Materials Today: Proceedings 33 (2020) 2174–2179

Contents lists available at ScienceDirect

Materials Today: Proceedings

journal homepage: www.elsevier.com/locate/matpr

Studies on the hypsochromic shifted optical properties of gold nanoparticles embedded electrospun poly(methyl methacrylate) (PMMA) nanofibers

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ARTICLE INFO

Article history:
Received 10 November 2019
Received in revised form 24 March 2020
Accepted 27 March 2020
Available online 11 April 2020

Keywords:
Electrospinning
PMMA
Surface plasmon resonance
Gold nanoparticles
Photoluminescence

ABSTRACT

Electrospinning is always a fascinating fiber formation technique in the material science world. The characteristic properties and functionalities of the electrospun nanofibers keep them attractive always and everywhere. Here PMMA electrospun nanofibers with 60–150 nm are produced and characterised by various characterisation techniques. Gold nanoparticles (AuNPs) incorporated electrospun PMMA nanofibers are produced by dispersion of the prepared PMMA nanofibers in colloidal AuNPs. The homogenous distribution of AuNPs on PMMA fiber surface is proved by TEM, FESEM, XRD, FTIR etc. and the optical characterisations are done by UV and PL analyses. PL spectra of the AuNPs incorporated PMMA nanofibers showed the characteristic absorptions of both PMMA and AuNPs in the visible region which shows the successful incorporation of the gold nanoparticles to PMMA nanofibers. The PL spectrum shows a characteristic blue shift in peak position with increase in excitation wavelength. The AuNPs incorporated PMMA nanofibers show enhanced photoluminescence than pure PMMA nanofibers which points to the host matrix nature of PMMA to noble metal nanoparticles like AuNPs.

Selection and peer-review under responsibility of the scientific committee of the 2nd International conference on Advanced Materials – Materials for a Better Living.

1. Introduction

Electrospun PMMA nanofibers are a matter of concern in the research world where it plays an important role in our day to day life. Electrospinning is a recently developed simple technique to produce nanofibers from solutions or melts. Electrospinning produces fibers in the submicron range with different architectures like pure, surface modified, porous, coaxial, coaxial hollow, blend etc. where each of which has a certain unique role and wide applications in various aspects of life. Electrospinning process is influenced by mainly three parameters like high voltage power supply, flow rate and tip to collector distance. It works on the basic principle that the polymer solution is subjected to an electric field and when it reaches the high voltage it overcomes the surface tension forces and a Taylor cone is produced at the tip of the needle; then the solvent(s) gets evaporated and the fibers are collected in the collector [1].

Electrospinning can be used to produce different polymeric compositions like PVDF-PMMA, [2–4] PEO-Chitosan, [5–7] PAN-PMMA, [8] PP-PA [9] etc. in addition to the production of pure nanofibers. PMMA plays an important role in various aspects of life and technology especially that related to optical field as it is a transparent polymer. Here PMMA is our choice because of its transparency, commercial availability, easy handling, low cost and resistance to moulds and enzymes etc. [10,11]. Gold nanoparticles have many applications in various areas like sensors, catalysts, biomedical etc. out of its properties like surface plasmon resonance (SPR) and others [12]. Colloidal gold nanoparticles can be prepared in different media and here we used starch.

Here the work is progressing in two stages where first one is the preparation of PMMA nanofibers through electrospinning followed by the synthesis of electrospun PMMA nanofibers incorporated with gold nanoparticles. The SPR of the donated gold metal nanoparticles are utilised here to investigate the optical properties. Here the novelty of the work is lying with the preparation of ultrafine PMMA nanofibers and studies on the optical properties of these nanofibers incorporated with gold nanoparticles. Many

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https://doi.org/10.1016/j.matpr.2020.03.681
2214-7853/
Selection and peer-review under responsibility of the scientific committee of the 2nd International conference on Advanced Materials – Materials for a Better Living.

works are being carried out in various research centres on PMMA thin films and gold metal nanoparticles. But here we focus on electrospun PMMA *nanofibers* incorporated with AuNPs which is not that much popular yet. It is easy to produce thin films by casting on a surface but the production of electrospun nanofibers with desired properties and functionalities are not that much easy as it depends on many internal and external parameters in addition to the major ones mentioned above.

2. Materials

Materials like poly(ethylene oxide)(PEO) (Sigma Aldrich), PMMA (Alfa Aesar), chloroform (Merk) and acetone (Merk), colloidal gold nanoparticles etc. used here to accomplish the work.

3. Methods

3.1. Preparation of PMMA nanofibers

PMMA nanofibers are produced by electrospinning. To get it, 1 g of PMMA is dissolved in a mixture of acetone and chloroform and is stirred well for 2 h to get a completely miscible solution and then it is subjected to electrospinning with suitable parameters like 20 kV voltage, 0.4 ML flow rate, 20 cm tip to collector distance etc. The diagrammatic representation of the procedure applied is shown in Fig. 1. Detailed elaboration and further information about the preparation of electrospun PMMA nanofibers are given in previously published papers [13,14].

3.2. Preparation of gold nanoparticles

The preparation method was followed from a previous study [15].

3.3. Preparation of PMMA nanofibers incorporated with gold nanoparticles

PMMA nanofibers incorporated with gold nanoparticles are prepared by dispersion method. Here 0.02 g of PMMA nanofibers are dispersed in 10 mL colloidal gold nanoparticles for 3 weeks. Then it is taken out, dried and kept for further analyses.

3.4. Characterisation

FTIR analyses of the samples were carried out using instrument Perkin Elmer Spectrum Two (Kerala, India). XRD analyses of the samples were carried out using Bruker AXS D8 Advance (STIC, CUSAT, Kerala, India). SEM analyses of the samples are carried out with JEOL Model - JSM 6390LV (STIC, CUSAT, Kerala, India). FESEM analysis is carried out using Nova NanoSEM 450 UoK (Trivandrum, Kerala, India). AFM analyses of the samples are carried out using Alpha300RA AFM & RAMAN (SAIF, MGU, Kerala, India). TEM analyses of the samples were carried out using JEM 2100 (IIUCNN, MGU, Kerala, India).

4. Results and discussion

4.1. Fourier transform infrared spectra (FTIR) analyses

The FTIR spectra of the electrospun PMMA nanofibers and those incorporated with gold nanoparticles are shown in Fig. 2(a)-(b).

PMMA shows main peaks at 2951 cm^{-1}, 1734 cm^{-1}, 1440 cm^{-1}, 985 cm^{-1}, 803 cm^{-1} etc. which corresponds to the PMMA C–H stretching band, PMMA C═O band, H–C–H bend in PMMA, C–C stretching PMMA and C═O in plane bending respectively. Detailed explanation of the FTIR details of PMMA nanofibers are given in the previously published papers [13,14]. A weak bond is formed between PMMA and AuNPs and the interaction between PMMA and AuNPs is referred here [16]. It is observed from the FTIR spectra of PMMA nanofibers incorporated with gold nanoparticles that certain new peaks are observed here and also the peaks of PMMA show a blue shift. The broad peak obtained at 3200–3600 cm^{-1}, 2918 cm^{-1}, 1623 cm^{-1}, 1215 cm^{-1}, 1019 cm^{-1} and 826 cm^{-1} respectively corresponds to the stretching vibrations of OH group, aliphatic C–H stretching vibrations, C═C stretching vibrations, OH bending vibrations, C-O stretching vibrations of phenolic group and aromatic ring. These bands arise from the alkaloids and various phytochemicals present in the leaf extract from which the gold nanoparticles are made [15]. Here the FTIR peaks of PMMA are shifted to 2955 cm^{-1}, 1739 cm^{-1}, 1456 cm^{-1}, 994 cm^{-1} and 805 cm^{-1} which denotes PMMA C–H stretching band, PMMA C═O band, H–C–H bend in PMMA, C–C stretching PMMA, C═O in plane bending respectively. This is due to the functional group interaction between PMMA and gold nanoparticles.

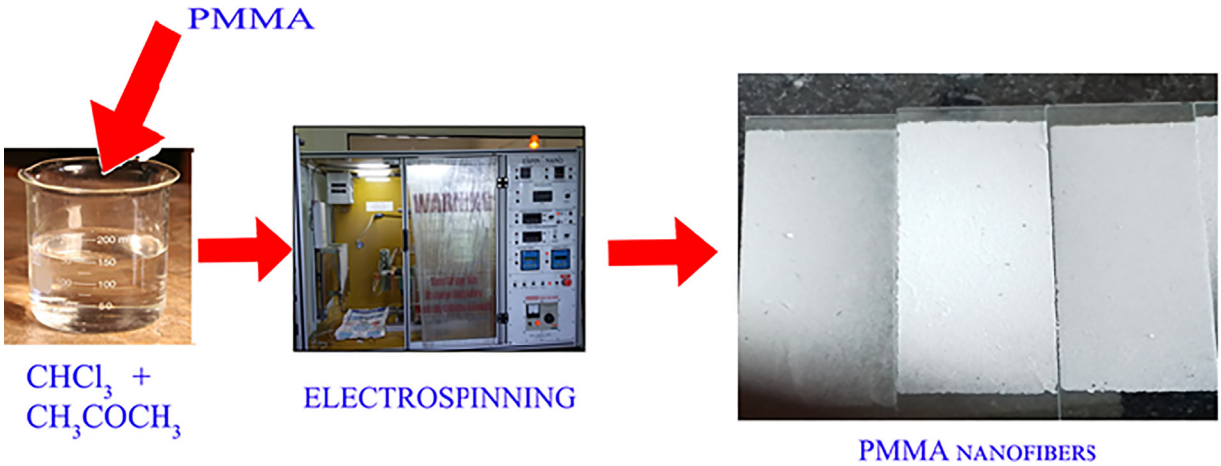

Fig. 1. Procedure for preparation of PMMA nanofibers.

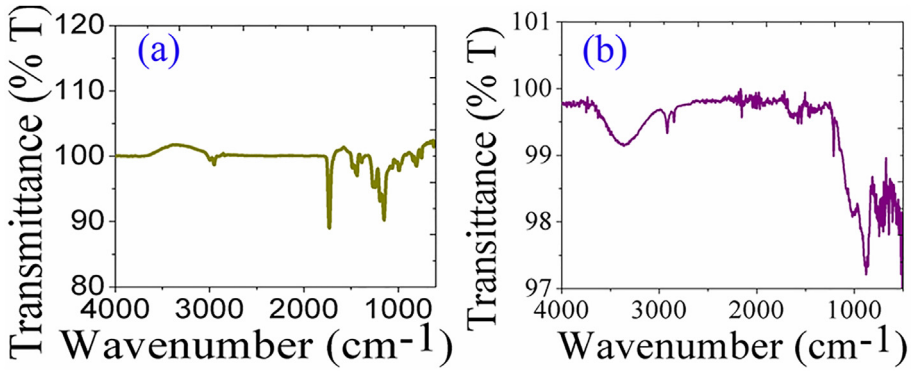

Fig. 2. FTIR spectra: (a) PMMA nanofibers (b) PMMA nanofibers incorporated with gold nanoparticles.

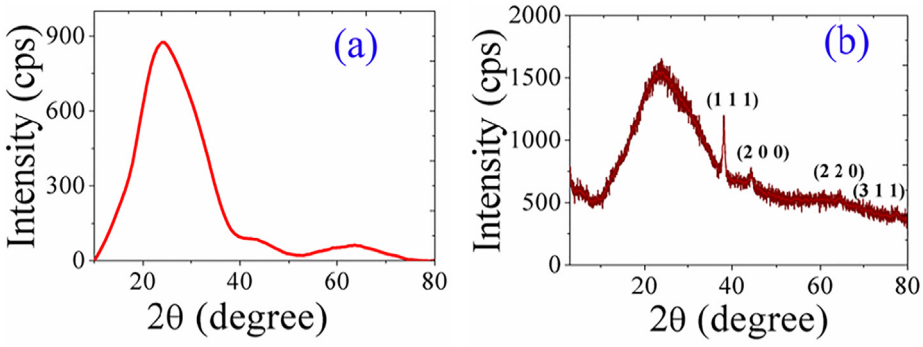

Fig. 3. XRD spectra: (a) PMMA nanofibers (b) PMMA nanofibers incorporated with gold nanoparticles.

4.2. X-Ray diffractometer (XRD) analysis

XRD spectra of the PMMA nanofibers and those incorporated with gold nanoparticles are shown in Fig. 3(a)-(b).

Pure PMMA nanofibers show XRD peaks at 24.2°, 43.3° and 63.1° [13,14] while they are shifted to 23.7, 41.5 and 62.5°after incorporating with gold nanoparticles. The shift in peaks due to interaction with AuNps supports FTIR results. The peaks obtained at 38.2°, 44.5°, 64.8° and 77.6° correspond to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) reflections of FCC structured gold nanoparticles [15]. Here the XRD spectrum shows the characteristic peaks of both PMMA and gold nanoparticles which prove the incorporation of gold nanoparticles to PMMA polymer matrix.

4.3. Field emission scanning electron microscope (FESEM) analysis

FESEM images of the PMMA nanofibers and those incorporated with gold nanoparticles are shown in Fig. 4(a)-(b). The diameter of the PMMA nanofibers is measured using WCIF Image J software and found to be below 100 nm. The details and further results are already published [13,14]. PMMA nanofibers show fine, smooth and well-arranged fiber form whereas the shape and uniformity of the sample is changed in a considerable way after incorporating

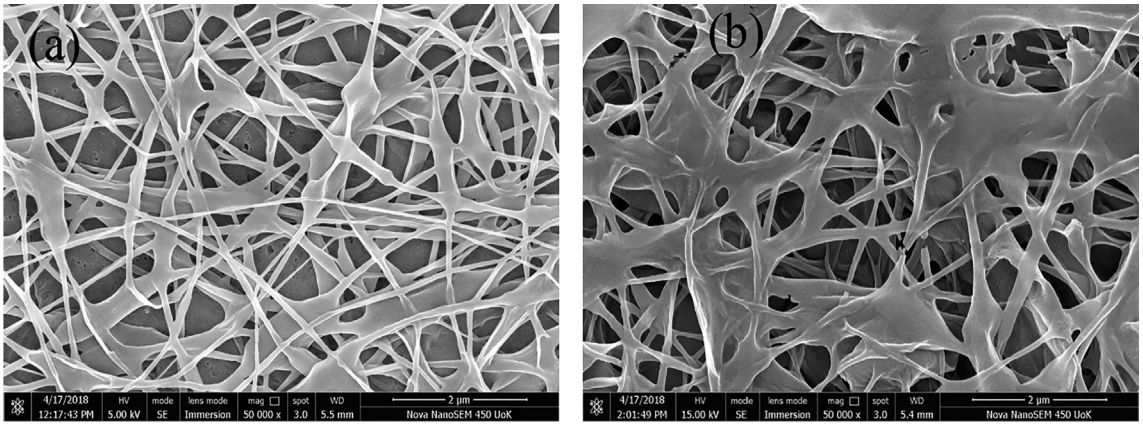

Fig. 4. FESEM images: (a) PMMA nanofibers (b) PMMA nanofibers incorporated with gold nanoparticles.

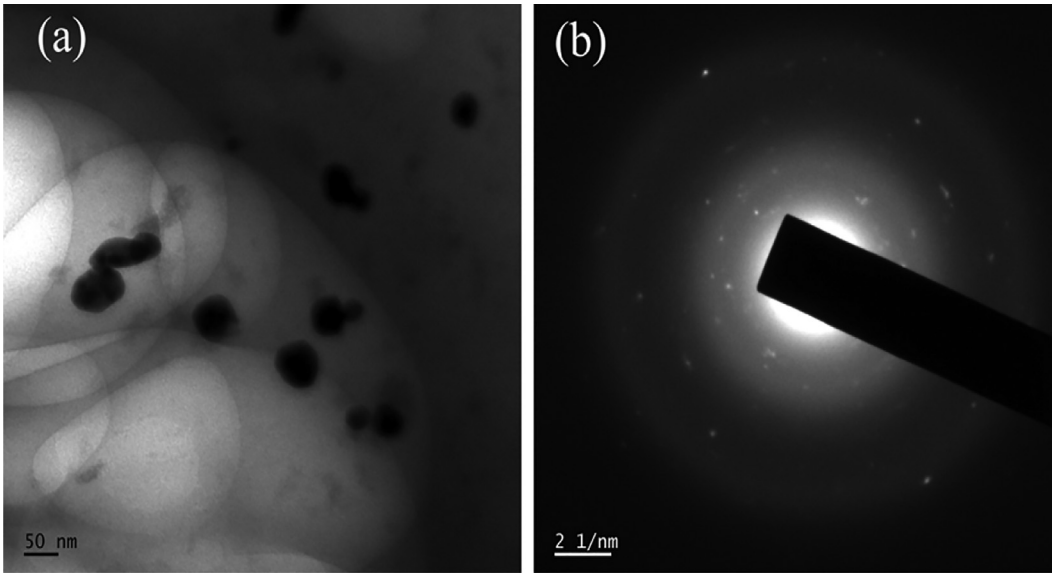

Fig. 5. (a) TEM image of PMMA nanofibers incorporated with gold nanoparticles (b) SAED pattern of PMMA nanofibers incorporated with gold nanoparticles.

the gold nanoparticles to it. This elucidates the incorporation of AuNPs to the polymer matrix.

4.4. Transmission electron microscope (TEM) analysis

The TEM image and SAED pattern of the electrospun PMMA nanofibers incorporated with AuNPs are shown in Fig. 5(a)-(b). TEM image proves the successful incorporation of AuNPs to it as shown in the figure and the SAED pattern also supports this incorporation. PMMA is an amorphous polymer and hence there is no possibility for such a SAED pattern as shown in Fig. 5(b). But here the SAED pattern shows a crystalline nature which is only due to the presence of crystalline AuNPs incorporated in the amorphous PMMA polymer.

4.5. Energy dispersive X-ray spectroscopy (EDX) analysis

The presence and elemental composition of the PMMA nanofibers incorporated with AuNPs is checked further by EDX analysis and the EDX spectrum is shown in Fig. 6. The data obtained is given

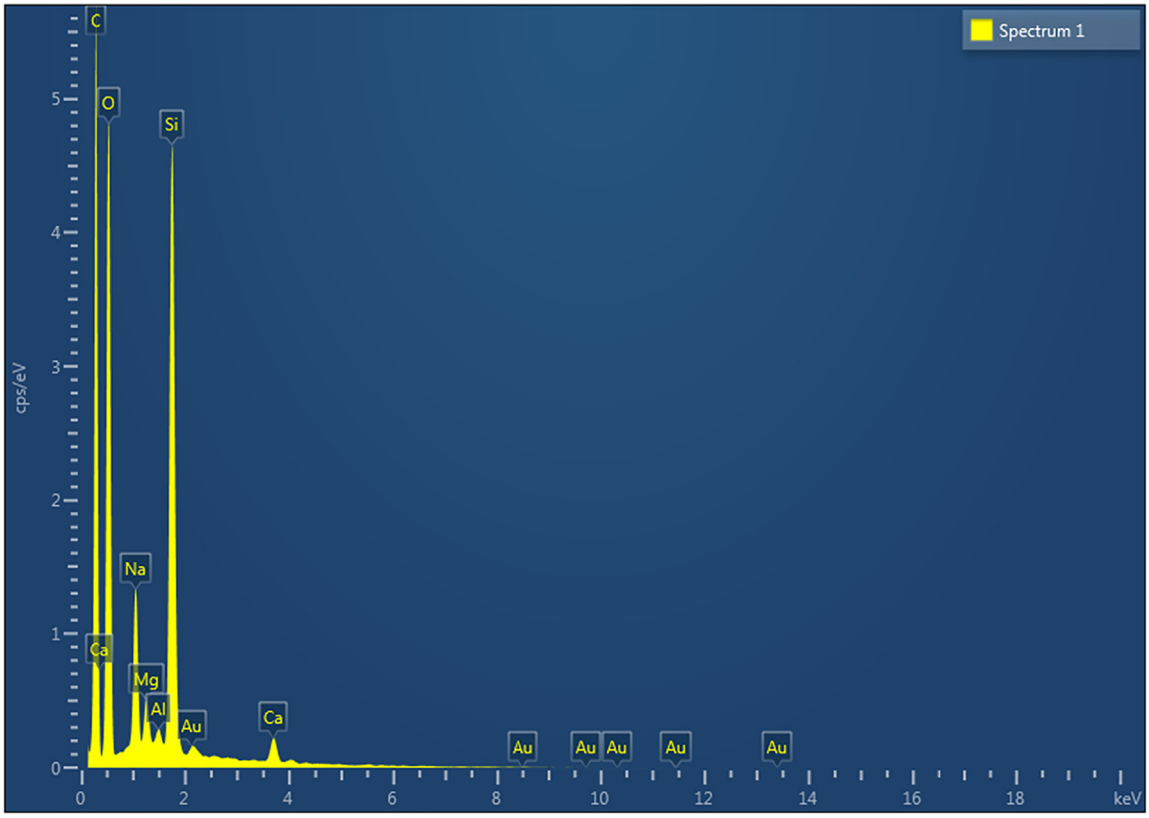

Fig. 6. EDX spectra: PMMA nanofibers incorporated with gold nanoparticles.

Table 1
Elemental composition of PMMA nanofibers incorporated with AuNPs.

Element	Line Type	Wt%	Atomic %
C	K series	49.81	59.54
O	K series	37.99	34.09
Na	K series	3.13	1.95
Mg	K series	0.64	0.38
Al	K series	0.18	0.1
Si	K series	7.29	3.73
Ca	K series	0.54	0.19
Au	M series	0.42	0.03
Total:		100	100

in Table 1 and it is mentioned in the table that the sample contains 0.42% of AuNPs. It is also noted that the particles are non-uniformly distributed here. This again supports the TEM, FESEM etc. results.

4.6. UV–Visible absorption analysis

The UV–Visible analysis spectra of PMMA nanofibers and these nanofibers incorporated with AuNPs are shown in Fig. 7(a)-(b). PMMA nanofibers show a broad absorption in the visible region which is characteristic of polymers [13,14]. Noble metal nanoparticles like AuNPs possess unique SR band which arises from the quantum size effect of them and these SPR bands make them suitable for many optical applications [17]. PMMA nanofibers incorporated with AuNPs also show an absorption in visible region but here it is entirely different in shape from the native form. Here the peak is very sharp while it is broad in the native form and hence it is a strong evidence for the incorporation of crystalline AuNPs to amorphous PMMA. The presence of crystalline AuNPs makes the peak sharp here. Here it doesn't show the separate peak corresponding to AuNPs whereas it shows two distinct emissions in PL analyses. Here in absorption spectra the peak of AuNPs may be shifted to lower wavelengths and merging with the peak of PMMA. This effect reduces the broadness of PMMA peaks to a great extent as shown in Fig. 7(b). The broad peak of PMMA nanofibers may be suppressing the peaks of AuNPs which are present only to a small extent.

4.7. Photoluminescence studies (PL)

The photoluminescence spectra of PMMA nanofibers and those incorporated with gold nanoparticles are given in Fig. 8(a)-(b).

PMMA nanofibers are excited at different excitation wavelengths and it shows a broad peak in the visible region in all excitations with maximum intensity at excitation wavelength 330 nm. PMMA nanofibers incorporated with AuNPs are also subjected to different excitation wavelengths from 270 nm to 310 nm. Here the PL spectrum shows three distinct peaks where one broad peak is in 400–500 regions which represents PMMA and the other is at 500–560 regions which corresponds to that of AuNPs and the peak at 650–750 regions correspond to that of plant extract contents from which AuNPs are prepared. Here the peaks of AuNPs are not that much visible since the concentration of AuNPs are very low. As the concentration of AuNPs increases the peak becomes clear as proved in our own further studies which are beyond the scope of this paper. PMMA nanofibers show maximum intensity at 501,148 cps while that incorporated with gold nanoparticles have 577,159 cps. This enhancement is due to the presence of luminescent AuNPs in transparent PMMA.

The photoluminescence intensity is found to increase with increase in excitation wavelength. Here the peak positions are shifted to lower wavelengths with increase in the excitation wavelength from 270 nm to 310 nm. The blue shift observed in peak position of PMMA nanofibers after incorporating AuNPs and the

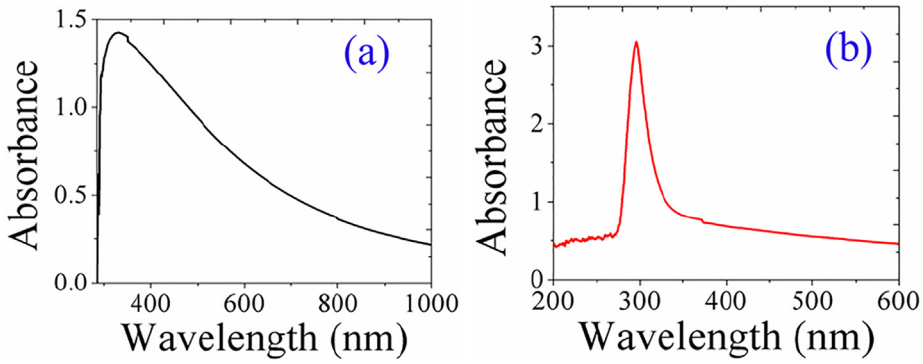

Fig. 7. UV–Visible analysis spectra: (a) PMMA nanofibers (b) PMMA nanofibers incorporated with gold nanoparticles.

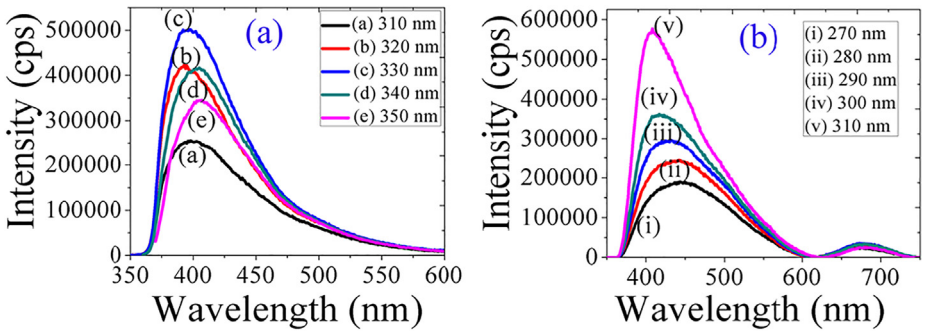

Fig. 8. Photoluminescence spectra: (a) PMMA nanofibers (b) PMMA nanofibers incorporated with gold nanoparticles.

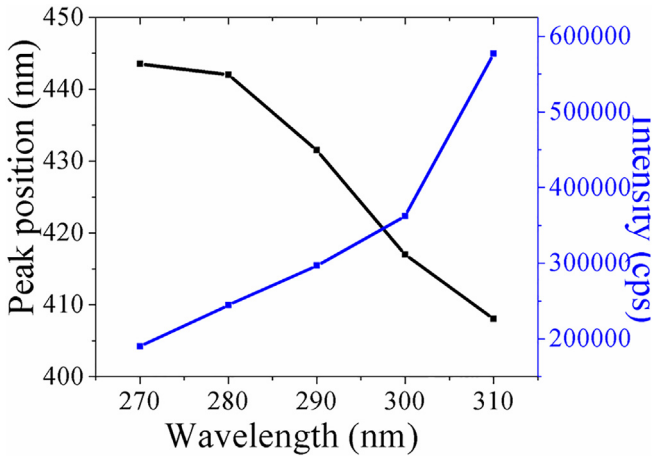

Fig. 9. PL shift in peak position and intensity: PMMA nanofibers incorporated with gold nanoparticles.

changes in intensity are collectively drawn together in Fig. 9. Thus the PL spectrum is characterised with enhancement in intensity and blue shift in peak position. The changes that occur in the peak position and intensity are due to the changes in luminescence transition of PMMA nanofibers and plasmon resonance [18]. Optical properties of the AuNPs depend on particle size as mentioned in the literature [17] and it is proved here also. These observations in intensity and peak positions prove that PMMA can act as a good host matrix to AuNPs with enhanced intensity which is an additional advantage to the transparent nature of PMMA. The polymer supports help to immobilize the nanoparticles, to maintain the size and shape dependent properties of nanomaterials and in making it useful for various applications [19].

5. Applications

PMMA nanofibers have many applications in optical fields due to their transparency, rigidity and stability compared to other polymeric systems. These characteristic properties of PMMA are combined with the SPR of AuNPs to use it in capacitors, light and flexible electronic devices, sensors etc [20,21]. The polymer matrix also acts as a good support to the AuNPs in catalysis [18]. Thus the PMMA nanofibers incorporated with AuNPs found applications in many areas. The incorporation of these AuNPs to structurally modified electrospun PMMA nanofibers like surface roughened and coaxial hollow PMMA forms offer much more unique properties and advantages than the AuNPs incorporated pure PMMA nanofibers and these works are progressing well which is beyond the scope of this paper.

6. Conclusion

Electrospinning is an evergreen technology for the production of polymer nanofibers having supreme properties and functionalities by tuning the process and parameters associated with it. Electrospun PMMA nanofibers are produced with diameter 60–150 nm and the AuNPs are incorporated to it for analysing the host matrix nature of PMMA to them and to understand the variation in the optical properties of PMMA nanofibers after incorporating AuNPs to it. PMMA nanofibers are characterised by different structural and molecular analyses to elucidate their morphological properties. The successful incorporation of the AuNPs to these PMMA nanofibers is proved by TEM, AFM, FESEM, XRD, FTIR etc. The optical properties of the samples are analysed by UV–Visible absorption studies and PL analyses. PL analyses of the samples showed peaks corresponding to PMMA and AuNPs. The peaks show blue shift with increase in wavelength and PMMA nanofibers incorporated with AuNPs show enhancement in intensity due to the luminescence transitions between PMMA and AuNPs. These analyses give a solid evidence for the host matrix nature of PMMA nanofibers to noble metal nanoparticles like AuNPs. The transparency of PMMA nanofibers are combined with SPR of AuNPs to make them useful in many optical fields.

CRediT authorship contribution statement

Princy Philip: Conceptualization, Methodology, Investigation, Visualization, Writing - original draft. **Tomlal Jose:** Validation, Supervision, Resources, Project administration, Funding acquisition. **K.C. Philip:** Supervision, Resources. **P. Manoj:** Data curation, Formal analysis. **T. Sajini:** Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors thank UGC and KSCSTE for providing fund for electrospinning machine. We sincerely thank the instrument operators in Mahatma Gandhi University (IIUCNN & SAIF), Cochin University (STIC, CUSAT) and Kerala University, Trivandrum in India for providing the timely technical assistance.

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