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Structural, Optical, And Frequency Dependent Conductivity Properties Of PANI/Ceo_2 Nanocomposites By In Situ Polymerization Method

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Abstract- This article explain a novel synthesis for producing Polyaniline / CeO_2 nanocomposites with five weight percentage (5wt%) by in situ polymerization technique. The synthesized nanocomposites were analysing using many measurements like X ray diffraction (XRD), absorption UV spectroscopy, FTIR, and impedance spectroscopy. An XRD result tells that the structures of nanocomposites are nanocrystalline. The grain size of the nanocomposites was calculated by XRD analysis, has around 9.8 (nm). The optical studies response for the nanocomposites, shows the possible visible absorption peaks for PANI/CeO_2 nanocomposites in the region of 273, 342, 634 and 872 (nm). Band gap energy of nanocomposites is discussed and calculated, it is 3.3 (eV). The FTIR characterization was analyzed and was confirmed the functional group of the nanocomposites materials. AC Conductivity properties are done and conductivity (σ) at various logarithm frequencies (log f) and various temperature are reported. Hopping of electron between ions is the nice of the nanocomposites and hopping mechanism was discussed.
Index Terms- Conductivity; Nanocomposite; Polymerization; Absorption; Peak

1. INTRODUCTION

Conducting polymer and metal oxide nanocomposites have engaged nice attention for their potential applications in many fields like as secondary battery, sensors, and electrodes [1]. Conducting polymer and metal oxide nanocomposites hold very high hardness and strength of inorganic materials [2] and hold ability of polymer. Recent years, many properties have intense on the polyaniline-metal oxide nanocomposites to get materials with supportive nature between polyaniline and metal oxide [3]. However, the crystalline behaviour of these nanocomposites is getting been low [4]. So, search new polyaniline / cerium dioxide nanocomposites have with good crystalline nature, nice stability, and easy preparation [5], we have chosen this work.

Among the various metal oxides, CeO_2 are the most valuable materials for normal use in the world [6]. They display good crystalline behaviour, high density and semiconducting behaviour [7]. Also it has good UV blocking to product sensitive materials [8], as coating materials. CeO_2 have many applications like as LPG sensors, solid fuel cell and electrode for electrochemical devices [9]. The theoretical and experimental has displays that, CeO_2 metal is an ion [10]. In this property, recently, a few articles were
carried out on polyaniline/cerium oxide nanocomposites. The electrical and optical properties of PANI/CeO_2 nanocomposites can be adjust by managing the preparation, with concentration of CeO_2 nanomaterials.

In the easy method of preparing nanocomposites require conventional synthesis methods. Several preparation techniques have been developed to synthesis nanocomposites with nanoparticle size and similarity like as hydrothermal method, sol-gel method and in situ polymerization [11] methods. The in situ polymerization method, in addition to decrease crystalline size and uniformly, has proved to be a nice tool for the preparation of materials, like as nanocrystalline, alloys, amorphous alloys and ceramic materials. Hence, in the percent work, PANI/CeO_2 nanocomposites were synthesised using in situ polymerization method. The prepared samples were analysis by X ray diffraction (XRD), absorption UV spectroscopy, FTIR, and impedance spectroscopy.

2. MATERIALS AND METHODS

2.1 Materials

The HCl (2M), APS (Ammonium per sulphate), CeO_2 nanoparticles, and Polyaniline were used materials.

2.2 Preparation (Five Weight Percentage) of PANI/CeO_2 Nanocomposites Powder

Preparation of PANI/CeO_2 nanocomposites (5wt%) as follows: 4.5 (ml) of polyaniline and 70 (millilitre) of HCl (2M) are mixed and

continuously stirred at constant temperature of 40^0C. In solution, 0.45 (g) (5 wt%) of synthesised cerium oxide was added and stirred 3 hours. During the stirring, synthesised APS was added into the solution. The finally got green colour powder and it was dried for room temperature on one week.

2.3 Experimental Technique

The powder XRD was analysis by PAN analytical model diffractometer (Kα = 1.54056 Å at 35kV, 10 mA). The FTIR spectrum was recorded by 8400S Shimadzu spectrometer. The UV spectrum was recorded by UV Visible spectroscopy. AC conductivity was analysis using by Zahnner zennium IM meter.

3. RESULTS AND DISCUSSION

3.1 Powder X Ray Diffraction Analyses

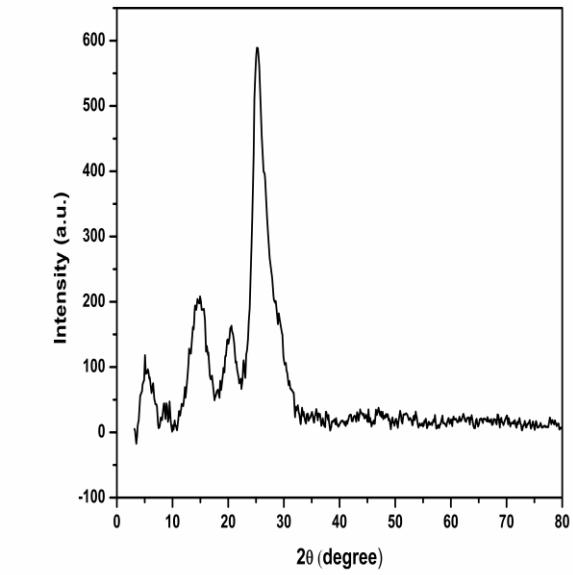

Fig. 1. XRD pattern of PANI/CeO_2 Nanocomposites

Figure 1 shows the powder X ray diffraction of the PANI/CeO_2 nanocomposites (5wt%) occurred by in situ polymerization methods. The prepared nanocomposites pattern show the many broad peaks, these peaks indicates that the particles are very small size. These nanocomposites particles are crystalline behaviour. From figure 1, the nanocomposite has four broad and strong peaks at $2\theta = 5.3^o$, 14.9^o, 20.4^o and 25.2^o. The peak 25.2^o is corresponds to the peak of pure PANI [12], another three peaks also are corresponds to the pure PANI and shifted towards the CeO_2 nanoparticles. The peak 25.2^o is overlap to the peak of pure PANI. The intensity of the peaks was enhanced by concentration of weight percentage, as prepared nanocomposites peaks intensity are maximum, due to the concentration also high (5wt%). The crystalline boundary size of the as prepared PANI/CeO_2 nanocomposites were calculated by obtained from the full width half maximum value in x-ray diffraction results, using Scherrer's formula. The average crystalline size is about 9.8 (nm). This nanoparticle nano size is due to the good polymerization with Polyaniline and cerium dioxide.

3.2 UV Analyses

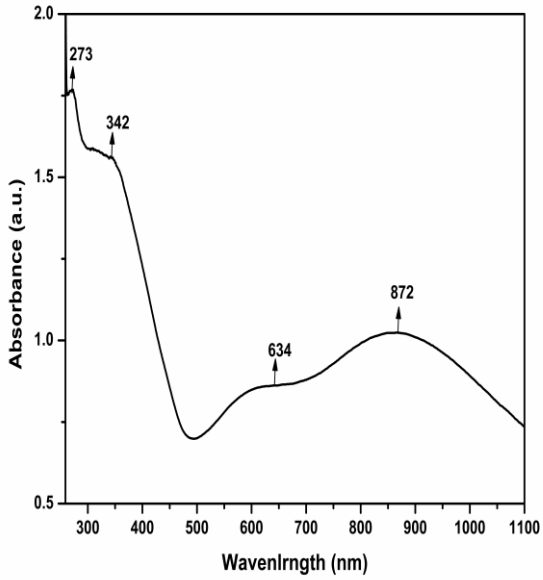

Fig. 2(a). UV Spectra of PANI/CeO_2 Nanocomposites.

Figure 2(a) shows that, UV absorbance spectra of PANI/CeO2 nanocomposites. The UV absorbance spectra can be serving in discernment electronic structure of the energy band gap. UV absorption in the very near arising from the sample, electronic transitions occurred. The UV absorbance of the PANI/CeO2 nanocompopsite was recorded in between the range of wavelength 200 to 1200 (nm). UV absorption peaks are not possible in the pure CeO_2 nanoparticle [13], but pure PANI has absorbance peaks. From the figure, the nanocomposites are observed absorption peaks in presence of polyaniline, four strong absorption peaks have observed at 273, 342, 634 and 872 (nm). The absorbance wavelength of 872 (nm) was broad, it concluded that, are self-assembled the nanocomposites. The variations of absorption wavelength have been occurred due to compared to the pure and composite materials. The UV absorption wavelength change is occurred due to the reason of the doping mechanism, it is depends on doping concentration in nanocomposites materials. The variation of absorption wavelength indicates the changes of band gap energy (E_g) [15]. In UV absorption spectra, the absorption

wavelength decreases will be seen towards with increase in doping concentration (5wt%).

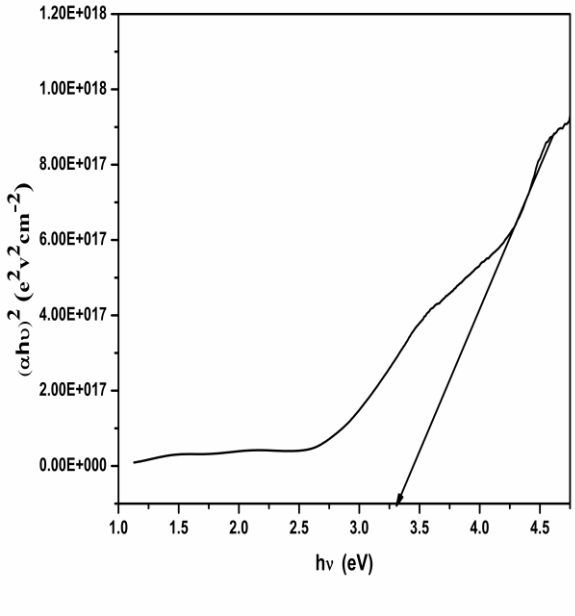

Fig. 2(b). Bands gap of PANI/CeO_2 Nanocomposites.

The band gap energy for the PANI/CeO_2 nanocomposites were calculated by the formula of $\alpha h\gamma = (h\gamma - E_g)^{1/2}$. Where α is absorbance and hγ is a photon energy in (eV). Figure 2(b) is plotted between the hγ versus $(\alpha h\gamma)^2$ and E_g is calculated. The band gap is obtained, to taking straight line of intercept of extrapolation to x axis with zero absorbance. The band gap value of nanocomposites is 3.31 (eV), these Eg value depends on the methods of synthesis and influence of the particle grain size. This good band gap energy value indicates that the CeO_2 incorporated in PANI as expected. In this calculated nanocomposites band gap energy is high compared to the pure CeO_2 nanoparticles. The pure CeO_2 nanoparticles E_g value is 3.19 (eV) from some published articles [15].

3.3 FTIR Analyses

Figure 3, shows the spectral analysis pattern of PANI/CeO_2 nanocomposites. The vibration peaks of the as-prepared nanocomposite sample at 507.24, 588.25, 698.18, 805.18, 1130.21, 1242.07, 1299.93, 1473.51, 1745.46, 2366.49, and 2817.8 (cm^{-1}) correlate with peaks and correspond to the pure PANI and CeO_2 nanoparticles. Compared to the above peaks value, indicates that navigation has confirmed to the between of PANI and CeO_2. Small sharp peaks 1299.93 (cm^{-1}) related to a main polymer chain of amine has clearly seen. The wide and sharp peaks at 1130.21 (cm^{-1}) have been a description from bending vibration of C-H, which has a formation of new structure in B-H^+H-CL, Q = N^+H-CL, and N = Q = N during the process of HCl doped with PANI [16]. The very small and clear peaks at 805.18 cm^{-1} indicate to metal-oxygen bands. The peaks at 1473.51, 1242.07, and 507.24 (cm^{-1}) are indicating to the functional group of PANI. From the figure, residual water and hydroxyl group are not obtained. All the other peaks also have blue shifted.

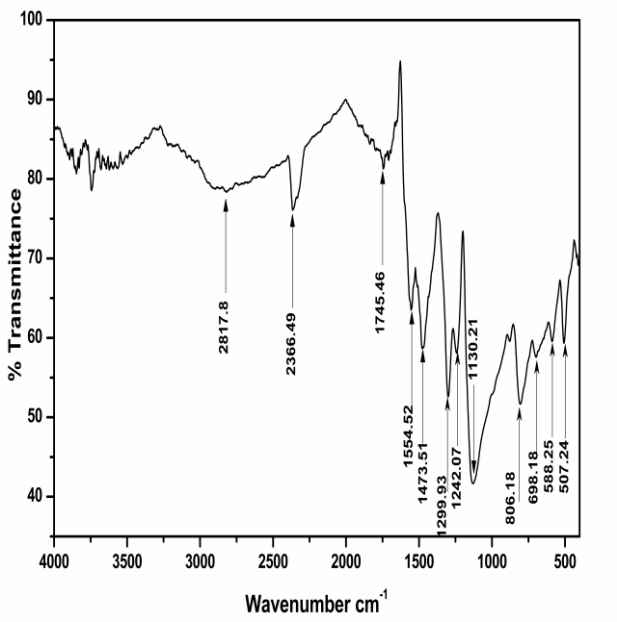

Fig. 3. FTIR Spectra of PANI/CeO_2 Nanocomposites.

3.4 AC Conductivity Analyses

Figure 5 shows the AC conductivity pattern of PANI/CeO_2 nanocomposites at 5 wt% from -1 (Hz) to 5 (MHz). From the conductivity diagram, up to 1 (MHz) has constant, display a frequency independent AC conductivity in the very low frequency. Up to 1 (MHz), the AC conductivity is constant and more than 1 (MHz) conductivity is measured to be increased. After that, conductivity is consciously increasing as the frequency increased. At 373 (K), conductivity is constant as the range of all frequency regions. Another all the temperature range, AC conductivity is consciously increased. The formation in AC conductivity of nanocomposites over polyaniline occurred, to be due to the distributing of CeO_2 in the polyaniline chain. Frequency-dependent AC conductivity explains that CeO_2 nanoparticle hopping through the polyaniline chain, due to the transports of charge carriers, conductivity increased. AC conductivity results are concluded that it was occurred intrinsic dipolar polarization [17].

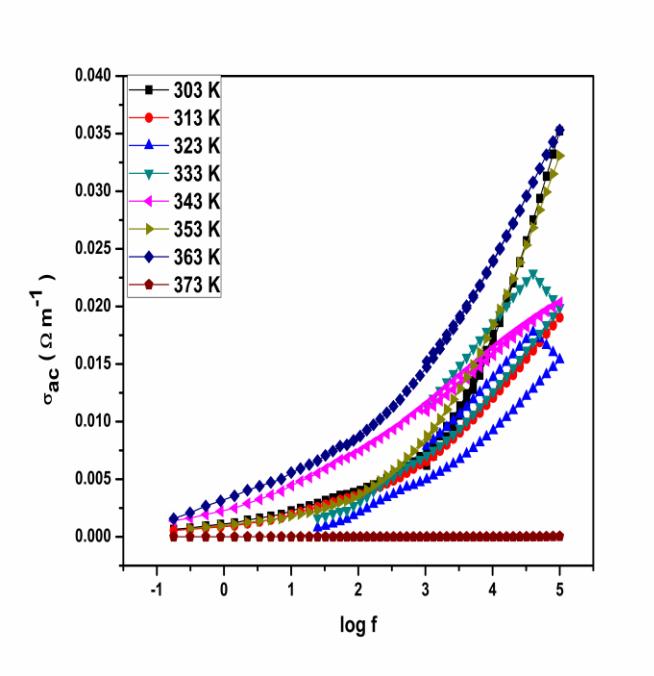

Fig. 5. Conductivity of PANI/CeO_2 Nanocomposites.

4. CONCLUSION

The metal oxide based polymer composites have been successfully prepared in situ polymerization methods with five weight percentage. From the XRD analyses, about the encapsulation of CeO_2 nanoparticles in the polyaniline chain, and have confirmed the crystalline nature. The average grain sizes as-prepared nanocomposites powders are also calculated. The blue-shift occurrences of absorption UV entrance have been carried out, explained. Band gap energy of the nanocomposites was found from the UV absorption. From the FTIR analysis, the formation of composite materials and a functional group of the prepared nanocomposite sample were confirmed. The frequency dependent AC conductivity investigation was carried out, conductivity remains constant at low-frequency region and increased at high frequency-region.

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