Synthesis, Characterization and photocatalytic Application of nano ZrO_2 and MoO_3-ZrO_2 mixed oxide Nano Particles

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Abstract

Nano MoO_3-ZrO_2 mixed oxides were prepared 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 by UV, FTIR,TEM, and photocatalytic studies. The absorption peak for MoO_3- ZrO_2 mixed oxide has been found to be at 290 and 308nm**.** The size of synthesized nanoparticles were further confirmed by TEM and it was found to be 50nm. The prepared mixed metal oxide nanoparticles shows a good photocatalytic activity,thus it can be used as a photocatalysts.

Keywords: MoO_3-ZrO_2 , UV,FTIR,TEM.

1.Introduction

Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale size-dependent properties are often observed. Thus, the properties of materials change as their size approaches the nano scale and as the percentage of atoms at the surface of a material becomes significant. [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 properties in any material[2]. Zirconium dioxide is one of the most studied ceramic materials. ZrO_2 adopts a monoclinic crystal structure at room temperature and transitions to tetragonal and cubic at higher temperatures. The change of volume caused by the structure transitions from tetragonal to monoclinic to cubic induces large stresses, causing it to crack upon cooling from high temperatures.[3] When the zirconia is blended with some other oxides, the tetragonal and/or cubic phases are stabilized.[4] Molybdenum-bearing enzymes are by far the most common bacterial catalysts for breaking the chemical bond in atmospheric molecular nitrogen in the process of biological nitrogen fixation. At least 50 molybdenum enzymes are now known in bacteria, plants, and animals, although only bacterial and cyanobacterial enzymes are involved in nitrogen fixation.[5]

The photocatalytic activity of any semiconductor catalyst strongly depends upon adsorption capacity and the electron-hole pair separation efficiency of the catalyst. The adsorption capacity can be improved by increasing the specific surface area of catalysts. On the other hand, electron–hole separation efficiency could be significantly enhanced by doping the pure catalysts with rare earth and/or transition metals impurities. Doping with rare earth and/or transition metals creates quasi-stable energy states within the band gap and behaves as trap site for electrons and holes. Electron trapping due to higher defect sites leads to increase in the photocatalytic efficiency provided the electron-hole pair recombination rate is lower than the rate of electron transfer to adsorbed molecule.[6]

2.EXPERIMENTAL METHODS

2.1 PREPARATION OF ZrO_2 NANO METAL OXIDE

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 NANO MIXED OXIDE

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 molybdate solutions were mixed.Sodium hydroxide solution(100ml,1M) was added dropwise to 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 PHOTOCATALYTIC MEASUREMENT

The photocatalytic activity of mixed metal oxide nanoparticles were examined by studying the degradation of Methyl orange dye[$C_{14}H_{14}N_3NaO_3S$] aqueous solution under laboratory made Visible spectrophotometer[7]. For a typical photocatalytic experiment, 0.2g of the prepared sample was added to 100 ml of 3.2 g of Methyl Orange aqueous solution. The prepared sample was dispersed under ultrasonic vibration for 10 min. The aqueous suspension was put under constant stirring in dark for 1hr, so that the Methyl Orange dye atoms are adsorbed on the surface of nanocrystals. The stable suspension was then exposed to the UV- radiation with continuous magnetic stirring. About 10 ml of suspension solution was

taken out after every 10 min of UV light exposure. The photo degradation of Methyl Orange dye mixed with each synthesized samples were examined using Visible absorption values.

3. CHARACTERIZATION

Computer controlled JASCO V-530 was used to study UV-VIS spectral behavior. The FT-IR spectra were recorded using a SHIMADZU instrument. 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.

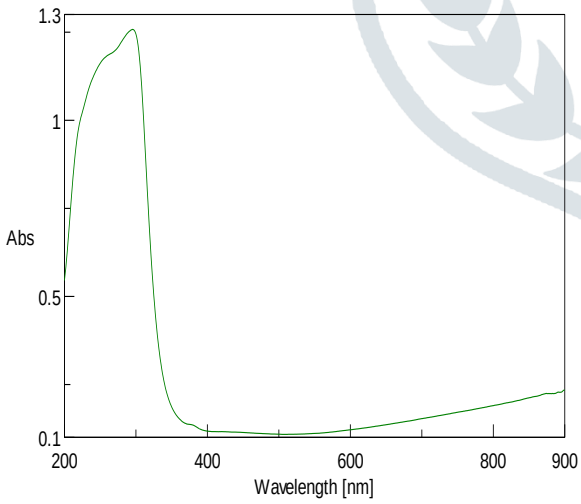
4.RESULT AND DISCUSSION

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.

4.1 STUDIES OF UV-VISIBLE SPECTROSCOPY

Optical properties of the ZrO_2 nanoparticles sample are 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 and absorbance for ZrO_2 nanoparticles appears at about 295nm and 1.3 [8].

UV-Vis absorption spectra of MoO_3-ZrO_2 mixed oxide is recorded in the range of 200-800nm and it is shown in (Fig:2).The absorption peak for MoO_3-ZrO_2 mixed oxide has been found to be at 290 and 308nm and absorbance at 1.32. The variation in the absorption peaks for simple and mixed oxide nanoparticles are due to the smaller size of nanoparticles[9]. The absorption peaks of simple and mixed oxide appeared at shorter wavelength region and are thus used as a solar UV blockers.[10]



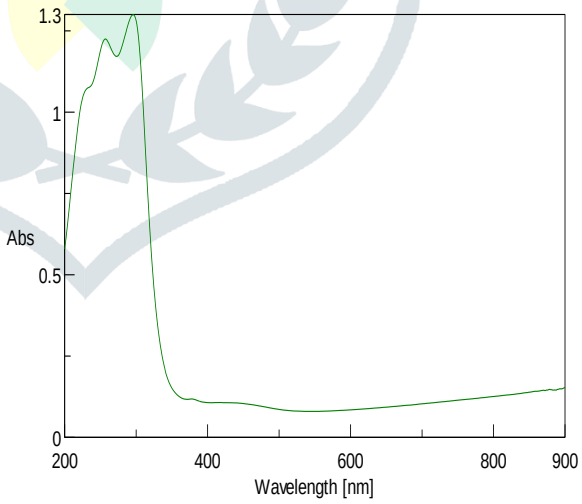


Fig:1 UV-VIS Spectrum of ZrO_2 nanoparticles Fig:2 UV-VIS Spectrum of MoO_3-ZrO_2 Mixed oxide nanoparticles

4.2.FOURIER TRANSFORM INFRA-RED SPECTROSCOPY(FTIR)

FT-IR spectra of metal oxide nanoparticles are recorded in the range of 400-4000cm^{-1}.Fig:3 shows FT-IR spectra of ZrO_2 nanoparticles (Fig:3) showed characteristic peak at 1380.82cm^{-1}is assigned to O_2 stretching frequency of ZrO_2 [11].The peak observed at3443.68cm^{-1} is attributed to O-H stretching frequencies of water. Few less intense peaks centered at 2924.57 cm^{-1} and 2361.17cm^{-1} are probably due to presence of asymmetric C-H stretching vibration and O-H stretching respectively [12]. The band observed at 1065.55cm^{-1} clearly indicates the presence of inorganic ion[13]. . The peak at 856..86 cm^{-1} was due to the formation of Zr ion [14]. The characteristic peak appeared at 453.74cm^{-1} could be attributed to the metal oxygen (Zr-O) bond [15].

FT-IR spectra of MoO_3-ZrO_2 mixed oxides are shown in (Fig.4).The frequencies observed at 938cm^{-1}and 856cm^{-1} are attributed to Mo-O bond. The signal at 463cm^{-1} is assigned to the Mo^{6+}stretching and bending vibrations in the Mo-O-Mo units[16].The peak observed at 1383.12cm^{-1} is assigned to O_2 stretching frequencies of ZrO_2.The band observed at 1575cm^{-1} corresponds to bending mode of adsorbed water[17].The broad band at 3343.87 cm^{-1} is assigned to the stretching vibration of the –OH group connected to the Mo cation [16]. The peak at 851.50 cm^{-1} 463.23 cm^{-1} could be attributed to the metal oxygen(Mo- O-Zr) bond.

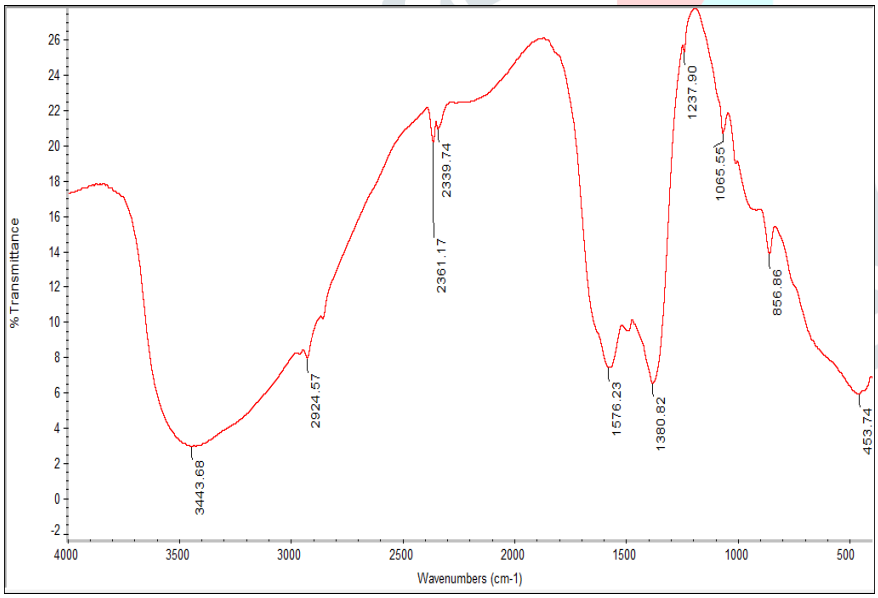


Fig:3 FTIR Spectrum of ZrO_2 nanoparticles

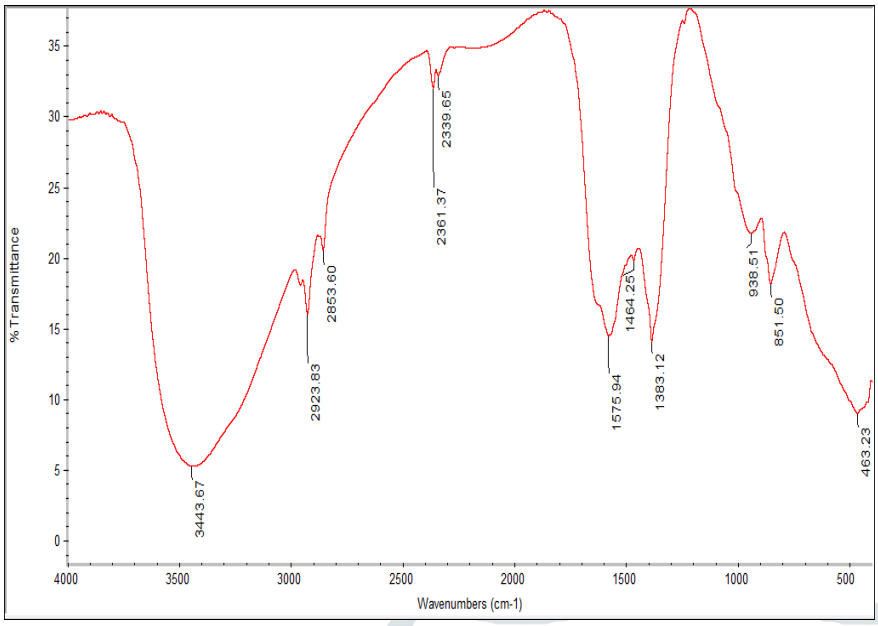


Fig:4 FTIR Spectrum of MoO_3-ZrO_2 mixed oxide nanoparticles

4.3.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 (Figs:5). These images shows that the particles formed are of nearly stone shape of morphology. The size of nano MoO_3-ZrO_2 mixed oxide is found to be nm (Fig:5).

The selected-area diffraction pattern of nano MoO_3-ZrO_2 oxide is shown in (Fig:6). It revealed that the samples are amorphous phase. From the results obtained it has been demonstrated that the size of nano MoO_3-ZrO_2 oxide is accumulated in nm. The patterns display distinct as opposed to being the powder pattern type confirm that the amorphous growth of nanoparticles. The Selected Area Electron Diffraction pattern exhibiting several uniform bright rings suggested that the nano crystals are amorphous nature.

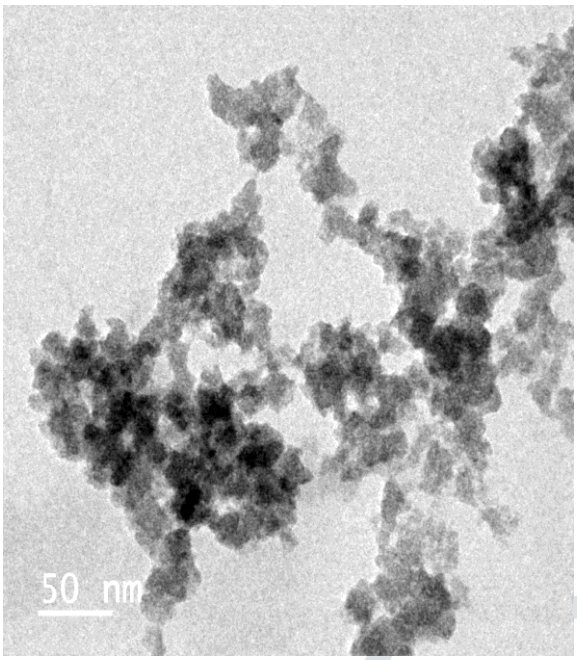


Fig:5 TEM images of MoO_3-ZrO_2 mixed oxide nanoparticles

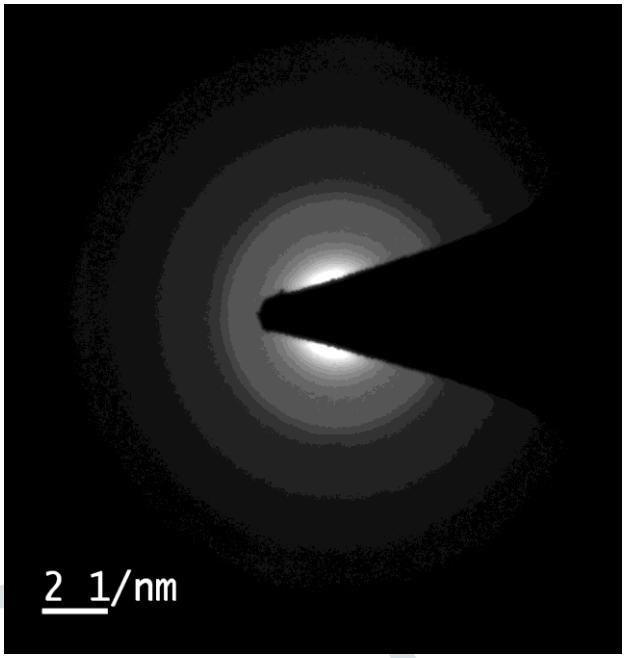


Fig:6 SAED pattern of MoO_3-ZrO_2 mixed oxide nanoparticles

4.4. PHOTOCATALYTIC ACTIVITY

The photocatalytic activity of mixed metal oxide nanoparticles was examined by studying the degradation of Methyl Orange dye [$C_{14}H_{14}N_3NaO_3S$] aqueous solution under laboratory made Visible spectrophotometer.Present measurements report the photocatalytic activity of mixed metal oxide nanoparticles by degradation of Methyl Orange dye under UV light exposure.

The UV–Vis absorbance values of Methyl Orange solution shows absorption wavelength at 462 nm. The characteristic absorption value at 462 nm was used to track the photocatalytic degradation process. Absorption values of pure Methyl Orange dye with and without UV radiation exposure is shown in (Table-1). It can be clearly noticed from the recorded values that no significant changes of the concentration of Methyl Orange after 3 hr irradiation, which indicated that pure MB solution cannot be easily degraded by UV light. The absorption values of Methyl Orange dye solution mixed with MoO_3-ZrO_2 nanoparticles under different duration (80min) of UV-radiation is shown in (Table-2). It is clear from the (Table-4) that the absorbance of Methyl Orange dye decreases after 80 minute exposure of UV light. The above results clearly indicates that the prepared mixed metal oxide nanoparticles shows a good photocatalytic activity,thus it can be used as a photocatalysts[18].

Table-1

Time in hours	Absorbance
1 hour	0.156
2 hour	0.116
3 hour	0.105

Table-2

Time in minutes	Absorbance
10	0.197
20	0.074
30	0.058
40	0.044
50	0.035
60	0.028
70	0.021
80	0.016

CONCLUSION

Nano MoO_3-ZrO_2 mixed oxides are synthesized by wet chemical method. The mixed metal oxide nanoparticles are characterized by UV,FTIR, TEM and photocatalytic activity. UV –Visible spectra of ZrO_2 and MoO_3-ZrO_2 mixed metal oxide nanoparticles exhibihited absorption at 295 nm and 308 nm. FT-IR spectral results revealed that the presence of Zr-O and Mo-O bonds of nano mixed oxides. TEM Microscope also confirmed the particle size of the mixed oxide nanoparticles are in the nano scale range. From this investigation the synthesized mixed metal oxide nanoparticles have been observed as photocatalysts.

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