Synthesized vanadium doped ZnO through the co-precipitation method

N F Djaja, A Taufik and R Saleh

1. Introduction
Zinc oxide (ZnO) has attracted a large amount of attention in scientific investigation due to its unique qualities as for example an ample direct band gap of 3.37 eV and a higher exciton binding energy of 60 meV than that of ambient thermal energy [1]. ZnO has numerous applications in the chemical industry such as in rubber manufacturing, the ceramic industry, medicine, cigarette filters, food additive, pigment, UV absorbers, coatings, in the corrosion prevention in nuclear reactors and in methane reforming [2]. However, in several applications, ZnO still are limited, for example, in photocatalytic applications, ZnO with wide band gap energy could not be activated under visible light irradiation [3]. Therefore, modified ZnO nanoparticles are of vast interest due to their unique properties for several applications.

Doping ZnO with transition metals has been widely investigated to improve the physical properties of ZnO nanoparticles. Between the transition metals, vanadium has been considered as a promising dopant. Vanadium could potentially improve the physical properties ZnO nanoparticles, these enhancements would include applications as a coating for surfaces and in the development of ferromagnetic materials [4].

Therefore, this study evaluates the formation of vanadium doped ZnO synthesized through a co-precipitation method. The prepared samples were then characterized by X-ray diffraction (XRD), energy dispersive X-ray (EDX), UV-Vis diffuse reflectance spectroscopy (DRS) and Electron Spin Resonance Spectroscopy (ESR).

2. Materials and methods
2.1. Synthesis of the vanadium doped ZnO nanoparticles
The employed reagents for the synthesis were used as purchased: vanadium oxide (V₂O₅, 99%, Merck) and zinc (II) sulfate (ZnSO₄·7H₂O, 99%, Merck). Precursor solutions of different ZnSO₄·7H₂O and V₂O₅...
compositions were made with distilled water. An ultrasonic bath was employed to mix these solutions at 57 kHz for a period of time of 2 h. To adjust the pH of precursor solutions, an alkaline solution was prepared by mixing 440 mL of de-ionized water with 44 mmol of NaOH. After ultrasonic mixing, the precursor solutions were pH adjusted to a PH of 12 by drop wise addition of the alkaline solution, this solution was stirred at laboratory temperature. The solutions were stirred for half an hour and kept at laboratory temperature for a period of 18 h. The precipitate formed these solutions was washed with ethanol and distilled water. The precipitate formed from these solutions was washed with ethanol and distilled water. The final precipitate was dried in a vacuum oven at 200 °C for 1 h.

2.2. Characterisation of the synthesis nanoparticles

An X-Ray Leo 420 instruments was used to determine the elemental analysis of the vanadium doped zinc oxide nanoparticles (i.e. the samples). The range of operation was from 0 to 10 keV. An XRD Philips PW 1710 instrument was used to determine the structural properties of the samples. This instrument operates with monochromatic Cu–Kα (\(\lambda = 1.54060 \text{ Å}\)) with the conditions of 40 kV and 20 mA; 2θ = 10–80°, the set up and was calibrated with a standard. XRD patterns were evaluated by MAUD software where the lattice parameters and crystal structure were fitted by the Rietveld fitting method. The grain size was determined by the Williamson–Hall plot (equation (1)):

\[
\beta_{hkl} = \left(\frac{h \lambda}{D}\right) + 4 \varepsilon \sin (\theta)
\]

(1)

where \(\beta_{hkl}\): full width at half maximum (FWHM), \(D\): average crystallite size, \(k\): shape factor (selected as 0.9), \(\lambda\): wavelength of the Cu–Kα radiation, and \(\varepsilon\): microstrain parameter.

A Shimadzu UV–vis spectrophotometer was used for optical characterizations of the diffuse reflectance spectra. This instrument has an integrating sphere attachment and spectral on reflectance standard. All spectra of the samples were evaluated in the range of 250 to 800 nm. The band gap energy was determined by the Kubelka-Munk function as described by equation (2):

\[
F(R) = \frac{(1 - 2R)^2}{2R}
\]

(2)

where \(R\): reflectance spectra of the samples, and the band gap energy is obtained by extrapolation of the function \(F(R) = 0 \text{ vs energy}\).

Electron Spin Resonance (ESR) measurements were performed in the range of 0–71 T field to obtained the information about the site occupancy and oxidation state.

3. Results and discussion

Figure 1 shows the EDS spectra of V-doped ZnO with different vanadium loading. The figure shows the Zn, O and V atomic compositions of all the prepared samples. Thus, vanadium has successfully been incorporated into the ZnO structure. The vanadium peak height at 4.91 keV increases with the increased vanadium loading. After integrating the whole spectra, the vanadium loading was determined to be 5, 8, and 16 at.% The additional peak from carbon atom is from the sample holder used to measure the samples.
The structural properties of all the prepared samples characterized by XRD measurement are plotted in figure 2. This figure shows that all the prepared samples reveal several diffraction peaks at $2\theta \approx 31.65^\circ$, 34.27°, 36.09°, 47.29°, 56.57°, 62.74°, 66.22°, 68.15°, and 69.69° that correspond to the (100), (002), (101), (102), (110), (103), (200), (112), and (201) planes, respectively. Thus, diffraction peaks correspond to the hexagonal wurtzite structure from ZnO nanoparticles, and no undesired peak was detected that indicates the samples were the desired structure. The lattice parameters were determined by the Rietveld refinement method and are shown in table 1. The table shows that the lattice parameter of the ZnO nanoparticles incorporated with vanadium is slightly changed compared to the lattice parameter of pure ZnO nanoparticles. This change is probably due to the substitution of vanadium on the zinc lattices. Vanadium of different valence states and ionic radii such as V$^{5+}$ ($r_{V^{5+}} = 0.54\text{Å}$) [6], V$^{4+}$ ($r_{V^{4+}} = 0.63\text{Å}$) [7], V$^{3+}$ ($r_{V^{3+}} = 0.74\text{Å}$) [8, 9], and V$^{2+}$ ($r_{V^{2+}} = 0.93\text{Å}$) [10] could substitute Zn$^{2+}$ ($r_{Zn^{2+}} = 0.74\text{Å}$) ions [5]. Vanadium of different oxidation states has different ionic radii, Zn$^{2+}$ substitution by V ions of larger radius would increase its lattice parameters and vice versa [4].

The W-H plots used to determine the crystallite sizes of the samples are plotted in figure 3. The figure shows that the W-H plot possesses good coefficient correlation for all samples. The calculated grain sizes of the samples are presented in table 1. The table shows that the grain size of the V-doped

| V at.% | lattice parameters | volume | grain size (nm) |
|-------|-------------------|--------|----------------|
| 5     | 3.2514, 5.2121    | 47.7187| 18.99          |
| 8     | 3.2507, 5.2101    | 47.6794| 18.25          |
| 16    | 3.2449, 5.2003    | 47.4209| 17.30          |

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**Table 1.** Lattice parameters, cells volume, and grain size of nanoparticles V-doped ZnO

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Table 2. Lattice parameters, cells volume, and grain size of nanoparticles V doped ZnO

| V at. % | Energy gap (eV) |
|---------|-----------------|
| 5       | 3.352           |
| 8       | 3.351           |
| 16      | 3.350           |

Figure 5. UV-Vis diffuse reflectance spectra of V-doped ZnO with different V contents.

Figure 6. Kubelka-Munk analysis V-doped ZnO with different vanadium contents.

ZnO with different vanadium contents decreased compared to pure ZnO nanoparticles, indicating that the incorporation vanadium reduces the crystallization process of ZnO.

The ESR spectra of V-doped ZnO with different V dopant concentrations are shown in figure 4. The most abundant naturally occurring vanadium is the \(^{51}\)V isotope. The Pourbaix diagram of V\(_2\)O\(_5\) indicates that the vanadium stable oxidation state is V\(^{5+}\) at pH of 12. The reaction between Vanadium and Zinc from the precursor solution makes vanadium to be reduced to V\(^{4+}\). The V\(^{4+}\) ion is paramagnetic with a 3d electronic configuration and an electronic spin (S) of 1/2. The nuclear spin (I) of the \(^{51}\)V isotope is 7/2. With these parameters, we have considered that the eightfold hyperfine structure found in figure 4 to be related to a dipole–dipole interaction between the magnetic and electronic moments of \(^{51}\)V nucleus and the V\(^{4+}\) ions.

The UV-Vis reflectance spectra of V-doped ZnO are shown in figure 5. This figure shows that the reflectance ability of V-doped ZnO tends to decrease with increased vanadium content. In addition, the reflectance spectra of the samples correspond with the absorbance ability of the prepared samples. Kubelka-Munk analyses were also performed, and the Kubelka-Munk results were plotted in figure 6. The figure shows that the absorbance ability of V-doped ZnO in the visible range increased with increased vanadium content. The band gaps calculated using Kubelka-Munk analysis are presented in table 2. The table shows a decrease from 3.352 eV to 3.350 eV of the band gap energy of the V-doped ZnO as a function of vanadium content from 5 at.% to 16 at.%. These results are very important in several applications that use visible light radiation as a source of energy such as the photocatalytic processes.

4. Summary

V-doped ZnO with different vanadium content has been successfully synthesized by a co-precipitation technique. Structural analysis indicates that the V-doped ZnO samples possess a hexagonal wurtzite structure. However, the decreasing lattice parameter of ZnO indicates a substitution between zinc and vanadium atoms. In addition, the results show that the absorbance ability of V-doped ZnO of visible light radiation increased with increased vanadium loading. These results will be incorporated in further projects to develop photocatalysts under visible light radiations.
References
[1] M. M. Ovhal, A. S. Kumar, P. Khullar, M. Kumar 2017 Mater. Chem. Phys. 195 58–66
[2] A. N. Kadam, T. G. Kim, D. S. Shin, K. M. Garadkar, and J. Park 2017 J. Alloys Compd. 710 102–13
[3] U. Alam, A. Khan, W. Raza, A. Khan, and M. Muneer 2017 Catal. Today 284 169–78
[4] E. Sarica and V. Bilgin 2016 Surf. Coat. Technol. 286 1–8
[5] L. Wang, L. Meng, V. Teixeria, S. Song, Z. Xu, and X. Xu 2009 Thin Solid Films 517 3721–5
[6] Y.C. Yang, C. Song, F. Zeng, F. Pan, Y.N. Xie, and T. Liu 2007 Appl. Phys. Lett. 90 242903
[7] H. Colak and O. Turkoglu 2012 J. Mater. Sci. -Mater. Electron. 23 1750–1758
[8] S.F. Olive-Mendez, C.R. Santillan-Rodriguez, R.A. Gonzalez-Valenzuela, F. Espinosa-Magana, and J.A. Matutes-Aquino 2014 Nanoscale Res. Lett. 9 1–7
[9] Z. Wen-Chen, W. Shao-Yi, D. Hui-Ning, and Z. Jian 2002 Spectrochim. Acta A 58 537–41
[10] T. Akilan, N. Srinivasan, R. Saravanan, P. Chowdury 2014 Manuf. Process. 29 780–8