

Preparation and Characterization for a New ZnO - Montmorillonite Hybrid from Iraqi (Traifawi) Clay Minerals

Mohammed H. Abdul Latif

Department of Chemistry, Ibn Al Haitham College of Education, University of Baghdad, Adhamiya,
Al- Dilal Square, Baghdad, Iraq
Email: mohammed21latif@yahoo.com

Abstract

A new hybrid materials of zinc oxide with Iraqi (Traifawi) montmorillonite were synthesized by mixing 15 g. of H – form initiated montmorillonite with 100 ml saturated aqueous solution of Zinc chloride ($ZnCl_2$) with continuous agitation at 60 °C, and the mixture was allowed to react for 24 h. to ensure maximum interlayer Zn^{+2} cations intercalation. The resulting Zn – intercalated montmorillonite solid was separated by centrifugation, washed several times with deionized water for free (HCl), dried at 100 °C for 24 h. and calcined at 900 °C using Muffle Furnace. ZnO –montmorillonite hybrid was characterized by X-ray diffraction (XRD), FT-IR spectroscopy, scanning electron microscopy (SEM), and Fluorescence spectroscopy. The appearance of the reflections due to ZnO crystal in the XRD patterns of ZnO–montmorillonite and Zn – montmorillonite was ascribed to the formation of ZnO and Zn^{+2} ions on the solid surfaces. ZnO – montmorillonite hybrid (SEM) images show the flower-shaped structures on the external surface of clay mineral in a complete flower like morphology composed with sharp tipped hexagonal Nano rods. The enhancement in emission intensity of the zinc oxide hybrids may be probably due to increase in oxygen vacancies defect arose by the surrounding environment of montmorillonite.

Keywords: Characterization, Iraqi (Traifawi), ZnO - Montmorillonite, hybrid.

1. Introduction

Among many ordered or constrained systems utilized to organize reactants, layered materials offer a two-dimensional expandable interlayer space for organizing guest species. The motivation to study intercalation reactions arises because the optical and electronic properties of both guest and host can be altered by the reactions. The microscopic structure can be tailored by selecting and designing both the guests and hosts and also by Co adsorption. From X-ray diffraction studies, interlayer distances are measured and the orientation of the intercalated species is estimated. Layered alkali silicates are also capable of incorporating guest species in the interlayer space to form intercalation compounds. The mechanism of the intercalation can be classified into two broad types. One involves cation exchange with interlayer exchangeable cations; the other concerns adsorption of polar molecules by ion–dipole interactions with interlayer cations and/or hydrogen bonding with the surface oxygen atom of the silicate sheets [1]. Smectite, a 2:1 type layered silicate, including montmorillonite exhibit beneficial properties, such as large surface area, swelling behavior, adsorptive property and ion exchange property [2]. The surface of montmorillonite can be used to prevent the guest particles from aggregation. Taking advantages of Smectite for nanoparticle preparation and immobilization, the hybrid materials of Smectite semiconductor particles, including metal, metal oxides, and metal sulfides have been successfully prepared and evaluated [3]. Montmorillonite–zinc oxide hybrid (MMT–ZnO) has recently been synthesized by a sol–gel intercalation reaction. It was found that MMT–ZnO had novel physicochemical properties [4]. ZnO is a key technological material. The lack of a center of symmetry in quartzite, combined with large electromechanical coupling, results in strong piezoelectric and Pyro electric properties and the consequent use of ZnO in mechanical actuators and piezoelectric sensors. In addition, ZnO is a wide band-gap (3.37 eV) compound semiconductor that is suitable for short wavelength optoelectronic applications. The high exciton binding energy (60 meV) in ZnO crystal can ensure efficient excitonic emission at room temperature and room temperature ultraviolet (UV) luminescence has been reported in disordered nanoparticles and thin films. ZnO is transparent to visible light and can be made highly conductive by doping [5]. The fluorescence spectroscopy was generally used to elucidate the nature of traps/vacancies formed with the incorporation of dopants. The type of vacancies formed depends upon the ZnO synthesis conditions and techniques used [6]. Generally, three emission bands are observed in ZnO Nano crystals. The first band centered at 357 nm indicates band-to-band transition, the second band at 387 nm is for the radiative recombination of an electron and a hole, i.e. the excitonic emission and the third emission at 420 nm may be attributed to the interstitial oxygen [7]. In this study, we report a new easy method of preparation of ZnO - montmorillonite hybrid depending on the good ion exchange property of Iraqi montmorillonite clay minerals. Involving intercalation mechanism for Zn^{+2} cations present in the interlayer gap.

2. Experimental

Iraqi (Traifawi) Smectite (Ca – montmorillonite) clay used in the present study obtained from the General

Company for Geological Survey and Mining in Baghdad, Iraq. The cation exchange capacity (CEC) of Ca – montmorillonite is 80 meq. /100 g of clay, and the Ca – montmorillonite percent in crude is between (60 – 65 %). The clay sample was sieved to produce particle size of 45 μ m, dried for 24 h. at 100 °C in an electric oven, and stored in a desiccator until use. Activated H – form Amberlight orange ion exchanger and Zinc chloride (ZnCl₂) were purchased from Fluka-BDH Chemicals. Distilled and deionized water with a conductivity value of 1.5 x 10⁻⁵ S Cm⁻¹ was used. Iraqi (Traifawi) CA – montmorillonite was benefitted to improve its montmorillonite content and cation exchange capacity (CEC) by attrition – scrubbing at high concentration (15 %) and at high impeller speed (2500 r.p.m.) for 1 h., using Flotation Cell. The resulting solid was separated by centrifugation, washed several times with deionized water and dried at 100 °C for 24 hour. ZnO – montmorillonite hybrid was prepared by converting (Ca – montmorillonite 15% solution) to (H – montmorillonite) using Activated H – form Amberlight orange ion exchange at the molar ratio of 1:1, followed by agitation for 24 h. at 150 r.p.m. and 60 °C using thermo stated shaker bath (Alba Tch.). Clay suspension was separated from Amberlight orange ion exchange granules using 75 μ m sieve. The resulting solid was separated by centrifugation, washed several times with deionized water and dried at 100 °C for 24 h.

A 15 g. of the resulting H – form initiated montmorillonite was mixed with 100 ml saturated aqueous solution of Zinc chloride (ZnCl₂) with continuous agitation at 60 °C, and the mixture is allowed to react for 24 h. to ensure maximum interlayer Zn⁺² cations intercalation. The resulting Zn – intercalated montmorillonite solid was separated by centrifugation, washed several times with deionized water to free Hydrochloric acid (HCl), dried at 100 °C for 24 h. and calcined at 900 °C using Muffle Furnace to convert Zn – intercalated montmorillonite to ZnO –montmorillonite hybrid.

X-ray diffraction (XRD) data were obtained on Shimadzu x- ray diffraction P 04 – XRD – 6000. SEM Micrographs were carried out on VEGA3 – TESCAN Scanning Electron Microscope. Fourier Transform – Infrared (FT-IR) spectra were recorded on Shimadzu FT-IR Spectrophotometer – 30000:1/ IRAFF. The Fluorescence emission spectrum of powdered solid sample (using 45 μ m sieve) Zn – intercalated Montmorillonite, and ZnO – Montmorillonite hybrid was measured at two excitation wavelengths using ELICO – SL174 – Spectra – Fluorimeter at Excitation band pass = 20nm and Emission band pass = 20nm with Scan speed = 400nm / minute.

3- Result and discussion

The XRD patterns of ZnO–montmorillonite hybrid and Zn – intercalated montmorillonite are shown in (Figure 1) together with that of Purified initiated Montmorillonite crude. The reflections of ZnO appeared clearly in (Figure 1 a) located at d= 0.287, and 0.25 nm. This indicates the presence of high zinc oxide in the clay Hybrid. The basal spacing (d₀₀₁) of Purified initiated Montmorillonite crude was observed at a low angle region (2 θ < 10°, d=1.22 nm) (Figure 1c), and after the reactions, the d₀₀₁ peak of ZnO–montmorillonite (2 θ = 6.6°, d=1.326 nm) (Figure 1a), and Zn – montmorillonite (2 θ = 5.6°, d=1.558 nm) (Figure 1b), shifted towards to lower angle side when compared with Purified initiated Montmorillonite crude and the reflections due to ZnO were also seen at higher angle region. This indicates the emergence of a new peak involving clay hybrid. The basal spacing of ZnO–montmorillonite and Zn– montmorillonite were 1.558 (Figure 1b) and 1.326 nm (Figure 1a), respectively, and that is due to the shrinkage of basal height by burning at 900 °C. The gallery heights were determined to be 0.366 for ZnO–montmorillonite and 0.598 nm for Zn –montmorillonite by subtracting the thickness of the silicate layer (0.96 nm) [4], showing the expansion of the interlayer spaces that may thought to be caused by the intercalation of ZnO particles and/or Zn⁺² ions. All of the reflections at d=0.28, 0.26 and 0.25 nm of ZnO and the hybrids are well confirmed to a ZnO hexagonal quartzite lattice, according to JCPDS card number 36-1451. The appearance of the reflections due to ZnO crystal in the XRD patterns of ZnO–montmorillonite and Zn – montmorillonite was ascribed to the formation of ZnO and Zn⁺² ions on the solid surfaces.

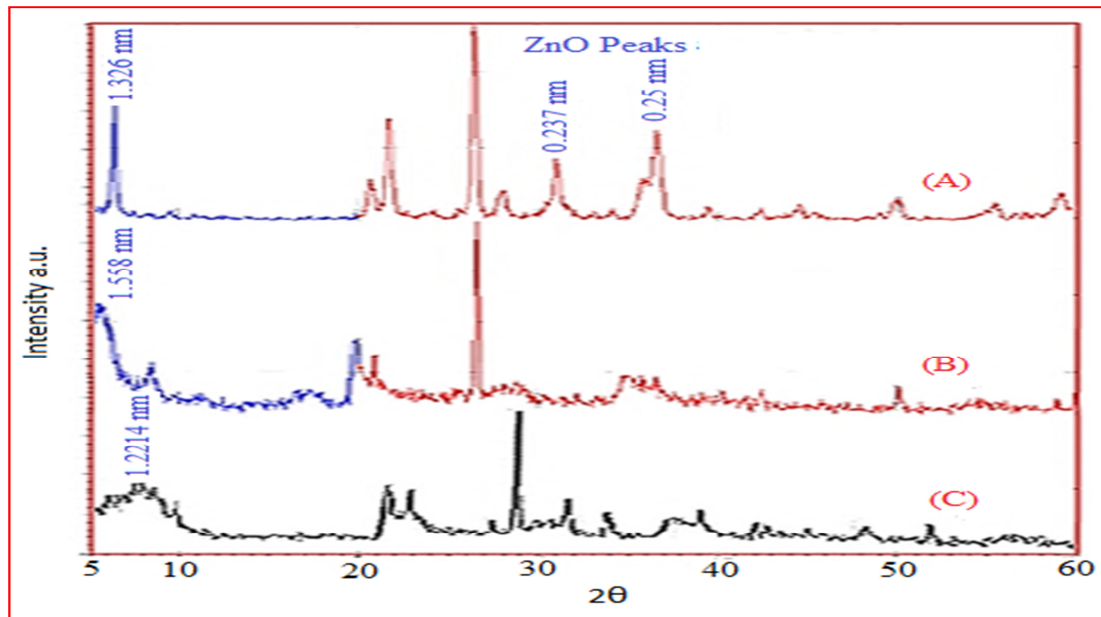


Figure 1: Powder XRD Patterns of (A) ZnO – montmorillonite hybrid, (B) Zn – intercalated montmorillonite, And (C) initiated crude Montmorillonite

Morphologies of the products were examined by SEM and TEM analyses. The images of ZnO (Figure 2) showed a flower like microstructures (averaged diameter of CA. 1.5 μm) composed of hexagonal ZnO rods.

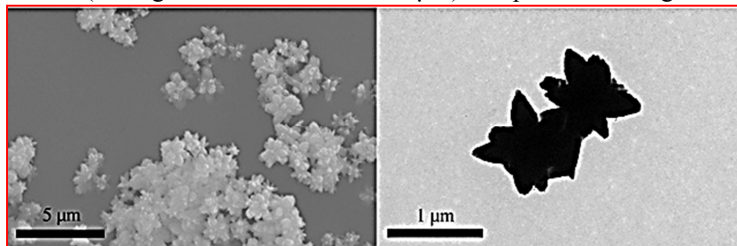


Figure 2: SEM and TEM images of ZnO [3].

Low and high magnification SEM images (Figure 3A, 3D & 3G) of initiating montmorillonite show a normal characteristic of layered shape Montmorillonite Clay, But note in (Figure 3B, 3E & 3H) of Zn – intercalated montmorillonite a change in the nature of the Montmorillonite clay surface due to high intercalation of Zn^{+2} ions on the external surface of clay mineral and in the interlayer space of montmorillonite. This was shown clearly in high magnification SEM images (Figure 3E & 3H) by having a new texture to the clay surface. Through an accurate vision of (Figure 3C, 3F & 3I) of ZnO – montmorillonite hybrid the flower-shaped structures were seen on the external surface of clay mineral in a complete flower like morphology composed with sharp tipped hexagonal Nano rods. These images indicate the success of the process of intercalation of Zn^{+2} ions and the success of the method of calcining to convert Zn – intercalated montmorillonite to ZnO –montmorillonite hybrid.

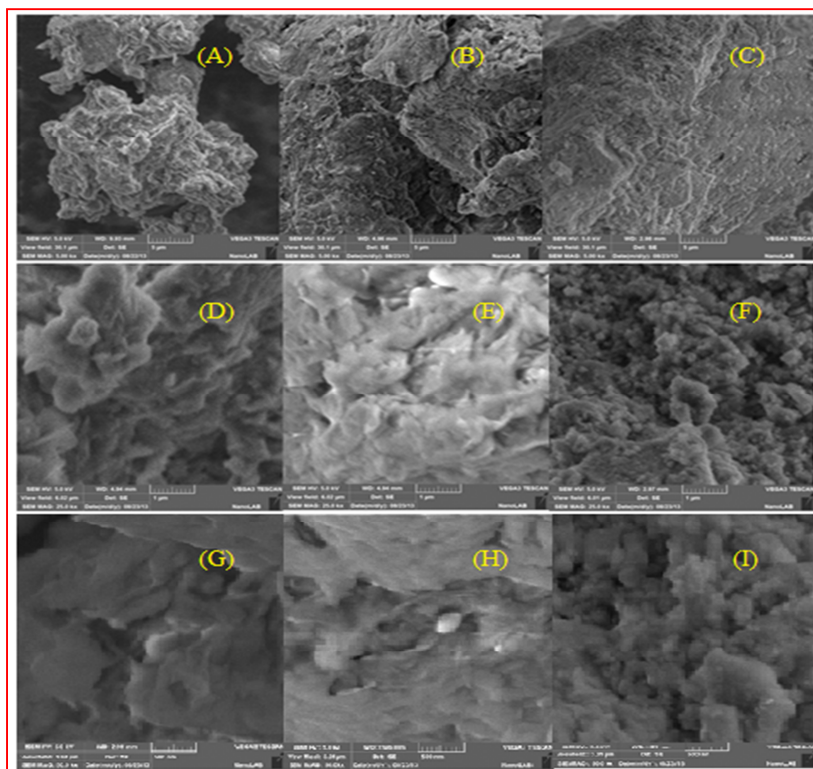


Figure 3: Low and high magnification SEM images (A, D &G) of initiating montmorillonite, (B, E &H) of Zn – intercalated montmorillonite, and (C, F &I) of ZnO – montmorillonite hybrid.

The FT-IR spectrum of ZnO – Montmorillonite hybrid shows the ZnO absorption band at (467.13 cm^{-1}), and that is near the standard peak of zinc oxide which observed in the range of ($426- 440\text{ cm}^{-1}$) [6-8], and that will support the results derived from Low and high magnification SEM images (Figure 3C, 3F &3I) of ZnO – montmorillonite hybrid. While the FT-IR spectrum of Zn - intercalated Montmorillonite, and initiated crude Montmorillonite (Figure 4G) shows the Montmorillonite triplet. A weak –OH absorption bands at 1622.13 cm^{-1} (Figure 4E) and 3444.87 cm^{-1} (Figure 4F) (Figure 3C, 3F &3I) of ZnO – montmorillonite hybrid indicate the presence of low moisture content, probably due to high calcining temperature ($900\text{ }^{\circ}\text{C}$). While the FT-IR spectrum of Zn - intercalated Montmorillonite (Figure 4B), and the FT-IR spectrum of initiating crude Montmorillonite (Figure 4C) shows strong –OH peaks due to the high moisture content.

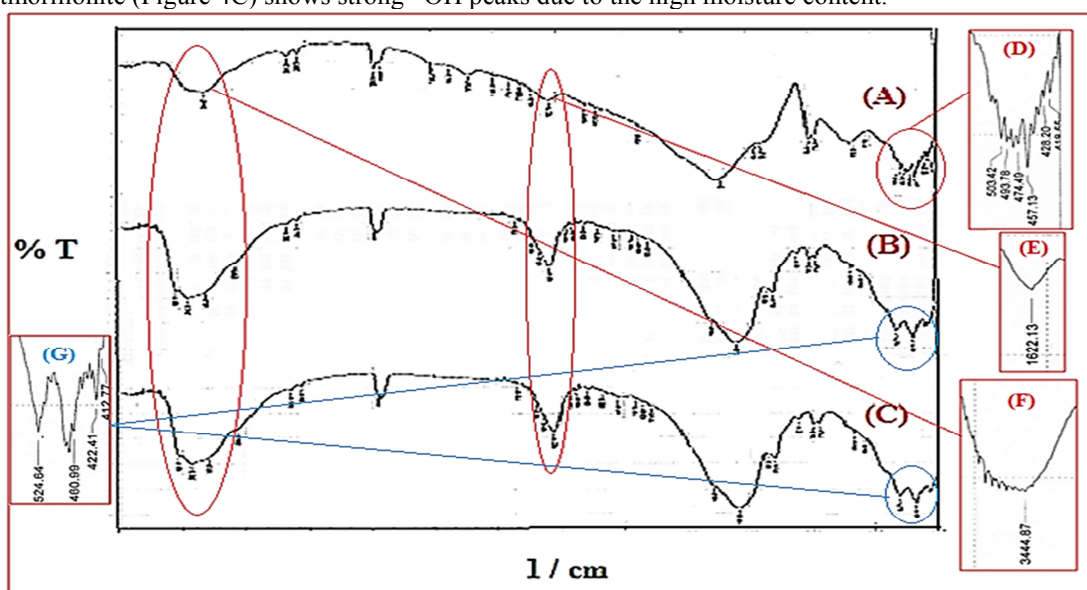


Figure 4: FT-IR Spectrum of (A): ZnO – Montmorillonite hybrid calcined at $900\text{ }^{\circ}\text{C}$, (B): Zn - intercalated Montmorillonite, and (C): initiated crude Montmorillonite.

The UV–visible spectrum of ZnO showed an absorption onset at 383 nm (3.31 eV) [3]. The characteristic absorption onsets wavelengths of Zn – intercalated Montmorillonite, and ZnO – Montmorillonite hybrid were recorded by ELICO – SL174 – Spectra - Fluorimeter at 410 (ca. 3.02 eV) from (Figures 5&7) and 430 nm (ca. 2.88 eV) from (Figures 6&8), respectively for both materials. In the fluorescence spectra (Figures 5) an emission peaks appears at [430 nm (ca. 2.88 eV) & 848 nm (ca. 1.46 eV)] (λ excitation = 420 nm), which is attributed to the as prepared ZnO–montmorillonite hybrid and this clearly confirms the presence of the ZnO nanoparticles. When we rise the excitation lambda (λ excitation = 440 nm) (Figures 6) a red shift of emission peaks happen, and the emission peaks appears at [450 nm (ca. 2.75 eV) & 887 nm (ca. 1.39 eV)]. Also In the fluorescence spectra (Figures 7) an emission peak appears at [430 nm (ca. 2.88 eV) & 849 nm (ca. 1.46 eV)] (λ excitation = 420 nm), which is attributed to the as prepared Zn – intercalated Montmorillonite and this clearly confirms the presence of the ZnO nanoparticles due to the site exchange between Zn^{+2} ions and Al^{+3} of Montmorillonite mineral layer ($4SiO_2 \cdot Al_2O_3 \cdot H_2O$). Also when we rise the excitation lambda (λ excitation = 440 nm) (Figures 8) a red shift of emission peaks happen, and the emission peaks appear at [450 nm (ca. 2.75 eV) & 888 nm (ca. 1.39 eV)]. We note that the excitation at the blue region of spectra leads to emission fluorescence at near the IR - spectrum region of each Zn – intercalated Montmorillonite, and ZnO – Montmorillonite hybrid materials. The enhancement in the emission intensity of the zinc oxide hybrids may be probably due to increase in oxygen vacancies defect arose by the surrounding environment of montmorillonite.

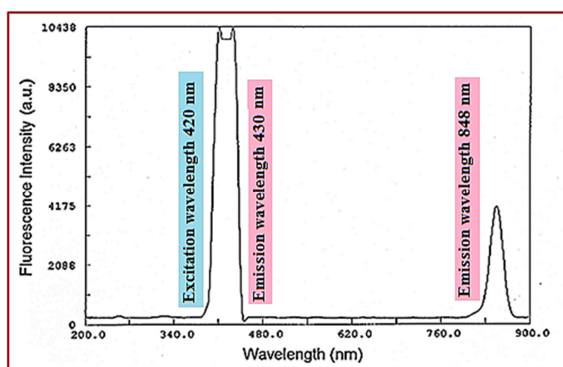


Figure 5: Fluorescence emission spectrum of ZnO – Montmorillonite hybrid (Ex. λ = 420 nm).

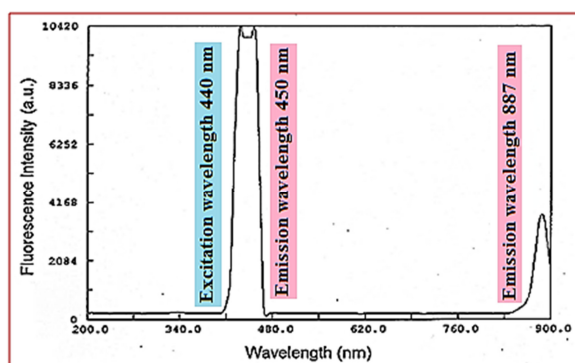


Figure 6: Fluorescence emission spectrum of ZnO – Montmorillonite hybrid (Ex. λ = 440 nm).

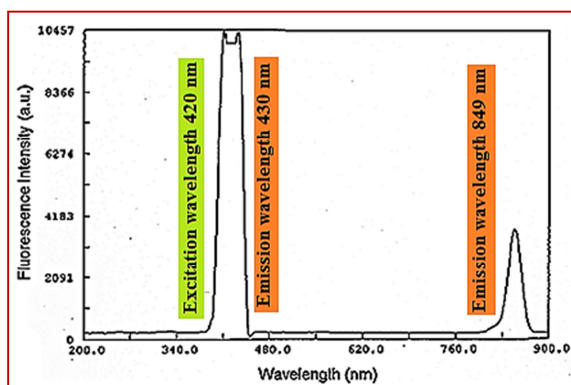


Figure 7: Fluorescence emission spectrum of Zn –intercalated Montmorillonite (Ex. λ = 420 nm).

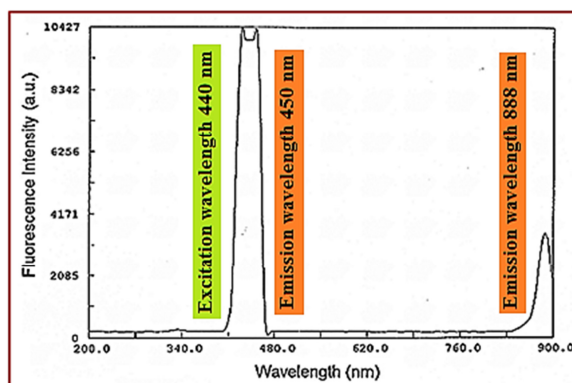


Figure 8: Fluorescence emission spectrum of Zn –intercalated Montmorillonite (Ex. λ = 440 nm).

4. Conclusions

A new and simple method of preparation of Zinc oxide–montmorillonite hybrids was applied, depending on ion exchange technique, and converting of Zn^{+2} intercalated ions to Zinc Oxide by calcining of final product of clay minerals. Powder X- ray diffraction spectra confirmed the formation of zinc oxide. The FT-IR spectrum of ZnO – Montmorillonite hybrid shows the ZnO absorption band at (467.13 cm^{-1}), and that is near the standard peak of zinc oxide which observed in the range of ($426- 440\text{ cm}^{-1}$), and that will support the results derived from SEM images of ZnO - montmorillonite hybrid. The enhancement in the emission intensity of the zinc oxide hybrids may be probably due to increase in oxygen vacancies defect arose by the surrounding environment of montmorillonite.

Acknowledgments

We would like to acknowledge Dean of the Faculty of Education Ibn al-Haitham, and the Chemistry department for their support.

References

- [1] Ogawa M. Photo process in clay–organic complexes. In: Auerbach SM, Carrado KA, Dutta PK, editors. *Hand book of Layered Materials*. New York: Marcel Dekker; 2004. pp. 191–260.
- [2] Lagaly G, Ogawa M, Dékány I. Clay Mineral Organic Interactions. In: Bergaya F, Theng BKG, Lagaly G, editors. *Handbook of Clay Science, Developments in Clay Science*, volume 1. Amsterdam: Elsevier; 2006. pp. 309–77.
- [3] Nithima Khaorapapong, Nuttaporn Khumchoo, Makoto Ogawa, Preparation of zinc oxide–montmorillonite hybrids, *Materials Letters* 65, 2011, 657–660.
- [4] Fatimah, I., Wang, S.B., Wulandari, D., ZnO / montmorillonite for photo catalytic and photo chemical degradation of methylene blue. *Appl.Clay Sci.*, 2011. 53, pp.553–560.
- [5] Zhong Lin Wang, Zinc oxide nanostructures: growth, properties and applications, *J. Phys.: Condens., Matter*, 16, 2004, pp.829 – 858.
- [6] Lakowicz, JR: *Principles of Fluorescence Spectroscopy*, 4th printing. Springer Science, Heidelberg, 2006.
- [7] Modak, S, Acharya, S, Bandyopadhyay, A, Karan, S, Roy, SK, Chakrabarti, PK: Microstructural investigations and paramagnetic susceptibilities of zinc oxide, europium oxide and their Nano composites. *J. Mag. Mater.*, 2010, p. 322, 283.
- [8] R. Wahab, S.G. Ansari, Y.S. Kim, H.K. Seo, H.S. Shin, Room temperature synthesis of needle - shaped ZnO Nano rods via sono chemical method, *Appl. Surf. Sci.* 253, 18, 2007, pp.7622- 7626.
- [9] R. Wahab, S.G. Ansari, Y.S. Kim, H.K. Seo, G.S. Kim, G. Khang, H.S. Shin, Low temperature solution synthesis and characterization of ZnO nano-flowers, *Mater. Res. Bull.* 42, 9, 2007, pp.1640 -1648.
- [10] R. Wahab, S.G. Ansari, H. Kee Seo, Y.S. Kim, E.K. Suh, H.S. Shin, Low temperature synthesis and characterization of rosette-like nanostructures of ZnO using solution process, *Solid, State. Sci.* 11, 2, 2009, pp.439 - 443.

The IISTE is a pioneer in the Open-Access hosting service and academic event management. The aim of the firm is Accelerating Global Knowledge Sharing.

More information about the firm can be found on the homepage:

<http://www.iiste.org>

CALL FOR JOURNAL PAPERS

There are more than 30 peer-reviewed academic journals hosted under the hosting platform.

Prospective authors of journals can find the submission instruction on the following page: <http://www.iiste.org/journals/> All the journals articles are available online to the readers all over the world without financial, legal, or technical barriers other than those inseparable from gaining access to the internet itself. Paper version of the journals is also available upon request of readers and authors.

MORE RESOURCES

Book publication information: <http://www.iiste.org/book/>

Academic conference: <http://www.iiste.org/conference/upcoming-conferences-call-for-paper/>

IISTE Knowledge Sharing Partners

EBSCO, Index Copernicus, Ulrich's Periodicals Directory, JournalTOCS, PKP Open Archives Harvester, Bielefeld Academic Search Engine, Elektronische Zeitschriftenbibliothek EZB, Open J-Gate, OCLC WorldCat, Universe Digital Library, NewJour, Google Scholar

