Green Synthesis and Characterization of Nickel Tungsten Bimetallic Oxide Nanoparticles via Microwave Irradiation Technique

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Abstract
Nickel tungsten bimetallic oxide nanoparticles were synthesised in ethylene glycol using microwave irradiation technique. Nickel and tungsten oxide nanoparticles were synthesised separately using microwave assisted polyol synthesis method. The respective systems are combined together in ratio 1:1 molar and are subjected to microwave irradiation to get Ni-W bimetallic oxide. The structure and composition of nanoparticles were characterised by UV-Visible Spectroscopy, FT-IR Spectroscopy, X-Ray Diffraction (XRD), Energy Dispersion Spectroscopy (EDS), Transmission Electron Microscopy (TEM), Photoluminescence Spectroscopy (PL) and Magnetic Susceptibility measurements. From the XRD and FT-IR measurements, nanocrystalline Wolframite structure of Ni-W bimetallic oxide nanoparticles was established.

The emperical formula of the nanoparticle is found as $Ni_{0.4}W_{0.6}O_{2.6}$*. The composition may be varied by changing the ratio of Ni and W. A maximum absorbance of 385nm was obtained in UV-Visible spectrum and three emission peaks were obtained in the visible region of photoluminescent studies. Further studies can be done on the catalytic and electrochromic properties of the substance.*

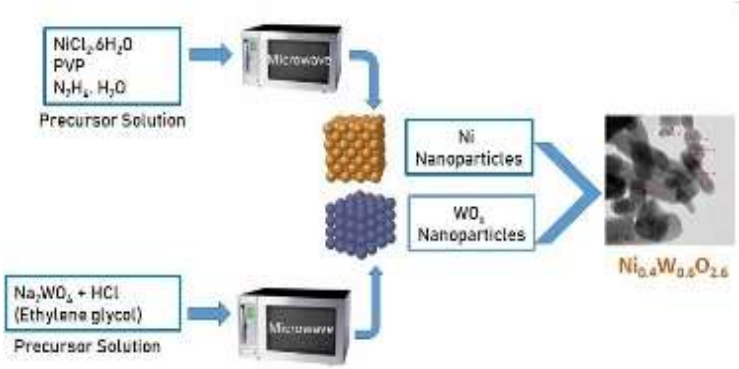
Keywords: Bimetallic oxide nanoparticles, Nickel-Tungsten, Microwave irradiation, Green synthesis.

Introduction

The study on bimetallic oxide nanoparticles is of great interest nowadays because of the increased potential application for which they can be applied, particularly in industrial catalytic applications. The bimetallic oxide nanoparticles have greater advantage over monometallic oxide as they incorporate nano-dimension properties of more than one element within a single nanosystem. This obviously enhances the properties through synergetic interaction between corresponding elements.

Nickel tungsten bimetallic oxide nanoparticles are of greater importance since they possess several applications. These can be used in electrochromic smart windows and possess catalytic activity etc.[1,4,9,15] They can be used in humidity sensors too. Bimetallic oxide nanoparticles are generally synthesized by various methods like sol-gel synthesis, hydrothermal synthesis, microwave irradiation, chemical vapor deposition, combustion technique, pyrolysis, mechanical grinding, laser ablation and sputtering[7]. In the present work, microwave assisted green synthesis of nickel-tungsten bimetallic oxide by polyol method using ethylene glycol as solvent, hydrazenium hydroxide as reducing agent and poly vinyl pyrrolidone (PVP) as capping agent is used. It is an efficient method in terms of time and energy compared to other conventional methods[14]. It takes only minutes to complete the reaction using microwave irradiation whereas conventional procedures take several hours.

Polyol synthesis is the most convenient method for the synthesis of metal oxide nanoparticles of uniform size due to high boiling point and penetration power[14]. Nickel-tungsten bimetallic oxide possesses LSPR (Localized Surface Plasmon Resonance) properties, electrochromic properties and optical properties[2,3]. Due to the electrochromic properties, it can be used as electrochromic smart window, in catalytic applications and electrochemical applications.



Here we consider the synthesis of Ni-W bimetallic oxide in the ratio 1:1 M and characterization is done by using powder XRD, FT-IR, TEM and EDS analysis. Optical characteristics were evaluated using UV-Visible Spectroscopy and photoluminescence. Magnetic susceptibility measurements are done to assess the magnetic behavior of nanoparticles.

Material and Methods

Materials: The following chemicals are used: Nickel chloride hexahydrate ($NiCl_2.6H_2O$), Sodium tungstate (Na_2WO_4), Ethylene glycol, Hydrazenium hydroxide, PVP (Polyvinylpyrolidone), Sodium Carbonate (Na_2CO_3) and Sodium Hydroxide (NaOH).

Apparatus: Powder XRD was taken using Bruker D8 Advance X-Ray Diffractometer over a 2θ range 10 to 80^0, the IR spectra of bimetallic oxide nanoparticles were recorded in the frequency range 400-4000cm^{-1} on Shimadzu DR-43S FT-IR spectrophotometer, High Resolution Transmission Electron microscopic measurements were made by LaB6 source with a magnification of 2000x-1500000x using Joel/JEM 2100 High Resolution Transmission Electron Microscope. Electron Diffraction Spectroscopic studies were made by using Carl Zeiss EVO 18 Secondary Electron Microscope with EDS.

UV-Visible spectroscopy measurements were conducted in absorption mode over a wavelength range of 200-800nm using Perkin Elmer Lambda 25 UV/VIS Spectrometer. Fluorescence measurement was made by using Xe lamp source in a wavelength range 370-680nm on JASCO FP-8300 Fluorescence Spectrometer. Magnetic susceptibility measurements of nickel tungsten oxide nanoparticles were done by using Sherwood Scientific Magnetic Susceptibility balance.

Synthesis of Ni nanoparticles: 1M $NiCl_2$ solution is mixed with 0.1M Na_2CO_3 solution, poly vinyl pyrrolidone (PVP) solution, 0.1M NaOH solution, 0.6mL of hydrazenium hydroxide ($N_2H_4.H_2O$) and ethylene glycol. The mixture solution was irradiated under microwave for 120 seconds, filtered, washed and dried.

Synthesis of WO_x nanoparticles: Sodium tungstate is heated with Conc. HCl and distilled water. Yellow coloured tungstic acid is dissolved in 20mL ethylene glycol and microwave irradiated for 2 min with hydrazenium hydroxide and PVP. Filter, wash and dry.

Synthesis of bimetallic oxide nanoparticles: 0.58g Ni nanoparticles were dispersed in 20 mL ethylene glycol and 2.31g WO_3 nanoparticles were added to it. To this, 4mL PVP solution and 0.6mL hydrazenium hydroxide were added. The mixture was irradiated in a microwave oven for 2 to 3 minutes until a dark coloured solution is obtained. Filter, wash with water, dry and calcinate at 500^0C for 1 hour.

Results and Discussion

The XRD measurements were carried out using Brucker D8 Advance X-Ray Diffractometer. The X-Rays were produced using a sealed tube and the wavelength of X-Ray was 1.5406Å. Figure1 shows powder XRD patterns for nickel tungsten oxide nanoparticles prepared by microwave synthesis with PVP as capping agent. The diffraction patterns produced by parent NiO (JCPDS card 78-0429) and WO_3 (JCPDS card 43-1035) are shown by Juan et al[8]. The main diffraction peaks of WO_3 were observed at 23.20 and 24.12, 34.39°.

In the XRD pattern of $Ni_xW_{1-x}O_y$ besides strong peaks corresponding to WO_3, new peaks at 15.79, 19.42, 25.10, 31.10, 36.74, 41.82 and 54.78° are observed. New diffraction peaks were observed as the principal peaks of the monoclinic $NiWO_4$ phase (JCPDS card 72-1189). The intensity of $NiWO_4$ peaks varies with the Ni content. With the increase in Ni content, peaks of WO_3 become weaker and correspond to $NiWO_4$ becoming stronger in intensity. From the θ values, it was found that the diffraction peaks corresponding to (010), (100), (011), (110), (111), (002), (200) and (202) were indexed and are in agreement with the monoclinic Wolframite structure of nickel tungstate.

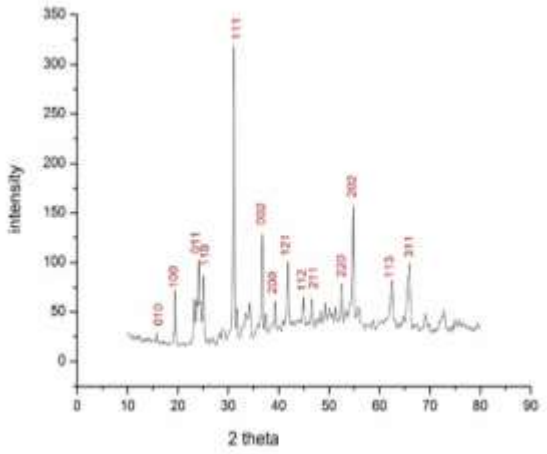


Fig. 1: XRD of Ni-W oxide

The FT-IR spectrum of nickel tungsten oxide nanoparticle is shown in fig. 2. This spectrum shows IR absorption due to different vibrational modes. Characteristic major peaks are observed at 1002.98, 864.11, 671.23, 640.37, 611.43, 530.42 and 449.41 cm^{-1}.

In comparison to the previous investigation[6], these peaks attributed to the Wolframite type structure. It has been reported that the main absorption bands of Wolframite type structure[11] were observed in a range of 450-1000 cm^{-1}. In comparison to previous investigation, these peaks are attributed to the vibrational bands of $NiWO_4$. The band appearing at 864.11 cm^{-1} arises from the vibration of WO_2 entity present in W_2O_8 groups. The absorption bands at 671.23cm^{-1} and 640.37cm^{-1} are typical of two oxygen bridges (W_2O_2) and correspond to asymmetric stretching of same group. The band at 1002.98 cm^{-1} corresponds to stretching modes of W=O terminal bonds.

Also the observed spectra below 500 cm^{-1} are due to vibrations of NiO_6 polyhedra. The spectrum of calcinated sample confirms the formation of crystalline particles. Particle size of nanoparticles was measured by Debye-Scherrer equation and is found to be of the order of 30-40nm.

Electron diffraction studies were carried out using Scanning Electron Microscope with EDS. The EDAX spectrum of nickel tungstate is shown in the figure 3. The peaks of EDAX pattern confirmed the presence of nickel and tungsten in the product. The average atomic weight percentage of Ni and W is about 11.96 and 65.91% respectively. The elemental analysis confirms the empirical formula of the product as $Ni_{0.4}W_{0.6}O_{2.6}$.

Fig. 4 shows the TEM micrograph of nickel tungsten bimetallic oxide particles that were synthesised by microwave irradiation method in a green route. Based on TEM analysis, the average size of the nickel-tungsten oxide nanoparticles was found to be 40nm. TEM images show that the size distribution of nanoparticles was almost homogenous and most of the nanoparticles were in spherical geometry with an average size of 40nm and also rod shaped in length of about 119nm. The high resolution TEM images display slight agglomeration of the nanoparticles.

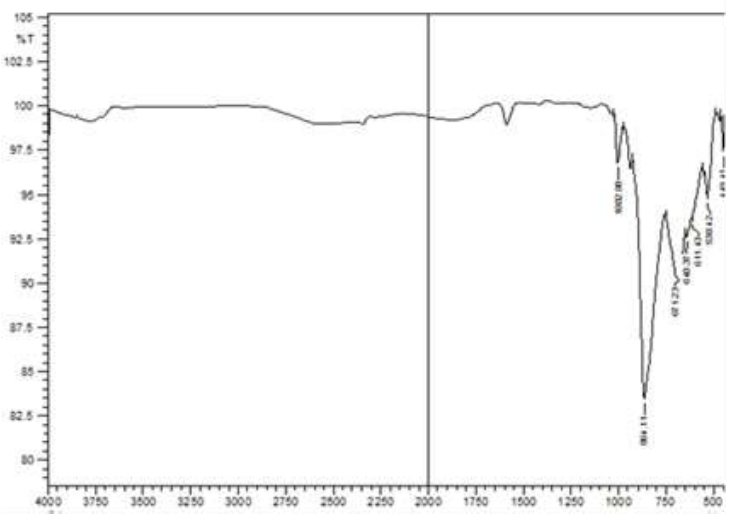


Fig. 2: FT-IR Spectrum of Ni-W oxide

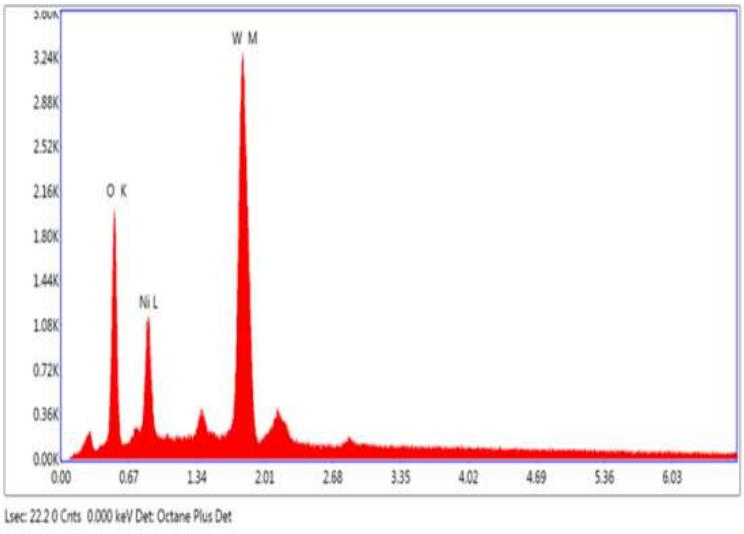


Fig. 3: EDS Spectrum of Ni-W oxide

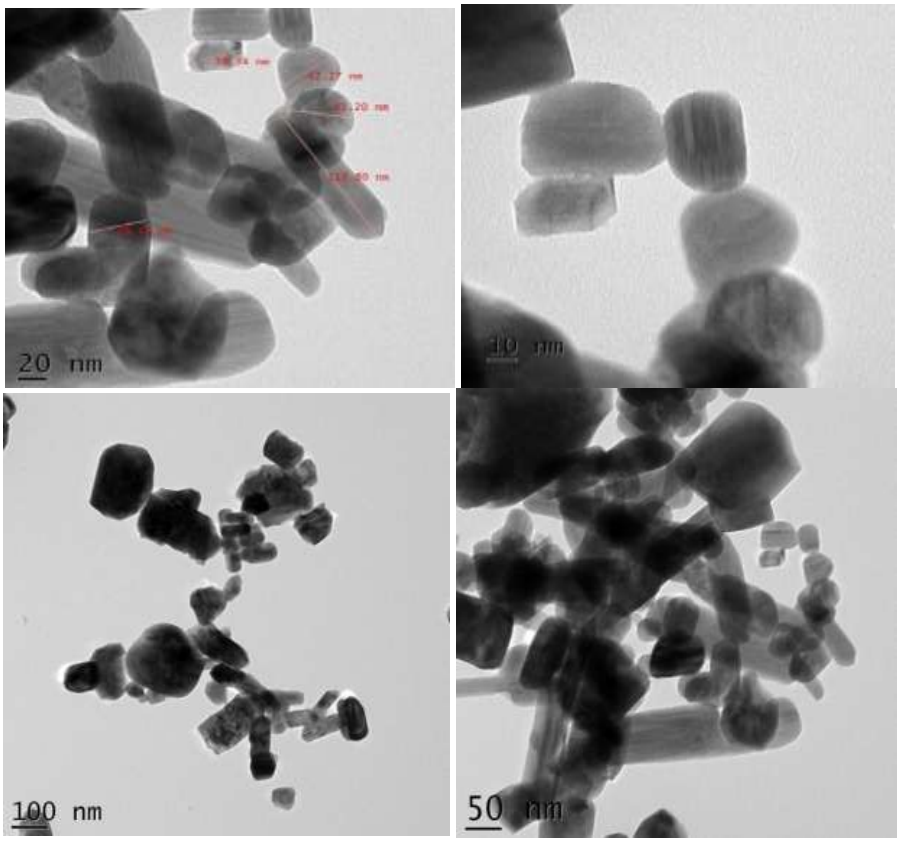


Fig. 4: TEM Micrograph images of Ni-W bimetallic oxide

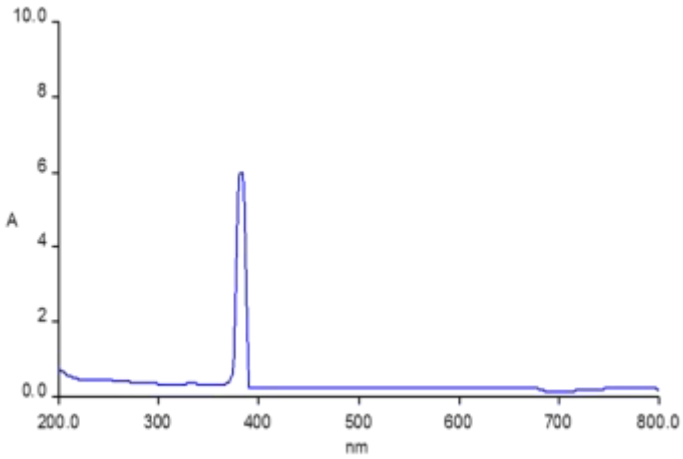


Fig. 5: UV-Vis spectrum in ethylene glycol

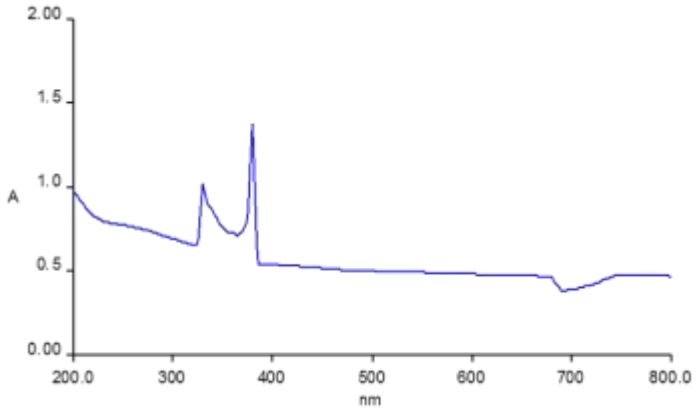


Fig. 6: UV-Vis spectrum in water

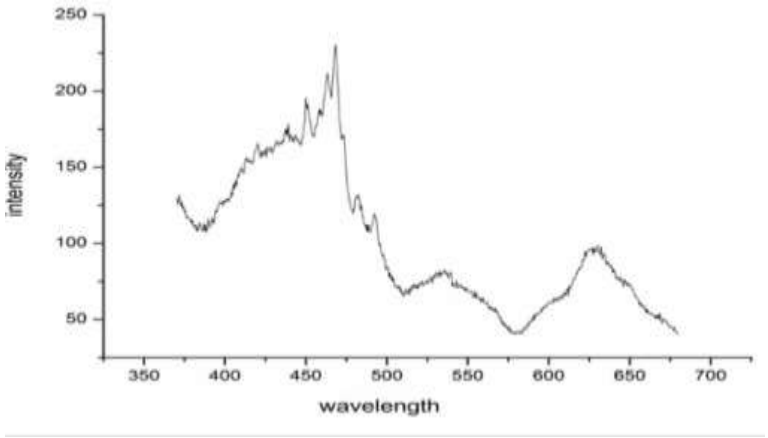


Fig. 7: Photoluminescence Spectra of Ni-W oxide

The absorption spectra of nickel tungsten oxide nanoparticles were recorded using UV-Vis spectrophotometer (Lambda25 UV/VIS Spectrometer) in the range of 200-800nm. The optical absorption spectrum of nickel tungsten oxide dispersed in ethylene glycol and water is shown in the figures 5 and 6 respectively. In ethylene glycol, a maximum intensity peak is found at 385nm. But in water, 2 peaks at 330nm and 380nm were observed. The peak at 330 nm may be due to magnetic Ni NPs. This peak is not found in ethylene glycol.

This may be due to the magnetic force of nickel that causes them to precipitate[5]. It is attributed to small crystal size and relating quantum confinement of the excitonic transition for nano-structures[10]. This work shows a red shift from the previously reported data[13]which may be due to the difference in particle size of the sample. UV–Vis result reveals that $NiWO_4$ nano-particles have good light absorption properties not only in the ultraviolet region but also in the visible light wavelengths[10].

Fluorescence measurements of the sample were carried out using a Xe lamp source by exciting the molecule at its absorption frequency of 385 nm. Figure 7 shows fluorescence emission spectra of nickel tungsten oxide nanoparticles prepared by microwave irradiation. Employing 370 nm as excitation wavelength, the photoluminescence spectra display an electronic transition within Wolframite molecular complex connected with intrinsic emission. The emission of synthesised nanoparticles was in the wavelength range of 390-670 nm. The obtained pattern has emission bands due to WO_6^{6-} complex along with some defects in the crystal structure.

Previous studies[12] proposed that blue and green emissions are due to intrinsic WO_6^{6-} complex. The double emission from $^3T_{1u} \rightarrow {}^1A_{1g}$ may be responsible for this. The blue emission peak at 467nm could be due to excitonic photoluminescence process in which non radiative transitions of excited electrons from conduction band bottom to different sub bands occur first and subsequent radiative transition from sub band to valence band top can take place[16]. The yellow-orange emission is attributed to the recombination of electron-hole pairs localised at oxygen atom deficient tungstate ions. Also the transitions of $T_{2u} \rightarrow T_{2g}$ and $T_{1g} \rightarrow T_{2g}$ are responsible for green and yellow bands.

In general, the excitonic photoluminescence spectrum mainly arises due to defects in semiconductors. Hence the blue emission peak may show the presence of interstitial oxygen atom inside NiO matrix due to addition of tungsten oxide. Magnetic susceptibility measurements confirmed the paramagnetic behaviour of the compound with unpaired electrons.

Conclusion

Nanoparticles of Ni-W bimetallic oxide with Wolframite structure were successfully synthesised by microwave assisted polyol method in a reliable, fast, efficient and cost effective manner. The composition and structure of nanoparticles were characterised by TEM, EDS, FT-IR and XRD measurements. Optical characteristics were obtained by UV-Vis and photoluminescence studies and magnetic properties using magnetic susceptibility measurements.

Initially, the absorption properties of the sample in UV as well as visible region were observed with a maximum absorbance at 385nm in ethylene glycol medium. In FT-IR spectra, characteristic vibrations corresponding to NiO, WO_2, W_2O_8 and W═O were observed which confirm the wolframite structure of Ni-W oxide NPs. The EDS study confirms the empirical formula of sample as $Ni_{0.4}W_{0.6}O_{2.6}$. XRD analysis showed characteristic 2θ peaks of Ni-W bimetallic oxide and supports its formation.

Particle size of nanoparticles was measured by Debye-Scherer equation and was found to be of the order of 30-40nm. TEM images confirm particle size of the prepared Ni-W bimetallic oxide nanoparticles. Magnetic susceptibility measurements show that the compound is paramagnetic with unpaired electrons. Hence the synthesis of Ni-W bimetallic oxide in a green method using microwave radiation was confirmed and further studies have to be carried out in the electrochromic and catalytic activity of the compound.

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