Synthesis and Characterization of Co3O4-ZnO-ZrO2 Ternary Nanoparticles

S. Alwin David, V. Veeraputhiran, C. Vedhi*

Department of Chemistry, V.O. Chidambaram College, Tuticorin – 628 008, Tamil Nadu, India.

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Abstract

Nano Co3O4-ZnO-ZrO2 mixed metal oxides were synthesized by wet chemical method by mixing of equimolar solutions of cobalt chloride, zinc sulfate and zirconium oxychloride in aqueous sodium hydroxide and refluxed at elevated temperature. The synthesized mixed nano oxides were characterized by FT-IR, XRD, UV-Vis DRS, TEM, SAED, SEM, EDAX and AFM. The FTIR spectra expose the presence of M-O bonds (M = Co, Zn, Zr). From XRD studies, the size of the Co3O4-ZnO-ZrO2 NPs are found to be 28.11 – 52.36 nm through Scherrer’s formula. The XRD patterns also reveal that the particle size is drastically increased with increasing concentration of precursors. From UV-Vis diffuse reflectance spectra (DRS), band gap energies of the [0.1 – 0.5] Co3O4-ZnO-ZrO2 NPs are found to be in the range of 2.41-2.68 eV. The TEM, SEM and AFM micrographs of 0.1 M Co3O4-ZnO-ZrO2 NPs display irregular shape with size ranging from 20-45 nm. SAED pattern confirms the crystalline nature of these nanoparticles. EDAX analysis indicates the presence of Co, Zn and Zr.

1. Introduction

Large surface-to-volume ratio and small size of the nanoparticles can guide to the different physical and chemical properties which are altered from those of their bulk counterparts. In recent times, there has been an increasing attention in the synthesis of nano mixed metal oxides. Co3O4 is an important p-type semiconductor which has been widely used in supercapacitor, lithium-ion batteries, solar cells, electrocatalysis, photocatalysis and sensing devices [1, 2]. ZnO is one of the most widely utilized n-type semiconductor due to its applications in UV-light emitting diodes, piezo-electric transducers, solar cells, memory devices, photodiodes, photodetectors, light emitting diodes, anticancer therapeutic agent, sensors, industrial wastewater treatment and photocatalysis [3, 4]. ZrO2 is a noteworthy n-type semiconductor because of its applications in many fields such as high temperature ceramics, restorative dentistry, electrochemical capacitor electrodes, sensor, fuel cells, optical devices and photocatalysis [5, 6].

Therefore, the research limelight has twisted towards reasonably priced metal oxides such as Co3O4, ZnO and ZrO2. In this work, Co3O4-ZnO-ZrO2 NPs were obtained by wet chemical method. The synthesized ternary metal oxide nanomaterials were characterized by FT-IR, XRD, DRS, TEM, SAED, SEM, EDAX and AFM.

2. Experimental Methods

2.1 Materials

The precursors CoCl2•6H2O, ZnSO4•7H2O, ZrOCl2•8H2O and the precipitant (NaOH) were purchased from Merck. All solutions were prepared using deionized water.

2.2 Synthesis of Co3O4-ZnO-ZrO2 Nanoparticles

About 25 mL of 0.1 M CoCl2•6H2O was added to the aqueous solution of 7.5 mL of 1.0 M NaOH solution and stirred well. To this mixture 25 mL of 0.1 M ZnSO4•7H2O and 25 mL of 0.1 M ZrOCl2•8H2O were added. The resulting mixture was stirred well and refluxed at an elevated temperature for 3 hours. The product was filtered, washed with water and dried. Similar procedure was carried out to synthesize different concentrations of [0.2 M – 0.5 M] Co3O4-ZnO-ZrO2 nanoparticles.

3. Results and Discussion

3.1 FTIR Analysis

FTIR spectra of Co3O4-ZnO-ZrO2 NPs are shown in Fig. 1. The bands in the low frequency region, 568-962 cm⁻¹ correspond to the lattice vibration modes of M-O (M = Co, Zn, Zr) [7, 8]. IR bands observed at around 1113 – 1116 cm⁻¹ are due to the presence of Symmetric stretching of Zr-O [8].
The band appears at 1384 cm\(^{-1}\) in the FTIR spectra indicates the presence of M-O rocking in plane vibration \((M = \text{Co, Zn, Zr})\) [9]. The absorption peaks at around 1465 cm\(^{-1}\) are assigned to the stretching vibration of Co-O bond [10].

### 3.2 XRD Analysis

The XRD patterns of the Co\(_3\)O\(_2\)-ZnO-ZrO\(_2\) NPs are presented in Fig. 2, the diffraction peaks at 2\(\theta\) values of 19.18\(^{\circ}\), 31.90\(^{\circ}\), 36.35\(^{\circ}\), 38.25\(^{\circ}\) and 56.13\(^{\circ}\) are attributed to (111), (200), (311), (220) and (422) planes of CoO\(_3\) (ICPDS card no. 76-1802) respectively [11]. The diffraction peaks at 2\(\theta\) values of 32.94\(^{\circ}\), 47.75\(^{\circ}\), 62.94\(^{\circ}\) and 68.06\(^{\circ}\) are due to (002), (102), (103) and (112) planes of ZnO (ICPDS card no. 36-1451) respectively [12]. The diffraction peaks at 2\(\theta\) values of 35.10\(^{\circ}\), 51.15\(^{\circ}\) and 58.97\(^{\circ}\) are assigned to the (200), (220) and (311) planes of ZrO\(_2\) (ICPDS card no. 50-1089) respectively [5].

Similar diffraction peaks are also observed in all the samples as given in the Fig. 2. The average particle sizes of the Co\(_3\)O\(_2\)-ZnO-ZrO\(_2\) NPs as estimated using the Scherrer’s formula are in the range of 28.11-52.36 nm. As the concentration of the precursors increases from 0.1 M to 0.5 M, the size of the nanoparticles also increases to an extent due to agglomeration of the small metal oxide nanoparticles.

![Fig. 2 XRD Patterns](image)

![Fig. 3 UV-Visible diffuse reflectance spectra](image)

### 3.3 UV-Visible Diffuse Reflectance Spectroscopic Analysis

The light absorbance properties of Co\(_3\)O\(_2\)-ZnO-ZrO\(_2\) NPs are investigated using UV-Vis diffuse reflectance spectrophotometer in the wavelength range of 200-900 nm. As shown in UV-Vis diffuse reflectance spectra (Fig. 3), two absorbance bands centered between 250-252 nm and 370-394 nm with a hump at around 670 nm, suggest that the samples can be activated by both UV and visible light irradiations [11].

There is a red shift in absorption bands (from 370 nm to 394 nm) observed in Co\(_3\)O\(_2\)-ZnO-ZrO\(_2\) NPs (from 0.1 M to 0.5 M) synthesized. This red shift is due to the increase in the particle size as well as decrease in the inter particle distance of Co\(_3\)O\(_2\)-ZnO-ZrO\(_2\) NPs (from 0.1 M to 0.5 M) [13].

The band gap \((E_g)\) of the NPs can be determined using well-known Tauc relation, \((a h v)^n = A (hv - E_g)\), where \(a\), \(h\), \(v\) and \(A\) are the absorption coefficient, Plank constant, light frequency and a constant, respectively. While \(n = 2\) for direct inter band transition. The \(E_g\) value can be estimated by plotting \((a h v)^2\) versus \(h v\) and extrapolating the linear part of curve to energy axis at \(a = 0\).

The calculated band gap energies are 2.68, 2.58, 2.52, 2.50 and 2.41 eV for 0.1 M, 0.2 M, 0.3 M, 0.4 M and 0.5 M Co\(_3\)O\(_2\)-ZnO-ZrO\(_2\) NPs, respectively. The band gap energy values suggest that these Co\(_3\)O\(_2\)-ZnO-ZrO\(_2\) NPs are visible light sensitive, capable to be photocatalysts under visible light illumination [11].

### 3.4 TEM Analysis

TEM images shown in Fig. 5, reveal that Co\(_3\)O\(_2\)-ZnO-ZrO\(_2\) NPs formed are irregular in shape and non-uniform in size ranging from 20-45 nm. It may be noted that the value obtained from TEM is in good agreement with that obtained from XRD measurements. The SAED pattern taken from the 0.1 M Co\(_3\)O\(_2\)-ZnO-ZrO\(_2\) NPs (Fig. 5(d)) shows strong diffraction rings and associated diffraction spots that indicate the crystalline nature of these nanoparticles.

![Fig. 4 Plot of (a (hv)^2 versus (hv) of a) 0.1 M Co\(_3\)O\(_2\)-ZnO-ZrO\(_2\) NPs b) 0.2 M Co\(_3\)O\(_2\)-ZnO-ZrO\(_2\) NPs c) 0.3 M Co\(_3\)O\(_2\)-ZnO-ZrO\(_2\) NPs d) 0.4 M Co\(_3\)O\(_2\)-ZnO-ZrO\(_2\) NPs and e) 0.5 M Co\(_3\)O\(_2\)-ZnO-ZrO\(_2\) NPs](image)

![Fig. 5 TEM image of 0.1 M Co\(_3\)O\(_2\)-ZnO-ZrO\(_2\) NPs in (a) 20 nm scale (b) 50 nm scale (c) 100 nm scale (d) SAED pattern of 0.1 M Co\(_3\)O\(_2\)-ZnO-ZrO\(_2\) NPs](image)
3.5 SEM Analysis

SEM micrographs of Co3O4-ZnO-ZrO2 NPs synthesized at five different concentrations of CoCl2, ZnSO4, and ZrOCl2 (0.1 M, 0.2 M, 0.3 M, 0.4 M, and 0.5 M) are shown in Fig. 6. The prepared Co3O4-ZnO-ZrO2 NPs display granular appearances with some rod-like morphology. The SEM micrographs also reveal that the granule size is drastically increased with increasing concentration of the precursors.

3.6 EDAX Analysis

EDAX analysis was performed to confirm the elemental composition of the synthesized Co3O4-ZnO-ZrO2 NPs. The presence of cobalt (Co), zinc (Zn), zirconium (Zr) and oxygen (O) signals peaks in the EDAX spectrum confirms that the metal oxides are dispersed well in Co3O4-ZnO-ZrO2 NPs (Fig. 6f). The atomic percent of Co, Zn and Zr is 9.85, 8.20 and 9.51 respectively. Obviously, the atomic ratio of Co, Zn and Zr is close to their molar ratio of their precursor (1:1:1) in the synthetic procedure.

Fig. 6 SEM image of a) 0.1 M Co3O4-ZnO-ZrO2 NPs b) 0.2 M Co3O4-ZnO-ZrO2 NPs c) 0.3 M Co3O4-ZnO-ZrO2 NPs d) 0.4 M Co3O4-ZnO-ZrO2 NPs and e) 0.5 M Co3O4-ZnO-ZrO2 NPs.

3.7 AFM Analysis

The AFM images that illustrate the surface morphology and roughness of Co3O4-ZnO-ZrO2 NPs are shown in Fig. 7. The shape of Co3O4-ZnO-ZrO2 NPs is irregular elongated sphere and the size is in the range of 20-45 nm. From the surface roughness analysis, it is observed that the surface roughness of the Co3O4-ZnO-ZrO2 NPs is estimated to be about 1.144 nm for the root mean square roughness (Srms) and 8.877 nm for the average surface roughness (Savg).

4. Conclusion

Nano Co3O4-ZnO-ZrO2 mixed oxides were synthesized effectively by wet chemical process. XRD patterns and SAED confirm the crystalline nature of Co3O4-ZnO-ZrO2 NPs with average particle size of 28.11–23.6 nm. Co3O4-ZnO-ZrO2 NPs are found to be irregular in shape with variable size ranging from 20–45 nm, as apparent by SEM, TEM and AFM. The band gap energies for the Co3O4-ZnO-ZrO2 NPs are found to be 3.15–3.35 eV.

References