ECO-FRIENDLY GREEN SYNTHESIS OF METAL OXIDE NANOCOMPOSITES FOR ELECTROCHEMICAL DETECTION OF HEAVY METALS IN WATER

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Keywords:

Combustion, nanocomposite, XRD, FT-IR, SEM, TEM, UV-DRS, Electrochemical sensing.

Introduction:

Chemicals used during the synthesis of Nanoparticles for the aggregation prevention are highly toxic and pollute the environment significantly. Therefore, it is aimed at the development of nanomaterials employing green chemistry approaches utilizing plant substituents such as, plant latexes and extracts which could offer combined effects due to their ability to act as fuels, reducing, capping and stabilizing agents and such approaches produce superior photo catalysts. Several synthetic methods to prepare metal oxide Nanocomposites have been reported earlier such as spray pyrolysis, solvothermal, hydrothermal processes and solution combustion processes.[1] Of all these, solution combustion synthesis process has received considerable attention since they offer the possibilities for controlling homogeneity, purity of phase, size distribution, surface area and microstructural uniformity. Nanocomposites have been proven to be competent photo catalysts for environmental applications because of their strong redox ability, non-toxicity, long term stability and low cost.[2]

Scope of The Work:

Removal of contaminants in waste water, such as heavy metals, has become a severe problem in the world. Numerous technologies have been developed to deal with this problem. As an emerging technology, nanotechnology has been gaining increasing interest and many nanomaterials have been developed to remove heavy metals from polluted water, due to their excellent features resulting from the nano scale effect. Nanomaterials such as TiO_2, ZnO, SnO_2, ZrO_2, and Fe_3O_4 are very promising for use in the ecological direction, especially as sorbents, photocatalysts, and sensitive layers of gas sensors.[3] The crystallochemical characteristics, surface structure, and surface phenomena that occur when they enter the water and air environment are given for these metal oxides, and it is shown that they play a significant role in obtaining the sorption and catalytic characteristics of these nanomaterials. Use of metal-oxide nanocomposites for environmental applications will lead to the development of new effective environmentally and economically feasible technologies.[4]

Objectives:

1. Eco-friendly facile green synthesis of metal oxide nanocomposites (CeO_2-ZnO, ZnO-NiO).
2. Characterization of the above synthesized nanocomposites using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), UV-Vis spectroscopy, UV-DRS and morphological studies with the aid of Scanning electron microscopy (SEM), Transmission electron microscopy (TEM).
3. The study of the above characterized nanocomposites as a catalyst in electrochemical detection of heavy metals such as cadmium, lead, mercury, copper in water.[5]

Methodology:

The synthesis was carried through solution combustion method.

The fuel was prepared by using the *puppalia lappaceae* leaves. *Puppalia lappaceae* has high contents of Alkaloids and alcohols along with carbohydrates and proteins and lipids. The leaves were dried in room temperature, crushed into powder form. The extract was prepared by refluxing the 10g of the powder with 100ml distilled water in a 250ml round bottom flask for 4 hours followed by filtering the extract. The extract is stored in refrigerator for further use.[6]

In this typical solution combustion method, 148.7mg of $Zn(NO_3)_2\,6H_2O$ and 145.3mg of $Ni(NO_3)_2\,6H_2O$ and 5ml of fuel (extract) taken in a crucible. The precursors were mixed thoroughly and placed in a preheated muffle furnace at 400 ±10°C for 15 minutes followed by the calcination for 3 h.[7]

similarly CeO_2-ZnO nanocomposite was synthesized by using 274.1 mg of $(NH_4)_2Ce(NO_3)_2$,148.7mg $Zn(NO_3)_2\,6H_2O$ with 5ml of fuel. The reaction is exothermic, vigorous reaction leads to the formation of metal oxide Nanocomposites. The obtained product kept in an airtight container for further analysis. The metal composites obtained were characterized by XRD, FT-IR, SEM and TEM.

Figure 1: Synthesis of nanoparticles by solution combustion method

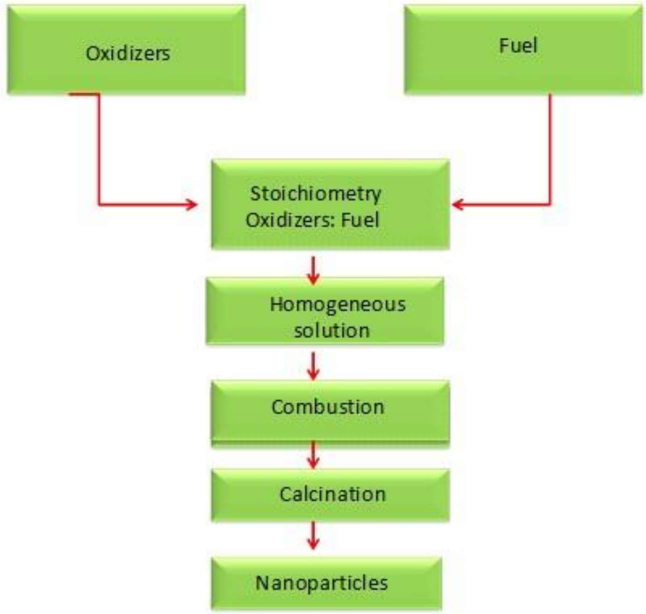

Figure 2: Flow chart for the solution combustion method

Results And Discussions:

1. The synthesized metal oxide nanocomposites were analyzed by X ray diffraction studies which confirms the presence of nanocomposites.
2. Intermolecular interactions were studied by FT-IR Spectroscopy.
3. Surface area, crystal structure and morphology were studied using SEM.
4. Band gap of the synthesized nanocomposites was determined using UV-DRS Spectroscopy.

XRD studies:

X ray diffraction pattern of CeO_2-ZnO nanocomposites (Fig 3) were found to be matching with standard JCPDS No: CeO_2- 34-394 and ZnO- 5-664. The average crystallite size (D) of nanoparticles was calculated using the Scherrer equation and found to be 5 nm.

X ray diffraction pattern of ZnO-NiO nanocomposites (Fig 4) are found to be matching with standard JCPDS No: ZnO- 5-664 and NiO- 65-2901. The particle size was found to be 4.5 nm.

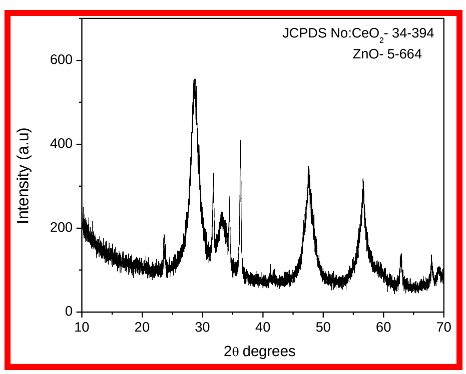

Figure 3: XRD pattern of CeO_2-ZnO nanocomposites

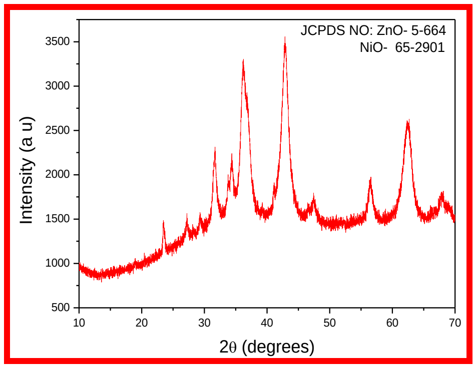

Figure 4: XRD pattern of ZnO-NiO nanocomposites

FT-IR studies:

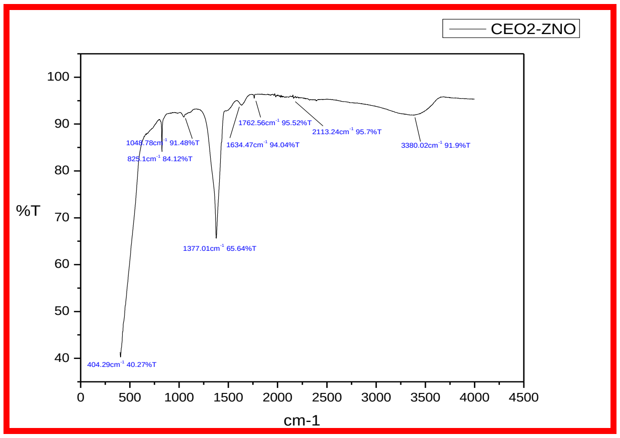

Figure 5: FT-IR Spectrum of CeO2-ZnO nanocomposites

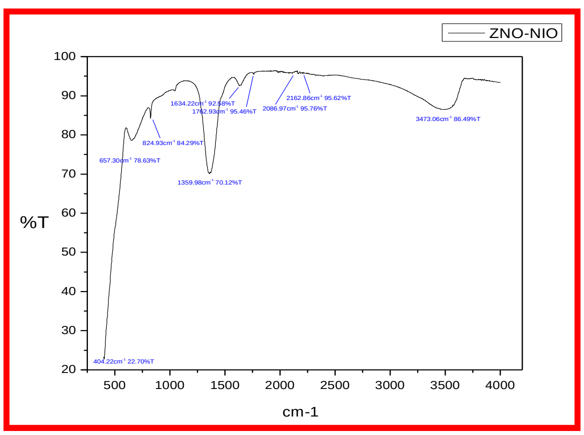

Figure 6: FT-IR Spectrum of ZnO-NiO nanocomposites

The FT-IR spectrum (Fig 5) shows several significant absorption peaks in the range of 4300 cm^{-1} to 400 cm^{-1}. 3380 cm^{-1}, 404.22 cm^{-1} and 825.1 cm^{-1} represents the -OH stretching, Zn-O stretching and Ce-O stretching, respectively.

The FT-IR spectrum (Fig 6) shows several significant absorption peaks in the range of 3473 cm-1 to 404 cm-1. 3473.06 cm-1, 404.22 cm-1 and 657.3 cm-1 represents the -OH stretching. Zn-O stretching and Ni-O stretching, respectively.

Scanning electron microscopic studies:

Figure 7 and 8 shows the images of CeO2-ZnO and ZnO-NiO nanocomposites. Both shows porous, agglomerated structure. This type of porous network with lot of voids is typical of combustion synthesized powders due to escaping gases.

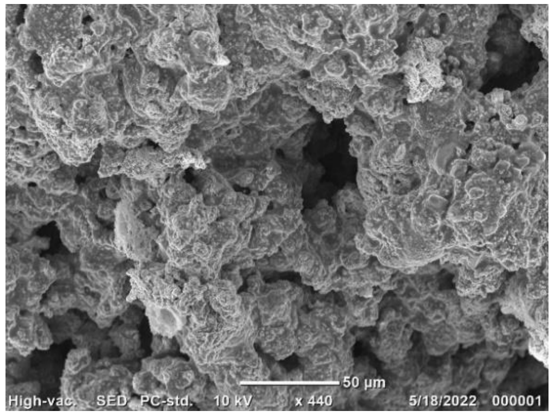

Figure 7: SEM images of CeO_2-ZnO nanocomposites

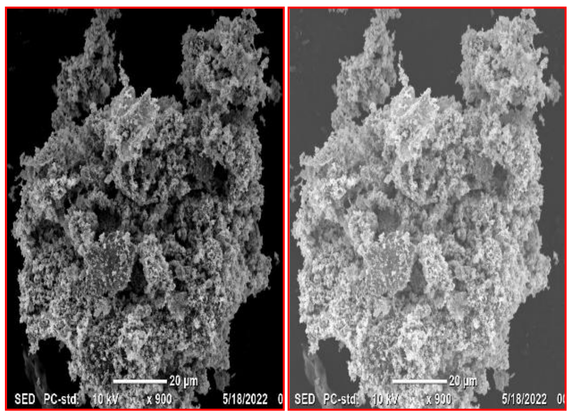

Figure 8: SEM images of ZnO-NiO nanocomposites

UV-diffuse reflectance spectra:

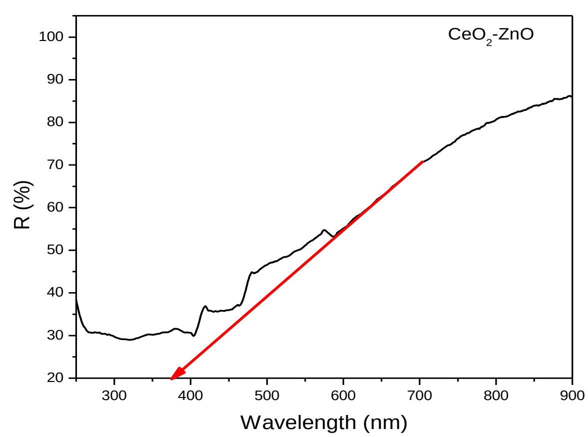

Figure 9: UV-DRS Spectroscopy of CeO_2-ZnO nanocomposites

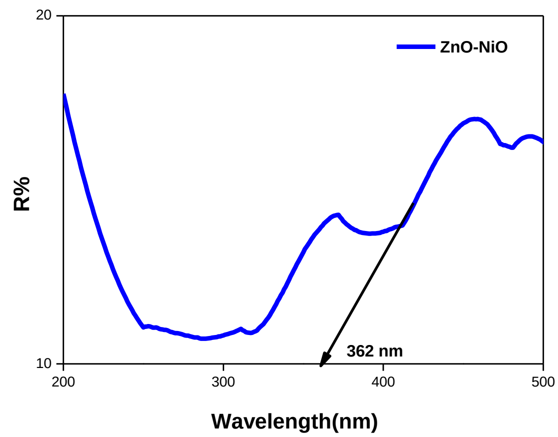

Figure 10: UV-DRS Spectroscopy of ZnO-NiO nanocomposites

UV-DRS spectra are used to determine the band gap of the Semiconductor metal oxides. Band Gap energy was determined and it is found to be 3.4 eV for CeO2-ZnO nanocomposites and 1.69 eV for ZnO-NiO nanocomposites.

Applications:

Electrochemical studies:

Cd^{2+}, Pb^{2+} and other heavy metals released from mining, waste gas and waste water can contaminate the food chain and environment and pose a threat to human health. Cd^{2+} and Pb^{2+} are the most widely used heavy metals in human society, and are also the main metal pollutants in the environment. Cd^{2+} and Pb^{2+} pollution mainly come from human activities, such as mining, manufacturing and burning fossil fuels. Cd^{2+} and Pb^{2+} in the atmosphere are carried into water and soil by wind and rain water, and industrial wastewater is the main source of lead and cadmium pollution of drinking water. These activities release large amounts of lead and cadmium into the environment, resulting in lead and cadmium always co-existing in the environmental medium. In addition to the toxicity of these ions, they also have synergistic effects on human health.[8] Hence, simultaneous specificity detection of lead and cadmium is very much important.

Synthesized nanocomposites were studied for their electrochemical activity, i.e, electrochemical detection of heavy metals, such as Cd^{2+} and Pb^{2+} in water. These studies are carried out by using modified electrodes. Glassy carbon electrodes are modified with CeO_2-ZnO and ZnO-NiO nanocomposites. Modification of electrode involves polishing of glassy carbon electrode with various sizes of alumina powder. Polished glassy carbon electrode was further washed with distilled water. 5 mg of the sample was weighed and dispersed in 1 mL of water and sonicated for 5 min. This sonicated sample was drop casted on the surface of the glassy carbon electrode and dried for 6 hours. This modified electrode was further used as a working electrode along with the counter and reference electrode.

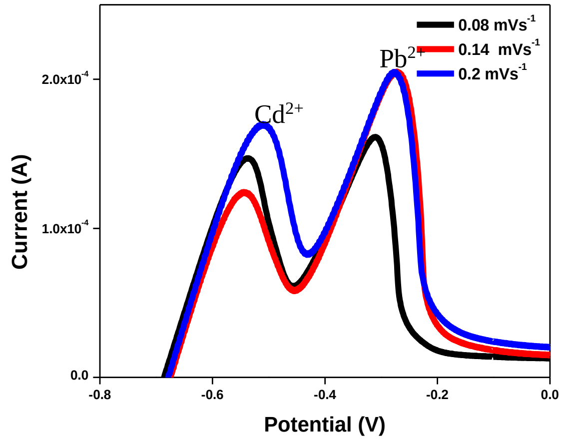

Figure 11. Detection of Cd^{+2} and Pb^{+2} using ZnO-NiO modified electrode

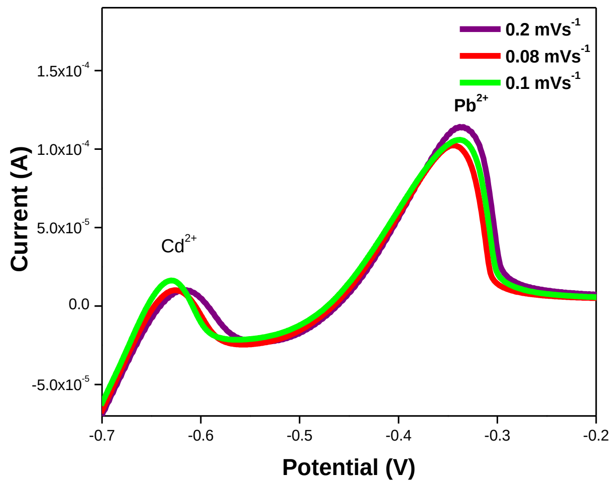

Figure 12. Detection of Cd^{+2} and Pb^{+2} using for CeO_2-ZnO modified electrode

Cyclic voltammogramm's were obtained at 3 different scan rates in presence of 1 mM solution of both Cadmium and lead solution. Peak currents were found around -0.6 V is the indication of presence of Cd2+ in the sample. Whereas, the peak currents around -0.3 V is the indication of presence of Pb2+ in the sample. From this, it was concluded that synthesized nanomaterials are very much effective in detecting the heavy metals at very lower concentrations.

Further studies is being carried out to evaluate the interference of other metals ions also with 1:1 and 1:10, 1:100 ratios.

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