Abstract— In this paper we report the preparation of sulfonated polyaniline emeraldine salt (PANI-ES) by chemical oxidation route using ammonium per sulphate as oxidant and H_2SO_4 as dopant. Composite of PANI (micro sheets) with 15% copper (II) oxide nano particles was synthesized by placing CuO powder gradually in the polymerization solution of aniline while polymerization by keeping monomer to additive ratio 1: 0.15. PANI microsheets, nano particles of CuO and Micro ribbon structure of PANI/15% CuO have been examine by SEM micrographs. UV-vis spectrograph reveals the 1.385 near UV absorbance of PANI/15% CuO composite at 309 nm. Also the composite has been characterized by powder XRD and FTIR spectroscopy. Assigned bonds on FTIR spectrographs reveal the formation of PANI and PANI/CuO.

Keywords— CuO, PANI/CuO , micro ribbons.

I. INTRODUCTION

Among the organic conducting polymers, polyaniline (PANI) has attracted much attention due to its wide range of conductivity from insulating to metallic regime, abundant morphologies, good environmental stability, low cost monomer, ease of synthesis and various promising applications such as organic light emitting diodes, photovoltaic cells, sensors, protection of metallic corrosion and electrostatic discharge [1,4]. The charge carriers of the PANI are generally considered to be polaron and bipolaron stabilized by counter ions incorporated into the polymer during preparation. Therefore conducting and physical properties of PANI depend on the choice of counter ions is called dopant. Copper oxide (CuO) a versatile semiconductor materials, has been attracting attention because of the commercial demand for optoelectronic devices operating at blue and ultraviolet regions [5]. CuO is a monoclinic n-type semiconductor with narrow band gap energy of 1.5-1.8 eV, and it has very large excitation binding energy (60 meV) at room temperature [6, 7]. CuO has recently more attracted by researchers due to its exotic properties and wide applications from heterogeneous catalysts, gas sensors, field-emission emitters to high temperature superconductors and solar cells, lithium ion electrode materials, and etc. [8,9]. Because it has good mechanical flexibility and environmental stability, and its resistivity could be controlled with acid /base (doping/undoping), it has reach application in various areas such as lightweight battery electrode, electromagnetic shielding device, anticorrosion coating, solar cells, photo detectors and sensors [10,11].

PANI were greatly influenced by the addition of metal oxide such as iron oxide [12], CdO [13], Al_2O_3[14], ZnO [15]. However, only very few reports are found on the use of CuO on PANI. We et al investigates a new technique for tuning the properties of possible future organic device based on CuO incorporating conducting PANI [11]. At present no such report available on PANI composite with 15 wt % of CuO. Here we have reported the synthesis and characterization of polyaniline - CuO composites.

II. EXPERIMENTAL

2.1 Materials and method

All chemicals used are from MERCK of GR grade. The monomer aniline was doubly distilled prior to use. Ammonium persulphate ([NH_4)_2S_2O_8], copper oxide (CuO), sulphuric acid (H_2SO_4) were procured and were used as received.

2.2 Preparation of polyaniline

PANI-ES was synthesized by chemical oxidation method. Pre cooled (0-4°C) 100-ml solution of 0.4 M ammonium persulphate in 1 M sulphuric acid was added drop wise to 100 ml precooled (0-4°C) solution of 0.4 M aniline in 1 M sulfuric acid for 1 hour with constant stirring. After completion of the oxidant addition, stirring was continued for another 7 hours at 0-4°C to ensure completion of the reaction. During polymerization the sequence of colorations of the reaction mixture was light blue, blue green and finally greenish black precipitate. Dark green color ensures the formation of conductive PANI salt. The reaction mixture was kept overnight. Then precipitated emeraldine salt was filtered, washed with distilled water until the filtrate became colorless and finally with methanol and dried in oven at 70-80°C for 8 hours.

2.3 Synthesis of Polyaniline/CuO Composites

The composite of PANI-ES with CuO was synthesized by chemical oxidation method. The method was same as that of PANI synthesis, and CuO powder was added in aqueous solution of aniline containing sulphuric acid before addition of oxidant, ammonium persulphate. The CuO powder was added in pre- cooled (0-4°C) 100-ml solution of 0.4 M aniline in 1M sulphuric acid by keeping various weight % (10%, 15%, 20%, 25%, 30%, 35% and 40%) of CuO with aniline monomer.
The another solution of 100 ml precooled (0-4°C) solution of 0.4 M ammonium persulphate in 1 M sulfuric acid was added to the former solution for 1 hour with constant stirring. After completion of the oxidant addition, stirring was continued for another 7 hours at 0-4°C to ensure completion of the reaction. During polymerization, the sequence of colorations of the reaction mixture was light blue, blue green and finally greenish black precipitate. Dark green color ensures the formation of conductive composite PANI salt/CuO. The reaction mixture was kept overnight. Then precipitated was filtered, washed with distilled water until the filtrate became colorless and finally washed with methanol, and dried in oven at 70-80°C for 8 hours.

III. RESULT AND DISCUSSION

3.1 Scanning electron microscopy (SEM)

Fig.1(a), (b) and (c) shows the SEM micrographs displaying surface morphology of conducting PANI-ES, PANI/15%CuO composite and CuO. Fig. 1(a) shows the micro sheets of PANI. The micro ribbons structure of PANI/15%CuO having widths 495.18nm, 216.33nm and 202.84nm is shown in fig. 2(b). SEM image of pure CuO shows the spherical structure of CuO in fig. (c).

![Fig. 1: SEM micrographs of (a) PANI-ES (b) PANI-15%CuO and (c) CuO](image)

3.2 X-ray diffraction

![Fig-2: X-ray diffraction of (a) PANI-ES, (b) pure CuO and (c) PANI/CuO (15%)](image)

XRD graphs of PANI, CuO and PANI/15% CuO are shown in fig.2. The characteristics peak at 2 theta =25° confirms the formation of pure PANI. It shows the partial crystallinity. XRD pattern of PANI/15%CuO shows the presence of oxide peaks corresponding to 2theta = 8.55°, 20°, 25°and 29° are due to (250), (245), (200) and (575) respectively. In the spectra of pure CuO the major peaks are obtained at 2θ =35.6°, 38.8° and the other observed peaks are at 2θ = 49.9°, 53.5°, 58.3°, 61.6°, 66.32°, 68.16°, 72.53°, 75.15°.

3.3 FTIR study

Fig. 3(a) shows the IR spectra of pure PANI, with prominent peaks at 1564 cm⁻¹ (C=N stretching in quinoid ring of PANI), 1480 cm⁻¹ (C=C stretching in benzonid ring of PANI and C-C of para-substituted benzene). The peak at 1108 cm⁻¹ is due to the B-NH= Q vibration, indicating that PANI is conductive in the form of emeraldine salt. Fig.3b shows the FTIR spectra of PANI-CuO(15%) composite. The spectrum enriched with peaks reveals the presence of PANI and shows peaks below the 1000 cm⁻¹ clearly shows presence of copper oxide. Some additional peaks and shifts in vibrational frequency were also observed on comparison with pure PANI and (CuO) spectrum. This confirms the formation of PANI-CuO (15%) and fig 3(c) shows the FTIR spectrum of pure CuO.
For a further rise in weight % of CuO from 20 % to 25 % this absorption peak shows again red shift, 311 nm to 335 eV with decreasing band gap, 3.9971 eV to 3.7108 eV.

An identity peak of CuO in the UV range shifted at 291 nm for the composites having 15 %, 20 %, 30 %, 35% and 40% weight of CuO. In the same composite PANI/CuO, the first identity peak of PANI in the visible range lapse. Second absorption peak shifted with the weight % of CuO in the composite. It shows the red shift, 799 nm to 789 nm from 10 % to 25 % weight of CuO in the composite with increasing band gap, 1.5755 eV to 1.5815 eV respectively. With the rise in weight % of CuO in composite, from 15 % to 20 %, this peak shows blue shift, 786 nm to 662 nm with increasing band gap, 1.5815 eV to 1.8778 eV respectively. With further increment in weight % of CuO, from 20 % to 25 %, the same peak shows again red shift, 662 nm to 787 nm with decreasing band gap, 1.8778 eV to 1.5795eV respectively. Similarly for increasing the weight percentage of CuO absorption peak shows again red shift for 25 % to 30 % and 30 % to 35 % with decreasing band gap. Whole this UV-VIS spectroscopic data shows the well intercalation of CuO in the PANI. Band gaps of PANI/ZnO composite, in both, UV and visible range are decreasing as comparable to PANI.

**3.4 Optical spectroscopy (UV-vis)**

Optical spectroscopy is an important techniques to understand the conducting states corresponding to the absorption bands of inter and intragap states of conducting polymers. Fig.4 (a), (b) and (c) shows optical absorption with respect to wavelength for PANI, PANI-CuO (15%) and CuO. Fig. (b) shows the major absorption peak at 309 nm which confirms formation of \( \pi- \pi^* \) transition of benzeniod ring in the composite PANI/CuO (15%). In case of PANI, two characteristics bands appear at 291nm, and 788nm which are attributed to \( \pi- \pi^* \), exciton and polaron transition respective. In pure CuO only one peak appears in uv-visible range spectra. Second absorption peak lapses in the visible range.

UV –VIS spectrograph of CuO shows the absorption peaks at 291 nm in the UV range. The identity peaks of CuO lapse out on the UV-VIS spectrographs of the composites. With increasing weight % of CuO in the PANI/CuO composite from 10 % to 15 %, the first absorption peak shows the red shift, 309 nm to 315 nm with decreasing band gap 4.0230 eV to 3.9464 eV. For the rise in weight % of CuO in the composite from 15% to 20 % this absorption peak shows the blue shift, 315 nm to 311 nm with increasing band gap, 3.9464 eV to 3.9971 eV.
IV. CONCLUSIONS

Polyaniline and series of PANI-CuO composites with different weight % have been synthesized by in-situ polymerization method. SEM Micrograph reveals that the formation of micro sheets and micro ribbons of PANI and PANI-CuO15%. UV-vis spectrograph reveals the 1.385 near UV absorbance of PANI/CuO 15% composite at 309nm. XRD and FTIR study shows the formation of \( \pi - \pi^* \) transition of benzeniod ring.

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