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The study of adsorption of conducting polymer based new precursor PANI-cuo nanocomposites on thin film and its characterization

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ABSTRACT

Thin film of PANI-CuO nanocomposites were successfully prepared by the chemical oxidative method of the aniline in acidic medium with potassium dichromate ($K_2Cr_2O_7$) as an oxidant. The composition, morphology and structure of the PANI-CuO nanocomposites were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), EDS-spectrum and cyclic voltammetery technique. Due to formation of H-bonding between amine group of PANI polymer chain and CuO, the characteristic FTIR peaks of PANI were found to shift to higher or lower wave number in PANI–CuO composites. XRD results indicated that the crystallinity of PANI was more pronounced after addition of CuO. In scanning electron micrograph (SEM) analysis the micrographs clearly reveal that granules are developed in the PANI – CuO film. CV curve present the super capacitive properties of PANI-CuO thin films prepared in this research.

Keywords: PANI-cuo, Thin film, SEM, XRD, cyclic voltammetery

INTRODUCTION

Recent decade, developments of conducting polymers on nanometer scale have been receiving significant attention due to its electronic properties, such as high electron affinities and low ionization potentials. CP also used as impedance type gas sensors for low cost, highly sensitive and selective room temperature. CP has been used in the areas of bio--analytical science due to their high mobility of the charge carriers and bio-compatibility. CP have been used in the preparation of biosensors in various fields, such as environmental monitoring and food analysis immunosensors, health care, DNA sensors due to their sensitivity towards very minor perturbations.

Polyaniline (PANI) is the most attractive CP [1-3]. It is used in various field such as electronic devices [4], supercapacitors [5], sensors [6,7], batteries [8] due to its physical and chemical properties, low cost, good electrical conductivity (p-type), high environmental stability, [9,10]. PANI emaraldine salts (PANI-Cl, PANI-Br, PANI-ClO4) are used as sensors for some organic and inorganic solvents [11]. There are different CP was produced for special purpose like PANI $NiFe_2O_4$ [12] and can be used as suitable electrode material for redox super capacitors. The electrodeposited PANI – Ag shows high capacitance properties [13].

CP thin film will not get spread uniformly all over the substrate; it acquires a small fraction on the surface of the substrate. Only few sites of substrate will get occupied first i.e. *nuclei* or *clusters*. The nuclei grow laterally or in height. The gap between different nuclei, gradually decreases and convert into thin film. The critical size of nuclei depends on super saturation, the more the super saturation lesser will be the critical size. Another factor which affects nucleation is interface structure. There are several stages in the growth process of a thin film. These include nucleation, coalescence, cleaned formation, hole formation and continues film. It is evident that nucleation takes place at different edges and interfaces of substrate making island structure. Further deposition will lead to spread these spots and making a liquid like structure, which may be described as coalescence structure. This will further grow to a network of the film with channels in between. In the channels secondary nucleation takes place and channels will shrink into holes. This on further deposition forms a continuous film. During deposition various defects such as points, dislocation, twinning, stacking faults etc. may develop and it is also possible to dope some metal oxides within

the thin film. Although many researcher devoted to the electro-polymerization of aniline and the characterization of the PANI-modified electrodes but there is not much information on the properties of the polymeric films formed by the electro-oxidation of the aniline derivatives.

Now-a-days, many researchers reported the PANI nanocomposites with the inorganic nano-scale such as TiO2, CdS, Silica, Ag, CeO2, Fe3O4, Zn and MnO2 etc. but about PANI–CuO nanocomposites there is less attention. CuO is a nontoxic, p-type semiconducting material with a good photocatalytic activity that has direct narrow band gap (1.2 eV). The structure and morphology of CuO have an adverse impact on its properties and applications such as reaction time, rate of evaporation and precursor concentration are found to determine the growth of CuO nanostructures like nanoparticles and nanospheres, it also used in dry batteries.

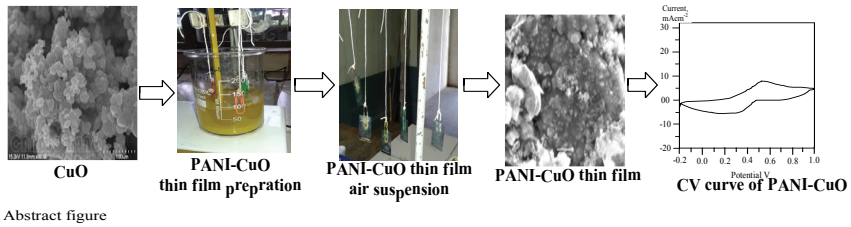
In present work, PANI-CuO nanocomposites and its thin film were prepared by in situ oxidative polymerization of aniline monomer with potassium dichromate ($K_2Cr_2O_7$) in acidic media. PANI-CuO was characterized FTIR, XRD, SEM and EDS spectrum. The main aim of the development of thin film PANI–CuO nanocompositeis applying it as a chemical sensor.

EXPERIMENTAL

Preparation of Thin Film of PANI–cuo nanocomposite

A series of CuO-doped PANI latex was synthesized via in situ emulsion polymerization. A typical procedure to prepare the CuO-doped PANI is given as follows: 0.45 gm of CuO was mixed with 0.05 mol (4.5 g) of aniline monomer in 100 mL of 1 molar HCl. The mixture was stirred for 30 minutes at 15-20°C, to form a homogeneous dispersion of aniline-CuO complex. Meanwhile $K_2Cr_2O_7$ (0.50 gm) dissolved in 1 molar HCl solution (20 ml). Dichromate solution was added dropwise into the emulsion with continuous vigorous stirring at 15-20°C temperature. After completion of addition reaction mixture was stirred for 4 hrs at same temperature, greenish to dark brownish Colour precipitate is the first confirmative evidence for formation of CuO-PANI nanocomposite. After completion of reaction glass substrate was immersed into the greenish to dark brownish Colour precipitate of CuO-PANI nanocomposite (shown in Figure 1a). The solution was stirred continuously for several hrs with the help of magnetic stirrer. The glass substrate is taken out of the solution after particular time interval (such as 30, 60, 90, 120, 150 minutes) and clamped in air to dry and drain the excess of PANI (Figure 1b) then the precipitate was collected on a 4G cintered filtration assembely and repeatedly rinsed with water. The products were then dried in an oven for 10-12 hrs.

All chemicals used were from S.D.Fine Chem. Ltd. Doubled glass distilled water was prepared in the laboratoryusing all glass quick fit apparatus.



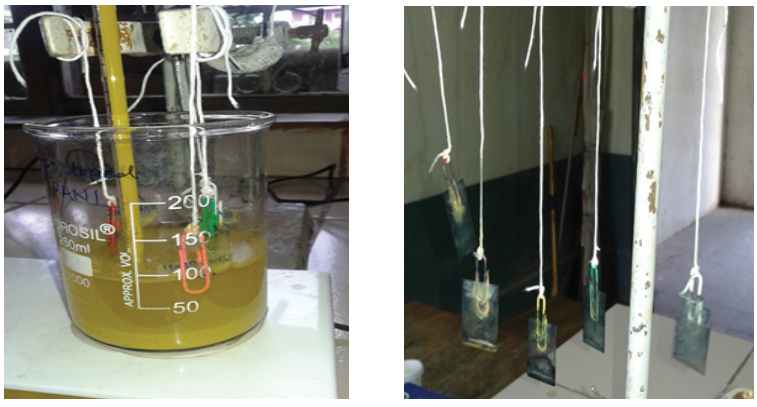
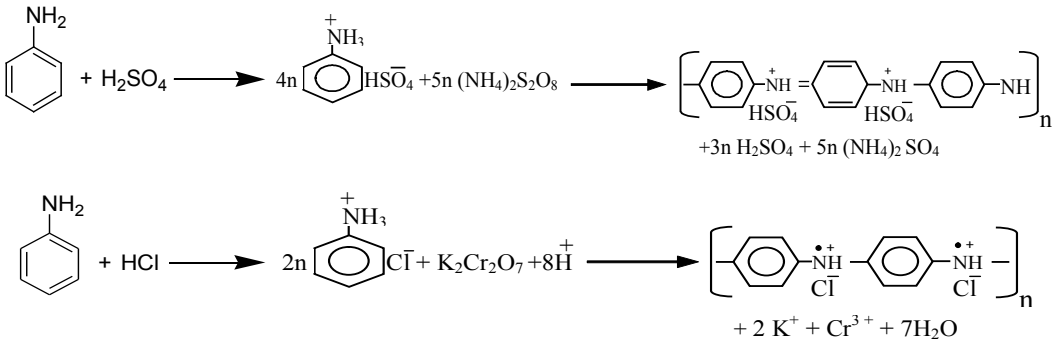


Figure 1. (a) Expt. set up thin flim PANI-CuO. **(b)** Air suspension of thin PANI-CuO.

RESULTS and DISCUSSION

Literature survey shows that the aniline reacts with sulphuric acid to give anilinium hydrogen sulphate salt and then oxidised with ammonium persulphate to get PANI (Scheme 1). In the present investigation aniline oxidized with strong oxidizing agent Potassium Dichromate in 1N HCl solution to get PANI scheme 2.



Thin film is gaining more importance due to its varied applicability in the field of electronics, optics, space science, aircraft, defence etc. A nontoxic, p-type semiconducting CuO doped into PANI synthesized by above method with the view of its wide range of application to get thin film of PANI-CuO nanocomposites.

Formation mechanism of PANI–CuO nanocomposites:

A feasible mechanism for the formation of the PANI–CuO nanocomposites is shown in Figure 2.

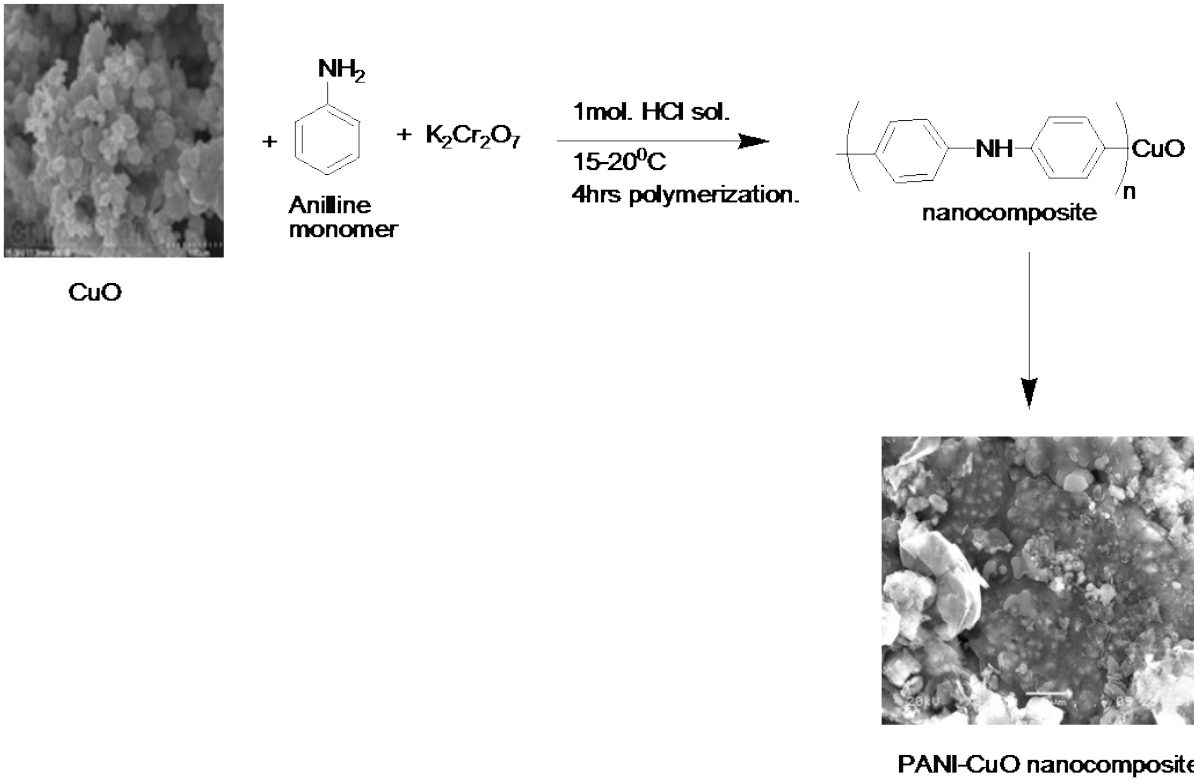


Figure 2: Fesible Mechanism of PANI-CuO nanocomposite.

FTIR

PANI and PANI–CuO nanocomposites were characterized by using the FTIR technique. In PANI–CuO nanocomposites, a broad peak observed at 3413cm^{-1} which can be associated to the interaction between CuO and PANI due to the hydrogen bonding between H–N of PANI and oxygen of CuO (Figure 3).

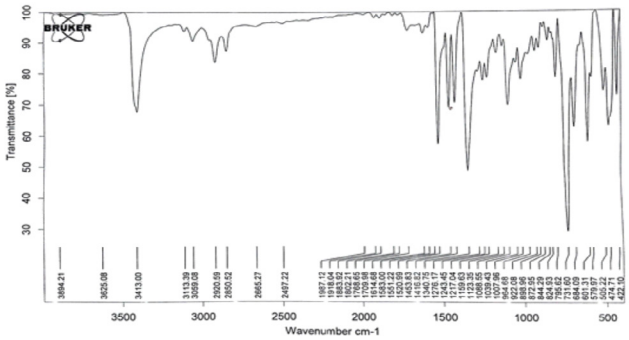


Figure 3: FTIR pattern of PANI-CuO nanocomposites.

XRD

XRD analysis was used to examine the structure of the CuO and PANI–CuO nanocomposites and investigate the effect of the doping CuO on the PANI structure. Figure **4** shows the Wurtzite Structure Model of Cu-O.

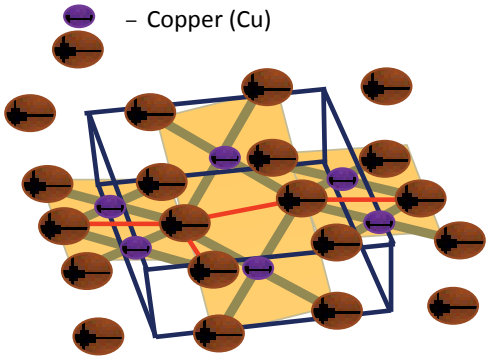


Figure 4: The Wurtzite Model of CuO.

The XRD reveals that the structure of the CuO doped PANI is found to be Monoclinic Phase. The unit cell edge parameters of the crystal is found to be a(4.82338 A˚), b(3.45593 A˚) and c(5.24087A˚). And the angles between edges (axes) are α(89.965˚), β(90.070˚) and γ(89.965˚) respectively. The volume occupied is observed to be 75.65728 $A^{\circ 3}$. The XRD pattern of PANI-CuO nanocomposite is shown in Figure 5**.** By comparing XRD pattern of PANI-CuO nanocomposites with the literature it is clearly shows that intensity of the peaks was increased by doping of CuO monomer which means that there is an interaction of CuO monomer and PANI by formation of hydrogen bonding between H–N and oxygen of CuO.

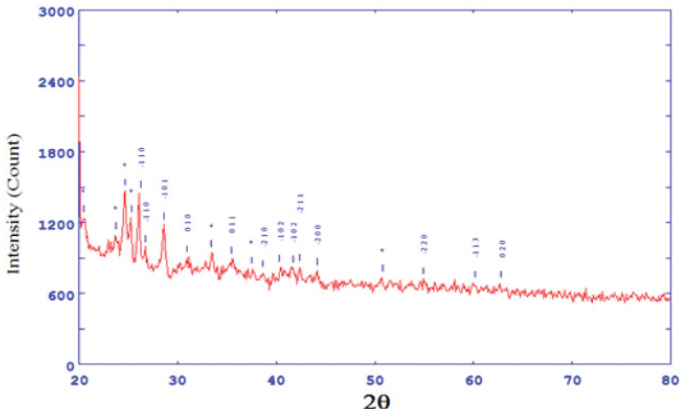
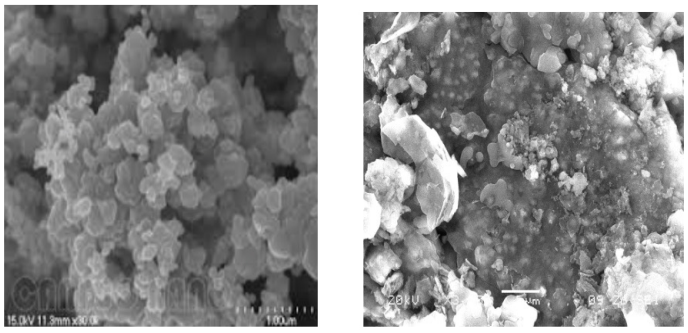


Figure 5: PANI-CuO Monoclinic Phase XRD Pattern

SEM

The SEM images of substrate shows PANI nano films with metal oxides in the cavities. Hence porosity is less at

surfaces. The micrographs clearly reveal that there are random growths of fibres; the granules are developed in the PANI – CuO film. It represented that morphology of single CuO depends on substrate temperature. The morphology of CuO deposits depend on different conditions, the structure varies sometimes spherical, hierarchical, continuous deposits plate and rod structure, hexagonal nano rings etc. The granules are also observed in CuO thin films. Morphologies of the CuO, PANI–CuO nanocomposite and thin film are shown in Figure 6.



(a) CuO (b) PANI - CuO thin film

Figure 6: Scanning Electron Micrograph (SEM)

The SEM images help us draw a conclusion that the doping of CuO has a strong effect on the morphology of PANI and develop granules. These nanocomposites should give the opportunity to obtain improved capacitance due to surface effects, since PANI has various structures such as granules, nanofibers, nanotubes, nano-spheres, microspheres and cracks.

EDS

The EDS spectrum of the composite has been recorded and are shown in the Figure 7 for PANI-CuO nanocomposites and Elements detected are also represented in tabular form in Table 1**.**

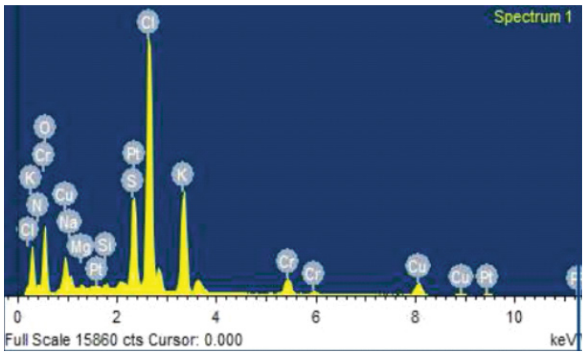


Figure 7: EDS Graph for Elements Present in the PANI-CuO nanocomposite.

Table 1: Elements Detected in the Composites.

	Element	N	O	Na	Mg	Si	S	Cl	K	Cr	Cu	Totals
PANI – ZnO	Weight%	9.49	44.75	1.40	0.26	0.22	6.27	20.09	9.46	2.86	5.19	100
	Atomic%	14.44	59.57	1.29	0.23	0.17	4.17	12.07	5.14	1.17	1.74	

Cyclic voltammetery

The cyclic voltammetery technique was used to investigate the super capacitive properties of the thin films prepared shown in Figure 8. The thin film electrodes are studied in the potential window of - 0.2 to + 0.8 XvsSCE. The scan rate was maintained 5m/s. The thin film shows pseudo capacitors behaviour. PANI theoretical specific capacity of about 145 mAh/g (without for anion - dopant) at dopant degree equal to 0.5, is one of the most interesting conducting conjugated polymer, but in reality, PANI doped with different acids prepared by common chemical methods, hardly achieved capacity of 100 mAh/g. During cycling in aqueous solutions, PANI undergoes two redox transitions and its instability appears due to over oxidation that lowers Coulomb efficiency of PANI.

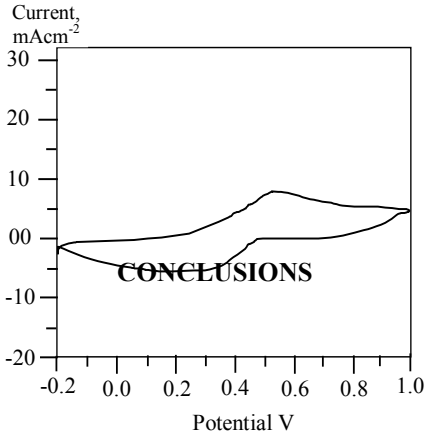


Figure 8: CV curves PANI-CuO thin Flim.

CONCLUSIONS

Spectroscopic analytical methods such as XRD, FTIR, SEM, EDS, CV indicate that PANI–CuO nanocomposite is successfully prepared in this research prepared by in situ chemical oxidative polymerization at atmospheric pressure. A possible mechanism for the formation of the PANI–CuO nanocomposites was proposed. XRD and FTIR results show that interaction between CuO and PANI is based on the formation of hydrogen bonding at 3413 cm^{-1}. The XRD reveals that the structure of the CuO doped PANI is found to be hexagonal structure. A SEM image shows that the granules are developed in the PANI – CuO film. The cyclic voltammetery technique was investigating the super capacitive properties of the thin films prepared in this research.

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