



## Synthesis, Electrochemical Characterization Of MoO<sub>3</sub>-CeO<sub>2</sub> Mixed Oxide Nano Particles

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**Abstract** : Nano MoO<sub>3</sub>-CeO<sub>2</sub> 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<sub>3</sub>-CeO<sub>2</sub> mixed oxides were characterized by UV-Vis, TEM and CV studies. The absorption peak for MoO<sub>3</sub>-CeO<sub>2</sub> 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 50nm. Cyclic Voltammetric studies exhibit good adherent behaviour on electrode surface and good electroactivity at pH 1.0.  
**Keywords:** MoO<sub>3</sub>-CeO<sub>2</sub>, UV-Vis, Cyclic Voltammetry, TEM.

### Introduction

In recent years, Synthesis[38-48] of metal Nanoparticles using plant leaf extract has attracted attention of many researchers because of availability of materials, inexpensive and process is easy to carry out in any laboratory, use of non-toxic reagent[1]. Nanotechnology plays an important role in modern research. Nanotechnology that can be applied almost all fields such as pharmaceutical, electronics, health care, food and feed, biomedical science, drug and gene delivery, chemical industry, energy science, cosmetics, environmental health, mechanics and space industries[2].

In recent decades, semiconducting oxide nanostructure based research stimulating more attention[3]. The optical, luminescence and catalytic properties arises from the availability of the shielded 4f levels with only one electron in the 4f state, Ce<sup>3+</sup>[4]. Ceria (CeO<sub>2</sub>) is an important rare-earth oxide that has been attracting a-growing attention because of its varied applications in fuel cells,[5]-[9] oxygen gas sensors,[10] polishing agents,[11] oxygen permeation membrane systems,[12][13] and as catalysts for different technologically important processes.[14]-[19] 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,[20] removal of total organic carbon from waste,[21] automobile exhaust gas conversion, and in deNO<sub>x</sub> reactions[22][23]. The possibility of transformation from Ce<sup>3+</sup> and Ce<sup>4+</sup> aids in accepting or removing oxygen from ceria. In addition, the fluorite structure of ceria or doped ceria has superior chemical and physical stability[24]. Pure CeO<sub>2</sub> 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<sub>2</sub> reduce drastically, but it also loses its redox properties and oxygen storage capacity[25] 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[26]. 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[27].

Molybdenite the 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, molybdenite can be used to blacken a surface or as a solid lubricant[28]. 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[29]. Weak oxidation of molybdenum starts at 300 °C. It has one of the lowest coefficients of thermal expansion among commercially used metals[30].

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-highest melting 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.[31]

## Experimental Details

### Materials Used

Cerium nitrate

Ammonium molybdate

Sodium hydroxide

### Preparation of CeO<sub>2</sub> NANO Metal Oxides

Ceria nanoparticles were synthesized by using 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 70-80°C 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<sub>3</sub> nanoparticles using Ammonium molybdate as precursors.

### Preparation of MoO<sub>3</sub>-CeO<sub>2</sub> Mixed Oxide

MoO<sub>3</sub>-CeO<sub>2</sub> 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 deionised water. 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 70-80°C. Sodium hydroxide is used as a precipitating agent. The white precipitate was obtained. The obtained precipitate was filtered and the filtrate 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<sub>2</sub> nanoparticles 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. In this spectrum  $\lambda_{max}$  is observed at 292nm. This indicates that the absorption shifts towards shorter wavelength because of the particle size reduction[32]. The absorption edge has been obtained at a shorter wavelength. The broadening of the absorption spectrum could be due to the quantum confinement of the nanoparticles[33].

UV-Vis absorption spectra of MoO<sub>3</sub>-CeO<sub>2</sub> mixed oxide is recorded in the range of 200-800nm and it is shown in (Fig:2 ). The absorption peak for MoO<sub>3</sub>-CeO<sub>2</sub> 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[34]. 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[35].

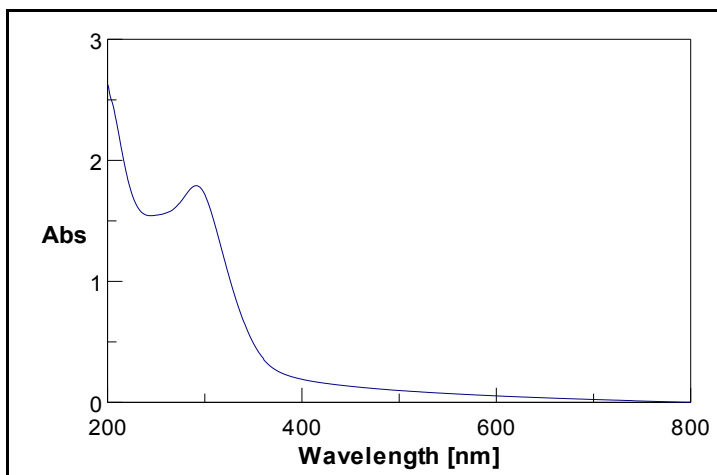


Fig:1 UV-VIS Spectrum of CeO<sub>2</sub> nanoparticles

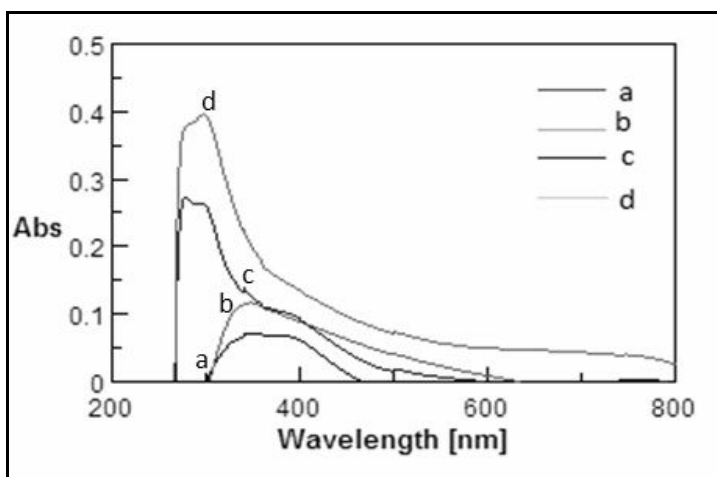


Fig:2 UV-VIS Spectra of a)0.05M MoO<sub>3</sub>-CeO<sub>2</sub> b)0.1M MoO<sub>3</sub>-CeO<sub>2</sub> c)0.15M MoO<sub>3</sub>-CeO<sub>2</sub> d) 0.2M MoO<sub>3</sub>-CeO<sub>2</sub>

## TEM

The shape and size of synthesized nanoparticles were analysed by TEM[36]. Fig:3 shows the TEM image of synthesized MoO<sub>3</sub>-CeO<sub>2</sub> nano mixed oxides. The synthesized MoO<sub>3</sub>-CeO<sub>2</sub> nano mixed oxides are in the nano range. The size of nano MoO<sub>3</sub>-CeO<sub>2</sub> mixed oxide is found to be 50 nm[37].

The selected-area diffraction pattern of nano MoO<sub>3</sub>-CeO<sub>2</sub> 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<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> and nano MoO<sub>3</sub>-CeO<sub>2</sub> mixed oxides are in the range of 50 nm. The Selected Area Electron Diffraction pattern exhibiting several uniform bright rings suggested that the nanocrystals are semicrystalline.

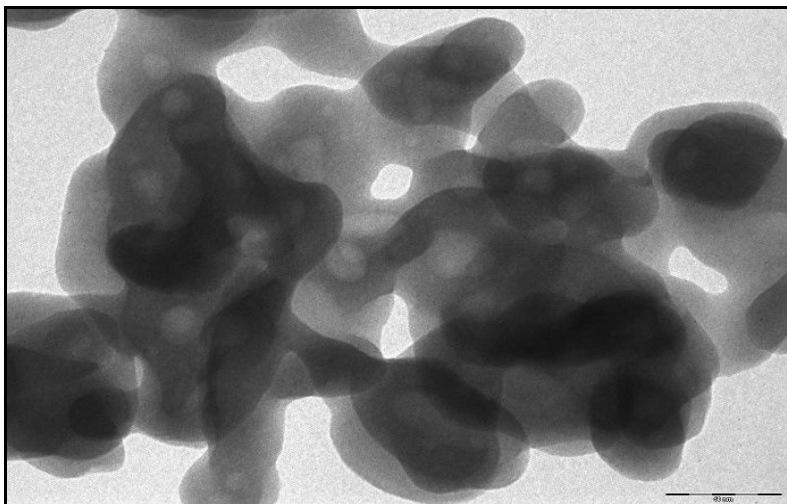


Fig:3 TEM images of nano MoO<sub>3</sub>-CeO<sub>2</sub> mixed oxide

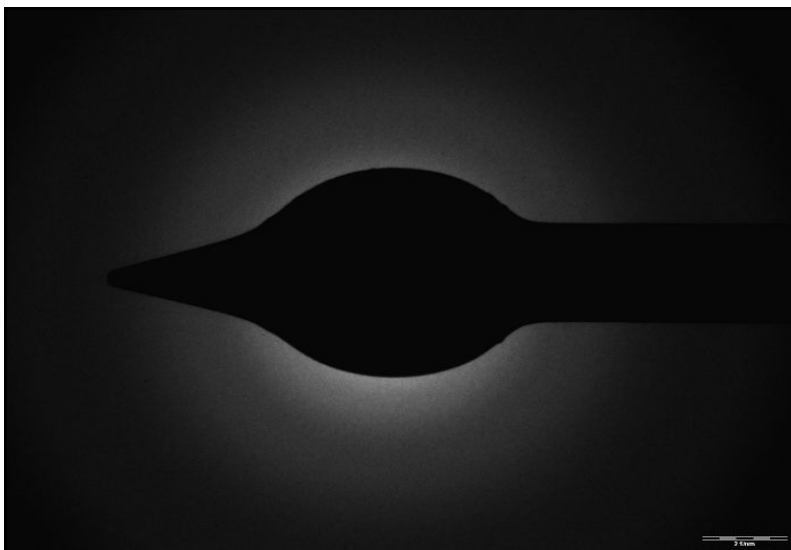


Fig:4 SAED pattern of nano MoO<sub>3</sub>-CeO<sub>2</sub> mixed oxide

## 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. Cyclic voltammetric behaviour of CeO<sub>2</sub> showed one oxidation peak (Fig:5) at -0.1175V which is due to the presence of CeO<sub>2</sub>. Cyclic voltammetric behaviour of MoO<sub>3</sub> showed one oxidation peak (Fig:6) at 1.856V and reduction peak at 2.752V which is due to the presence of MoO<sub>3</sub>. The nano MoO<sub>3</sub>-CeO<sub>2</sub> (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  $\text{MoO}_3$  confirms the formation nano  $\text{MoO}_3\text{-CeO}_2$  mixed oxide(Fig:7).

Cyclic voltammetric behaviour of  $\text{MoO}_3\text{-CeO}_2$  mixed oxides at different scan rates are shown in (Fig:8).The plot of peak current versus scan rate for nano  $\text{MoO}_3\text{-CeO}_2$  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  $\text{MoO}_3\text{-CeO}_2$  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.

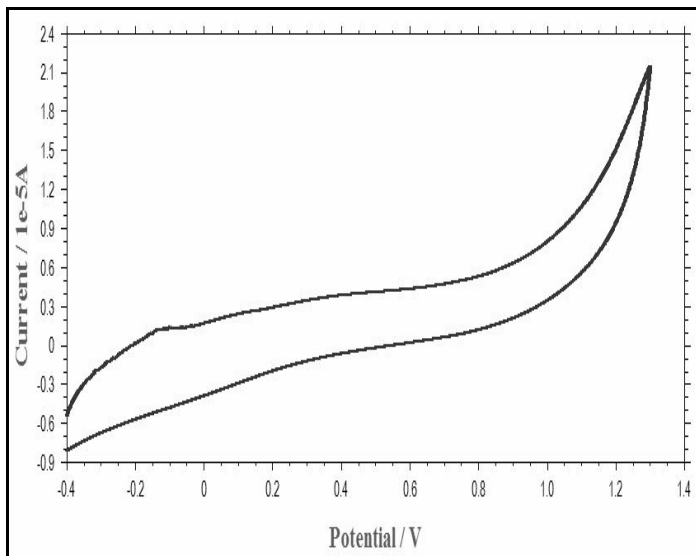


Fig:5 Cyclic Voltammogram of  $\text{CeO}_2$  nano particle

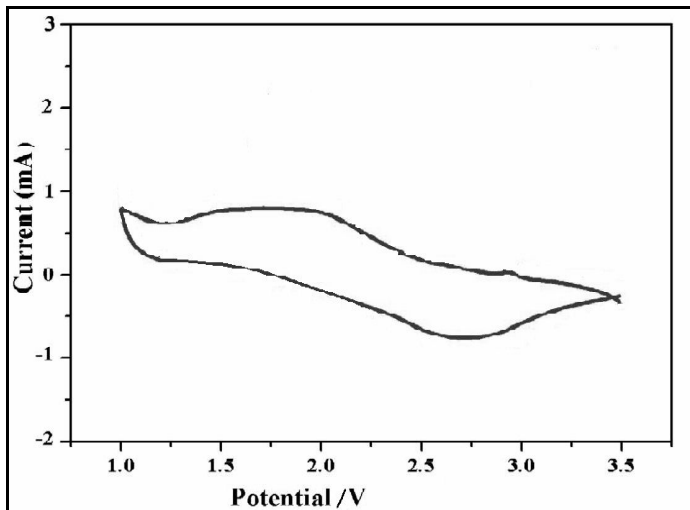
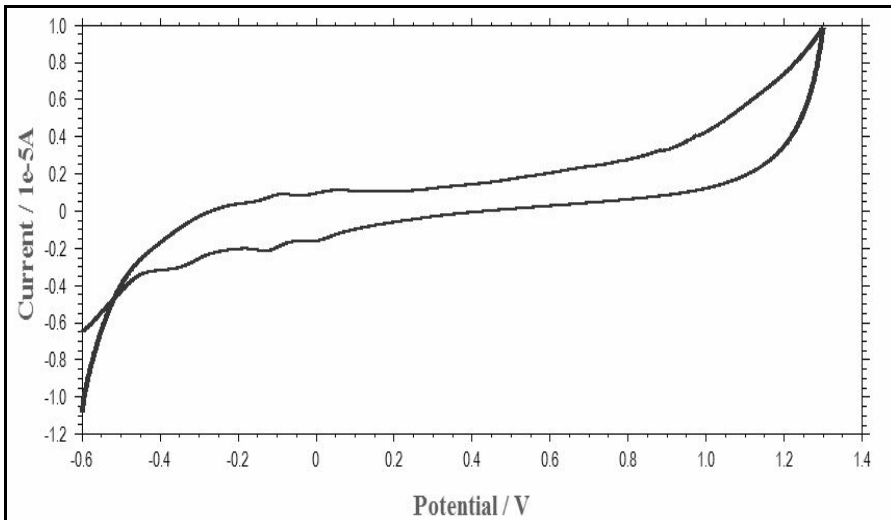
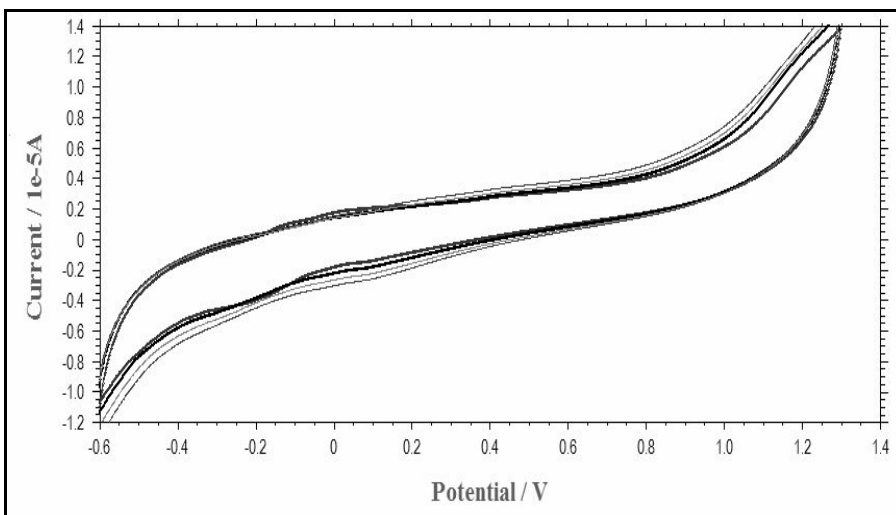


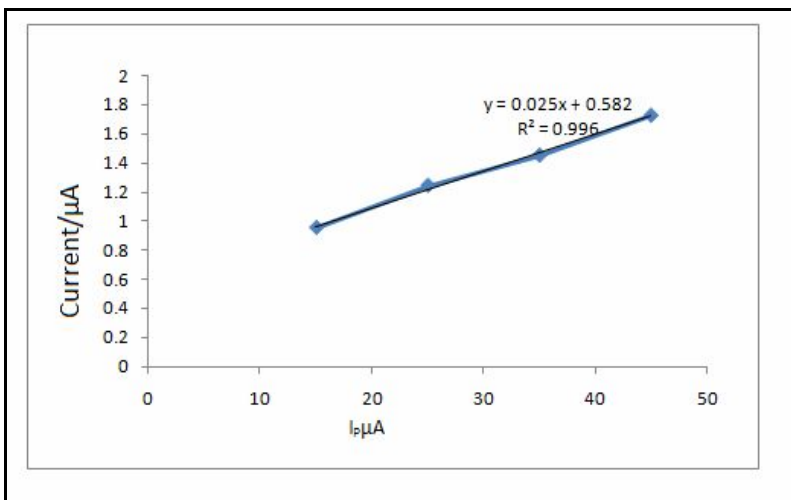
Fig: 6Cyclicvoltammogram of  $\text{MoO}_3$  nano particles



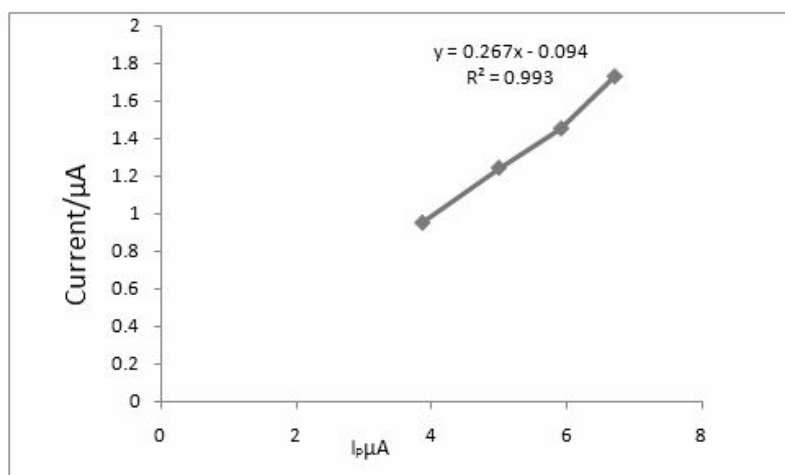
**Fig:7** Cyclic Voltammogram of nano MoO<sub>3</sub>-CeO<sub>2</sub> mixed oxide



**Fig:8** Cyclic voltammetricbehaviour of nano MoO<sub>3</sub>-CeO<sub>2</sub> mixed oxides at different scan rates 15,25,35 and 45mVS<sup>-1</sup>



**Fig :9** Plot of peak current Versus scan rate for nano MoO<sub>3</sub>-CeO<sub>2</sub> mixed oxide



**Fig :10 Plot of peak current Versus square root of scan rate for nano MoO<sub>3</sub>-CeO<sub>2</sub> mixed oxide**

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### Conclusion

Nano MoO<sub>3</sub>-CeO<sub>2</sub> 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 Cyclic voltammetric 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.

### References

1. V.D.kulakarni, K.K.jare, P.D.patole, S.B.ode, P.S.kulkarni,biosynthesis of copper nanoparticles using aeglemarmeloos leaf extract, Indian Streams Research Journal, ISSN:-2230-7850.
2. K. Saranyaadevi, V. Subha, R. S. Ernest Ravindran, S. Renganathan, .Zeylanica Extract,vol.6, No.10, pp 4533-4541, International Journal of ChemTech Research 2014, coden (USA): IJCRGG ISSN : 0974-4290.
3. Dutta M., Mridha S., Basak D., Optoelectronic characteristics of UV photodetector based on ZnO nanowire thin films, Appl. Surf. Sci. 2008, 254, 2743–2747.
4. ElJouad M., AlaouiLamrani M., Sofiani Z., Addou M., El Habbani T., Fellahi N., Bahedi K., Dghoughi L., Monteil A., Sahraoui B., Dabos S., Gaumer N., Roughness effect on photoluminescence of cerium doped zinc oxide thin films. Optical Materials, Opt. Mater. 2009, 31, 1357–1361.
5. ParkS.J,Vohs J.M andGorte R.J: Direct oxidation of hydrocarbonsin a solid-oxide fuel cell. 2000, Nature 265, 404.
6. MurrayE.P,Tsai T and Barnett A : A direct-methane fuel cellwith a ceria-based anode. 1999, Nature 400, 649.

7. Maki Y, Matuda Mandkudo T: U.S. Patent No. 3 1971 [607] 424.
8. Kharton V.V, Figueiredo F.M, Navarro L, Naumovich E.N, Kovalevsky A.V, Yaremchenko A.A, Viskup P., Carneiro A, Marques F.M.B and Frade J.R: Ceria-based materials for solid oxide fuel cells. *J. Mater. Sci.* 2001, 36, 1105.
9. Tok A.I.Y., Luo L.H., Boey F.Y.C and Ng S.H: Consolidation and properties of Gd<sub>0.1</sub>Ce<sub>0.9</sub>O<sub>1.95</sub> nanoparticles for solid oxide fuel cell electrolytes. *J. Mater. Res.* 2006, 21, 19.
10. Izu N, Shin W and Murayama N: Fast response of resistive type oxygen gas sensors based on nano-sized ceria powder. *Sens. Actuators*, 2003 B 93, 449.
11. Kirk N. and Wood J.V: Glass polishing. *Br. Ceram. Trans.* 1994, 93, 25.
12. Yin X, Hong L and Liu Z-L: Development of oxygen transport membrane La<sub>0.2</sub>Sr<sub>0.8</sub>CoO<sub>3-d</sub>/Ce<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>2-d</sub> on the tubular CeO<sub>2</sub> support. *Appl. Catal., A* 2006, 300.
13. Yin X, Hong L and Liu Z-L: Oxygen permeation through the LSCO-80/CeO<sub>2</sub> asymmetric tubular membrane reactor. *J. Membr. Sci.* 2006, 268, 2.
14. Damayanova S and Bueno J.M.C: Effect of CeO<sub>2</sub> loading on the surface and catalytic behaviors of CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-supported Pt catalysts. *Appl. A. Catal.*, 2003, 253, 135.
15. Yao Y. F. and Kummer J.T.: Low-concentration supported precious metal catalysts prepared by thermal transport. *J. Catal.* 1987, 106, 307.
16. Su E.C, Montreuil C.N and Rothschild W.G: Oxygen storage capacity of monolith three-way catalysts. *Appl. Catal.* 1985, 17, 75.
17. Imamura S, Fukuda I and Ishida S: Wet oxidation catalyzed by ruthenium supported on cerium (IV) oxides. *Ind. Eng. Chem. Res.* 1998, 27, 718.
18. Mishra V.S, Mahajani V.V and Joshi J.B: Wet air oxidation. *Ind. Eng. Chem. Res.* 1995, 34, 2.
19. Trovarelli A, de Leitenburg C, Boaro M, and Dolcetti G.: Redox chemistry over CeO<sub>2</sub>-based catalysts: SO<sub>2</sub> reduction by CO or CH<sub>4</sub>. *Catal. Today* 1999, 50, 381.
20. Zhao S and Gorte R.K.: A comparison of ceria and Sm-doped ceria for hydrocarbon oxidation reactions. *Appl. Catal., A* 2004, 277, 129.
21. Kawi S., Tang Y.P, Hidajat K. and Yu L.E: Synthesis and characterization of nanoscale CeO<sub>2</sub> catalyst for deNO<sub>x</sub>. *J. Metastable Nanocryst. Mater.* 2005, 23, 95.
22. Neylon M.K., Castagonla M.J, Castagonla N.B and Marshall C.L: Coated bifunctional catalysts for NO<sub>x</sub> SCR with C<sub>3</sub>H<sub>6</sub>: Part I: Water-enhanced activity. *Catal. Today* 2004, 96, 53.
23. Colon G, Navio J.A, Monaci R and Ferino I.: CeO<sub>2</sub>-La<sub>2</sub>O<sub>3</sub> catalytic system Part I. Preparation and characterisation of catalysts. *Phys. Chem. Chem. Phys.* 2000, 2, 4453.
24. Krishna K., Bueno-Lopez A., Makkee M and Moulijn J.A: Potential rare earth modified CeO<sub>2</sub> catalysts for soot oxidation. I. Characterisation and catalytic activity with O<sub>2</sub>. *Appl. B. Catal.* 2007, 75, 189.
25. Hennings U and Reimert R.: Noble metal catalysts supported on gadolinium doped ceria used for natural gas reforming in fuel-cell applications. *Appl. Catal. B* 2007, 70, 498.
26. Liu F.X, Wang C.Y, Su Q.D, Zhao T.P and Zhao G.W: Optical properties of nanocrystalline ceria. *Appl. Opt.* 1997, 36, 2796.
27. Deshpande, Sameer; Patil, Swanand; Kuchibhatla, Satyanarayana VNT; Seal, Sudipta. "Size dependency variation in lattice parameter and valency states in nanocrystalline cerium oxide". *Applied Physics Letters* 87, 2005 (13): 133113.
28. Lansdown, A. R. (Elsevier) (1999).
29. Lide, David R., ed. *CRC Handbook of Chemistry and Physics* 4, Chemical Rubber Publishing Company 1994, p. 18.
30. Emsley, John, s. Oxford: Oxford University Press: 2001, pp. 262-266.
31. AZoM.com Pty. Limited. 2007. Retrieved 2007-05-06.
32. Thenneti Raghavulu, Ramesh Kumar G., Gokul Raj S., Mathivanan V., Mohan R.J., Crystal growth, 2007, 307, 112.
33. Suresh Sagadevan et al/ *Int. J. Chem Tech Res.* 2014-2015, 7(6), pp 2620-2624.
34. Singh D. K, Pandey D. K, Yadav R. R. and Devaraj Singh Pramana - *J. Phys*, May 2012, Vol. 78, No. 5, 759-766.
35. Hongying Yang, Sukang Zhu, Ning Pan August 2003.
36. Aswathy Aromal S, Daizy Philip. Green synthesis of gold nanoparticles using *Trigonella foenum-graecum* and its size-dependent catalytic activity. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy.* 2012; 97: 1-5.



37. Sivakumar P, NethraDevi C, Renganathan S. Synthesis of Silver Nanoparticles using Lantana Camara Fruit Extract and its effect on pathogens. *Asian.J.Pharma.Clini.Res.* 2012; 5(3): 3 1-5
38. Amita Verma, Pathak Prateek, Anjali Thakur, Parjanya Kr Shukla, Piperazine bridged 4-aminoquinoline 1,3,5- triazine derivatives: Design, Synthesis, characterization and antibacterial evaluation, *International Journal of ChemTech Research*,2016, Vol.9, No.04 pp 261-269.
39. Ahmed Kareem Obaid, SaadonA.Aowda, Ameer Hassan Idan, Ahmed HabeebRadhi , Synthesis and characterization of new Isoniazid Prodrug as anticancer agent, *International Journal of ChemTech Research*,2016, Vol.9, No.04 pp 521-528.
40. R.R.Muthuchudarkodi,S.Kalaiarasi,Synthesis,Electrochemical Characterization Of MoO<sub>3</sub>-CeO<sub>2</sub> Mixed Oxide Nano Particles, *International Journal of ChemTech Research*,2016, Vol.9, No.04 pp 699-706.
41. S.Devasenar, N.Hajara Beevi, S.S.Jayanthi, Synthesis and characterization of Copper Nanoparticles using Leaf Extract of *Andrographis Paniculata* and their Antimicrobial Activities., *International Journal of ChemTech Research* ,2016, Vol.9, No.04 pp 725-730.
42. Synthesis, Spectral Characterization, Biological Activity and Dna Cleavage Studies of Cu(II), Ni(II) AND Zn(II) SCHIFF Base Complexes Derived from 2,4-Dihydroxy Benzaldehyde and P-Chloroaniline, *International Journal of ChemTech Research* ,2016, Vol.9, No.03 pp 277-285.
43. R.Nandhikumar, K.Subramani, Synthesis and Characterization of Mikanecic acid diesters using different Catalysts and Their Comparison study, *International Journal of ChemTech Research* ,2016, Vol.9, No.03 pp 297-302.
44. G.SenthilNathan, K.Vetrivel, I.Pugazhenthii, K.Anver Basha, Mohammed Bilal, Synthesis, Characterization and Thermal Studies of Poly (5-Indanyl Methacrylate –co- Glycidyl Methacrylate), *International Journal of ChemTech Research* ,2016, Vol.9, No.03 pp 363-371.
45. Mani Jayanthi, Thirugnanam Lavanya, SriRangarajan Chenthamarai, Kaveri Satheesh, Synthesis, Optical Characterization And Electrochemical Properties Of Cd<sub>(1-x)</sub>Ni<sub>(x)</sub> S/ Reduced Graphene Oxide Nanocomposites, *International Journal of ChemTech Research* ,2016, Vol.9, No.02 pp 156-164.
46. M. Paul Johnpeter and A. Paulraj, Synthesis and Characterization of New Mannich Base of 1-[(2-Hydroxy-Phenyl)-Phenyl Amino-Methyl]-Pyrrole-2-5-dione (L) with some Transition Metal Complexes, *International Journal of ChemTech Research* ,2016, Vol.9, No.02 pp 176-181.
47. Subramani Dorothy, Kaliaperumal Punithamurthy, Kaveri Satheesh, One pot easy synthesis and optical characterization of Cd<sub>1-x</sub>Co<sub>x</sub>S/rGO composites starting from graphite oxide by co precipitation method and its electrochemical Properties, *International Journal of ChemTech Research*,2016, Vol.9, No.01 pp 226-232
48. B. E. Ezema, J. I. Ayogu, P.C. Uzoewulu, S.A. Agada, Convenient Syntheses and Antimicrobial Screening of Some Derivatives of Complex Benzoxazinophenothiazines, *International Journal of ChemTech Research* ,2016, Vol.9, No.01 pp 338-346.

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