaction was kept in the dark away from sunlight because the silver and carbazole are photosensitive.

Characterization: The morphology of silver nanowires and Ag@polycarbazole nanocomposite was analyzed by SEM (TESCAN MIRA3XMU TESCAN scanning electron microscope. 90), UV-Vis (Shimadzu UV 1800 spectrophotometer), FT-IR (Nicolet iS10), nanoparticle analyzer SZ-100 (Horiba SZ-100), EDX, photoluminescence and zeta potential (Malvern Instruments zeta sizer).

RESULTS AND DISCUSSION

Morphology and apparent outlook of pure silver nanowires and Ag@PCz nanocomposites were characterized by SEM as shown in Fig. 1(a, b), respectively. The SEM revealed that the silver nanowires were monodispersed and have a diameter in the range of 60-100 nm and 3-5 µm long. The outer surface is smooth, but nanowires were randomly arranged. Iron (III) acetate served as an oxidant and it helped to initiate the polymerization. The monomers of carbazole were utilized to form polycarbazole over the nanowires. The diameter of coated wires was found to be 80-100 nm. The presence of carbazole monomer layer on surface of nanowires indicates the presence of polycarbazole composite. The SEM images illustrate that pure silver nanowires surface was quite smooth compared to Ag@PCz composite. The nanocomposite forms polymeric interconnected network around the silver wires. Therefore, carbazole polymer had grown around the wires, moreover, growing tendency of the polymer around the nanowires decreased the silver nanowires from coalescence.

The nanoparticle analyzer (SZ100) was used to measure the zeta potential, size of particles and molecular weight, respectively. An average Z-potential and PI range of pure nanowires and Ag@PCz composites are presented in Table-1. Fig. 2 demonstrates the dominant peaks and the Z-potential of pure silver nanowires and polycarbazole composite. The average zeta potential difference between pure silver nanowires and composite was found to be 1048.5.

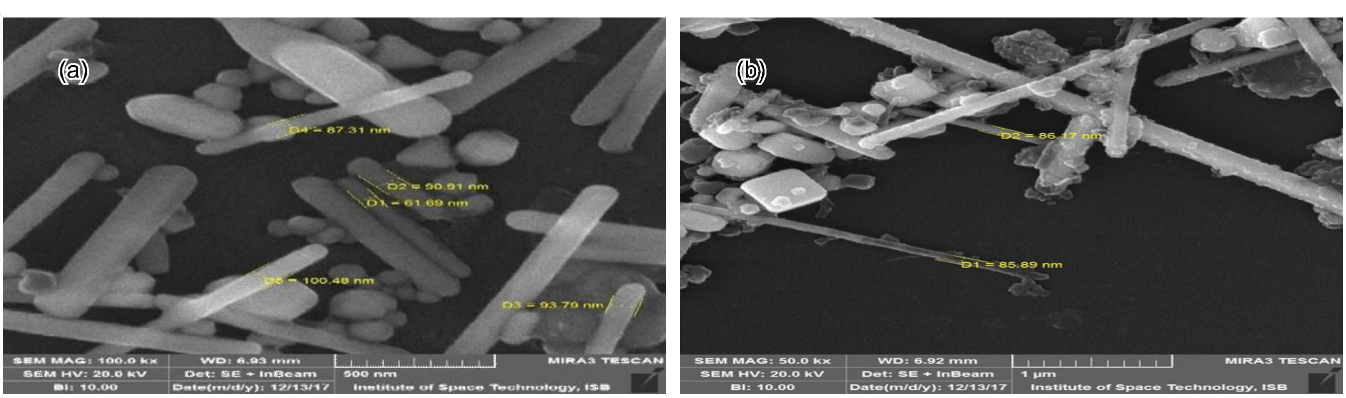

Fig. 1. SEM micrographs of pure silver nanowire (a); and Ag@PCz nanocomposite (b)

TABLE-1
SZ-100 DATA OF PURE SILVER NANOWIRES AND Ag@PCz NANOCOMPOSITE

Peak No.	S.P. area ratio		Mean (nm)		S.D. (nm)		Mode (nm)	
	Pure Ag nanowires	Ag@PCz	Pure Ag nanowires	Ag@PCz	Pure Ag nanowires	Ag@PCz	Pure Ag nanowires	Ag@PCz
1	0.11	0.39	182.7	361.3	15.5	44.7	182.1	369.5
2	0.89	0.61	5887.1	5642.3	704.9	957.4	5664.1	5588.7
3	–	–	–	–	–	–	–	–
Total	1.00	1.00	6069.8	6003.6	720.4	1002.1	5846.2	5958.2

Pure Ag nanowires = Z-average = 3629.7 nm, PI = 1.181; Ag@PCz = Z-average = 2581.2 nm, PI = 0.968

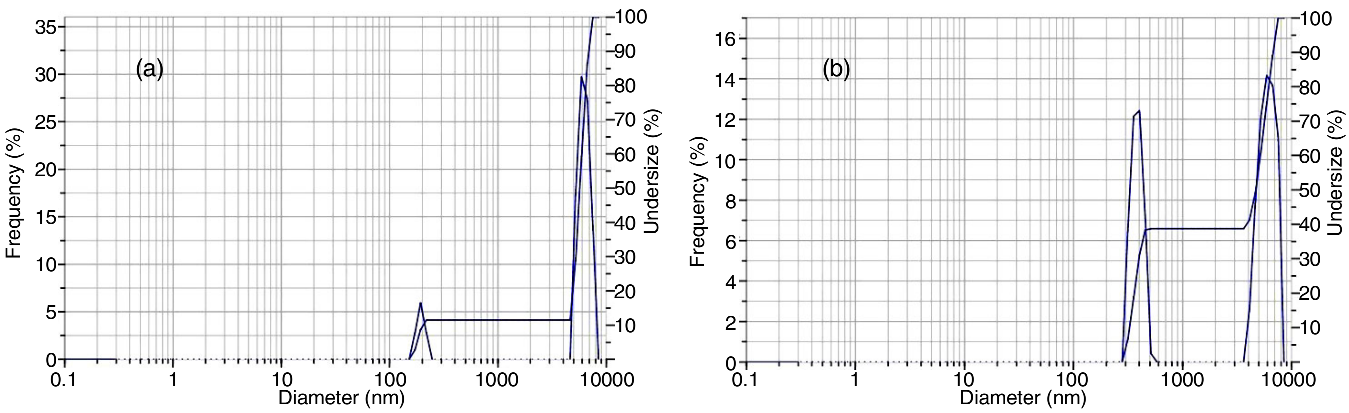

Fig. 2. The nanoparticle size spectraum of pure silver nanowire (a); and Ag@PCz nanocomposite (b)

The prepared material was further characterized by zeta potential as shown in Fig. 3. This characterization is used to evaluate the activity of the polymer to improve the stability of pure nanowires and reduce the propensity for agglomeration. The major aim of this characterization is to elaborate the effect of polymer on the thickness and dispersion of silver nanowires. The zeta potential of pure silver nanowires is -3.18 mV but after adsorption of Fe^{3+} ions on the composite with polymer coating around the wires, the value of polycarbazole nanocomposite is -3.87 mV. The value of zeta potential of pure silver nanowires cannot be greater than -24.5 mV [22]. However, the value changes from -3.18 mV to -3.87 mV after polymer encapsulation and Fe^{3+} adsorption.

Zeta potential of the composite was negative because Fe^{3+} ions were adsorbed on the surface of pure nanowires. A positive millivolt indicates that the nanowires/particles contain positive charge on the sample surface. Zeta potential indicates stability of the sample when the sample has a greater absolute value. There are two conditions in which the value becomes negative. One is the overcharging and the second is the presence of multivalent cation. The zeta potential indicates the ability to disperse the silver nanowires and has a negative value of -3.18 mV. This enhances the polycarbazole coating around the wires. The high stability helps to orient the nanocomposite in specific direction by using the electric field. The wires and composite dispersion stability help to determine the different properties like conductivity and anisotropic.

The UV-visible spectroscopy (Fig. 4a) shows the presence of bands at 345 and 410 nm, which confirms the presence of silver nanowires. The polycarbazole nanocomposite in which Fe^{3+} ions were adsorbed on the surface of pure silver nanowires is shown in Fig. 4b. It shows that SPR decreased due to low molar absorptivity of silver nanowires. The π to π^* transition found in the spectrum of Ag@PCz shows that such transitions only exist when PCz polymer was present in high density [23].

The FT-IR spectrum of Ag@PCz nanowires is shown in Fig. 5. The given spectrum elucidates the complete structural morphology of the prepared of pure silver nanowires. The FTIR

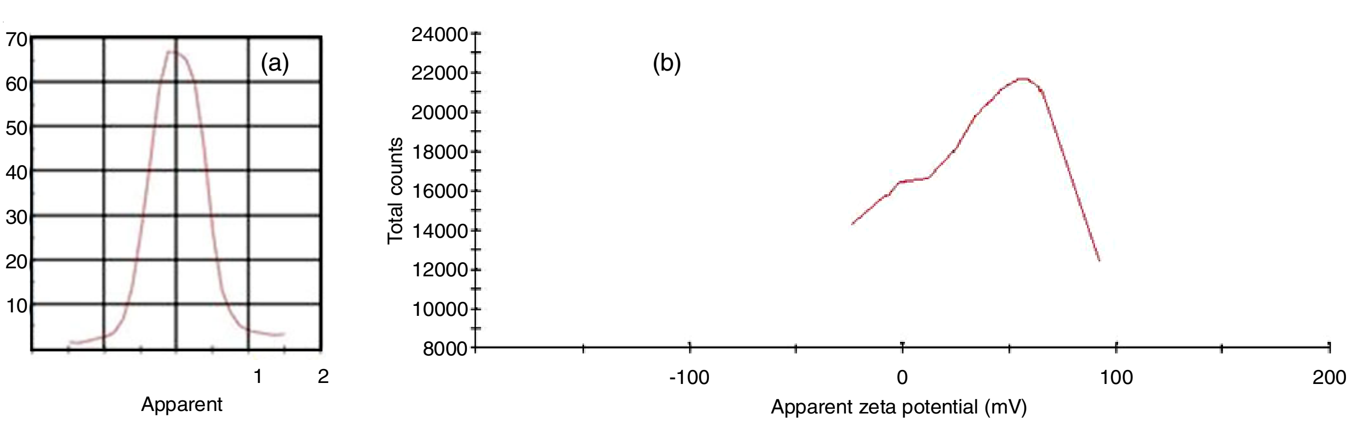

Fig. 3. Zeta potential of pure silver nanowire (a); and Ag@PCz nanocomposite (b)

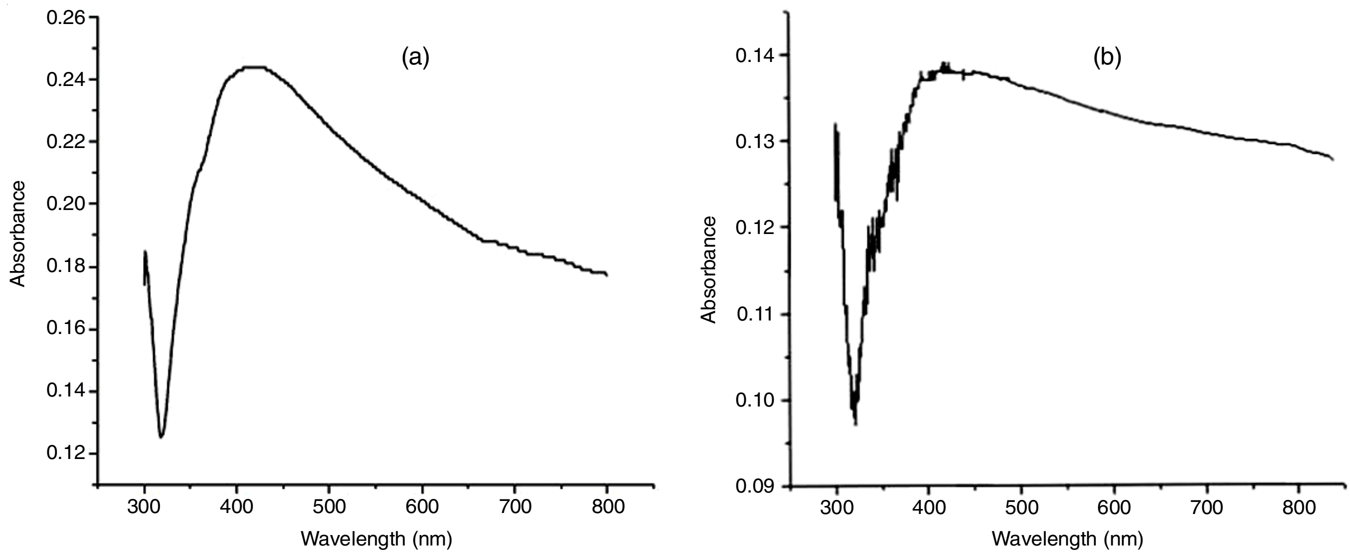

Fig. 4. UV spectrum of pure silver nanowire (a); and Ag@PCz nanocomposite (b)

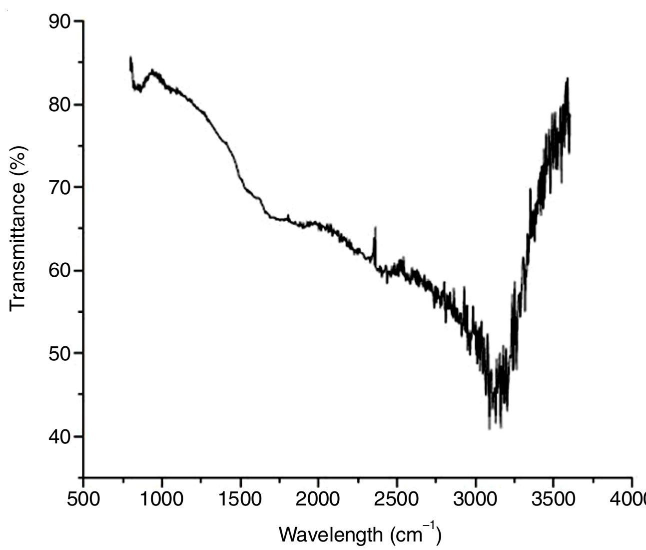

Fig. 5. FT-IR spectrum of synthesized Ag@PCz nanocomposite

spectrum shows N-H stretching near 3300 cm^{-1} and alkene aromatic stretching at 1600 cm^{-1}. Another band appears at near 950 cm^{-1} represents the substituted ring of carbazole and the deformation of C-H [24]. The band at 1000 cm^{-1} shows the presence of C-N stretching that is very significant in case of Fe^{3+} because it has greater thickness of polymer surface and less important in case of Ag^{+}. The band at 1557 cm^{-1} shows the presence of doped polycarbazole. Based on these characterization it can be concluded that Ag@PCz can be synthesized as nanocomposites. In both spectra, there is a strong presence of transition metal which results in all the bands not being well resolved and were found diffused except for the band at 1557 cm^{-1}.

Similarly, in case of photoluminescence (PL), ferric acetate had low intensity but in Ag@PCz, intensity of nanocomposite increased. The PCz luminescence comes in the blue and violet region [25]. So, it carries no effect on the silver nanowires, where PL intensity is in the green region. Basically, this technique helps to balance the surface cation which affects the PL intensity of nanowires. Photoluminescence of silver nanowires, Fe^{3+} loaded silver nanowires and polycarbazole polymeric sheathed around the silver nanowires is shown in Fig. 6. The pure nanowires were irradiated with 410 nm UV light. It produced the emission near 800 nm. The Ag@PCz composite was irradiated with 390 nm excitation energy and

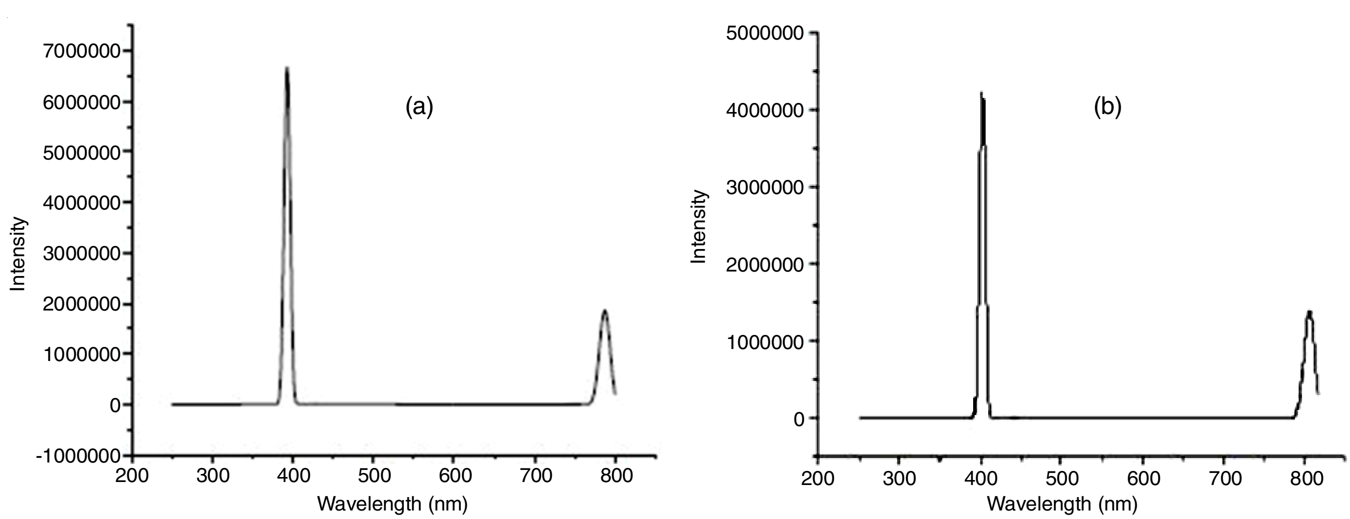

Fig. 6. Photoluminescence spectrum of pure silver nanowire (a); and Ag@PCz nanocomposite (b)

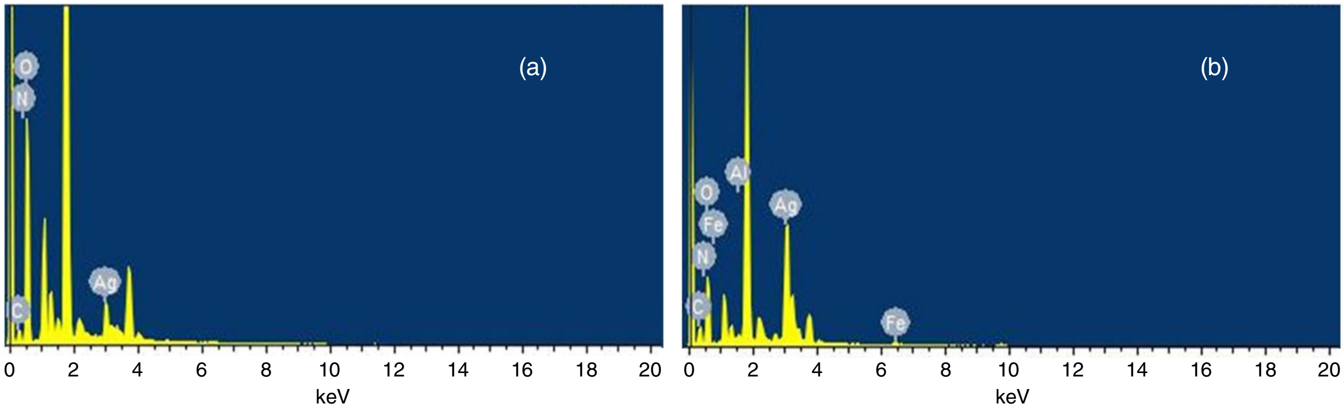

Fig. 7. The EDX spectrum of pure silver nanowire (a); and Ag@PCz nanocomposite (b)

the emission was near 750 nm. The luminescence of Fe^{3+} containing nanowires had a lower intensity but after treating with polycarbazole, the PL intensity increased. So, from all observations it was proved that polycarbazole wass very effective to balance the PL intensity of silver nanowires. Moreover, it was very significant that it increased the luminescence from violet region to blue. The value of PL transition was enhanced by electronic transition among the higher d-band and conduction sp-band in the metals [26]. It is more beneficial to examine the density and quantum confinement factors of electrons. Furthermore, the SPR behavior and PL mechanism of silver nanowires does not behave equally. The SPR intensity decreased when silver nanowires was coated with polymers, but on oxidant adsorption, the value was high. The conduction *sp*-band also effected by the oxidative ions and it can be used to understand the electron conduction band for more optical phenomena [27].

EDX analysis: Fig. 7a indicates the weight percentage of each element in the pure silver nanowires. EDX result confirms the presence of silver in the nanowires. The weight percentage of each elements present in the sample of pure nanowires is given in Table-2, which shows the compositional ratio of each element in the pure silver nanowires. Oxygen and nitrogen were also present in the nanowires due to surface oxidation.

TABLE-2
EDX DATA OF PURE SILVER NANOWIRES AND Ag@PCz NANOCOMPOSITE

Element	Weight (%)		Atomic (%)	
	Pure Ag nanowires	Ag@PCz	Pure Ag nanowires	Ag@PCz
O K	79.34	48.48	87.39	73.77
N K	1.87	1.80	2.36	3.13
Ag L	18.79	41.56	3.98	9.38
C K	–	6.06	–	12.29
Al K	–	1.09	–	0.99
Fe K	–	1.01	–	0.44

Fig. 7b shows the elements which are present in Ag@PCz nanocomposites. The EDX spectrum also shows the presence of Ag and Fe. Fig. 7b indicates that Al, Si, S and C were present in minor quantity in the nanocomposite, which were due to the glass slide and the oxidation effect on the wires. The oxygen appears in the spectrum in larger quantity because the sample is affected by surface oxidation during the formation process.

Conclusion

Synthesis of silver nanowires encapsulated by polycarbazole (PCz) were carried out in two stages. First, pure silver nanowires were synthesized by polyol method and in the second stage, ion adsorption process were used to fabricate the PCz around wires by using Fe^{3+} as oxidants and Ag^{+} ions. The SEM confirmed the polymer coating around the nanowires. The diameter of polymer coated wires was within 80-100 nm range. The measured value of zeta potential for Ag@PCz composite was -3.87 mV. The UV bands at 345 and 410 nm decreased due to the molar absorptivity of polymer coating around the wires. The photoluminescence of Ag@PCz nanocomposite was in the blue and violet area, while the pure nanowires were in the green region. Optical behaviour was found to be present when the nanowires were coated with PCz polymer. The PCz coated nanowires had significantly high dispersion, which can be also very useful in applications of electrochemical and electroanalytical point of view in future.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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