

Enhance the Sensitivity of Polyaniline Doped with Strontium Oxide Nanocomposites by H₂S GAS

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Abstract: *The conducting Polyaniline-Strontium Oxide (PANI/SrO) nanocomposites were synthesized in the laboratory by chemical oxidation in-situ polymerization technique with variable weight percentages of 10, 20, 30, 40 and 50 of pure Strontium oxide in Polyaniline. The size of nanocomposites were characterized by X-ray diffraction (XRD) and it is found to be 25nm. The surface morphology of the nanocomposites was studied by scanning Electron Microscope (SEM) and it is found to be porous and sponge like nanomaterials. The porous nanomaterials is very useful for gas sensor applications. The sensitivity of various wt. % of PANI-SrO nanocomposites as a function of time at room temperature. Among all the samples 50wt. % of PANI-SrO nanocomposites shows highest sensitivity for 100ppm of H₂S gas injected into the gas chamber. For pure polyaniline and 10wt% of PANI/SrO nanocomposites shows low sensitivity.*

Keywords: Nanocomposites, Sensitivity, Gas sensor, Hydrogen sulphide gas, Polyaniline

1. Introduction

The conducting polymer-metal oxide nanocomposites having unique physical properties that have attracted more and more attention. Conductive polyaniline (PANI) has been studied extensively because of its ease synthesis, low cost, environmentally friendly, electrical, electronic and other properties [1-5]. Conducting polymers are widely used for gas detection due to their electrochemical properties. SrO has been attracted much attention as cathodes in rechargeable battery, selective gas sensors such as H₂S, ammonia because of their high surface area and redox activity. One of the important aspects of the SrO is its layered lamellar structure. Many studies have been conducted to form PANI/SrO nanocomposites structures controlling internal morphology has still remained a challenge. In this paper, authors report synthesis, characterization, gas sensor properties of polyaniline /SrO nanocomposites [6-15].

2. Experimental Methods

Materials and Method All the reagents were analytical grade only and were used as received. Aniline monomer was distilled under reduced pressure and kept below 0-5 °C prior to use. Aniline monomer, hydrochloric acid (HCl), ammonium per sulphate [(NH₄)₂S₂O₈] and Strontium Nitrate were purchased from Merck chemicals ltd.

2.1 Synthesis of SrO and Pure PANI

The strontium oxide nanoparticles were synthesized by self – propagating low temperature combustion method, employing strontium oxalate as precursor. The precursor is prepared by dissolving equimolar quantity of ammonium persulphate and oxalic acid in distilled water.

Synthesis of PANI was carried out by in-situ chemical oxidation polymerization technique. Aniline (0.1M) was mixed in 1M hydrochloric acid and stirred for 30 min to form aniline hydrochloride solution. To this solution, add 0.1M of ammonium per sulphate (APS), which acts as an oxidizer was

slowly added one drop per second with continuous stirring under ice bath at temperature of 0-5°C for 6 hrs to get it completely polymerized. The precipitate was filtered, washed with double distilled water and acetone. Finally dried PANI placed in hot air oven at 70°C for 24hrs to achieve a constant mass.

2.2. Synthesis of PANI/SrO nanocomposites

Synthesis of PANI/SrO nanocomposites was carried out by In-situ chemical oxidation polymerization technique. Aniline (0.1M) was mixed in 1M hydrochloric acid and stirred for 15-20 min to form Aniline hydrochloride. SrO powder is added in the mass fraction to the above solution with vigorous stirring in order to keep the SrO homogeneously suspended in the solution. To this solution, add 0.1M of ammonium persulphate (APS), which acts as an oxidizer was slowly added drop-wise with continuous stirring at 0-5°C for 4-6 hours to be completely polymerized. The precipitate was filtered, washed several times with deionized water and acetone. Finally dried in hot air oven for 24hrs to achieve a constant mass. In this way, polyaniline/SrO nanocomposites with various weight percentages of SrO (10%, 20%, 30%, 40% and 50%) were synthesized. Later, the synthesized samples were made a fine powder with the help of agate mortar.

3. Characterization

X-Ray diffraction studies were performed using Philips X-ray diffractometer with CuK α as the radiation source. The morphology of the nanocomposites in the form of powder were investigated using scanning electron microscope (SEM) Model-EVO-18 (Special Edison, Zeiss, Germany). The variation of resistance of PANI and various weight percentage of PANI/SrO nanocomposites for H₂S gas and fresh air injected in the gas sensor chamber was studied by using Keithley 2400 source meter at room temperature. The samples were prepared in the pellet form of 10 mm diameter and 3mm thickness by applying pressure of 1ton in Athane hydraulic machine Mumbai. The pellets were coated with

silver paste on both sides.

a) X-ray Diffraction (XRD)

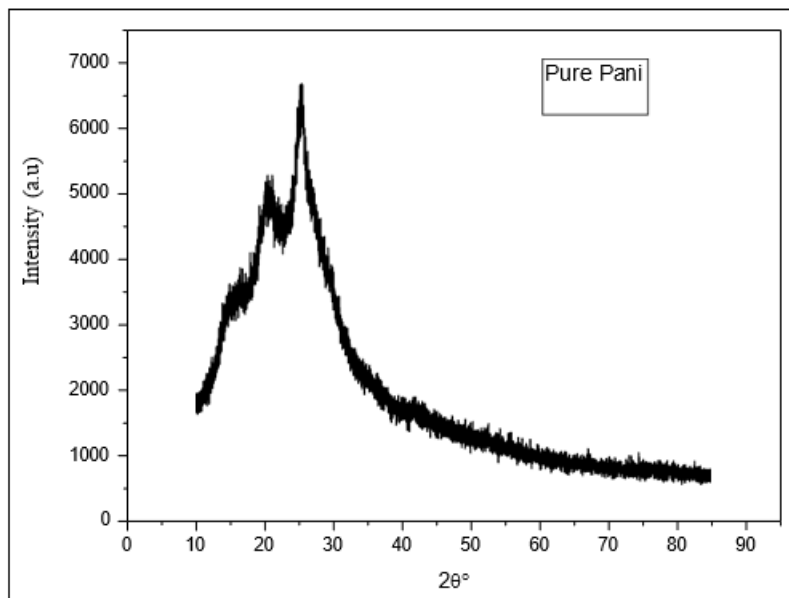


Figure 1: XRD graph of pure PANI

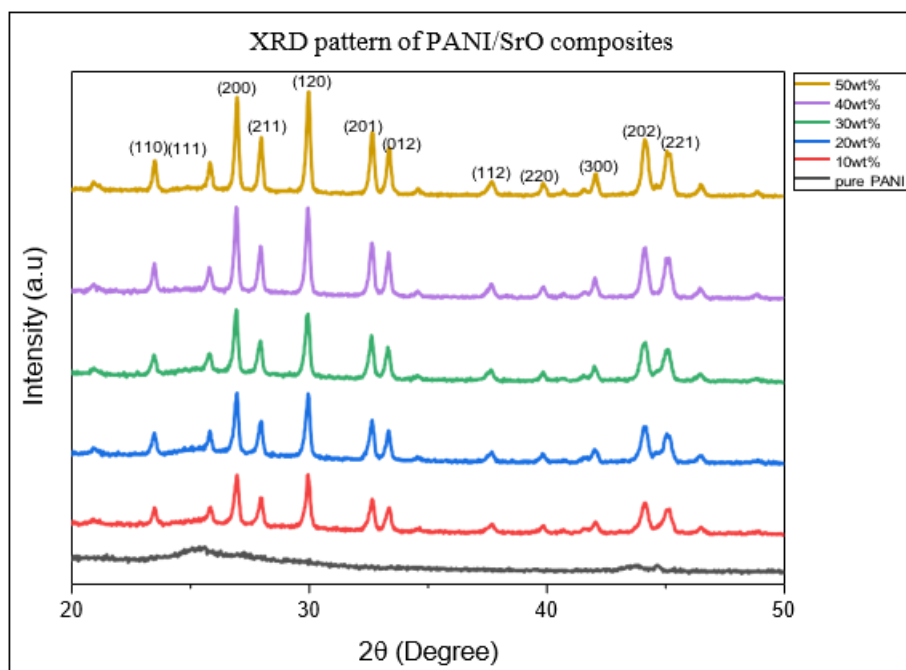


Figure 2: XRD graph of Various wt% of PANI/SrO Nanocomposites

XRD Analysis figure 1 shows the graph of X-ray diffraction pattern of Pure Polyaniline. The analysis of x-ray diffraction of Polyaniline suggests that it has amorphous nature with a broad peak centered on $2\theta \approx 25.53^\circ$ which corresponds to (200) diffraction plane.

Figure 2 shows graph of X-ray Diffraction pattern of various weight % of PANI/SrO nanocomposites. These nanoparticles have shown good crystallinity because of existence of sharp peaks in XRD pattern. The Crystallite size of the synthesized PANI/SrO nanoparticles was calculated using Scherer's formula given by $D = 0.9\lambda / \beta \cos\theta$ where D is the average crystallite size, λ is the wavelength of X-ray (1.5405Å) and β

is the full width half maximum in radian. The average crystallite size is found to 45nm. In the XRD pattern, different lines attributed to the (100), (111), (200), (002), (201), (012), (112) and (202) planes are good agreement with data of PANI/SrO powder file, which corresponds to orthorhombic crystalline structure. The resulting diffractogram shows a perfect crystalline structure which may be due to the presence of SrO. The comparison of XRD pattern of SrO and nanocomposite suggests that there is no change in the structure of SrO due to its dispersion in polyaniline during polymerization reaction.

b) Scanning Electron Micrographs (SEM)

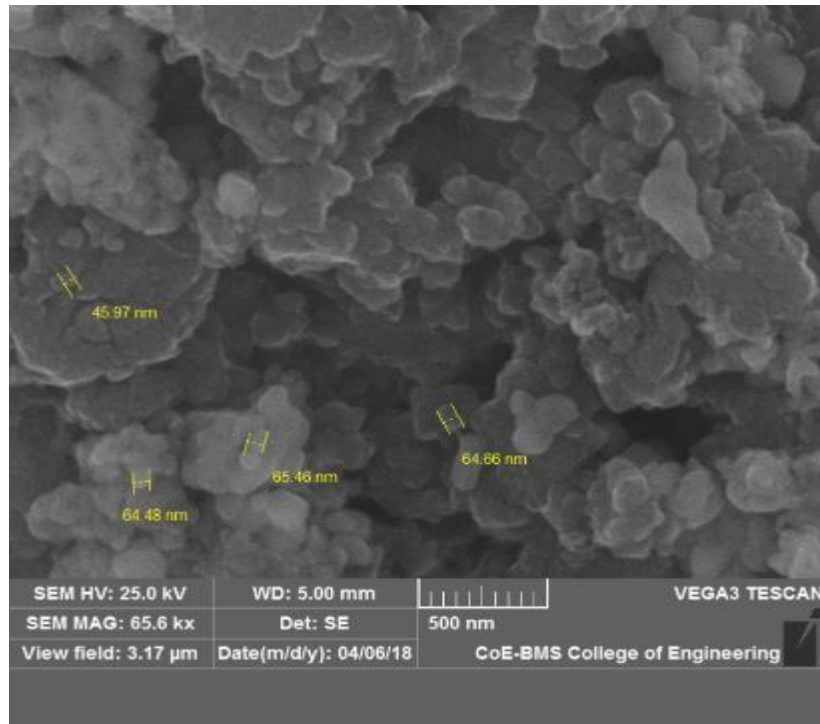


Figure 3: SEM image of Pure PANI

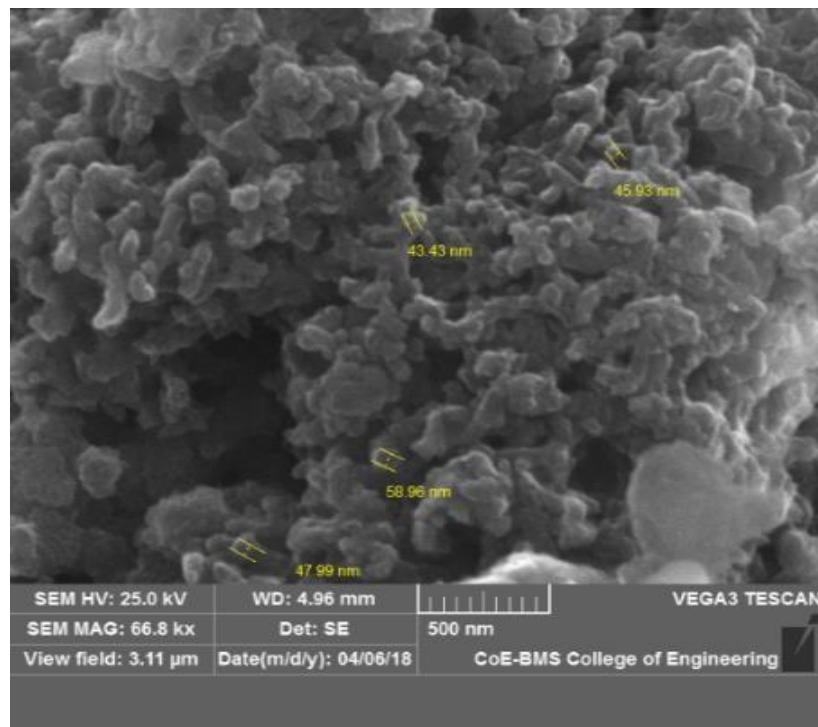


Figure 4: SEM image of Pure SrO

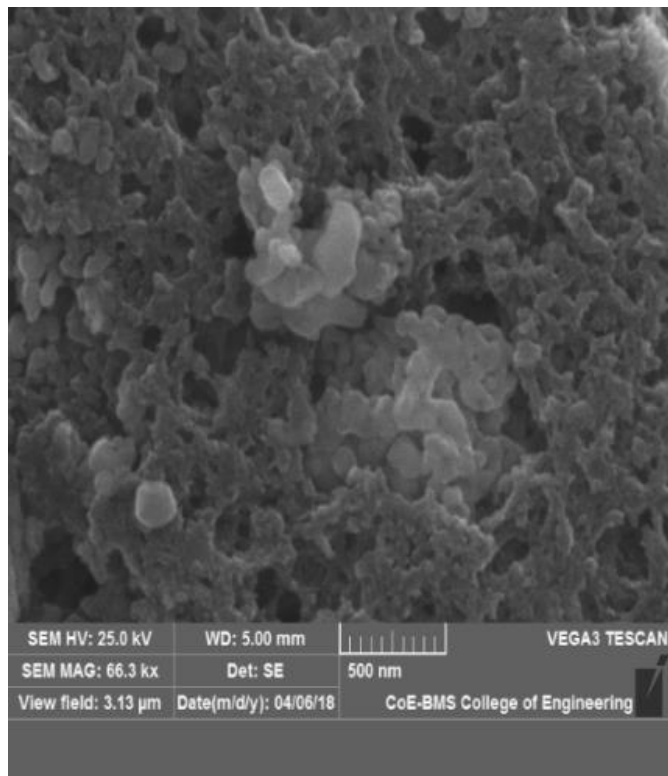


Figure 5: SEM image of 50wt% of PANI/SrO nanocomposites

Figure 3 shows SEM image of Pure Polyaniline. It is found that Polyaniline grains have well interaction with one another. The average size was calculated by using linear intercept formula and it is found to be 45nm to 65nm.

Figure 4 shows SEM image of pure strontium oxide and it is seen to be porous like structure. The average grain size was found to be 55nm. the grains are found to be well interconnected with each other which indicate that they have enough binding energy to combine with neighbors grains or

molecules.

Figure 5 shows the SEM image of 50wt. % of PANI/SrO nanocomposites and it is found to be sponge like structure.

4. Result and Discussion

Sensor Study

Gas Sensor analysis:

The PANI/SrO nanocomposite were tested for 100 ppm of H₂S gas at room temperature. For the pellets having silver paste contact having metallic contacts were kept in the test vacuum chamber of known volume with the electrical leads taken out for electrical measurements. 100ppm of H₂S gas was injected into the test chamber. Resistance of the composites measured with time until it reached steady value. this procedure was followed once again after removing H₂S gas and exposing the test chamber to air. This steps were repeated.

H₂S gas sensing mechanism:

The physical properties of conducting polymers strongly depend on their doping levels. Fortunately, the doping levels of conducting polymers can be easily changed by chemical reactions at room temperature. This provides a simple technique to detect the analytes. Most of the conducting polymers are doped / undoped by redox reactions. Therefore, their doping level can be altered by transferring electrons from or to the analytes. Electron transferring can cause the changes in electrical resistance and work function of the sensing material. This process occurred when pellets of PANI are exposed with H₂S gas. Electron acceptors can remove electrons from the aromatic rings of conducting polymers. When this occurs at a p-type conducting polymer, the doping level as well as the electric conductance of the conducting polymer is enhanced. An opposite process will occur when detecting an electron donating gas.



Figure 6: Shows experimental set up of gas sensor device.

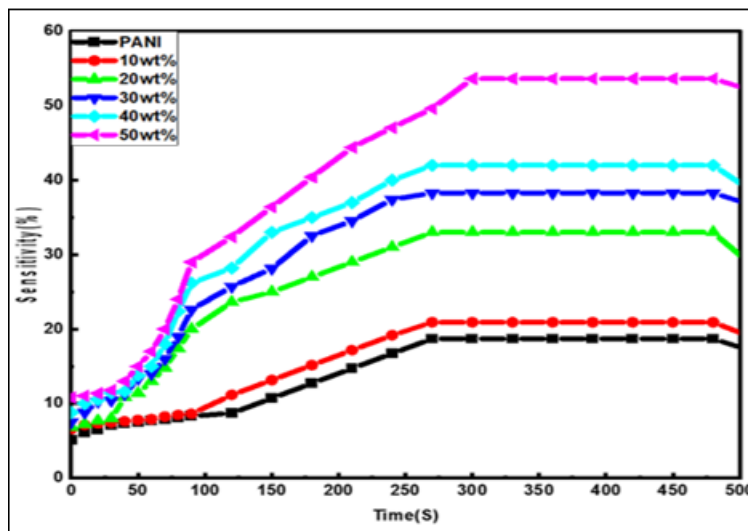


Figure 7: Shows sensitivity of gas with weight percentage of pure PANI and various wt. % of PANI/SrO nanocomposites material.

Figure 7 graph shows that among all the samples 50wt% of PANI/SrO nanocomposites show highest sensitivity due to larger surface area and more adsorption. 10wt% of PANI/SrO nanocomposites has lowest sensitivity due to lower surface area and low adsorption at room temperature for 100 ppm of H₂S gas.

5. Conclusion

Polyaniline/ SrO nanocomposites were synthesized by chemical oxidation in-situ polymerization method. The XRD pattern confirms size and crystallite of nanocomposites. The SEM image shows the presence of SrO nanoparticles which are uniformly distributed throughout the nanocomposites sample. H₂S Gas sensor properties were studied in the presence of SrO nanoparticles in polyaniline which shows sensitivity were maximum for 50wt% of PANI/SrO nanocomposites and minimum for 10wt% of PANI/SrO nanocomposites.

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References

- [1] Jiahua Zhu, a Suying Wei, Lei Zhang, Yuangbing Mao, Jongeun Ryu, d Amar B. Karki, e David P. Younge and Zhanhu Guo, (2011) 342.
- [2] Wong H P, Dave B C, Leroux F et al, J Mater Chem, 8 (1998) 1019.
- [3] Kanatzidis M G, Wu C G. J Am Chem Soc, 111 (1989) 4139.
- [4] Pokhodenko V D, Krylov V A, Kurys Y I et al. Phys Chem Chem Phys, 1 (1999) 905.
- [5] Lora-Cantu M, Gomez-Romero P. J New Mater Electrochem Syst, 2 (1999) 141.
- [6] Heinze J. Top Curr Chem, 2 (1990) 152.
- [7] Epstein A J, Mac Diarmid A. G Makromol Chem, Macromol Symp, 51 (1991) 217.
- [8] Yang Y, Heeger A J Appl Phys Lett, 64 (1994) 1245.
- [9] Ramesh Patil, Ashish Roy, Kopplalkar R, Anilkumar,

- Shrikant Ekhelkar, J. App. Poly. Sci; 121 (2011) 262.
- [10] Kopplalkar R, Anilkumar, A. Parveen, G. R. Badiger, M. V. N. Ambika Prasad, Physica B, 404 (2009) 1664.
- [11] Ashish Roy, Kopplalkar R, Anilkumar, M. V. N. Ambika Prasad; J appl. Poly. Sci, 121 (2011) 675.
- [12] M. I Gautu and P. J. G. Romero, J of Solid- State Chemistry, 147 (1991) 601.
- [13] Ramesh Patil, Ashish Roy, Kopplalkar R, Anilkumar, K. M. Jadhav a, Shrikant Ekhelkar Composites Part B, 42 (2012) 3406.
- [14] Kaushik A, Kumar R, Arya SK, et al. organic-inorganic hybrid nanocomposites- based gas sensor for environmental monitoring Chem Rev, 2015; 115: 4571-4606.