

Sonosynthesis and characterization of nano ZnO/Montmorillonite nano clay composite via Sol-Gel method

M. Modaresi Tehrani, N. Molahasani, Sh. Aghabeygi*

Department of Chemistry, East Tehran Branch, Islamic Azad University, Tehran, Iran

Received: 1 May 2016; Accepted: 4 July 2016

ABSTRACT: Nano ZnO/ montmorillonite composite were prepared by sol gel method under ultrasonic irradiation from directly mixing montmorillonite nano clay into Zinc gel. The $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and montmorillonite nano clay was used as precursor. The zinc acetate was dissolved in DI water and, NH_3 (aq) solution was dropped into the zinc solution until pH 9 consequently the zinc gel was produced. The montmorillonite nano clay was mixed into Zinc gel, after stirring for two days, the mixture was irradiated 30 min by ultrasonic probe. The filtrated composite gel was calcinated at 400°C for 3h in furnace. The morphology of prepared catalysts were characterized by field emission scanning electronic microscopy (FESEM), Fourier transform infrared (FT-IR) and X-ray diffraction (XRD). The XRD patterns confirm that synthesized catalysts had highly crystalline nature. The calcination temperature of 400°C and aging time of 48 h for preparation of this nanocomposite was found to be the optimum condition.

Keywords: Montmorillonite, Clay, Nano ZnO, Photo-catalyst, Sol-gel, Ultrasonic irradiation

INTRODUCTION

Nano ZnO as the well-known semiconductor has been intensively investigated in the fields of photo-catalysis, solar cell and gas sensors due to their special electronic and optical properties (Guan, *et al.*, 2004, Yu, *et al.*, 2008, Zhang, *et al.*, 2009, Pan, *et al.*, 2010, Xiong, *et al.*, 2010). Semiconductors, such as ZnO, play the most promising roles in several areas of research. The ZnO/Air/UV system is the most effective one. The heterogeneous photo-catalytic behavior of ZnO under UV irradiation, due to which electron and hole pairs are generated at conduction and valence bands respectively, has been studied extensively (Wang, *et al.*, 2005, Zhou, *et*

al., 2007, Khodadadi, *et al.*, 2016, Silva, *et al.*, 2013). ZnO, as a semiconductor, is also usually used as photocatalyst to destroy the organic pollutants in water because its high photo-sensitivity and large band gap can offer the high driving force for reduction and oxidation processes. It is proved that ZnO may exhibit a better efficiency than TiO_2 in photocatalytic degradation for some dyes (Gouvea, *et al.*, 2000, Dindar, *et al.*, 2001, Fu, *et al.*, 2012, Nezamzadeh-Ejehieh, *et al.*, 2015). Intense research has also been conducted on the effect of ZnO particle size on its photo-catalytic activity. It is well known that in the nano-meter size range, the physical and chemical properties of the semiconductor

(*) Corresponding Author - e-mail: saghabeygi@yahoo.com

are found to be modified as compared with those of the bulk semiconductor. Decrease in the size of the particles causes an increase in the photo-catalytic activity of the semiconductor. Therefore control of the size, to which particles grow in, a nano-meter range, becomes necessary (Anpo, *et al.*, 1987, Murugesan, *et al.*, 2002, Tang, *et al.*, 2013).

One strategy to obtain ZnO with defined particle size can be the use of various supports such as silica and clay, etc, and dispersal of the catalyst particles on them (Vafayi, *et al.*, 2015, Danwittayakul, *et al.*, 2013, Hadjltaief, *et al.*, 2016). Zinc oxide is a II–VI group, n-type direct band gap semiconductor that possess some great characteristics, including a wide energy band gap (3.3 eV) (Mohamed, *et al.*, 2005, Nezamzadeh-Ejhieh, *et al.*, 2014, Zhao, *et al.*, 2015, Nezamzadeh-Ejhieh, *et al.*, 2012, Tsay, *et al.*, 2010). In general, clays are other promising additives due to their high surface area, high mechanical and chemical stability and high adsorption capacity. Furthermore, they are also low cost and eco-friendly and they possess many hydroxyl groups on its surface which enhances the photo-catalytic efficiency. The interaction between clay and metal oxides is another reason for addition of clay in the metal oxide-clay composites which leads to an improvement of the contact between the catalyst surface and irradiation (Aghabeygi, *et al.*, 2016, Vaezi, 2008).

In this research we synthesized the high dispersed nano ZnO on montmorillonite nano clay as a composite with high surface area by using ultrasonic irradiation.

EXPERIMENTAL

Materials

All the chemical reagents used in this research were analytical grade and without further purification. Deionized water (DI) was used in all experiments.

Sono- synthesis of Nano ZnO/montmorillonite composite

Preparation of ZnO gel : 4.4 g $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was firstly dissolved in DI water (100 ml) and stirred to get a precursor solution, the 20 ml (2M) NH_3 (aq)

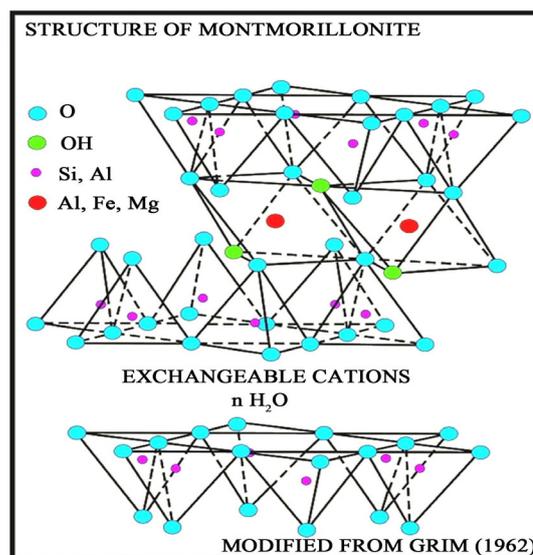
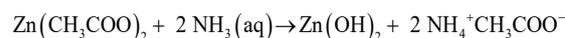


Fig. 1. Structural formula of montmorillonite clay

was dropped into the precursor solution, one drop per second, until pH of mixture was adjusted 9 during stirred solution, and the white suspension of $\text{Zn}(\text{OH})_2$ was appeared.



The montmorillonite clay (Fig. 1) directly incorporated into the ZnO gel, to get the ZnO/ montmorillonite composite gel. As aging time, the mixture of reaction continuously stirred for two days. The solution was sonicated by an Ultrasound Horn (Bandelin, SONOPULS 20 kHz) at 85% amplitude delivering power of 200W by the Titanium Flat tip of probe for 30 min with 0.5 s pulse and 0.5 s silent period cycles to achieve a ZnO/montmorillonite clay homogeneous gel. After filtering the product was calcinated in furnace at 500°C for 3h. The white powder of nano ZnO/ montmorillonite clay was prepared (Khatamian, *et al.*, 2010, Mukasa-Tebandeke, *et al.*, 2015).

Characterization

The IR spectra performed as KBr disks from 4000 to 400 cm^{-1} on a Bruker Tensor 27 FT-IR spectrometer. X-ray powder diffraction (XRD) measurements were performed using an X'pert diffractometer (Philips Company) with monochromatized Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$). The samples were characterized with a Field Emission Scanning Electron Microscope (Hitachi S4160 Cold Field Emission) with gold coating.

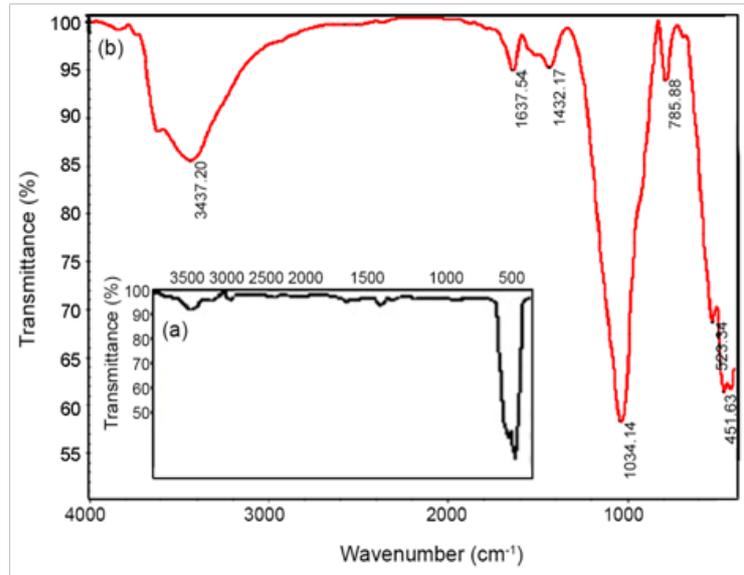


Fig. 2. FT-IR spectra of (a) nano ZnO and (b) nano ZnO /montmorillonite composite

RESULTS AND DISCUSSION

FT-IR spectra

The FT-IR spectra of nano ZnO /montmorillonite composite and pure nano ZnO (wurtzite) is shown in (Fig. 2). In comparison of (Fig. 2a and b) is shown, in (Fig. 2b) the water molecules was trapped in montmorillonite pores therefore the broad peak at 3437 cm^{-1} has assigned to the symmetry and asymmetry stretching vibrations of water and M-O-H and the peak at 1637 cm^{-1} is resulted from bending vibrations of water, in (Fig. 2b) is larger than nano ZnO (Fig. 2a). In (Fig. 2b), the peak at 1432 cm^{-1} has been related to the surface M-O-H bending (M= Al, Fe, Mg). The peak at 1034 cm^{-1} has been resulted bending and stretching vibration of, O-Si-O bonds and M-O-Si of montmoril-

lonite. The peaks at 785, 523 and 461 cm^{-1} have been related to the bending and stretching of the Zn-O-Zn bonds and flexion (Wang, *et al.*, 2005).

XRD Analysis

Fig. 3 presents the XRD patterns of the sonosynthesized nano ZnO hexagonal wurtzite and nano ZnO/ montmorillonite nano clay composite. In (Fig. 3a), the peaks indicate the respective Joint Committee on Powder Diffraction Standards (JCPDS) card No. 36-1451, for hexagonal wurtzite structure of ZnO. In (Fig. 3b), the diffraction peaks appear at 2θ , 6.390, 8.585, 19.810, 20.845, 22.535, 26.625, 28.825, and 32.560 are related to the montmorillonite clay. These values of 2θ are observed that have a good agreement with the data of the montmorillonite in the

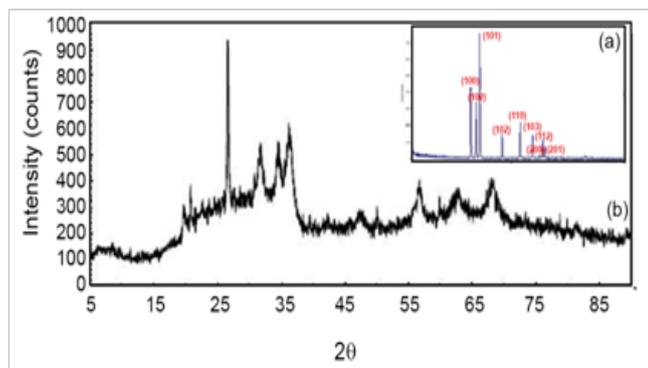


Fig. 3. XRD Patterns of (a) nano ZnO and (b) nano ZnO /Montmorillonite composite

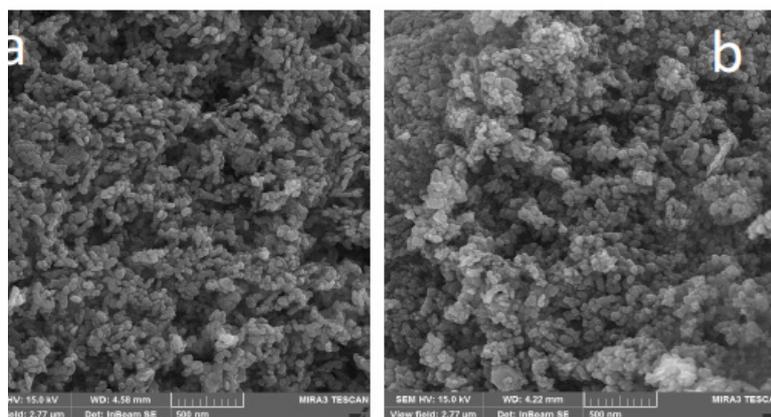


Fig. 4. FESEM images of (a) nano ZnO and (b) nano ZnO /montmorillonite composite

library of the instrument (Zhao, *et al.*, 2015).

The average crystallite size of samples D_v was calculated based upon the XRD pattern for quantitative purpose using the Debye- Scherer equation:

$$D_v = \frac{K\lambda}{\beta \cos \theta}$$

Where: D_v is the “volume weighted” crystallite size = $\frac{3}{4} d$ (crystallite diameter) K is the “Scherer constant” (around 0.89), λ is the wavelength of the X-rays here is 1, $\text{CuK}\alpha = 1.541 \text{ \AA}$, θ is the Bragg angle for the peak at 2θ , β is the “integral breadth” of the peak at 2θ . The $\beta = (\pi/2)$ FWHM (full width at half maximum) for a Gaussian shaped peak. According to XRD Patterns, the mean crystallite size of nano ZnO and nano ZnO / montmorillonite nano clay composite are calculated to be 26 and 17 nm respectively.

FESEM images

Fig. 4 shows the FESEM images of the nano ZnO and ZnO /montmorillonite nano composite. Surface and particle morphology of the synthesized nano ZnO and nano ZnO /montmorillonite composite have been studied and their FESEM images are shown in (Fig. 4a and 4b) respectively. The ZnO NPs are being located on the inner surface of montmorillonite clay the morphology of the nano ZnO and ZnO /montmorillonite nanocomposite are similar together. The particles size of nano ZnO and ZnO /montmorillonite clay nanocomposite is in the range 35-45 nm and 25-35 nm respectively.

CONCLUSIONS

In this work, nano ZnO and nano ZnO/montmorillonite nano clay composite have been synthesized by a facile sol-gel method using ultrasonic irradiation. $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and montmorillonite nano clay have been used as starting materials. The composite of ZnO gel and montmorillonite was calcinated at 400°C . Comparison of the FT-IR spectra of ZrO_2/ZnO nanocomposite with the pure ZnO nanoparticles, have been showed formation of nano ZnO/montmorillonite nano clay composite. Crystal phase and particle size of NPs can be detected by XRD. According to XRD Patterns, the calculated value as crystallite size of nano ZnO hexagonal wurtzite and nano ZnO/montmorillonite nano clay composite was obtained 54 and 37 nm respectively. The FESEM images have been shown that the nano ZnO are been inner surface of montmorillonite.

ACKNOWLEDGMENT

We are grateful to East Tehran Branch, Islamic Azad University for financial support of this research.

REFERENCES

Aghabeygi, S., Kia Kojoori, R., Vakili-Azad, H., (2016). Sonosynthesis characterization and photocatalytic degradation property of nano ZnO/zeo-

- lite A. Iran. J. Catal., 6(3): 275-279.
- Anpo, M., Shima, T., Kodama, S., Kubokawa, Y., (1987). Photocatalytic hydrogenation of propyne with water on small-particle titania: size quantization effects and reaction intermediates. *J. Phys. Chem.*, 91(16): 4305-4310.
- Danwittayakul, S., Jaisai, M., Koottatep, T., Dutta, J., (2013). Enhancement of photocatalytic degradation of methyl orange by supported zinc oxide nanorods/zinc stannate on porous substrates, *Ind. Eng. Chem. Res.*, 52(38): 13629-13636.
- Dindar, B., Icli, S., (2001). Unusual photoreactivity of zinc oxide irradiated by concentrated sunlight. *J. Photochem. Photobiol. A: Chem.*, 140(3): 263-268.
- Fu, D., Han, G., Chang, Y., Dong, J., (2012). The synthesis and properties of ZnO-graphene nano hybrid for photodegradation of organic pollutant in water. *Mater. Chem. Phys.*, 132(2-3): 673-681.
- Guan, G., Kida, T., Kusakabe, K., Kimura, K., Abe, E., Yoshida, A., (2004). Photocatalytic reactivity of noble metal-loaded ETS-4 zeolites. *Inorg. Chem. Commun.*, 7(5): 618-620.
- Gouvea, K., Wypych, F., Moraes, S.G., Duran, N., Nagata, N., Peralta-Zamora, P., (2000). Semiconductor-assisted photocatalytic degradation of reactive dyes in aqueous solution. *Chemosphere*, 40(4): 433-440.
- Hadjltaief, H.B., Zina, M.B., Galvez, M.E., Cořta, P.D., (2016). Photocatalytic degradation of methyl green dye in aqueous solution over natural clay-supported ZnO-TiO₂ catalysts. *J. Photochem. Photobiol. A*, 315: 25-33. .
- Khataee, A., Sheydaei, M., Hassani, A., Taseidifar, M., Karaca, S., (2015). Sonocatalytic removal of an organic dye using TiO₂/Montmorillonite nanocomposite. *Ultrason. Sonochem.*, 22: 404-411.
- Khatamian, M., Hashemian, S., Sabae, S., (2010). Preparation and photo-catalytic activity of nano TiO₂-ZSM-5 composite. *Mater. Sci. Semicond. Process*, 13(3): 156-151.
- Khodadadi, B., Bordbar, M., (2016). Sonochemical synthesis of undoped and Co-doped ZnO nanostructures and investigation of optical and photocatalytic properties. *Iran. J. Catal.*, 6(1): 37-42.
- Mohamed, R.M., Ismail, A.A., Othman, I., Ibrahim, I. A., (2005). Preparation of TiO₂-ZSM-5 zeolite for photodegradation of EDTA. *J. Mol. Catal. A: Chem.*, 238(1-2): 151-157.
- Murugesan, V., Sakthive, I.S., Shankar, M.V., Palanichamy, M., Arabindoo, B., (2002). Photocatalytic decomposition of leather dye. *J. Photochem. Photobiol. A*, 148(1-3): 153-159.
- Nezamzadeh-Ejhih, A., Khorsandi, S., (2014). Photocatalytic degradation of 4-nitrophenol with ZnO supported nano-clinoptilolite zeolite A. *J. Ind. Eng. Chem.*, 20(3): 937-946.
- Nezamzadeh-Ejhih A., Bahrami M., (2015). Investigation of the photocatalytic activity of supported ZnO-TiO₂ on clinoptilolite nano-particles towards photodegradation of wastewater-contained phenol. *Des. Water Treat.*, 55(4): 1096-1104.
- Pan, J.H., Dou, H., Xiong, Z., Xu, C., Ma, J., Zhao, X.S., (2010). Porous photocatalysts for advanced water purifications. *J. Mater. Chem.*, 20(22): 4512.
- Silva, C.G., Monteiro, J., Marques, R.R.N., Silva, A.M.T., Martínez, C., Canle, M., Faria, J.L., (2013). Photochemical and photocatalytic degradation of trans-resveratrol. *Photochem. Photobiol. Sci.*, 12(4): 638-644.
- Tang, Y., Miao, S., Mo, L., Zheng, X., Brent, H. Shanks, (2013). One-step hydrogenation/esterification activity enhancement over bifunctional mesoporous organic-inorganic hybrid silicas. *Top. Catal.*, 56(18-20): 1804-1813.
- Vafayi, L., Gharibe, S., (2015). Enhancement of photocatalytic activity of ZnO-SiO₂ by nano-sized Pt for efficient removal of dyes from wastewater effluents. *Iran. J. Catal.*, 5(4): 365-371.
- Zhao, L., Liu, Z.C., Liu, Z.F., (2014). Synthetic zeolite supported ZnO nanoparticle materials for photocatalytic applications. *Synth. Mater. Tech.*, 30(1): 60-64
- Nezamzadeh-Ejhih, A., Banan, Z., (2012). Sunlight assisted photodecolorization of crystal violet catalyzed by CdS nanoparticles embedded on zeolite A. *Desalination*, 284: 157-166.
- Tsay, C.Y., Fan, K.S., Chen, S.H., Tsai, C.H., (2010). Preparation and characterization of ZnO transparent semiconductor thin films by sol-gel method. *J. Alloys Compd.*, 495(1): 126-130.
- Mukasa-Tebandeke, I.Z., Ssebuwufu, P.J.M., Nyanzi,

- S.A., Schumann, A., Nyakairu, G.W.A., Ntale, M., Lugolobi, F., (2015). The elemental, mineralogical, IR, DTA and XRD analyses characterized clays and clay minerals of central and eastern uganda. *Adv. Mater. Phy. Chem.*, 5: 67.
- Vaezi, M.R., (2008). Two-step solochemical synthesis of ZnO/TiO₂ nano-composite materials. *J. Mater. Process Technol.*, 205(1-3): 332-337.
- Xiong, H.M., (2010). Photoluminescent ZnO nanoparticles modified by polymers. *J. Mater. Chem.*, 20(21): 4251.
- Wang, L.J, Chang, Y., Li, J.S., Yang, Y.C., Sun, X.Y., (2005). Preparation and characterization of nano-sized ZSM-5 zeolites in the absence of organic template. *Mater. Lett.*, 59(27): 3427-30.
- Yang, G., Yanb, Z., Xiao, T., (2012). Preparation and characterization of SnO₂/ZnO/TiO₂ composite semiconductor with enhanced photocatalytic activity. *Appl. Surf. Sci.*, 258(22): 8704-8712.
- Yu, V., Meteleva, F., Roessner, G., Novikov, F., (2008). Synthesis and optical properties of zeolite-semiconductor composites new photocatalysts. *J. Photochem. Photobiol. A*, 196(2-3): 154-158.
- Zhang, Q., Dandeneau, C.S., Zhou, X., Cao, G., (2009). ZnO Nanostructures for dye-sensitized solar cells. *Adv. Mater.*, 21(41): 4087-4108.
- Zhou, G., Deng, J., (2007). Preparation and photocatalytic performance of Ag/ZnO nano-composites. *Mater. Sci. Semicond. Process*, 10(2-3) 90-96.

AUTHOR (S) BIOSKETCHES

Mona Modaresi Tehrani, M.Sc., Department of Chemistry, East Tehran Branch, Islamic Azad University, Tehran, Iran

Nasibeh Molahasani, Assistant Professor, Department of Chemistry, East Tehran Branch, Islamic Azad University, Tehran, Iran

Shokufeh Aghabeygi, Associate Professor, Department of Chemistry, East Tehran Branch, Islamic Azad University, Tehran, Iran, Email: saghabeygi@yahoo.com