Novel sodium dodecyl sulphate-assisted synthesis of $\text{Zn}_3\text{V}_2\text{O}_8$ nanostructures via a simple route

Fatemeh Mazloom, Maryam Masjedi-Arani, Maryam Ghiyasiyan-Arani, Masoud Salavati-Niasari *

Institute of Nano Science and Nano Technology, University of Kashan, Kashan, P.O. Box 87317-51167, I. R. Iran

*Corresponding author: Tel.: +98 315 591 2383, Fax: +98 3155913201.

E-mail address: Salavati@kashanu.ac.ir

Abstract

Zinc vanadate ($\text{Zn}_3\text{V}_2\text{O}_8$) nanostructures were prepared via a simple precipitation approach in the presence of anionic sodium dodecyl sulphate (SDS) surfactant as size and morphology controller. The effect of different parameters such as precursor of Zn, reaction time, temperature, solvent and pH on the size, morphology and uniformity of prepared products were investigated. As-prepared products were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) spectrum, Electron Dispersive X-ray spectroscopy (EDX), Photoluminescence and ultraviolet-visible (UV-Vis) spectroscopy. The photocatalytic activity of $\text{Zn}_3\text{V}_2\text{O}_8$ nanostructures were evaluated by degradation of anionic and cationic dyes in aqueous solution under UV light irradiation. Moreover, the cyclic voltammetry analysis of $\text{Zn}_3\text{V}_2\text{O}_8$ nano and bulk structures were investigated.

Keywords: Zinc vanadate; Nanostructure; Precipitation; Optical property; Photocatalytic activity.

1. Introduction

Nanomaterials have attracted extensive attention because of their novel properties in different fields in comparison with their bulk counterparts. Artificial colors are used in different sectors of industries but due to

their strong sustainability and toxicity are a major problem for our life environment [1]. Photocatalytic degradation is a simple way to eliminate of water pollutants. Metal vanadates are a significant class of inorganic nanomaterials that have received main interest as complex oxides due to their potential application in various fields including photocatalytic activity. Lots of research has been focused on the preparing of metal vanadates of silver, copper, manganese, iron, bismuth and indium from different routes. Among them, zinc vanadate nanomaterials have interested special attention since zinc is a cheap, abundant and environmental- benign metal, and vanadium has multiple valence states leading to rich structures of its compounds. Zinc vanadate ($\text{Zn}_3\text{V}_2\text{O}_8$) as a semiconductor photocatalyst material has attracted significant consideration. Nanostructured $\text{Zn}_3\text{V}_2\text{O}_8$ is widely used in applications such as lithium ion batteries [2], photocatalysis [3] and luminescence [4, 5]. A variation of possible methods including hydrothermal method [6], sol-gel [7], wet chemical approach [3], coprecipitation [2] and solid state [5, 8] have been applied to obtain different types of zinc vanadate. The precipitation method is more promising in terms of low cost, simply control the shape and particle size, short reaction time, low processing temperature, simplicity and potential for large scale production. This method has become an important tool in synthesis of nano-sized materials with different size and morphology in recent years [9-11]. In this paper, $\text{Zn}_3\text{V}_2\text{O}_8$ nanoparticles were synthesized via a precipitation method in presence of anionic SDS surfactant as a size and morphology controller and ethylenediamine as novel basic agent to adjust the pH value to 8-9. In addition to SDS, The carbon chain of ethylenediamine can provide great steric hindrance to control the size and morphology of $\text{Zn}_3\text{V}_2\text{O}_8$ nanoparticles. It is good to know that nanoparticle size and morphology have a great effect on the properties of them [12-16]. So, controlling morphology and particle size via investigation of different reaction condition is important. In this work, the role of precursor of Zn, reaction time, temperature, solvent and pH on the size, morphology and uniformity of the $\text{Zn}_3\text{V}_2\text{O}_8$ nanocrystals were evaluated. The photocatalytic degradation activity of eosin Y and methylene blue as anionic and cationic dyes is

compared to study the catalytic properties of as-produced $\text{Zn}_3\text{V}_2\text{O}_8$ nanostructures, respectively. Moreover, the cyclic voltammetry analysis of $\text{Zn}_3\text{V}_2\text{O}_8$ nano and bulk structures were evaluated.

2. Experimental

2.1. Materials and Physical Measurements

$\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, NH_4VO_3 and ethylenediamine (en) were purchased from Merck Company. All of the chemicals were used as received without further purifications. For characterization of the products, X-ray diffraction (XRD) patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu $\text{K}\alpha$ radiation. GC-2550TG (Teif Gostar Faraz Company, Iran) were used for all chemical analyses. Scanning electron microscopy (SEM) images were obtained on Philips XL-30ESEM. Transmission electron microscopy (TEM) image was obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 200 kV. Fourier transform infrared (FT-IR) spectra were recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets. Optical analyses were performed using a V-670 UV–Vis–NIR Spectrophotometer (Jasco). Room temperature photoluminescence (PL) was studied on a Perkin Elmer (LS 55) fluorescence spectrophotometer.

2.2. Synthesis of pure $\text{Zn}_3\text{V}_2\text{O}_8$ nanoparticles

Zinc vanadate nanostructures were prepared by reaction between $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and NH_4VO_3 with molar ratio of 3:2 in the presence of SDS surfactant. In a typical experiment, an aqueous solution of NH_4VO_3 (2 mmol) was added dropwise into a solution including 3 mmol of $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 0.5 g of SDS surfactant. In this process, a yellow suspension appeared gradually. Finally, basic agent was added to adjust the pH value of the solution to about 8-9, after the mixture had been stirred for about 2 hours. The final products were collected by centrifugation, washed with deionized water and ethanol. The as-obtained products were dried at 80 °C under vacuum for 2 h, then calcinated at 600 °C for another 2h. The preparation conditions for synthesis $\text{Zn}_3\text{V}_2\text{O}_8$ nanostructures have been illustrated in Table 1.

2.3. Photocatalytic measurements

The photocatalytic activity of $\text{Zn}_3\text{V}_2\text{O}_8$ nanoparticles was tested by using eosin Y and methylene blue solution. The degradation reaction was carried out in a quartz photocatalytic reactor. The photocatalytic degradation was carried out with 5×10^{-5} M of solutions containing 0.05 g of nanostructures. This mixture was aerated for 30 min to reach adsorption equilibrium. Then, the mixture was placed inside the photoreactor in which the vessel was 40 cm away from the UV. The quartz vessel and light sources were placed inside a black box equipped with a fan to prevent UV leakage. The experiments were performed at room temperature and pH of the solutions was adjusted 3. Aliquots of the mixture were taken at periodic intervals during the irradiation, and after centrifugation, they were analyzed with the UV–Vis spectrometer. The dyes degradation percentage was calculated as follows:

$$D.P.(t) = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

Where A_0 and A_t are the absorbance value of solution at 0 and t min, respectively.

2.4. Cyclic voltammetry analysis

$\text{K}_3\text{Fe}(\text{CN})_6$, $\text{K}_4\text{Fe}(\text{CN})_6$, phosphoric acid (H_3PO_4) and sodium hydroxide (NaOH) were purchased from MERCK (Germany).

Voltammetric studies were carried out by Sama 500 potentiostat, Isfahan, Iran. A three electrode system comprising of a glassy carbon electrode (GCE) (Metrohm, Switzerland) modified $\text{Zn}_3\text{V}_2\text{O}_8$ nanostructures, a saturated $\text{Ag}/\text{AgCl}/\text{KCl}$ (Metrohm, Switzerland) and Pt wire (Metrohm, Switzerland) were used as working, reference and counter electrode, respectively. A model 691 pH meter (Metrohm, Switzerland) was used to adjust the pH of the 0.2 M phosphate buffer solution, which was applied as a supporting electrolyte in the voltammetric experiments.

3. Results and discussion

In order to confirm the crystal phase and purity of $\text{Zn}_3\text{V}_2\text{O}_8$ nanostructures, XRD analysis was carried out. XRD pattern of the product synthesized after calcination at 600 °C is shown in Fig. 1. In Fig. 1 most of the reflection peaks can be attributed to the orthorhombic phase $\text{Zn}_3\text{V}_2\text{O}_8$ with space group of Abam and cell constants $a = 8.2990 \text{ \AA}$, $b = 11.5284 \text{ \AA}$, and $c = 6.1116 \text{ \AA}$ (JCPDS card No. 34-0378) and some weak diffraction evidence of residual $\text{Zn}_2\text{V}_2\text{O}_7$ phase (JCPDS card No. 29-1396). the crystallite diameter (D_c) of $\text{Zn}_3\text{V}_2\text{O}_8$ nanostructures obtained using the Scherrer equation [17]: $D = K\lambda/\beta\cos\theta$; where β is the breadth of the observed diffraction line at its half intensity maximum, K is the so-called shape factor, which usually takes a value of about 0.9, and λ is the wavelength of X-ray source used in XRD. Calculated crystalline domain sizes have been found to be 31 nm for sample of calcined at 600 °C.

To examine the role of the Zn precursor on the morphology and size of the products, $\text{Zn}_3\text{V}_2\text{O}_8$ nanostructures were synthesized by $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. SEM images of synthesized products using different Zn precursors such as $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ are illustrated in Fig. 2(a–c), respectively. These results show that using $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ precursors lead to synthesis of agglomerated products. However, by using $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ precursor, nanostructure products are obtained. According to the Fig. 2(a), it can be seen that the as-prepared product by using $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ precursor have uniform morphology and fine size. The effect of reaction time and temperature on the morphology and particle size of the zinc vanadate samples were investigated. For this propose, reactions were performed at different times and temperatures. SEM image of $\text{Zn}_3\text{V}_2\text{O}_8$ sample prepared at 80 °C is shown in Fig 3(a). By increasing the reaction temperature from 25 (sample No.1) to 80 °C (sample No.4), bulk structures are synthesized. Fig 3(b) shows the SEM image of sample prepared at the reaction time of 18 h. Increasing the reaction time to 18 h (sample No.5), causes larger particle size. In the process of nucleation, with increasing reaction time nuclei grow to form larger nanoparticles and finally agglomerated particles are prepared. In order to investigate the effect of solvent on the size and morphology of the products, the reaction carried out in

different solvents of water, propylene glycol and methanol. Fig 3(c, d) show the SEM image of products prepared in presence of propylene glycol and methanol, respectively. Propylene glycol is suitable solvent for synthesis of $\text{Zn}_3\text{V}_2\text{O}_8$ nanoparticles with fine size and uniform size distribution. Using the methanol as a solvent lead to synthesis of bulk structures. Fig 3(e) shows $\text{Zn}_3\text{V}_2\text{O}_8$ nanostructure prepared with pH=11 (sample No.8). for the investigation of influence SDS surfactant on the size, morphology and uniformity of the products, blank test was carried out. Fig 3(f) shows the SEM image of $\text{Zn}_3\text{V}_2\text{O}_8$ sample without SDS surfactant (sample No.9). Bulk structure products were synthesized without presence of SDS as a capping agent. These results indicate that the presence of the anionic surfactant of SDS is very favorable to produce fine and uniform $\text{Zn}_3\text{V}_2\text{O}_8$ nanoparticles. As SDS plays a suitable role in the reaction, we are very interested in how it works. The possible mechanism is shown as follows. The $\text{Zn}_3\text{V}_2\text{O}_8$ surfaces are occupied by hydroxy groups. As the SDS molecule has an anionic group of SO_4^- and zinc vanadate has many hydroxy groups on the surface, SDS will entwine the $\text{Zn}_3\text{V}_2\text{O}_8$ surface tightly as shown in Scheme 1. But $\text{Zn}_3\text{V}_2\text{O}_8$ obtained without anionic surfactant is highly agglomerated. The probable mechanism of SDS surfactant on the size, morphology and uniformity of products are shown in Scheme 1.

The size and shape of zinc vanadate nanoparticle prepared in presence of the SDS surfactant and propylene glycol solvent was elucidated by TEM image. Fig. 4 shows the TEM image of sample No. 6 which contains spherical nanoparticles with the particle size of 27-155 nm. The purity of the nanostructures was also confirmed by energy dispersive X-ray spectroscopy. EDX analysis of $\text{Zn}_3\text{V}_2\text{O}_8$ nanoparticles (sample No. 6) is illustrated in Fig. 5. The lines of Zn, V and O are obviously observed.

The surface conditioning of as-prepared $\text{Zn}_3\text{V}_2\text{O}_8$ nanoparticle was recorded using FT-IR spectrum in order to detect the residual organic compounds. Fig. 6 shows FT-IR spectrum of sample No. 6. The absorption bond centered at 3440 cm^{-1} and weak peak at 1618 cm^{-1} can be assigned to the stretching and bending vibrations of the hydrogen-bonded OH groups of the adsorbed water, respectively. The vibration bonds at 840 and 663 cm^{-1}

are attributed to tetrahedral VO₄ vibration modes in the network. The absorption around 417 cm⁻¹ correspond to the stretching vibration Zn-O band, which is consistent with octahedral ZnO₆ [18, 19]. The very weak vibration peaks about 1100-1220 cm⁻¹ are assigned to S-O and absorption of CO₂ molecules from atmosphere [20, 21]. Very weak peaks around 2920 and 2850 cm⁻¹ can be attributed to the asymmetric and symmetric stretching vibrations of aliphatic groups (-CH₂-) n, respectively [22]. From the FT-IR results, it can be concluded that probably a small amount of SDS surfactant and propylene glycol solvent are attached to the surface of Zn₃V₂O₈ nanoparticles which may have a well role in preventing nanoparticles agglomeration.

The UV-Vis Diffuse Reflectance spectroscopy of sample No. 6 is shown in Fig 7(a, b). The fundamental absorption edge in most semiconductors follows the exponential law. Using the absorption data, the band gap was estimated by Tauc's relationship:

$$\alpha = \frac{\alpha_0(h\nu - E_g)^n}{h\nu} \quad (2)$$

where α is absorption coefficient, $h\nu$ is the photon energy, α_0 and h are the constants, E_g is the optical band gap of the material, and n depends on the type of electronic transition and can be any value between 1/2 and 3 [23]. The energy gap of the Zn₃V₂O₈ sample has been determined by extrapolating the linear portion of the plots of $(\alpha h\nu)^2$ against $h\nu$ to the energy axis (Fig. 7 b). The E_g value is calculated 3.25 eV for the sample No. 6. Moreover, Optical properties of Zn₃V₂O₈ nanocrystals were investigated by using PL technique. Optical properties of zinc vanadate nanocrystal is of great importance as they provide information for the uses of these materials in photocatalytic applications. Fig. 7(c) shows the PL spectrum of Zn₃V₂O₈ nanostructure (sample No. 6) that measured at room temperature using an excitation wavelength of 340 nm. A strong visible light emission ranging from 450 to 600 nm can be found in the PL spectrum. The PL spectra show a broad emission band centered at around 457 nm for sample No 6. The determined band gap of sample No. 6 in ethanol solution is 2.71 eV [5, 18].

The photocatalytic activity of $\text{Zn}_3\text{V}_2\text{O}_8$ nanoparticles (sample No. 6) were investigated by monitoring the degradation of eosin Y and methylene blue as water pollutants in an aqueous solution under UV light irradiation. The obtained results are shown in Fig. 8. As shown in Fig. 8, the eosin Y and methylene blue degradation percentage of $\text{Zn}_3\text{V}_2\text{O}_8$ nanoparticles increased rapidly after the Osram lamp turned on. According to photocatalytic calculations by Eq. (1), the eosin Y and methylene blue degradation were about 60 and 81 % after 150 min irradiation of UV light, respectively. These results indicated that $\text{Zn}_3\text{V}_2\text{O}_8$ nanocrystals are suitable photocatalyst under UV light in the short time. It is well known that the size, crystallinity, morphology and surface areas of nanostructures as photocatalyst have significant effect on the photocatalytic activity [24]. On the other hand, the defects in crystals, such as zinc vacancy, oxygen vacancy, especially on the surface can supply more active sites are considerable to photocatalyst during the catalytic process [25]. In this work, the modified photocatalytic activity may be attributed to convenient distribution of the pores, numerous hydroxyl contents and high separation rate of photoinduced charge carriers [26].

The electrochemical behavior of $\text{Zn}_3\text{V}_2\text{O}_8$ nanostructures was investigated by cyclic voltammetry (CV) technique at the surface of a GCE. The CV experiments were performed in a 5.0 mM redox probe ($\text{K}_3\text{Fe}(\text{CN})_6 + \text{K}_4\text{Fe}(\text{CN})_6$) phosphate buffer solution at a scanning rate of 100.0 mV s^{-1} . The cyclic voltammograms of GCE- $\text{Zn}_3\text{V}_2\text{O}_8$ nanostructure (sample No. 6) and GCE- $\text{Zn}_3\text{V}_2\text{O}_8$ bulk structure (sample No. 9) were shown in Fig. 9. As can be observed, the electrochemical properties of GCE after modification by $\text{Zn}_3\text{V}_2\text{O}_8$ nanostructures are better than the bulk structures. The increase in current response of GCE is clear evidence of the catalytic effect of GCE- $\text{Zn}_3\text{V}_2\text{O}_8$ nanostructures.

4. Conclusions

We employed a facile precipitation route to synthesize $\text{Zn}_3\text{V}_2\text{O}_8$ nanoparticles with aid of ethylenediamine as basic agent and SDS as the capping agent. The effect of different parameters such as precursor of Zn, solvent, pH, reaction time and temperature on the size, morphology and uniformity of prepared products were

investigated. $\text{Zn}_3\text{V}_2\text{O}_8$ nanocrystals were characterized by XRD, SEM, TEM, EDS, FT-IR, PL and DRS. Different morphology and size of products were prepared. The photocatalytic behavior of nanoparticles was evaluated using the degradation of eosin Y and methylene blue aqueous solution under UV light irradiation. The results show that $\text{Zn}_3\text{V}_2\text{O}_8$ nanostructures are good candidate with excellent performance in photocatalytic applications for degradation of anionic and cationic dyes under UV irradiation in a short time.

Acknowledgments

Authors are grateful to the council of Iran National Science Foundation and University of Kashan for supporting this work by Grant No (159271/342).

References

- [1] W. Ma, J. Li, X. Tao, J. He, Y. Xu, J. C. Yu and J. Zhao, Efficient degradation of organic pollutants by using dioxygen activated by resin-exchanged iron (II) bipyridine under visible irradiation, *Angew. Chem., Int. Ed.* 42 (2003) 1029–1032.
- [2] L.H. Gan, D. Deng, Y. Zhang, G. Li, X. Wang, L. Jiangb, C.R. Wang, Zn₃V₂O₈ hexagon nanosheets: a high-performance anode material for lithium-ion batteries, *J. Mater. Chem. A* 2 (2014) 2461-2466.
- [3] C. Mondal, M. Ganguly, A.K. Sinha, J. Pal, R. Sahoo, and T. Pal, Robust cubooctahedron Zn₃V₂O₈ in gram quantity: a material for photocatalytic dye degradation in water, *Cryst.Eng Comm*, 15 (2013) 6745-6751.
- [4] Shreyas.S. Pitale, Mukut. Gohain , I.M. Nagpure, O.M. Ntwaeaborwa, Barend C.B. Bezuidenhoudt, H.C. Swart, A comparative study on structural, morphological and luminescence characteristics of Zn₃(VO₄)₂ phosphor prepared via hydrothermal and citrate-gel combustion routes, *Physica B*. 407 (2012) 1485-1488.
- [5] T. Li, J. Luo, Z. Honda, T. Fukuda, N. Kamata, Sintering Condition and Optical Properties of Zn₃V₂O₈ Phosphor, *Adv. Mater. Phys. Chem*, 2 (2012) 173.
- [6] R. Shi, Y. Wang, F. Zhou and Y. Zhu. Zn₃V₂O₇(OH)₂(H₂O)₂ and Zn₃V₂O₈ nanostructures: controlled fabrication and photocatalytic performance, *J. Mater. Chem.* 21 (2011) 6313-6320.
- [7] L. Xiao, Y. Zhao, J. Yin and L. Zhang, Clewlike ZnV₂O₄ hollow spheres: Nonaqueous sol–gel synthesis, formation mechanism, and lithium storage properties, *Chem. Eur. J.* 15 (2009) 9442-9450.
- [8] D. Wang, J. Tang, Z. Zou, J. Ye, Photophysical and Photocatalytic Properties of a New Series of Visible-Light-Driven Photocatalysts M₃V₂O₈ (M: Mg, Ni, Zn), *Chem. Mater.* 17 (2005) 5177-5182.
- [9] Z. Shahri, M. Bazarganipour, M. Salavati-Niasari, Controllable synthesis of novel zinc molybdate rod-like nanostructures via simple surfactant-free precipitation, *Superlattices and Microstructures*. 63 (2013) 258-266.
- [10] S. Zinatloo-Ajabshir, M. Salavati-Niasari, Novel poly(ethyleneglycol)-assisted synthesis of praseodymium oxide nanostructures via a facile precipitation route, *Ceramics International*. 41 (2015) 567-575.

- [11] F. Mohandes, M. Salavati-Niasari, M. h. Fathi, Z. Fereshteh, Hydroxyapatite nanocrystals: Simple preparation, characterization and formation mechanism, *Materials Science and Engineering*. 45 (2014) 29-36.
- [12] A. Sobhani, M. Salavati-Niasari, A new simple route for the preparation of nanosized copper selenides under different conditions. *Ceram. Int.* 40 (2014) 8173–8182.
- [13] A. Sobhani, M. Salavati-Niasari, Hydrothermal synthesis, characterization, and magnetic properties of cubic MnSe_2/Se nanocomposites material, *J. Alloys Compd.* 617 (2014) 93–101.
- [14] A. Sobhani, M. Salavati-Niasari, A Polyethylene Glycol-assisted Hydrothermal Synthesis of FeSe_2 Nanoparticles and $\text{FeSe}_2/\text{FeO}(\text{OH})$ Nanocomposites. *J. Alloys Compd.* 625 (2015) 26–33.
- [15] F. Ansari, A. Sobhani, M. Salavati-Niasari, Sol-gel auto-combustion synthesis of $\text{PbFe}_{12}\text{O}_{19}$ using maltose as a novel reductant. *RSC Adv.* 4 (2014) 63946–63950.
- [16] A. Sobhani, M. Salavati-Niasari, CdSe nanoparticles: Facile hydrothermal synthesis , characterization and optical properties. *J. Mater. Sci.: Mater. Electron.* 26 (2015) 6831–6836 .
- [17] M. Masjedi-Arani, M. Salavati-Niasari, A simple sonochemical approach for synthesis and characterization of Zn_2SiO_4 nanostructures, *Ultrasonics Sonochemistry*. 29 (2016) 226–235.
- [18] S. Ni, X. Wang, G. Zhou, F. Yang, J. Wang, D. He, Crystallized $\text{Zn}_3(\text{VO}_4)_2$ Synthesis, characterization and optical property, *J. Alloys Compd.* 491 (2010) 378-381.
- [19] M. Wang, Y. Shi, G. Jiang, Synthesis, characterization and photocatalytic properties of nanobelt-assembled flower-like $\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ microcrystals, *Mater Lett.* 122 (2014) 66-69.
- [20] M. Salavati-Niasari, L. Saleh, F. Mohandes, A. Ghaemi, Sonochemical preparation of pure t-LaVO_4 nanoparticles with the aid of tris(acetylacetonato)lanthanum hydrate as a novel precursor, *Ultrason. Sonochem.* 21 (2014) 653-662.
- [21] Dong, Z. Du, Y. Zhao, D. Zhou, Preparation of surface modified nano- $\text{Mg}(\text{OH})_2$ via precipitation method, *Powder Technol.* 198, (2010), 325.

- [22] J. Liu, Y. Wang, D. Sun, Enhancing the performance of dye-sensitized solar cells by benzoic acid modified TiO₂ nanorod electrode, *J. Renew. Energy*. 38 (2012) 214-218.
- [23] J. Tauc, R. Grigorovici, A. Vancu, Optical Properties and Electronic Structure of Amorphous Germanium, *J. Phys. Status Solidi B*. 15 (1966) 627-637.
- [24] H. Huang, H.F. Chen, Y. Xia, X.Y. Tao, Y.P. Gan, X.X. Weng, W. Zhang, Controllable synthesis and visible-light-responsive photocatalytic activity of Bi₂WO₆ fluffy microsphere with hierarchical architecture, *J Colloid Interface Sci*. 370 (2012) 132-138.
- [25] X.J. Wang, Q.L. Zhang, Q. Wan, G.Z. Dai, C.J. Zhou, B.S. Zou, Controllable ZnO architectures by ethanolamine-assisted hydrothermal reaction for enhanced photocatalytic activity, *J Phys Chem C*. 115 (2011) 2769-2775.
- [26] J. Zhong, J. Li, F. Feng, Y. Lu, J. Zeng, W. Hu, Z. Tang, Improved photocatalytic performance of SiO₂-TiO₂ prepared with the assistance of SDBS, *J. Mol. Catal. A Chem*. 357 (2012) 101-105.

Table. 1. Preparation conditions for the synthesis of $\text{Zn}_3\text{V}_2\text{O}_8$ nanostructures.

Sample No.	Effect	Precursor of Zn	Temperature	Time of reaction (hour)	solvent	surfactant	pH
1	precursor	$\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	25 °C	2	water	SDS	8
2	precursor	$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$	25 °C	2	water	SDS	8
3	precursor	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	25 °C	2	water	SDS	8
4	temperature	$\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	80 °C	2	water	SDS	8
5	time of reaction	$\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	25 °C	18	water	SDS	8
6	solvent	$\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	25 °C	2	Propylene glycol	SDS	8
7	solvent	$\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	25 °C	2	methanol	SDS	8
8	pH	$\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	25 °C	2	water	SDS	11
9	blank	$\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	25 °C	2	water	-	8

Figure Captions:

Fig. 1. XRD patterns of synthesized sample after calcination at 600 °C (Sample No. 6).

Fig. 2. SEM images of $\text{Zn}_3\text{V}_2\text{O}_8$ nanostructures prepared by different precursors (a) $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, (b) $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and (c) $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$.

Fig. 3. SEM images of $\text{Zn}_3\text{V}_2\text{O}_8$ nanostructures prepared at different conditions (a-f) Sample Nos. 4-9, respectively.

Fig. 4. TEM image of $\text{Zn}_3\text{V}_2\text{O}_8$ nanostructures by SDS surfactant (sample No. 6).

Fig. 5. EDS pattern of $\text{Zn}_3\text{V}_2\text{O}_8$ nanoparticles (sample No. 6).

Fig. 6. FT-IR spectrum of $\text{Zn}_3\text{V}_2\text{O}_8$ nanoparticles (sample No. 6).

Fig. 7. (a) UV–Vis diffuse absorption spectra, (b) plot of $(\alpha h\nu)^2$ versus $(h\nu)$ and (c) Room temperature photoluminescence of sample No. 6.

Fig. 8. Photocatalytic degradation of $\text{Zn}_3\text{V}_2\text{O}_8$ nanoparticles under UV irradiations.

Fig. 9. Cyclic Voltammogram of (a) GCE- $\text{Zn}_3\text{V}_2\text{O}_8$ nanostructures and (b) GCE- $\text{Zn}_3\text{V}_2\text{O}_8$ bulk structures.

Scheme. 1. Schematic diagram of formation of nanostructures and effect of SDS surfactant on the particle size and morphology.

Scheme 1.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8. Photocatalytic degradation of $\text{Zn}_3\text{V}_2\text{O}_8$ nanoparticles under UV irradiations.

Fig. 9.