Morphology Controlled Hexagonal Nanoflakes of Spinel NiCo₂O₄ Using Ethylene Glycol

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Abstract: The present work is focussed on the morphology controlled synthesis of hexagonal nanoflakes of Nickel cobaltites (NiCo₂O₄) by simple reflux condensation technique. At first mixed metal molecular complexes were prepared for the different mole concentrations of organic fuelling ligand 'guanidinium carbonate" and a mixture of water and Ethylene Glycol (EG) as solvents. As synthesized molecular precursors were analyzed through FTIR and Raman studies to understand their chemical environment. Both the Spectral observation clearly indicates that the presence of guanidinium moiety and metal glycolate formation in the precursor samples. Later these bimetallic precursors were subjected to calcination at 600° C for 4 hrs to obtain NiCo₂O₄ hexagonal flakes. The functional, crystallinity and morphologies of the residues (NiCo₂O₄) were characterized by FTIR, XRD and FESEM measurements. FESEM analyses reveal that ethylene glycol plays an important role (i.e) 'interlinking role" to determine the morphology of the hexagonal nanoflakes of NiCo₂O₄ and the mechanism was proposed. Finally hexagonal nano flakes NiCo₂O₄ were applied as photo catalyst for methylene blue degradation.

Keywords: Spinel oxides, organic bases, Ethylene glycol

1. Introduction

Mixed metal oxide (MMO) nanoparticles are called as hetero metal oxide nanoparticles, as they can incorporate more than two metals into the mixed metal oxide. The electronic and magnetic properties vary, when combining two metals in an oxide matrix. Mixed metal oxide nanoparticles exhibit unusual surface morphologies and possess more reactive surface, because of the presence of high concentrations of edge/corner sites and other defects. Furthermore, the combination of two metals in an oxide matrix can produce materials with novel structural or electronic properties that can lead to superior catalytic activity or selectivity. At structural level, a dopant can introduce stress into the lattice of an oxide host, inducing in this way the formation of defects that have a high chemical activity. On the other hand, the lattice of the oxide host can impose on the dopant element non-typical coordination modes with a subsequent perturbation in the dopant chemical properties. Finally, metal \leftrightarrow metal or metal \leftrightarrow oxygen \leftrightarrow metal interactions in mixed-metal oxides can give electronic states not seen in single-metal oxides.

In a traditional catalyst, metal nanoparticles are dispersed over an oxide 0support with the presumption that the main role of the support is to stabilize and disperse the metal particles along its surface. Typically, there is a low concentration of chemically active sites in the oxide and these may be blocked by the anchoring of the metal particles. By using a second oxide as a support (host), one can create a multifunctional configuration in which the catalyst exposes metal nanoparticles and chemically active oxide nanoparticles to the reactants. Thus, the reactants can interact with defect sites of the oxide nanoparticles, metal sites, and metal–oxide interfaces.

2. Structural Analysis (Powder XRD)

To confirm the crystalline phase of the nickel cobaltite powders powder X-ray diffraction were carried out and it is shown in **Fig 1.2**. All the diffraction peaks are corresponds to the pure cubic spinel phase of NiCo₂O₄ with fd3m space group (JCPDS card NO.73-1702). [3]

The single phase formation of $NiCo_2O_4$ indicates the advantage of guanidine molecule (i.e) it facilitates the combustion during crystallization and providing the resultant material with desired phase.



Figure 1.2: X-ray diffraction pattern for NiCo₂O₄

3. Surface Analysis

Fig 1.3 shows the field emission scanning electron microscope images of the NiCo₂O₄ sample prepared using guanidine carbonate under reflux conditions (absence of ethylene glycol). The morphology of the nickel cobaltite is aggregated spherical particles with micron sized crystals (Average particle size of ~70 nm). Generally under very

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slow growth conditions, the crystal growth habit is predominantly spherical in appearance to lower surface free energy. Therefore, nanoparticles are first formed in solution. With time increasing, self-assembly of nanoparticles into secondary aggregate spherical structures with micron size is realized. The schematic representation is shown in **Fig 1.4**.

Figure 1.3: FESEM images of NiCo₂O₄for0.9 M of GC (without Ethylene Glycol)



Figure 1.4: Schematic representation for the formation of NiCo₂O₄without EG

Nicobaltite nanopowders obtained with the help of guanidine molecule indicates that the fueling property of this molecule during crystallization.

Figure 1.5: Spectra for Nickel Cobalt precursor samples



Figure 1.6: Raman spectra for mixed metal complexes

In all the three samples the intense Raman band at 1009, $1011and1011cm^{-1}$ is attributed to the symmetric stretching of the CN₃ frame of guanidinium group. The absence of this CN₃ stretching vibrations in the FTIR spectrum of precursor samples clearly denotes that in all the prepared metal complexes guanidine ispresent as guanidinium (Gu⁺).

4. Structural Analysis

Powder X-ray diffraction studies were performed to determine crystalline nature and phase purities of the samples. The X-ray powder diffraction patterns of $NiCo_2O_4$ samples prepared with different moleconcentrations of metal complexes are shown in Fig(1.8).



Figure 1.8: X-ray diffraction patterns for NiCo₂O₄

Fig (1.6) shows the recorded Raman spectrum of molecular complexes with different mole concentration of GC in mixture of solvents (EG and water). Generally guanidinium ion has perfect D_{3h} symmetry in crystalline phase and in the solid state it has C_{3V} point group symmetry. The fundamental vibration modes of this molecule are assigned by the group frequencies of CN₃ and NH₂ functional groups.

All diffraction peaks in this pattern can be ascertained as cubic spinel structured NiCo₂O₄ with a space group of Fd3m (JCPDS Card no. 73-1702) [12]. Thesix well-defined diffraction peaks, including not only the peak position, but also their relative intensities, canbe indexed and assigned to (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) plane reflections of the spinel nickel cobaltite. From the XRD pattern it is observed that as the mole concentration of the GC increases the crystallite peaks seem to be improving in intensity. Using Scherrer equation average grain size (~20 nm) and lattice parameterofnickel cobaltites **a=8.065** Å is calculated.



Figure 1.9: FESEM images of NiCo₂O₄ for different mole concentrations of GC a) 0.7 M b) 0.9M c) 1.0M

FESEM images depicts that (**Fig 1.9(a-c**)), all the three products of nickel cobaltite prepared through reflux condense technique have uniform hexagonal nanoflakes morphology. These hexagonal flakes composed of small grains of spherical flakes in it. Schematic representation for the formation of NiCo₂O₄ with EG.

The above FESEM results clearly evident the role of ethylene glycol in the present work. Here ethylene glycol plays a dual role as complexing agent (metal glycolate formation) as well as morphology directing agent for the formation of perfect bilayer pattern in to hexagonal flakes.



Figure 1.10: Schematic representation for the formation of $NiCo_2O_4$ with EG

5. Role of Ethylene Glycol

In the present case it is believed that the ethylene glycol plays a vital role in the formation of hexagonal nanoflakes of $NiCO_2O_4$.

In general ethylene glycol is an optimal solvent and it has ability to form coordination complexes with metal cations. It is also used as reducing agent to synthesize metal nanoparticles from their respective metal salts [13].From the above information we expected that metal glycolate present in the mixed metal complexes $((Gun)^{2+}[NiCo(Gly)^{2-}_3].H_2O)$ in which the Ni and Co ions are bridged by the glycolate ions to form a nuclei(formation of flake likes) under appropriate synthetic conditions. After certain time interval these nuclei are started to grow and forming a perfect bilayer pattern of (M-OCH₂CH₂O-M) with increased surface free energy. After calcinating the as prepared metal complexes the bridged glycolate molecules were detached in to individual layers and resulting in hexagonal flakes of NiCo₂O₄ and it is schematically represented in Fig 1.10. This observation is also good for other metal oxide systems [14,15].



Paper ID: ETPTA-135

6. Experimental Techniques

Preparation of Mixed Metal Complex (Using guanidine carbonate)

Cobalt (II) chloride hexahydrate (CoCl₂.6H₂O, 0.2 mmol), Nickel (II) chloride hexahydrate (NiCl₂.6H₂O, 0.1 mmol), are dissolved in 5mL of DI water.Meanwhile Guanidine Carbonate (GC=0.9M) (H₂NC(=NH)NH₂)₂.H₂CO₃) is dissolved in 5mL DI water to form a transparent solution in water bath. The GC solution is added drop wise to the reaction mixture solution of metal chlorides with stirring to immediate formation of precipitate is observed.

The reaction mixture is stirred for 15 minutes, pH = 10 is measured. Then the resulting solution is transferred to boiling flask and connected to a Liebig or vigorous condenser, heated to 120°C and kept at that temperature for 24 hours. The products are washed with DI water three times, and dried for one hour. Then the as prepared molecular complexes are calcinated at 600°C for 4 hours to obtain nickel cobaltite.

Preparation of Metal Complex: (Presence of Ethylene Glycol)

Cobalt (II) chloride hexahydrate (CoCl₂.6H₂O, 0.2 mmol), Nickel (II) chloride hexahydrate (NiCl₂.6H₂O,

0.1mmol), are dissolved in 5mL of DI water and 5mL of Ethylene Glycol. The reaction mixture is stirred for one hour at room temperature. Meanwhile Guanidine Carbonate (GC) $(H_2NC(=NH)NH_2)_2.H_2CO_3)$ is dissolved in 5mL of DI water and 5ml of Ethylene Glycol to form a transparent solution in the water bath. The GC solution is added drop wise to the reaction mixture solution of metal chlorides with stirring. The immediate formation of precipitate is observed.

The reaction mixture is stirred for 15 minutes, pH is measured. Then the resulting solution is transferred to boiling flask and connected to a Liebig or vigorous condenser, heated to 120°C and kept at that temperature for 24 hours.

The products are washed with DI water three times, and dried for one hour. The same procedure is followed different molar ratio of Guanidine Carbonate as 0.9M, 1.0M (keeping the metal concentration as same).

Preparation of NiCo₂O₄

Nickel cobaltites nanopowders have been obtained through calcinating the precursor sample inside the muffle furnace at 600°C for 4 hours. The as prepared and calcinated compound are analyzed by FTIR, TGDTA, XRD, SEM, and study their chemical composition, thermal, structural and morphological properties respectively.

7. Results and Discussion

The present work is focused on the morphology controlled synthesis of hexagonal nanoflakes of Nickel cobaltites $(NiCo_2O_4)$ by simple reflux condensation technique. In

order to attain the goal we made two attempts. In the first case bimetallic (NiCo) molecular complexes were prepared with the help of organic fuelling ligand 'Guanidinine carbonate' Then the as prepared molecular complexes were subjected to calcinations to obtain NiCo₂O₄ nanopowders.

Characterization of Nickel Cobaltite Powders Using Guanidine Carbonate: (Absence of Ethylene Glycol)

Nickel cobaltite nanopowders are prepared using organic base guanidine carbonate molecule For a representative example, here in nickel cobaltite prepared using 0.9 mole concentration added guanidine carbonate sample is reported. FTIR, XRD and FESEM results obtained from this sample are discussed below.

FTIR Analysis

Fig (1.1) shows FTIR spectra of the as prepared mixed metal complex using 0.9 mole concentration of guanidine carbonate. The as prepared metal complexes exhibit broad band in the region $3500-3200 \text{ cm}^{-1}$ includes N-H stretching and OH stretching modes of guanidine and water molecules respectively. The intense and sharp peak at 1665 cm⁻¹ is attributed to the characteristic stretching vibration of C=N group of guanidine [1].



Figure 1.1: FTIR spectrum for mixed metal complexes

The small peaks at 853 cm⁻¹and 684cm⁻¹ is corresponds to the C-H group vibrational modes of guanidine [2]. Interstingly the carbonate group vibrational frequencies (883 cm⁻¹) get shifted in the precursor samples indicates the possibility for carbonate ions can act as anionic spices in the as prepared metal complexes. In plane ring mode of CN₃group is also observed at 580cm⁻¹. The presence of ligand bands (C=N,NH₂ modes of vibration) in the as prepared metal complexes clearly indicates that guanidine group is involved in the complex formation.Thenthe as prepared precursor sample is calcinated at 600°C for 4 hours to obtain NiCo₂O₄.

Characterization of Nickel Cobaltite

Powders Using Ethyleneglycol

Here in mixed metal molecular complexes prepared with different mole concentrations of organic fuel guanidinium

carbonate (0.7M, 0.9M, and 1M)and a mixture of water and ethylene glycol as solvents and the results are discussed below.

FTIR Analysis

To confirm the presence of guanidinium and to understand the chemical environment present in the as prepared mixed metal molecular complexes FTIR spectrum were recorded. Fig 1.5 shows the FTIR spectra of free guanidine carbonate (a) in comparison with that of molecular complexes prepared at different mole concentrations of guanidine (**b-d**) in a mixture of ethylene glycol and water as solvents. The infrared spectra of the pure GC (a) shows the fundamental modes of vibrations at 1660cm⁻¹(vC=N), 3300-3200 cm⁻¹(vN-H) and the peak at 883 cm⁻¹ corresponds to (C-H) interaction between the guanidinium and carbonate group of the molecule [2,4].IR spectrum of the mixed metal complexes exhibits characteristic ligand bands at 1680 cm⁻¹(vC=N) and at 3200 cm⁻¹(N-H stretching vibrations) with slight shift in intensity as compared to pure GC. Moreover the carbonate group vibrational frequencies (883 cm⁻¹) are not present in the precursor samples. This indicates during the reflux conditions carbonate ions are eliminated. The above IR spectral observation clearly indicates the presence of guanidinium moiety with complex formation in the precursor samples.

Raman Analysis

Raman spectroscopy is a non destructive and structure sensitive spectroscopic technique, for understanding the crystalline nature and material structure. The as prepared precursors were further probed for Raman analysis to confirm the observation from FTIR spectrum.

A similar type of band has also been noted in earlier from guanidine compounds [1,6,7]. The vibrational modes appear at 537 cm⁻¹in the samples corresponds to the in plane CN₃ modes of vibrations. The existence of ethylene glycol in the precursor samples is also accounted from the Raman spectrum. The highly intense raman band at 1091 cm⁻¹, 1091 cm⁻¹ and 1089 cm⁻¹ belongs to the gauche conformation mode of ethylene glycol and it is due to C-O stretching between the C and OH groups of ethylene glycol [8,9]. Thus the presence of this vibration reveal that there is a possibility for the formation of metal glycolates (i.e.) ethylene glycol is coordinated with the metal ion. In the entire Raman spectrum precursor samples exhibits strong raman band at 144 cm⁻¹ and itisassociated to theisobestic point of ethylene glycol (EG) - water mixtures [10]. Therefore from both the FTIR and Ramen spectroscopic studies the as prepared precursor can be mostly figure out as (Gun) $_{2}^{+}$ [NiCo(Gly)²⁻₃].H₂O. It is schematically represented below:



Schematic representation of formation mechanism for mixed metal complex

Characterization of Hexagonal Nanoflakes of Nickel Cobaltite

FTIR Analysis

Formation of Nickel cobaltites by the thermal decomposition of the mixed metal complexes $((Gun)_2^+[NiCo(Gly)^{2-3}].H_2O)$ has been confirmed by the IR spectrum(**Fig1.7**).Mixed metal oxides show two strong vibrational bands in the region of 664-569 cm⁻¹ corresponding to the metal oxygen stretching from tetrahedral and octahedral sites, of nickel and cobalt respectively.These are the characteristic vibration of nickel cobaltites [11].IR spectra of the residue indicates that the organic fuels are all most eliminated during calcinations.



Figure 1.7: FTIR spectrum for NiCo₂O₄

Morphological Analysis

Surface morphology of the as prepared Nickel cobaltite nanopowders synthesized using different mole concentrations of guanidinium carbonate (O.7M, 0.9M, 1M) in mixture of solvents (ethylene glycol and water) were analyzed through field emission scanning electron microscope.

8. Application

Photocatalyst Test



1.10 UV-Vis absorption spectra during photocatalytic reaction of MB

In the present work the as prepared NiCo₂O₄ hexagonal nanoflakes were dispersed in the methylene blue dye solution and illuminated UV light for different time intervals (0-4 hours) and their absorption were recorded. The absorption results are shown in **Fig 1.10**. Absorption results indicate that NiCo₂O₄hexagonal nanoflakes exhibits poor degradation efficiency. This may be attributed to poor surface area and high electron hole recombination rate present in NiCo₂O₄.

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