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RESEARCH ARTICLE

Corrosion Behavior of Ag Doped Bi_2O_3 Nano Composite†

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Abstract: Nano particles of silver and bismuth oxide have been synthesized by an eco-friendly, cost effective green mediated method using methanolic extract of Cleistanthus Collinus. Also, Ag doped Bi_2O_3 nano particles have been prepared and characterized using XRD, SEM and EDAX analysis. The Ag doped Bi_2O_3 nanoparticles have been coated over mild steel substrate and the corrosion behaviour has been studied.

Keywords: Green synthesis, Cleistanthus Collinus, Corrosion

Introduction

Nano systems are expected to find various unique applications. Nanostructured materials can be made with unique nanostructures and properties. This field is expected to open new venues in science and technology[1]. Metal and oxides of metal nano particles are of particular interest for their mechanical, electrical, magnetic, optical, chemical and other special properties[2-11]. They have better malleability and ductility compared to bulk materials. These are made of tight cluster of very small particles resulting in overlapping electron clouds that induce quantum effect resulting in more efficient conduction of light or electricity[12]. Nano structured silver and bismuth oxide have more important applications in various fields such as catalysis, sensors and biomedicine[13-15]. The physicochemical and optoelectronic properties of metallic nano particles are strongly dependent on the size, shape and its distribution[16,17]. Bismuth oxide having enhanced photon scattering due to classical size effects can be realized without compromising the electronic conduction via nano-scale material inclusion to scatter heat conducting phonons[18,19]. So far most advances of thermo electric performance via nano structuring have been attained through this approach and the quantum confinement can increase thermopower. The silver and bismuth oxides are prepared by using chemical methods like sol gel method[19-23], hydrothermal[24] and Co precipitation method[25,26]. These chemical methods are toxic, capital intensive and have low productivity[27]. In the past few years, the living organisms such as bacteria[28], fungi[29], yeast[30] and plant biomass like plant extract[31-32] are used for the biosynthesis of various metals and metal oxide nano particles. This is simple, cost -effective and eco-friendly method with control

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over the size and shape. The size control and morphology of the resultant nanostructures can be related to the interaction between biomolecules and metal atoms.

Cleistanthus Collinus contains lignan lactone glucosides like Cleistanthin A and Cleistanthin B. Genin (Diphyllin) is the major metabolite of these lignan lactone glycosides. The other lignin glycosidein in this plant is Collinusin. These are toxic aryl naphthalene lignin lactones. Cleistanthin A is used in chinese medicine as sheng bai xin[33]. So this extract was chosen for the synthesis of the silver and bismuth oxide nanoparticles. In the present study silver and bismuth oxide nano particles have been synthesized by using Cleistanthus Collinus methanolic extract. Finally this silver is doped in bismuth oxide by using simple chemical method.

Metals used for manufacturing automobile parts, building materials *etc*., tend return to their more stable state, the oxidised state which causes surface deterioration and changes on structural metal properties. It can be damaging and expensive to control. The present work analysed the corrosion inhibition effect of this product was carried out by using mild steel in 3.5% sodium chloride environment.

Experimental

All analytical reagents used in this experiment were of highest purity and obtained from Sigma Aldrich (Bangalore, India) and media components were purchased from Hi-Media (Mumbai, India) and fresh, green leaves of Cleistanthus Collinus plant were collected from Mallur village (Tamil Nadu, India) in Salem district.

Preparation of plant extract

The leaves of Cleistanthus Collinus plant were dried at room temperature and powdered well. Then 10 g of dried powder was mixed with 100 mL of ethanol and the mixture was heated at 60 ^{o}C for 2 h. It was filtered by using Whatman filter paper (No.1) and the filtrate was collected. This ethanolic extract was used as stock solution for the study.

Synthesis of silver nanoparticles

10 mL of Cleistanthus Collinus plant ethanolic extract was mixed with 90 mL of 1 mM $AgNO_3$ aqueous solution in 250 mL conical flask. The reaction mixture was heated at 80 ^{o}C for one hour. The light brown coloured solution changed into dark reddish brown which shows the reduction of Ag^+ ions to metallic Ag.

Synthesis of Bi_2O_3 nanoparticles

The procedure adopted was followed above for synthesizing Bi_2O_3 nanoparticles. The colour change from yellow to light brown which showed the formation of bismuth oxide nanoparticles.

Synthesis of Ag doped Bi_2O_3 nanoparticles

The Bi_2O_3 and Ag nanoparticles synthesized were combined together in the ratio of 2:1 and refluxed for 2 h. It was centrifuged at 8000 rpm and dried to get Ag doped Bi_2O_3 nanoparticles.

Characterization

IR Spectroscopy

The binding properties of Ag, Bi_2O_3 nanoparticles synthesized from methanolic extract of Cleistanthus Collinus leaf and Ag doped Bi_2O_3 nanoparticles were investigated by bruker vertex70 FTIR spectrometer. Dried and powdered Ag nanoparticles were pelleted with Potassium bromide and the results were recorded (Figure 1).

XRD

The Ag, Bi_2O_3 nano particles synthesized by Cleistanthus Collinus leaves extract and Ag doped Bi_2O_3 nanoparticles were subjected to the x-ray diffraction. This was carried out using Cu-Kα radiation source in PANalytical X'per PRO model x-ray powder diffractometer. XRD was done using nanoparticles coated glass substrate at an operating voltage of 45kV and a current of 40 mA. Full width at half maximum (FWHM) data was used in Scherer's formula to determine mean particle size. The equation is as follows:

$$d = 0.9 \lambda / \beta \cos\theta$$

Where d is the mean diameter of the nanoparticles, λ is wavelength of x-ray radiation source, β is the angular FWHM of the XRD peak at the diffraction angle θ.

SEM and EDAX

After the bioreduction of silver ions, Bi_2O_3 and Ag doped Bi_2O_3 nano particles were mounted on specimen stubs and analysed by using the EDAX attached SEM which was characterized provided the size, shape of nano particles and confirmed the presence of specific element (Figures 4-6).

Corrosion studies

Steel plate with an area 1 cm^2 with 1.5 mm thickness was used as the cathode, the Ag doped bismuth oxide mixed with 0.01 g PVA in ethanol. Then the paste was coated on steel plate by using spin coating method. Then the plate was dried at 120 ^oC in hot air oven for 10 minutes. The coated steel plate was used for corrosion studies. For electrochemical corrosion measurement a biologic science instrument was used with EC Lab Software, a three electrode open cell with nano structured Ag doped Bi_2O_3composite coatings as working electrode (WE), Platinum electrode as counter electrode (CE) and calomel electrode as reference electrode(RE). As 3.5% NaCl solution was used at room temperature.

EIS measurements were done using initial frequency 10000 mHz and final frequency 0.01 Hz AC sine wave amplitude of 10 mV; frequency per decade 10 Hz delay before integration 1S. The impedance spectra were recorded on sample after 30 minutes. All the recorded impedance spectra were analysed as nyquist diagrams.

For polarisation measurements were done, the polarisation curves were recorded after 30 minutes of immersion. I_{corr} for the particular steel specimens was determined by extrapolating the anode and the cathode Tafel curves.

Results and Discussion

The FT-IR broad band at 3410 cm^{-1} due to the stretching vibration and deformation vibration mode of hydroxyl group.2917.34 cm^{-1} refers to the stretching C-H vibration of alkyl group. The IR bands at 900 cm^{-1} to 1383.36 cm^{-1} could be assigned to Bi-O-Ag Stretching vibrations.

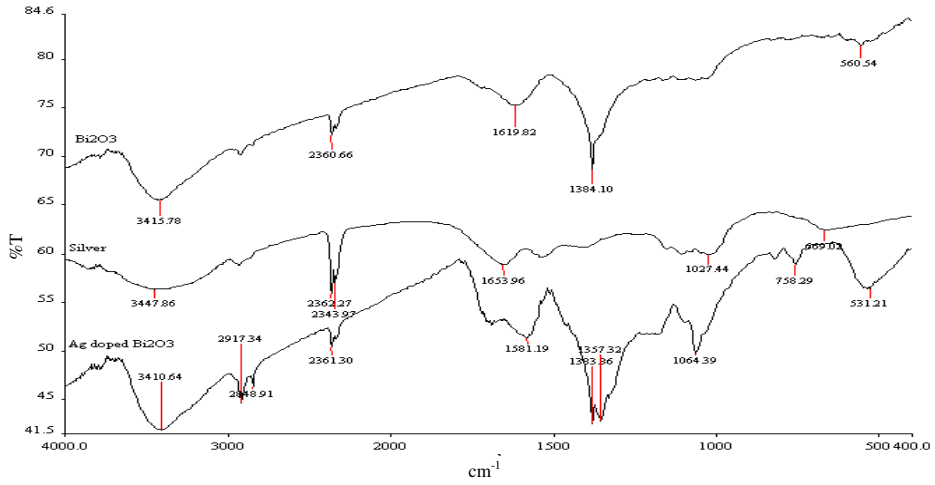
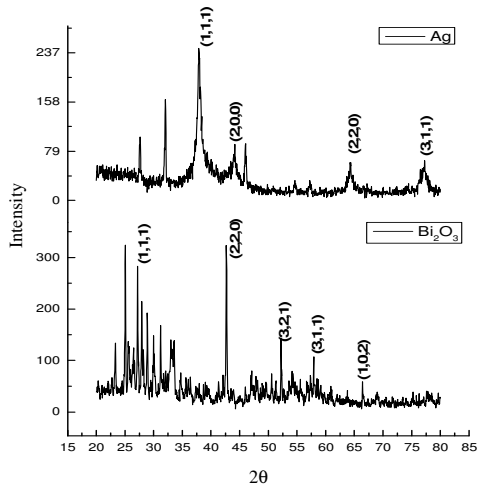


Figure 1. The FT IR results for (i) Bi_2O_3 (ii) Ag (iii) Ag doped Bi_2O_3



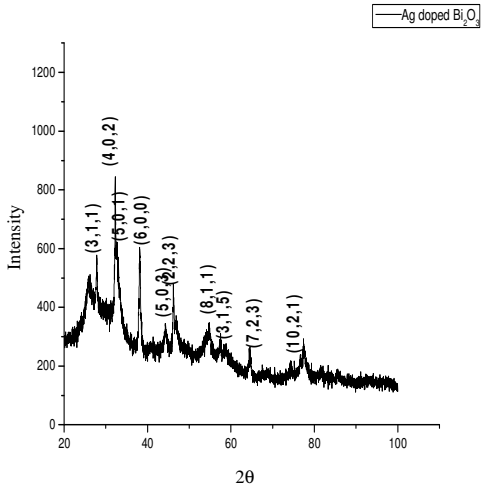


Figure 2. The XRD results of (i) Ag (ii) Bi_2O_3 **Figure 3.** The XRD result of Ag doped Bi_2O_3

Figure 2 and 3 shows XRD of Ag, Bi_2O_3 and Ag doped Bi_2O_3.These peaks are attributed to crystal planes (110), (200), (220), (311), Bi_2O_3 for Ag , (110),(220),(321),(311),(102) for Bi_2O_3 and (311),(402),(501),(600),(503),(223),(811),(315),(723),(1021) for Ag doped Bi_2O_3. It shows the formation of Ag doped Bi_2O_3 and its in orthorhombic system and its primitive lattice (pdf Number-87-0866).The grain size of Ag doped Bi_2O_3 was 39.22 nm.

SEM and EDAX

EDAX results for (i) Ag (ii) Bi_2O_3 (iii) Ag doped Bi_2O_3

Figure 4 & 5 shows the formation of Ag and Bi_2O_3 showed predominantly cubic shaped Ag and monoclinic Bi_2O_3 nanoparticles .Also the results the uniform distribution of Ag and Bi_2O_3 nanoparticles. The average size of Ag nano particle was 131 nm and Bi_2O_3 was 170.5 nm. In EDAX results (Figure 6 a & b), the silver nanoparticles was exhibited an optical

absorption band peak at 3 keV and Bi_2O_3 was exhibited an optical absorption band peak at 2.5 keV. This represents the typical absorption of Ag and Bi_2O_3 nanoparticles .The SEM and EDAX results confirm the presence of noble Ag and Bi_2O_3 nanoparticles.

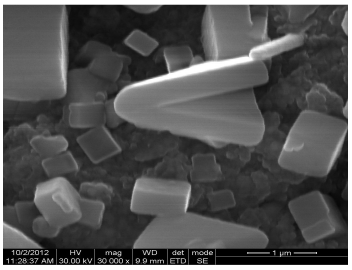


Figure 4. The SEM for Ag nanoparticles

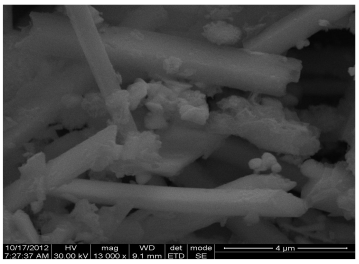


Figure 5. The SEM for Bi_2O_3 nanoparticles

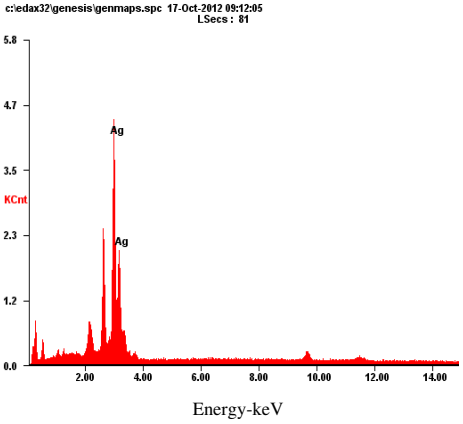


Figure 6 (a). EDAX results for Ag nanoparticles

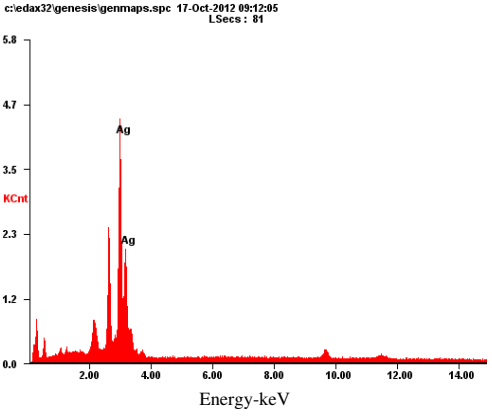


Figure 6 (b). EDAX results for Bi_2O_3 nanoparticles

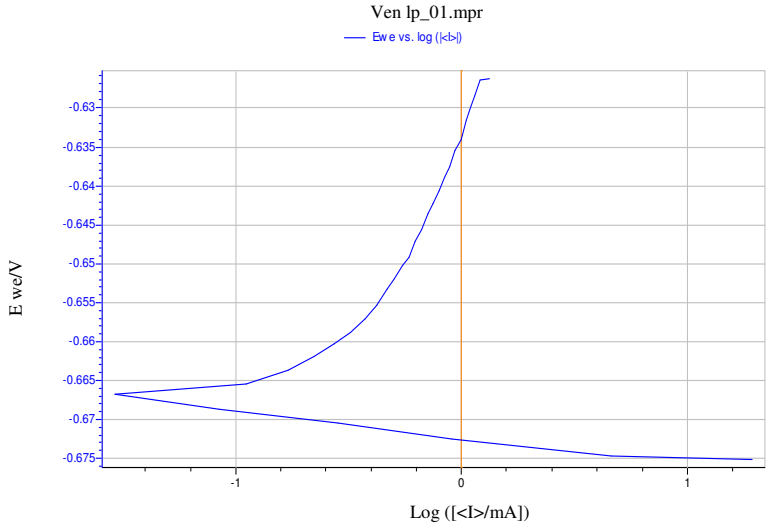


Figure 7. Tafel diagram for bare mild steel (Blank)

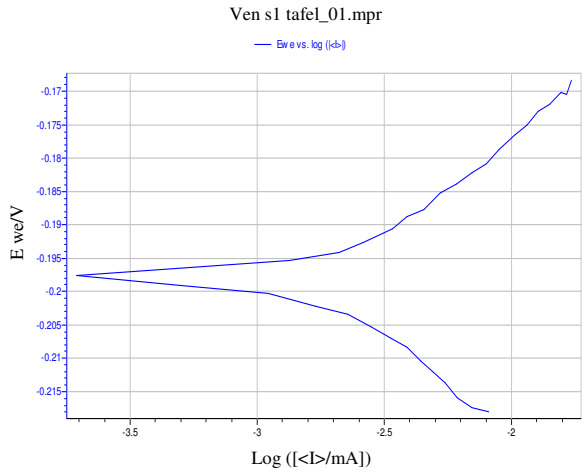


Figure 8. Tafel diagram for Ag doped Bi_2O_3

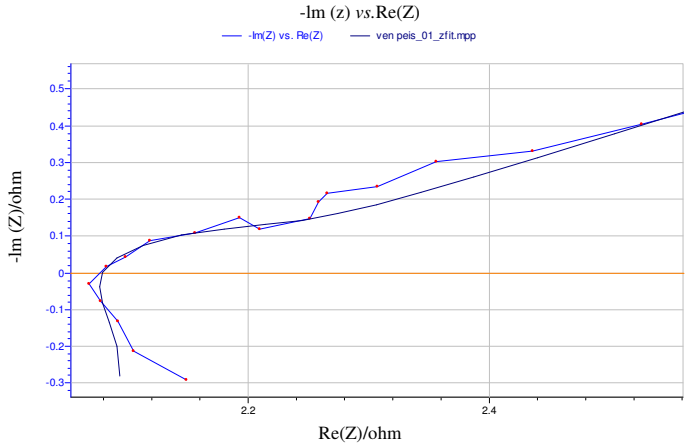


Figure 9. Nyquist impedance diagram for mild steel

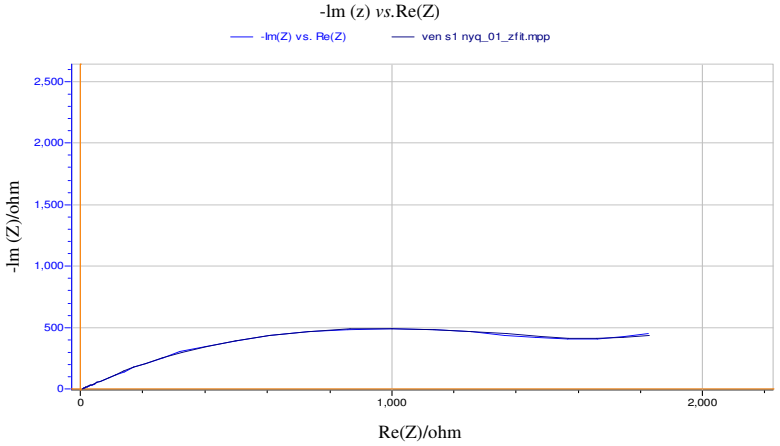


Figure 10. Nyquist impedance diagram for Ag doped Bi_2O_3

Corrosion studies

The corresponding polarisation resistance (Figure 7 & 8) and capacitance values from impedance diagrams (Figure 9 & 10) for bare mild steel and Ag doped Bi_2O_3 nano composite in 3.5% NaCl using equivalent circuit are tabulated. For blank, after 30 minutes of immersion of steel plate, the polarization resistance was decreased and the polarisation resistance of nano composite coatings in 3.5% NaCl was increased.

The performed potentiometric polarization results for nano structured Ag doped Bi_2O_3 composite coating on mild steel in 3.5% NaCl are presented in Table 1. The quantitative information on corrosion currents and corrosion potentials were extracted from the slope of the curves using the sterm-Geary equation,

$$i_{corr} = \frac{1}{2.303Rp}\left[\frac{\beta a + \beta c}{\beta a + \beta c}\right]$$

- i_{corr} is the corrosion current density in Amps/cm^2;
- Rp is the corrosion resistance in ohms cm^2;
- βa is the anodic Tafel slope in Volts/decade or mV/decade of current density;
- βc is the cathodic Tafel slope in Volts/decade or mV/decade
- The quantity, $(\beta a \cdot \beta c)/(\beta a + \beta c)$, is referred to as the Tafel constant.

The corrosion potential is shifted to more negative values for nanostructured coatings in 3.5% NaCl (-200.50 mV). The rate of corrosion was calculated from the i_{corr}, corrosion current density, D the density, M the atomic mass of specimen and v the valence entered in tafel calculation box.

$$\text{Rate of corrosion (mmpy)} = \frac{i_{cor\,r}(A/cm^2)xM(g)}{D(g/cm^3)xV} x3270$$

The blank and coated specimens were compared in terms of impedance and polarisation values in 3.5% NaCl. The improvement of corrosion resistance could be due to the fine surface structure of composite coating compared to blank. The experimental data showed the corrosion rate as 2.2712 mmpy (Blank) and 0.016818 mmpy (coated sample).

Table 1. Corrosion potential (Ecorr), Current density (Icorr), Anodic /Cathodic tafel slopes (β a & β c) and Corrosion rate of Ag doped Bi2O3 coated mild steel.

Solution (3.5% NaCl)	E_{corr}, mV	i_{corr}, μA/cm^2	β_a, mV/decade	B_c, mV/decade	Rate of corrosion, mmpy
Blank	-671.656	283.325	70.0	2.1	2.271 3
Sample coated steel	-200.500	2.108	31.5	34.8	0.0169

Conclusion

It could be concluded that the coating layers of Ag doped Bi_2O_3 was homogeneously distributed on the mild steel surface. The effect of Ag doped Bi_2O_3 could be an effective protective coatings for mild steel against corrosion in 3.5% NaCl solution.

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