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Synthesis,Electrochemical Characterization Of MoO_3-CeO_2 Mixed Oxide Nano Particles

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Abstract: Nano MoO_3-CeO_2 mixed oxides were prepared by wet chemical method by mixing equimolar solutions of Ammonium molybdate(0.1M) and Cerium nitrate(0.1M) in aqueous Sodium hydroxide and refluxed at elevated temperature. The prepared nano MoO_3-CeO_2 mixed oxides were characterized by UV-Vis,TEM and CV studies. The absorption peak for MoO_3-CeO_2 mixed oxide has been found to be at 348nm.The blue shifted absorption peaks of simple and mixed metal oxide nano particles showed nano scale effect.The size of synthesized nano particles were further confirmed by TEM and it was found to be 170nm. Cyclic Voltammetric studies exhibit good adherent behaviour on electrode surface and good electroactivity at pH 1.0.
Keywords:MoO_3-CeO_2 ,UV-Vis, Cyclic Voltammetry, TEM.

Introduction

Metal oxides play a very important role in many areas of chemistry, physics and materials science[1]. The metal elements are able to form a large diversity of oxide compounds[2]. These can adopt a vast number of structural geometries with an electronic structure that can exhibit metallic, semiconductor or insulator character. In technological applications, oxides are used in the fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings for the passivation of surfaces against corrosion, and as catalysts. In the emerging field of nanotechnology, a goal is to make nano structures or nano arrays with special properties with respect to those of bulk or single particle species[3].

Ceria (CeO_2) is an important rare-earth oxide that has been attracting a-growing attention because of its varied applications in fuel cells,[4]-[8] oxygen gas sensors,[9]polishing agents,[10] oxygen permeation membrane systems,[11][12] and as catalysts for different technologically important processes.[13]-[18] Ceria is an essential component of the three-way catalyst (TWC), which is being used for environment cleaning purposes, as well as different emerging fields of catalysis such as oxidation of hydrocarbons,[19] removal of total organic carbon from waste,[20] automobile exhaust gas conversion, and in deNOx reactions[21][22]. The possibility of transformation from Ce^{3+} and Ce^{4+} aids in accepting or removing oxygen from ceria. In addition, the fluorite structure of ceria or doped ceria has superior chemical and physical stability[23]. Pure CeO2 alone as a catalyst is probably of little interest because of its low textural stability under high-temperature conditions, usually encountered in exhaust gases. At high temperatures, not only does the surface area of CeO_2 reduce drastically, but it also loses its redox properties and oxygen storage capacity[24] It has been observed that ceria with suitable dopants (specially rare-earth oxide) improves its stability toward sintering and the catalytic activity of the resulting catalysts[25]. The versatility of rare-earth doped ceria depends on availability of the 4f

shell. On substitution of the trivalent rare-earth element, the oxygen vacancies increase, which in turn improves oxygen mobility and oxygen storage capacity[26].

Molybdenitethe principal ore from which molybdenum is now extracted was previously known as molybdena. Molybdena was confused with and often utilized as though it were graphite. Like graphite, molbdenite can be used to blacken a surface or as a solid lubricant[27].In its pure form, molybdenum is a silvery-grey metal with a Mohs hardness of 5.5. It has a melting point of 2,623 °C (4,753 °F); of the naturally occurring elements, only tantalum, osmium, rhenium, tungsten, and carbon have higher melting points[28]. Weak oxidation of molybdenum starts at 300 °C. It has one of the lowest coefficients of thermal expansion among commercially used metals[29].

Molybdenum does not occur naturally as a free metal on Earth, but rather in various oxidation states in minerals. The free element, which is a silvery metal with a gray cast, has the sixth-highestmelting point of any element. It readily forms hard, stable carbides in alloys, and for this reason most of world production of the element (about 80%) is in making many types of steel alloys, including high strength alloys and super alloys.[30]

Experimental Details

Materials Used
Cerium nitrate
Ammonium molbdate
Sodium hydroxide

Preparation of CeO_2 Nano Metal Oxides

Ceria nanoparticles were synthesized byusing cerium nitrate 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 cerium nitrate was prepared in 50ml of deionised water and then aqueous solution of (50ml, 2M) Sodium hydroxide was added dropwise to this solution making a final volume of 100ml. This mixture was stirred well and refluxed for 2-3 hours at 70-80ºC which resulted in the formation of light yellow ceria 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. Similar procedure was carried out for the preparation of MoO_3 nanoparticles using Ammonium molybdate as precursors.

Preparation of MoO_3-CeO_2 Mixed Oxide

MoO_3-CeO_2 mixed oxide nanoparticles were prepared at room temperature by wet chemical method.50ml of 0.1M solution of cerium nitrate, 50 ml of 0.1M solution of ammonium molybdate and 100ml of 2M solution of sodium hydroxide were prepared by deionisedwater.Cerium nitrate and ammonium molybdate solutions were mixed.Sodium hydroxide solution(100ml.2M) was added dropwise to the above mixture. The resulting solution was refluxed for 2-3 hours at 70-80ºC.Sodium hydroxide is used as a precipitating agent. The white precipitate was obtained. The obtained precipitate was filtered and the filterate was washed several times with deionised water to remove the impurities. The precipitate was dried at room temperature.Similar procedure was repeated for the preparation of different concentrations of mixed metal oxide nanoparticles by varying the concentrations of both Ammonium molybdate and Cerium nitrate in the range of 0.05-0.2M.

Characterization

Computer controlled JASCO V-530 was used to study UV-VIS spectral behaviour. The exact nano meter size of the particle was characterized by computer controlled PHILIPSCM 200 operating voltages: 20-200kv resolution.2.4A° Transmission Electron Microscopy was used(TEM). Cyclic Voltammetric studies were carried out using electrochemical workstation (mode 650c), CH-Instrument.

Result and Discussion

UV-Visible Spectroscopy

Optical properties of the CeO_2nanoparticles samples were studied by UV-Vis spectrum. It can be seen from the (Fig :1) that there is an intensive absorption in the ultraviolet band of about 200-800nm. The absorption wavelength appears at about 292nm for CeO_2 nanoparticles[31].

UV-vis absorption spectra of MoO_3-CeO_2 mixed oxide is recorded in the range of 200-800nm and it is shown in (Fig:2).The absorption peak for MoO_3-CeO_2 mixed oxide has been found to be at 348nm. The variation in the absorption peaks for simple and mixed oxide nanoparticles are due to the smaller size of nanoparticles[32]. The mixed oxide nanoparticles exhibited more than 40nm blue shift compared with that of the simple oxide nanoparticles. The blue shift of the absorption peaks of metal oxide nanoparticles result from certain unique effects of nano materials such as nanoscale effect and the blue shift reduces absorption of UV rays of longer wave length and is thus undesirable for UV protection. The absorption peaks of mixed oxide appeared at shorter wavelength region and are thus used as a solar UV blockers[33].

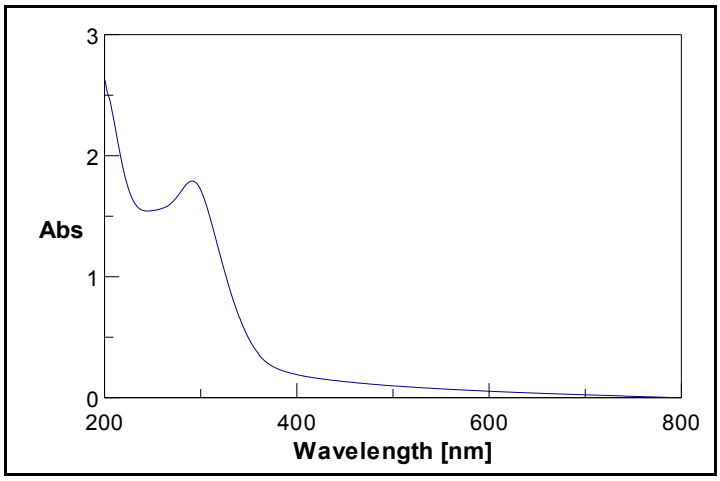

Fig:1 UV-VIS Spectrum of CeO_2 nanoparticles

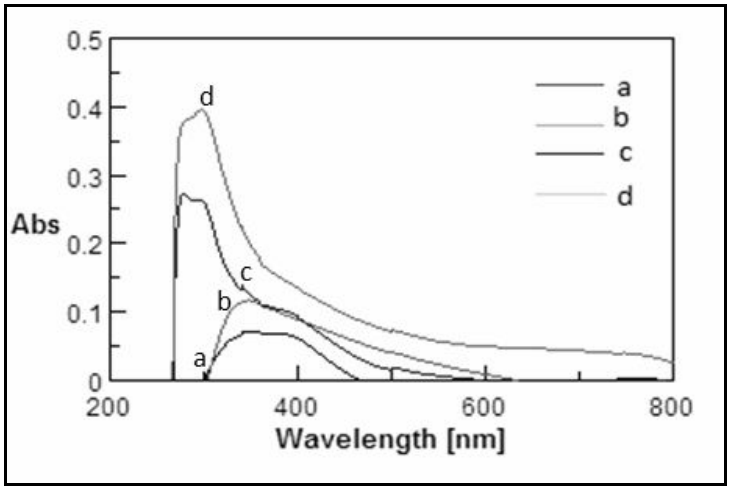

Fig:2 UV-VIS Spectra of a)0.05M MoO_3-CeO_2b)0.1MMoO_3-CeO_2 c)0.15MMoO_3-CeO_2 d) 0.2MMoO_3-CeO_2

TEM

The size of synthesized nanoparticles were further confirmed by TEM. The transmission electron microscopy (TEM) image of MoO_3-CeO_2mixed oxides are prepared from 0.1M concentration of Mo ion are shown in (Figs:3). The size of nano MoO_3-CeO_2 mixed oxide is found to be 50 nm.

The selected-area diffraction pattern of nanoMoO_3-CeO_2 mixed oxides are shown in (Fig:4). It revealed that the samples are semicrystalline (110),(111) and (111) phase. From the results obtained it has been demonstrated that the size of nano Al_2O_3-CeO_2 and nano MoO_3-CeO_2 mixed oxides are in the range of 50 nm. The Selected Area Electron Diffraction pattern exhibiting several uniform bright rings suggested that the nanocrytals are semicrystalline.

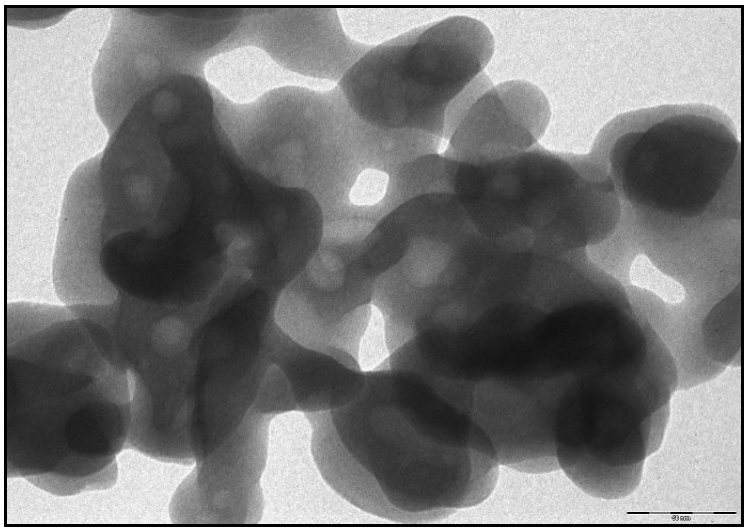

Fig:3 TEM images of nano MoO_3-CeO_2 mixed oxide

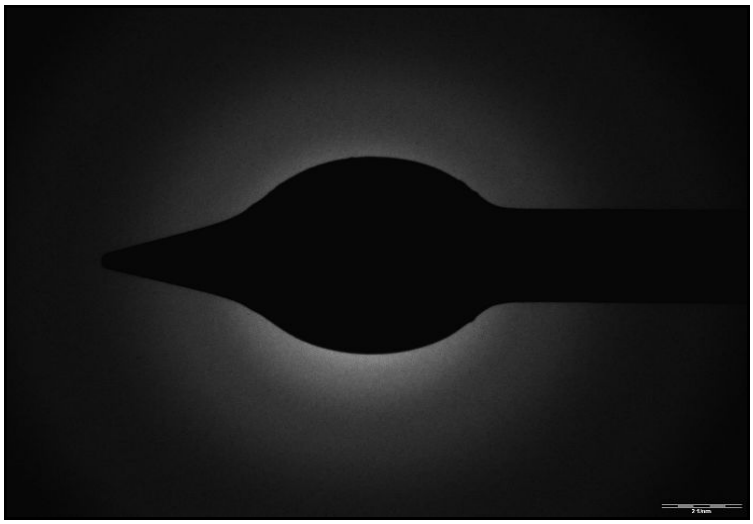

Fig:4 SAED pattern of nano MoO_3-CeO_2 mixed oxide

Cyclic Voltammetry

Cyclic voltammetric behaviour of the nano mixed oxides are recorded. The potential window is between -0.6 to 1.4V on GCE at 50mv/s.Cyclicvoltammetricbehaviour of CeO_2 showed one oxidation peak(Fig:5) at -0.1175V which is due to the presence of CeO_2.Cyclic voltammetric behaviour of MoO_3 showed one oxidation peak(Fig:6) at 1.856V and reduction peak at 2.752V which is due to the presence of MoO_3.The nano MoO_3-CeO_2 (0.1M)mixed oxide shows one oxidation peak at -0.0992V and reduction peak at -0.1293V

which is entirely different from the behaviour of MoO_3confirms the formation nano MoO_3-CeO_2 mixed oxide (Fig:7).

Cyclic voltammetric behaviour of MoO_3-CeO_2 mixed oxides at different scan rates are shown in (Fig:8).The plot of peak current verus for scan rate for nano MoO_3-CeO_2 mixed oxides (Fig:9) gave a straight line indicating a good adherent behaviour on electrode. Thus the mixed oxides act as corrosive resistance agents. Peak current of nano MoO_3-CeO_2 are correlated with the square root of scan rate ,(Fig:10) a straight line is observed. These facts revealed that the voltammetric redox behaviour of mixed metal oxide nano particles are controlled by adsorption process.

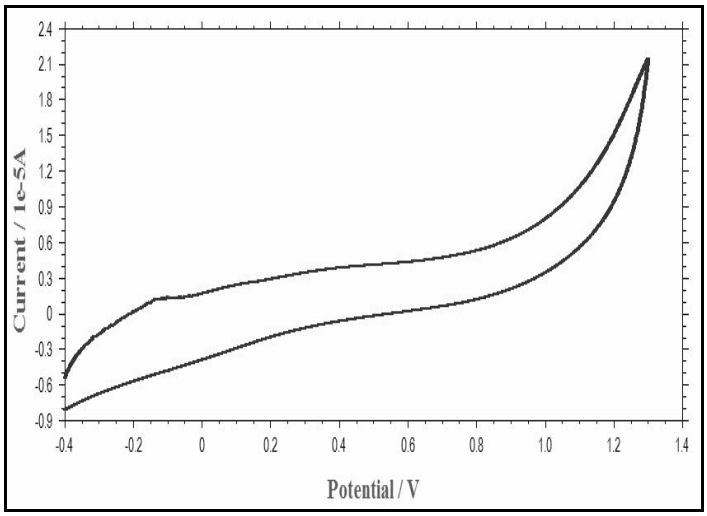

Fig:5 Cyclic Voltammogram of CeO_2 nano particle

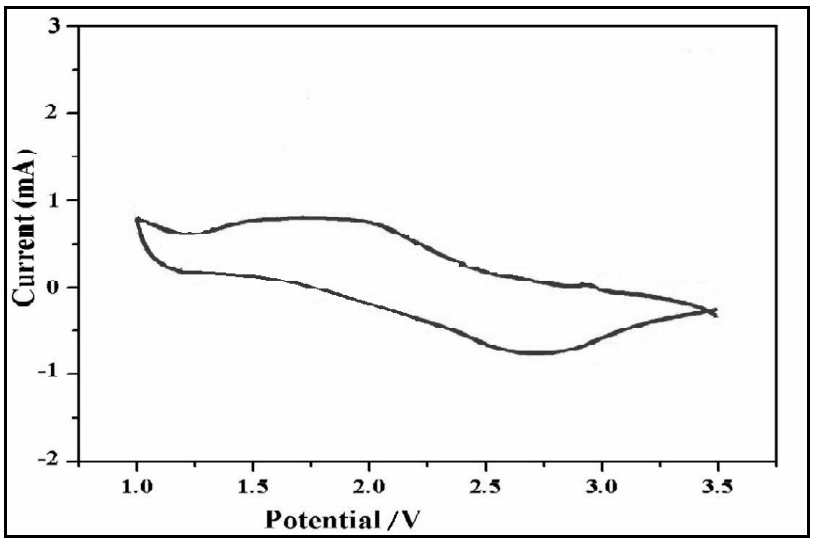

Fig: 6Cyclicvoltammommogram of MoO_3 nano particles

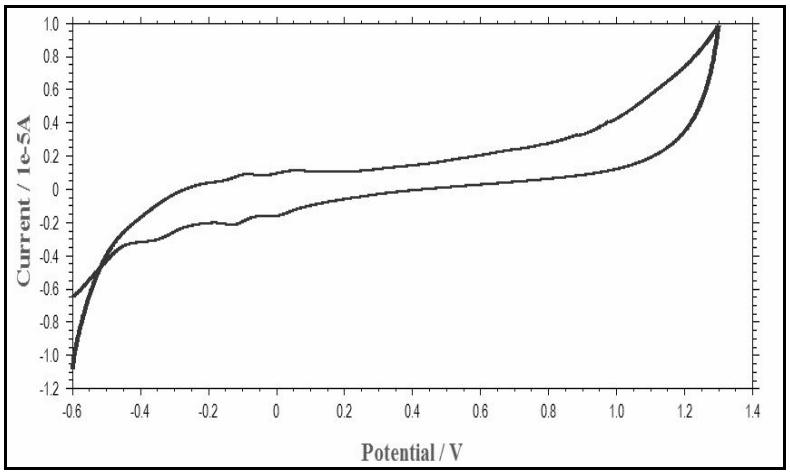

Fig:7 Cyclic Voltammogram of nano MoO_3-CeO_2 mixed oxide

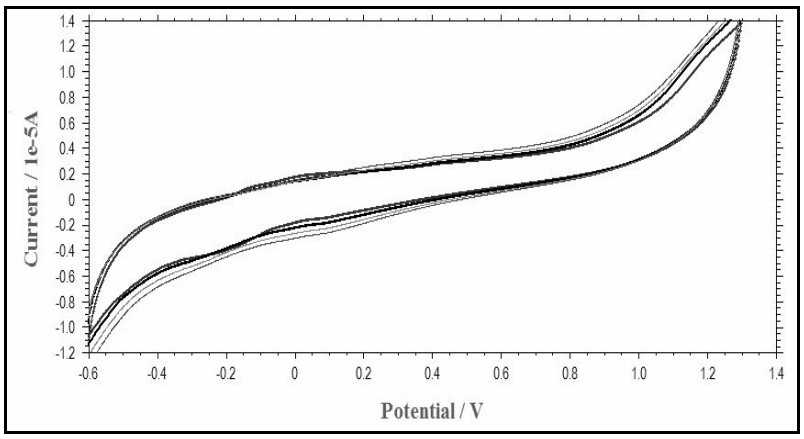

Fig:8 Cyclic voltammetricbehaviour of nano MoO_3-CeO_2 mixed oxides at different scan rates 15.25,35 and 45mVS^{-1}

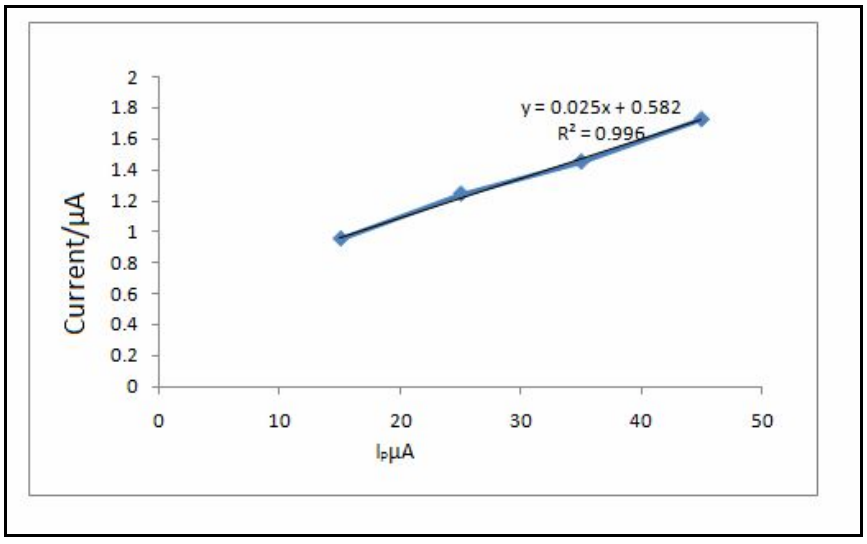

Fig :9 Plot of peak current Versus scan rate for nano MoO_3-CeO_2 mixed oxide

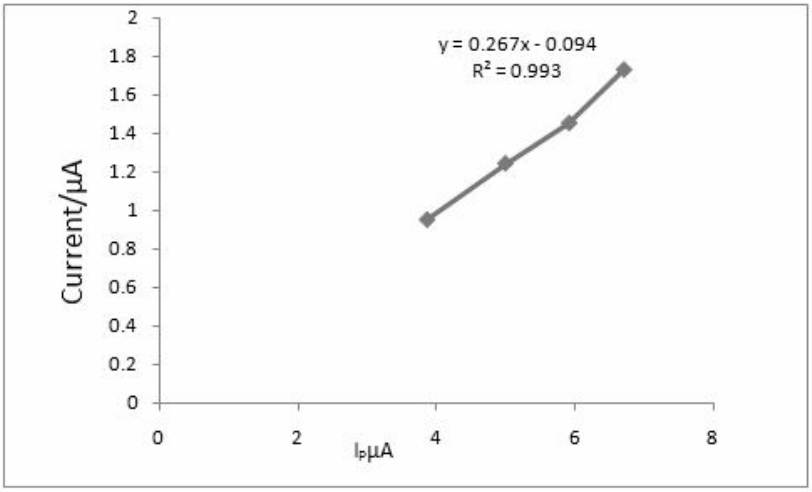

Fig :10 Plot of peak current Versus square root of scan rate for nano MoO_3-CeO_2 mixed oxide

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Conclusion

Nano MoO_3-CeO_2 mixed oxides are synthesized by wet chemical method. The mixed metal oxide nanoparticles are characterized by UV,TEM and Cyclic Voltammetry. The blue shifted absorption peaks of simple and mixed metal oxide nanoparticles showed nano scale effect. The surface morphology of the synthesized mixed oxide nanoparticles exhibited different structures. TEM Microscope also confirmed the particle size of the mixed oxide nanoparticles are in the nano scale range. .From Cyclicvoltammetric studies the mixed metal oxide nanoparticles exhibited good adherent behaviour on electrode surface and are adsorption controlled and revealed good electroactivity.

From this investigation the synthesized mixed metal oxide nanoparticles have been observed as corrosive resistant.Thus the mixed oxides can be used as a potential photocatalyst, electrode material and for further medicinal applications.

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