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Synthesis and Characterization of Co_3O_4 - CuO - ZrO_2 Ternary Nanoparticles

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Abstract : Nano Co_3O_4 - CuO - ZrO_2 mixed oxides were synthesized by wet chemical method by mixing of equimolar solutions of cobalt chloride, copper sulphate and zirconium oxychloride in aqueous sodium hydroxide and refluxed at elevated temperature. The prepared mixed nano oxides were characterized by FT-IR, XRD, UV-DRS, TEM, SAED, SEM, EDAX and AFM. The FTIR spectra exposed the presence of M-O bonds (M = Co, Cu, Zr). From XRD studies, the size of the Co_3O_4 - CuO - ZrO_2 NPs are found to be 12.93 - 23.83nm through Scherrer's formula. The XRD patterns also reveal that the nanoparticle size is drastically increased with increasing concentration of the precursors. From UV-Vis diffuse reflectance spectra (DRS), band gap energy of the (0.1 – 0.5M) Co_3O_4 - CuO - ZrO_2 NPs are found to be in the range of 3.13 - 3.24eV. The TEM, SEM and AFM micrographs of 0.1MCo_3O_4 - CuO - ZrO_2 NPs display irregular shape with size ranging from 10 - 40nm. SAED pattern confirms the crystalline nature of these nanoparticles. EDAX analysis indicates the presence of Co, Cu, Zr and O.

Keywords: Co_3O_4 - CuO - ZrO_2 NPs, Mixed nano oxides, Wet chemical method, Band gap energy.

Introduction

Metal oxides play a very important role in many areas of chemistry, physics and materials science. The metal elements are able to form a large diversity of oxide compounds.

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 [1].

Co_3O_4 is acceptable as an important p-type semiconductor which has been widely utilized in lithium-ion batteries, supercapacitor, solar cells, sensing devices, electrocatalysis and photocatalysis [2, 3].

CuO has been established as a technologically important p-type semiconductor with its numerous applications such as gas sensors, solar photovoltaics, lithium ion electrode, superconductors, field emission emitters, magnetic storage media, field transistors, biosensors and photocatalysis [4, 5].

ZrO_2 is a significant n-type semiconductor because of its potential applications in many fields such as restorative dentistry, high temperature ceramics, sensor, electrochemical capacitor electrodes, optical devices, fuel cells and photocatalysis [6, 7].

Therefore, the research spotlight has turned towards inexpensive metal oxides such as Co_3O_4, CuO and ZrO_2. In this work, wet chemical method was applied to synthesize Co_3O_4 - CuO - ZrO_2 NPs. The developed ternary metal oxide nanomaterials were characterized by FT-IR, XRD, DRS, TEM, SAED, SEM, EDAX and AFM.

Experimental Details

Materials

The precursors of $CoCl_2$. $6H_2O$, $CuSO_4$. $5H_2O$, $ZrOCl_2$. $8H_2O$ and NaOH were purchased from e-merck. All solutions were prepared using deionized water.

Preparation of Co_3O_4 - CuO - ZrO_2 NPs

About 25mL of 0.1M $CoCl_2$. $6H_2O$ was added to the aqueous solution of 75mL of 1.0M NaOH solution and stirred well. To this mixture 25mL of 0.1M $CuSO_4$. $5H_2O$ and 25mL of 0.1M $ZrOCl_2$. $8H_2O$ were added. The resulting mixture was stirred well and refluxed at an elevated temperature (100-120^o C) for 3 hours. The product was filtered, washed with distilled water and dried. Similar procedure was carried out to prepare different concentrations of (0.2M - 0.5M) Co_3O_4 - CuO - ZrO_2 NPs.

Characterization

FTIR measurements of prepared samples as KBr disks were performed on a Thermo Scientific Nicolet iS5 FTIR spectrometer. The average size of nanoparticles was determined by XPERT-PRO X-ray diffractometer using Cu K_α radiation. UV-Vis diffuse reflectance spectra were recorded with JascoV-600 spectrophotometer. Philips-CM200 Transmission Electron Microscopy (TEM) was used to study the shape, particle size and lattice image of the nanoparticles. The morphology and composition of the nanoparticles were determined by JEOL JSM 6390 Scanning Electron Microscopy (SEM) with EDAX. Atomic force microscopy (AFM) images were recorded on a Nanosurf Easyscan 2 AFM instrument to obtain topographical images of the nanoparticles.

Results and Discussion

FTIR analysis

The FTIR analysis are depicted in figure 1. The bands in the low frequency region, 583 – 1018 cm^{-1} correspond to the lattice vibration modes of M - O (M = Co, Cu, Zr) [8, 9]. IR bands observed at around 1113 – 1115 cm^{-1} are due to the presence of symmetric stretching of M - O (M = Cu, Zr) [9]. The band appears at 1384 cm^{-1} in the FTIR spectra indicates the presence of M - O rocking in plane vibration (M = Co, Cu, Zr) [10]. The absorption peaks at around 1462 cm^{-1} are assigned to the stretching vibration of Co - O bond [11].

XRD analysis

Figure 2 explain the X-ray diffraction patterns of Co_3O_4 - CuO - ZrO_2 nanoparticles in which the diffraction peaks at 36.72° (311) and 59.25° (511) are ascribed to Co_3O_4 (JCPDS card no. 76-1802) [12]. The diffraction peak at 2θ value of 38.92° (111) is assigned to CuO (JCPDS card no. 80-1916) [13]. The diffraction peaks at 2θ values of 35.11° (200) and 62.83° (222) can be attributed to ZrO_2 (JCPDS card no. 50-1089) [6].

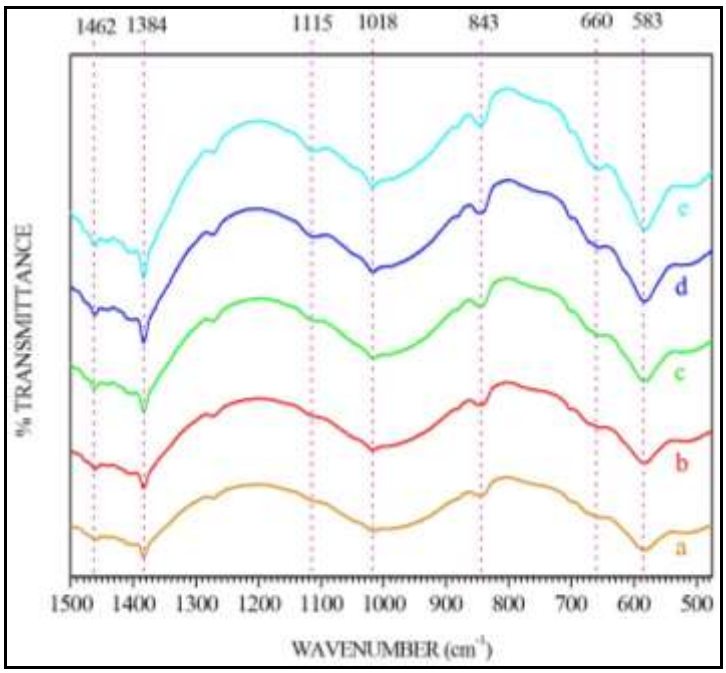

Figure 1 FTIR Spectra of a) 0.1M Co_3O_4 - CuO - ZrO_2 NPs b) 0.2M Co_3O_4 - CuO - ZrO_2 NPs c) 0.3M Co_3O_4 - CuO - ZrO_2 NPs d) 0.4M Co_3O_4 - CuO - ZrO_2 NPs e) 0.5M Co_3O_4 - CuO - ZrO_2 NPs

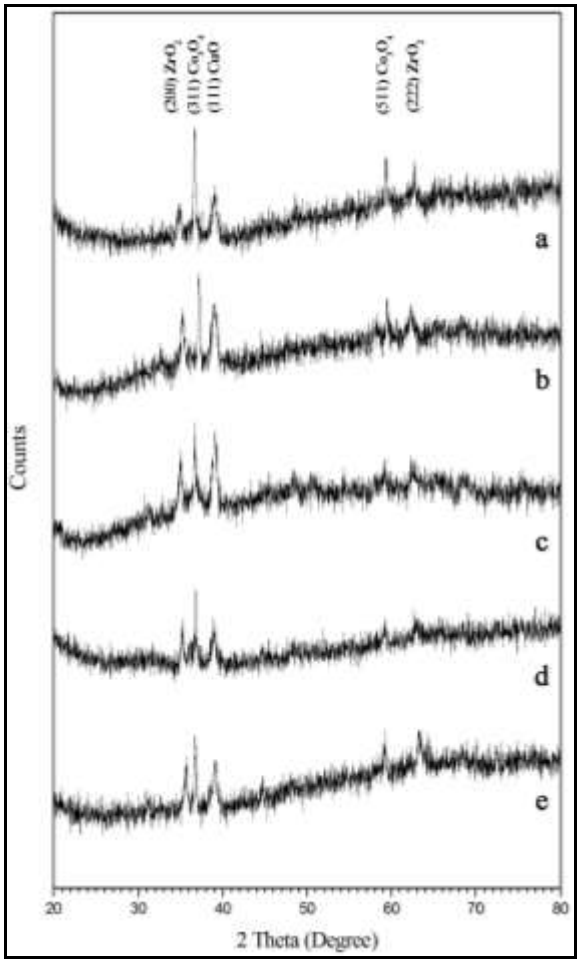

Figure 2 XRD Pattern of a) 0.1M Co_3O_4 - CuO - ZrO_2 NPs b) 0.2M Co_3O_4 - CuO - ZrO_2 NPs c) 0.3M Co_3O_4 - CuO - ZrO_2 NPs d) 0.4M Co_3O_4 - CuO - ZrO_2 NPs e) 0.5M Co_3O_4 - CuO - ZrO_2 NPs

Similar diffraction peaks are also observed in all the samples as given in the figure 2. The average particle sizes of the Co_3O_4 - CuO - ZrO_2 NPs as estimated using the Scherrer formula are in the range of 12.93 – 23.83nm. As the concentration of the precursors increases from 0.1M to 0.5M, the size of the nanoparticles also increases to an extent due to agglomeration of the small metal oxide nanoparticles.

UV-Visible diffuse reflectance Spectroscopic analysis

As shown in figure 3, these five samples display similar absorption spectra. Two absorption bands and a hump are observed locating at around 253 – 254 nm, 383 – 396 nm and 700nm respectively. These values suggest that the samples can be activated by both UV and visible light irradiations [12]. There is a red shift in absorption bands (from 383nm to 396nm) observed in Co_3O_4 - CuO - ZrO_2 NPs (from 0.1M to 0.5M) synthesized. This red shift is due to the increase in the particle size as well as decrease in the inter particle distance of Co_3O_4 - CuO - ZrO_2 NPs (from 0.1M to 0.5M) [14].

The band gap energy (Eg), an index to evaluate the light-absorption ability, can be estimated according to the equation

$Eg = hc/\lambda = 1240/\lambda$ (eV)

Where h is plancks constant, c is speed of light and λ is the absorption edge wavelength (nm).

The band gap values obtained for the Co_3O_4 - CuO - ZrO_2 NPs are 3.24eV (0.1M), 3.21eV (0.2M), 3.16eV (0.3M), 3.15eV (0.4M), and 3.13eV (0.5M). This clearly shows that the synthesized Co_3O_4 - CuO - ZrO_2 NPs can potentially be used as a photocatalyst, and excitation of electrons from valence to the conduction band using UV- visible radiation is possible [12].

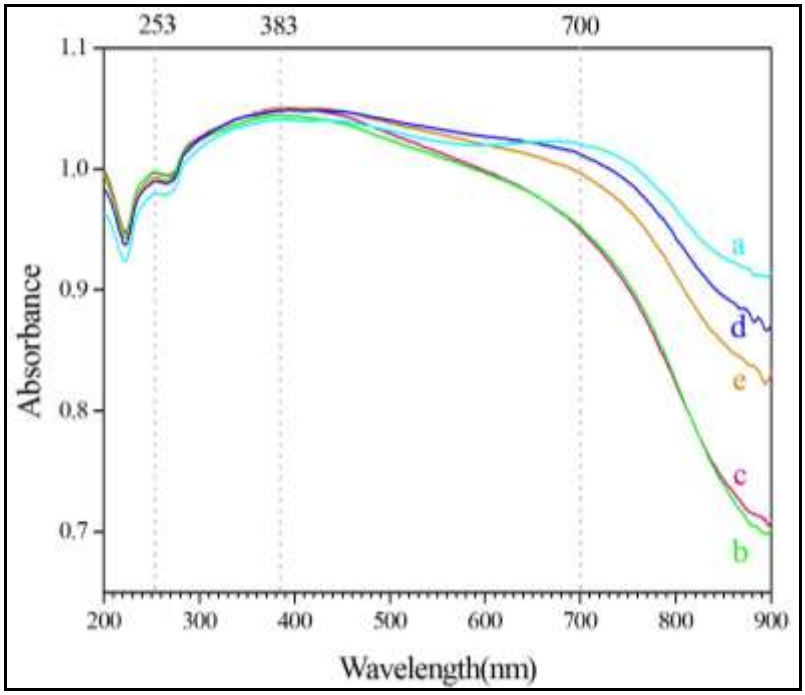

Figure 3 UV-Visible diffuse reflectance spectra of a) 0.1M Co_3O_4 - CuO - ZrO_2 NPs b) 0.2M Co_3O_4 - CuO - ZrO_2 NPs c) 0.3M Co_3O_4 - CuO - ZrO_2 NPs d) 0.4M Co_3O_4 - CuO - ZrO_2 NPs e) 0.5M Co_3O_4 - CuO - ZrO_2 NPs

TEM analysis

TEM image of 0.1M Co_3O_4 - CuO - ZrO_2 NPs (figure 4a) shows the typical morphology of the synthesized nanoparticles having several irregular shaped particles with some rod shaped particles. The size of these nanoparticles is in the range of 10 – 40nm which is agreement with the XRD results. The ring-like

diffraction pattern and the approximately circular nature of the selected area electron diffraction (SAED) spots indicated in Figure 4(b) reflects that the particles are crystalline in nature.

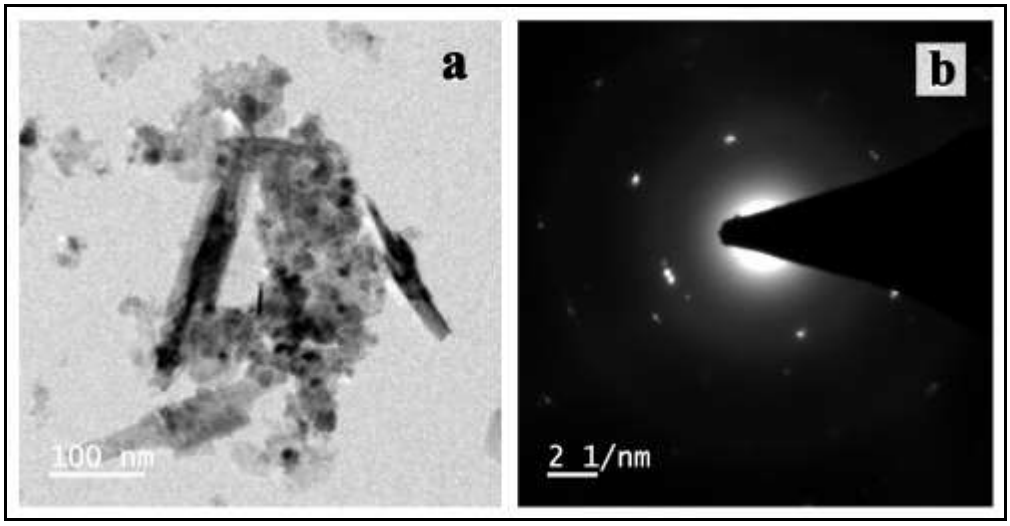

Figure 4 (a) TEM image of 0.1M Co_3O_4 - CuO - ZrO_2 NPs (b) SAED pattern of 0.1M Co_3O_4 - CuO - ZrO_2 NPs

SEM analysis

SEM micrographs of Co_3O_4 - CuO - ZrO_2 NPs synthesized at five different concentrations of $CoCl_2$, $CuSO_4$ and $ZrOCl_2$ (0.1M, 0.2M, 0.3M, 0.4M, 0.5M) are shown in Figure 5. The prepared Co_3O_4 - CuO - ZrO_2 NPs display granular flakes like morphology. The SEM micrographs also reveal that the granule size is drastically increased with increasing concentration of the precursors.

EDAX analysis

EDAX analysis was performed to confirm the elemental composition of the synthesized Co_3O_4 - CuO - ZrO_2 NPs. The presence of cobalt (Co), Copper (Cu), zirconium (Zr) and oxygen (O) signals peaks in the EDAX spectrum confirms that the metal oxides are dispersed well in Co_3O_4 - CuO - ZrO_2 NPs (Figure 5f). Obviously, the atomic ratio of Co, Cu and Zr (10.56, 12.15 and 8.42 respectively) is close to their molar ratio of their precursor (1:1:1) in the preparation procedure

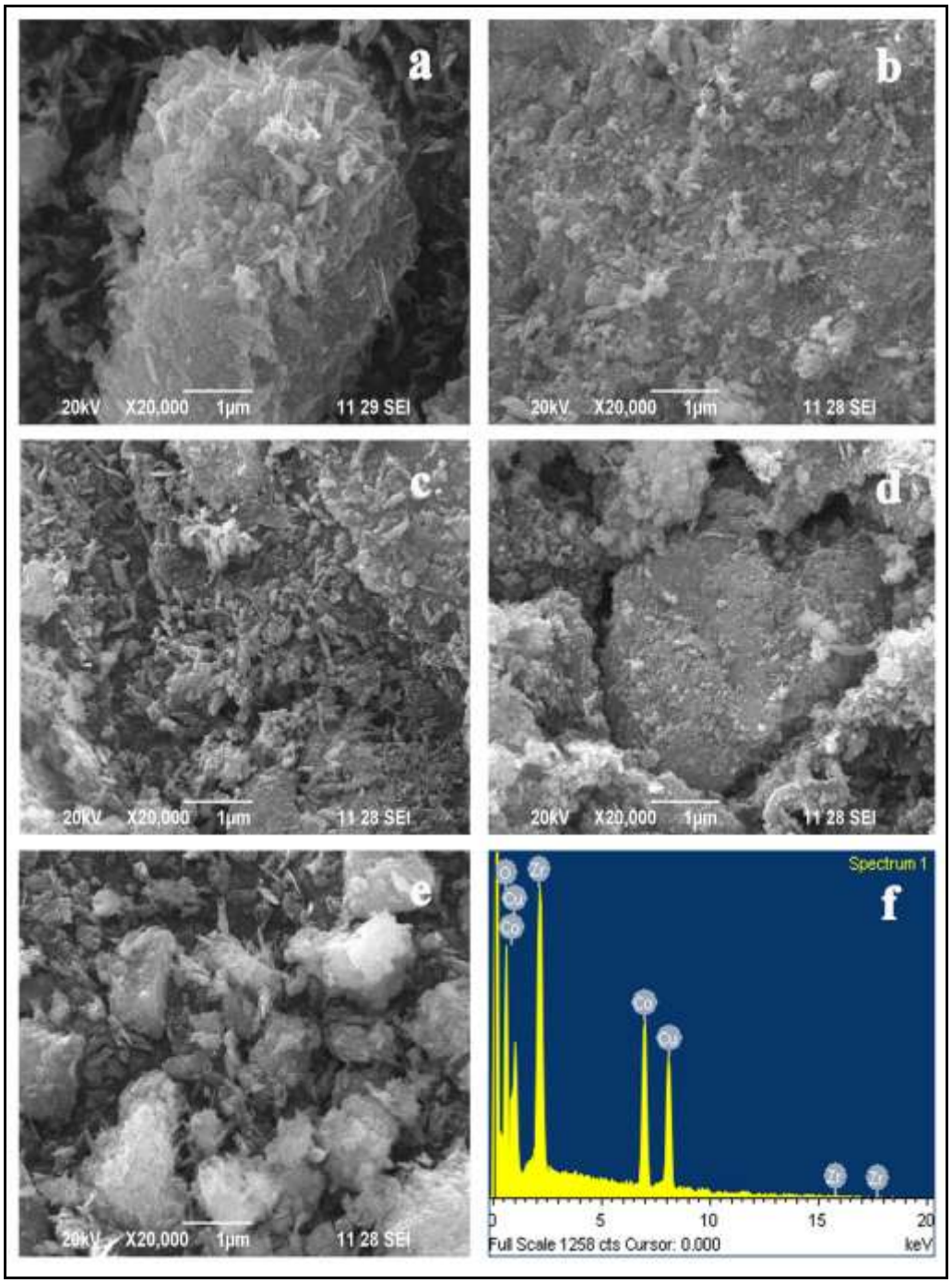

Figure 5 SEM image of a) 0.1M Co_3O_4 - CuO - ZrO_2 NPs b) 0.2M Co_3O_4 - CuO - ZrO_2 NPs c) 0.3M Co_3O_4 - CuO - ZrO_2 NPs d) 0.4M Co_3O_4 - CuO - ZrO_2 NPs e) 0.5M Co_3O_4 - CuO - ZrO_2 NPs f) EDAX of 0.1M Co_3O_4 - CuO - ZrO_2 NPs

.AFM analysis

The AFM image of Co_3O_4 - CuO - ZrO_2 NPs (Figure 6) reveals irregular elongated spheres morphology with lateral diameters of 10–40 nm. The average surface roughness (S_a) and the root mean square roughness **(**S_q**)** of the Co_3O_4 - CuO - ZrO_2 NPs are 8.487nm, 11.036nm respectively.

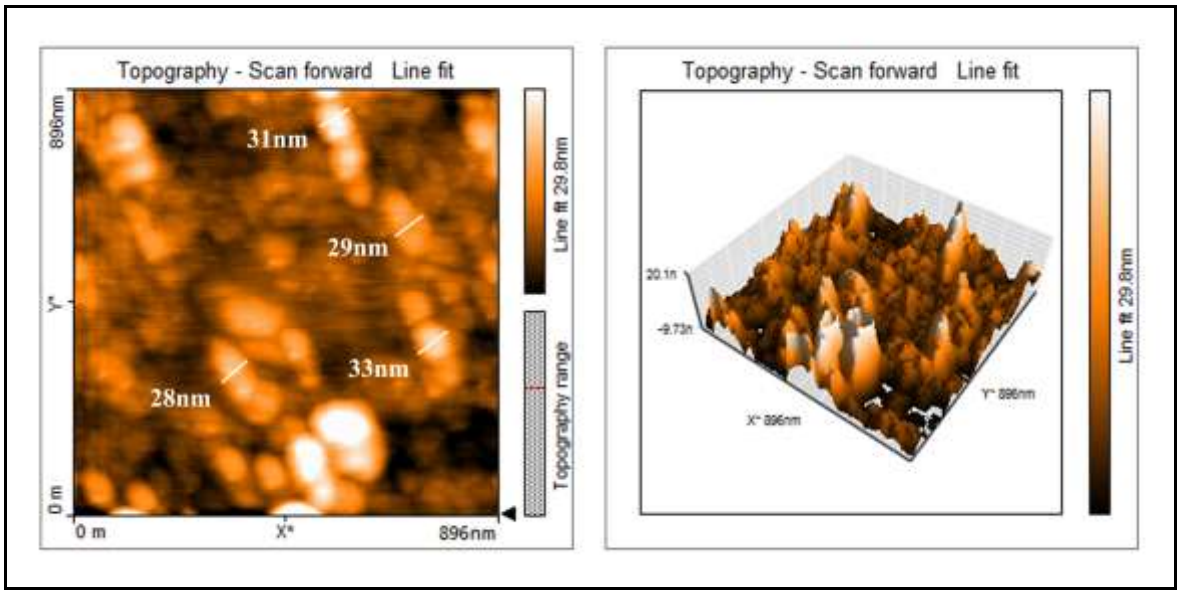

Figure 6 AFM images of 0.1M Co_3O_4 - CuO - ZrO_2 NPs

Conclusions

Nano Co_3O_4 - CuO - ZrO_2 mixed metal oxides were synthesized successfully by wet chemical method. SAED and XRD patterns confirm the crystalline nature of Co_3O_4 - CuO - ZrO_2 NPs with average particle size of 12.93 - 23.83nm. Co_3O_4 - CuO - ZrO_2 NPs are found to be irregular in shape with variable size ranging from 10 to 40 nm, as evident by TEM, SEM and AFM. The band gap values for the Co_3O_4 - CuO - ZrO_2 NPs are 3.13 - 3.24eV. This clearly indicates that the synthesized Co_3O_4 - CuO - ZrO_2 NPs can be used as a photocatalyst.

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