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Optical Characterization of Co:ZnO Films Fabricated by Anodization for Photocatalytic Water Purification

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Abstract

While the sixth sustainable development goal to be achieved by 2030 is clean water and sanitation, there is still a global challenge in the supply of adequate clean water due to population growth and urbanization. This necessitates coming up with more affordable approaches of managing wastewater for re-use. Photocatalytic degradation of pollutants has proved to be one of the promising ways of purifying water. This study aimed at preparing Cobalt doped ZnO films to be used in photocatalytic water purification. ZnO films were fabricated by anodization and Cobalt incorporated. Heat treatment was done at 250^0C. Optical characterization was done using a UV-VIS NIR spectrophotometer to obtain reflectance data which aided in determining the optical properties of the films. Data analysis showed a decrease in ZnO reflectance and optical band gap on incorporation of Cobalt. This implied an increase in the absorption of the films which is a fundamental property in photocatalytic water purification. Hence Cobalt doped ZnO films have good photocatalytic properties and can be used for photocatalytic water purification.

Keywords: Photocalysis, ZnO, pigmentation, optical characterization, water purification.

1.0 Introduction

Photocatalysis has proved to be one of the most promising techniques for purification of waste water by the chemical utilization of solar energy where hazardous organic pollutants are degraded, Hoffman *et al*., (1995). ZnOwhich is a wide band gap semiconductor with a band gap of 3.31eV has been widely used in designing of diodes, biosensors, as antibacterial agents and photocatalysts because it is cheap, readily available and non-toxic. In photocatalysis it is used to speed up the degradation rate.Its wide band gap however limits its photocatalytic activity hence the need to improve its activity.

In a study of the photocatalytic activity of ZnO nanoparticles synthesized by combustion method done by Nagaraju *et al.,* (2017) who showed the band gap of *ZnO* as 3.29 eV. Photocatalytic results in this study showed ZnO as a promising photocatalytic material. Kuriakose *et al.,*(2014), studied enhanced photocatalytic activity of Co doped *ZnO* nanodisks and nanaorods prepared by wet chemical method and reported that doping *ZnO* nanodisks and nanorods with Co enhanced their photocatalytic activity. Poongodi *et al.,* (2015) stated that Cobalt doped *ZnO* was seen to be more photocatalytic than the pure *ZnO*. They attributed this to the increase in ZnO crystal size when doped with Cobalt.Borhani and Amrollahi (2017) observed a shift in the ZnO band edge towards longer wavelengths on doping with Cobalt. They also reported a decrease in the

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absorption coefficient with increasing wavelengthand an increase with the extinction coefficient with Cobalt doping.

Metal ions such as Mn^{2+}, Cu^{2+}, Ag^{2+} and Co^{2+} have been used to alter the optical and photocatalytic properties and Cobalt ions are preferred because their ionic radius(0.745Å)is similar to that of Zinc(0.74Å), Woo *et al*., (2014). ZnO:Co films can be fabricated using different techniques such as spray pyrolysis, sol-gel, sputtering and anodization, Kulkrani and Shirsa (2015).In this study, we seek to fabricate Co:ZnO films by anodization and characterize them optically consequently its application in photocatalytic water purification since optical properties determine the photocatalytic activity. Optical properties of a material affect its photocatalytic activity in terms of the amount of energy absorbed. The amount of solar energy absorbed depends on its band gap energy. Materials with wide band gap absorb less energy hence lower activity and vice versa.According to Bennoet al. (2003) the absorption coefficient of thin films can be obtained using the relation 1:

$$R(\lambda) + T(\lambda) = e^{-\alpha d} \qquad (1)$$

When $T(\lambda) = 0$, $R(\lambda) = e^{-\alpha d}$ giving

$$\alpha = \frac{1}{d}\ln\left[\frac{1}{R(\lambda)}\right] \qquad (2)$$

In band gap determination of semiconductors,the transition of an electron from the valence to the conduction band is guided by the equation, Depla and Mahieu (2008):

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \qquad (3)$$

where A is a constant, E_g is the band gap energy, v is the frequency of the radiation, h is the planck's constant and n is a number dependent on the transition type: n=1/2 for direct allowed transition, n=3/2 for direct forbidden transition, n=2 for indirect allowed transition, and n=3 for indirect forbidden transition.

2. Methods and materials

2.1 Sample preparation

Zinc plates were mirror polished, sonicated in ethanol, rinsed and dried in air. Pure ZnO plates were prepared by anodization method. The schematic diagram for anodization method is shown in figure 1. A constant voltage of 10V was maintained for 60 minutes using 0.5M oxalic acid as the electrolyte, zinc as the working electrode and graphite the counter electrode.This was done at room temperature after which the anodized zinc sheets were rinsed in distilled water and dried in air. Cobalt was electrodeposited in some of the anodized ZnO for 20s and 60 seconds using a 20V ac power supply so as to vary the amount of Cobalt deposited in the ZnO samples. Post anodization heat treatment done by heating the plates at 523K for 2 hours in air.

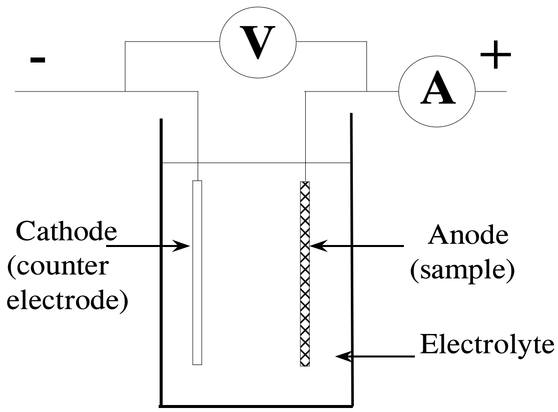


Figure 1: Schematic diagram for anodization method. Nemes *et al.,* (2011)

2.2 Optical characterization

Optical characterization was done using a perkin elmer UV/VIS/NIR Lambda 19 spectrophotometer equipped with an integrating sphere to evaluate the optical properties of the pure and Cobalt pigmented ZnO films. Reflectance measurement was done in the solar range 300nm < λ < 2500nm. Further data analysis was done using the SCOUT software which aided in the determination of the optical properties of the fabricated films. This was done by fitting experimental data onto simulated data within the software as illustrated in figure 2. This aided in the determination of the film thickness, absorption coefficient and band gaps.

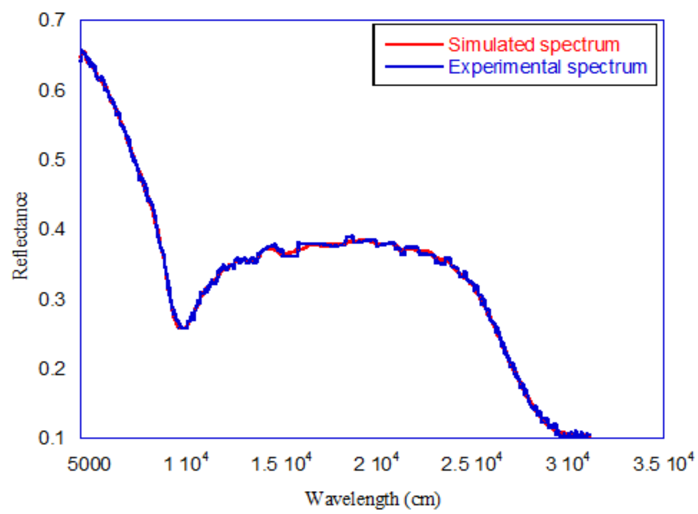


Figure 2: An illustration of fitting of the experimental to simulated spectra using the SCOUT software

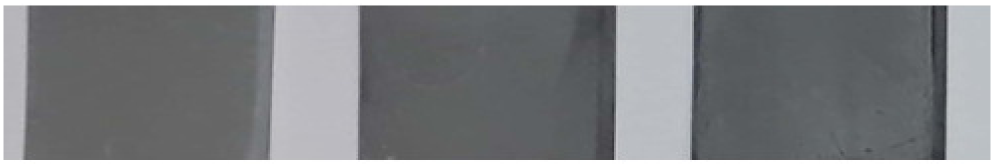
The film thickness obtained from the software was used to determine the absorption coefficient using the relation (2) indicated in section 1.The transmission $T(\lambda)$ waszero since the substrate used was opaque.

The optical band gap of the prepared films was determined using the relation (3) indicated in section 1 where n is ½ since ZnO is a direct band gap semiconductor.

3. Results and Discussion

3.1 Reflectance measurements

The prepared films were observed to darken as Cobalt was introduced. Figure 3 shows a photo of the films before without Cobalt and with varying amounts of Cobalt.



ZnO ZnO:Co 20s ZnO:Co60s

Figure 3: A photo of the prepared films

Figure 4shows the spectra for the measured reflectance for the polished Zinc metal before anodization and the as deposited ZnO and Co:ZnO films.

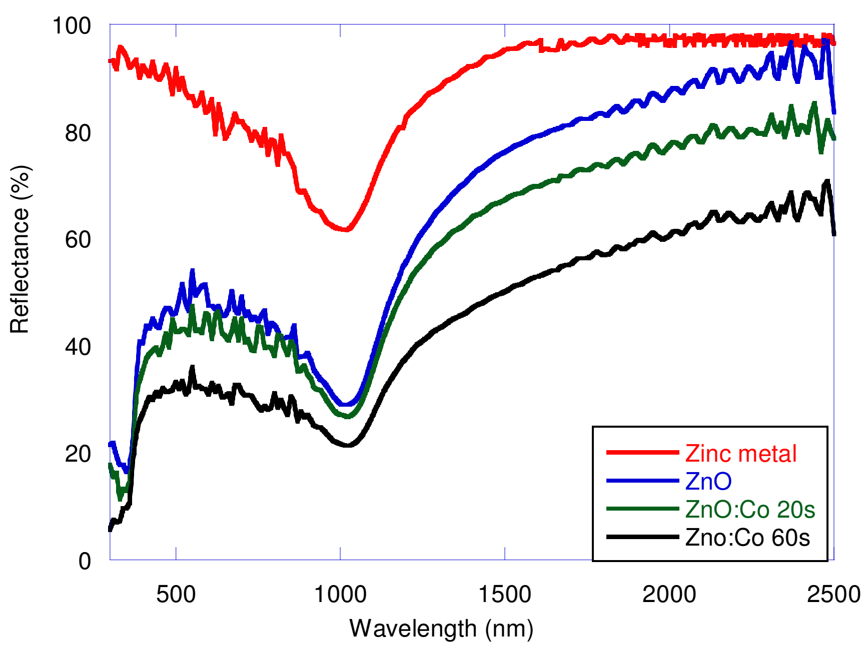


Figure 4: Measured reflectance spectra for polished zinc metal, pure ZnO and Co:ZnO

Polished zinc metal has a higher reflectance more than 60% because of its shiny nature. The reflectance for pure ZnO is higher thanfor Co:ZnO. This can be attributed to the darkening of the ZnO films when they are pigmented with Cobalt. A sharp decrease in the pure and Co:ZnO reflectance is observed at low wavelengths about 348nm. This decrease gives the absorption edge of the films which is agreement with the fact that ZnO absorbs in the UV region of the solar spectrum. The deep in the spectrum at about 1050nm in the spectrum is due to Zinc metal parallel band absorption as seen in the data presented by the handbook of optical constants, Palik (1998).

The decrease in reflectance of the Cobalt pigmented ZnO films is indicative of an increase in absorption. An increase in absorption indicates enhancement of its photocatalytic activity since more energy is absorbed.

3.2 Absorption coefficient measurements

The Thickness of the prepared films increased from 108.3nm, 109.0nm and 110.0nm. These thicknesses were used to determine their absorption coefficients. Figure 5 shows the absorption coefficient as a function of wavelength.

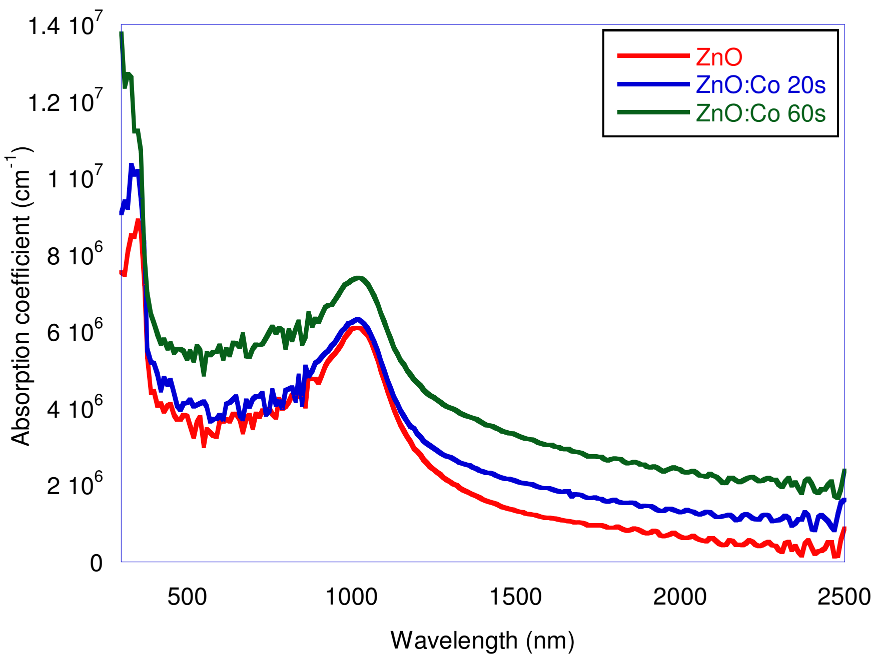


Figure 5: Absorption coefficient as a function of wavelength

The absorption coefficient for the pure and Cobalt pigmented ZnO films is observed to sharply increase at low wavelengths representing the UV region of the solar spectrum. This also further explains the high absorption of ZnO in the UV region due to its wide band gap. Cobalt pigmented ZnO has a higher absorption coefficient in the lower wavelengths than pure ZnO.

This is attributed to the decrease in reflectance on pigmenting hence an increase in absorption. At higher wavelengths, the absorption coefficient remains low showing low absorption by the films. Cobalt pigmented ZnO films have a higher absorption coefficient hence more photocatalytic.

3.3 Band gap measurements

A Tauc's plot gave the optical band gap for ZnO which is a direct band gap semiconductor as shown in figure 6.

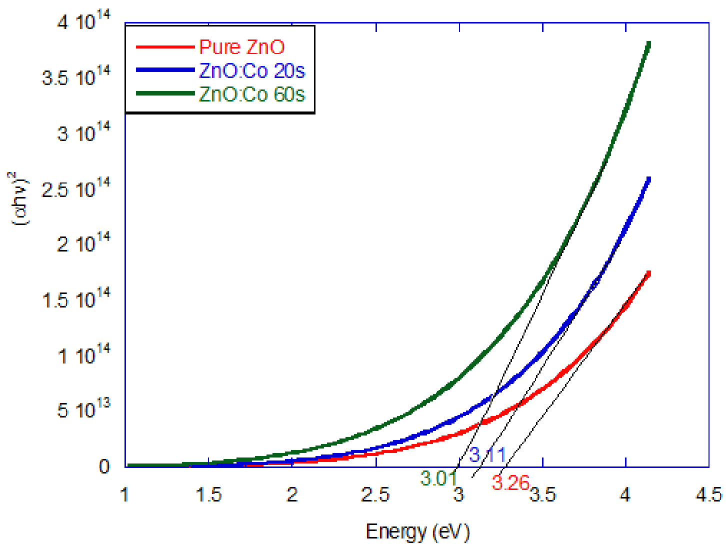


Figure 6: Graph showing the optical band gap of the fabricated films

The optical band gap of pure ZnO is 3.26e V. A decrease in the band gap is observed as the ZnO films are pigmented with Cobalt. The decrease in band gap is an indication of an increase in the absorption of the films as confirmed by the reflectance and absorption coefficient. This is attributed to the red shift in the absorption edge of the ZnO films which results from the Cobalt ions being incorporated into the ZnO crystal structure which results in formation of impurity levels between the ZnO band gap hence narrowing it as discussed in section 1.

4.0 Conclusion

ZnO films were successfully fabricated by anodization. Varying amounts of Cobalt were electrodeposited at 20s and 60s and it was seen that an increase in the amount of Cobalt affected its optical properties. The more the Cobalt content in the films, the more absorbing the films. This was attributed to the darkening of the films and the narrowing of the ZnO band gap by Cobalt. This showed that the photocatalytic activity of ZnO was enhanced by Cobalt doping.

5.0 Acknowledgement

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