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Probing Defects by Positron Annihilation Lifetime Spectroscopy in Electrochemically Synthesized ZNO Nanocomposites: A Comparative Study

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Abstract

The present article gives a detailed comparative description of the dopant and particle size dependant changes in the structural arrangement of intrinsic defects present in electrochemically synthesized ZnO:M or ZnO:MO nanocomposites. X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) have been carried out to find the shapes and sizes of the nanocrystalline ZnO composites. Presence of defects in detail is carried out using positron annihilation spectroscopy, which reveals the presence of zinc vacancy. The studies reveal that small particles which are spherical in nature around a critical size (~23 nm) are in receipt of better positive surface charge due to the higher occupancy of the doubly charged oxygen vacancy as compared to the larger nanostructures whereas singly charged oxygen vacancy predominates. This change in electronic structure has been acting as an initiator yet another interesting phenomenon, described as positron confinement inside nanocrystals. To conclude, based on all the above mentioned techniques, a model of the structural arrangement of the intrinsic defects in the present samples has been reconciled.

Keywords: *Dopant, Positrion Annihilation Lifetime Spectroscopy, Scanning Electron Microscopy, X-ray Diffraction, ZnO Nanocomposite*

1.0 Introduction

In this article, a large number of nanocrystalline ZnO composites with varied size and dopants have been inspected. The type of defects present in these nanocrystals has been examined by Positrion Annihilation Lifetime Spectroscopy (PALS). It has been found that the particle size and dopant materials are strongly correlated with positron annihilation parameters. With the data obtained from PALS examination, a defect in structural arrangement in the nanocrystals has been identified with prediction which describes the mechanism with noteworthy points about the defect related visible region emission. The positron annihilation lifetime values give the picture of positively charged oxygen vacancy at the surface which inturn creates a potential barrier leading to the interesting phenomenon of confinement of positrons within the nanocrystals[1].

1.1 Importance of ZnO Nanocrystals

ZnO nanocrystals have been a easy accessible material for design and development of new technological applications in the field of communication, storage of both energy and data, sensing, optics, in protecting environment, cosmetology, biology and medicine due to their very important properties related to optical, electrical, and magnetism. In particular, the unique and specific

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properties have lots of advantageous benefits in making use of nanoparticles. This arises from many similarities in properties including the size of nanoparticles and biomolecules such as proteins and nucleic acids. To be more specific among all these, metal oxide nanoparticles outstand as one of the most useful materials, due to their wide variety of properties and functionalities. The major dominating material in metal oxide nanoparticles is Zinc Oxide (ZnO) nanoparticles because it is involved in many areas of application, *e.g.,* in the field of development of sensors, new cosmetics, as storage aids in data and energy, optical and electrical devices, materials for displays, and in drug-delivery[2,3].

2.0 Experimental

2.1 Electrochemical Synthesis of ZnO:Cu, ZnO:MgO, ZnO:Sn, ZnO:ZrO_2 and $AgRuO_2$ Nanocomposites

A keen selection and setup of experimental conditions like choice of the electrolyte, electrodes, time of run of the experiment, parameters that can be varied with like current, electrolyte concentration, post experimental techniques for recovery of the metal oxide nanoparticles adopted like centrifugation, washing and drying at high temperature ~400°C, aided in obtaining the maximum yield of the desired products without much wastage *i.e.,* room temperature was employed in the synthesis of the ZnO:Cu, ZnO:MgO, ZnO:Sn, ZnO:ZrO_2 and $AgRuO_2$ nanocomposites[4].

2.2 X-Ray Powder Diffraction

The crystallographic studies and analysis were carried out by X-ray diffractometer (Rigaku, Mini Flex II desktop XRD) using Cu Kα wavelength (λ= 1.54059) and range of scanning varied from 10° to 70°. Williamson-Hall plot using Full Width Half Maximum (FWHM) data was used to calculate the average particle size and micro strain after careful and close correction of the instrumental broadening[4].

2.3 Scanning Electron Microscopy

The morphological studies to obtain the features of the ZnO nanoparticles under analysis was determined by Scanning Electron Microscopy (SEM model LEO 440)[4].

2.4 Positron Annihilation Lifetime Spectroscopy (PALS)

The defect concentration study and analysis of the samples were carried on and quantified by Positron lifetime spectrometer which consists of a fast-fast coincidence system with BaF_2 scintillators coupled to photo multiplier tubes of type XP2020/Q with quartz window as detectors. Twin pellets of 9 mm diameter and size 2 mm thick of the sample were sandwiched with 17 μCi ^{22}Na positron source deposited on a pure Kapton foil of 0.0127 mm thickness[5]. The sandwich that is created between source and sample was placed between two detectors of PALS to obtain lifetime spectrum. The spectra were studied in detail and analyzed into two lifetime components with the help of PATFIT-88 and RESOLUTION programs. The function of resolution that was determined was used in the present analysis of positron lifetime spectra[5,6].

3.0 Results and Discussion

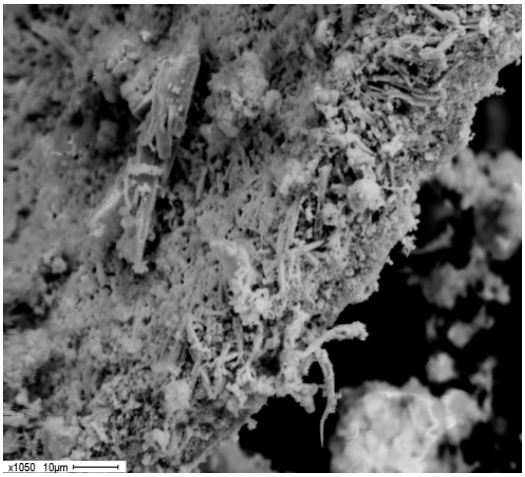
3.1 Characterization

3.1.1 X-ray Diffraction

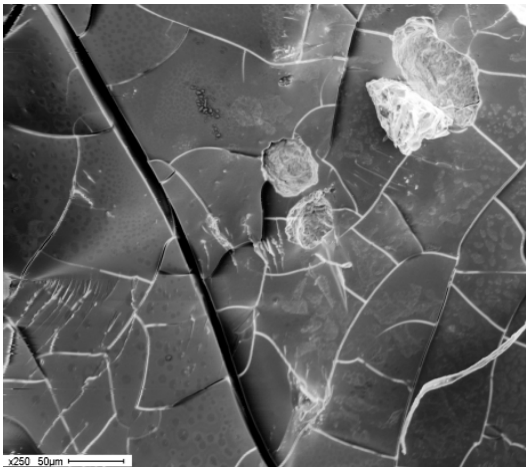
The X-ray diffraction data and studies of the prepared materials revealed the size of the particulates in nanometers. ZnO:Cu (9.9 nm), ZnO:MgO (17.5 nm), ZnO:Sn (37.0 nm), ZnO:ZrO_2 (12.5 nm) and $AgRuO_2$ (34.5 nm) calculated by the Williamson-Hall plot. Tauc plot derived from the UV-V is spectrum revealed the bandgap values of the nanocomposites. ZnO:Cu (3.05 eV), ZnO:MgO (3.9 eV), ZnO:Sn (3.1 eV), ZnO:ZrO_2 (2.5 eV) and $AgRuO_2$ (2.85 eV). The bandgap values are therefore helpful in predicting whether the photocatalyst is active under UV light or visible light. From the above values we can say that ZnO:MgO and show enhanced photocatalytic activity under UV light compared to the ZnO:Cu, ZnO:Sn , ZnO:ZrO_2 and $AgRuO_2$ which show high activity under sunlight[4,7].

3.1.2 Scanning Electron Microscopy

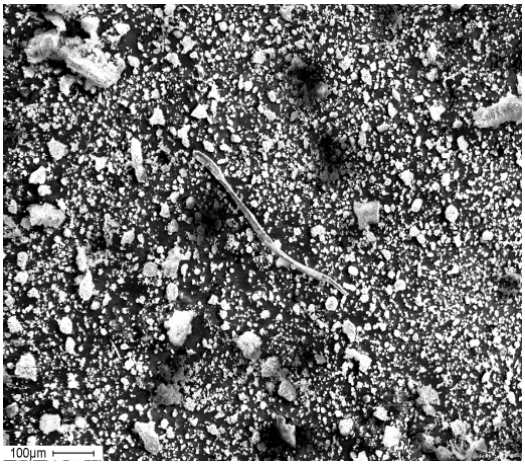
Size and surface area of the particle have major impact on the photocatalytic degradation activities



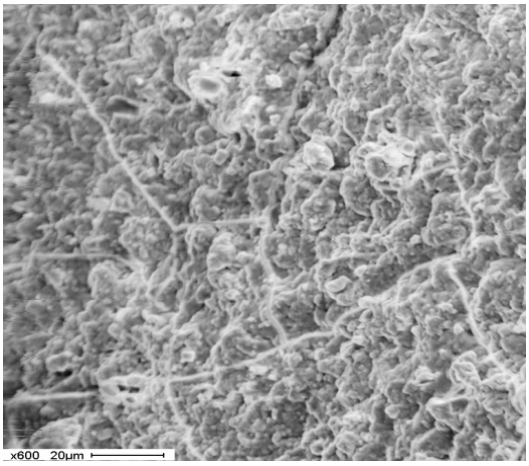
ZnO:Cu



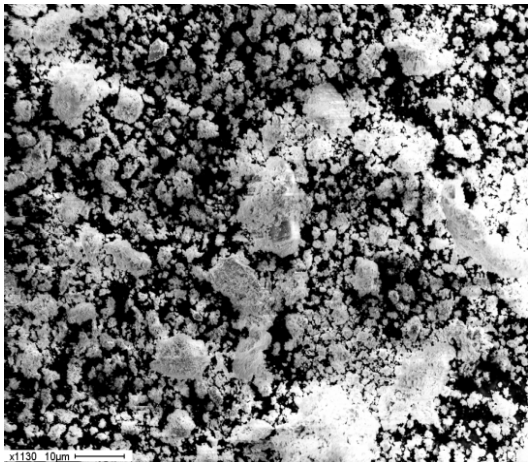
ZnO:MgO



ZnO:Sn



ZnO:ZrO_2



$AgRuO_2$

Figure 1. Scanning electron micrographs of ZnO:Cu, ZnO:MgO, ZnO:Sn, ZnO:ZrO_2, $AgRuO_2$

of ZnO:M or ZnO:MO photocatalysts. The skeletal structure of the samples was detected by using SEM. The SEM micrographs of the ZnO:M or ZnO:MO nanocomposites show that they consist of agglomerated particles[4].

3.1.3 Positron Annihilation Lifetime Spectroscopy

Vacancies of both zinc and oxygen are found in ZnO/ ZnO:M / ZnO:MO. Zn vacancies only can be identified and observed by PALS technique as they process negative charge state and therefore it acts as strong seducingareas for positrons[6].

3.2 Probing Defects by Positron Annihilation Lifetime Spectroscopy

From Table 1, it is concluded that, both chemical and physical properties of copper are very much alike to those of zinc which is termed as synergism. This is the reason that doping of ZnO with copper does not have much effect in formation of intrinsic point defects. τ2 of ZnO:Cu (562 ps) is more compared to ZnO (230 ps), the defect concentration of ZnO:Cu is lesser compared to other metal doped nanometal oxides due to the synergistic nature of Zn and Cu as mentioned. The increase of τ2 for ZnO:Sn (530 ps), ZnO/MgO (644 ps), ZnO/ZrO_2 (654 ps) compared to ZnO (230 ps) is because the compounds consists of a mixture of many oxides, many defects which includes vacancies and interstitial atoms of both species. The high τ2 value and defect concentration of ZnO:Sn, ZnO/ZrO_2 compared to ZnO increases the photocatalytic degradation activity of the nanocrystals. These defects are the major throwbacks in making the photocatalys absorb the light in visible region and making them more efficient $AgRuO_2$ nanostructures[6]. Second life time τ2 is due to annihilation of positron trapped at defect in the medium. It is also seen that even though τ2 of Ag-RuO_2 (410 ps) is more compared to ZnO (230 ps), the defect concentration of Ag-RuO_2 is lesser but still it shows higher activity than ZnO.

Table 1. PALS results

Parameters	ZnO	ZnO:Cu	ZnO:MgO	ZnO:Sn	ZnO:ZrO_2	$AgRuO_2$
τ_1(ps)	171	260	231	228	245	211
I_1 (%)	-	91.52	84.09	87.88	85.31	90.04
τ_2 (ps)	230	562	644	530	654	410
I_2 (%)	-	8.48	15.91	12.12	14.69	9.959
τ_{mean} mean lifetime (ps)	-	285	297	264	305	231
τ_B Bulk lifetime(ps)	181	272	257	245	269	222
λ_B Bilk annihilation rate $(ns)^{-1}$	-	3.671	3.884	4.083	3.705	4.508
K Trapping rate $(10^9)s^{-1}$	-	0.175	0.441	0.303	0.374	0.229
τ_2/τ_B size of vacancy cluster	1.27	2.06	2.505	2.16	2.43	1.84
Defect concentration C=Ad (K/μ) (10^{15}) cm		4.847	12.201	8.374	10.358	2.775

3.3 Correlation Between Defect Concentration and PALS Results

Table 2. The overall summarized results in the present study

Compound	Crystallite Size (nm)	PXRD JCPDS No	Lattice Parameters (A)	Unit Cell Volume (A3)	Band Gap (eV)
ZnO:Cu	9.9	09-0492	a=17.28 b=8.10 c=7.34	1028.5	3.05
ZnO: MgO	17.5	48-0418 31-1468	a=9.46 b=9.20 c=8.93	778.81	3.9
ZnO:Sn	34.0	74-2184	a=2.89 b=2.89 c=8.22	934.31	3.1
ZnO:ZrO	12.5	32-1482	a=13.67 b=6.01 c=3.74	308.17	2.5
$AgRuO_2$	34.5	85-0295	a=8.50 b=8.50 c=12.78	926.03	2.85

3.4 Photocatalytic Degradation of Organics and Effluents

Table 3. The overall photodegradation results in the present study[7,8,9]

Compound	Organic Effluents Treated	Initial COD ppm	Final COD ppm	Photodegradation Efficiency %
ZnO:Cu	Cibacron brilliant yellow Textile dyeing and printing industry effluent	3989.32 2787.12	234.12 874.36	94.13 68.62
ZnO: MgO	Eosin yellow	2490.84	392.11	84.25
ZnO:Sn	Rhodamine B	2987.36	984.23	67.05
ZnO:ZrO	Fast green FCF Paper dyeing and printing industry effluent	4252.0 2147.31	217.2 257.21	94.89 88.02
$AgRuO_2$	Fast green FCF Parathion pesticide	4252.0 4617.67	115.9 1794.32	97.27 61.14

4.0 Conclusions

The order of photodegradation efficiency is as follows:

$Ag\text{-}RuO_2 > ZnO:ZrO_2 > ZnO:Cu > ZnO:MgO > ZnO:Sn > ZnO$

~ 97% ~ 95% ~ 94% ~ 84% ~ 67% ~ 57%

- The photocatalytic decomposition of dyes using the prepared ZnO:M or ZnO:MO nanocomposite cryatals may be considered as an efficient and environmental friendly technique, as it makes the breakdown of the complex dye molecules into simpler non-toxic molecules very much easier.
- The study of various time dependant parameters like initial concentration of dye, pH of the medium, amount of catalyst, effect of intensity of light, helped in finding the optimum conditions of the reaction[10].
- The above mentioned statements motivated us to make use of sunlight as the source of illuminating radiation in the photodegradation reaction which is also considered as safe and cost effective.
- The decomposition of few industrial effluents were also carried out successfully using the as prepared metal oxide nanocomposite materials. The COD values decreased significantly which demonstrates the destruction of the organic molecules present in the effluent[11,12].

5.0 Future Aspects

There are various reports and articles related to ZnO and modified ZnO nanoparticles, but the gap researchers are finding are in the synthesis protocol in terms of size and shape of the particles which is hindering its possible application in biomedical sciences.

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