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OPTO-ELECTRONIC AND ELECTROCHEMICAL EVALUATIONS OF PARTICULATE WO_3 AND SnO_2 IN ELECTROCODEPOSITED Zn- TiO_2 NANOCOMPOSITES COATINGS FOR SENSOR APPLICATION

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Abstract

This study synthesized, characterized and determined the electronic and optical properties of Zn-TiO_2, Zn-TiO_2-WO_3 and Zn-TiO_2-SnO_2 nano-composite coatings on low carbon steel. It has also determined the effect of these coatings on the corrosion of mild steel in saline environment. This was with a view to produce an active coating to providing alternative to hazardous chromium coating. Active multi functional nano crystalline coatings of the composites were electrolytically fabricated on low carbon steel from Zinc bath, with its Cation and nanoparticulates of TiO_2, SnO_2 and WO_3 were uniformly codeposited in the Zn matrix. The nano-powders were characterized with Scanning Electron Microscope/Energy Dispersive Spectrometer (SEM/EDS) analyses for confirmation of the chemical compositions and purity. The electrocodeposition bath compositions were developed with 120 gram per litre of $ZnCl_2$, 30 gram per litre of KCl along sides with the nanopowders. Other additives including cetylpridinum chloride, 2- Butyne 1,4diol were added as surfactants and Thiourea was added as stabilizer. The coated specimens were sectioned into parts, some of which were characterized with electrical meters and solar simulator to determine the electrical conductivity and solar response of the coated samples respectively. Samples were also subjected to corrosion experiment in 3.5% NaCl (saline) media to study their corrosion resistance properties in the test media through Potentiodynamic polarization method. The results, the electrical conductivity of the generated nano-composite coatings displayed a better electrical conductivity of 2.45E-01$\Omega^{-1}m^{-1}$ which made it a better sensor material and outstanding corrosion resistance with corrosion rate at 0.10116 mm/year. The study concluded that both matrices with the Nano Particulate WO_3 and SnO_2 can be use as sensor materials but the WO_3 matrix showed a better electrical conductivity both in the presence and absence of uv light and enhanced corrosion protection under light and dark conditions, thus a better sensor's material.

Keywords: Sensors, Electrical resistivity, Corrosion rate, Nanocomposites, Opto-digital microscopy.

1.0 INTRODUCTION

A sensor can be defined as an electrical or electronic device which detects certain form of input from a physical environment and process it to an output usually inform of signal. This input may be light, sound, motion, moisture etc [1-2]. However, in the nanotechnology age, efforts are shifting towards the fabrication of nanosensors which are flexible, versatile, sensitive and specific [3]

[4] reviewed and evaluated the behaviour of one-dimensional nanostructured metal-oxide gas sensors based on. MoO_3. SnO_2, ZnO, WO_3, TiO_2, In_2O_3, Fe_2O_3, $AgVO_3$, CdO and CuO, TeO_2. The study summarized the merits and demerits with respect to their sensing mechanism. The authours further presented a general idea of various nanomaterials and how they have been employed for biosensing (Table 1). [5] investigated the application of Nanosensors as promising emerging tools in food production and agriculture. The study thoroughly reviewed various applications of nanosensors in food and agricultural industries.

Several materials, such as SnO_2, ZnO, ZnO-CuO, In_2O_3 and WO_3-In_2O_3 have been discovered to be good materials in Carbon monoxide and hydrogen sensors for environmental and industrial monitoring [6-7]. They also found that material of the sensing films determine the sensitivity of gas sensors. Despite the significant amount of research studies reported, research on active nano composites coatings is yet to be fully explored because of their versatility and wide field of applications. [8-9], for example, studied the use of nanocomposite energy storage materials in green building design, reported the comparative studies of tribo characteristics, the microstructure and electrochemical behaviours of Zn-TiO_2-WO_3 and Zn-TiO_2 nano-composite coatings. The results demonstrated the excellent coatings stability and corrosion resistance of the material.

Also, [10] studied the nanoparticulates loading effect of WO_3 on the mechanical behaviour, microstrure, and corrosion protection ability of WO_3 in Zn /TiO_2- nanocomposite coatings designed to be applied in marine structures. The results displayed a potential unique coating material for that aggressive environment. Likewise, [11] investigated Optical and electrical properties of WO_3-ZnO-SnO_2 / Zn-TiO_2 nanocomposites matrix. The corrosion resistant trend was also investigated. From the results, the materials behaved excellently and the effect of the ternary nanocomposites in Zn-TiO_2 was helpful and novel. In this similar vein, [12] reported data on the outcome of current density relationship on the alloy (super) composite coating using electrolytic method.

The data generated were unique and could be basis for engineering applications. More so, [13] elaborated on the effect of current concentration (density) and zinc oxide nano particles influence on the morphology and mechanical strengthening properties of zinc/ titanium(iv)/ zinc(iv) alloys deposited at constant deposition time. Furthermore, [14] worked on the study of rapid heat treatment on the microstructure evolution and surface characteristics of the electrodeposited modify Zn/TiO_2 composite coatings on low carbon steel. They were able to identify the condition for optimal coating stability. Moreover, [15] investigated the structural behaviour, electrical, optical, and corrosion resistant properties of electrodeposited tungsten(vi)oxide integrated on zinc/titanium(iv)oxide electrolyte applied in defence application. The results obtained from the findings revealed the potency and suitability of the coatings for defence application. Also [16] evaluated the effect of titanium(iv)oxide particulate fortification on the morphological and mechanical behaviour of binary nano-composite on mild steel. The results indicated the uniqueness of the coating and corroborate the view that nanoparticulates properties cannot always be extrapolated from their bulk property.

Also, [17] investigated the wear trend of plasma coated composite coatings using self generated alumina, it was inferred from their findings the production route dependent nature of the ceramic coating. [18] explored nanocomposite materials for biomedical and energy storage applications. The review demonstrated the immense applications of nanocomposite materials in different fields of biomedicine and engineering. However, this study compared the optoelectronic and electrochemical characteristics of two unique energy storage nanoparticulates oxides (WO_3 and SnO_2) in Zn-TiO_2 nanocomposites matrices for the purpose of their sensor application's potential.

Table 1: Different nanomaterials for the detection of different analyses by using various sensing techniques [3]

Target	Nanomaterials	Detection element	Sensing method
Microorganisms	Silver nanorods	Electrostatic attraction	Surface-enhanced Raman spectroscopy
Spores	Lanthanide doped Nanoparticles	Ethylene diamine tetraacetic acid	Photoluminescence
Bacteria	Magnetic Nanoparticles	Antibodies	Magnetic susceptibility
Bacteria	Gold Nanoparticles	Complementary oligonucleotide	Colorimetry
M. tuberculosis	Carbon nanotubes	Complementary oligonucleotide	Impedance
Pathogenic organisms	Heterogeneous nanowires	Antibodies	Reflectance/PL
Toxin	Quantum dots	Single nucleotide chain	Fluorescence resonance energy transfer
DNA	Magnetic NPs	Electrostatic forces	Polymerase chain reaction

2.0 EXPERIMENTAL PROCEDURE

2.1 Preparation of Substrate

The steel sample dimension (substrate) with composition presented in Table 2 and zinc anode sheet sundergone adequate surface preparation similar to [11].

Table 2: Compositional analysis of the carbon steel [11]

Element %	Content	Element %	Content	Element %	Content
C	0.134	Mo	0.083	Ti	<0.002
Si	0.119	Ni	0.019	V	0.0048
Mn	0.237	Cu	0.044	W	0.024
P	<0.003	Al	0.050	B	>0.016
S	>0.156	Co	0.012	Sn	0.0046
Cr	0.094	Nb	<0.005	Fe	97.70

2.2 Coating Deposition

The low C-steel sample previously prepared was energized by using 10% hydrochloric acid solution for about 5 seconds and then water-rinsed. Before plating, the solution (coating) was prepared at room (normal) temperature by means of deionized water and analar-grade reagents.

To achieve stability of dispersion of the particles in the solution, the formulations of the bath were produced a day in advance and stirred constantly at a velocity of 400 rpm with continual heating at 70ºC throughout the process (plating) [19-21]. The bath formulations used for the different coating matrix was similar to that of [14]. The deposition parameter choice is consistent with research from earlier work [22, 15]. The result is presented in Table 3.

Table 3: Conditions and bath composition for the nano-composites

Sample order	Matrix sample	Time of deposition (min)	Current density (A/cm^2)
1	Zn/TiO_2	20	1.0
2	Zn/TiO_2	20	1.5
3	$Zn/TiO_2/SnO_2$	20	1.0
4	$Zn/TiO_2/SnO_2$	20	1.5
5	$Zn/TiO_2/WO_3$	20	1.0
6	$Zn/TiO_2/WO_3$	20	1.5

2.3 Characterization of the Deposited Coating

The produced coatings obtained were characterized with the scanning electron microscope, model (JSM – 7600F) which was attached with EDS. The three-electrode cell assembly was used in the electrochemical investigations with an PGSTAT 101 Metrohm Autolab Potentiostat in a 3.5% NaCl static solution at room normal temperature. A platinum electrode served as the counter electrode, Ag/AgCl served as the reference electrode, and the produced composite on the substrate functioned as the working electrode.

The electronic and electrical tests were carried out utilizing a four-point probe system and a Keithley 2400 Series meter (source), all of which were connected using multimeters and the Lab View Tracer software. For systems that require a tight connection to the measuring source, Keithley's 2400 Series Source meters were created. Resistance (Sheet) and I-V characteristics were also measured using it. In contrast to the low noise and high repeatability of multimeters, it has read back, precision and low noise power source features.

3.0 RESULTS AND DISCUSSION

3.1 Microstructural Investigations

Figures 1, 2 and 3 illustrate the SEM/EDS spectra of as-received nano particulates of TiO_2, WO_3 and SnO_2**.** The morphological analysis and elemental composition of the as-received nano powders were investigated using SEM and EDS. This was with the view to authenticate the as-received; nano-TiO_2, nano-WO_3, nano-ZnO and nano-SnO_2 respectively. The EDS results confirmed that, those powders were the ones actually ordered for as well as their high purity were evident, since no foreign element in each of the powder's composition.

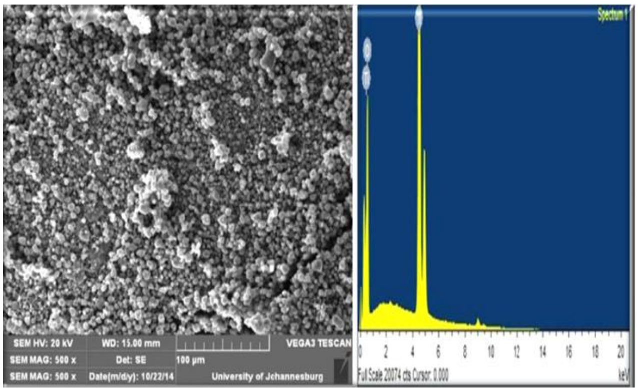

Figure 1: Spectra (SEM/EDS) of as-received nano-TiO_2

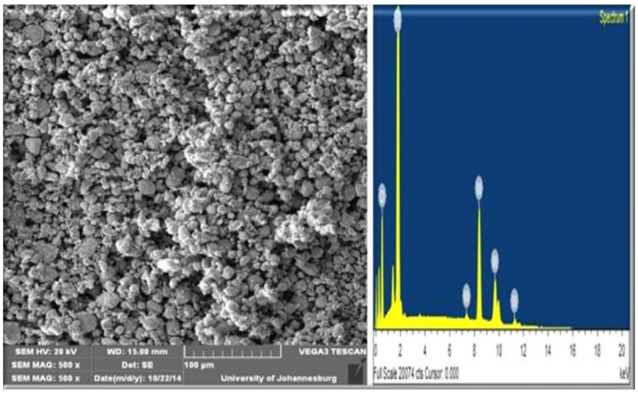

Figure 2: Spectra (SEM/EDS) of as-receivednano-WO_3

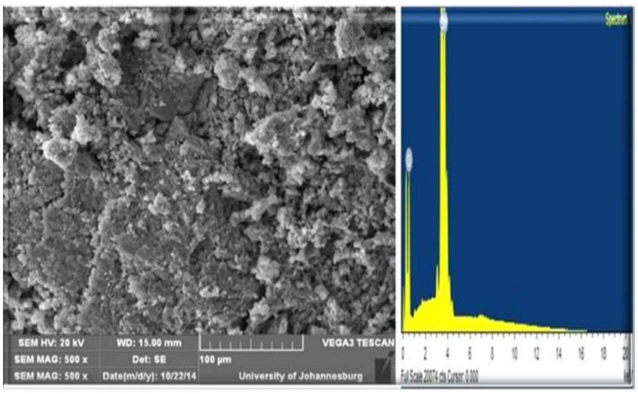

Figure 3: Spectra (SEM/EDS) of as-received nano-SnO_2

3.2 Polarization Measurements

The extrapolated values obtained from Tafel slope's E_{Corr}, I_{Corr}, corrosion rate (CR), as well as polarization resistance (RP) were shown in Table 4. The outcomes demonstrated the coatings' corrosion resistance behavior in a static solution of 3.5% NaCl at a constant scan rate. According to Figure 4 which is polarization diagram for "Zn/TiO_2/SnO_2" as well as "Zn/TiO_2/WO_3" coatings of the nano composite. The addition of SnO_2 and WO_3 nanoparticulate changed the shape of the curve (polarization) but significantly raised the E_{corr} value. These traits suggest that improving this procedure might need adding more additives. The electrochemical curve also shows that the "Zn-TiO_2-WO_3" component had a larger polarization voltage. The principal assessment for the coating with the leastrate of corrosion was Zn/TiO_2/WO_3 at 1.5A, indicating that the WO_3 addition improves the consequence of corrosion opposing capability.

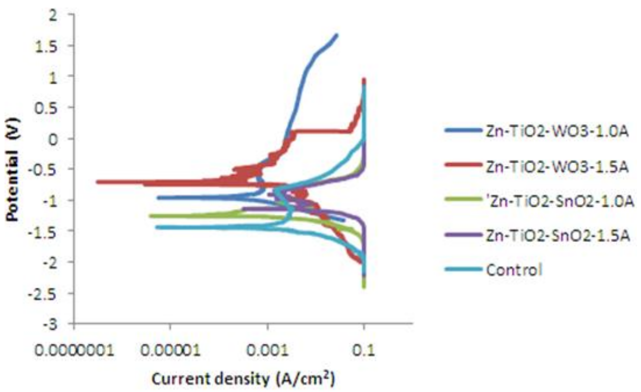

Figure 4: Polarization (Potentiodynamic) curves of the nano-composite coatings on mild steel in NaCl (3.5%) solution

This could be explained by firmness and the nature of the passive film formed by the ternary Zn-TiO_2-WO_3on the coated steel's surface. They display better corrosion resistance produced by ''Zn/TiO_2/WO_3 /1.5A'' on the coated steel's surface. They display better quality than the Zn/TiO_2 series. All coatings showed noticeably improved potential, which might be attributable to the coatings' effects on the film that precipitated at the Zn matrix interface [22]. In contrast to the coated species, the uncoated substrate has less passive coating produced on the surface, which causes strong corrosion attack by the chloride solution, which has a polarization potential of roughly -1.4V. All of the coatings had distinctive coating characteristics. The measurements of polarization results are presented in Table 4 and were based on Tafel extrapolated plots. The subsequent decline in potential might be attributed to a little breakdown of passivity that occurred as the WO_3 concentration was raised. 10-11].

Table 4: The extrapolated data of polarization obtained from Tafel corrosion slope for the nano-composite coatings

Sample	E_{corr} (V)	i_{corr} (A/cm^2)	Corrosion rate (mm/year)	Polarization resistance (Ω)
Control	-0.93099	0.008072	1.7633	2.0199
Zn-TiO_2-SnO_2-15g-1.0A	0.749207	0.002372	0.51816	8.6612
Zn-TiO_2-SnO_2-15g-1.0A	-0.858459	0.003284	0.76435	3.670
Zn-TiO_2-WO_3-8g-1.0A	-0.43435	0.001889	0.41263	7.8281
Zn-TiO_2-WO_3-8g-1.5A	-0.33654	0.001084	0.23677	19.975

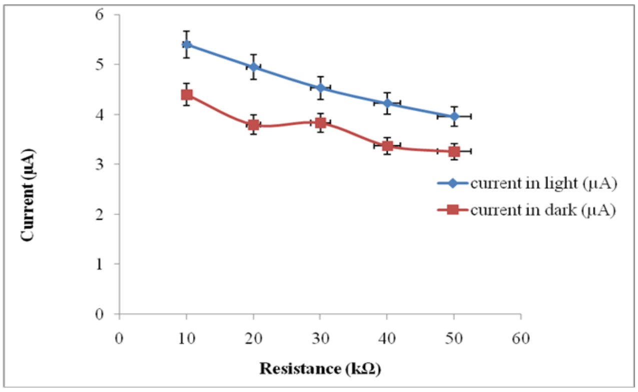

Figure 5: Characteristic plot of current-resistance (I-R) of the Zn-TiO_2 nano-composite coating viewed under dark and light conditions

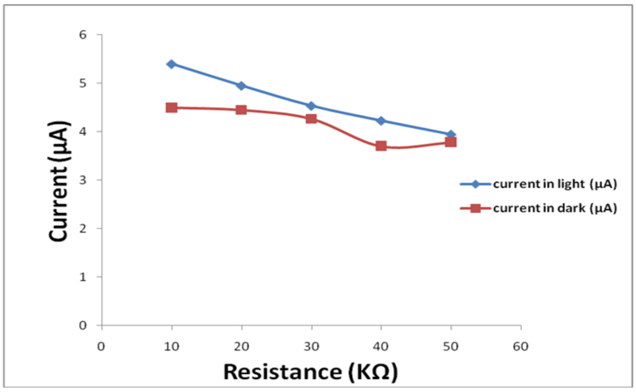

Figure 6: Characteristic plot of current-resistance (I-R) of the Zn-TiO_2-WO_3 nano-composite coating viewed under dark and light conditions

3.3 Opto-electronic Characterization

Figures 5, 6 and 7 present the I-R (Current-Resistance) characteristic plots of coatings Zn-TiO_2 as well as Zn/TiO_2/WO_3 and that of Zn/TiO_2/SnO_2 on the low carbon steel in the presence of light and dark environments while the opto-electronic properties of the nano-composite coating are presented in Table 5. The plots illustrate the trend in which the electric current flows through the nanocomposites coatings at varying resistance during dark and light periods. It was glaring that the irradiation of light favours the coatings current flow. Although, all the samples displayed better performance in the light's presence as compared to the period during dark which could be attributed to the better photo generated electrons transferred during illumination, however, ''Zn/TiO_2/WO_3'' showed the optimal performance [23, 13].

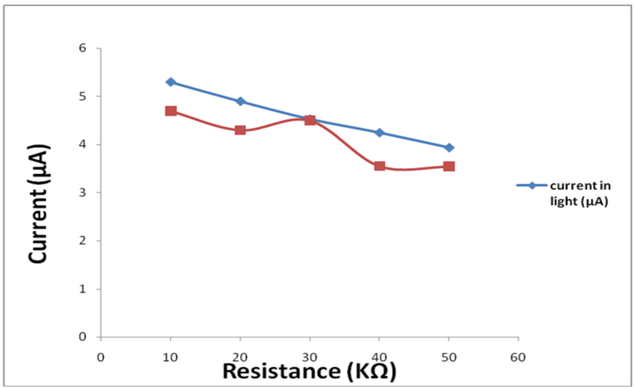

Figure 7: Characteristic plot of current-resistance (I-R) of the Zn-TiO_2-SnO_2 nano-composite coating viewed under dark and light conditions

The sinusoidal nature shown when it was dark condition (Figure 5) which could be as a result of presence of SnO_2 and WO_3 (material with the capability to store energy) in the coating matrix though WO_3 displayed a better performance which made it a better sensor material. The electrical conductivity of the nanocomposites coatings (Figure 8) further confirmed the enhanced electrical conductivity performance of particles loading effect of tungsten oxide and tin(iv)oxide nano composites with optimal performance using tungsten(vi)oxide. The result is also in good conformity with [23-24, and 13]

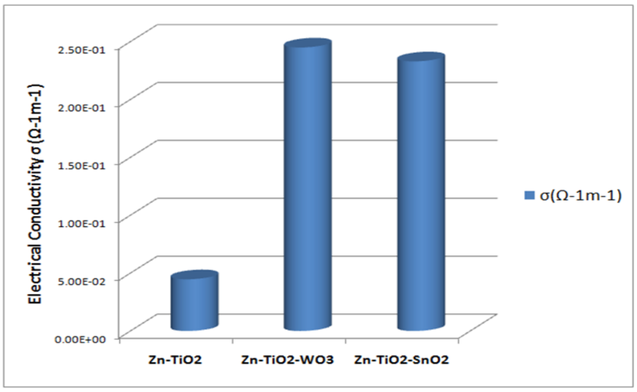

Figure 8: Electrical conductivity behaviour of the nanocomposites coatings

Table 5: The opto-electronic properties of the nano-composite coating

Sample	V/I (Ω)	R_S	t(µm)	ρ (Ω.µm)	ρ (Ωm)	$\sigma(\Omega^{-1}m^{-1})$	$\sigma(\Omega^{-1}cm^{-1})$
Zn-TiO_2	8.24E+04	3.73E+05	60	2.24E+07	2.24E+01	4.47E-02	4.47E+00
Zn-TiO_2-WO_3	2.25E+04	1.02E+05	40	4.08E+06	4.08E+00	2.45E-01	2.45E+01
Zn-TiO_2-SnO_2	2.05E+05	4.52E+04	95	4.29E+06	4.29E+00	2.33E-01	2.33E+01

4.0 CONCLUSION

1. SnO_2 as well as WO_3 nanoparticulates were used to fabricate nanocomposites of Zn-TiO_2-WO_3 coatings via chloride bath. The coatings were excellent with unique properties
2. the electrical conductivity of the Zn-TiO_2-WO_3 nano-composite coatings displayed a better electrical conductivity of 2.45E-01$\Omega^{-1}m^{-1}$
3. Zn-TiO_2-WO_3 nano-composite coated steel sample displayed better sensor potential

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