SPECIFIC ADVANCEMENTS MODIFIED CRO₄-ZNO THIN FILMS
CHARACTERIZATION AND APPLICATION OF PHOTOCATALYTIC
PURIFICATION OF CARCINOGENIC DYE AND SYNTHETIC DYE-
SENSITIZED SOLAR CELLS

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Abstract

The synthesis of semiconducting oxides CrO₄-ZnO thin films characterization has been effectively achieved deposited on glass substrates by spray pyrolysis approach at 500°C using aqueous Zinc was Zincacetylacetonate (Zn C₁₀ H₁₄ O₅) at the atomic concentration and then dissolved in the ethanol and (NH₄)₂Cr₂O₇. 2H₂O (0.1 M) dissolved in ethanol. The effect of CrO₄-ZnO Nanocomposite material on the structural, surface morphological, electrical and optical properties of CrO₄-ZnO thin films was studied. HR-SEM and HR-TEM image shows exposed that the surface morphology of the films nanoflake shaped structure. The presence of Chromate, Zinc and Oxygen are confirmed the presence of peaks, using EDS analysis. X-ray
diffraction (XRD) patterns accepted the successful growth of high quality thin films which is polycrystalline nature. The PL analysis shows in CrO$_4$-ZnO is certified to the low recombination of electron-hole pairs by transfer of electrons and holes between ZnO and UV-Vis DRS analysis. The photocatalytic activity of CrO$_4$-ZnO nanocomposite material was studied from Photodegradation study of Rhodamine B (Rh B) dye under UV-light irradiation. As a reaction of this the material was found to be stable and reusable, which extends to a high antibacterial activity and the electrochemical study from synthetic based DSSCs analysis showed increased current is short circuit by CrO$_4$-ZnO thin film nanocomposite material was industrial applications.

**Keywords:** Catalytic application. Medicina application, Electrochemical application, Spray pyrolysis,

1. **Introduction**

Several researchers have been study the performance of the Dye sensitizer solar cells using metal oxide such as TiO$_2$, ZnO, SnO$_2$ and CuI prepared nano composite metal oxide thin film to explore the possibilities of enhancing the efficiency of Dye sensitizer solar cells achieved by providing an effective path for electron transport and higher surface area for dye adsorption to maximize light absorption. A lot of presented result based on ZnO thin film, the TiO$_2$ metal oxide also has similar energy approximately the similar energy metal oxide have an excellent and extensive application much attention of researchers [1-7]. The mixed semiconduct oxide is Physicalpropertice and catalytic activity Jiang Yin et al. reported that MCrO$_4$ (Ba and Sr) has photocatalytic propertice
The photocatalytic work in used. Rhodamine B dye is commonly used in several industries such as food, cosmetics, paper and textiles. Such as dye for colorizing the foodstuffs. It is a dye degradation product such as aromatic amines which are greatly carcinogenic and hazardous. The advanced oxidation process is a photocatalysis in a waste water treatment is a technique and it is used for the total mineralization of organics [14-16].

2. Material method

Zinc acetylacetonate (Zn C₁₅H₁₄O₅), Ammonium dichromate dihydate analytical reagent (NH₄)₂Cr₂O₇. 2H₂O, hydrochloric solution, microscopic glass, Rh B dye, sodium sulfide, Fluorine doped Tin oxide (FTO-plate) and Ruthenium dye (535-bisTBA, N719) solution and ethanol solution was reagent of Sigma Aldrich and used as such. All glassware was cleaned acid followed by thoroughly washing with distilled water, deionized water and water is used as a throughout experiment.

2.1. Experimental procedure

CrO₄-ZnO thin films were processed on microscopic glass substrates, at a temperature of 500°C using spray pyrolysis technique. For making deposition, Zincacetylacetonate (Zn C₁₀H₁₄O₅) was dissolved in ethanol at the atomic concentration and then dissolved in the deionized water and Ammonium dichromate dihydate (NH₄)₂Cr₂O₇. 2H₂O solution. This synthesized solution was sprayed on the microscopic glass substrates, having the dimension of 75x25 mm² at the temperature of 500°C (Ts=500°C). Before the preparation of thin film, glass substrates were well cleaned with
hydrochloric (HCL) solution followed by water bath, acetone, rinsed with distilled water and allowed to dry in oven. Before making deposition, the substrates were pre-heated for specific time and then the synthesized solution was sprayed respectively. When a precursor aerosol droplets moving close to the heated substrate, a pyrolytic decomposition process exists, and as a result, high quality CrO$_4$-ZnO films were developed. After that, the deposited films were allowed to cool slowly up to room temperature, followed by washing with distilled water, dried and then annealed at 500°C in air. Finally, the thin films deposited were characterized.

2.2 Characterization Techniques

The structural characterization of the deposited films was reported by X-ray diffraction technique on SHIMADZU-6000 (monochromatic Cu-K$_\alpha$ radiation, $\lambda$=1.5406 Å). The XRD patterns were recorded in 2θ interval from 10° to 90° with the steps of 0.05° at room temperature. The surface morphology was studied by using HR-SEM (JEOL-JES-1600). Elementary Dispersive X-ray (EDX) evaluation experiments were performed on a FEI Quanta FEG 200 instrument with EDX analyzer facility at 25°C. High-resolution transmission electron microscopy (HR-TEM) images were taken using a JEOL-JEM-2010 UHR instrument operated at an acceleration voltage of 200 kV with a lattice image resolution of 0.14 nm.

Photoluminescence (PL) spectra at a room temperature were recorded using a Perkin-Elmer LS 55 fluorescence spectrometer. UV spectral measurements were done using a Hitachi-U-2001 spectrometer. Ultraviolet and visible (UV-vis) absorbance spectra
were measured over a range of 800-200 nm with a Shimadzu UV-1650PC recording spectrometer using a quartz cell with 10 mm of optical path length. The antibacterial activity was studied by disc diffusion method; the test compound was dissolved in DMSO (200 mg/mL) for about half an hour. Commercially available drug disc, Ciprofloxacin (10 mg/disc) was used as positive reference standard and The Photovoltaic properties of the material was characterized by recording the photo current voltage (I-V) curve under illumination of A.M.1.5 (100Mw/cm²).

3. Results and discussion

3.1. Surface morphology and composition analysis

3.1.1. HR-SEM and EDX Analysis

The exterior morphology of the synthesized CrO₄-ZnO thin films were discussed in the following way. The CrO₄-ZnO thin films have a affinity towards manners of agglomeration due to high temperature (T) and pressure (P) in the preparation process. HR-SEM images were recorded at advanced magnification and minor magnification at dissimilar locations. In Fig.1a were showed that nanoflake like nanostructure of CrO₄-ZnO thin films. Fig.1 and c Surface plot in selected area highlighted in fig(a) thin films. An EDX spectrum was acquired to examine the elemental composition of the catalyst, which confirms the existence of the expected elements Cr, Zn and O, it shown in Fig 2.
Fig. 1. Morphological analysis of HR-SEM image (a) CrO4-ZnO and (c) Surface plot in selected area highlighted in fig(a) thin films
3.1.2. HR-TEM analysis

The detailed morphological and structural characterizations of the prepared material were examined by TEM images in Fig. 3 exhibit the typical of intercrossed Nanosparical structure, The HRTEM images. The Fig show a distinguished interface and the continuity of Nanosparical structure between the CrO$_4$-ZnO thin films confirming the formation of chemical bonds between them it is established that the presence of particles are depicted from the HR-TEM micrographs of the mixed nanoparticles at 200 nm as intercrossed Nanosparical structure as obtained.
3.2. Crystallographic and Morphological analysis

Fig 4. XRD pattern of pure ZnO and CrO$_4$-ZnO thin films deposited on glass substrates at 500°C (optimized temperature). All the CrO$_4$-ZnO thin films are preferentially oriented along (002) plane c – axis with hexagonal wurtzite structure and free from the formation of secondary phases. The diffraction peaks detected for the films corresponding to (101), (002) and (100) planes are the indicative of hexagonal wurtzite structure (JCPDS card No 36 - 1451). No second phase is detected in XRD pattern of pure ZnO thin films. A reduce in intensity of plane and an increase in strong diffraction intensity is observed along with plane for CrO$_4$-ZnO thin films. However, there is no significant change in peak position of (100), (200), (112), (202) and (400) exhibited crystal plane structure.
Fig. 4 XRD patterns of (a) ZnO and (b) CrO4-ZnO thin film
3.3. Photoluminescence study

The PL fabrication spectrum of Fig.5 shows the broad intense green emission at 300-500 nm of ZnO and CrO$_4$-ZnO thin films synthesized nanocomposite were observed by room temperature. This PL emission occurred due to band-band transition on ZnO and other CrO$_4$-ZnO thin films synthesized nanocomposite exhibits broad band emissions attributed at 325,370 and 440 nm in the visible area. The strong emission band observed at 325 and 370 nm in close to UV-Visible region as in that order [17]. While recombination of electron-hole between conduction bands to valence band is suppression by adding ZnO. This may cause decrease in fluorescence energy this transition trap level decreases by mixing CrO$_4$-ZnO thin films material [18]. PL results excellent turn for surface phenonmenon in the photodegradation method.

![Photoluminescence spectrum of (a) ZnO and (b) CrO4-ZnO thin film](image-url)

Fig.5. Photoluminescence spectrum of (a) ZnO and (b) CrO4-ZnO thin film
3.4. UV-vis DRS Spectrum

The UV-vis DRS Spectrum of ZnO and Ag₂O-ZnO thin films as shown Fig. 6 a and b. Zn²⁺ strength covalently interact with ZnO and decrease its band gab. Ag₂O-ZnO thin films caused is a red shift in absorption edge. The result indicate in UV-vis spectrum in the diffuse reflectance mode (R) were trance formed to the Kubelka-Munk function F(R) to hole the degree of light absorption from diffusion. The band gab energy was obtained from the plot of the modified Kubelka-Munk function (F(R) E)¹⁄² Vs the energy of the absorbed light (E) (eq 1)

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(F(R) E)^{1/2} = \left( \frac{(1-R)^{1/2}}{2R} \right) \times \frac{X h \nu}{\text{(1)}}
\]

Fig.6. UV-Vis DRS spectrum of (a) ZnO and (b) CrO₄-ZnO thin film
The final result indicates the band gap energy of the ZnO and Ag$_2$O-ZnO thin films are 3.5 eV and 3.15 eV correspondingly. The lower band gap energy supports for higher photocatalytic activity [19].

3.5. Application; Photocatalytic Activity

3.5.1. Photocatalytic Purification of Rh B dye with Artificial UV-light Irradiation

The photodegradation study of purification of Rh B dye with artificial UV-light irradiation. Rh B dye aqueous solution in the presence of concentration 1x10$^{-4}$ M it was shown to the dark in colour. After the photodegradation time was 60 min in colour changes at irradiation times shown in monochrome solution was respectively. The reaction time affords the photodegradation of Rh B dye dye. The photodegradation of CrO$_4$-ZnO thin films and dye solution under UV-Light it shown in Fig. 7.

![Fig.7. The effect of Photodegradation study of Rh B dye under UV-light irradiation by (a) Dark (b) Nil catalysis (c) ZnO nano powder (d) ZnO and (e) CrO4-ZnO thin film](image-url)
This final result was observed to undergo degradation of 60 min (% of degradation: Dark 2.5%, Nil catalyst 9%, ZnO nano powder 38%, Prepared ZnO 67% and CrO$_4$-ZnO thin film 86%) the final result was observed CrO$_4$-ZnO thin film high photocatalytic activity that of ZnO thin film.

### 3.5.2. Reusability of Photocatalytic Activity

The stability of reusability of photocatalysts in very important analysis of CrO$_4$-ZnO thin film the photocatalytic degradation properties of the photocatalyst was investigated by repeating Rh B dye photocatalytic degradation experiments six times. After each cycle, the photocatalysts were washed thoroughly with water, and a fresh solution of Rh B dye was made before each photocatalytic run in the photoreactor under UV-light and the results are shown in Fig 8. Complete degradation 60 min report in occurred in the ZnO and CrO$_4$-ZnO thin film 4$^{th}$, 5$^{th}$ and 6th cycles obtained in (91 and 95%). The results indicated the prepared photocatalysts are stable and reusable. After the sixth cycle the efficiency of catalysts decreased about compared to the total degradation of Rh B dye. There is no significant change in reaction, indicating the stability of photocatalyst. This photocatalyst is nontoxic for wastewater treatment. This is due to the loss of catalysts, during the water washing of catalysts, which was not observed in the naked eye. Thus suggests that CrO$_4$-ZnO thin film photocatalysts have excellent stability and reusability for photodegradation of pollutants that of ZnO thin film. This Experiment used for waste water treatment analysis.
3.5.3. Mechanism of Photocatalytic Effect

The photocatalytic reaction was affords the photodegradation of Rh B dye exhibited deionizer water solution very advanced photocatalytic activity that of contaminated sea water by source of these observations, than recently photocatalytic activity work observed [20, 21]

a uncertain mechanism for photocatalytic degradation Rh B dye is proposed as follows:

CrO$_4$-ZnO used in photodegradation of Rh B dye exhibited deionizer water solution
1 \text{Rh B dye} + \text{hv} \rightarrow \text{Rh B dye} \quad \ldots(2)

1 \text{Rh B} + \text{ISC} \rightarrow 3 \text{Rh B dye} \quad \ldots(3)

\text{CrO}_4^{2-}\text{-ZnO (SC)} + \text{hv} \rightarrow e^-\text{(CB)} + h^+\text{(VB)} \quad \ldots(4)

\cdot \text{OH} + h^+ \rightarrow \cdot \text{OH} \quad \ldots(5)

\cdot \text{OH} + 3 \text{Rh B dye} \rightarrow \text{Leuco Rh B dye} \quad \ldots(6)

\text{Leuco Rh B dye} \rightarrow \text{Products} \quad \ldots(7)

Rh B dye absorbs radiation of desired wavelength and it forms excited singlet state. Further, it undergoes intersystem crossing (ISC) to give its more stable triplet state. Along with this, the CrO$_4$-ZnO thin film (SC) also utilizes this energy to excite its electron from valence band to the conduction band. An electron can be abstracted from hydroxyl ion by hole (h$^+$) present in the valence band of semiconductor generating OH radical. This hydroxyl radical will oxidize Rh B dye to its leuco form, which may ultimately degrade to products. It was confirmed that the OH radical participates as an active oxidizing species in the degradation of Rh B dye as the rate of degradation was appreciably reduced in presence of hydroxyl radical scavenger (2-propanol) [22] Shown in Scheme.1.
Scheme 1. Photodegradation of CrO₄-ZnO thin film on Rh B dye under UV-light irradiation

3.6. Antibacterial Activity

Antibacterial activity of (1) ZnO and (2) CrO₄-ZnO thin film showed activity against both gram-positive strains and also gram-negative strains by high Antibacterial activity. ZnO and CrO₄-ZnO thin film 20 and 22 mm inhibition zone was developed against *B. subtilis aureus and Escherichia coli* that of on gram-positive and gram-negative bacteria respectively it is shows in Fig 9. As the result proposed the of reading (2) CrO₄-ZnO thin film and increases value of the electron holes charge separation through decreasing the band gap energy with leads to a impediment in the recombination rate for
high antibacterial activity used in biomedical application and high photocatalytic activity [23].

Fig.9. Antibacterial activity [disc diffusion method]: (a) B. subtilis aureus and (b) Escherichia coli investigation of prepared (1) ZnO, (2) CrO4-ZnO thin film showed activity against both gram-positive strains and also gram-negative strains.
3.7. Application; Electrochemical Activity

3.7.1. Photovoltaic Properties

Electrochemical activity of synthetic based Dye Sensitized Solar cell (DSSCs). CrO$_4$-ZnO thin film act as photoelectrode are coated on Fluorine doped Tin oxide (FTO-plate) glass substrate. The routine solar cell is fabricated with synthesis film through Ruthenium dye (535-bisTBA, N719). From the data, it is clear that (N719) this CrO$_4$-ZnO thin film based cell gives the mainly brilliant activity with the use of dye as sensitizer reunite the maximum value of short-circuit current density, $J_{sc}$ (7.0 mA/cm$^2$) than ZnO (5.0 mA/cm$^2$), open-circuit voltage, $V_{oc}$ (500 mV), fill-factor, FF (0.94) and efficiency, $\eta$ (1.7%) it shows Figure 10. The result indicating Ag$_2$O-TiO$_2$ increases electron transfer in short circuit current density was obtained [24,25].

![Image](image-url)

**Fig.10.** Current density–voltage (J–V) curves for the DSSC’s fabricated from (a) ZnO coated GCE in 0.1 M KCl and (b) CrO4-ZnO thin film GCE in 0.1 M KCl by Synthetic Ruthenium dye (535-bisTBA, N719)
4. Conclusion

In summing up we have synthesized, characterization and application of CrO₄-ZnO thin film was prepared by spray pyrolysis approach at 500°C. The HR-SEM and HR-TEM images pure ZnO and CrO₄-ZnO thin film shows exposed that the surface morphology of the nanoflake shaped structure, HR-TEM morphology of the nanospherical shaped structured. EDX analysis confirm that Cr, Zn and O present. PL analysis CrO₄-ZnO thin film decrease intensity increase photocatalytic activity and UV-vis DRS Spectrum The lower band gap energy superior photocatalytic activity. This final result was observed CrO₄-ZnO thin film on Rh B dye dissolved in water solution undergoes high photocatalytic activity that ZnO thin film. This photocatalyst is nontoxic for wastewater treatment and excellent stability and reusability used for waste water treatment, CrO₄-ZnO thin film was high antibacterial activity that of ZnO thin film for medicinal application and Electrochemical activity of CrO₄-ZnO thin film based Dye Sensitized Solar cell (DSSCs) application of result indicating CrO₄-ZnO thin film increases electron transfer in short circuit current density that of ZnO was obtained this used for very industrial applications.
References


