ELECTROCHEMICAL AND OPTICAL BIMODAL SENSING OF CAFFEIC ACID BASED ON ELECTRODES OF NANORODS AuNPs: PEDOT: PSS AND BIOHYBRID CHITOSAN: PEDOT: PSS.

Salma Khan[1] and Anudeep Kumar Narula[1][*]

[1] Molecular Chemistry Laboratory, University School of Basic and Applied Sciences, Guru Gobind Singh Indraprastha University, Delhi-110078, India

*Corresponding author: +91-11-25302444

E-mail address: aknarula@ipu.ac.in (A. K. Narula)

Instrumentation

The characterization of the AuNPs and nanorods of AuNPs: PEDOT: PSS was performed on PHILIPS CM30 transmission electron microscope (TEM) working at 200 kV. A single drop of the aqueous solution of the AuNPs: PEDOT: PSS dispersion was placed onto a copper grid coated with a carbon film (400-mesh). The grid was left to dry in air for 24 hours at room temperature. UV-Visible spectrophotometer (Hitachi U-3010) was used to study about the surface Plasmon resonance of the nanocomposites. Optical sensing of caffeic acid was done by drop casting the each fabricated composites on glass slides separately, followed by adding 20 µl of different concentrations of caffeic acid on glass slide. The prepared samples for optical analysis were allowed for drying in vacuum oven for 24 hours. The structural characterizations of nanocomposites of AuNPs: PEDOT: PSS was done by FT-IR spectrophotometer (perkin Elmer RXI spectrometer in the range of 4000- 400 cm^{-1}), UV-Visible spectrophotometer, X-ray Diffraction pattern (Bruker Model D-8 Advance Diffractometer having Cu/Kα radiation with scanning speed of 10°/ min, recorded in the 2θ range of 10°-100°) . The interactions of fabricated composites (PEDOT: PSS, CHITOSAN: PEDOT: PSS and AuNPs: PEDOT: PSS) with caffeic acid were studied by X-ray Photoelectron emission spectroscopy (XPS). X-ray photoelectron spectroscopy (XPS) spectra were recorded by a VG Microtech ESCA 3000 Multilab spectrometer, possessing excitation source of AlK_{α} (hν D 1486.6 eV), a nine-channel detection system and a hemispherical analyser operating at a constant pass energy of 20 eV. The surface morphology was studied by SEM, (CARL ZEISS EVO 18). The electrochemical properties and sensing was accomplished on Autolab potentiostat by drop casting on the ITO (indium tin oxide) slide

having area (1x1) cm^2. The cyclic voltammogram were recorded on three electrode system namely graphite electrode as an auxiliary electrode, Ag/AgCl as a reference electrode. The working electrode dipped in the PBS saline electrolyte consisting along with 0.1 M of KCl as a supporting electrolyte. The voltammogram were scanned at different scan rates in the potential window of positive potential i.e. +1 volt to negative potential -1 volt.
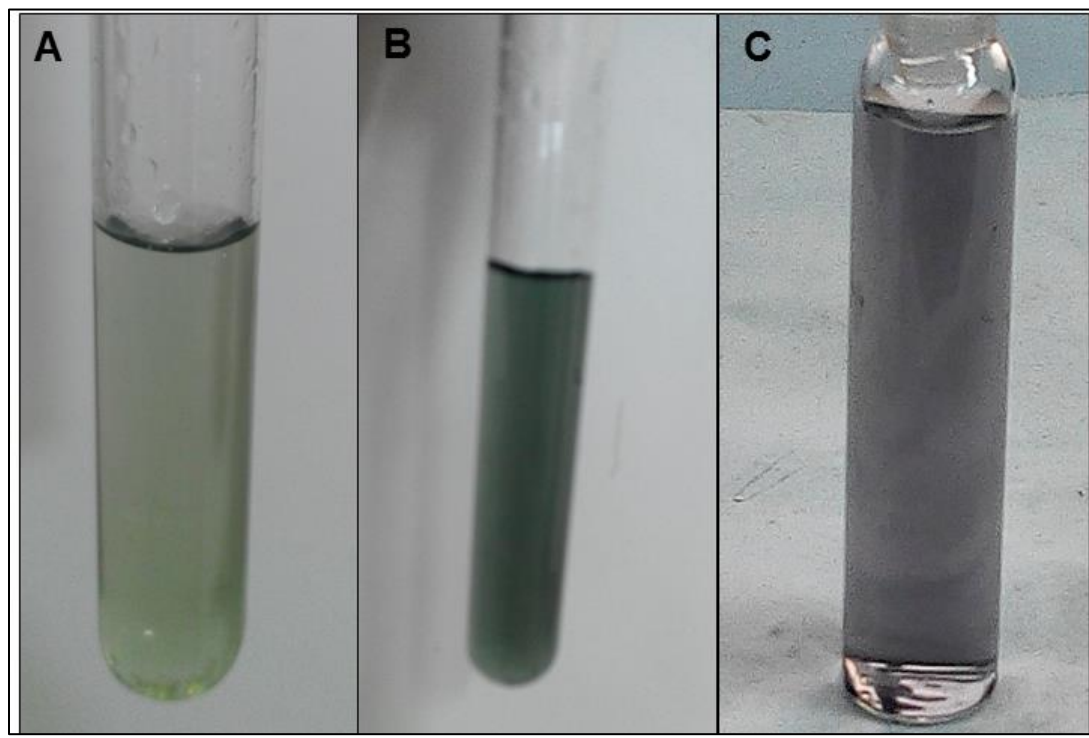
Fig. S1: Progress of polymerization of AuNPs: PEDOT: PSS after A) 1 hour B) 3 hours C) 48 hours.
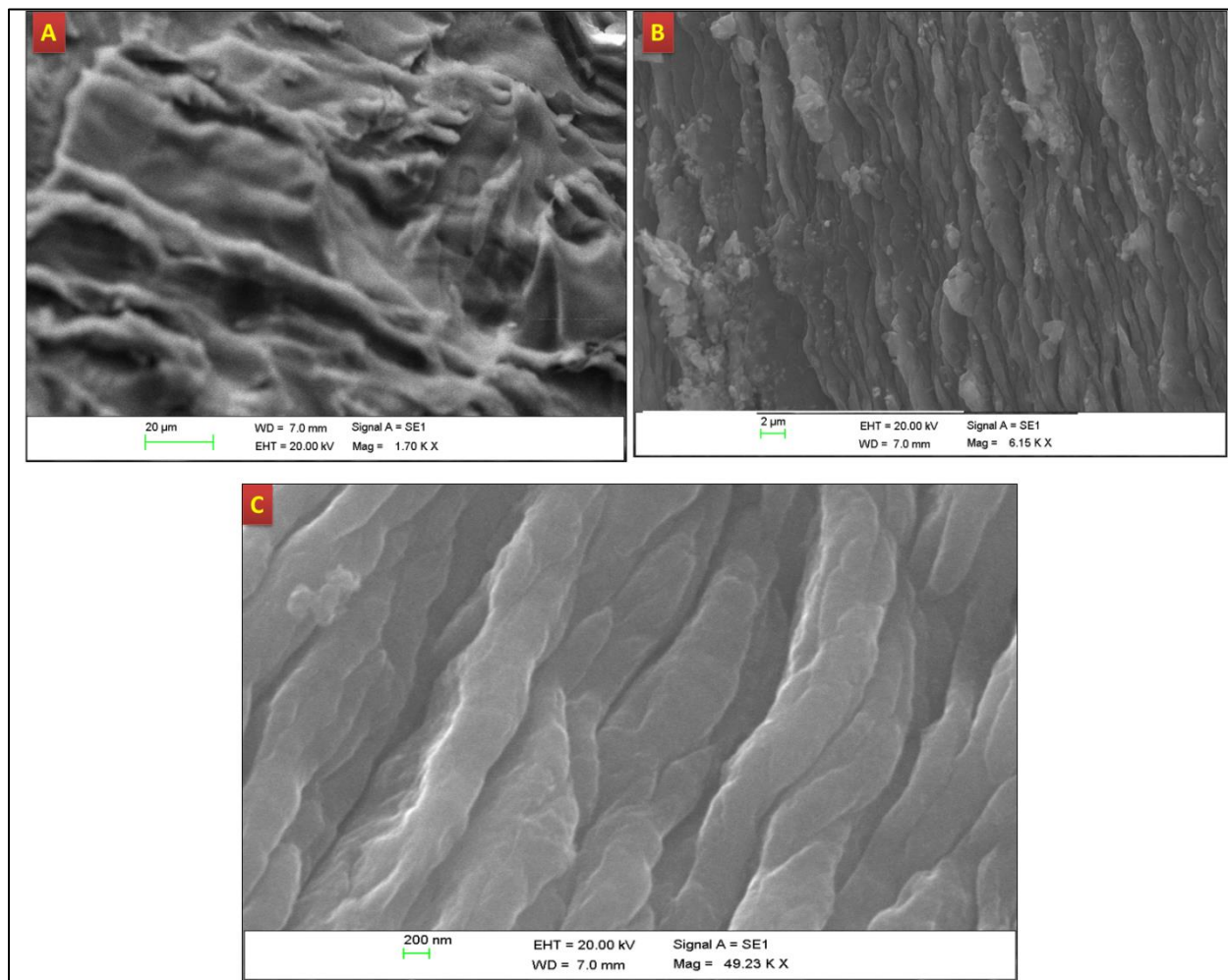
SEM

Fig. S2: SEM Microgrphs of fabricated composites A) PEDOT: PSS, B) and C) Nanorods AuNPs: PEDOT: PSS at different scale.
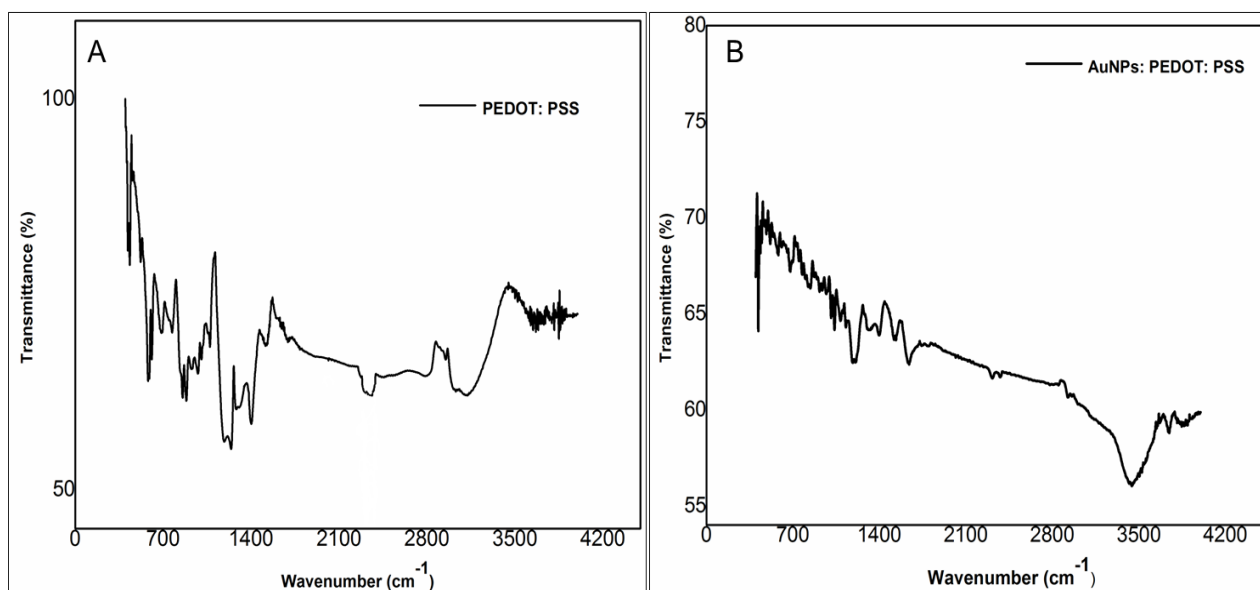
FTIR

Fig. S3 FT-IR spectrum of A) PEDOT: PSS B) nanorods of AuNPs: PEDOT: PSS

Fig. 2 showed the FT-IR spectrum of PEDOT: PSS and AuNPs: PEDOT: PSS. The spectrum of PEDOT: PSS, exhibited strong band at 1418 cm^{-1} and 1260 cm^{-1}, attributed to the   high level polymerization about – C$_\alpha$ – C$_\beta$- and –C$_\alpha$ – C$_\alpha$ –respectively, in thiophene ring. The transmittance peaks observed at 1191.87 cm^{-1} and 1080.92 cm^{-1} were designated to the bending modes of –C-O-C– bond of ethylenedioxy group (1). However, the FT-IR spectrum of nanorods of AuNPs: PEDOT: PSS showed comparable peak pattern as observed for PEDOT: PSS, suggested that AuNPs are held by weak physical Vander-Wal forces of interactions, henceforth the polymer structure remained unaffected by incorporation of gold nanoparticles.

Table S1: Comparison of the linear range and detection limit between the proposed method and other reported detection methods for CA.

METHOD	LINEAR RANGE	LOD	REFRENCE
Amperometric detection	2.0 to 14.0×10^{-6} M	1.0×10^{-6} M	(2)
Electrochemical detection	0.001 µM –55 µM	0.37 nM	(3)
HPLC Liquid chromatography	0.1 µg/ mL to 100 µg/ mL	0.17 µg/mL	(4)
UV-Visible Spectrophotometer	5×10^{-8} M to 2×10^{-3}M	$2.50 \times 10\text{-}8$	(5)
Voltammetric detection	1×10^{-8} to 5×10^{-7} M	4×10^{-9} M	(6)
Flouorometry	2–350 (µM)	0.2 (µM)	(7)
Cyclic voltammetry	2 µM to 10 mM	1.2E-02 M and 1.32E-02 M	This work

Table S2: XPS characterize peaks of fabricated composites with their respective atomic percent.

PEDOT: PSS

Name	Peak (BE) (eV)	Atomic (%)
C (1s)	284.39	79.82
O (1s)	532.61	20.18
S (2p)	162.24	05.54

CHITOSAN: PEDOT: PSS

Name	Peak (BE) (eV)	Atomic (%)
C (1s)	284.68	65.21
O (1s)	532.39	12.45
S (2p)	168.24	6.25
N (2p)	399.56	3.24

AuNPs: PEDOT: PSS

Name	Peak (BE) (eV)	Atomic (%)
C (1s)	284.68	65.21
O (1s)	532.39	12.45
S (2p)	168.24	6.25
N (2p)	399.41	3.24
Au (4f)	83.8	3.25

REFRENCES

1) Ely, F., Matsumoto, A., Zoetebier, B., Peressinotto, V.S., Hirata, M.K., Sousa, D.A. Maciel, R., 2014. Org. Electron. 15, 1062–1070.

2) Gomes, S.A.S.S., Nogueira, J.M.F., Rebelo, M.J.F., 2004. Biosen. Bioelectron. 20, 1211–1216.

3) Liu, Z., Lu,B., Gao, Y., Yang, T., Yue, R., Xu, J., Gao, L., 2016. RSC Adv. 6, 89157–89166.

4) Irakli, M. N., Victoria, F., Samanidou, Biliaderis, C. G., Ioannis, N., Papadoyannis, 2012. Food Chem. 134, 1624–1632.

5) Carlo, G.D., Curulli, A., Toro, R.G., Bianchini, C., Caro,T.D., Padeletti, G., Zane, D., Ingo, G. M., 2012. Langmuir. 28, 5471−5479.

6) Tyszczuk, K., Kamin´sk ,A.S., Woz´niak, A., 2011. Food Chem. 125, 1498–150.

7) Nan Cai, N., Li, Y., Chen, S., Su.X., 2016. Analyst. 141, 4456-4462.