Electronic Supplementary Material (ESI) for RSC Advances. This journal is © The Royal Society of Chemistry 2014

# Supplementary Information



Fig.1. Experimental set up for room temperature gas sensing measurement.



Fig.2. Photograph of CSA doped  $PPy/\alpha$ -Fe<sub>2</sub>O<sub>3</sub> hybrid sensor film .

#### **FTIR** analysis

The FTIR spectrum of the pure PPy,  $PPy/\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (50%) and 30% CSA doped  $PPy/\alpha$ -Fe<sub>2</sub>O<sub>3</sub> hybrid nanocomposite are shown in Fig. 3. FTIR spectrum of pure PPy [Fig.3 (a)] shows the characteristic peaks at 792 cm<sup>-1</sup> and 926 cm<sup>-1</sup> are due to the C–H wagging as well as peak at 1049 cm<sup>-1</sup> belongs to =C-H in plane deformation vibration. The characteristic peak at 1114 cm<sup>-1</sup> attributed to C-H in and out of plane deformations and the N–C stretching band observed at 1204 cm<sup>-1</sup>.While, =C–H in plane vibration observed at 1305 cm<sup>-1</sup>. The peak observed at 1474 cm<sup>-1</sup> and 1559 cm<sup>-1</sup> are due to vibration of pyrrole ring and ring stretching mode of pyrrole ring respectively. C-N stretching vibration is observed at 1684 cm<sup>-1</sup>.

The broad peak observed at 3117 cm<sup>-1</sup> is due to N-H stretching. The observed different characteristic peak assignments in FTIR spectrum confirms the formation of PPy and well matches with those observed in other studies [1-3]. In the FTIR spectra of  $PPy/\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (50%) nanocomposite [Fig.3 (b)], the main characteristic peaks of pure PPy at 792 cm<sup>-1</sup> shifted to 797 cm<sup>-1</sup>,926 cm<sup>-1</sup> shifted to 930cm<sup>-1</sup>,1114 cm<sup>-1</sup> shifted to 1116 cm<sup>-1</sup>,1204 cm<sup>-1</sup> shifted to 1213 cm<sup>-1</sup> <sup>1</sup>,1474 cm<sup>-1</sup> shifted to 1477cm<sup>-1</sup>, 1559 cm<sup>-1</sup> shifted to 1563 cm<sup>-1</sup> and 1684 cm<sup>-1</sup> shifted to 1689 cm<sup>-1</sup> respectively. Furthermore, the new peaks at 554cm<sup>-1</sup> and 680 cm<sup>-1</sup> belong to Fe-O bond stretching, which clearly indicate the presence of Fe<sub>2</sub>O<sub>3</sub> in the polymer matrix. While, shift in the peak positions attributed to some chemical interactions between PPy and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticle. The FTIR spectra of 30% CSA doped  $PPy/\alpha$ -Fe<sub>2</sub>O<sub>3</sub> [Figure 3(c)] also show the same characteristic peaks that of PPy/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite. However, the peak at 554 cm<sup>-1</sup> and 680 cm<sup>-1</sup> are shifted towards 560 cm<sup>-1</sup> and 683 cm<sup>-1</sup> respectively. Furthermore, peak at 797 cm<sup>-1</sup> shifted to 790 cm<sup>-1</sup>, 930 cm<sup>-1</sup> shifted to 924 cm<sup>-1</sup>,1049 cm<sup>-1</sup> shifted to 1045 cm<sup>-1</sup>,1477 cm<sup>-1</sup> shifted to 1472 cm<sup>-1</sup>,1563 cm<sup>-1</sup> shifted to 1560 cm<sup>-1</sup> and 1789 cm<sup>-1</sup> shifted to 1740 cm<sup>-1</sup>. These shifts are due to the chemical interaction between CSA and  $PPy/\alpha$ -Fe<sub>2</sub>O<sub>3</sub> hybrid nanocomposite.



**Fig.3.** FTIR spectrum (a) PPy, (b) PPy/α-Fe<sub>2</sub>O<sub>3</sub> (50%) and (c) 30% CSA doped PPy/α-Fe<sub>2</sub>O<sub>3</sub> hybrid nanocomposite.

## **E-DAX** analysis

The elemental presence of CSA doped  $PPy/\alpha$ -Fe<sub>2</sub>O<sub>3</sub> hybrid nanocomposite was analyzed by using energy dispersive X-ray (EDAX) spectroscopy and presented in Fig.4. E-DAX analysis confirms the existence of C, N, O, S and Fe elements in the deposited films and no noticeable impurity was observed. The detected element C, N and O are belongs to PPy and the element S belongs to camphor sulfonic acid. Furthermore, the Pt trace is due to the platinum coating applied to enhance the FESEM image.



**Fig.4.** E-DAX spectrum of 30% CSA doped  $PPy/\alpha$ -Fe<sub>2</sub>O<sub>3</sub> hybrid nanocomposite.

#### **XPS** study

XPS is an effective technique to illuminate chemical state of the element and the surface composition existing in the prepared material. Therefore, the formation of CSA doped PPy/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> hybrid nanocomposite was also confirmed by carrying out XPS analysis and the obtained XPS spectrum is shown in Fig. 5

The peaks C1s and N1s is located at the binding energies of 284 eV (C-C) and 399.82 eV (N-C) respectively, which are in good agreement with reported values of PPy [3]. The two peaks Fe2p1 and Fe2p3 is located at 725.99 eV and 710.53 eV respectively with an energy difference of 15.46 eV, which is characteristic of Fe<sup>3+</sup> state and confirms the presence of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> in the prepared

hybrid nanocomposite [4]. The peak O1s at 531.43 eV indicates the presence of oxygen and matches with reported value [4]. While, S2p peak is found at 167.97 ev, which is due to dopant CSA. Thus, XPS results in addition to XRD and FTIR spectroscopy confirms the formation CSA doped PPy/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> hybrid nanocomposite.



Fig. 5. XPS spectra of 30% CSA doped  $PPy/\alpha$ -Fe<sub>2</sub>O<sub>3</sub> hybrid nanocomposite.



Fig. 6 . The variation of NO\_2 response of CSA doped PPy/ $\alpha$ -Fe\_2O\_3 film with 10-90% RH.

## References

- [1] E. Pretsch, P. Buhlmann, M. Badertscher, "Structure determination of organic compounds tables of spectral data", 4th Ed. .pp 283.
- [2] S. T. Navale, M. A. Chougule, A. T. Mane, V. B. Patil, "Highly sensitive, reproducible, selective and stable CSA-Polypyrrole NO<sub>2</sub> sensor, Synth. Metals, 189 (2014)111.
- [3] A. Joshi, S. A. Gangal, S. K. Gupta, "Ammonia sensing properties of polypyrrole thin films at room temperature", Sens. and Actua. B, 156 (2011) 938.
- [4] A.P. Grosvenor, B.A. Kobe, M.C. Biesinger, N.S. McIntyre, "Investigation of multiplet splitting of Fe 2p XPS spectra and bonding in iron compounds", Sur. and Inter. Analy., 36 (2004) 1564.