Purine-Blended Nanofiber Woven Flexible Nanomats for SERS-Based Analyte Detection

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Materials and Instrument details:

Polyacrylonitrile (PAN) with average Mw 150000 (Typical) and rhodamine 6G were purchased from Sigma Aldrich. Adenine, thiourea, Bromine and $HAuCl_4$ were obtained from Spectrochem Pvt Ltd., Tri sodium citrate dihydrate was purchased from Rankem. Sodium hydroxide was acquired from Finar. Uric acid and n-propyl bromide were obtained from Alfa Aesar, India. Dimethylformamide and ethanol were purchased from Merck. Electrospun nanofibrous mats were prepared on a Super ES-2 model electrospinning unit. Field Emission Scanning Electron Microscope (FESEM) images were taken on an FEI Quanta 200 microscope equipped with a tungsten filament gun, operating at a 4 mm WD and an operating voltage of 10 kV. Transmission Electron Microscope (TEM) images were acquired using Thermo fischer FEI Technai T12-120 instrument operating at 120 kV, while High Resolution Transmission Electron Microscope (HRTEM) images were obtained using FEI Titan G2 60-300 instrument operating at 300 kV. FTIR analyses were done for fiber mats after making pellets with KBr on a Bruker Vector 22 FTIR spectrophotometer operating from 400 to 4000 cm^{-1}. X-ray diffraction (XRD) was performed with a PANalytical X'Pert PRO diffractometer with Cu Kα radiation (1.5405 Å), Netherlands. SERS spectra of analytes with various concentrations were recorded on Raman spectrometer (WiTec CRM 2000 Raman spectrometer, Germany), equipped with a He-Ne laser excitation source emitting at a wavelength of 532 nm. Raman spectra have been recorded on 5 different places for each sample to check the reliablity and also the raman spectra were repeated on 3 different set of samples to check the reproducibility.

Synthetic procedure

Synthesis of 8-mercapto-N9-propyladenine (L)

The titled compound was synthesized by following reported procedure.[1]

Preparation of electrospinning solution

Electrospinning solution **(A-D)** was prepared by blending of **L** with **PAN** in various proportions to get electrospun nanofiber mats namely **P1**, **P2**, **P3** and **P4** (Table 1).

Procedure for electrospinning solution (B-D): DMF solution of PAN with 9% w/v was prepared to which certain amount of **L** was added. The resulting solution was stirred at room temperature for 3 h. As-synthesized homogeneous viscous solution was subjected to electrospinning technique.

Electrospinning solution	PAN Concentration (% w/w)	L Concentration (% w/w)	Electrospun fibrous mats
A (control)	100	0	P1
B	90.9	9.1	P2
C	83.33	16.67	P3
D	66.66	33.34	P4

Table 1. Concentration of **PAN** and **L** in electrospinning solution

Procedure for electrospinning solution A:

As a control experiment, above mentioned procedure was followed in the absence of **L**.

Synthesis of electrospun fibers mat (P1-P4):

The following procedure was employed for all electrospinning solutions **(A-D)** to make corresponding fiber mats **(P1-P4)**. As-synthesized viscous solution was transferred in to a syringe with a needle which was connected to high voltage source. Electrospun was done under 14 kV with flow rate of 15 µL/min. Electrospun fibers were collected on non-woven cloth placed on metallic rotating drum.

Synthesis of citrate capped gold nanoparticles (AuNPs)

An aqueous solution of citrate capped gold nanoparticle with spherical shape was synthesized by modified reported procedure.[2] In brief, 150 ml of 1 mM $HAuCl_4$ aqueous solution was boiled under vigorous stirring. After 10 min, 15 ml of 38.8 mM trisodium citrate aqueous solution was added into the reaction medium. Stirring with heating the reaction mixture at 100 °C was continued for 30 min. Then Wine red colored

aqueous solution of AuNPs was cooled down to room temperature and was stored at 4 ℃ in refrigerator before use.

Fabrication of electrospun fiber/AuNPs composites

As-prepared all electrospun fibrous mats **(P1-P4)** were cut into 1 x 1 cm pieces and were allowed to interact with as-synthesized citrate capped AuNPs aqueous solution. Each nanofibrous mat was immersed into citrate capped AuNPs solution (4 ml) separately and kept in incubator shaker at 37 ℃ for 6 h. The wine red color of AuNPs solution containing **P2-P4** became almost colorless and a very slight dark grey precipitate was observed whereas, wine red color of AuNPs solution having **P1** remained unchanged. For the effective decoration of nanoparticles on the fibres, all the mats (**P1-P4**) were again immersed separately into fresh AuNPs solution as described above and the same procedure was repeated thrice and kept in shaker for 6 h, 24 h and 24 h respectively at the same temperature. The color of mats **P2-P4** changed from colorless to dark grey whereas, the mat **P1** remained almost colorless. Then all the mats were taken out from AuNPs solution followed by washing with water and kept at room temperature for drying in dark environment.

Sample Preparation for FESEM analysis:

As-prepared electrospun fibrous mats **(P1 -P4)** without and with AuNPs were cut into 0.5 × 0.5 cm pieces and were gold coated for 1 min prior to FESEM imaging.

Sample Preparation for TEM analysis:

AuNPs decorated electrospun fibrous mats **(P1-P4)** were cut into 0.2 × 0.2 cm piece and each mat was suspended in 0.5 ml of water. It was sonicated for 30 min and 4 µL of this water suspension was drop casted on a TEM grid. Then the sample was dried and the images were acquired followed by elemental mapping analysis.

Sample preparation for SERS measurements

Sample preparation of rhodamine 6G: AuNPs decorated electrospun fibrous mats **(P1-P4)** were cut into 0.3 x 0.3 cm on which 2 µL ethanolic solution of rhodamine 6G (10^{-15} M) was dropcasted. They were allowed to dry at room temperature in dark environment prior to raman spectroscopy analysis.

Sample preparation of uric acid: Analyte was prepared by following reported procedure.[3] In short, stock solution of 1 mM uric acid was prepared by adding 0.2 ml of 2% NaOH aqueous solution to 9.8 ml aqueous suspension of uric acid (1.68 mg). Aqueous solution of uric acid with lower concentrations 10^{-6}, 10^{-7} M were prepared by diluting stock solution of 1 mM uric acid with distilled water. AuNPs decorated electrospun fibrous mats **(P1-P4)** were cut into 0.3 x 0.3 cm and 2 µL of uric acid solution with various concentrations were drop casted on **AuNPs/PAN/L** nanofibers composites. They were allowed to dry at room temperature in dark environment prior to raman spectroscopy analysis.

P4 without AuNPs was cut into 0.3 x 0.3 cm on which, 2 µL of aqueous solution of uric acid (10^{-3} M) was drop casted. It was allowed to dry at room temperature prior to raman spectroscopy analysis.
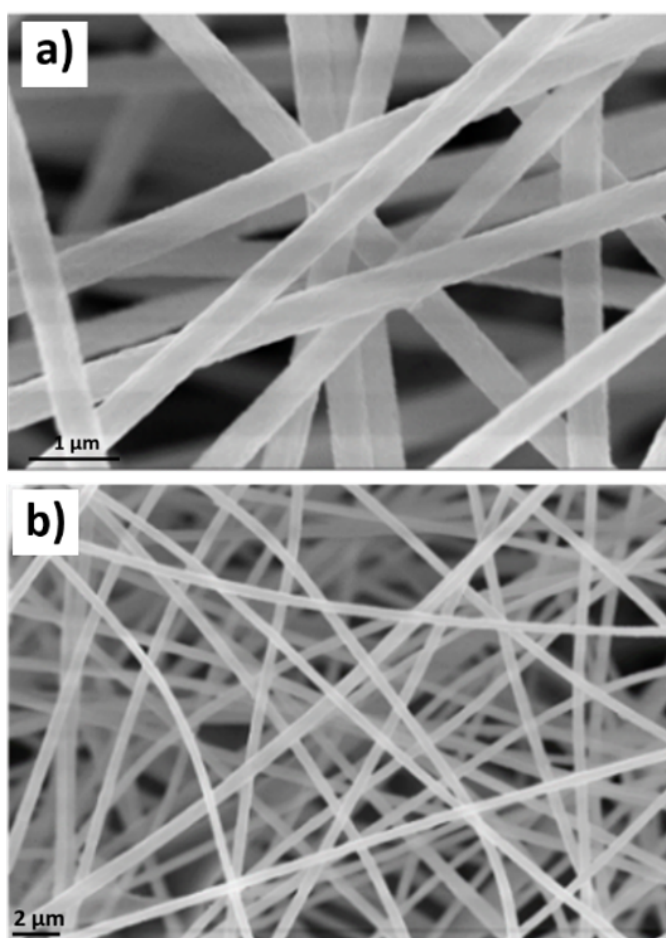

Fig. S1. FESEM images of **PAN/L** electrospun nanofibers with various blend ratio a) 90.9/9.1 **(P2)**; b) 83.33/16.67 **(P3)** (%w/w).
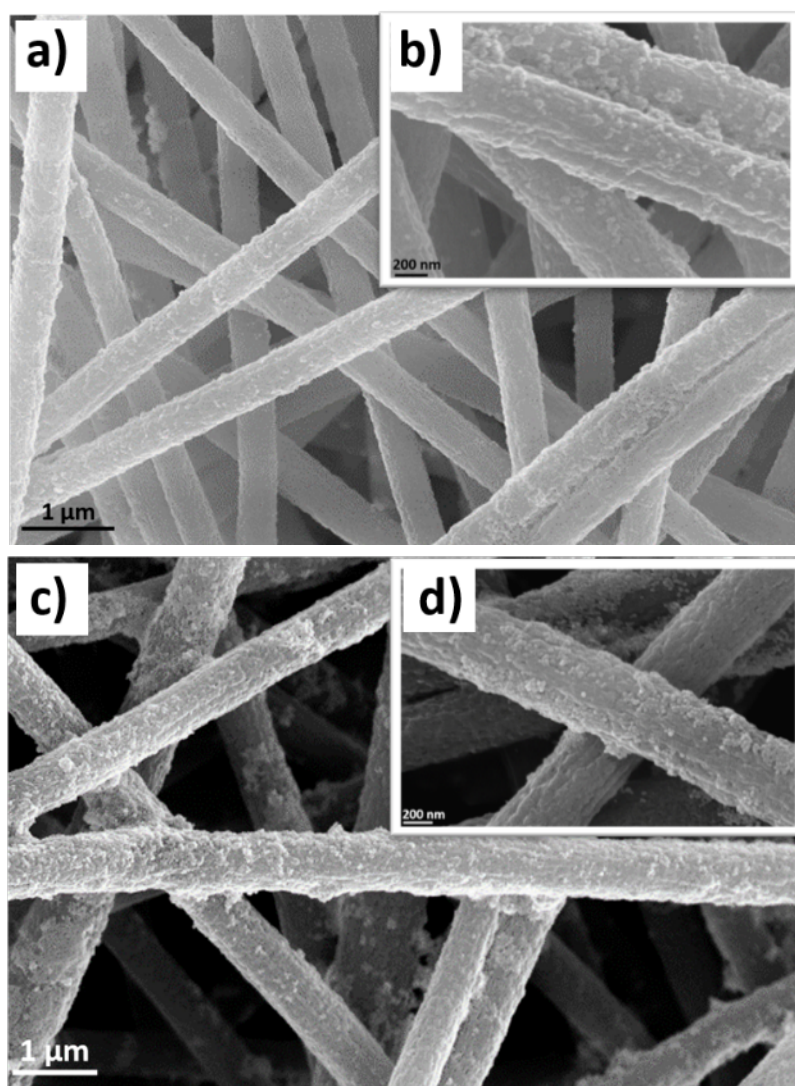
Fig. S2. FESEM images of AuNPs decorated **PAN/L** electrospun nanofibrous mats of **P2** (a,b) and **P3** (c,d).
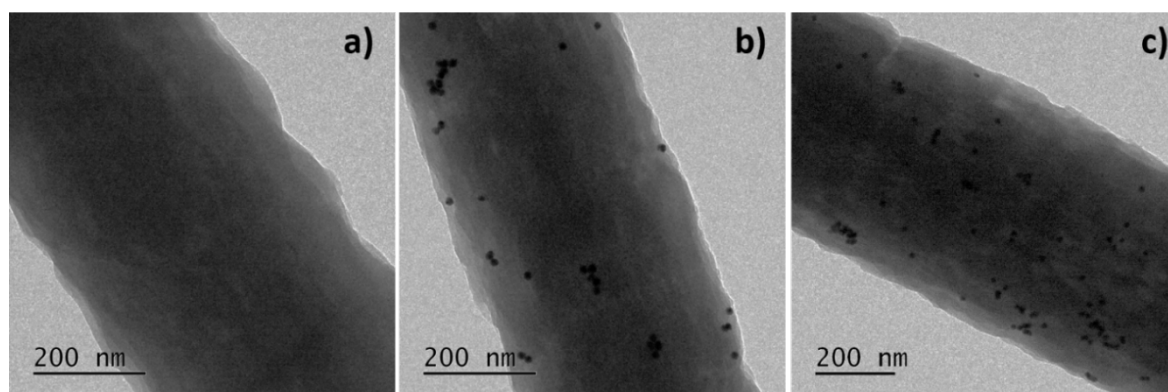

Fig.S3. TEM images of AuNPs decorated **PAN/L** electrospun fibers a) **P1** b) **P2** and c) **P3**.
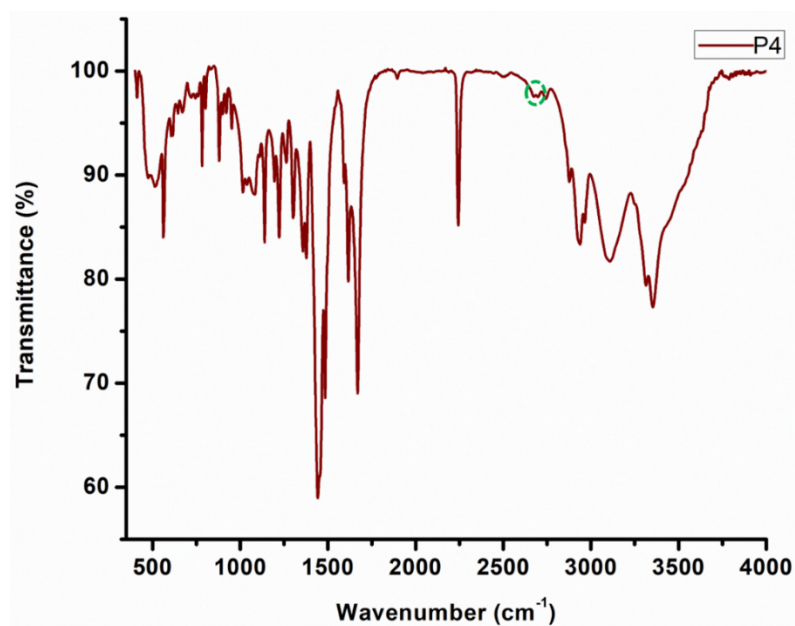
Fig. S4. FT-IR spectra of electrospun nanofibrous mat **P4.** Green dotted circle indicates the presence of S-H stretching frequency at 2674 cm^{-1}.
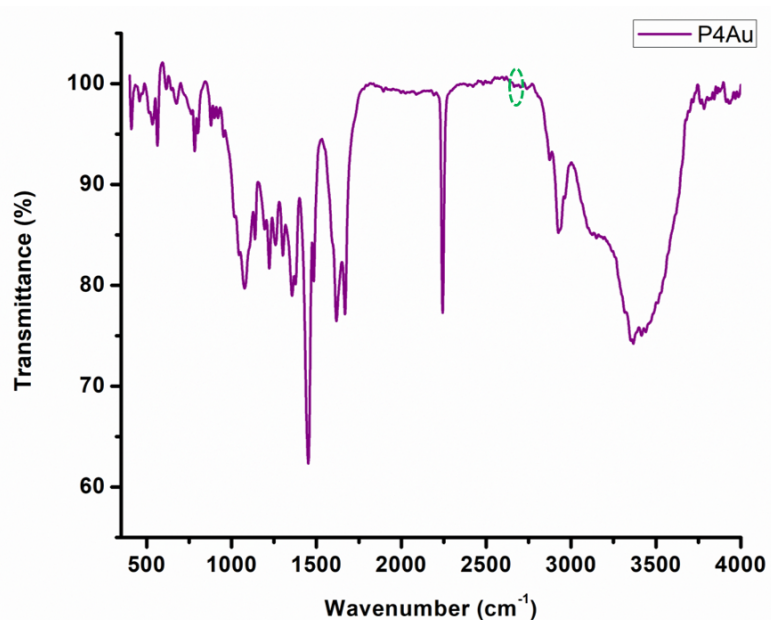

Fig. S5. FT-IR spectra of electrospun nanofibrous mat **AuNPs/P4**. Green dotted circle indicates the absence of S-H stretching frequency at 2674 cm^{-1} in **AuNPs/P4**.
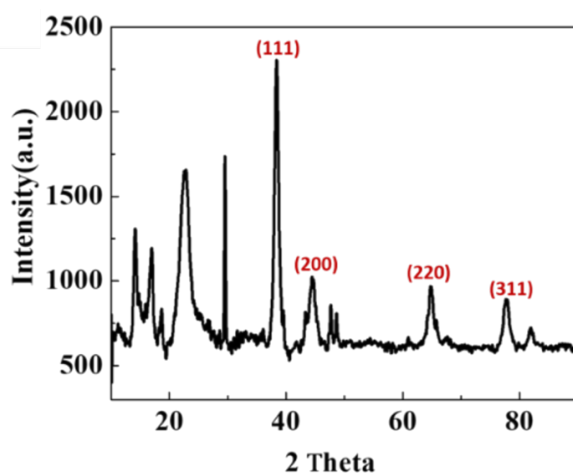
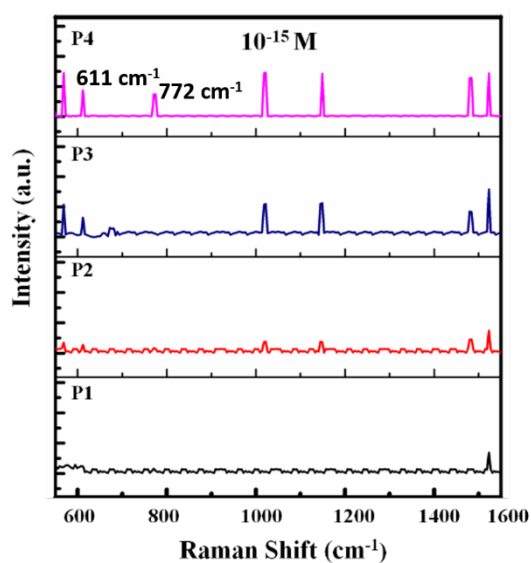**Fig S6.** XRD pattern of electrospun fibrous mat of **AuNps/P4**.

Fig. S7. Raman spectra of AuNPs decorated **PAN/L** electrospun fibrous mats (**P1-P4**) with 10^{-15} M of rhodamine 6G.
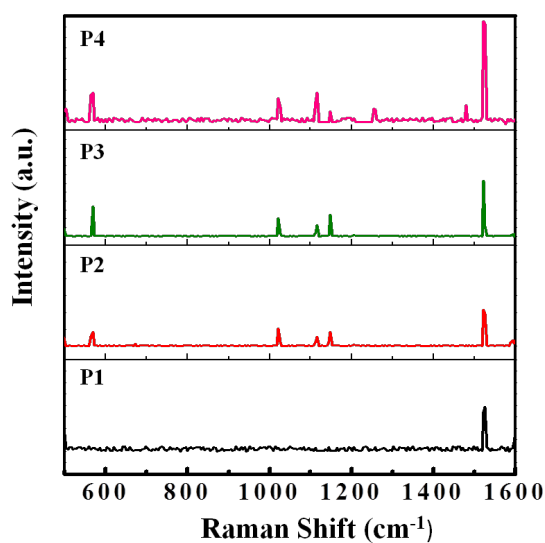

Fig. S8. Raman spectra of AuNPs decorated **PAN/L** electrospun fibrous mats (**P1-P4**) without uric acid.
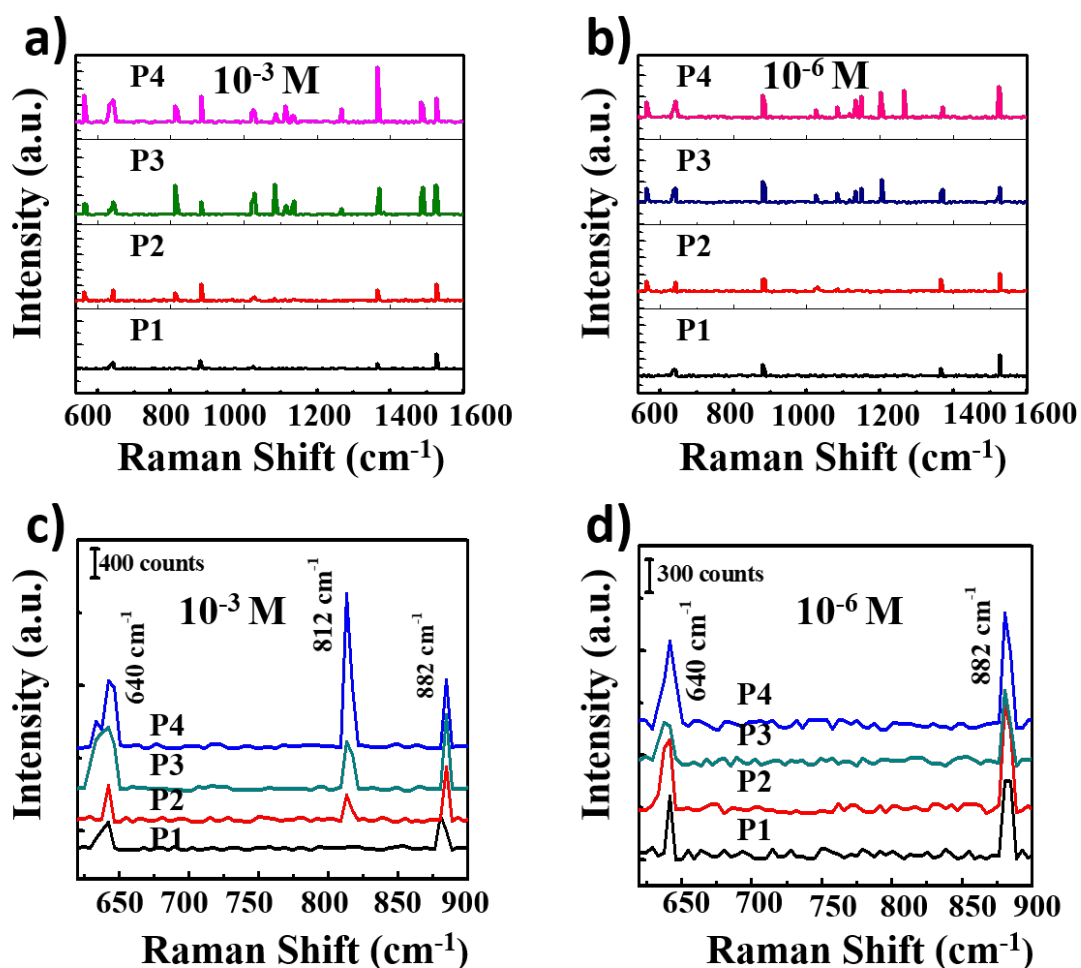
Fig. S9. Raman spectra of AuNPs decorated **PAN/L** electrospun fibrous mats (**P1-P4**) a) with 10^{-3} M of uric acid and b) with 10^{-6} M of uric acid. Raman spectra of uric acid on **AuNPs/PAN/L** nanofibers composites showing 640 and 882 cm^{-1} peaks of uric acid at 0% w/w (**P1**), 9% w/w (**P2**), 16% w/w (**P3**) and 33% w/w (**P4**) of **L** blended **PAN** electrospun nanofibers at c) 10^{-3} M and d) 10^{-6} M of uric acid.
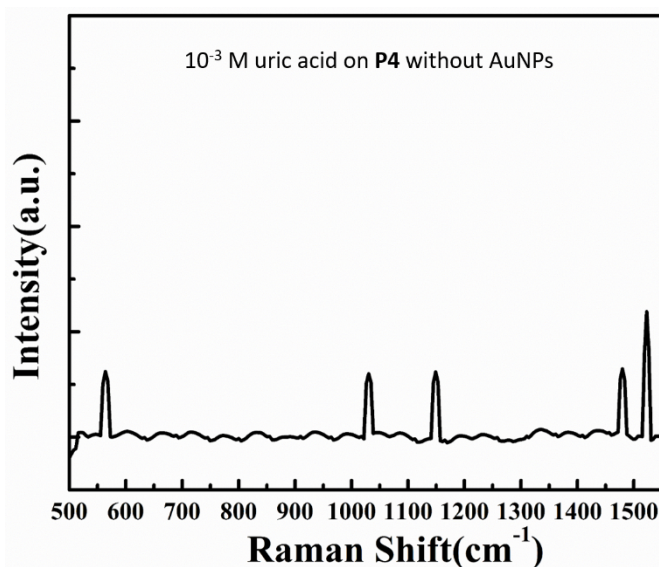

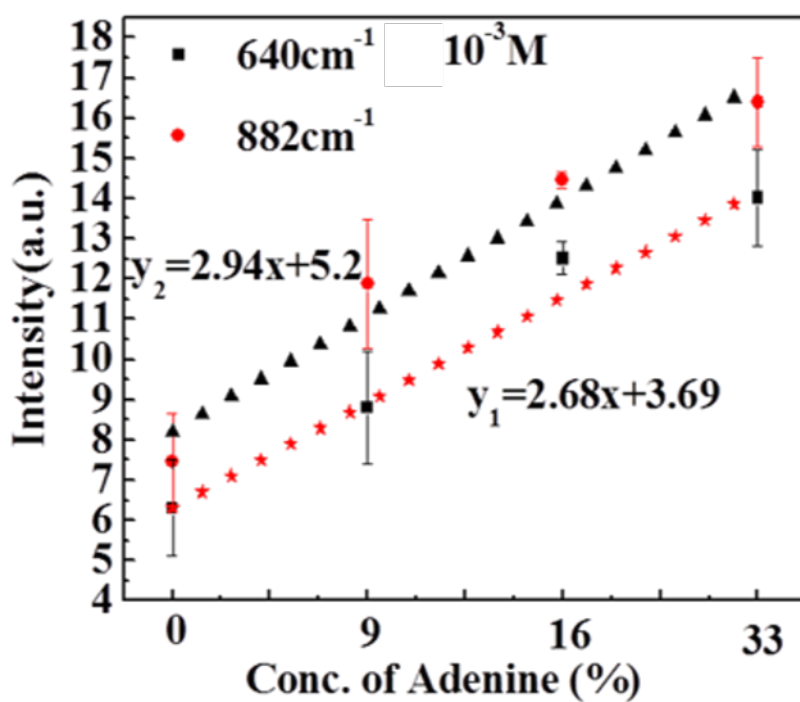**Fig. S10.** Raman spectra of **P4** with 10^{-3} M uric acid

Fig. S11. Variation of intensities of 640 and 882 cm^{-1} peaks of 10^{-3} M of uric acid on **AuNPs/PAN/L** composites with the percent of 8-mercapto-9-propyladenine (**L**).
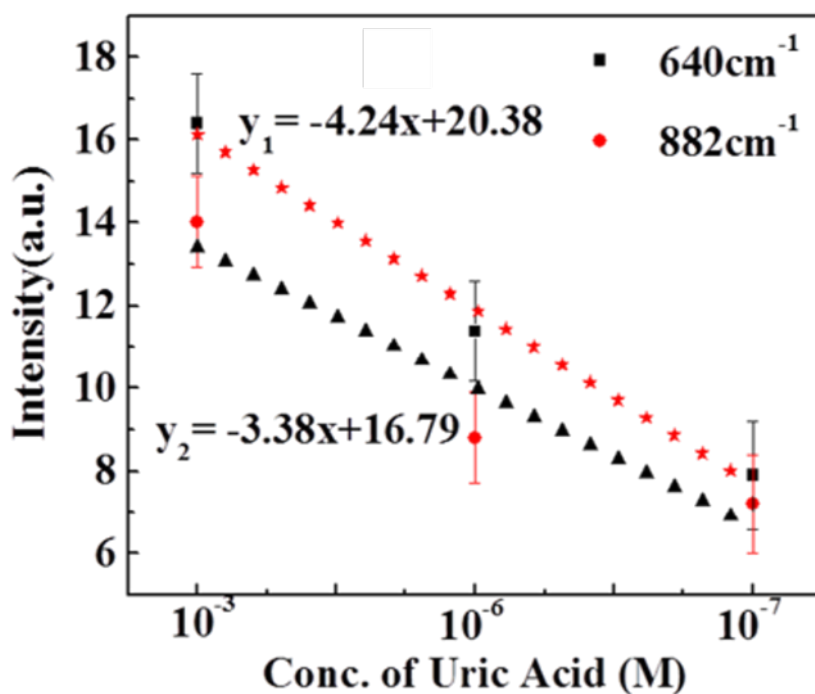

Fig. S12. Variation of intensities of 640 and 882 cm^{-1} peaks with the concentration of uric acid.

Average Enhancement factor calculation:

The estimated average enhancement factor (AEF) in SERS spectra was calculated using the following equation:[4]

$$AEF = I_{SERS}(C_R)/I_R(C_{SERS}) \qquad (1)$$

where, I_{SERS} is the SERS band intensity of an analyte using the synthesized **AuNPs/PAN/L** electrospun fibers composites, I_R is the Raman intensity of an analyte on **PAN** fiber (**P1**) (without **L**), C_{SERS} represents the corresponding concentration of an analyte on **AuNPs/PAN/L** electrospun fibers (10^{-7} M) and C_R is the concentration of an analyte on **PAN** fiber (**P1**) (10^{-3} M, without **L**), which produces the Raman signal, I_R. The calculated AEF values for uric acid are 1.14×10^4 (640 cm^{-1} band) and 1.058×10^4 (882 cm^{-1} band).
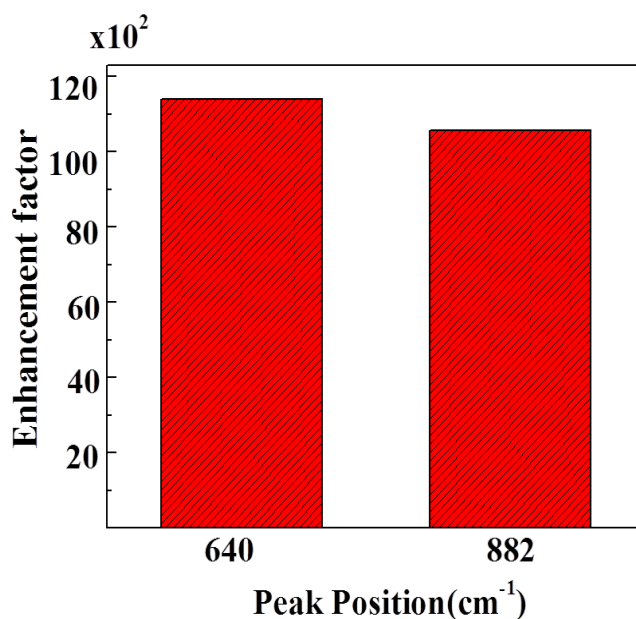

Fig. S13. Histogram showing the variation of enhancement factor of uric acid on **AuNPs/PAN/L** nanofibers composites for 640 and 882 cm^{-1} peaks.
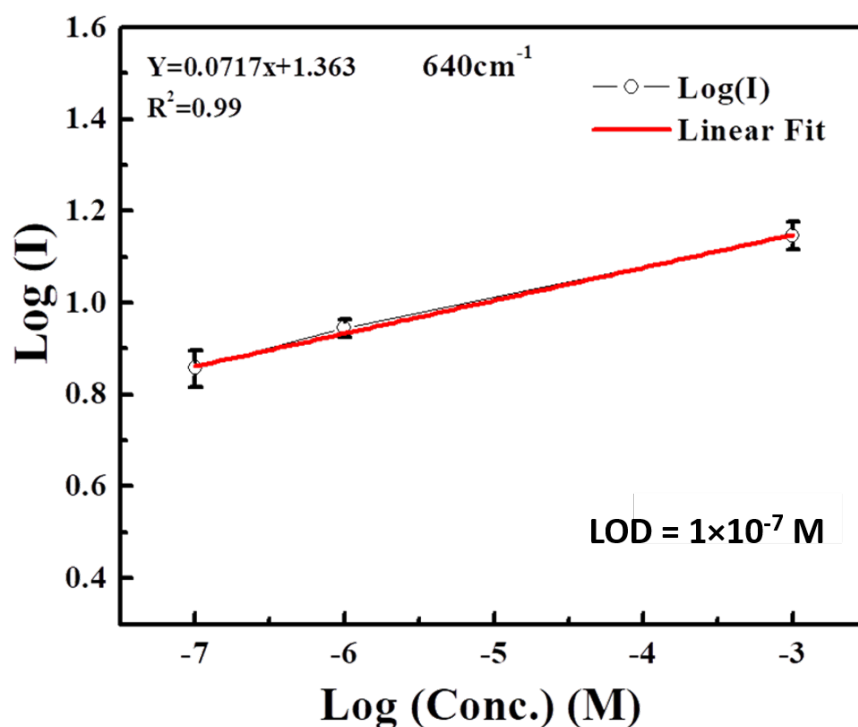
Fig. S14. Linear dependence of log plots of Raman mode intensity Vs Concentration for 640 cm^{-1} peak of uric acid.

References

1. V. Venkatesh, A. Shukla, S. Sivakumar and S. Verma, *ACS Appl. Mater. Interfaces*, 2014, **6**, 2185-2191.
2. A. D. McFarland, C. L. Haynes, C. A. Mirkin, R. P. Van Duyne and H. A. Godwin, *J. Chem. Educ.*, 2004, **81**, 544A.
3. M. Pucetaite, M. Velicka, J. Pilipavicius, A. Beganskiene, J. Ceponkus and V. Sablinskas, *J. Raman Spectrosc.*, 2016, **47**, 681-686.
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