

# Synthesis and characterization of organic-inorganic hybrid: Polyaniline-cerium tungstate nanocomposite

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**Abstract-** Polyaniline-Cerium tungstate (Pani-CeW), an 'organic-inorganic' composite material, was synthesized via sol-gel method using an electrically conducting polymer, polyaniline (Pani) and Cerium tungstate (CeW) prepared. The physico-chemical properties of the material were determined using FT-IR, TGA, XRD, SEM and EDX studies. The characterization results confirmed that there is a strong interaction between Pani and CeW. The thermal behavior of Pani, CeW and Pani-CeW composite were also investigated by thermogravimetric analysis (TGA) under nitrogen atmosphere and the Pani-CeW composite was found thermally more stable than pure Pani.

**Keywords-** Organic-inorganic hybrid, Polyaniline-cerium tungstate nanocomposite

## I. INTRODUCTION

Organic-inorganic hybrid material represent natural interface between the world of chemistry (organic-inorganic) each with very significant contribution to the field of material science and each with characteristic properties of each component trying to decrease or eliminate their drawbacks getting in an ideal way a synergic effect, which results in the development of new material with new properties. During the recent years there has been an explosive growth of research in the field of conducting polymers owing to their interesting electrical properties and their potential applications in various fields like electrochromic displays electronic devices, modified electrodes, chemical and biosensors. These polymeric materials can be obtained in various forms like powders, thin films. In order to select a material suitable for applications in various technological fields one has to overcome certain limitations such as poor mechanical properties and processibility, instability in ambient conditions. Several approaches have been made by many researchers to improve these properties. One of the best ways is the formation of conducting composites. Because of their light weight, low cost, low-temperature fabrication, good mechanical strength, and good environmental stability, polymer-based conducting composites have acquired an important position among technologies based on conducting and semiconducting materials [1].

Conducting polymers possess good tuneable electrical conductivity and are organic electrochromic materials with chemically active surface [2], such as polyaniline. It received great attention since its rediscovery by Shirakawa et al. [3], due to its wide range of application [4]. But they are chemically sensitive and have poor mechanical properties and thus pose a processibility problem. On the other hand, inorganic oxides or metal acid salts shows the presence of more sites for surface reactivity and are highly porous in sol form. They also have good mechanical properties and are good dispersants too [5]. Recently, several groups have combined conductive polymers with metal oxides to and structural stability [6]. The properties of composites of such kind are strongly dependent on concentration of polymer. generate hybrid composites that possess higher reversible capacity, redox cyclability

Among known conducting polymer, polyaniline are most frequently used in the commercial applications due to the high conductivity, long term stability of its conductivity and the possibility of forming homopolymers or composites with optimal mechanical properties. It is known for its stability in the oxidized state and interesting redox properties. The electrical and electronic properties exhibited by solid state materials are crucial in a large number of inorganic as well as organic-inorganic materials applications [7]. These unique electronic properties result from their extended structures, where strong interactions between the atoms, ions or molecules occur throughout the lattice. In terms of conductivity, the behavior ranges from insulating through semiconducting to metallic and superconducting.

In the past few years, researchers have shown much interest in the study of conducting behavior of 'organic-inorganic' composite materials [8]. Special interest today is focused on composite system having high conductivity at ambient temperatures, since they find unique applications such as separators in high power and rechargeable lithium batteries. Moreover, composite materials composed of oxides or polyvalent metal acid salts and conducting polymers have brought out more fields of applications, such as smart windows, toners in photocopying, and conducting paints [9] fuel cell, chemical sensors [10].

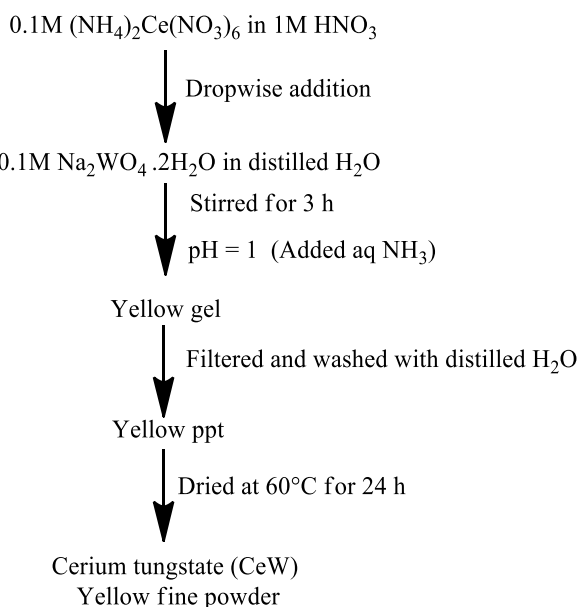
In this paper deals with the evaluation of conductive nanocomposite of organic-inorganic hybrid Pani-CeW nanocomposite has been prepared by in-situ with the method of chemical oxidative polymerization. The methods of preparation of Pani, CeW nanoparticle and Pani-CeW nanocomposites are reported. To the best of our knowledge, this the first ever attempt made to Synthesis and characterization of organic-inorganic hybrid: Polyaniline-cerium tungstate nanocomposite.

## II. EXPERIMENTAL

### 2.1. Chemicals and reagents.

Aniline was purified by distillation before use, aniline (99%) and ammonium persulphate were purchased from Merck. Ammonium ceric nitrate, sodium tungstate and anhydrous ferric chloride were purchased from Fischer scientific. All other reagents such as acids, metal salts and solvents were purchased from Merck and were of analytical reagent grade. Millipore water was used for solution preparation.

### 2.3. Synthesis of Cerium tungstate (CeW)



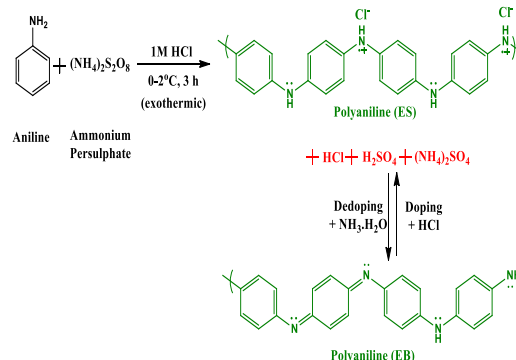
Scheme 1 Synthetic route for preparation of cerium tungstate (CeW).

The method of preparation of CeW (Scheme 1) was based on a modified version of that reported [11]. In a typical preparation CeW was prepared by adding 0.1 M ammonium ceric nitrate  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  in 1 M  $\text{HNO}_3$  to an aqueous solution of 0.1 M sodium tungstate ( $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ) in 1 : 1 molar proportion drop wise and with constant stirring. After complete addition of ammonium ceric nitrate, the yellow gel of CeW was obtained. The pH of the mixture (<1) was adjusted to

1 by adding aqueous ammonia. The solution along with the precipitates was stirred for 3 h. The precipitate was filtered, washed with conductivity water till the washings were chloride free, and dried at  $50^\circ\text{C}$ . The sample was then converted to the hydrogen form by immersion in 1 M  $\text{HCl}$ , the acid being intermittently replaced. The yellow fine powder obtained was used for the characterization and composite preparation.

### 2.2. Synthesis of Polyaniline-cerium tungstate nanocomposite (Pani-CeW)

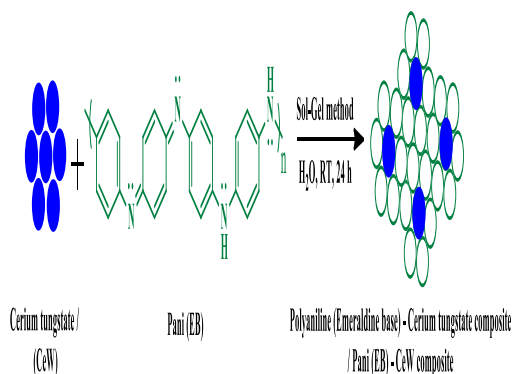
Polyaniline gel (Scheme 2) was synthesized by oxidative polymerization of aniline in the presence of hydrochloric acid using ammonium persulphate (acts as an oxidizing agent). For the synthesis, 10% aniline with 100 ml of 1M  $\text{HCl}$  in double distilled water was taken and stirred in a double wall flask at temperature  $0^\circ\text{C}$ . The solution (150 ml) of ammonium persulphate (0.1M in double distilled water) was added drop by drop in the double wall flask with continuous stirring. After 6 h, stirring was stopped and the solution was filtered in Buchner funnel and the residue was washed 3–4 times with distilled water and finally with methanol. The gel was kept in oven at  $50^\circ\text{C}$  for 24 h to dry.



Scheme 2 Synthetic route for preparation of (a) Pani (EB) and (b) Pani (ES).

Pani-CeW composites was prepared by the sol-gel method of polyaniline into the inorganic precipitate of Cerium tungstate with a constant stirring. A schematic presentation for the formation of Pani-CeW composites is shown in Scheme 3. The resultant mixture was turned slowly into greenish black colored slurries. The slurries were kept for 24 h at room temperature. Pani composite based gel was filtered off, washed thoroughly with distilled water to remove excess acid and any adhering trace of ammonium persulphate. The washed gel was dried at  $40^\circ\text{C}$  in an oven. The dried products were immersed in double distilled water to obtain small granules. The material was protonated by keeping it in 1M  $\text{HNO}_3$  solution for 24 h with occasionally shaking and intermittently replacing the supernatant liquid. The excess acid was removed after several washings with distilled water. The material was finally dried at

40°C and fine powder of composite was obtained by grinding the material with the help of pestle mortar. The powder of Pani-CeW composites kept in desiccator for further use. The pure Pani was synthesized (Scheme 2) by a similar method as the preparation of Pani-CeW composite without the CeW.



Scheme 3 Synthetic route for preparation of (a) Pani (EB) and (b) Pani (EB)-CeW composite.

### III. CHARACTERIZATION

FT-IR spectra were recorded by Thermo Nicolet FT-IR Spectrometer over the range of 4000–600  $\text{cm}^{-1}$ . The X-ray diffraction (XRD) studies of the CeW, Polymer and composite were carried out using Rigaku X-ray powder diffractometer with Cu anode ( $K\alpha \lambda = 1.54186 \text{ \AA}$ ) in the range of  $5^\circ \leq 2\theta \leq 80^\circ$  at 30 kV. The surface morphology and EDX were analyzed by scanning electron microscopy (SEM) using the instrument VEGA3 TESCAN. The TG-DTA measurements were performed using Perkin-Elmer thermal analyzer between 20°C and 800°C (in N<sub>2</sub>, rate 10°C/min).

### IV. RESULTS AND DISCUSSION

FT-IR spectra of the CeW particle, Pani and Pani-CeW composite (Fig.1) shows the formation of Pani-CeW composite from the Pani and CeW particle. The spectrum of the Pani shows the evidence of the vanishing of the CH=CH, CH=N, C=C and N-N stretching vibration band at 3104, 1590, 1406 and 1037  $\text{cm}^{-1}$  respectively. The position of this band in Pani-CeW composite is shifted slightly towards higher wave number. In Pani-CeW composite below 950  $\text{cm}^{-1}$  to 600  $\text{cm}^{-1}$  obtain broad band due to it is main characteristic stretching of CeW particle, however a peak at 835  $\text{cm}^{-1}$  in CeW spectrum is due to M–O bonding and the band between 1400 and 900  $\text{cm}^{-1}$  may be assigned to symmetric and antisymmetric stretching of the W–O bond in WO<sub>3</sub> groups. so it is clear evidence of CeW particle incorporate on Pani.

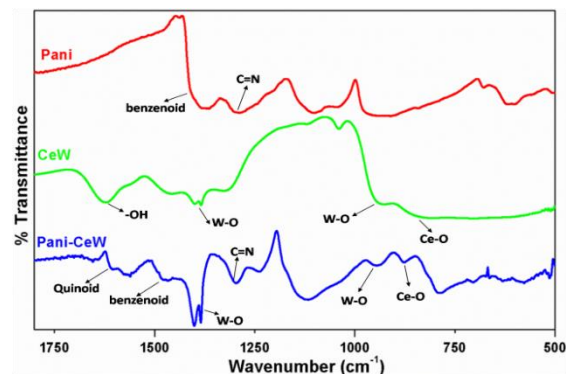


Fig. 1. FTIR spectra of (a) Pani (EB), (b) CeW, (c) Pani (EB)-CeW composite.

The XRD patterns of pure Pani, CeW, and Pani-CeW composite are shown in Fig. 2. The XRD pattern of CeW shows the sharp diffraction peak, attributed to crystal nature of CeW particle at  $2\theta \sim 23^\circ$ – $30^\circ$ . The diffraction peaks of CeW particle in composite shows a decrease in crystallinity which may be attributed to the dominant amorphous nature of Pani. The peak of CeW were in good agreement with JCPDS no.250192. The broadening of peak of CeW particle in Pani-CeW composite suggests successful incorporation of CeW particle in Pani-CeW composite. The results are also in agreement with the FTIR studies. The average particle size of the composite estimated by using the Scherrer equation. The particle size of the CeW particle and Pani-CeW composite is found to be  $\sim 2.32$  and  $0.89$  nm respectively.

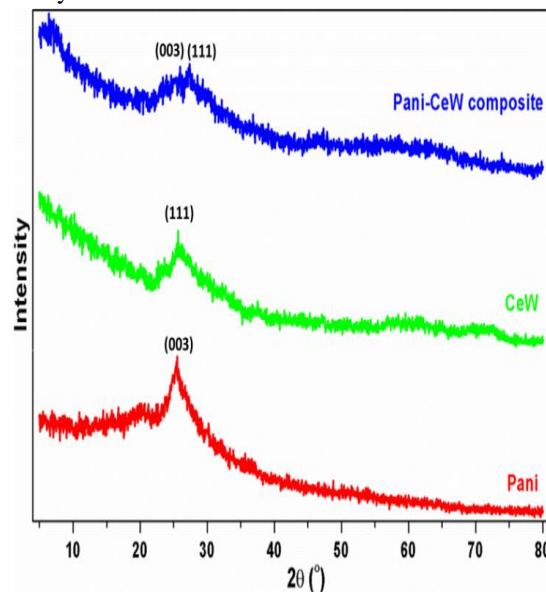


Fig. 2. XRD patterns of Pani, CeW and Pani-CeW composite.

TGA curves of Pani, CeW particle and Pani-CeW composite are shown in Fig. 3. There are two stages of weight loss, the first weight loss till 250, 263 and 320°C can be attributed to the loss of physisorbed water molecules and

volatile impurities, the second weight loss up to 400, 566 and 560°C can be ascribed to the degradation of the polymers unsaturated groups whereas from 400 to 900°C the polymer shows some stability and hardly any weight loss is seen. The total mass loss up to 900°C has been estimated to be about 25.50, 84.42 and 52.14% for the Pani, CeW particle, Pani-CeW composite respectively. From the observation thermal stability of the composite is higher than the polymer and the weight loss of the composite is lower than the polymer. These results confirm that the presence of CeW in the Pani-CeW composite is responsible for the higher thermal stability of the composite material in comparison to pristine Pani in N<sub>2</sub> atm.

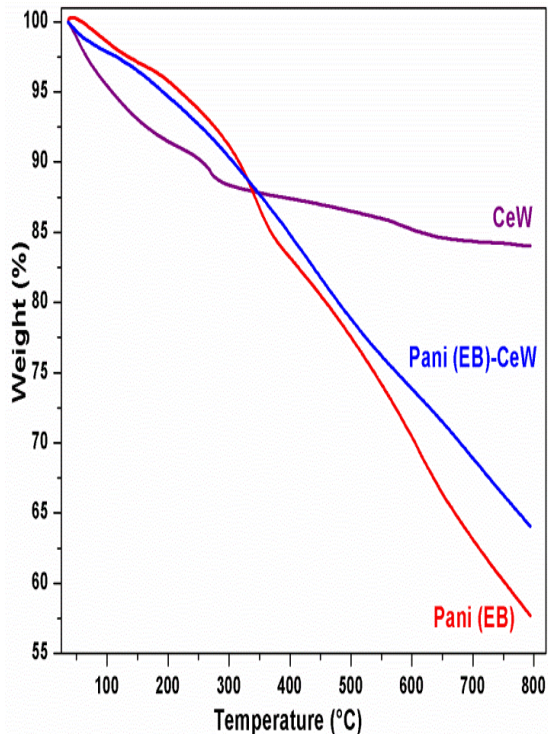


Fig.3. Thermo gravimetric plot of CeW, Pani and Pani-CeW composite.

The surface morphology of Pani, CeW nanoparticles and Pani-CeW nanocomposite was examined by SEM. The SEM picture of Pani (Fig. 4 (a)) expose the smooth surface of the Pani and CeW nanoparticle shows (Fig. 4 (b)) small grain texture. Pani-CeW nanocomposite (Fig. 4 (c)) shows high porous nature of the nanocomposite indicating the influence of CeW nanoparticle on the texture of the nanocomposite.

SEM-EDX spectra of CeW nanoparticles and Pani-CeW nanocomposite (Fig. 8) also confirmed the presence of CeW in Pani. The weight percentages of the elements in the sample are given in the plot. Peaks corresponding to Ce, W, O and Ce, W, O, C, N in the nanoparticles and nanocomposite respectively confirm their presence. EDX is not sensitive to the lighter atom H.

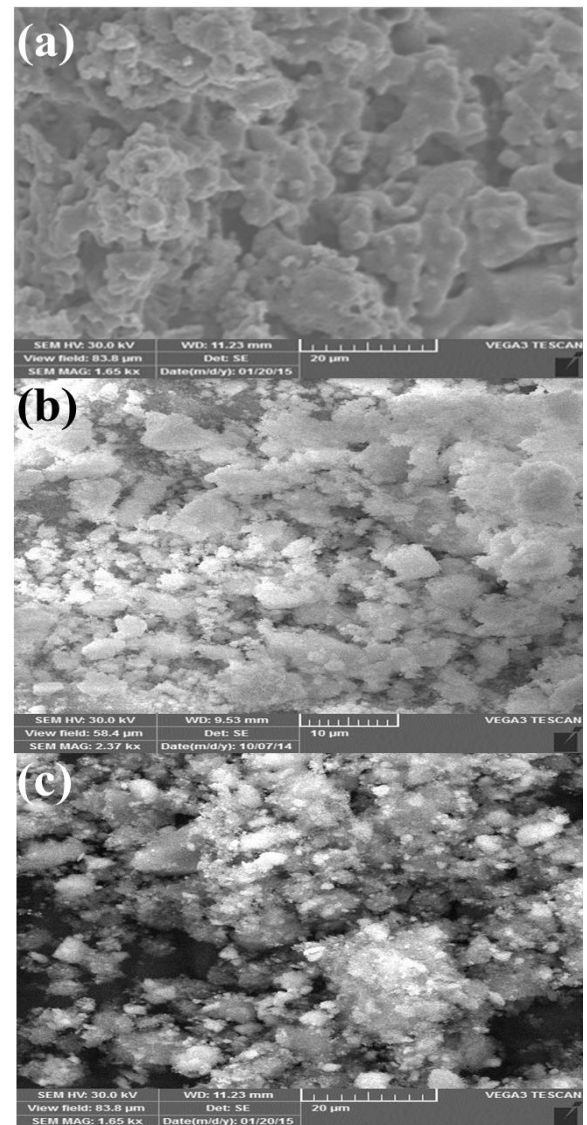
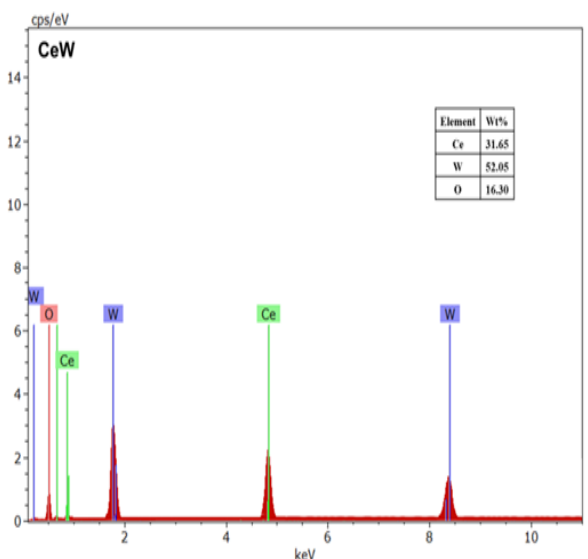


Fig.4. SEM images of (a) Pani, (b) CeW and (c) Pani-CeW composite



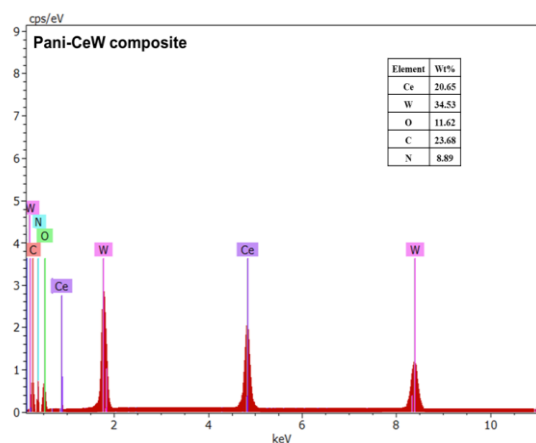


Fig.5. EDX spectrum of CeW and Pani-CeW composite.

## V. CONCLUSION

In this paper, the results of FT-IR, UV, XRD, SEM, EDX and TGA studies reveal that the polymerization of Pani have been successfully achieved on the surface of the CeW particles and indicate that there is a strong interaction between Pani and CeW particles. This electrically conducting Pani-CeW nanocomposite has been successfully synthesized by using an in situ chemical oxidative polymerization technique.

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