Aluminum-Doped Nano-Zinc Oxide Can Act as Good Carrier for Biomedicine

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Abstract Proper diagnosis of the cause of trouble, dose estimation and safe reaching of medicine to the destination (DDD model) would bring effective healing result. Technology/equipments help a lot to diagnosis and identify the location of the damage. Nanoscience and nanotechnology are occupying a major part in these regards. Medicine applied orally or by injection has to pass a long route through the body parts overcoming many obstacles before reaching to destination. Nanoparticles can move faster without distortion of the passage and interact largely with infected cells as its surface-to-volume ration is larger. Zinc oxide nanoparticles (ZnO NPs), as one of the most important metal oxide nanoparticles, are popularly employed in various fields of medical science and applications due to their peculiar physical and chemical properties. Aluminum-doped zinc oxide (AZO) nanoparticles are transparent as well as conducting (TCO) material and being used as an important component in a number of electronic and imaging devices including scanner, liquid–crystal displays, OLEDs, touchscreens and photovoltaics. Both these nanomaterials have been deposited in a simple and low-cost sol–gel method.

Keywords Nano-medicine · Drug carriers · ZnO · AZO · TCO material · Sol–gel method

1 Introduction

Recently emerging nanoscience and nanotechnology may bring revolution in different field of science and engineering. Accuracy in detection of infected cells and charging of precision amount of medicine can be increased by nanoscience and nanotechnology, particularly, in the field of medical science and treatment of different type of diseases. Over the last decade, nanoscience and nanotechnology are emerging as the operating as well as controlling parts of various fields of science and technology (Sirelkhatim et al. 2015; Siddiqi et al. 2018) which are essential for

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mankind. Nanoparticles are a part of nanomaterials that are defined as a single particle of 1–100 nm in diameter. From last few years, nanoparticles have been a common material for the development of new cutting-edge applications in communications, sensing, energy storage, data storage, optics, transmission, cosmetics, biology, environmental protection and medicine due to their important optoelectronic and peculiar physiochemical properties (Smijs and Pavel 2011).

Zinc oxide (ZnO), which can exhibit a wide variety of nanostructures, possesses unique semiconducting, optical and piezoelectric properties and hence has been investigated for a wide variety of applications. Most important features of ZnO nanomaterials are low toxicity and biodegradability and can be used as an additive in a variety of materials. Therefore, ZnO-based nanomaterials have been studied for a wide variety of applications such as drug delivery, gene delivery, anticancer, antibacterial and diabetes treatment; anti-inflammation; wound healing; bio-imaging and bio-sensing of a wide array of molecules of interest (Mishra et al. 2017; Zhang and Xiong 2015).

Aluminum-doped zinc oxide (AZO) nanoparticles has all properties of ZnO in addition with increased electrical conductivity. They are an important component in a number of electronic and biomedical imaging devices including liquid–crystal displays, OLEDs, touchscreens, photovoltaics, sunscreen**,** probes for imaging retinal hypoxia, etc. (Uddin et al. 2015).

Activity and reactivity of materials vastly vary with particle shape, size and concentration of nanoparticles, bonding strength of atoms, etc., which are been rooted during the synthesis process (Narjis et al. 2020). The sol–gel process has demonstrated as the high potential to control the size, bulk and surface properties of the oxides (Baraket and Ghorbel 1998). Moreover, it has advantages due to its excellent compositional control, homogeneity on the molecular level, simplicity, low cost, performing well in atmospheric pressure without the need for expensive vacuum equipment, lower crystallization temperature, and it can be used to deposit films over a large area with a very uniform thickness (Hench and West 1990). We report here the study of dependence of size, conductivity and transparency of the synthesized nanoparticles on various depositional conditions. For AZO samples, we have doped aluminum into ZnO through a simple sol–gel technique (Znaidi 2010).

2 Experimental

2.1 Synthesis of Undoped ZnO and Al-Doped AZO Nanoparticle

We have synthesized undoped and Al-doped ZnO (AZO) nanoparticles through a simple and low-cost sol–gel method (Znaidi 2010). Undoped ZnO samples were prepared by dissolving 0.5 M of zinc acetate dihydrate $Zn(CH_3COO)_2 \cdot 2H_2O$ into 30 ml of ethanol. This solution was stirred at 80 °C for 1 h. Then the solution is allowed for crystallization by slowly annealing to room temperature. To prepare the AZO nanoparticles, different amounts of aluminum acetate $Al(OH)(CH_3COO)_2$ were dissolved in a solution of zinc acetate dihydrate and polyethylene glycol as surfactant to gain concentration at 0% (AZO 0%), 2% (AZO 2%), 3% (AZO 3%) and 4% (AZO 4%) (g/mL), respectively. This precursor solution was sintered at 80 °C for 2 h with continuous stirring by magnetic stirrer. The solution is slowly converted to gel. Then the gel was dried to powder at 60 °C following by annealing process for crystallization. By this simple method, the nanoparticles have been successfully prepared.

2.2 Characterization

The characterizations were conducted by X-ray diffraction (XRD) and UV–visible spectroscopy, and the crystallite size was calculated using the Scherrer's formula:

$$D = k\lambda/(\beta \cos\theta) \tag{1}$$

where D is the average of crystallite size, β is the full width at the half maximum of the diffraction peak, θ is the Bragg angle, λ is the wavelength of X-ray used, and k is a constant.

3 Results and Discussions

3.1 X-Ray Diffractions

Crystal structures of the prepared undoped ZnO and Al-doped AZO samples were examined by X-ray diffraction in the diffraction angle range $2\theta = 10$–80°. X-ray diffraction [Fig. 1] shows the samples are polycrystalline nano-crystal. X-ray photographs also show that peak intensity is much higher for 3% Al-doping sample than 4%. It indicates that crystal homogeneity break and more disorder phase appear for higher Al concentrations.

The crystallite size was calculated using the Scherrer's formula in Eq. (1). Calculated size of crystallites is given in Table 1. Data show that the Al doping resulted in the increase in size of crystallites.

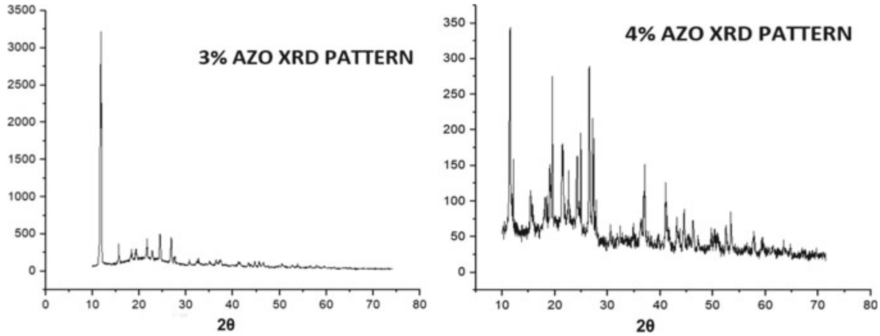

Fig. 1 XRD patterns of Al-doped ZnO at various Al concentrations

Table 1 From XRD data for 3 and 4% Al-doped ZnO

Samples	Peak position (2θ)	FWHM (full width half maxima)	Crystal size, *D* (nm)	Average crystal size, D_{av} (nm)
3% Al-doped AZO	11.74897	0.32112	24.86992009	26.99898166
	24.42357	0.30341	26.78952856	
	26.7863	0.27836	29.33749633	
4% Al-doped AZO	11.44373	0.28606	27.91046939	30.011019

3.2 *UV–Visible Optical Absorption*

Absorption spectra obtained in UV–visible spectroscopy show that pure ZnO has absorption peak at around 260 nm [Fig. 2a] and Al-doped samples have dual absorption peaks occurring at two positions: one at around 270 nm and other one at 300 nm [Fig. 2b and c].

This indicates that there are two types of lattices: unaffected ZnO lattice peaked at 270 nm and Al-doped AZO lattices peaked at 300 nm. Optical band gap of samples has been determined with the help of Tauc relation

$$(\alpha h\nu)^2 = A\left(h\nu - E_g\right) \tag{2}$$

where α represents absorption coefficient, A is a constant, and $h\nu$ is photon energy. Band gap value is found to be 3.6 eV for pure ZnO and 3.5 eV for AZO nanoparticles. It is also clear that band gap for these nanosamples are higher than the value of bulk ZnO.

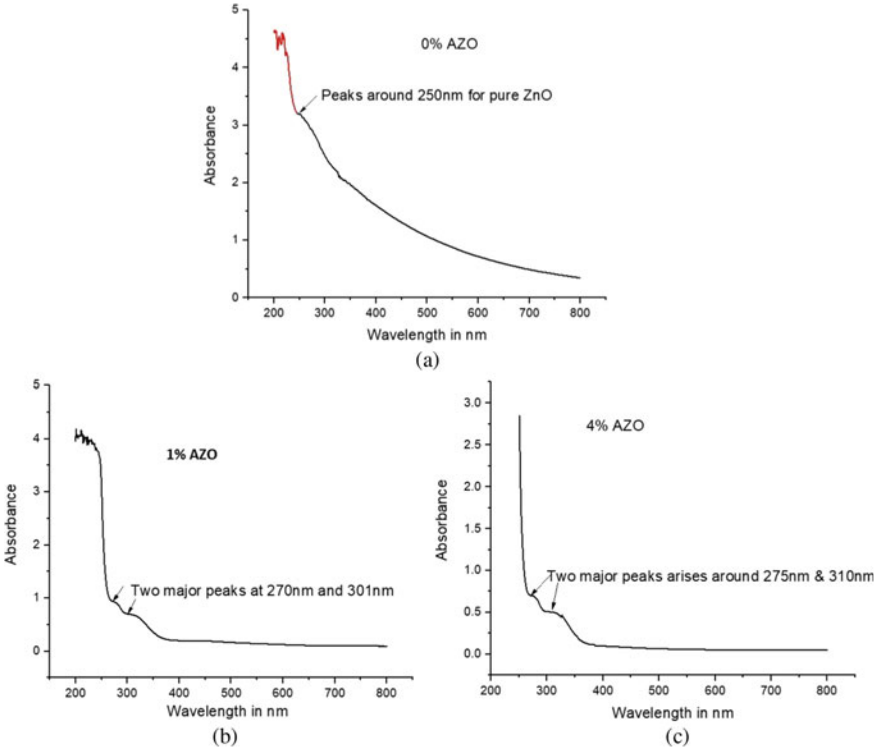

Fig. 2 UV–visible optical absorption of ZnO and AZO of different Al concentrations

3.3 Transmission or Transparency of the Materials

It is clear from the graph that undoped ZnO and Al-doped AZO samples below 4% Al concentration have transparency more than 80% and transparency reduces for higher Al concentrations [Fig. 3]. Reduction of transparencies may be due to scattering of photons by crystal defects created by doped aluminum atoms which took place in the interstitial positions or may be due to the impurity scattering present in the solution.

3.4 Study of Electrical Properties

For electrical and structural studies, DC electrical resistivity measurement has been done through a simple electrolysis method. Current–voltage characteristics of undoped and Al-doped ZnO nanoparticles with five different doping concentrations (0, 1, 3, 4, 6, 9%) are shown in Fig. 4. It is seen that the electrical current of the nanofluid increases with increasing Al dopant concentration upto 4% and then decreases for higher Al concentrations. To get a clear picture of this variation, we

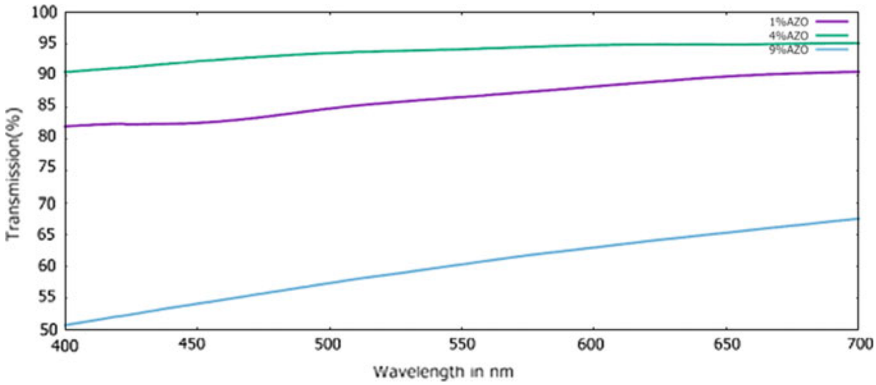

Fig. 3 Transmission of AZO for different % of Al doping

have calculated resistivity using the equation

$$\rho = R * A/L \tag{3}$$

where A is cross sectional area, L is the length of the dipped electrodes within the solution and $R = V/I$, is the resistance plotted in Fig. 5. Clearly, resistance decreases up to 4% Al concentrations and then decreases.

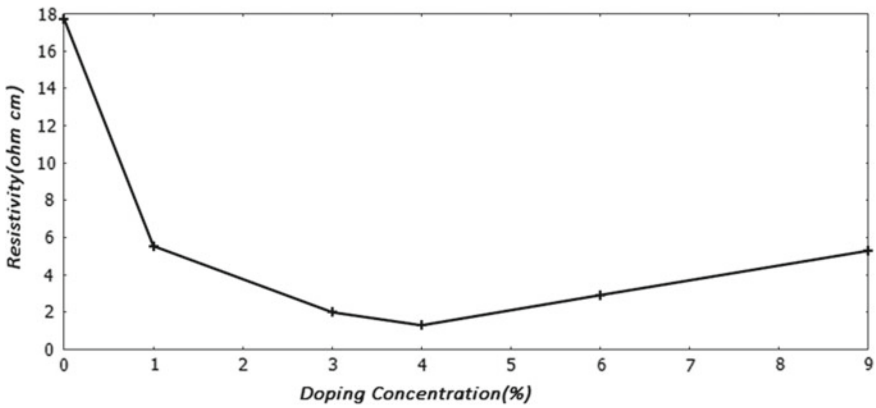

Fig. 5 Variation of resistivity of AZO samples for different Al concentrations

3.5 Discussion

All the above reported results show that Al doping into pure ZnO semiconductor crystal has a little effect on crystallinity and transmission. Possible explanation of the existence of two peaks is as follows.

- Atomic radius of Al is 125 pm which is less than Zn atom of radius ~139 pm.
- Lattice in which Zn atoms substituted by Al atoms might shrink in volume.
- Atoms of shirked lattice become closure, and there might be a change in electrons distribution.
- This new distribution might introduce shallow energy states within the band gap causing reduction in excitation energy of the valance electrons.

But all Zn ions could not be replaced by dopant Al atoms. So, obviously there are two types of lattice exist within the AZO materials: pure ZnO lattice which has a peak at around 270 nm and other one due to Zn substituted AZO lattice which has a peak at a lower energy at 310 nm. Doped Al atoms have two sites to sit within ZnO crystal: lattice site by substitution of Zn^{2+} ions and interstitial site of the crystal. Lattice site sited Al^{3+} gives one free electron and improves conductivity, but interstitial site sited Al atoms do not give free electron rather distort the crystal and introduce defects in the crystal which in turn absorb free electrons resulting decrease in conductivity.

- Initially when Al atom concentration in solution is low, Al atoms try to occupy first lattice position replacing Zn atoms through chemical reaction prioritized by their electron affinity. So, conductivity increases.
- When Al concentration is becoming high in solution, some Al atoms occupy interstitial positions. Interstitial Al creates volume defect and increases resistance of the sample.
- So for higher Al concentration, there is a competition between the effects of lattice Al and interstitial Al. Later effect dominates for higher Al concentrations.

Thus, this may be due to a competitive effect of carrier generation by substitutional Al with carrier trapping by interstitial Al. At lower concentrations, Al atoms occupy substitution position resulting increase in conductivity. But for higher concentration, more and more Al atoms occupy the interstitial positions producing defects and acting as carrier-trapping centers resulting reduction in conductivity.

4 Conclusions

Due to important optoelectronic and peculiar physiochemical properties of pure nano-ZnO can be used as drug delivery, gene delivery, anticancer, antibacterial and diabetes treatment, anti-inflammation, wound healing, bio-imaging and bio-sensing of a wide array of molecules of interest. Little toxic effect of ZnO can be used as for cancer and tumor treatments. Transparent and conducting properties of aluminum-doped AZO materials are mainly useful for imaging inside of the body system, touchscreen, etc., as well as drug carriers. AZO materials are less toxic and have no corrosive effects compared to other TCO materials available in market appealing for safer uses.

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