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Electrochemical, Optical and Morphological Characterizations of Cu Doped ZnO Nanostructure Thin Films Prepared by Spin Coating Method

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Abstract

From nanotechnology point of view where conductivity is crucial, although it is essential to determine the electrochemical properties Cu doped ZnO nanostructure thin films produced by spin coating, there are rare studies in the literature. Therefore, in this study, the aim was to examine thouroughly the electrochemical properties of nanostructure thin films which were grown on glass substrates by using a facile and cost-effective spin coating method. The effects of the dopant on the morphological, optical and electrochemical properties of ZnO nanostructure thin films doped with Cu at different concentrations (0-50%) were investigated by SEM, XRF, FTIR, UV-vis, mechanical profilometer, and cyclic voltametry. The absorption spectra of the samples revealed that the energy band gap value decreased by the incereasing of Cu doping concentration. SEM images depicted that more spherical and homogeneous nanostructures formed with the doping of Cu. Electrochemical results showed that increasing the Cu doping ratio in ZnO nanoparticles results in higher electron transfer indicating that the conductivity of ZnO nanostructured thin films increases with Cu doping. It can be concluded that it is possible to produce more homogeneous, wider spectrum absorption capable and more conductive nanostructure thin films by a simple and inexpensive method. It is envisaged that the thin films obtained are promising for a wide range of nanotechnology applications.

Keywords
Copper; Zinc Oxide; Cyclic Voltametry; Electrochemical; Thin Film; Spin Coating

Spin Kaplama Yöntemi ile Hazırlanan Cu Katkılı ZnO Nanoyapılı İnce Filmlerin Elektrokimyasal, Optik ve Morfolojik Karakterizasyonları

Öz

İletkenliğin hayati olduğu nanoteknoloji açısından bakıldığında, spin kaplama ile üretilen Cu katkılı ZnO nanoyapılı ince filmlerin elektrokimyasal özelliklerinin belirlenmesi çok gerekli olsa da literatürde sınırlı çalışmalar bulunmaktadır. Bu nedenle bu çalışmada, kolay ve uygun maliyetli spin kaplama yöntemi kullanılarak cam altlıklar üzerine büyütülen nanoyapılı ince filmlerin elektrokimyasal özelliklerinin derinlemesine incelenmesi amaçlanmıştır. Katkının, farklı konsantrasyonlarda (%0-50) Cu katkılı ZnO nanoyapılı ince filmlerin morfolojik, optik ve elektrokimyasal özellikleri üzerindeki etkileri SEM, XRF, FTIR, UV-vis, mekanik profilometre ve döngüsel voltametri ile araştırıldı. Örneklerin absorpsiyon spektrumları, Cu katkı konsantrasyonunun artmasıyla enerji bant aralığı değerinin azaldığını ortaya çıkardı. SEM görüntüleri, Cu katkısıyla daha küresel ve homojen nanoyapıların oluştuğunu gösterdi. Elektrokimyasal sonuçlar, ZnO nanoparçacıklarında Cu katkılama oranının arttırılmasının daha yüksek elektron transferi ile sonuçlandığını göstermiştir ki bu da ZnO nanoyapılı ince filmlerin Cu katkılaması ile iletkenliğinin arttığını göstermektedir. Basit ve ucuz bir yöntemle daha homojen, daha geniş spektrumlu absorpsiyon yeteneğine sahip ve daha iletken nanoyapılı ince filmler üretmenin mümkün olduğu sonucuna varılmıştır. Elde edilen ince filmlerin çok çeşitli nanoteknoloji uygulamaları için umut verici olduğu öngörülmektedir.

Anahtar kelimeler
Bakır; Çinko Oksit; Döngüsel Voltametri; Elektrokimyasal; İnce Film; Spin Kaplama

1. Introduction

Electrochemistry is a wide and multidisciplinary field concerned with either chemical changes caused by electric current or vice versa. So far, despite the basic principles of electrochemistry have been adequately explained for macro and micro dimensions, the application of electrochemical methods to nanoscale materials have not been studied extensively (Bard *et al*. 2001).

The electrochemical properties of nanomaterials including electronic, magnetic and optical features differs from large-scale materials (Aristov and Habekost 2015, Denuault, G. 2009). Nanomaterials can change their physicochemical features and structures depending on their physical environment, synthesis methods and process steps. This requires expertise of many research areas and the application of sophisticated tools and data analysis for the characterization of nanostructures. Previous studies have shown that electrochemical analysis is vital in nanostructure characterization as it provides the opportunity to improve performance. The electrochemical field is quite new in applying electrochemical methods to the testing of nanostructures by overcoming the limitations of traditional characterization approaches (Baer *et al*. 2008, Baer *et al*. 2013, Kuchibhatla *et al*. 2012, Grainger *and Castner 2008*).

Nanotechnology, which allows the development of new materials with unique and improved features, rapidly grow in many applications such as sensors, solar cells, fuel cells, photocatalysis, photodetectors, batteries, electrochromic displays, medicine, cosmetics, etc. Metal oxides are among the most preferred materials in nanotechnology field as they are cheap, non-hazardous, easy to synthesize and abundant (Xia *et al*. 2003, Thelander *et al*. 2006, Shen and Chen 2010, Carmo *et al*. 2011). Inorganic metal-oxide semiconductors such as CuO, Cu_2O, TiO_2, NiO, ZnO, etc. in nanomaterials production have been deeply investigated because of their improved optical and electrical properties. ZnO is considered as one of the front runners among metal oxide semiconductors due to its fascinating properties such as broad band gap of 3.36 eV and a large exciton binding energy of 60 meV, non-toxicity, biocompatibility, photochemical properties and chemical stability (Lien *et al*. 2014, Gawande *et al*. 2016, Saito *et al*. 2014, Mittiga *et al*. 2006, Park *et al*. 2012, Mahajan *et al*. 2020).

However, pure ZnO is particularly active in the ultraviolet light range due to its broad band gap due to the low photo-conversion efficiency in visible light efficient applications (Karthik *et al*. 2022). Therefore, there is an enormous need to adjust the absorption area of ZnO from ultraviolet (UV) to visible one (Salem *et al*. 2017). Doping of ZnO thin films is the most commonly used strategy for band gap adjustment, control of morphology and photo-electrochemical properties (Esgin *et al*. 2022). The physicochemical properties of ZnO thin films can be greatly developed by adding of convenient elements. It has been reported that these doping elements are effective in creating energy levels within the band gap and causing visible light absorption. Various transition metals such as Mo, Ga, Ni, Fe and Cu have been used as additives in ZnO (Ashokkumar and Muthukumaran 2015, Ashokkumar and Muthukumaran 2015). Among these additives, Cu has been of great interest. The Cu^{2+} ionic radii (0.73 Å) is near to the Zn^{2+} ion (0.74 Å) and is very advantageous as it can easily fills the emptiness of zinc in the lattice structure (Naik *et al*. 2021). However, there has been a need to develop techniques that provide controlled synthesis, favorable structural properties, low temperature and low cost production in order to successfully increase the commercialization of Cu doped ZnO nanostructured thin films. Up to now, several deposition techniques have been proposed for the production of Cu doped ZnO nanostructured thin films, such as pulsed laser deposition, spray pyrolysis, DC magnetron sputtering and magnetron co-sputtering. However, these deposition techniques are difficult and costly. Spin coating is a simple and low cost method that has been used for thin film production (Shewale *et al*. 2013, Allabergenov *et al*. 2014, Drmosh *et al*. 2013, Liu *et al*. 2016). In light of this, this study was focused on Cu doped ZnO thin films production by a simple, easily controlled and rapid spin coating. The electrochemical, morphological and optical properties of ZnO nanostructured thin films have been investigated by varying Cu concentration from 0 to 50%. Herein, it was aimed to report the commonly less investigated electrochemical properties of Cu doped ZnO nanostructured thin films produced by spin coating method. As will be seen below, the optical, morphological and electrochemical properties of ZnO nanostructured thin films improved as the Cu doping ratio increased indicating that the nanostructured thin films produced by spin coating have potential in many nanotechnology applications.

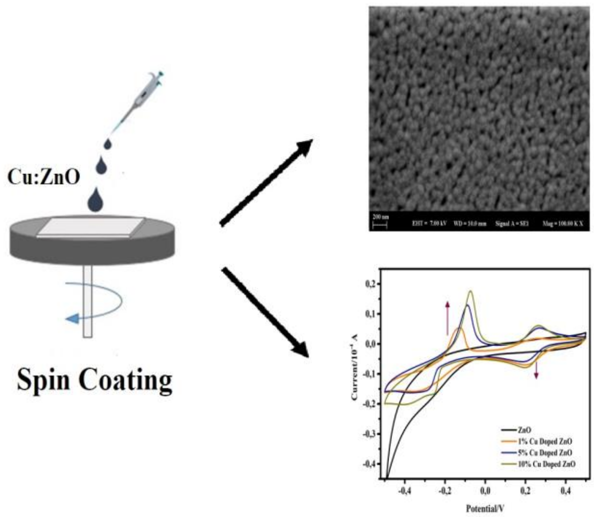

Figure 1. Schematic representation of the fabrication with spin coating method of ZnO nanostructure thin films doped with different concentrations (1-50%) of Cu

2. Experimental

All chemicals were supplied from Sigma Aldrich company. Cu doped ZnO nanostructured thin films were prepared on the microscope glasses by using sol-gel spin coating method. 1.5 cm x 1.5 cm glass substrates were cleaned in acetone and ethanol for about 15 minutes, respectively, to eliminate the contaminants and finally rinsed with deionized water in an ultrasonic bath. To prepare pure ZnO nanostructured thin films, 0.5 M zinc solution was prepared by dissolving zinc acetate dehydrate ($C_4H_{10}O_6Zn$) in dimethoxy ethanol ($C_4H_{10}O_3$) and three drops of monoethanolamine was droped as a complexing agent. Also, for the Cu doping, a 0.5 M copper solution was prepared by dissolving copper(II) acetate ($Cu(CH_3COO)_2 \cdot H_2O$) in dimethoxy ethanol ($C_4H_{10}O_3$) and similarly three drops of monoethanolamine was droped as a complexing agent. After the dissolution process, these two solutions were mixed in certain proportions to achieve the desired doping concentrations (0-50%). Then, all solutions were stirred at 70 °C for 1 hour on magnetic stirrer at atmospheric pressure. Afterwards, to prepare the thin films, the prepared solutions were droped on microscope glasses and spin coated at 3000 rpm for 60 s and dried at 250 °C for 10 min to evaporate the solvents from the samples (Fig. 1). 10 layers were coated by repeating the same processes. After the coating process was completed, the prepared samples were annealed in a muffle furnace at 600 °C for 6 hours.

After the annealing process, the prepared pure ZnO and 1-50% ratios Cu doped ZnO nanostructured thin films were analyzed morphologically, optically and electrochemically by scanning electron microscope (SEM), fourier transfer infrared spectrum (FTIR), ultraviolet–visible spectrophotometry (UV-vis), mechanical profilometer, and cyclic voltammetry (CV). The thickness and avarage roughness of the thin films were measured by Veeco Dektak profilometer. The optical characterizations of pure ZnO and Cu doped ZnO nanostructured thin films were determined in the wavelength range of 190–1100 nm using PerkinElmer Lambda2 UV–vis spectrophotometer. The composition of prepared thin films were determed by PANalytical Minipal4 X-ray fluorescence (XRF) spectrometer. The FTIR spectra of all samples were measured by a PerkinElmer spectrometer-ATR mode in the range of 4000-650 cm^{-1}. The surface morphology of the thin films were observed using a Zeiss EVO LS 10 SEM. CV were measured in the voltage range of -0.5-0.5 V at sweep rates 100 mVs^{-1}. The measurements were conducted in 0.1 M NaCl solution with a Au disc coated with pure and Cu doped ZnO nanostructured thin films as the working electrode. In the measurements, Ag/AgCl was used as the reference electrode and a Pt wire as the counter electrode. After the thin film was coated by dropping pure and Cu doped ZnO aqueous solutions on the Au disc of 2.0 mm in diameter and it was dried.

3. Results and discussion

XRF was used to determine the composition of nanostructured thin films. Figure 2 shows the quantitative results obtained from XRF measurement of pure ZnO, 1%, 10% and 50% Cu doped ZnO nanostructured thin films. As can be seen from Figure 2, in the pure ZnO spectrum, there is only the peak of the Zn element. The intensity of the Cu peak increased with the increase of the Cu doping ratio. Thus, XRF measurements have proved that the thin films produced in this study were doped with Cu.

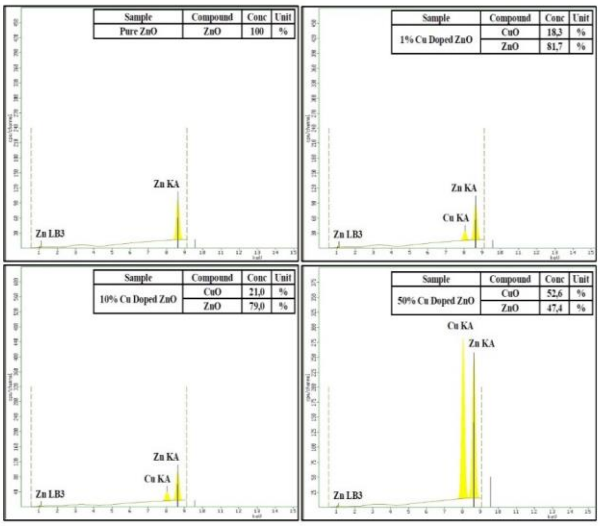

Figure 2. XRF spectra of pure ZnO, 1%, 10% and 50% Cu doped ZnO nanostructure thin films

SEM analysis was used to determine the effect of Cu doping on the morphology of the produced ZnO nanoparticled thin films. In Figure 3, SEM images illustrates the particle shapes and sizes varied by changing the Cu doping rates. In pure ZnO, the shapes of the nanostructures was not uniform and homogeneous, but as the Cu doping concentration increased, the nanostructures were more spherical and homogeneous. While the particle size for 1% Cu doped sample was about 35 nm, it increased up to 90 nm with the increasing Cu concentration. It has been observed that the films with higher Cu doping concentration have more homogeneous nanostructures. The results obtained from SEM images are consistent with the mechanical profilometer measurement results.

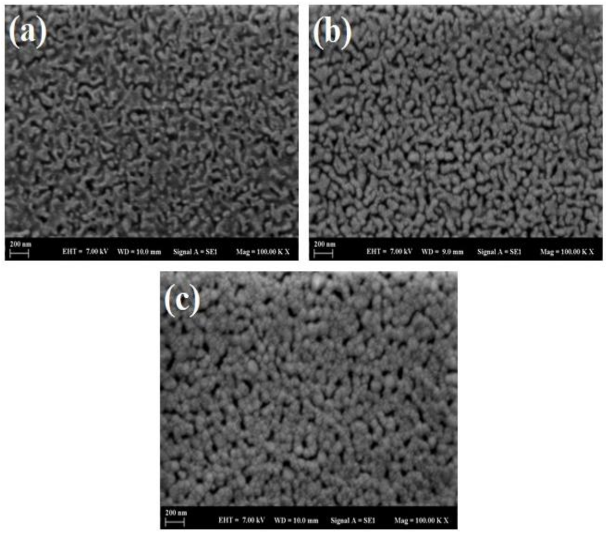

Figure 3. SEM images of (a) pure ZnO, (b) 1% and (c) 50% Cu doped ZnO nanostructure thin films

As the thickness and roughness of thin films affect their physical behavior, they have vital importance for applications based on thin films. Therefore, optimum thickness and roughness are focal parameters for thin film applications. Figure 4 shows, the thickness and roughness values measured by mechanical profilometer for pure ZnO, 1% and 50% Cu doped ZnO nanostructured thin films coated on glass substrates. The tables in Figure 2 show that the ratio of doping affected the roughness and thickness. The film thickness increased while the roughness values decreased as the doping ratio increased. As shown above, the SEM images reveal the homogeneity of the films changed as the Cu doping rate increased. With the doping of Cu ions to ZnO, the surface has become smoother as a result of the reduction of the gaps due to collection of more particles.

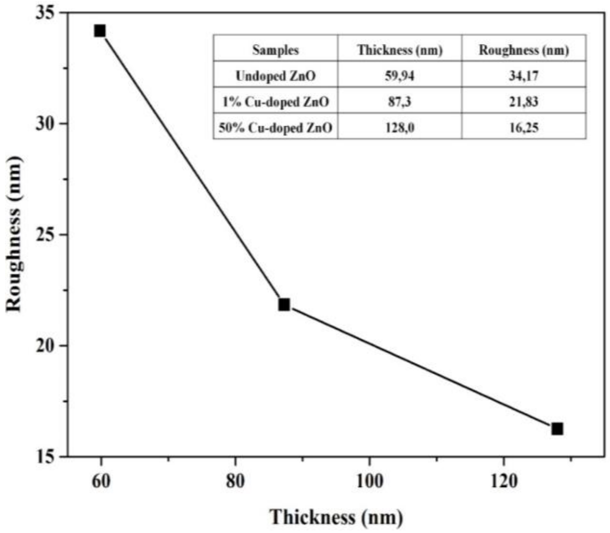

Figure 4. The average roughness of pure ZnO, 1% and 50% Cu doped ZnO nanostructure thin films

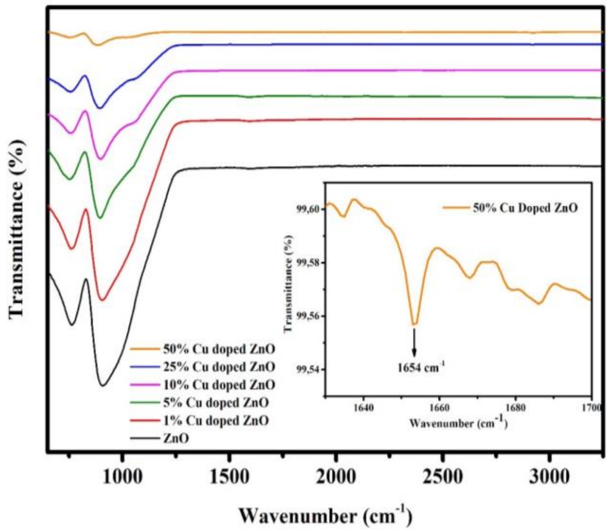

Figure 5. FTIR spectra of pure ZnO and ZnO nanostructure thin films with different concentrations (1-50%) of Cu

FTIR technique was used to analyze the structural interactions of ZnO and Cu. Figure 5 shows, the FTIR spectra of pure ZnO and different ratios (1-50%) Cu doped ZnO nanostructured thin films. The spectra was collected from wavenumber region of 650–4000 cm^{-1}. In the ZnO films, the peaks in the region between 700 and 1000 cm^{-1} correspond to Zn-O. The FTIR spectrum of undoped ZnO thin film has shown Zn-O absorption band near 763 cm^{-1}. The peak seen at 1654 cm^{-1} in the spectrum of 50% Cu doped ZnO nanostructured thin film corresponds to the stretching vibration of the Cu-O bond. As compared to FTIR spectra of pure ZnO films, a significant decrease in the intensity of bands and a shift in its positions towards lower wave number region is clearly seen in FTIR spectra with increasing Cu concentration (Handani *et al*. 2020, Yadav *et al*. 2021, Raul *et al*. 2014, Wang and An 2017). This result indicates that there is an interaction between Cu and ZnO.

UV-Vis spectroscopy is commonly used to determine optical properties of nanostructures. Figure 6 illustrates that the absorption spectra of pure and different ratios (1-50%) Cu doped ZnO nanostructured thin films in the wavelength range of 190-1100 nm. In the literature, there is an absorption peak at about 320 nm in the ZnO spectrum. However, an absorption peak can be seen at about 256 nm due to the different sizes of ZnO nanoparticles (Talam *et al*. 2012). The absorbance increased in the wavelength range of 200-400 nm with increasing doping concentration. This result is due to the increase in particle size and film thickness.

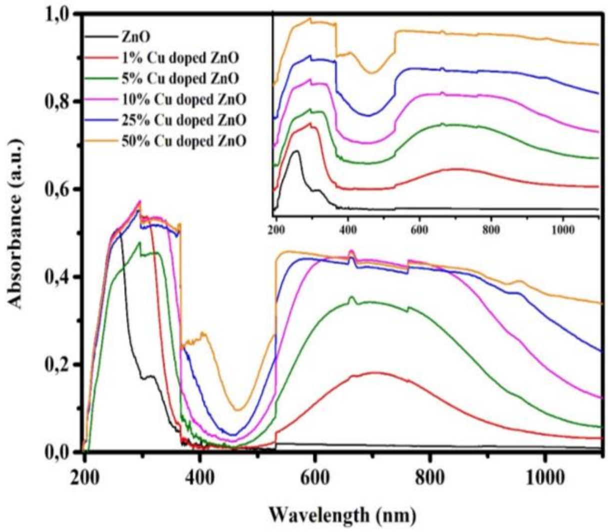

Figure 6. UV-Vis spectra of pure and ZnO nanostructure thin films with different concentrations (1-50%) of Cu

Doping of ZnO thin films with Cu shifted the absorption edge to the visible region. The reason for this shift could be due to the decreasing energy gap of ZnO calculated by Tauc plot method (Modwi *et al*. 2018). In addition, a new absorption peak with increasing intensity in the range of 500-900 nm was occured with the increasing concentration of Cu doping (Talam *et al.* 2012, Modwi *et al.* 2018, Patel *et al.* 2017, Wang *et al.* 2014). The optical band gaps of the prepared thin films were calculated using Tauc the equation:

$$\alpha h\vartheta = B\left(h\vartheta - E_g\right)^n \qquad (1)$$

where α, hν, E_g and B is the absorption coefficient, photon energy, optical band gap and band tailing parameter, respectively. n = 1/2 is taken for direct transition since ZnO is a direct band gap semiconductor. The optical band gap was calculated by extrapolating the linear portion of the curve between $(\alpha h\nu)^2$ and hν when α was equal to zero (Nouasria *et al.* 2021, Pon *et al.* 2021). The optical band gap of prepared nanostructure thin films were appraised by plotting $(\alpha h\nu)^2$ versus hν and extrapolated the linear part of the absorption peak to determine the intercept with x-axis as shown in Figure 7. The band gap were calculated from the Tauc plots as 3.45, 3.41 and 2.87 eV for pure ZnO, 1% and 25% Cu doped ZnO nanostructure thin films, respectively (Abderrahmane *et al.* 2021) . As can be seen from the UV results, the doping of Cu to the ZnO thin films caused absorption in the wider band gap region. This means that nano structures suitable for use in technological applications that are active in the visible region are produced.

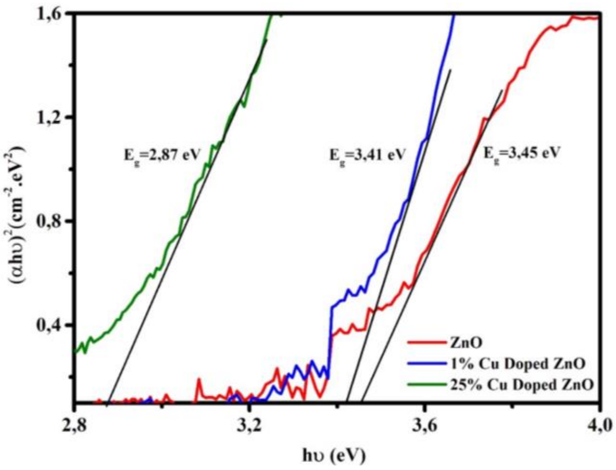

Figure 7. Tauc's plot evaluated from UV-Vis absorption spectrum for pure ZnO, 1% and 25% Cu doped ZnO nanostructure thin films

Nanostructured materials have active characteristics due to their physicochemical features depending upon their ambient conditions and synthesis processes. Therefore, studying the complex electrochemical characterizations of nanomaterials is of great importance. To investigate the effect of Cu doping on the electrochemical performance of the ZnO thin film were studied by CV was performed in the potential range from −0.5 to 0.5 V at a scan rate of 100 mV/s in 0.1 M NaCl aqueous solution. Figure 8 shows CVs of pure ZnO, 1%, 5% and 10% Cu doped ZnO nanostructure thin films. At CV curve of pure ZnO thin film, the distinguishable redox peaks has been not identified. Cyclic voltammetric behavior of 1% Cu doped ZnO nanostructure thin film has shown two oxidation peaks at 0.252 V and -0.122 V and two reduction peaks at -0.316 V and 0.214 V. 5% Cu doped ZnO nanostructure thin film has shown two oxidation peaks at 0.262 V and -0.086 V and two reduction peaks at -0.318 V 0.214 V. 10% Cu doped ZnO nanostructure thin film has shown two oxidation peaks at 0.266 V and -0.066 V and two reduction peaks at -0.342 V 0.204 V. As can be seen in voltamogram, the first oxidation peaks shift toward more possitive potential and this indicates that addition Cu leads to prevent oxidation. The shape of the CV loop of the nanostructured thin films have indicated that improved charge dissipation takes place at the electrode surface. It was seen that ZnOs doped with Cu performed better electrochemical properties than pure ZnO. This shows that Cu doping to ZnO thin films could improve the relative electron transfer. All prepared Cu doped nanostructure thin films has shown enhanced peak current compared to the pure ZnO. This indicates that the Cu doped electrode can be more prefareble in electrochemical applications. There has been an increase in peak current in almost all samples with increasing the concentration of Cu doping (Naik *et al*. 2021, Mahmoud *et al*. 2019).

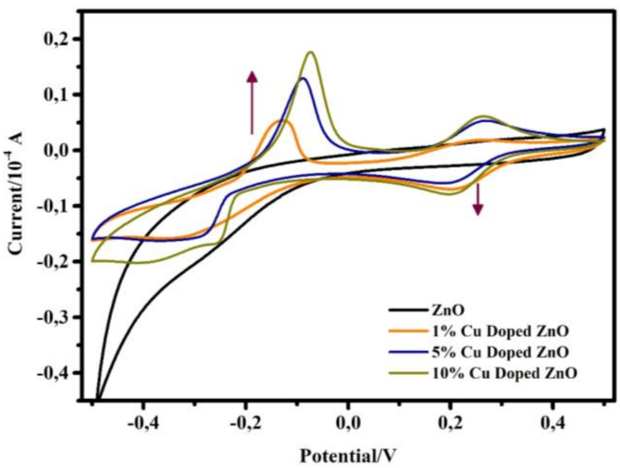

Figure 8. The cyclic voltammetry curves of pure ZnO, 1%, 5% and 10% Cu doped ZnO nanostructure thin films at a scan rate of 100 mV/s in 0.1 M NaCl aqueous solution

4. Conclusions

In this study, ZnO nanostructured thin films were prepared with Cu at different ratios (0-50%) by the spin coating which is an extremely simple and inexpensive technique. The chemical groups of prepared thin films were identified by FTIR spectra and prominent IR peaks were analyzed. From FTIR data, it was seen that Cu was doped to ZnO thin films due to the change in the intensity and positions of the Z-O peaks with increasing Cu concentration. The increase in the doping ratio of Cu was also confirmed by XRF measurement. Absorption spectra showed that the value of the energy band gap changes depending on the Cu doping ratio. The band gap energy value decreased as expected due to the increase in Cu doping ratio. As can be seen from the SEM images, more spherical and homogeneous nanostructures were formed with the doping of Cu. The film thickness increased and roughness decreased due to the homogeneous structure as the doping ratio increased Electrochemical measurements revealed that increase in Cu doping ratio in ZnO nanoparticles resulted in high electron transfer indicating that the conductivity of ZnO nanostructured thin films increased with Cu doping. All these results have shown that it is possible to produce more homogeneous, able to absorption in more wide spectrum and more conductive nanostructure thin films with a simple and inexpensive method. The thin films produced in this study are quite suitable for many nanotechnology applications.

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