The effect of Vanadium dopant on Bandgap Energy of Ni_{1-x}V_{x}Fe_{2}O_{4} nanospinel

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Abstract: V^{n+} doped NiFe_{2}O_{4}, Ni_{1-x}V_{x}Fe_{2}O_{4} (where x = 0.1, 0.3, and 0.5) nanomaterials were synthesized by sol-gel and freeze drying method simultaneously using nitrates of iron, and nickel, and ammonium vanadate as the starting materials. Powder X-ray Diffraction (XRD) showed that all composition was found to have cubic spinel, hexagonal and monoclinic structure. The average crystallite size using scherrer calculation was found to be in the range of 20 - 42 nm. The band gap energy (E_g) of undoped NiFe_{2}O_{4} was estimated to be 1.9 eV from UV-Vis diffuse reflectance spectroscopy (DRS). With the increase of V^{n+} dopant, the E_g value both decreased and increased from 1.6 eV to 2.0 eV, due to the difference of particle size of the samples.

Keywords: spinel, nanomaterial, dopant, bandgap energy

1. Introduction

Until now, the modification of the AB_{2}O_{4} nano spinel structure with the tetrahedral site A as the +2 valence cation and the octahedral site B as the +3 valence cation is still very interesting and has been widely carried out by researchers considering the unique properties possessed by these nano spinel compounds through substitution of cations A or B into A'B_{2}O_{4} or AB'_{2}O_{4} or partial substitution to A_{1-x}A'B_{2-x}O_{4} or A_{1-x}A'B'B'O_{4} [1-5]. This modification can give the normal spinel or inverted spinel structure where the +3 cation fills the tetrahedral site and the oxygen occupies a face-centered cube position in a tightly packed arrangement [6, 7]. One of these spinel materials is NiFe_{2}O_{4} nanomaterial which has many benefits in the field of catalysis [8, 9], magneto-optics [10, 11], supercapacitors [12, 13], photocatalytic [14, 15], and electronic devices [16, 17].

In the field of catalysts, the utilization of nanospinel nickel ferrite, NiFe_{2}O_{4}, is studied based on the unique properties of Lewis and Bronsted-Lowry [18, 19] acidity, surface area [20, 21], thermal and chemical stability [22, 23], oxygen mobility [24, 25] and adsorption-desorption [26, 27]. As for photocatalytic applications, in addition to the characteristics discussed earlier, a very needed property is the ease of promoting electrons from the valence band (HOMO) to the conductance band (LUMO). The easier to promote the electrons the less energy required or in other words, the distance between the valence band and the conductivity band is closer [28, 29].

The electrons promotion from the upper valence band to the lowest conduction band requires a minimum energy equivalent to the band gap energy (E_g). If the band gap energy is zero (E_g = 0 eV) or large (E_g > 4 eV), then they are either a metal or an insulator, respectively. If the band gap energy is between 0 and 4.0 eV, then the metal oxides or composites is a semiconductor. Furthermore, band gap energy is classified as direct and indirect. Direct means that the minimum energy of the lowest
The conduction band is just above the maximum energy of the valence band at the same crystal momentum. If this is not, it is called the indirect band gap energy, as shown in Figure 1 below.

![Figure 1. Schemes of band gap energy: (a) direct and (b) indirect transitions which are allowed](image)

The UV-Visible diffuse - reflectance spectrophotometer is a viable tool for the use of a simple method based on the Kubelka-Munk theory [30] and the Tauc [31] plot to obtain the band gap energy. Mathematically, the equation is expressed as follows: $\alpha h\nu = \beta (h\nu - E_g)^n$, where $h$ is the Planck constant (J·s⁻¹), $\beta$ the absorption constant, $\nu$ is the frequency of light (s⁻¹), $E_g$ is band gap energy (eV), and $n$ with respect to the types of electron transitions that are possible. The value of $n$ is 2 for the allowed indirect transition, 3 for the forbidden indirect transition, ½ for the directly allowed transition, and 3/2 for the forbidden direct transition.

The impact of adding dopants to a nanospinel can decrease or increase the energy band gap even though it is still in the $0 < E_g < 4.0$ eV range. If the addition of dopants to a nanospinel material decreases the band gap energy, a redshift will occur. But if the addition of dopant increases its bandgap energy, there will be a blue shift where the band gap energy magnitude will be related to the range of wave numbers used in the application [32, 33].

On this chance, we reported the effect of Vanadium dopant on band gap energy of Ni$_{1-x}$V$_x$Fe$_2$O$_4$ using the sol gel method and its possible application in photocatalytic reaction by analyzing the material using Diffuse Reflectance UV-Vis Spectroscopy, and X-Ray Diffraction for knowing its crystalline phases formed and crystallite size.

2. Experimental

2.1. Material

The materials used in this study were Ni(NO$_3$)$_2$·6H$_2$O (Merck, 99%), Fe(NO$_3$)$_3$·9H$_2$O (Merck, 99%), NH$_4$VO$_3$ (Merck, 99%), pectin and distilled water.

2.2. Instruments

The instruments used for characterization include X-Ray Diffraction (XRD) model PW 1710 with Cu-Kα radiation for structure identification, and Diffuse Reflectance UV-Vis Spectroscopy (Agilent Cary 60) to determine the band-gap energy.

2.3. Preparation of Ni$_{1-x}$V$_x$Fe$_2$O$_4$

The nanocatalyst was prepared by dissolving 8 grams of pectin in distilled water 400 mL using a magnetic stirrer at room temperature to obtain a homogeneous solution for around 4 hours. 25-30 mL Ammonia is added to reach pH of 11. For example, to prepare Ni$_{0.8}$V$_{0.2}$Fe$_2$O$_4$ as an example, then put the Ni-nitrates solution (1.994 g in 150 mL distilled water), Fe-nitrates solution (6.9407 g in 350 mL distilled water), and ammonium vanadate solution (0.2009 g in 100 mL destilled water)and poured...
slowly and simultaneously using an infusion tube, while continuing to stir until homogeneous. Then
heated while continuing to stir using a heating magnetic stirrer at a temperature of 80 °C, until the
precursor of Ni\(_{(1-x)}\)V\(_x\)Fe\(_2\)O\(_4\) gel was obtained. The gel was dried with a freeze dryer for 24-48 hours
and then calcined at 600 °C for 10 hours. The nanomaterial Ni\(_{(1-x)}\)V\(_x\)Fe\(_2\)O\(_4\) was obtained and ready to
analyze.

2.4. Characterization of Ni\(_{(1-x)}\)V\(_x\)Fe\(_2\)O\(_4\)

2.4.1. X-Ray Diffraction Analysis

The X-ray diffraction pattern Ni\(_{(1-x)}\)V\(_x\)Fe\(_2\)O\(_4\) was recorded at 2θ = 10-90º using a Philips diffractometer
model PW 1710 Cu-Kα radiation. Phase identification was carried out by matching the diffractogram
of the sample to the standard diffractogram using the JCPDF published by ICCD PDF. The crystallite
size was determined by the Scherrer method [34].

2.4.2. UV-Vis DR Spectroscopy Analysis

Determination of the Ni\(_{(1-x)}\)V\(_x\)Fe\(_2\)O\(_4\) band-gap energy, a number of samples were analyzed using UV-
Vis Diffuse Reflectance Spectroscopy and scanned at a wavelength of 200-800 nm [30].

3. Results and Discussion

3.1. Structural Analysis of X-Ray Diffractogram

Based on the results of the diffractogram analysis that has been carried out by the Rietveld
calculation, as shown in Figure 2 below, it can be said that Ni\(_{0.9}\)V\(_{0.1}\)Fe\(_2\)O\(_4\) spinels are formed and the
vanadium cation is in the NiFe\(_2\)O\(_4\) spinel structure. Furthermore, the increase in the number of
vanadium cations added to Ni\(_{(1-x)}\)V\(_x\)Fe\(_2\)O\(_4\) has an impact on the formation of the V\(_2\)O\(_5\) and Fe\(_2\)O\(_3\)
crystalline phases as described in the previous article [35].

![Figure 2. Difractogram of Ni\(_{(1-x)}\)V\(_x\)Fe\(_2\)O\(_4\) nanospinel {where (a) x=0.1, (b) x=0.3, and (c) x=0.5}](image)

Furthermore, by using the Scherrer method to calculate the crystal size [34], it was found that the
crystal size of Ni\(_{0.9}\)V\(_{0.1}\)Fe\(_2\)O\(_4\), Ni\(_{0.7}\)V\(_{0.3}\)Fe\(_2\)O\(_4\), and Ni\(_{0.5}\)V\(_{0.5}\)Fe\(_2\)O\(_4\), respectively 20.87, 42.08, and 39.97
nm as shown in the previous article [35].

3.2. Analysis of UV-Visible DRS Spectrum

To give the significant information in relation to the effect of crystallite size on the band gap energy ($E_g$) of spinel Ni$_{1-x}$V$_x$Fe$_2$O$_4$ samples, UV-Visible diffuse reflectance spectroscopy (DRS) analysis was carried out. The $E_g$ of the samples can be evaluated using the Kubelka-Munk method [30].

Optical absorption bands were detected on Ni$_{1-x}$V$_x$Fe$_2$O$_4$ nanospinel through the absorbance spectra of UV-Visible DRS versus the wavelength as shown in Figure 3 below, where the five bump or peaks at wavelengths of about 360, 460, 560, 630 and 750 nm show absorption peaks. The peaks indicate that there is an interaction between the 3d Fe$^{3+}$, 3d Ni$^{2+}$ and the 3d V$^{3+}$ orbitals with the 2p O$^{2-}$ orbitals, respectively, which are shown at the 360, 460 and 560 nm wavelengths of absorption, respectively. Most probably weak absorption bands at 630 and 750 nm belongs to d-d transition in Fe$^{3+}$ and Ni$^{2+}$/V$^{3+}$ ions in an octahedral and tetrahedral symmetries [22], which are influenced by replacing Ni with V in Ni$_{1-x}$V$_x$Fe$_2$O$_4$ nanospinel. Intra-atomic d-d transitions are of much lower intensity comparison to the inter-atomic transitions at region of fundamental absorption edge, as the amount of vanadium dopant more increase.

![Figure 3](image)

Figure 3. UV-Vis DR Absorption Spectra of Ni$_{1-x}$V$_x$Fe$_2$O$_4$ where (a) x = 0.1; (b) x=0.3; and (c) x=0.5

The calculated $E_g$ for all compositions of spinel Ni$_{1-x}$V$_x$Fe$_2$O$_4$ (where x = 0.0, 0.1, 0.3, and 0.5) nanomaterials are 1.9, 1.6, 1.8, and 2.0 eV, respectively [35]. It is inferred that there is a decrease and an increase in the $E_g$ of doped samples, when compared to the undoped NiFe$_2$O$_4$. The $E_g$ value of undoped NiFe$_2$O$_4$ is 1.9 eV, and hence, there is a red shift for x = 0.1, and 0.3 and blue shift for x = 0.5 of V$_x$-doped Ni$_{1-x}$Fe$_2$O$_4$ samples. Chavan and Naik [36] found a different value (2.82 eV) for undoped NiFe$_2$O$_4$ sample and increased as the amount of Mg dopant increased. The decrease in band gap energy may also be due to the sp-d exchange interaction between the localized d-electrons of V$^{3+}$/Ni$^{2+}$ ions and band electrons of spinel NiFe$_2$O$_4$ [22].
4. Conclusion

Based on the analysis of Ni_{1-x}V_xFe_2O_4 nanomaterial characteristics, it can be concluded that the addition of vanadium dopant into NiFe_2O_4 nanospinel affected on the structure of NiFe_2O_4 nanospinel where if the amount of vanadium dopants increases the crystalline phase of NiFe_2O_4 decreases due to the formation of other crystalline phases such as hexagonal Fe_2O_3 and monoclinic V_2O_5. Furthermore, the greater the amount of vanadium dopant added, the greater the crystalline size formed but the band gap energy more shifted to red and less shifted to blue.

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