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Comparison of electrical and photoluminescence properties of synthesized poly o-phenylenediamine and its sio_2 nanocomposites

J. Deepa[1*] and Jaya Shanthi R.[2]
Department of Chemistry, Auxilium College, katpadi, Vellore-6, India
deepachem20@gmail.com

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Abstract

Poly orthophenylenediamine and their silicon dioxide nanocomposites were synthesize using different concentration of SiO_2 nanoparticles like 5%, 10% and 15% by oxidative polymerization method using ammonium persulphate as an oxidant in the presence of HCl. The formation of polymers and their nanocomposites were confirmed from the UV-vis and IR spectroscopy and from the change of polymer colour from red to brown and found to exhibit band at 446nm in UV-visible spectroscopy. The crystalline nature of the synthesized polymers and their nanocomposites were determined from the XRD studies. The SEM images of the polymer recorded at different magnification shows rod like structure and found to change to flake like structures in the polymer nanocomposites synthesized at different concentration of SiO_2 nanoparticles. The TEM recorded at different angle confirms the core shell structures. The stability of the synthesized polymer and its nanocomposites were substantiated from thermal studies carried out using TGA, DTA and DSC. The comparative electrical conductivities of the polymer and its nanocomposites shows semiconducting nature and the conductivities are found to be higher for the nano composites than the polymer and the electrical conductivity was found to be higher for the polymer nanocomposite synthesized with 15% of SiO_2. Photoluminescence is the property which involves the process of photon excitation followed by photon emission. The PL spectrum of polymers and their nanocomposites were recorded with 5, 10, and 15% SiO_2 nanoparticles and are found to fall under the green light emission region. Thus the synthesized polymer and its nanocomposites can be used as a green light emitter in different applications.

Keywords: Poly (o-Phenylenediamine), Nanocomposites, Thermal property, Electrical conductivity.

Introduction

The components which have at least one dimension like length, width or thickness in the size range of 1-100 nm are defined as Nanocomposites[1] and it differ from traditional composites in their properties and applications[2]. It contains organic polymers and inorganic particles which provide a completely new class of materials with novel properties and various industrial and biological applications[3]. SiO_2 is an excellent catalyst support because of its chemical inertia, thermal stability and adsorption of reactants[4]. Silicon oxide is normally generated from sand that is extracted after a fusion of high temperature. Characterisation temperature was determined via the temperature at which the highest Specific Surface Area (SSA) and highest amount of silica present and they were observed at 700°C[5].

The polymer nanocomposites can modify and improve the physical properties like mechanical and thermal exhibit some unique properties[6]. The combination of conductive polymers with inorganic metal oxides generates hybrid composites that possess higher reversible capacity, redox cyclability and structural stability and it strongly dependent on concentration of polymer[7-11]. The electroactive polymers are used in the fields of Light Emitting Diodes, solar cells, transistors, photovoltaic cells, and lasers etc[12].

In the present study, Poly orthoPhenylenediamine (PoPDA) and its metal oxide SiO_2 nanocomposites were synthesized using different concentrations of SiO_2 like 5, 10 and 15% by chemical oxidative polymerization method using the oxidant ammonium persulphate and were characterized by different techniques. The electrical conductivities and the photoluminicence (PL) properties of the polymer and its nanocomposites were also studied.

Materials and methods

Materials: Monomer Poly (o-Phenylenediamine) (PoPDA), Ammonium persulphate (APS), silicon dioxide are product of sigma- Aldrich and Hydrochloric acid were procured from Merck Ltd., India. The chemicals used in the present studied were of analytical reagent grade.

Methods: Synthesis of Poly o-Phenylenediamine and its nanocomposites: The chemical oxidative polymerization technique was adopted to synthesize Poly ortho Phenylenediamine and its metal oxide nanocomposites using a standard procedure with slight modification[13,14]. The precipitated polymer and its nanocomposites were washed with distilled water until the filtrate was colourless then with solvent acetone and methanol to remove excess initiator (HCl)

monomer and oligomers. Finally the resultant polymer precipitate was dried at room temperature for 24 hours.

Characterization techniques: The synthesized polymer and its nanocomposites were characterized by FT-IR spectroscopy of using ABB-MB-3000 spectrometer in KBr medium at room temperature. Perkin Elmer Lamba spectrophotometer was used to record the UV-vis spectra by dissolving the polymers in DMSO as a solvent. The XRD of polymers and its nanocomposites were recorded on an analytical diffractometer (Cukα) radiation source by applying a step scanning method (2θ ranged from 0-70°) with the scanning speed of 4° min^{-1}. The morphological study of the synthesized polymers was carried out using Scanning Electron Microscopy (SEM model: Jeol 6390 LV) with accelerating voltage of 0.5kV to 30kV. Transmission electron microscopy (TEM model Tecnai T20 G2 S-TWIN) was used to investigate the dispersion of PoPDA/ SiO_2 composites. TGA/DTA was recorded using Perkin Elmer Diamond under a nitrogen atmosphere up to 700°C using a heating rate of 10°C/min. Differential scanning calorimetry (DSC) was measured using Mettler Toledo DSC 822^e from room temperature to 500°C. The electrical conductivity was measured at room temperature by the four-point probe technique using LCR meter HP484A. HITACHI 850-type visible-ultraviolet spectrophotometer with a Xe lamp as the excitation light source was used to study the fluorescence properties of the synthesized compounds at room temperature.

Results and discussion

FT-IR spectroscopy: FT-IR spectrum of the PoPDA and PoPDA/SiO_2 nanocomposites synthesized at 5%, 10% and 15% of SiO_2 are given in Figure-1. The single peaks at 3227cm^{-1} is due to the N–H stretching vibrations of the –NH– group[15]. The two peaks at 3380 and 2953cm^{-1} are associated with the asymmetrical and symmetrical N–H stretching vibrations of the NH_2 group. Two strong peaks at 1629cm^{-1} and 1531cm^{-1} are assigned to the C=C and C=N group in phenazine ring[16]. The peak at 1359cm^{-1} and 1286cm^{-1} are associated with C-N-C stretching in the benzenoid and quinoid rings[17]. Further, the bands at 718cm^{-1} and 609cm^{-1} are the characteristic of C–H out-of- plane bending vibrations of benzene nuclei in the phenazine skeleton[18]. However with addition of SiO_2 nanoparticles, the characteristic peaks are slightly shifted to the lower wave numbers with slight increase in their intensities. The shifts in the frequencies are due to the interaction between the SiO_2 nanoparticles and polymer chain which affect the electron densities and bond energies[19]. A strong absorption band at 1073 and 804cm^{-1} are due to the stretching and bending vibration of SiO_2 present in the polymeric backbone[20].

UV-vis spectroscopy: The UV-vis spectra of PoPDA and PoPDA/SiO_2 nanocomposites with different wt% of SiO_2 nanoparticles (5, 10 and 15%) are given in Figure-2. The UV-Vis absorption spectra of PoPDA show two absorption peaks at 316 and 452nm transition of the benzenoid and phenazine ring[21]. The PoPDA/SiO_2 nanocomposites exhibited two major peaks at 280 and 446nm and the peak at 280nm is due to π–π* transition of the benzenoid and quinoid ring[22]. The π–π* transition associated with the phenazine ring conjugated to the lone pair of electrons present on the nitrogen of the NH_2 groups[23] are confirmed from the absorption peak at 446 nm. A blue shift was observed in the absorption maximum when the change of pH of the solution changed from 2 to 7[24].

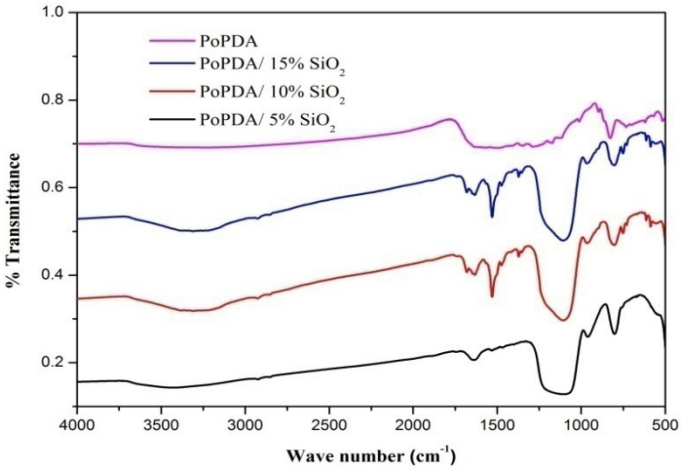


Figure-1: FT-IR spectra of PoPDA and its SiO_2 nanoparticles at different concentrations.

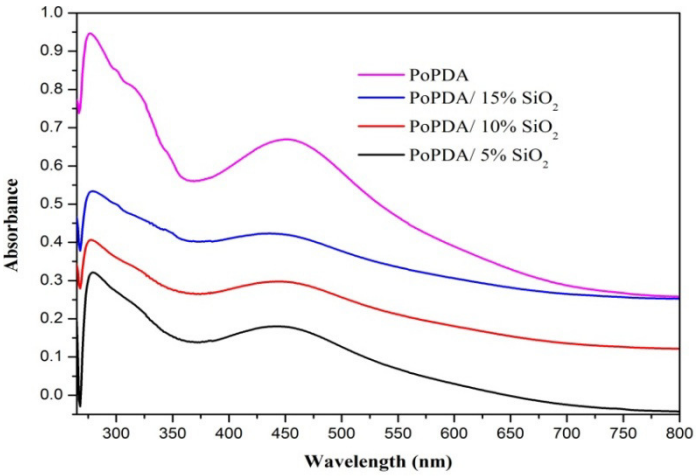


Figure-2: UV-vis spectra of PoPDA of its SiO_2 nanoparticles at different concentrations.

XRD: The XRD of PoPDA shows two sharp peaks at 2θ= 24.95 and 25.59. The inter-planar distances are found to be 40.95nm and 38.74nm and this is responsible for the crystalline nature of the polymer as shown Figure-3. The average crystalline size is calculated using Debye – Scherer equation d=[0.89]/[βcosΘ]. Where, β is full width of half maxima and the crystalline size of the polymer is found to be 8.340 nm. The XRD studies of the synthesized poly Phenylenediamine shows crystalline in nature but the poly phenylenediamine nanocomposites shows amorphous in nature[25].

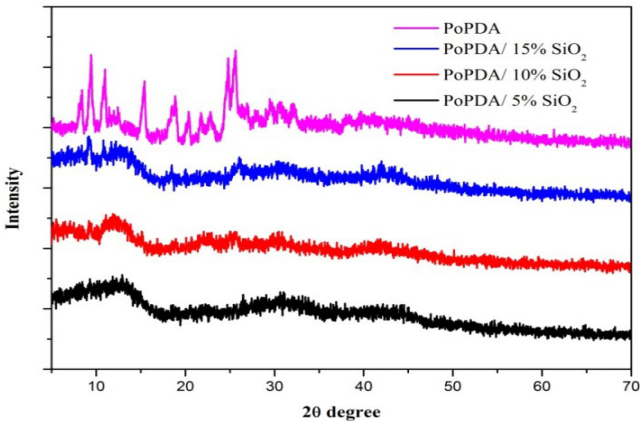
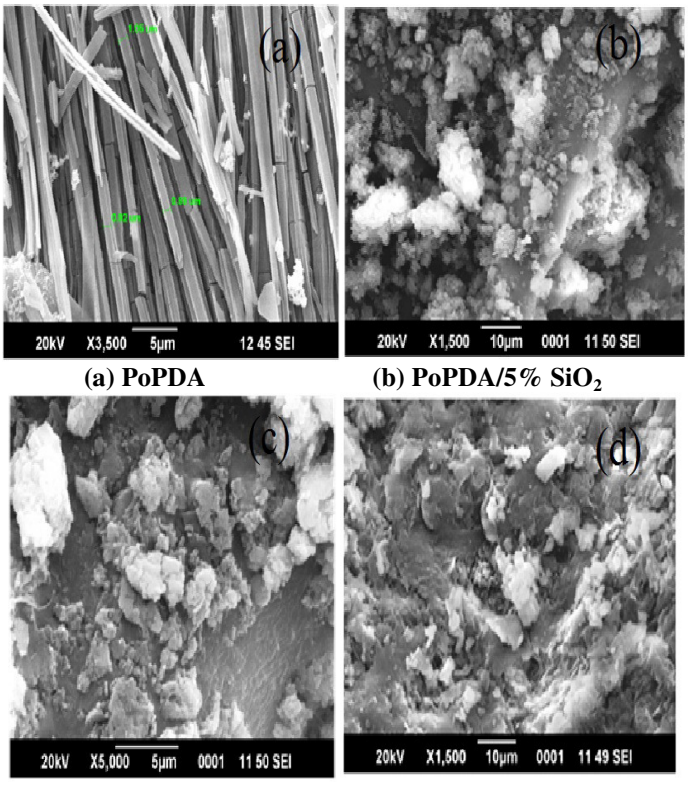


Figure-3: XRD of PoPDA and its SiO_2 nanoparticles at different concentrations.

Scanning Electron Microscopy: The SEM images of PoPDA and PoPDA/SiO_2 nanocomposites are given in Figures 4a-d. Figure 4a shows the SEM image of PoPDA which is found highly rod like structure. The SEM morphology of polymer nanocomposites with 5%, 10% and 15% of SiO_2 nanoparticles are found to be highly agglomerated. The poly nanocomposite synthesized with 5%, 10% and 15% of SiO_2 shows granular (4b), spherical (4c) and flake (4d) like structure. The SEM images are also clearly shows decreases in the intragranular distance as the concentration of SiO_2 increases and the morphology changes from granular to flake like structure[26].



(a) PoPDA **(b) PoPDA/5% SiO_2**

(c) PoPDA/10% SiO_2 **(d) PoPDA/15% SiO_2**

Figure-4: SEM images of PoPDA and its SiO_2 nanoparticles at different concentrations.

Thermogravimetric analysis: TGA is used to study the thermal stability of PoPDA and PoPDA/SiO_2 synthesized at different concentration of SiO_2 nanoparticles like 5, 10 and 15%. The polymer and its nanocomposites are found to have three stages of thermal transition as shown in Figure-5 and the thermal degradation of the polymer and its nanocomposites are almost similar. The first thermal transition occurred at 128°C is mainly due to the removal of moisture[27]. The second thermal transition at 287°C may be attributed to the removal of dopant[28] and the final weight loss at 483°C-700°C correspond to the degradation of the polymer[29]. The total residue was found to be 39.12% (wt %) for PoPDA and for the polymer nanocomposites the total residues are found to increase slightly to 42.05%, 43.85% and 45.78% (wt %) for 5%, 10% and 15% SiO_2 nanoparticles. The residue obtained shows that, as the concentration of the metal nanoparticles increases the residue obtained are found to increase.

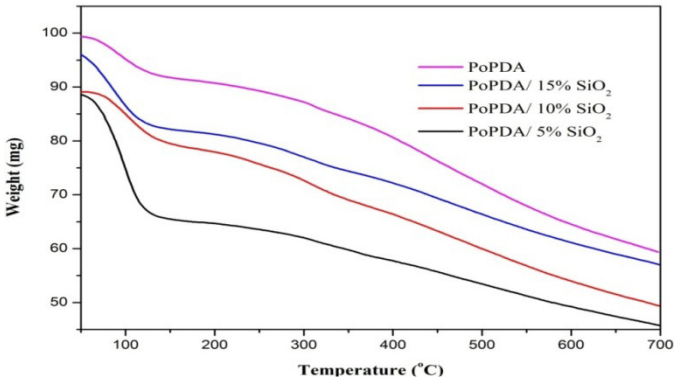


Figure-5: TGA of PoPDA and its SiO_2 nanoparticles at different concentrations.

Differential Scanning Calorimetry: The DSC of PoPDA and PoPDA/5% SiO_2, PoPDA/10% SiO_2 and PoPDA /15% SiO_2 are given Figure-6. The PoPDA shows peak at 95.86 °C which is due to the glass transition temperature [Tg]. The peak at 387.13 °C is characteristic of melting temperature [Tm]. The PoPDA/SiO_2 nanocomposite at different concentration shows an endothermic peak at 96.47°C which is due to the glass transition temperature [Tg]. The polymer starts to melt are shown by endothermic peak at 370°C which is characteristics of melting temperature[30]. TGA shows that the polymer nanocomposites are increased to the temperature compared to the polymer.

Transmission Electron Microscopy: Transmission Electron Microscopy images of polymer nanocomposites with 15% of SiO_2 nanoparticle at different angles are given in Figure-7 and it found to have aggregated spherical like morphology. The TEM image shows that the particle size of synthesized polymer nanocomposites ranges from 40-45nm. Moreover the outer core of the TEM image of the nanocomposite is more bright compared with the dark inner core and this forms the core- shell feature of the PoPDA/SiO_2 nanocomposites[31]. The formation of PoPDA/SiO_2 core shell nanocomposites may be due to the strong electrostatic interaction between polymer and SiO_2 nanoparticles.

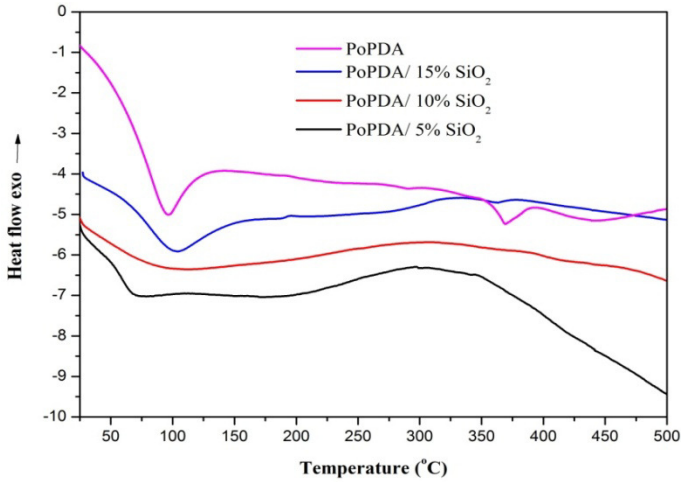


Figure-6: DSC of PoPDA and its SiO_2nanoparticles at different concentrations.

Electrical conductivity: The electrical conductivity of PoPDA and PoPDA/SiO_2 (5wt%, 10wt% and 15wt %) were determined using four-point-probe technique at room temperature and the results are given in Figure-8. The conductivity of PoPDA and its nanocomposites were evaluated using bulk resistance (R_b) using the formula: $\sigma = (t / A) (1 / Rb)$ S/cm, Where, t is the thickness of the pellet, A is the area of pellet and R_b is the bulk resistance of the pellet. The electrical conductivity of the PoPDA and PoPDA synthesized with 5, 10, and 15% SiO_2 nanoparticles are found to be 1.79 $x10^{-8}$ S/cm, 1.59 $x10^{-7}$, 2.13 x 10^{-7} and 2.78 $x10^{-7}$ S/cm. The results clearly show that the conductivity increases from polymer to the polymer nanocomposites and as the concentration of the SiO_2 increases, the conductivity increases slightly. When added different concentration of metal oxide nanopowder, it was found that the electrical conductivity of polymer SiO_2 nanocomposites was found to improve[32].

Photoluminescence: Perkin Elmer says Photoluminescence (PL) is the property which involves the process of photon excitation followed by photon emission and most of the molecules occupy the lowest vibrational level of the ground electronic state. The absorption of light is elevated to produce the excited states and from the molecules occupied in the excited states, again loses energy and reaches the lowest vibrational level of the first excited state. From the first excited level, the molecules return to the vibrational levels of the ground state emitting its energy in the form of fluorescence[33]. The PL property of the PoPDA and PoPDA/SiO_2 nanocomposite synthesized at different concentrations of SiO_2 are given in figure 9. From the figure, it is evident that the PL spectrum pattern shows strong green light emission band around at 530 nm. The ionized oxygen vacancy present in SiO2 may be responsible for the green emission and the emission may result from the recombination of a photogenerated hole with an electron occupying the oxygen vacancy[34].

Conclusion

The PoPDA and PoPDA /SiO_2 nanocomposites have been successively prepared via chemical polymerization methods. The synthesized polymer and composites were characterized using FT-IR, UV-vis spectroscopy and confirmed the formation of the polymers. The morphologies of the polymer and its nanocomposites carried out using SEM studies shows different morphology for the synthesized polymer and its nanocomposite. The XRD studies reveal the amorphous in nature polymer nanocomposite unlike the polymer. The formation of core shell type morphology of SiO_2 nanoparticles was confirmed from TEM analysis. The thermal stabilities of the polymers and its composites were confirmed from the TGA and DSC studies. The conductivity studies of the polymer nanocomposites of PoPDA shows semiconducting in nature and the conductivity is higher in polymer nanocomposites than the polymer. The study of the fluorescence shows that the polymer and its nanocomposites are cabable of emitting green light and this confirms that the synthesized polymer and its nanocomposites can be applied in different technological applications in future.

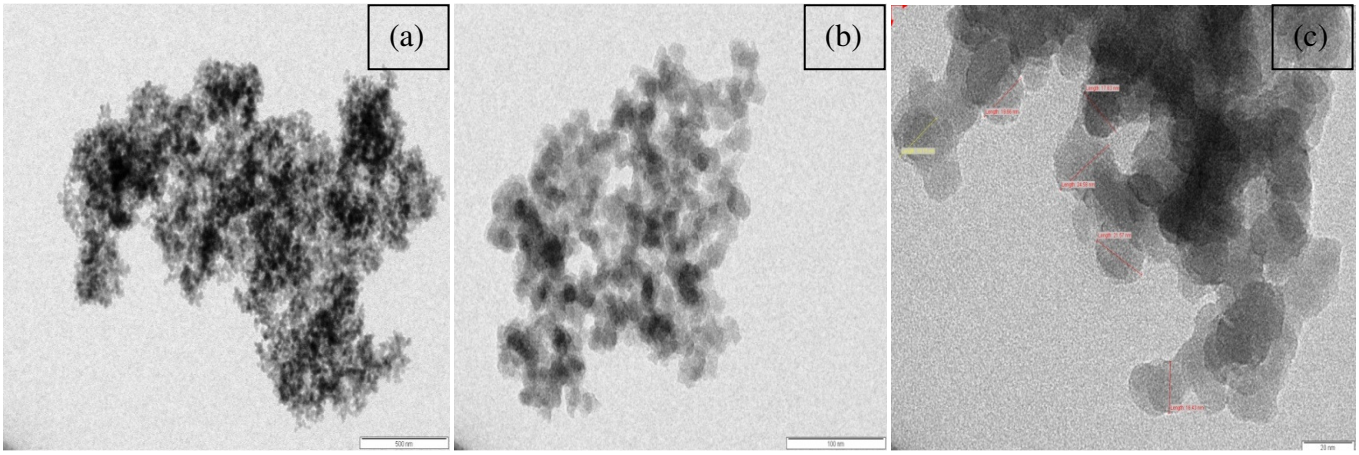


Figure-7: TEM images of PoPDA/ 15% SiO_2 nanocomposites at different angles.

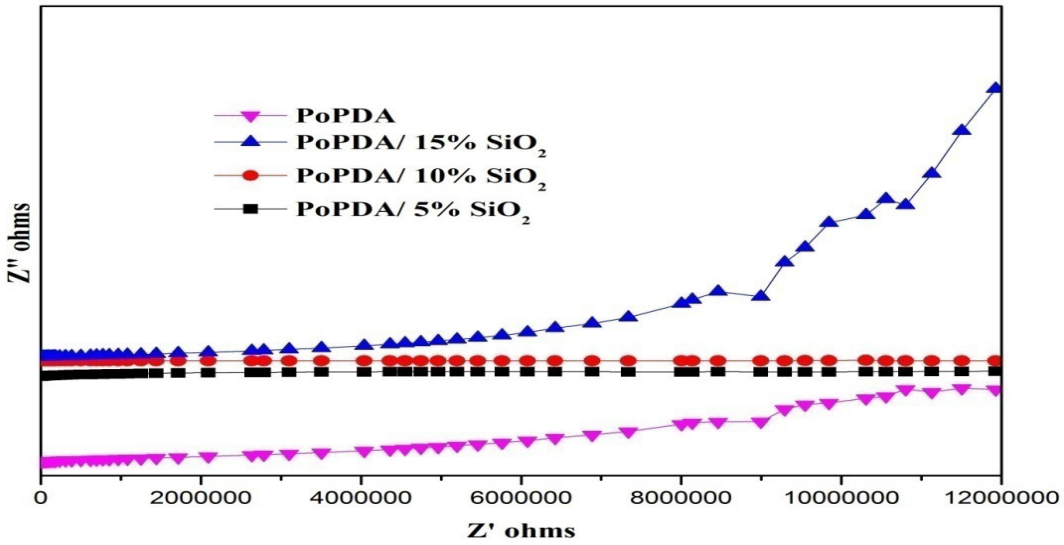


Figure-8: Electrical conductivities of PoPDA and its SiO_2 nanoparticles at different concentrations.

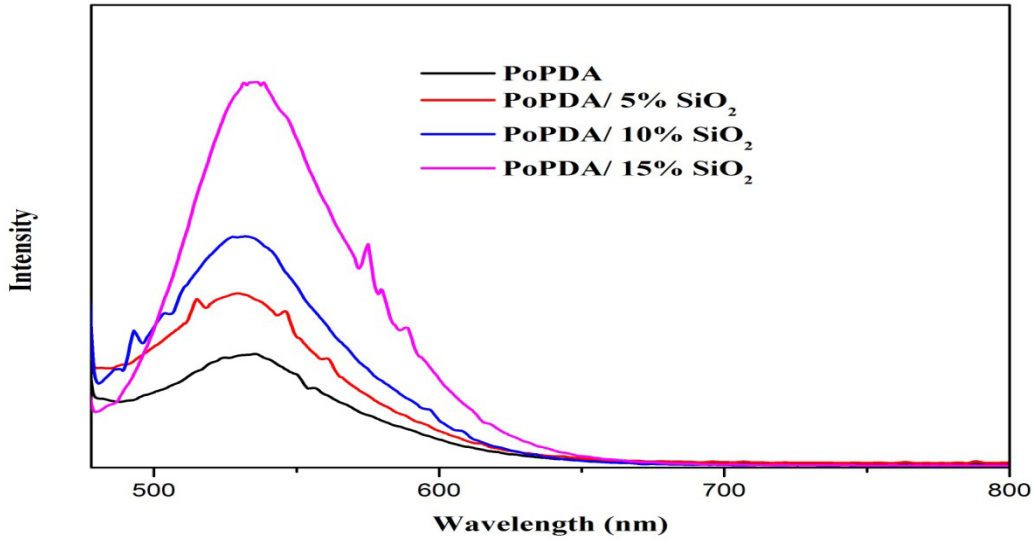


Figure-9: Photoluminescence of PoPDA and its SiO_2 nanoparticles at different concentrations.

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