Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Ultrafast on-site selective visual detection of TNT at Sub ppt level using fluorescent gold cluster incorporated single nanofiber

Anitha Senthamizhan, Aslı Celebioglu, Tamer Uyar**

Experimental details

Materials:

Tetrachloroauric acid trihydrate ($HAuCl_4 \cdot 3H_2O$), bovine serum albumin (BSA), poly ethylene oxide (PEO) (M_w 900,000), mercuric acetate, zinc acetate and copper acetate were purchased from Sigma–Aldrich. Sodium hydroxide pellet was obtained from Merck. All chemicals were of analytical grade and were used without further purification. De ionized water used as solvent for throughout the experiment.

Preparation of BSA capped fluorescent gold cluster:

The preparation was performed according to the previously reported method with trivial alteration. Briefly, 10 mM of $HAuCl_4$ solution (10ml) was mixed with equal amount of BSA solution (75 mg mL^{-1}) at 37 °C under vigorous stirring. The BSA concentration has been optimized and finalized as 75 mg/ml. Two minutes later, 1 ml of 1 M, NaOH solution was introduced in the mixture, and the reaction was allowed to proceed under vigorous stirring at 37°C for 12 h. The prepared gold cluster emitting red fluorescent under UV light, which is further incorporating into the nanofibers.

Preparation of Au.BSA@PEO nanofibers:

The PEO and Au.BSA@PEO nanofibers were prepared as follows. PEO is dissolved in deionised water by magnetic stirring at room temperature. The compositions of Au.BSA to PEO were optimized as 1:1. The processing parameters (collection distance, solution flow rate, applied voltage) significantly affects the fiber's morphology, which has been carefully optimized to get defect free nanofibers with desired diameter and composition.

The details of optimized experimental conditions are listed in Table 1. The electrospinning process was carried out at room temperature in a closed plexiglass box. The density of the composite fibrous membrane was controlled by altering the time of collection of nanofibers. The electrospun nanofiber obtained here was used for further characterization.

Table S1: Experimental conditions to produce defect free PEO and composites of Au.BSA and Au.BSA@PEO-NFs by electrospinning

Sample	Concentration (wt %, w/v)	Voltage (kV)	Electrode separation (cm)	Flow rate (mL/hour)
PEO	3.5	15	10	0.5
Au.BSA@PEO-NF	1:1	10	10	0.3

Instrumentation:

The morphology and diameter of the nanofibers at various stages were measured by scanning electron microscope (Quanta 200 FEG). The size and presence of elements in the Au.BSA and Au.BSA@PEO-NF were analyzed by using Tecnai G2 F30-Transmission Electron Micrposcopy (TEM). Fluorescence emission spectra were measured by Time resolved fluorescence spectrophotometer (FL-1057 TCSPC). The chemical composition of the Au.BSA and Au.BSA@PEO-NFM were performed using Thermo K-Alpha-Monochromated high-performance XPS spectrometer. The functional groups present in the sample were analyzed using Bruker Tensor 37-Fourier Transform Infrared Spectroscopy (FTIR) in the wave number ranging from 4000-400 cm^{-1}. Confocal Laser Scanning microscopy images were recorded using Zeiss LSM 510, excitation sources was fixed at 488 nm for all experiments and the images were captured at 20x magnification. Samples were directly coated on a glass slide using electrospinning method.

Contact Mode Visual Detection of TNT

Two different types of TNT solution were prepared by dissolving TNT in acetonitrile, termed as TNT-I and acetonitrile:water, TNT-II (0.5:9.5) mixture. Further, different concentrations of TNT have been diluted from the stock solution of 50 ppm TNT according to our need. For contact mode detection, the nanofibrous membrane were dipped in different concentration of TNT-I separately and taken out immediately. The color of the membrane were noticed to change suddenly while evaporating the solvent.

For TNT-II, the desired concentration was spotted on the Au.BSA@PEO-NFM since PEO is highly soluble in water. In order to ensure consistent analysis, all experiments were repeated and analyzed. After solvent evaporation, the membrane was illuminated with UV light to ensure the changes in the color. The experiment procedure was repeated for filter paper also. Similar procedure of TNT-I was applied for DNT and TNT-II were applied for different metal ions in water (Hg^{2+}, Cu^{2+} and Zn^{2+}) as well. For CLSM, the fibers were coated on glass slides and dipped half portion of the slide in TNT solution for minute. After drying the solvent images were taken at 20X magnification.

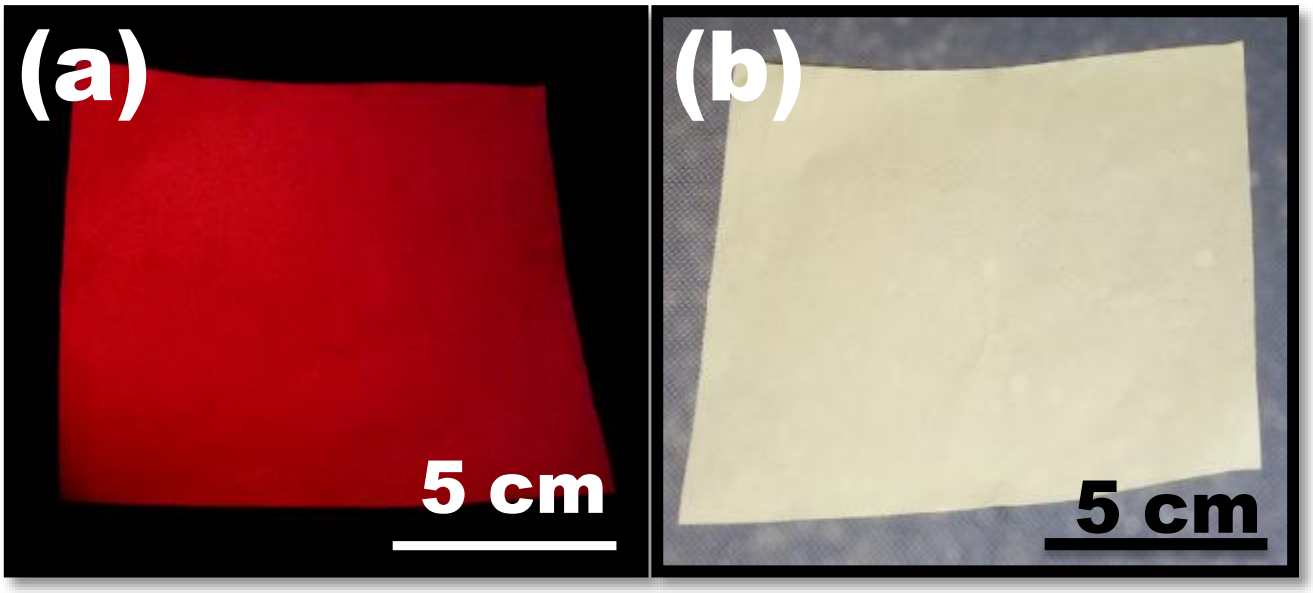

Figure S1: Photographs of the Au.BSA@PEO-NFM under (a)UV light (λext = 366 nm) and (b) white light.

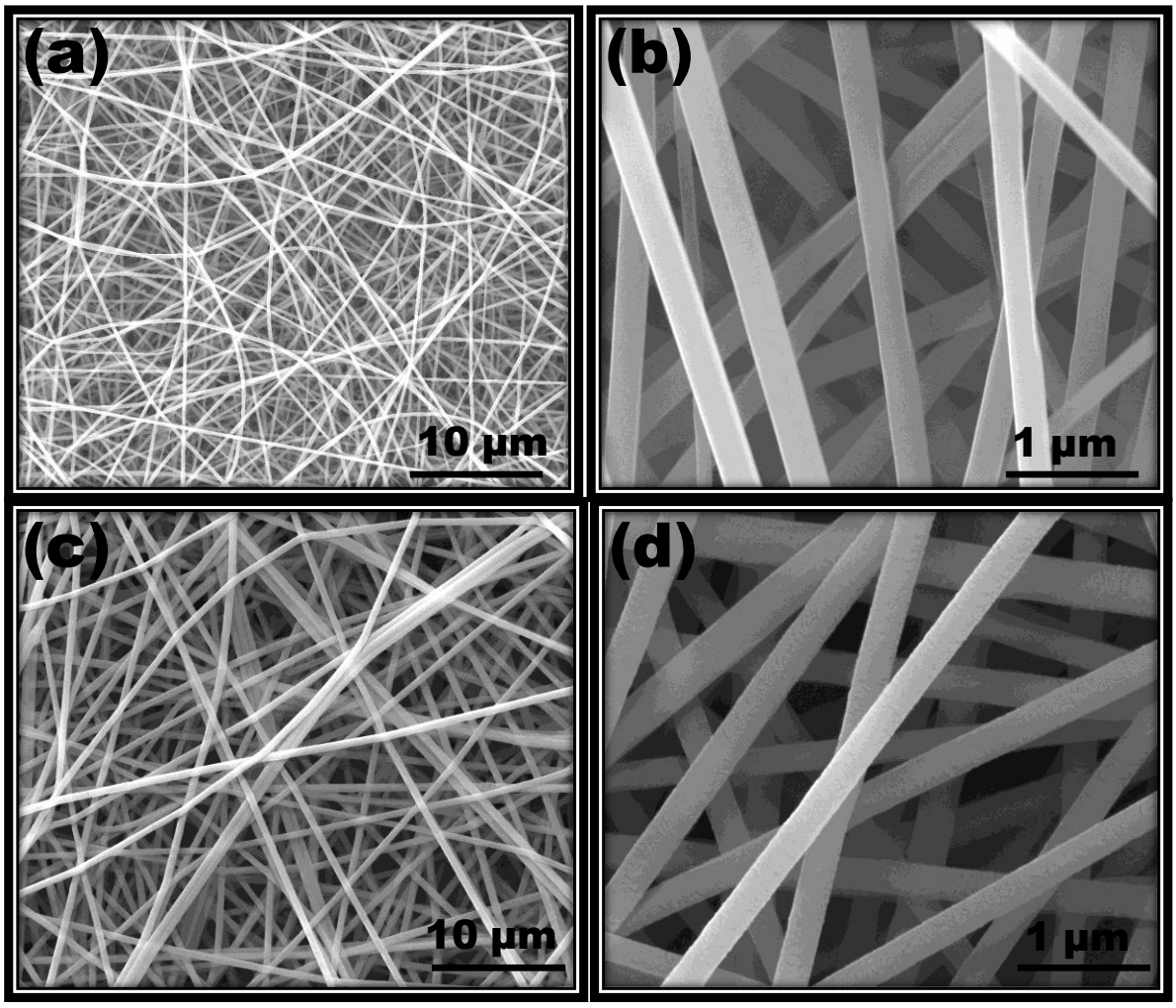

Figure S2: SEM images of the PEO (a-b) and BSA incorporated PEO nanofibers (c-d) at lower and higher magnification.

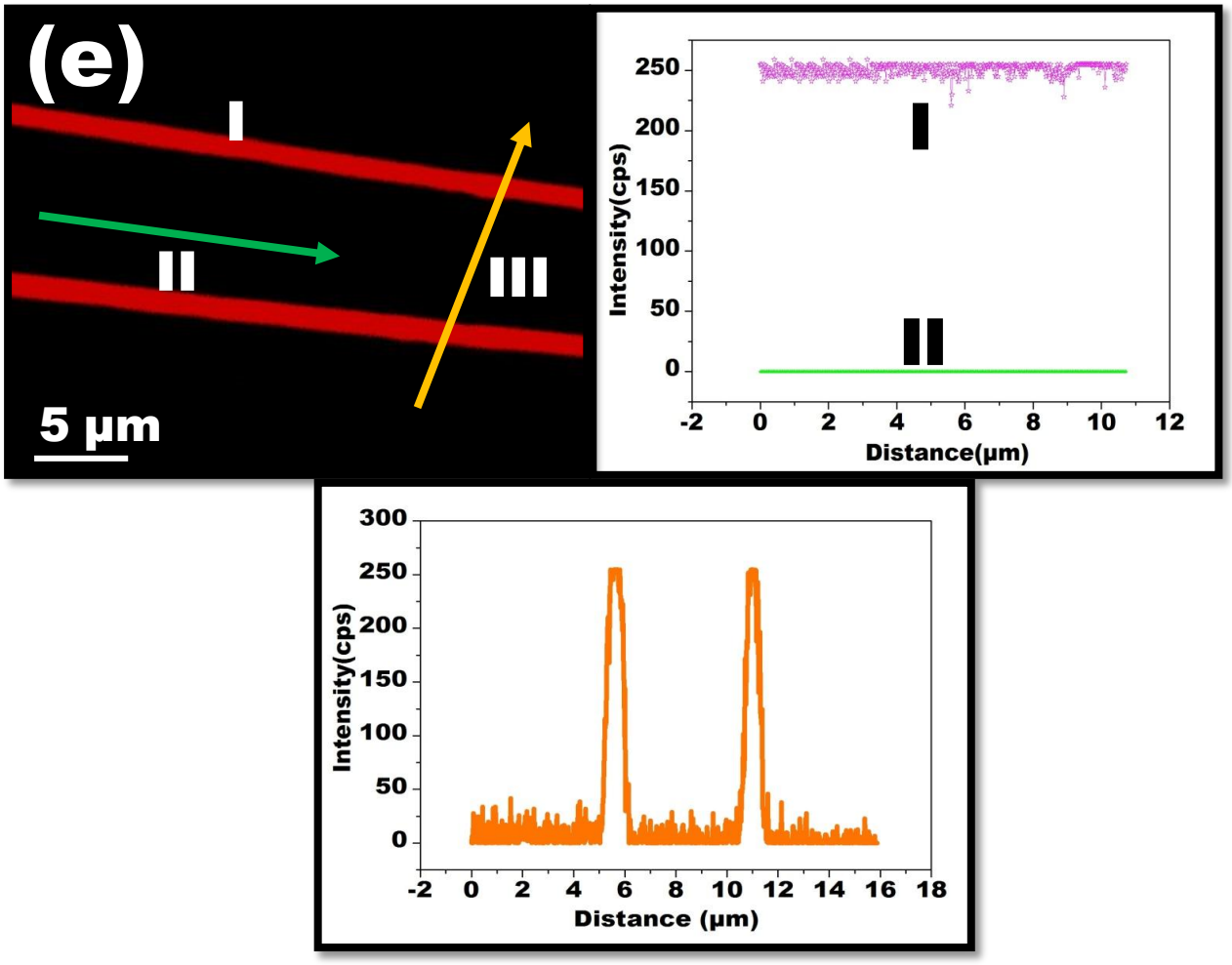

Figure S3: CLSM image of the two individual Au.BSA@PEO NFs and their intensity data collected from their surface.

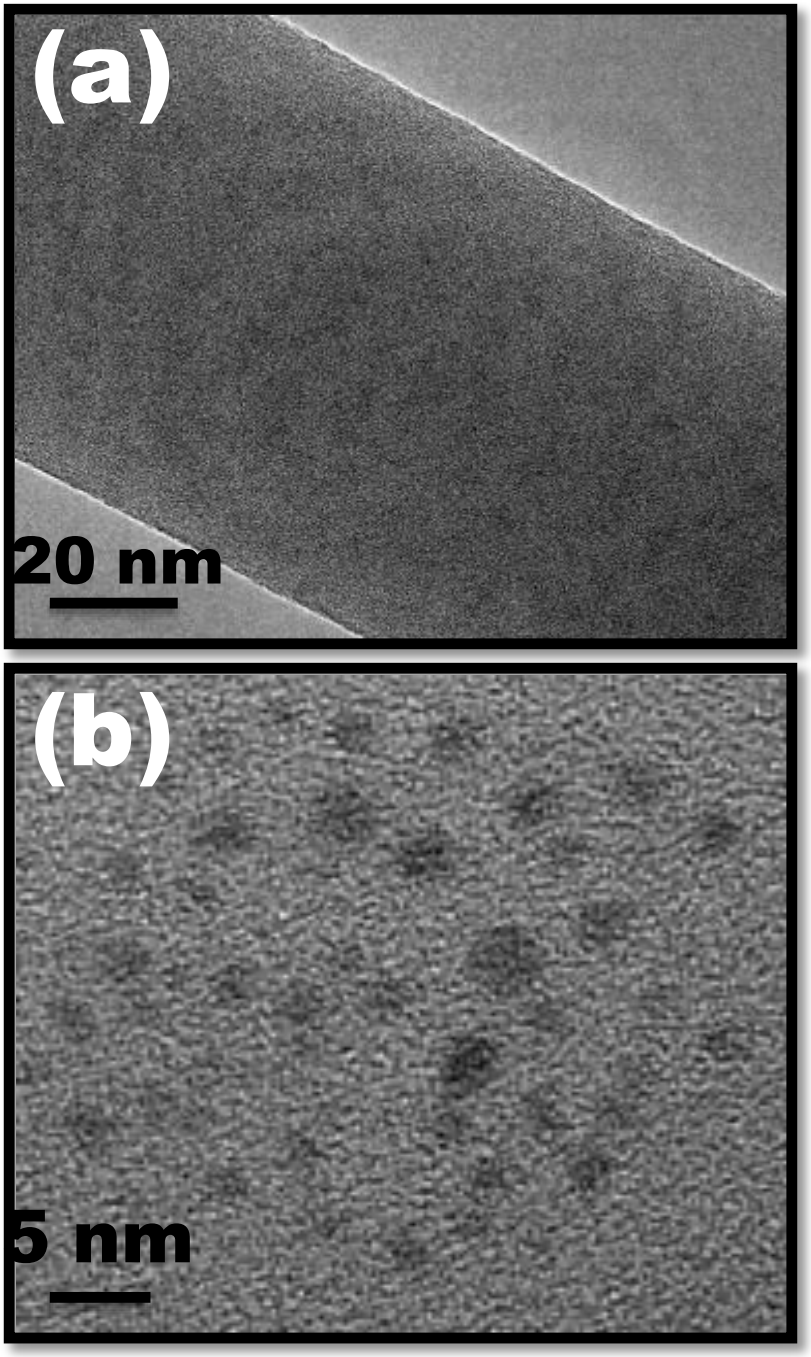

Figure S4 : HRTEM image of the Au.BSA@PEO-NF and Au.BSA

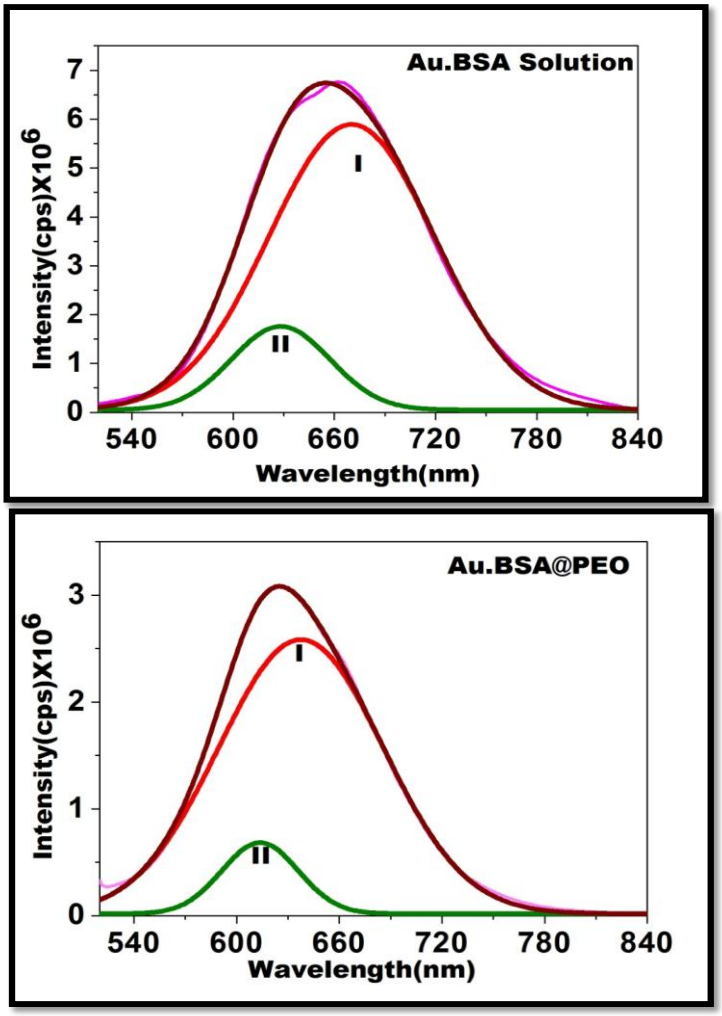

Table -II				
Sample	**Band**	**Central wave-length(nm)**	**Full width Half Maximum(FWHM)**	**Intensity ra-tio(I/II)**
Au.BSA	Band I	670	98	3.80
	Band II	628	58	
Au.BSA@PEO	Band I	638	96	3.33
	Band II	614	45	

Figure S5: Deconvoluted photoluminescence spectra of Au.BSA and Au.BSA@PEO-NFM. The parameters are given in Table II.

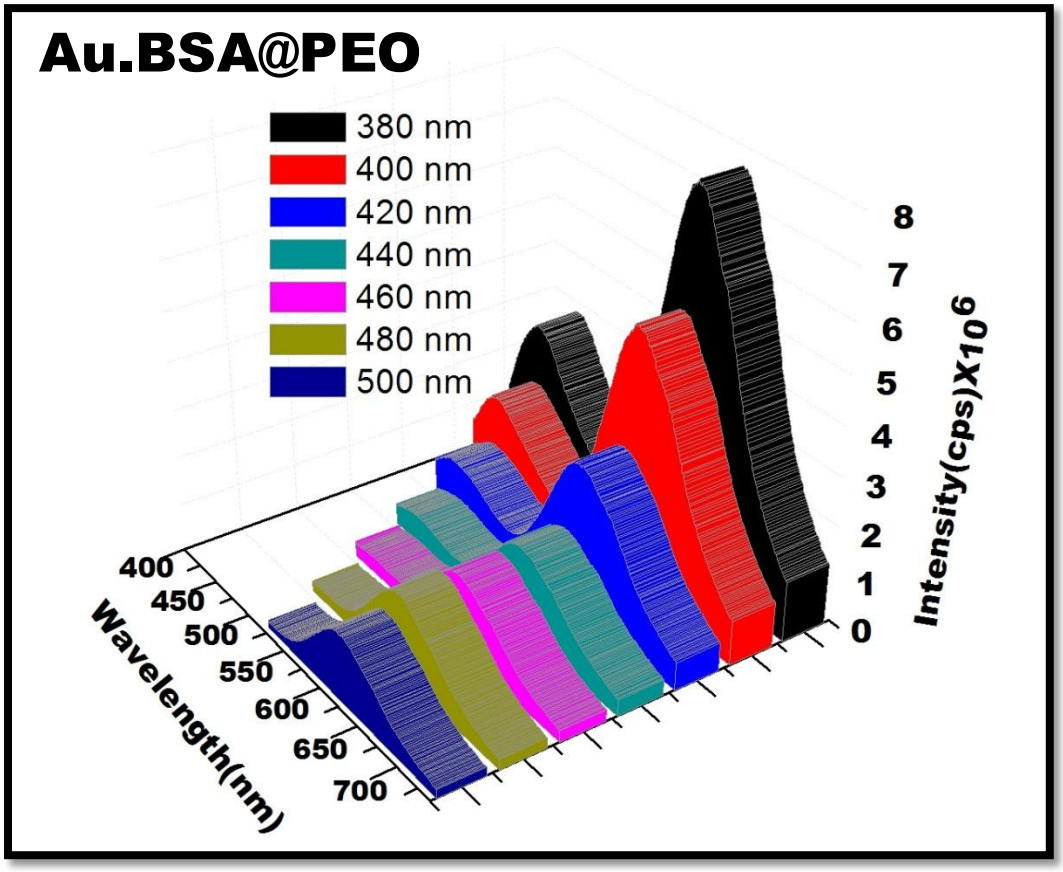

Figure S6: Emission spectra of Au.BSA@ PEO-NFM at different excitation wavelengths.

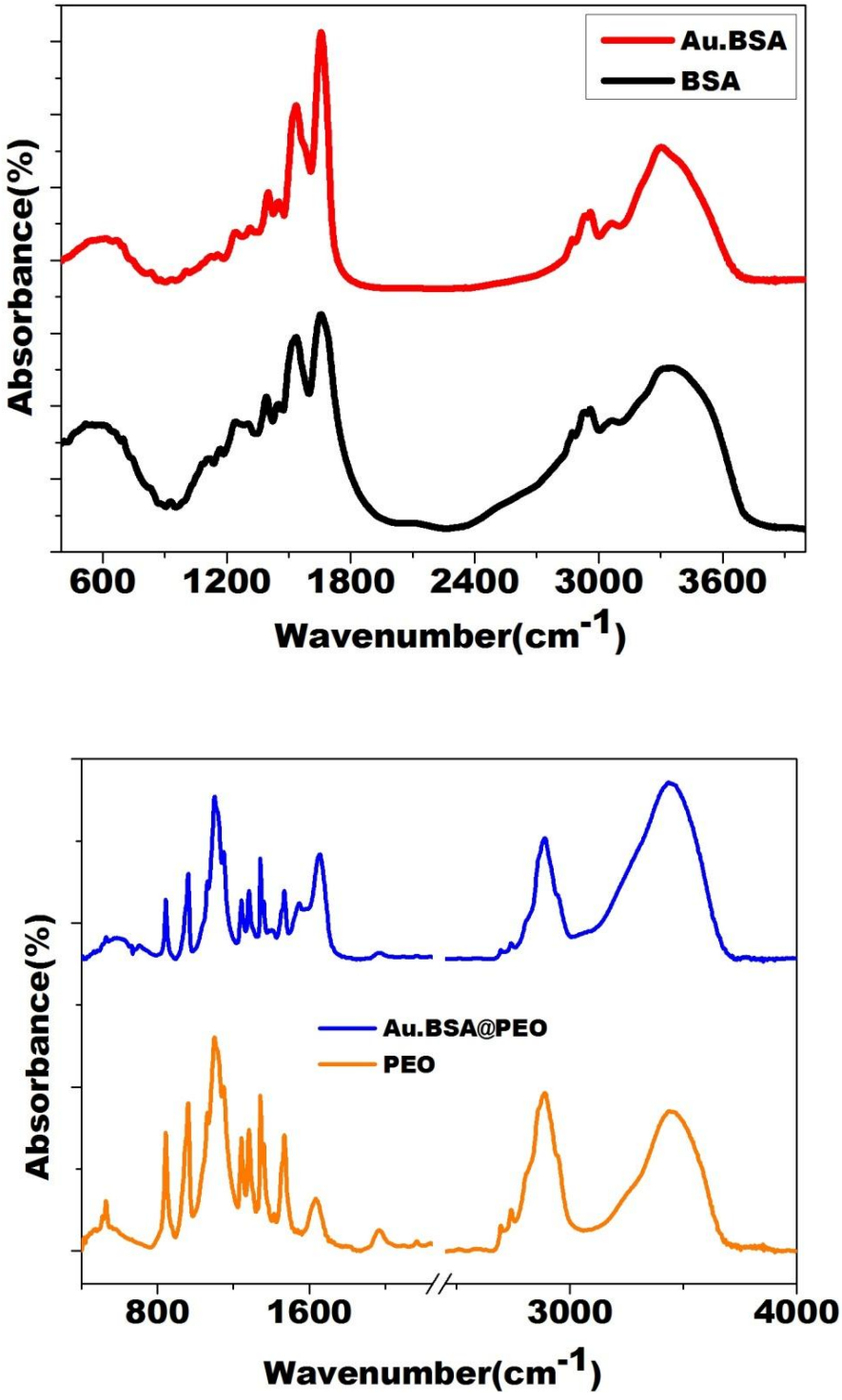

Figure S7: FTIR spectra of BSA powder, BSA stabilized gold cluster, PEO and Au.BSA@PEO-NFM. The observed spectra of BSA and Au.BSA looking very similar and also there is no hardly changes in the spectra suggesting that the character of BSA is preserved.

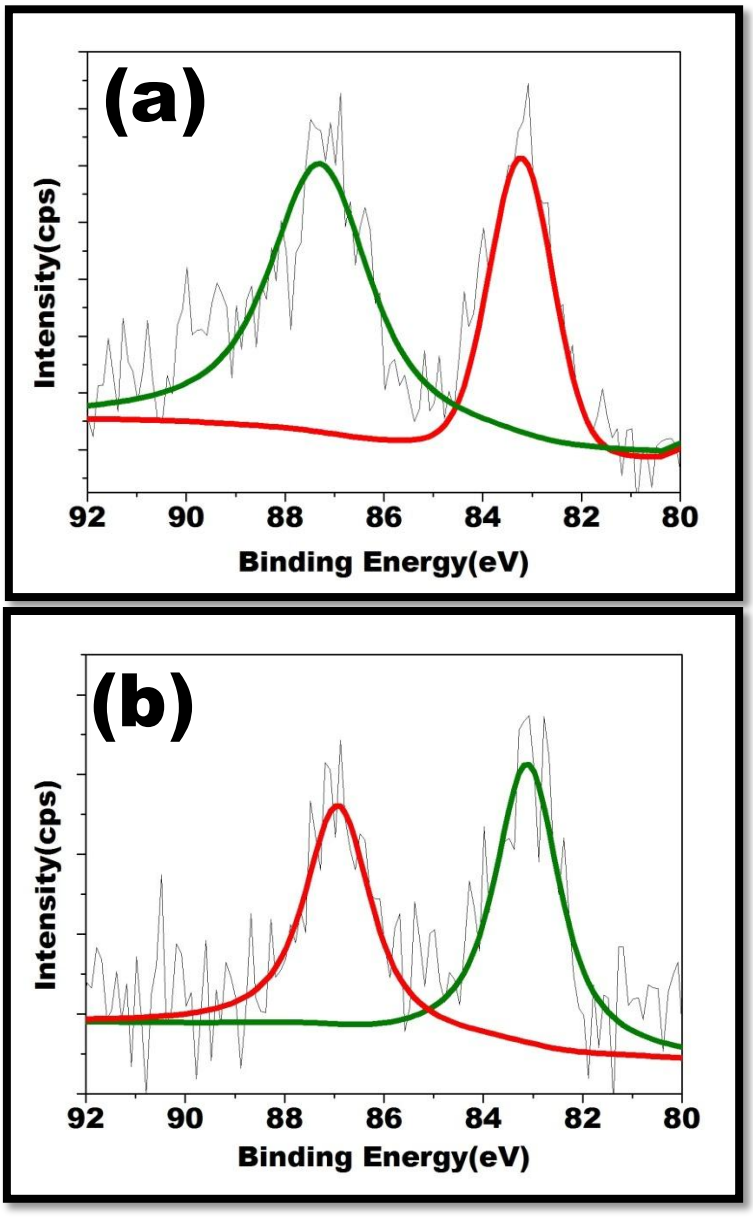

Figure S8: XPS spectra of Au 4f peak in Au.BSA (a) and Au.BSA@PEO-NFM (b)

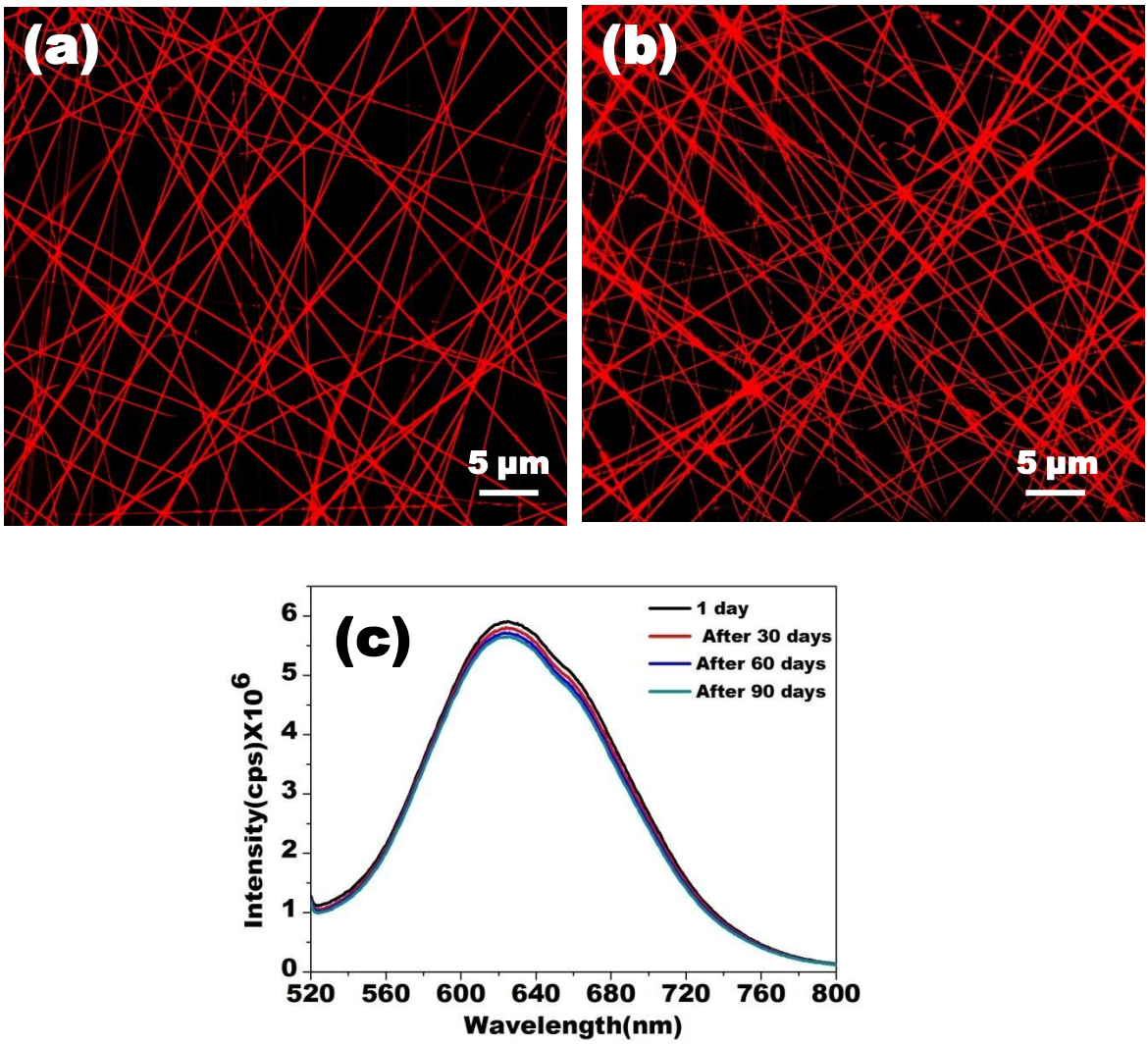

Figure S9: CLSM images of Au.BSA@PEO-NFM. Images are collected from the same glass slide after one and three months (Note that the images were taken from different points). (c) Fluorescence spectra of nanofibrous membrane were recorded at different time periods.

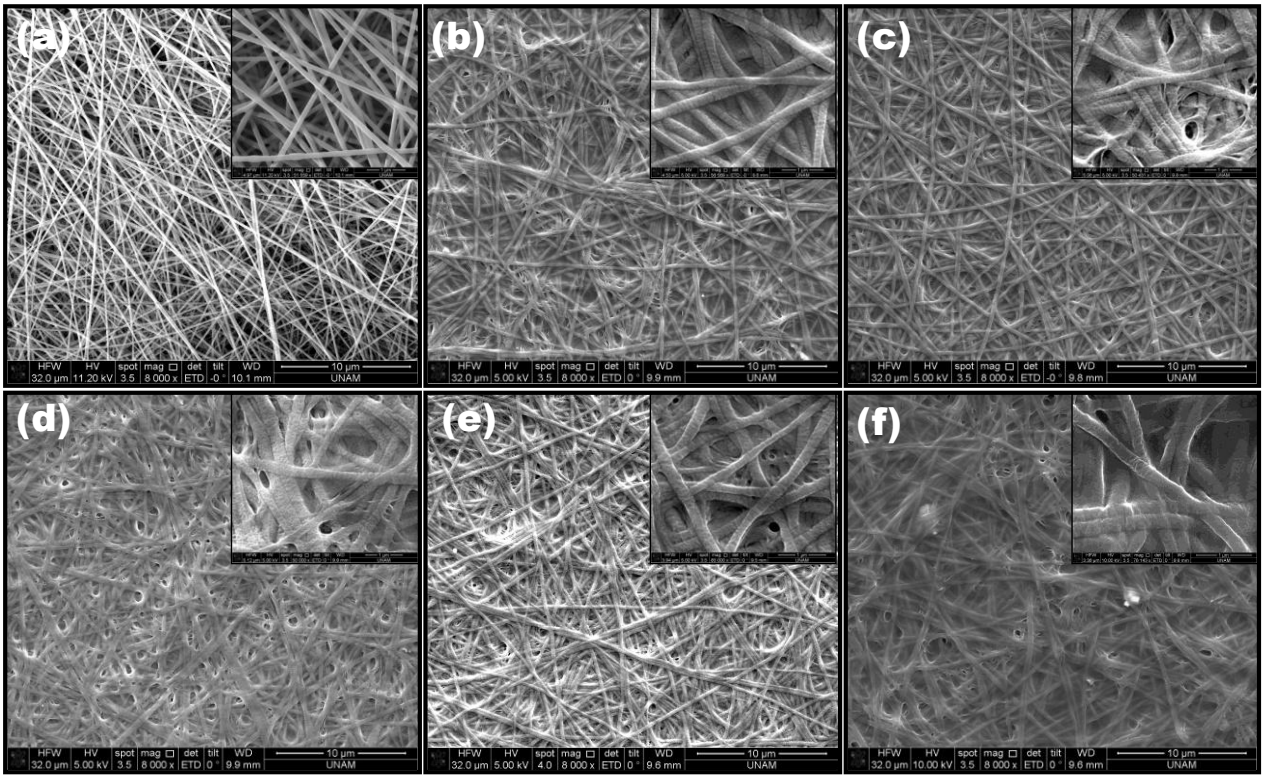

Figure S10: SEM images of the Au.BSA@PEO-NFM before (a) and after treatment of TNT at various concentrations (b) 1 ppm, (c) 100ppb, (d) 50ppb, (e) 10ppb, (f) 1ppb.

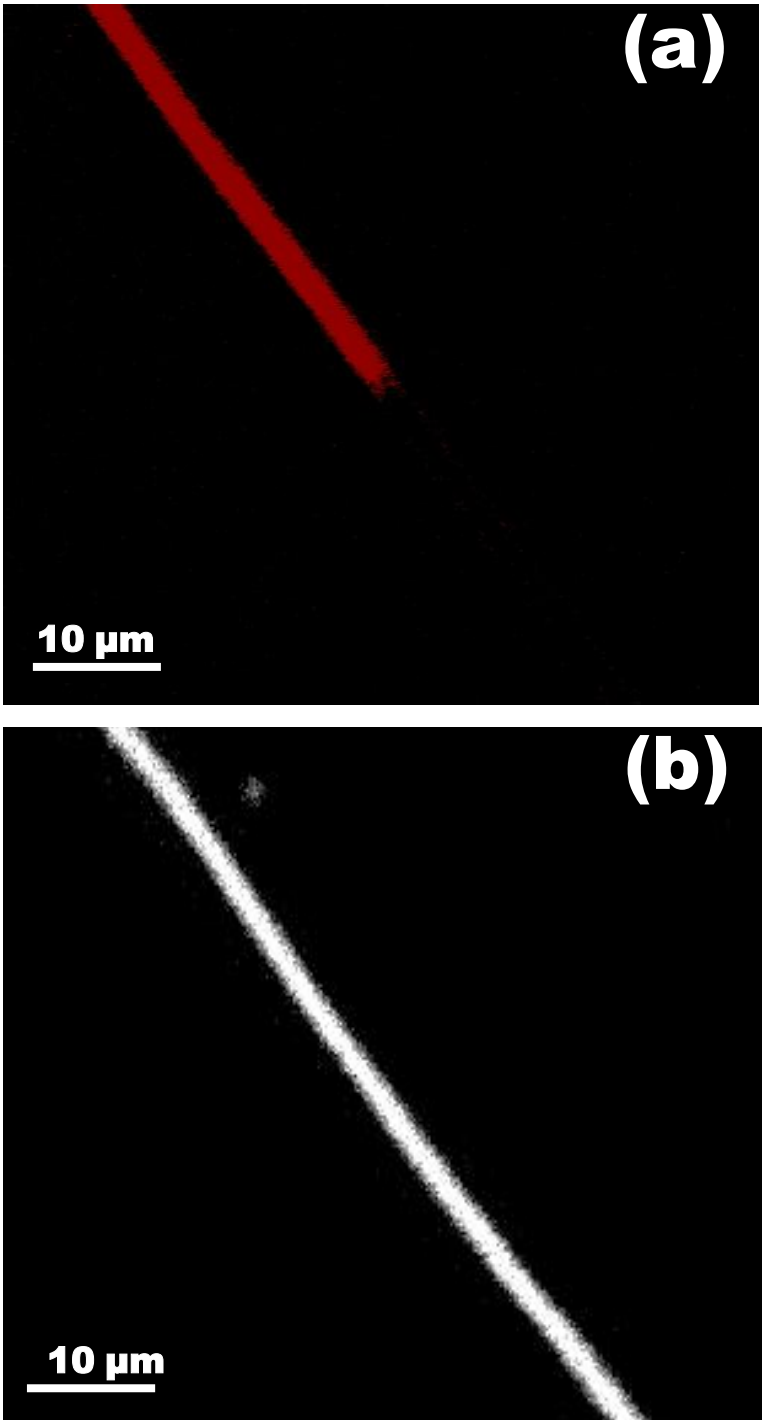

Figure S11: CLSM and optical images of Au.BSA@PEO-SNF. The half portion of the single nanofiber was treated with TNT and the remaining part at rest.

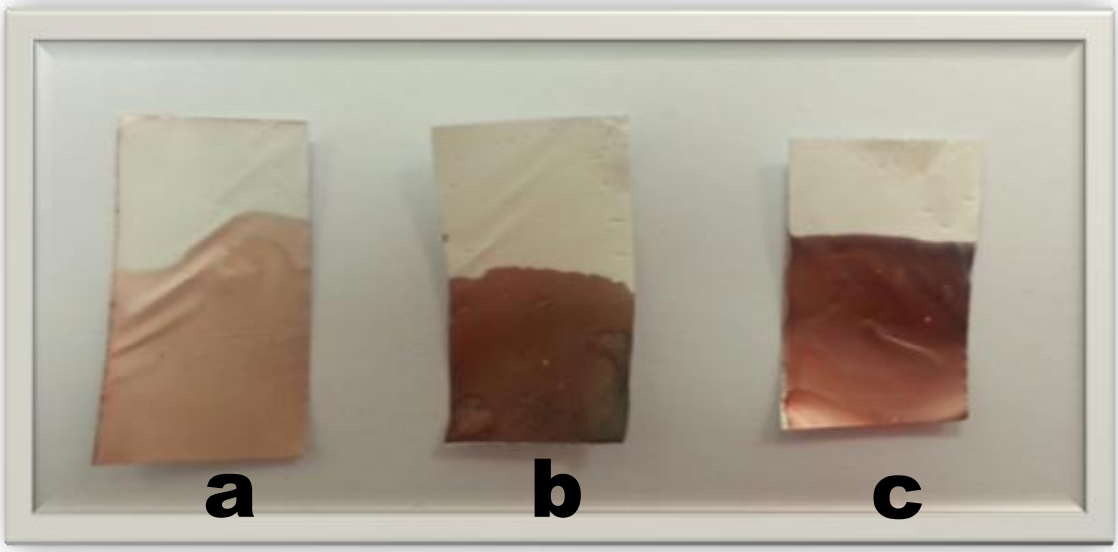

Figure S12: Sensing performance of TNT with respect to thickness of the nanofibrous mat at contact time of ~10 seconds. The nanofibers were collected for a)1, b) 5, and c) 15 minutes period.

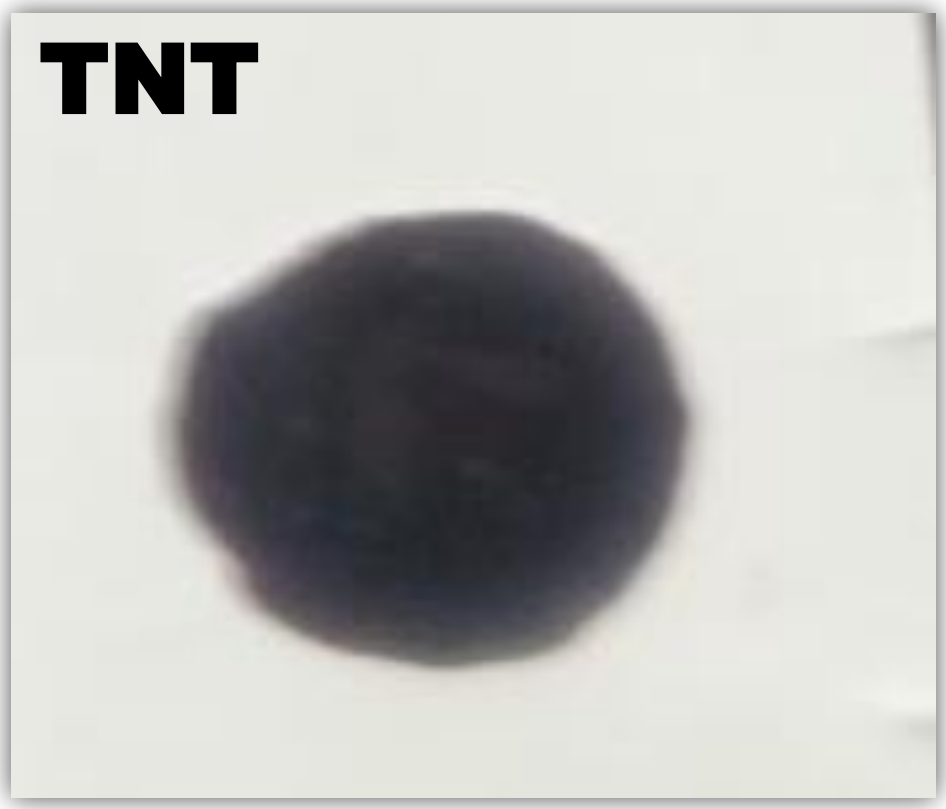

Figure S13: Sensing performance of Au.BSA@PEO-NFM upon exposure of TNT in water

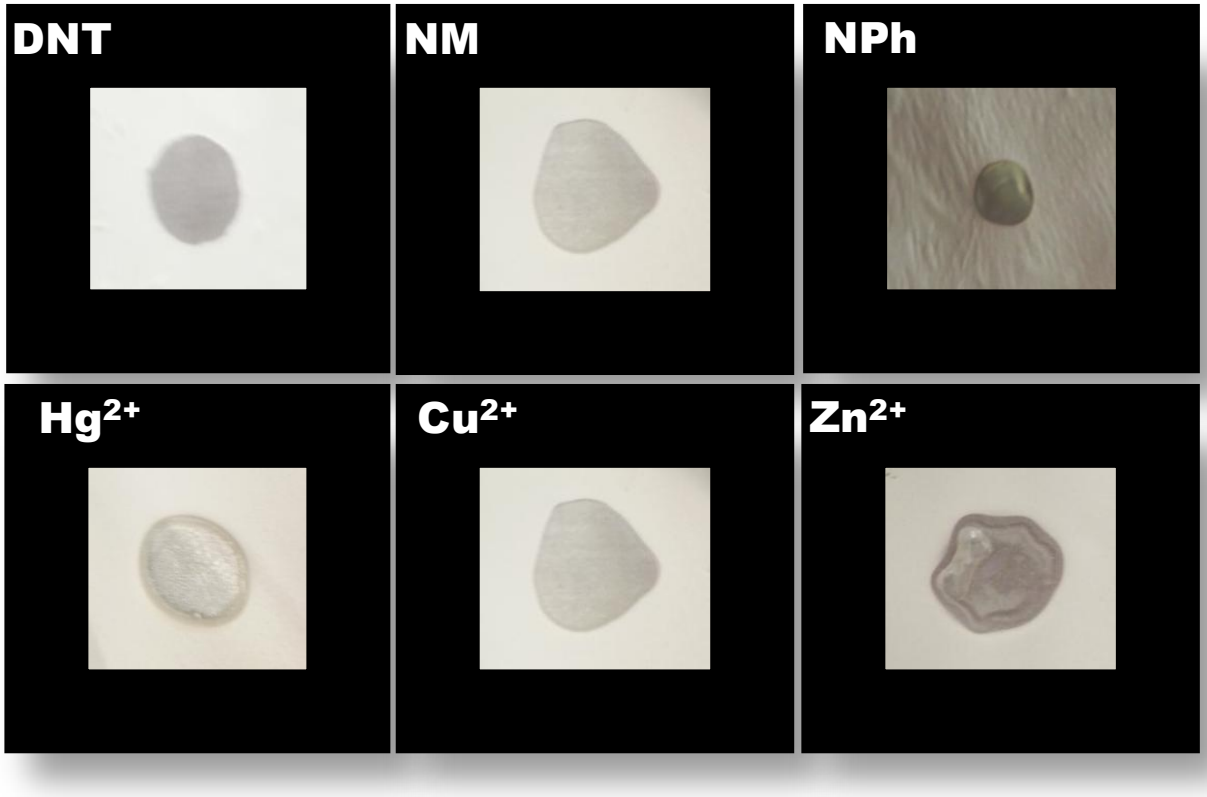

Figure S13: Sensing performance of Au.BSA@PEO-NFM upon exposure to other nitro aromatic compounds (DNT-2,4-Dinitrotoluene, NM-Nitromethane and NPh- 4-nitrophenol) and different metal ions in water. The concentration of all impurities were fixed at 50 ppm. Photographs were taken under normal light condition.

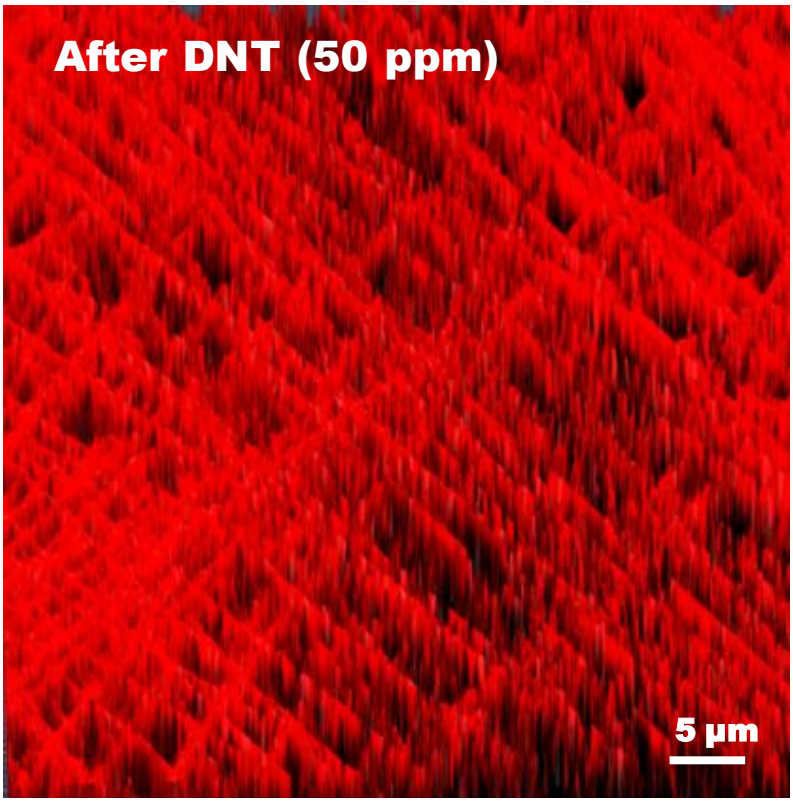

Figure S15: CLSM images of Au.BSA@PEO-NFM after treatment of DNT at 50 ppm concentration.

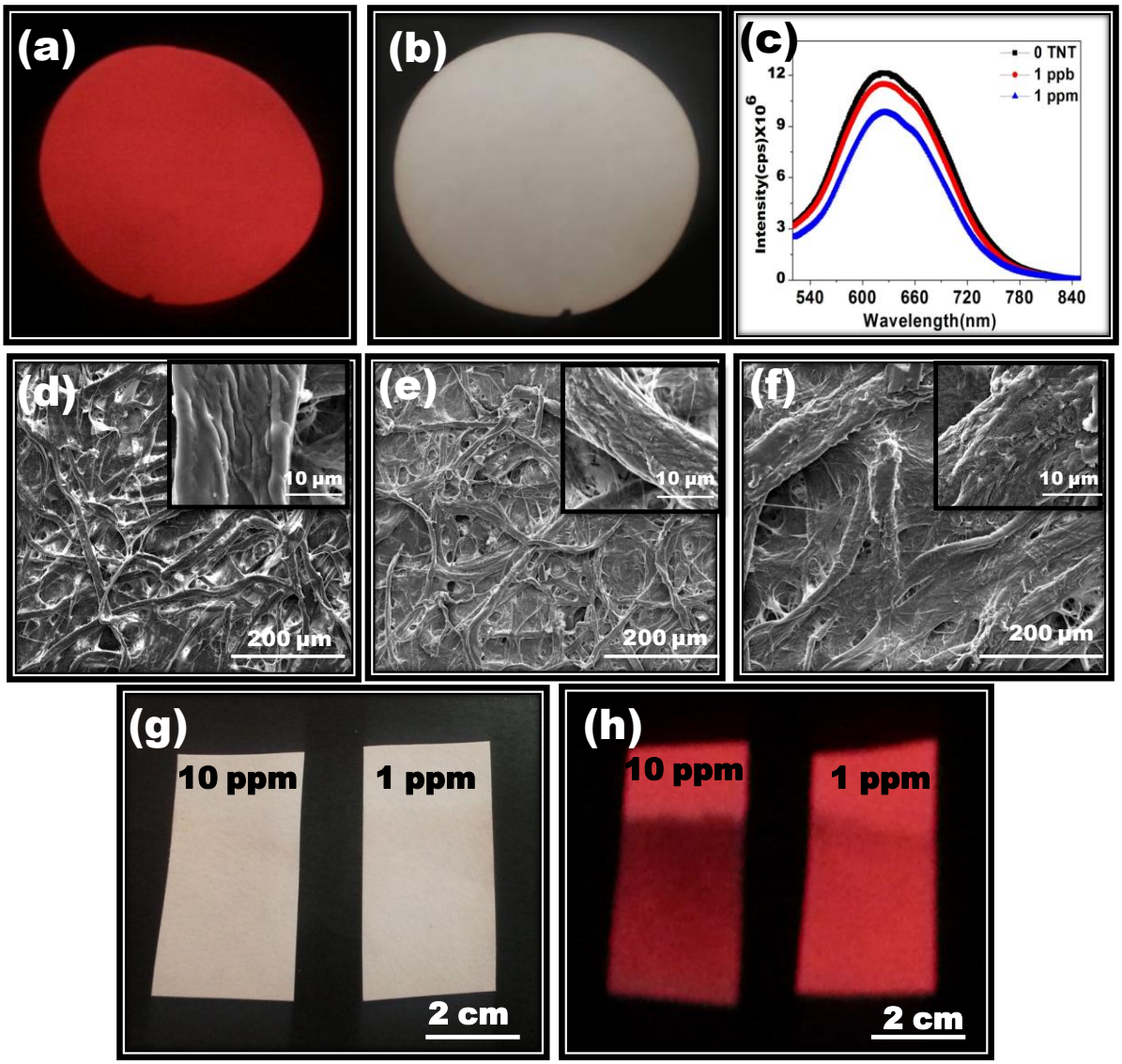

Figure S16: Sensing performance of Au.BSA coated filter paper termed as Au.BSA @FP. (a-b) Au.BSA @ FP under UV and normal light condition. (c) Fluorescence spectra of Au.BSA @ FP before and after treatment of TNT at various concentration. SEM image of (d) filter paper (e) Au.BSA @FP (f) after treatment of TNT and their photos under UV light were presented in figure (g-h).