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Synthesis, Characterization and Photocatalytic Activity of $NiWO_4$ Nanoparticles

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Abstract. Nanocrystalline $NiWO_4$ powder sample is synthesized by simple direct chemical precipitation method. The phase purity, crystal structure and morphology of $NiWO_4$ nanoparticles are investigated by X-ray diffraction and transmission electron microscopy. Vibration modes of as prepared sample are analyzed using Fourier transform infrared spectroscopy. Using UV-Vis spectroscopy and photoluminescence spectroscopy, optical properties of the sample are explored. The photo catalytic activities of the $NiWO_4$ nanoparticles are investigated for the degradation of methylene blue (MB) dye. The photochemical reaction follows first-order decay kinetics and a degradation rate of 46.26% is obtained.

INTRODUCTION

The transition metal tungstate with formula MWO_4 have attracted much attention due to their wide range of applications in the fields of photo anodes, laser hosts, optical fibre, scintillation detectors, catalysts, humidity sensors and pigments.[1-3] In this group of MWO_4, synthesis of $NiWO_4$ nanopowder has gained considerable importance due to its appropriate potential for application in electronic, catalysis and optical fields. In the present work nanocrystalline $NiWO_4$ powder sample is successfully synthesized by simple chemical precipitation method without using any surfactant, templates or catalyst. The low cost, low corrosion, high stability and appropriate band gap energy of $NiWO_4$ nanoparticles make them ideal photo-catalyst for waste water treatment through the degradation of organic pollutants. The degradation of methylene blue (MB) dye solution over the surface of $NiWO_4$ photo catalysts was reported previously in the range of 10- 15 % for a long irradiation time.[4] The current work demonstrates high photo catalytic performance of $NiWO_4$ nanoparticles for the degradation of MB.

EXPERIMENTAL DETAILS

Materials and Sample preparation

Analytical grade Nickel (II) nitrate hexa hydrate, $Ni(NO_3)_2.6\ H_2O$ (98%, Merck) and Sodium tungstate, $Na_2WO_4.2H_2O$ (98%, Merck) are used without further purification for the synthesis of nanocrystalline $NiWO_4$. Distilled water is used in all the synthesis procedures. In a typical synthesis, 0.1 M solutions of $Ni(NO_3)_2\ .6\ H_2O$ (sol A) and $Na_2WO_4.2H_2O$ (sol B) were made. Sol B was added to sol A and stirred using a magnetic stirrer. After completing the precipitation, above solution was washed several times with distilled water to remove unreacted nitrate and sodium ions from the obtained product. Then the precipitate obtained was dried at 80^0C for 15 h. The dried powder was calcined at 600 °C for 3 h to get the sample.

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Characterization

X-ray powder diffraction (XRD) pattern of as-prepared $NiWO_4$ sample was taken by a Bruker D8 Advance X-ray diffractometer with Cu-Kα radiation (λ = 1.5406Å, X –ray tube voltage = 35 kV and current =35 mA) in the 2θ range from 0 to 80^0 at increments of 0.02^0 with a step time of 29.1s. Transmission electron microscopy (TEM) images of powder sample was taken from a JEOL/JEM 2100 (Source: LaB6 and voltage: 200 kV). Fourier transform infrared (FTIR) spectrum of the $NiWO_4$ sample was recorded by FTIR spectrophotometer (Thermo Nicolet, Avatar 370) in the range 4000 to 400 cm^{-1}. Absorption spectrum of the sample was obtained using a double-beam UV–Visible spectrophotometer (Cary 5000 model) with a scan rate 600 nm/min. Photoluminescence (PL) spectrum of the sample was recorded by fluorescence spectrometer, RF- 5301 (slit width of 5.0 nm), using an excitation wavelength of 320 nm at room temperature.

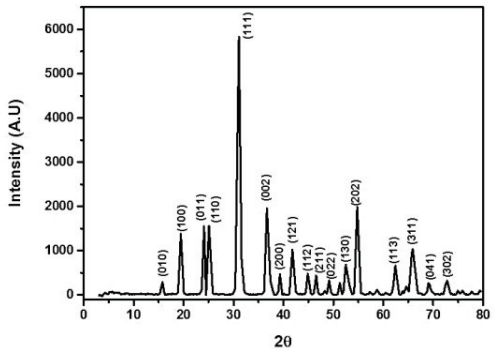
Photocatalytic experiment

The photocatalytic activity of the $NiWO_4$ particles were examined using aqueous MB dye under UV light irradiation (40 W) at room temperature at the λ_{max} of 665nm. The initial concentration of MB of 10 ppm in the presence of 0.050g of catalyst was sonicated for 30 min to obtain desorption/absorption equilibrium before irradiating the solution. The solution was irradiated and aliquots were drawn at regular intervals of time, centrifuged and the solution was analyzed for absorbance using UV- Vis spectrophotometer. A_0 is the absorbance of dye at initial stage and A_t is absorbance of dye at time t, Percentage degradation = $(A_0-A_t)/A_0$ X 100.

RESULTS AND DISCUSSION

X-Ray Diffraction Analysis

The X-ray diffraction pattern of the $NiWO_4$ sample is shown in Fig.1. The XRD patterns obtained agrees well with the Joint Committee on Powder Diffraction Standards (JCPDS) file No. 72-0480 and the sample corresponds to wolframite monoclinic structure with space group P2/C. This confirms that the experimental conditions used are favorable for the formation of the $NiWO_4$ nanoparticles, and oxygen atoms are hexagonally closely packed and the metal ions occupy a quarter of all the octahedral sites. The average crystallite size of $NiWO_4$ nanoparticles is calculated using Scherrer equation[5] and the value obtained is 25.13 nm.



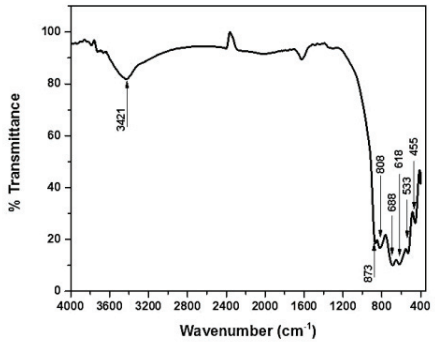


FIGURE 1. X-Ray diffraction patterns of $NiWO_4$ sample. **FIGURE 2**. FTIR spectrum of $NiWO_4$ sample

FT-IR Spectroscopy

FT-IR spectrum of the sample is shown in Fig.2. The main absorption bands of wolframite type structure appear in the range of 450-1000 cm^{-1}.[6]The bands at 873 and 808 cm^{-1} arise from vibrations of the WO_2 entity present in the W_2O_8 groups.[7] The absorption band at 618 cm^{-1} is typical of a two-oxygen bridge (W_2O_2) and corresponds to the asymmetric stretching of the same units.[8] The observed absorption below 500 cm^{-1} corresponds to the asymmetric stretching vibrations of the NiO_6 polyhedra.[1,2]

TEM analysis

TEM bright field image, HRTEM image and selected area diffraction pattern (SAED) of the sample are shown in Fig.3.The particle size obtained from TEM image ranges from 24 to 26 nm, which are in agreement with the XRD results. The HRTEM image shows polycrystalline nature. The interplanar spacing for sample is found to be 0.34 nm. The SAED pattern shows bright spots that confirm the crystalline nature of the sample.

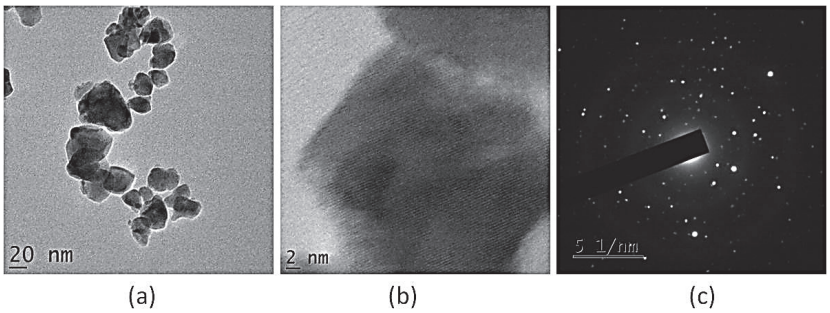


FIGURE 3. (a) Bright field image, (b) HR-TEM image and (c) SAED of $NiWO_4$ nanoparticles

UV-Visible Spectroscopy

Figure 4(a) gives the absorption spectrum of the sample. The main absorption peak in the region 290 nm may be attributed to the charge transfer transition in the WO_6 matrix. The two peaks in the visible region around 450 and 740 nm are due to the forbidden and allowed electronic transitions respectively. The band around 825 nm can be assigned to the presence of $Ni^{2+}O_4$ arising due to dislocation of Ni^{2+} from the octahedral to tetrahedral sites.[9] A broad absorption band is observed in the IR wavelength range 1300-1600 nm. The band gap energy of $NiWO_4$ sample is measured by plotting $(\alpha hv)^2$ as a function of photon energy as shown in Fig. 4(b). From the graph, the optical band gap estimated for the sample is 2.89 eV.

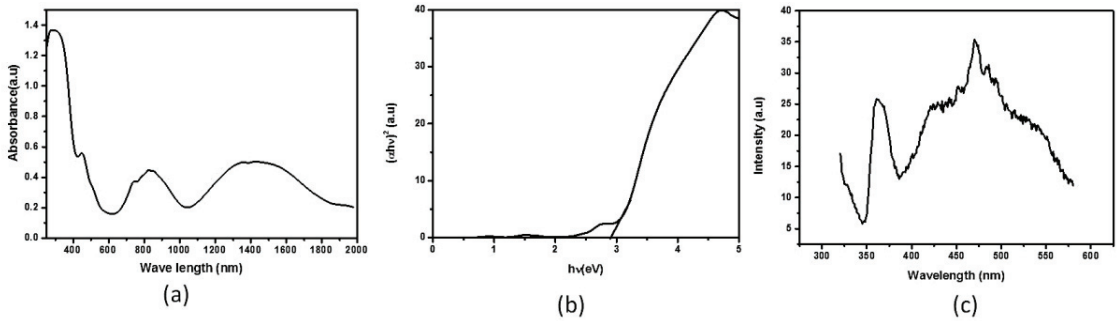


FIGURE 4. (a) Absorbance spectrum of $NiWO_4$ sample (b) Graph of $(\alpha h\nu)^2$ vs. hν for $NiWO_4$ sample (c) PL spectrum of $NiWO_4$ nanoparticle

Photoluminescence spectroscopy

Figure 4(c) shows room temperature PL emission spectrum of the synthesized $NiWO_4$ nanoparticles. Using 320 nm as excitation wavelength, the PL emissions for $NiWO_4$ nanoparticles are obtained at a wavelength range of 350-550 nm. The observed patterns may be originated from the WO_6^{6-} anion along with some defects in the crystal structure.[10] The emission peak at 360 nm is mainly attributed to charge transfer transitions within the WO_6 octahedra.[11] The emission peaks of 470, 483, 494 nm are related to the intensive transition from the ground state to the excited state of Ni^{2+} ($3d^8$) ions in distorted octahedral co-ordination.

Photocatalytic activity

The photo-degradation of aqueous MB dye over the surface the $NiWO_4$ nanoparticles under UV radiation is investigated using the UV-Vis absorption spectra at the maximum absorbance value of 665 nm for 210 min (Fig. 5a). The absorption band intensities of the MB dye solution are reduced with time under irradiation of UV, indicating the degradation of MB dye on the surface of the $NiWO_4$. Figure 5(b) shows the percentage photo-degradation of the MB dye solution with time. Within 210 min, 46.26% of the MB dye is degraded under UV irradiation. In order to study the kinetics of the photochemical reactions, the linear plot of $\ln(A_t/A_0)$ versus time is drawn (Fig. 5c) for the photo-degradation of MB dye with the $NiWO_4$. The rate constant of the photochemical reactions is estimated from the linear slope fitting curve. The photochemical reactions follow first-order decay kinetics. The value of the rate constant (k) is found to be 0.0028 min^{-1}. So $NiWO_4$ nanoparticles are suggested as a potential candidate to remove organic pollutants present in water by simple photocatalysis at room temperature.

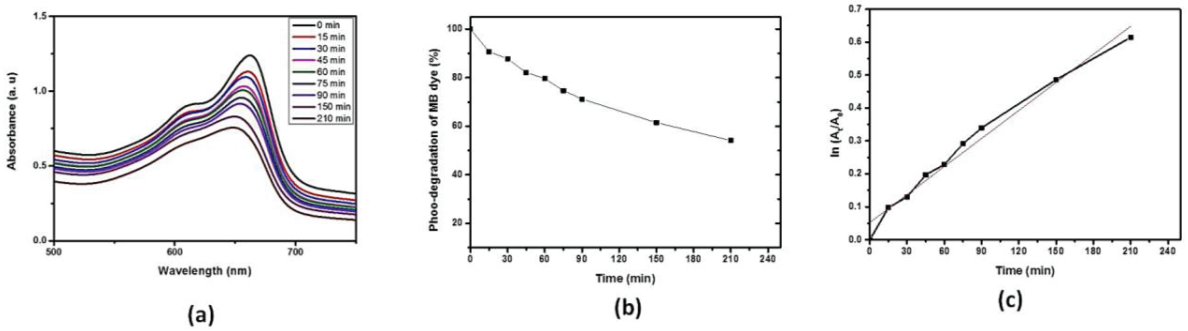


FIGURE 5. (a) Absorption spectra, (b) percentage degradation of MB with $NiWO_4$ and (c) linear plots of photo-degradation of MB with the $NiWO_4$

CONCLUSIONS

$NiWO_4$ nanoparticles with average crystallite size of 25.13 nm and polycrystalline nature are obtained by direct chemical precipitation method. FT-IR spectrum confirms the presence of all characteristic bonds in $NiWO_4$. The sample with an optical band gap of 2.89 eV shows greenish blue emission in photoluminescence. $NiWO_4$ sample is found to be a photocatalyst with 46.26% of degradation for MB with a photochemical reaction rate of 0.0028 min^{-1}.

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