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Chemical Synthesis, Thermochemical, Electrochemical and biological behaviour of MoO_3-ZrO_2 mixed oxide nanoparticles

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Abstract

Nano MoO_3-ZrO_2 mixed oxides were prepared by using wet chemical method by mixing equimolar solutions of Ammonium molybdate(0.1M) and Zirconium oxychloride(0.1M) in 1M aqueous Sodium hydroxide and it refluxed at elevated temperature. The prepared nano MoO_3-ZrO_2 mixed metal oxide nanoparticles were characterized byTEM, TGA,DTG,DSC,CV and antibacterial activity studies. The size of synthesized nanoparticles was further confirmed by TEM and it was found to be nm. Synthesized mixed oxide nanoparticles withstand thermal stability as they possess high surface area. Cyclic voltammetric studies the mixed metal oxide nanoparticles exhibited good adherent behaviour on electrode surface and revealed good electroactivity. The mixed metal oxide nanoparticles are moderately sensitive to Antimicrobial organisms.

Keywords:TEM,MoO_3-ZrO_2, CV,Antibacterial activity.

1. Introduction

Nanotechnology can be defined as the manipulation of matter through certain chemical and/or physical processes to create materials with specific properties, which can be used in particular applications [1]. Oxide Nanoparticles can exhibit unique physical and chemical properties due to their limited size and a high density of corner or edge surface sites. Particle size is expected to influence three important groups of proxperties in any material [2].

Nano scale particles have emerged as novel antimicrobial agent owing to the high surface area to volume ratio, which is coming up as the current interest in the researchers due to the growing microbial resistances against metal ions, antibiotics and the development of resistant strains [3].

Antimicrobial agents are of high relevance in numerous commercial applications such as in packaging industries, environmental, textiles and medical products to name a few [4]. However indiscriminate use of antibiotics has led to bacterial resistance to the antimicrobial drugs thereby triggering a greater need for efficient antimicrobial agents to which bacteria might not develop resistance [5].

The thermo gravimetric data collected from a thermal reaction is compiled into a plot of mass or percentage of initial mass on the y axis versus either temperature or time on the x-axis. This plot, which is often smoothed, is referred to as a TGA curve. The first derivative of the TGA curve (the DTG curve) may plotted to determine inflection points useful for in-depth interpretations as well as differential thermal analysis.A TGA can be used for materials characterization through analysis of characteristic decomposition patterns.

Differential scanning calorimetry or DSC is a thermo-analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. The main application of DSC is in studying phase transitions, such as melting, glass transitions,or exothermic decompositions. These transitions involve energy changes or heat capacity changes that can be detected by DSC with great sensitivity.

2. Experimental Methods

2.1 Preparation of ZrO_2nano metal oxide nanoparticles

Zirconia nanoparticles were synthesized by using Zirconium oxychloride and sodium hydroxide as precursors. All the reagents were of analytical grade and used without further purification. The entire process was carried out in deionised water for its inherent advantages of being simple and environment friendly. In a typical preparation, solution of 0.1M Zirconium oxychloride was prepared in 100ml of deionised water and then aqueous solution of (100ml, 1M) Sodium hydroxide was added dropwise to this solution making a final volume of 100ml. This mixture was stirred well for 1hour and refluxed at 70-80ºC which resulted in the formation of white powder of zirconia nanoparticles.The precipitate was separated from the reaction mixture,washed several times with deionised water to remove the impurities.The precipitate was dried at room temperature.

2.2 Preparation of Moo_3-ZrO_2 mixed oxide nanoparticles

MoO_3-ZrO_2 mixed oxide was prepared at room temperature by wet chemical method. 100ml of 0.1M solution of Zirconium oxychloride, 100 ml of 0.1M solution of Ammonium molybdate and 100ml of 1M solution of sodium hydroxide were prepared by deionised water. Zirconium oxychloride and Ammonium molybdatesolutions were mixed.Sodium hydroxide solution(100ml,1M) was added dropwiseto the above mixture. The resulting solution was stirred for 1hour and this solution was refluxed for 2-3 hours at 70-80ºc which resulted in the formation of white powder of mixed oxide nanoparticles. Sodium hydroxide is used as a capping agent.The precipitate was filtered and the filterate was washed several times with distilled water to remove the impurities.The precipitate was dried at room temperature.

2.3 Characterization

The exact nano meter size of the particle was characterized by computer controlled PHILIPSCM200 operating voltages: 20-200kv resolution. 2.4A° Transmission Electron Microscopy was used.The electrochemical behavior of metal oxide nanoparticles have been investigated throug CH-Instrument Inc., TX, USA.Thermal analysis studies were carried out by using Differential Scanning Colorimeter(DSC), Thermogravimetric Analysis(TGA) and Differential Thermogravimetry(DTG).

2.4 Antibacterial Activity

2.4.1 Preparation of test micro organisms

A roomful of the test organism was transferred to already sterilized 10 ml Nutrient agar and incubated overnight at 37^0C for bacteria and 30^0C for fungi. *Aspergillusniger* was cultured as a slant culture in an acidified PDA (Potato Dextrose Agar) media. 25 ml of sterilized Muller-Hinton Agar (MHA) (Hi Media, Mumbai, India) was poured in petriplates and allowed to solidify at room temperature on which the test organisms were inoculated.

2.4.2 Antimicrobial assay

The antimicrobial activity was measured by Disc Diffusion method. The sterile discs were impregnated with the known concentration of the various extracts (15 µl) and standard drugs. The discs were then placed on the already inoculated petridishes containing the inoculum of test microbes in such a way that there is no overlapping of the zones of inhibition. The seeded plates were then incubated at 37^0C for 24 hours and 48 hours for bacteria and fungi respectively. The antimicrobial activity of the animal extracts was recorded as the mean diameter of the resulting inhibition zone of growth measured in millimetres.

From the results, the Active Index (AI) and Proportion Index (PI) were calculated using the following formulae,

$$\text{Active Index (AI)} = \frac{\text{Inhibition zone of the test sample}}{\text{Inhibition zone of the standard}}$$

$$\text{Proportion Index (PI)} = \frac{\text{Number of positive results obtained for individual extract}}{\text{Total number of tests carried out for each extract}}$$

3. Result and Discussion

The characterization results of the synthesized mixed metal oxide nanoparticles are described below by various techniques. The results obtained are discussed in detail as follows.

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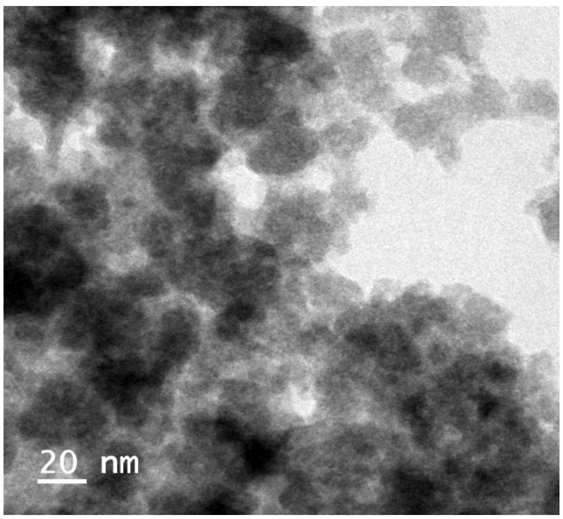
3.1 TEM ANALYSIS

The size of synthesized nanoparticles were further confirmed by TEM. The Transmission Electron Microscopy (TEM) image of MoO_3-ZrO_2 mixed oxide is prepared from 0.1M concentration of Zr and Mo ion are shown in (Fig:1). These images shows that the particles formed are of nearly spongy shape of morphology. The size of nano MoO_3-ZrO_2 mixed oxide is found to be nm (Fig:1)[6]

Fig: 1 TEM images of MoO_3-ZrO_2 mixed oxide nanoparticles



3.2 TGA, DTG and DSC Analysis

The TGA curve of MoO_3-ZrO_2 mixed oxide nanoparticles shows that in Fig: 2. The TGA curveofMoO_3-ZrO_2 mixed oxide nanoparticles degradation about 300˚C and the temperature of decomposition was around 600˚C(Fig: 2).TGA curve result indicated that the mixed oxide nanoparticles increased at higher temperature and maximum amount is found that 25% by weight.The TGA/DTG curve of mixed oxide nanoparticles shows that peak appears at 84˚C and derivative weight loss of mass4%.The TGA/DTG curve of mixed oxide nanoparticles shows that one endothermic peak at 84˚C [7][8].

The Differential Scanning Calorimeter (DSC) is a primary technique for measuring the thermal properties of materials to establish a connection between temperature .It can also be used to study the oxidative stability of samples and optimum storage conditions. The gradual loss of water starts from the surface of nanoparticles at 40^0C up to 200^0C. The MoO_3-ZrO_2 sample heat from 40°C to 995°C at 20°C/min. The sample showing different reactions were happened. In the MoO_3-ZrO_2 mixed oxide nanoparticle shows that one endothermic peak at 950°C. This is due to change of phases at that temperature[9].

The glass transition temperature (T_g),Crystallization temperature(T_C) and melting point(T_M) of nano MoO_3-CeO_2 mixed oxides are determined from the DSC curve(Fig:2). The Tg value of MoO_3 is 52.88^{0}C, T_C value of MoO_3 is 64.68^{0}C and it is melted at a temperature of 84.79^{0}C.

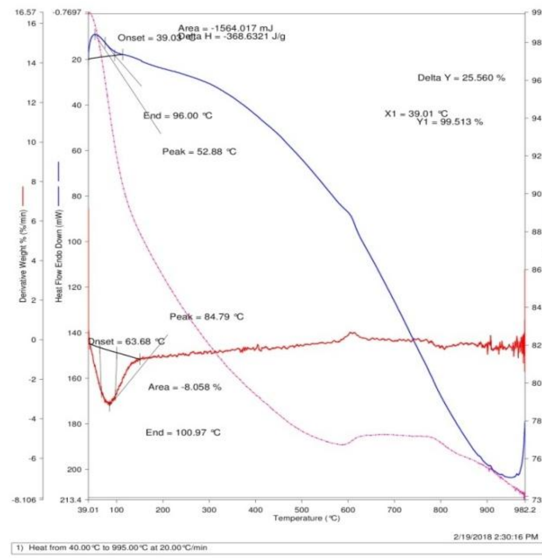


Fig:2 TGA,DTG and DSC curve of MoO_3-ZrO_2 mixed oxide nanoparticles

3.3 Cyclic Voltammetry

Cyclic voltammetricbehavior of the nano mixed oxides are recorded. The potential window is between 0 to 0.5V on GCE at 50mv/s. Cyclic voltammetricbehavior of ZrO_2 showed one oxidation peak (Fig: 3) at 0.167V which is due to the presence of ZrO2.

Cyclic voltammetricbehavior of nano MoO_3-ZrO_2 (0.1M) mixed oxide shows one oxidation peak at 0.185V which is entirely different from the behavior of MoO_3 confirms the formation nano MoO_3-ZrO_2 mixed oxide(Fig:4). Cyclic voltammetricbehavior of ZrO_2 mixed oxide at different scan rates are shown in (Fig: 5). Cyclic voltammetricbehaviorof MoO3-ZrO_2 mixed oxides at different scan rates are shown in (Fig: 6). Thus the mixed oxides act as a good adherent behavior on electrode. Thus the mixed oxides act as corrosive

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resistance agents. These facts revealed that the voltammetric redox behavior of mixed metal oxide nanoparticles are controlled by adsorption process.[10]

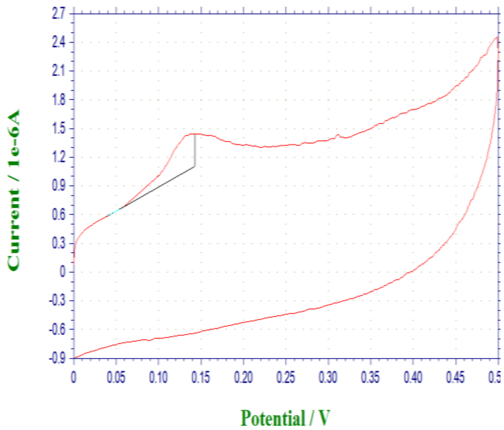

Fig:3 Cyclic Voltammogram of ZrO_2

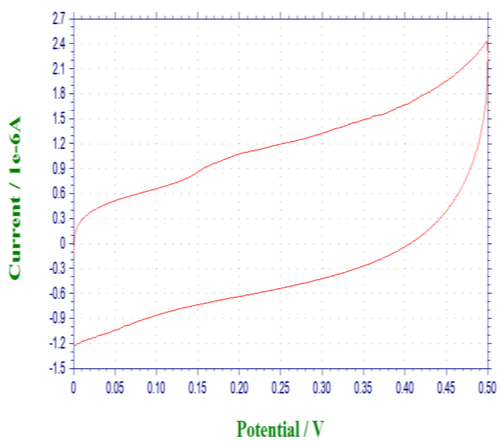

Fig:4 Cyclic Voltammogram of nanoparticles MoO_3-ZrO_2 nanoparticles

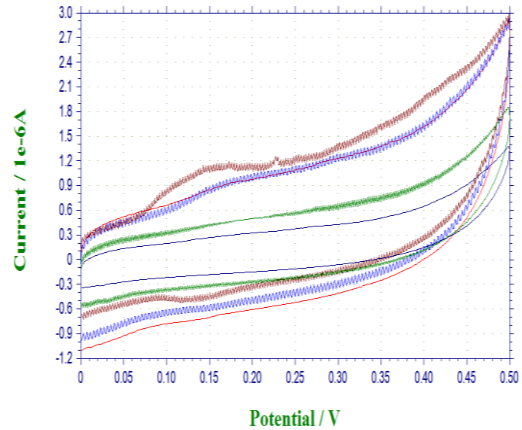

Fig: 5 Cyclic Voltammogram of ZrO_2

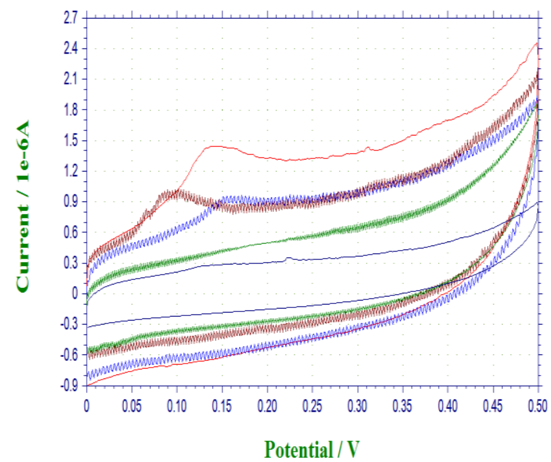

Fig: 6 Cyclic Voltammogramof MoO_3- ZrO_2

Nanoparticlesat different scanrate nanoparticles at different scan rate (0.05, 0.04,0.03,0.02,0.01mVS^{-1})

3.4Antibacterial Activity

The antibacterial activity of ZrO_2 nanoparticles was evaluated by measuring the zone of inhibition against the test organisms. The sizes of the zones of growth inhibition are presented in Table. The results indicated that ZrO_2 nanoparticles synthesized and showed effective antibacterial activity against all tested strains. ZrO_2 nanoparticles showed antibacterial activity against pathogenic *E.Coli*, *S. Typhi*, *K.pneumonia*respectively compared to standard Oflaxcin values. Moreover, the antibacterial activity of Oflaxcin is famous. The presented ZrO_2

Name of the organism	Zone of Inhibition (mm)										
	Petroleum ether (40^0-60^0C)		Benzene		Chloroform		Ethanol		Water		Standards
	DIZ*	AI#	DIZ*	AI#	DIZ*	AI#	DIZ*	AI#	DIZ*	AI#	
Bacillus Cereus	9	0.92	7	0.07	16	1.16	14	1.14	12	1.12	7
Bacillus subtilis	-	0	-	0	-	0	-	0	-	0	8
Staphylococcus aureus	-	0	11	1.11	-	0	-	0	-	0	12
Escherichia coli	-	0	-	0	-	0	14	1.13	14	1.14	11
Klebsiella pneumonia	-	0	-	0	-	0	16	1.22	21	1.28	16
Salmonella typhi	-	0	-	0	-	0	20	1.24	18	1.19	14

Name of the sorganism	Zone of Inhibition (mm)										
	Petroleum ether (40^0-60^0C)		Benzene		Chloroform		Ethanol		Water		Standards
	DIZ*	AI#	DIZ*	AI#	DIZ*	AI#	DIZ*	AI#	DIZ*	AI#	
Bacillus Cereus	-	0	-	0	-	0	-	0	-	0	7
Bacillus subtilis	-	0	-	0	-	0	3	0.08	2	0.06	8
Staphylococcus aureus	-	0	-	0	-	0	-	0	-	0	12
Escherichia coli	-	0	-	0	-	0	11	1.02	14	1.07	11
Salmonella typhi	-	0	-	0		0	21	1.29	15	1.06	14

nanoparticles are compounds obtained by using biological material. In addition, ZrO_2 nanoparticles show similar efficacy.

The antibacterial activity of mixed MoO_3-ZrO_2 nanoparticles was evaluated bymeasuring the zone of inhibition against the test organisms. The sizes of the zones of growth inhibition are presented in Table. The results indicated that MoO_3-ZrO_2 nanoparticles synthesized and showed effective antibacterial activity against all tested strains. MoO_3-ZrO_2 showed antibacterial activity against pathogenic *E. Coli, S. Typhi, K.pneumonia*respectively compared to standard Oflaxcin values. Moreover, the antibacterial activity of Oflaxcin is famous. The presented MoO_3-ZrO_2 nanoparticles are compounds obtained by using biological material. In addition MoO_3-ZrO_2 nanoparticles show similar efficacy.

3.4.1 Antibacterial Activityof ZrO_2 nanoparticles

3.4.2 Antibacterial Activityof MoO_3 –ZrO_2 nanoparticles

Conclusion

TEM microscope also confirmed the particle size of the mixed oxide nanoparticles are in the nano scale range.TGA, DTG and DSC studies revealed the thermal stability of the synthesized mixed oxide nanoparticles.Synthesized mixed oxide nanoparticles withstand thermal stability as they possess high surface area.Cyclic voltammetric studies the mixed metal oxide nanoparticles exhibited good adherent behaviour on electrode surface and are adsorption controlled and revealed good electroactivity.The mixed metal oxide nanoparticles are moderately sensitive to Antimicrobial organisms and thus it can be investigated for further medicinal applications.

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