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RESEARCH PAPER

Degradation of Organic Pollutant in Waste Water via $CdMoO_4$ Nanostructures as an Effective Photocatalyst; Ultrasound-assisted Preparation and Characterization

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ABSTRACT

Sphere-like cadmium molybdate ($CdMoO_4$) nanostructures have been synthesized by a large scale and simple sonochemical method by using $Cd(Sal)_2$ (Sal=salicylidene) and $Na_2MoO_4.2H_2O$ for the first time. The effects of sonochemical irradiation time, sonochemical power, temperature, solvent, surfactant and cadmium source were considered to obtain a controlled shape. The as-prepared nanostructured cadmium molybdate was analyzed by UV–Vis diffuse reflectance spectroscopy (DRS), energy dispersive X-ray microanalysis (EDX), Fourier transform infrared (FT-IR) spectroscopy, field emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD). It was established that morphology, particle size and phase composition of the final products could be greatly affected by these parameters. The photocatalytic activity of the synthesized products has been compared for the photo- degradation activity of methylene blue (MB). The distinguished degradation activity of cadmium molybdate photocatalyst can be ascribed to the powerful UV light absorption, excellent charge separation efficiency, nice particle size distribution and proper band gap of the nanostructures.

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INTRODUCTION

Water purification is one of the most significant topics in environmental science [1–7] and synthetic dyes are the major pollutant groups of wastewater [8–11]. Even in low quantities, presence of dyes can occasion critical environmental problems, for instance, growth of aquatic bacteria can be prevented by the interference of influence of sun light in to water by organic dye molecules [8–11]. Hence, much attempt has been made to decline the concentration of organic dyes in the wastewater [8–15]. Utilize of photocatalysts has been evaluated as one of the most promising approaches of eliminating organic compounds from water [16, 20–24].

Dye is an essential chemical utilized in variouse industries such as those involved in generating fabric, food, furniture and paint, representing a significant threat to the environment because of its toxicity and potentially carcinogenic nature [23- 34].

In current years, molybdates are materials that have involved the benefit of many researchers because of their broad potential to industrial application involving optic fiber, humidity sensor, catalysts, scintillation detector, solid-state lasers, photoluminescent devices, microwave applications, and so on. Molybdates are significant luminescent materials with scheelite-type tetragonal structure, membership I41/a space group with two formula units per primitive cell. Every of X atoms (X=Mo) is surrounded by four equivalent O atoms composing the $[XO_4]^2$ tetrahedral configuration and every divalent metal shares corners with eight adjacent O atoms of $[XO_4]^2$ tetrahedrons [35–39].

In this investigation, a novel sonochemical way was offered to prepare $CdMoO_4$ nanostructures.

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Besides, the morphology of $CdMoO_4$ nanostructures can be regulated by adjusting the processing parameters.

The reaction proceeded in an open system at atmospheric pressure. No other additives were used. This approach has obvious benefits like simple experimental set-up, easy handling, short reaction time, environmental friendliness and the procedure is very easy, attracting and novel by focusing large amount of sonochemical in to the solutions to prepare pure products. To the best of our knowledge, no such studies have ever been reported.

MATERIALS AND METHODS

Materials and experiments

All the chemicals used in our experiments were of analytical grade, were purchased from Merck and used as received without further purification. A multiwave ultrasonic generator (sonicator UP400-A; TOP Sonics , Iran), equipped with a converter/transducer and titanium oscillator (horn), 25 mm in diameter, operating at 20kHz with a maximum power output of 400W, was used for the ultrasonic irradiation. The ultrasonic generator was automatically adjusted as needed. The XRD patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni- filtered Cu Kα radiation. SEM images were obtained on Philips XL- 30 ESEM equipped with an energy dispersive X-ray spectroscopy. Fourier transform infrared spectroscopy (FT-IR) was recorded with Shimadzu Varian 4300 spectrophotometer in KBr pellets. EDS analysis was obtained on Philips EM208.

Synthesis of $Cd(Sal)_2$ complex

$[Cd(Sal)_2]$ was prepared as follows: cadmium(II) nitrate $[Cd(NO_3)_2.4H_2O]$, 2mmol, was dissolved in 25 ml distilled water, a solution of salicylaldehyde, 4mmol ,dissolved in the same volume of ethanol was drop wise added to the above solution under magnetic stirring. After addition of all reagents, the mixture was refluxed for about 6h.The precipitate was collected and then washed with ethanol and dried in vacuum oven in 60 ˚C.

Preparation of $CdMoO_4$ nanostructures (Photocatalyst preparation)

$CdMoO_4$ nanostructures were synthesized by simple sonochemical approach. In a typical process, an aqueous solution of Cd(Sal)2 in the presence of various surfactants, such as cetyl tri methyl ammonium bromide (CTAB), sodium dodecyl sulfate (SDS) and poly vinyl pyrrolidone(PVP) was mixed with $Na_2MoO_4.2H_2O$ aqueous solution and the solution under low frequency sonochemical at room temperature for 20 min. The yellow precipitate was centrifuged, washed out with distilled water and methanol for three times and dried under vacuum at 60 ˚C. The effects of surfactant and power source on the morphology and the particle sizes of $CdMoO_4$ nanostructures were considered.

Photocatalytic procedure

The photocatalytic activities of the samples were distinguished by the degradation of aqueous methylene blue (MB) under UV light. About 5 mg of the sample was first inserted to a reactor that contained $5*10^{-6}$ M of aqueous MB. The suspension was transferred in to a self-designed glass reactor, and stirred in darkness to achieve the adsorption equilibrium. In the research of photo- degradation by UV light, a 125W high pressure mercury lamp with a water cooling cylindrical jacket was employed. The concentration of MB was checked on the basis of its UV–visible absorption peak at 664 nm.

RESULTS AND DISCUSSIONS

FT-IR spectroscopy

Fig. 1 reveals FT-IR spectra of $Cd(Sal)_2$ precursor and $CdMoO_4$ nanostructures. Vibrations of $CdMoO_4$ are categorized in to the internal and external modes [40]. The first belongs to the vibration inside $[MoO_4]^{2-}$ units. Their centers of masses are stationary. The second is called lattice phonon mode which corresponds to the motion of Cd^{2+} cations and the rigid molecular units [20–22]. In the case [Cd(Sal)2] (Fig. 1a), the peaks at 1520 and 1635cm^{-1} belong to the C-O stretching vibrations ($\upsilon_{C\text{-}O}$) and the peak at 1430cm^{-1} belongs to C-C stretching vibrations (υ_{C-C}) of the salicylaldehyde. Free salicylaldehyde $\upsilon_{C\text{-}O}$ appears at 1685 and 1665cm^{-1}, and υ_{C-C} appears at 1495 and 1385cm^{-1}. Upon complex formation, these stretching vibrations shifted to lower regions. Fig. 1b exhibits FT-IR spectra of $CdMoO_4$ nanostructures acquired in methanol as solvent and CTAB as surfactant. The spectra indicate a band of Mo-O stretching vibration in MoO_4^{2-} tetrahedrons [18] at 795–930cm^{-1}. It is one of the internal modes illustrate as anti-symmetric stretching vibrations [18] of the three products. Weak Mo-O bending vibrations

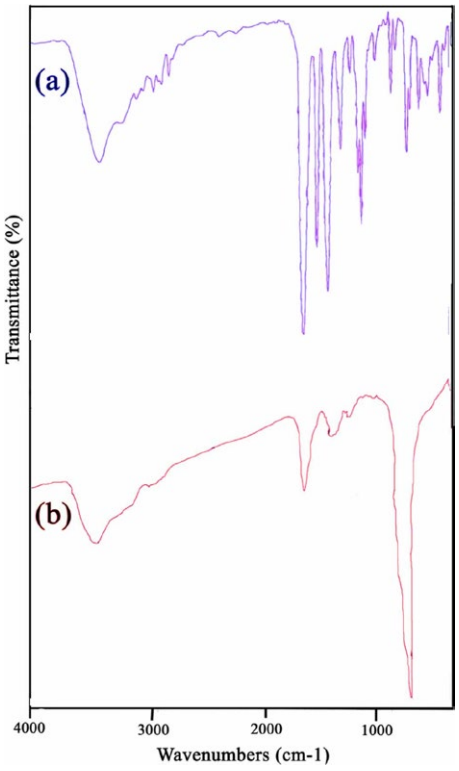

Fig. 1. FT-IR spectra of: (a) $Cd(Sal)_2$, (b) $CdMoO_4$ nanostructures

[41] were also discerned at about 405 cm^{-1} for $CdMoO_4$ nanostructures. The broad absorption band nearby 3330cm^{-1} in Fig. 1b is assigned to the stretching vibrations of absorption water. Absorption peaks at 460–945 cm^{-1} are because of Cd–O band, there are no absorption bands nearby this range in salicylaldehyde.

X-ray diffraction patterns

The crystal structure and the composition of the as-prepared products were exhibited by XRD. The XRD patterns of the cadmium molybdates has been presented in Fig. 2. All peaks in Fig. 2, correspond to the reflections of octahedral phase of $CdMoO_4$ which are in a good accord with the reported data (JCPDS: 85-0888). No considerable diffractions of other phases can be found in the figure, exhibiting that a pure $CdMoO_4$ phase has been formed.

EDX analysis

EDX analysis measurement was applied to investigate the chemical composition and purity of as-synthesized $CdMoO_4$ nanostructures. The EDX pattern of $CdMoO_4$ in Fig. 3 exhibits that the

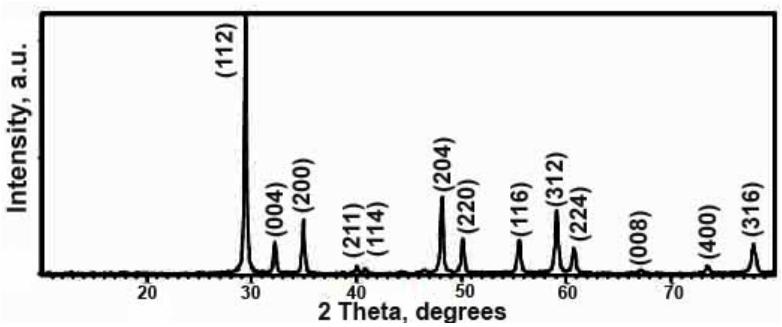

Fig. 2. XRD patterns of $CdMoO_4$ nanostructures

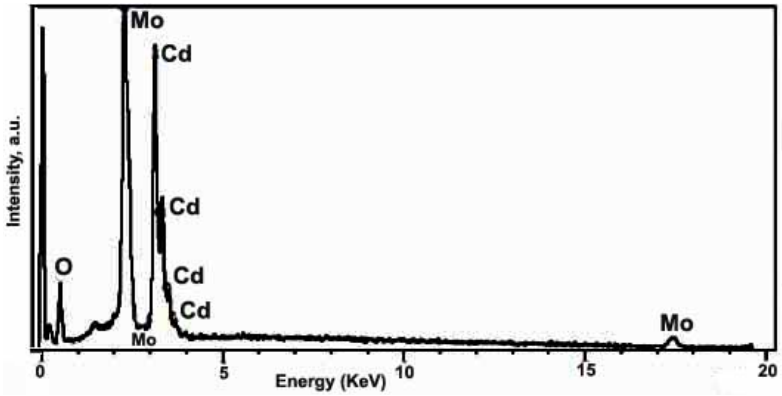

Fig. 3. EDX pattern of $CdMoO_4$ nanostructures

only elements which existed were Cd, Mo, and O. No peak of any impurity was detected, indicating the high purity of the product.

Optical properties

Fig. 4 reveals the $(\alpha h\upsilon)^2$ vs $h\upsilon$ curve of $CdMoO_4$ nanostructures which were estimated by their UV–visible absorbance utilizing the equation designed by Wood and Tauc revealed Eq. (1) [42] below.

$$\alpha h\upsilon=(h\upsilon-E_g)^n \quad (1)$$

where α is the absorbance, h the Planck constant, υ the photon frequency, E_g the energy gap, and n is the pure numbers associated with the various types of electronic transitions. For n=1/2, 2, 3/2 and 3, the transitions are directly allowed, indirectly allowed, directly forbidden, and indirectly forbidden, respectively. Each energy gap was specified by extrapolation of each linear portion of the curves to α=0. In the current consideration, the $CdMoO_4$ offers directly allowed electronic transition (n=1/2) [42], and the energy gaps of $CdMoO_4$ nanostructures is 3.8 eV.

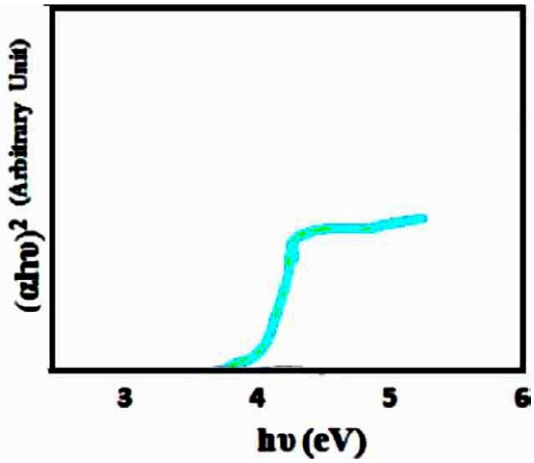

Fig. 4. The $(\alpha h\upsilon)^2$ vs $h\upsilon$ plot of $CdMoO_4$ nanostructures.

Photocatalytic decolorization of MB dye

The photocatalytic activity of the $CdMoO_4$ nanostructures was evaluated by monitoring the degradation of methylene blue (MB) in an aqueous solution, under irradiation with UV light (Fig. 5). Without light or nanostructures, nearly no MB was breakdown after 60min, revealing that the contribution of self-degradation was negligible. However, $CdMoO_4$ nanostructures exhibited high photocatalytic activity. The heterogeneous photocatalytic processes including many steps, such as diffusion, adsorption and reaction, convenient distribution of the pore is beneficial to diffusion of reactants and products, which prefer the photocatalytic reaction. In this paper, the improved photocatalytic activity may be ascribed to convenient sharing of the pore, high hydroxyl content and high separation rate of photo induced charge carriers [43].

SEM images

The morphology of the samples was considered by SEM images. Fig. 6 exhibits SEM images of the samples prepared at 30 °C, for 15 min with different surfactant via sonochemical approach. SEM images of the samples attained in the presence of CTAB, PVP and SDS have been illustrated in Fig. 6a, b, and c, respectively. The SEM images which revealed sphere-like nanostructures were organized in the presence of the surfactants. In the presence of PVP as surfactants, more regular sphere-like nanostructures were organized.

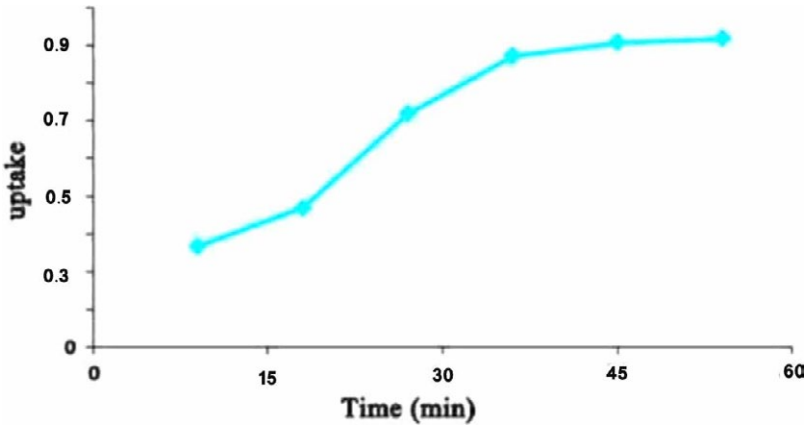

Fig. 5. Decolorization of MB dye of $CdMoO_4$ nanostructures.

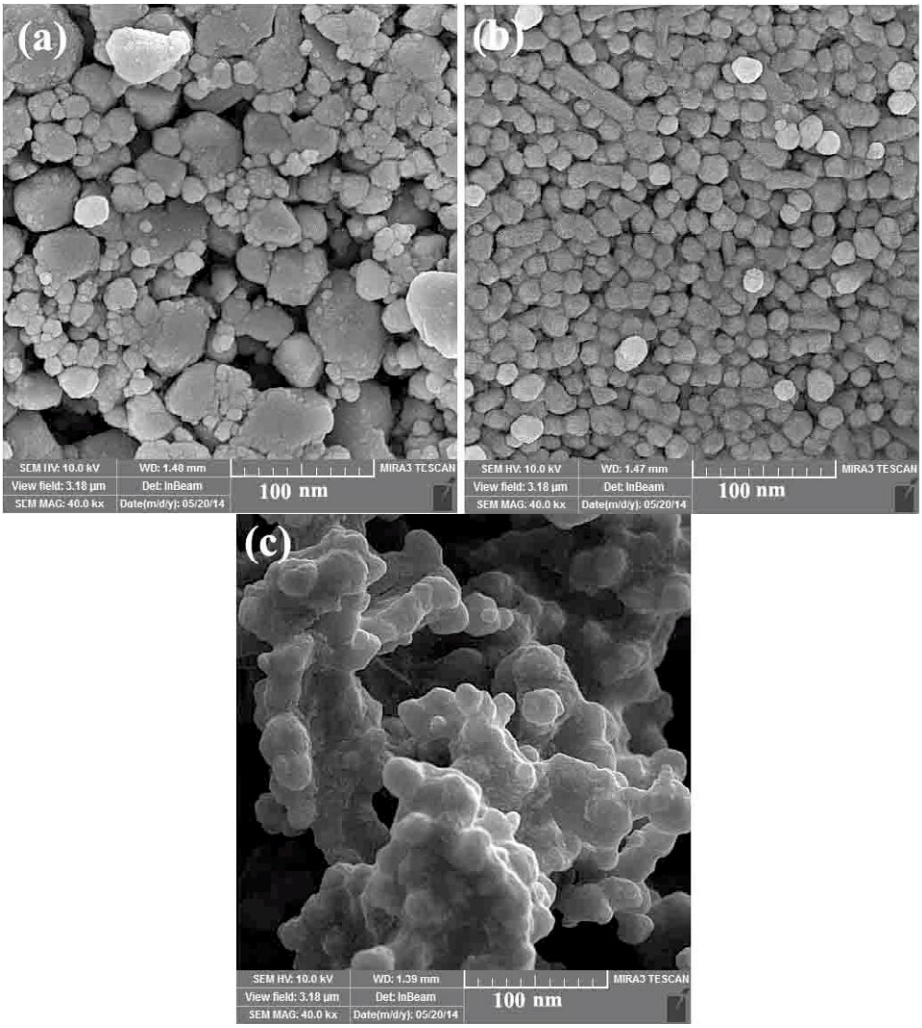

Fig. 6. SEM images of $CdMoO_4$ nanostructures gained from $Cd(Sal)_2$ and $Na_2MoO_4.2H_2O$ via sonochemical approach with different surfactants:(a) CTAB (b) PVP and (c) SDS in 400W and 20 min.

To investigate the effect of sonication power on the morphology of the products, the reaction was carried out in the presence of three different powers in water, 30 ˚C and 20 min SEM images of the samples were attained in the power of 200, 300 and 400W have been exhibited in Fig. 7a, b, and c, respectively. The SEM images displayed sphere-like nanostructures were formed in the three different powers without presence of any surfactant. In the power of 400W, sphere-like nanostructure sizes were increased.

CONCLUSIONS

In brief, sphere-like cadmium molybdate nanostructures have been successfully prepared from $Cd(Sal)_2$ and $Na_2MoO_4.2H_2O$ utilizing a sonochemical approach, under low temperature and pressure. By regulating the surfactant and power source, we could gain cadmium molybdate nanostructures morphology. To the best of our knowledge, it is the first time that $Cd(Sal)_2$ is utilized as Cd source for the synthesis of cadmium molybdate nanostructures by sonochemical process. The prepared cadmium molybdate nanostructures can be used in some analytical applications such as removal of methylene blue dye, since the % uptake was found to be >90% within 60 min.

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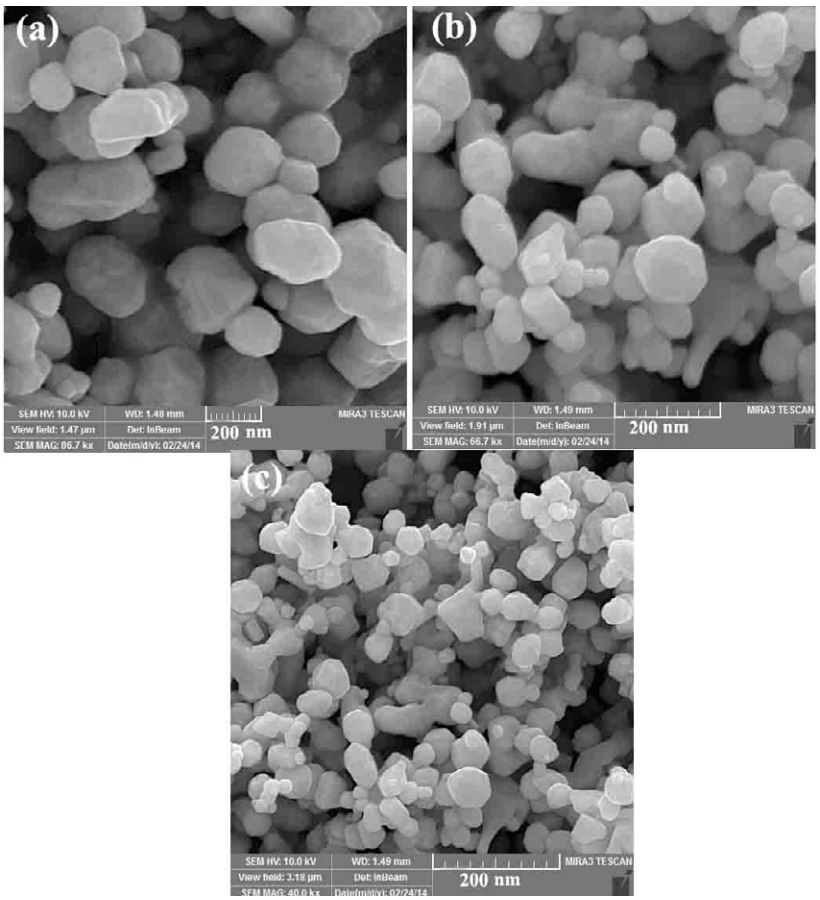

Fig. 7. SEM images of sphere-like $CdMoO_4$ nanostructures gained from $Cd(Sal)_2$ and $Na_2MoO_4.2H_2O$ in water via sonochemical approach in:(a) 200 ,(b) 300 and (c) 400 W in 20 min.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

REFERENCES

1. Seo HO, Sim CW, Kim K-D, Kim YD, Lim DC. Nanoporous TiO2/SiO2 prepared by atomic layer deposition as adsorbents of methylene blue in aqueous solutions. Chemical Engineering Journal. 2012;183:381-6.
2. Sreeprasad TS, Maliyekkal SM, Lisha KP, Pradeep T. Reduced graphene oxide–metal/metal oxide composites: Facile synthesis and application in water purification. Journal of Hazardous Materials. 2011;186(1):921-31.
[3] Zhao D., Jaroniec M., Hsiao B.S., Editorial for themed issue on advanced materials in water treatments, J. Mater. Chem. 2010; 20: 4476–4477.
4. Ma H, Burger C, Hsiao BS, Chu B. Ultra-fine cellulose nanofibers: new nano-scale materials for water purification. Journal of Materials Chemistry. 2011;21(21):7507.
5. Pan JH, Dou H, Xiong Z, Xu C, Ma J, Zhao XS. Porous photocatalysts for advanced water purifications. Journal of Materials Chemistry. 2010;20(22):4512.
6. Dey NK, Kim MJ, Kim K-D, Seo HO, Kim D, Kim YD, et al. Adsorption and photocatalytic degradation of methylene blue over TiO2 films on carbon fiber prepared by atomic layer deposition. Journal of Molecular Catalysis A: Chemical. 2011;337(1-2):33-8.
7. Ding Z, Hu X, Lu GQ, Yue P-L, Greenfield PF. Novel Silica Gel Supported TiO2Photocatalyst Synthesized by CVD Method. Langmuir. 2000;16(15):6216-22.
8. Dutta S, Parsons SA, Bhattacharjee C, Jarvis P, Datta S, Bandyopadhyay S. Kinetic study of adsorption and photo-decolorization of Reactive Red 198 on TiO2 surface. Chemical Engineering Journal. 2009;155(3):674-9.
9. Robinson T, Chandran B, Nigam P. Removal of dyes from an artificial textile dye effluent by two agricultural waste residues, corncob and barley husk. Environment International. 2002;28(1-2):29-33.
10. Özer A, Dursun G. Removal of methylene blue from aqueous solution by dehydrated wheat bran carbon. Journal of Hazardous Materials. 2007;146(1-2):262-9.
11. Özer D, Dursun G, Özer A. Methylene blue adsorption from aqueous solution by dehydrated peanut hull. Journal of Hazardous Materials. 2007;144(1-2):171-9.
12. Han F, Kambala VSR, Srinivasan M, Rajarathnam D, Naidu R. Tailored titanium dioxide photocatalysts for the degradation of organic dyes in wastewater treatment: A review. Applied Catalysis A: General. 2009;359(1-2):25-40.

13. Xiong Z, Ma J, Ng WJ, Waite TD, Zhao XS. Silver-modified mesoporous TiO2 photocatalyst for water purification. Water Research. 2011;45(5):2095-103.
14. Yang D, Fan T, Zhou H, Ding J, Zhang D. Biogenic Hierarchical TiO2/SiO2 Derived from Rice Husk and Enhanced Photocatalytic Properties for Dye Degradation. PLoS ONE. 2011;6(9):e24788.
15. Fan T-X, Chow S-K, Zhang D. Biomorphic mineralization: From biology to materials. Progress in Materials Science. 2009;54(5):542-659.
16. Pupp C, Yamdagni R, Porter RF. Mass spectrometric study of the evaporation of BaMoO4 and BaWO4. Journal of Inorganic and Nuclear Chemistry. 1969;31(7):2021-9.
[17] Sun Y., Ma J., Fang J., Gao C., Liu Z., Effect of MgO/CaO ratio on the micro structure of cordierite-based glass-ceramic glazes for floor tiles, Ceram. Int. 2011; 31: 683–686.
18. de Azevedo Marques AP, de Melo DMA, Paskocimas CA, Pizani PS, Joya MR, Leite ER, et al. Photoluminescent BaMoO4 nanopowders prepared by complex polymerization method (CPM). Journal of Solid State Chemistry. 2006;179(3):671-8.
19. Zhang C, Shen E, Wang E, Kang Z, Gao L, Hu C, et al. One-step solvothermal synthesis of high ordered BaWO4 and BaMoO4 nanostructures. Materials Chemistry and Physics. 2006;96(2-3):240-3.
20. Afanasiev P. Molten salt synthesis of barium molybdate and tungstate microcrystals. Materials Letters. 2007;61(23-24):4622-6.
21. Ryu JH, Yoon J-W, Lim CS, Shim KB. Microwave-assisted synthesis of barium molybdate by a citrate complex method and oriented aggregation. Materials Research Bulletin. 2005;40(9):1468-76.
22. Shahri Z, Bazarganipour M, Salavati-Niasari M. Controllable synthesis of novel zinc molybdate rod-like nanostructures via simple surfactant-free precipitation route. Superlattices and Microstructures. 2013;63:258-66.
[23] Stylidi M., Kondarides D.I., Verykios X.E., Pathways of solar light-induced photocatalytic degradation of azo dyes in aqueous TiO_2 suspensions, Appl. Catal. B, 2003; 40: 271–286.
24. Zhong Jb, Li Jz, Feng Fm, Lu Y, Zeng J, Hu W, et al. Improved photocatalytic performance of SiO2–TiO2 prepared with the assistance of SDBS. Journal of Molecular Catalysis A: Chemical. 2012;357:101-5.
25. Gholami T, Salavati-Niasari M, Bazarganipour M, Noori E. Synthesis and characterization of spherical silica nanoparticles by modified Stöber process assisted by organic ligand. Superlattices and Microstructures. 2013;61:33-41.
26. Salavati-Niasari M, Shoshtari-Yeganeh B, Bazarganipour M. Facile synthesis of rod-shape nanostructures lead selenide via hydrothermal process. Superlattices and Microstructures. 2013;58:20-30.
27. Noori E, Bazarganipour M, Salavati-Niasari M, Gholami T. Synthesis and Characterization of Silica Nanostructures in the Presence of Schiff-Base Ligand Via Simple Sonochemical Method. Journal of Cluster Science. 2013;24(4):1171-80.
28. Goudarzi M, Bazarganipour M, Salavati-Niasari M. Synthesis, characterization and degradation of organic dye over Co3O4nanoparticles prepared from new binuclear complex precursors. RSC Adv. 2014;4(87):46517-20.
29. Mandizadeh S, Bazarganipour M, Salavati-Niasari M. A low-cost and eco-friendly viable approach for green synthesis of barium haxaferrite nanostructures using palm oil. Ceramics International. 2014;40(10):15685-91.
30. Ghaed-Amini M, Bazarganipour M, Salavati-Niasari M. Calcium molybdate octahedral nanostructures, hierarchical self-assemblies controllable synthesis by coprecipitation method: Characterization and optical properties. Journal of Industrial and Engineering Chemistry. 2015;21:1089-97.
31. Gholamrezaei S, Salavati-Niasari M, Bazarganipour M, Panahi-Kalamuei M, Bagheri S. Novel precursors for synthesis of dendrite-like PbTe nanostructures and investigation of photoluminescence behavior. Advanced Powder Technology. 2014;25(5):1585-92.
[32] Nabiyouni G., Ghanbari D., Ghasemi J., Yousofnejad A., Microwave-assisted Synthesis of MgFe2O4-ZnO Nanocomposite and Its Photo-catalyst Investigation in Methyl Orange Degradation, J Nanostruct. 2015; 5: 289-295.
[33] Nabiyouni G., Ghanbari D., Karimzadeh S., Samani Ghalehtaki B., Sono-chemical Synthesis Fe3O4-Mg(OH)2 Nanocomposite and Its Photo-catalyst Investigation in Methyl Orange Degradation, J Nanostruct. 2014; 4: 467-474.
[34] Soofivand F., Sabet M., Seyghalkar H., Salavati-Niasari M., Using the $[Co(oct)_2]$ as a New Precursor for Simple Synthesis of CoS_2 Nanoparticles and Kinetics Studies on Photocatalytic Activities Under UV Irradiation, J Nanostruct. 2018; 8: 75-81.
35. Phuruangrat A, Thongtem T, Thongtem S. Cyclic microwave-assisted synthesis and characterization of nano-crystalline alkaline earth metal tungstates. Journal of the Ceramic Society of Japan. 2008;116(1353):605-9.
36. Cavalcante LS, Sczancoski JC, Tranquilin RL, Joya MR, Pizani PS, Varela JA, et al. BaMoO4 powders processed in domestic microwave-hydrothermal: Synthesis, characterization and photoluminescence at room temperature. Journal of Physics and Chemistry of Solids. 2008;69(11):2674-80.
37. Cavalcante LS, Sczancoski JC, Espinosa JWM, Varela JA, Pizani PS, Longo E. Photoluminescent behavior of BaWO4 powders processed in microwave-hydrothermal. Journal of Alloys and Compounds. 2009;474(1-2):195-200.
38. Cavalcante LS, Sczancoski JC, Lima LF, Espinosa JWM, Pizani PS, Varela JA, et al. Synthesis, Characterization, Anisotropic Growth and Photoluminescence of BaWO4. Crystal Growth & Design. 2009;9(2):1002-12.
39. Sczancoski JC, Cavalcante LS, Joya MR, Varela JA, Pizani PS, Longo E. SrMoO4 powders processed in microwave-hydrothermal: Synthesis, characterization and optical properties. Chemical Engineering Journal. 2008;140(1-3):632-7.
40. Basiev TT, Sobol AA, Voronko YK, Zverev PG. Spontaneous Raman spectroscopy of tungstate and molybdate crystals for Raman lasers. Optical Materials. 2000;15(3):205-16.
[41] Thongtema T., Phuruangrat A., Thongtem S., Sonochemical synthesis of $MMoO_4$ (M=Ca, Sr and Ba) nanocrystals, J. Ceram. Process. Res. 2008; 9: 189–191.
42. Thongtem T, Kungwankunakorn S, Kuntalue B, Phuruangrat A, Thongtem S. Luminescence and absorbance of highly crystalline CaMoO4, SrMoO4, CaWO4 and SrWO4 nanoparticles synthesized by co-precipitation method at room temperature. Journal of Alloys and Compounds. 2010;506(1):475-81.
43. Zhong Jb, Li Jz, Feng Fm, Lu Y, Zeng J, Hu W, et al. Improved photocatalytic performance of SiO2–TiO2 prepared with the assistance of SDBS. Journal of Molecular Catalysis A: Chemical. 2012;357:101-5.