IOP Conference Series: Materials Science and Engineering

PAPER • OPEN ACCESS

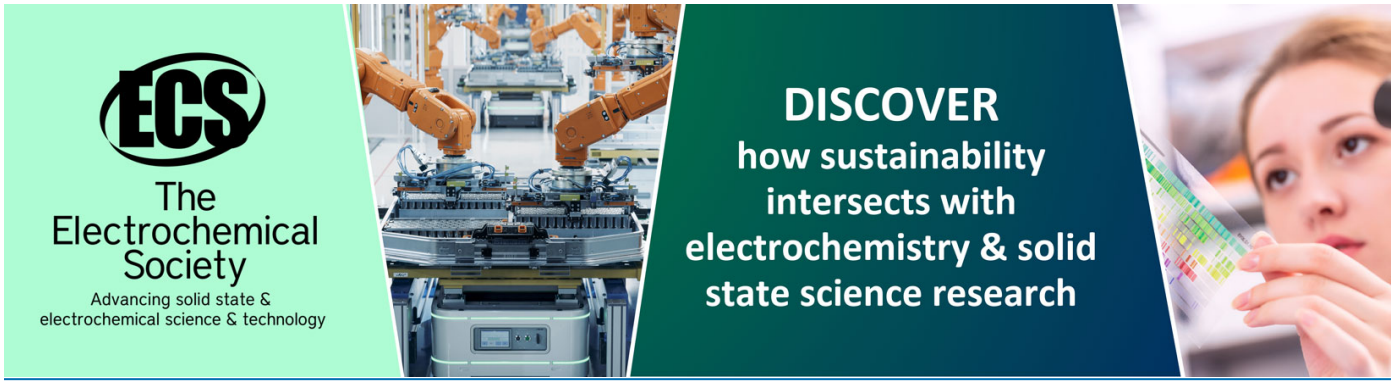
Preparation of $ErMnO_3$ by Sol-gel Method and its Photocatalytic Activity for Removal of Methyl Orange from Water

To cite this article: X Y Xie *et al* 2018 *IOP Conf. Ser.: Mater. Sci. Eng.* **362** 012021

View the article online for updates and enhancements.

You may also like

- Assessing the effect of calcination on adsorption capability of Mg/Al layer double hydroxides (LDHs)
Bayu Wiyantoko, Puji Kurniawati, Tri Esti Purbaningtias et al.
- Green synthesis of vanadium oxide-zirconium oxide nanocomposite for the degradation of methyl orange and picloram
Parsa Rasheed, Sirajul Haq, Muhammad Waseem et al.
- Implications of Reaction Mechanism and Kinetics on the Synthesis of Stoichiometric $LiNiO_2$
Chun-Chieh Chang, Jin Yong Kim and Prashant N. Kumta



This content was downloaded from IP address 3.18.104.220 on 21/05/2024 at 02:58

IOP Conf. Series: Materials Science and Engineering **362** (2018) 012021 doi:10.1088/1757-899X/362/1/012021

Preparation of $ErMnO_3$ by Sol-gel Method and its Photocatalytic Activity for Removal of Methyl Orange from Water

X Y Xie, J N Yang, L L Yu, J Y Min, D D Sun, P S Tang and H F Chen

Department of Materials Engineering, Huzhou University, Huzhou 313000, China
E-mail: tangps@163.com, headder@zjhu.edu.cn

Abstract. The single phase perovskite $ErMnO_3$ was synthesized using $Er(NO_3)_3$, manganese acetate, citric acid and urea by a facile sol-gel method. The gel of $ErMnO_3$ precursor was kept for 36 hours in 100 ℃ oven to get the xerogel. Then, the xerogel was calcined at 800 ℃ for 12 hours in muffle furnace to prepare single phase $ErMnO_3$. The prepared sample was characterized by thermogravimetry differential scanning calorimetry (TG-DSC), X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). Under ultraviolet light, the photocatalytic activity of $ErMnO_3$ was studied with methyl orange of 20 mg/L as the simulated sewage. The results show that the $ErMnO_3$ sample particle size distribution is relatively uniform, the average grain size is mainly around 100 nm. The photocatalytic experiment demonstrates that $ErMnO_3$ is highly photocatalytic activity for removal of methyl orange from water. When methyl orange of 20 mg/L is degraded for 120 min in the presence of $ErMnO_3$, the degradation rate of methyl orange can reach about 95%. The degradation of methyl orange accords with first order kinetic model in presence $ErMnO_3$ sample, and the apparent rate constant is 0.022 min^{-1}.

1. Introduction

As a new type of semiconductor material, the application of perovskite rare-earth manganate $ErMnO_3$ in photocatalytic degradation of sewage has not been reported [1-2]. At present, the methods of prepared $ErMnO_3$ are mainly hydrothermal method [3] and solid state reaction method [4-5] and so on. The sol-gel has the advantages which chemical reaction is easily controlled, with high purity, small granularity and good uniformity of powders [6-8]. In addition, the preparation of perovskite $ErMnO_3$ by sol-gel method has never been reported. Therefore, it is of great significance to prepare $ErMnO_3$ by sol-gel method and to investigate its photocatalytic activity for removal of methyl orange from sewage [9-10].

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

In this paper, using erbium nitrate, manganese acetate, citric acid and urea as the main raw materials, $ErMnO_3$ was prepared by a facile sol-gel method. The morphology and structure of prepared $ErMnO_3$ were characterized by TG-DSC, XRD, FT-IR and SEM. Under ultraviolet light conditions, the photocatalytic activity of $ErMnO_3$ was evaluated using methyl orange as simulated sewage.

2. Experimental details

2.1 Preparation of $ErMnO_3$

$Er(NO_3)_3$ $5H_2O$, manganese acetate, citric acid and urea were purchased from Aladdin reagent company. All reagents were analytical grade without further purification. In a typical process, at room temperature, the $Er(NO_3)_3$ $5H_2O$ of 0.01 mol, citric acid of 0.01 mol and manganese acetate of 0.01 mol were successively dissolved into the 80 mL deionized water to get the solution under magnetic stirring, and then urea of 0.005 mol was added to the solution. After stirred for 1h at room temperature, the resulted solution was kept for 36 hours in 100 ℃ oven to get the xerogel. Then the xerogel was calcined at 800 ℃ for 12 hours in muffle furnace to prepare $ErMnO_3$ sample.

2.2 Characterization methods

$ErMnO_3$ sample was measured by the American TA-SDTQ600 thermal analyzer. The temperature range of the TG-DSC is from 30 ℃ to 1100 ℃, and the heating rate is 10 ℃/min. Phase composition of sample was performed with a XD-6 X-ray diffraction (Beijing Purkinje General Instrument Co. Ltd.) using Cu Kα radiation (λ=0.15406 nm) operated at 36 kV and 20 mA. The surface adsorbents of $ErMnO_3$ sample were analyzed by Nicolet 5700 Fourier transform infrared spectroscopy of the US Thermo Corporation, using the KBr pressing plate method, and the scanning wave number range was 4000-400 cm^{-1}. The morphology of $ErMnO_3$ sample was observed by Hitachi S-3400N scanning electron microscope of Hitachi Company with an accelerating voltage of 15 kV.

2.3 Photocatalytic activity testing.

The photocatalytic experiment was carried out in a self-assembled apparatus which included a light source of 150 W high-pressure mercury lamp. Typically, 20 mg $ErMnO_3$ powder was added to a 10 mL methyl orange aqueous solution (20 mg/L). Then, the solution was held for 10 min in the darkness to obtain the adsorption–desorption equilibrium, followed by the UV-light irradiation. After a set irradiation time, the suspension was centrifuged. The supernatant was subjected to the UV–visible absorption measurement. Finally, the concentration of the residual MO was evaluated by the absorbance at 464 nm, then finding its degradation rate by standard curve method.

3. Results and discussion

Figure.1 shows TG-DSC curve of the dried gel powders by sol-gel. There is a small endothermic peak appearing on the DSC curve at about 56 ℃, and the TG curve has a weight loss of 1.9% from room temperature to 150 ℃, which is the desorption of adsorbed water to absorb heat. A large exothermic peak appeared at about 350℃, and there is a weight loss of 5.2% from 150 ℃ to 500 ℃, which is the result of combustion of residual organics such as citric acid adsorbed on the surface. There is a weight loss of 2.3% from 500 ℃ to 900 ℃, the homologous DSC curve appeares a small exothermic peak at 790 ℃, probably owing to the exothermic process of chemical reaction. According to the TG-DSC curve, the precursor products of $ErMnO_3$ was calcined at 800 ℃ to prepare pure $ErMnO_3$ samples.

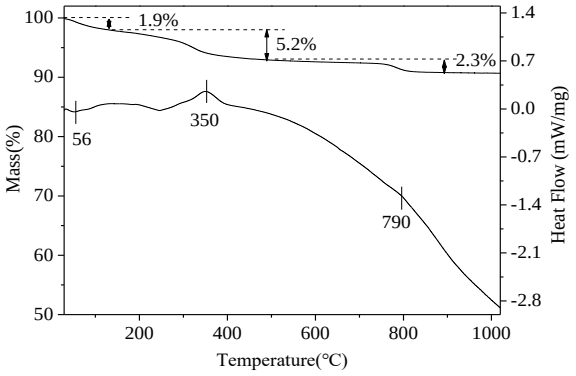


Figure.1 TG-DSC curves of the dried gel powders.

Figure.2 shows XRD pattern of the as-prepared $ErMnO_3$ sample. All peaks can be indexed to the characteristic XRD peaks of the $ErMnO_3$ according to the standard perovskite $ErMnO_3$ (PDF#14-0689) and there are no additional peaks observed, which indicates the successful synthesis of monophasic $ErMnO_3$ without external impurities.

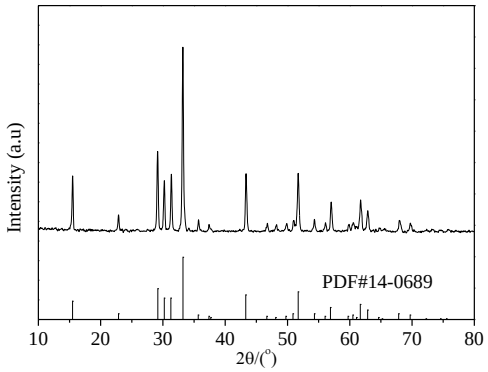


Figure.2 XRD pattern of the as-prepared $ErMnO_3$ sample.

Figure.3 is FT-IR spectrum of the as-prepared $ErMnO_3$ sample. From figure.3, there are mainly six peaks for $ErMnO_3$ sample, which are 3415 cm^{-1}, 2380 cm^{-1}, 1375 cm^{-1}, 1140 cm^{-1}, 900 cm^{-1}, 530 cm^{-1} respectively. The peaks of 1375 cm^{-1} and 3415 cm^{-1} are the -OH stretching vibration peak of sample surface absorbing water molecules. The peak around 2380 cm^{-1} is Er=O stretching vibration peak for $ErMnO_3$. The peak around 1140 cm^{-1} is Er=O torsional vibration peak for $ErMnO_3$. The peaks of 530 cm^{-1} and 900 cm^{-1} should be the vibration peak of Mn-O for $ErMnO_3$.

Figure.4 shows SEM image of the as-prepared $ErMnO_3$ sample. From figure.4, SEM image shows that the average grain size of $ErMnO_3$ sample is mainly about 100nm, the particle size distribution is relatively uniform, and there are also large particles of agglomeration. The average grain size of $ErMnO_3$ is about 100nm which has established a great foundation for the excellent photocatalytic activity of $ErMnO_3$.

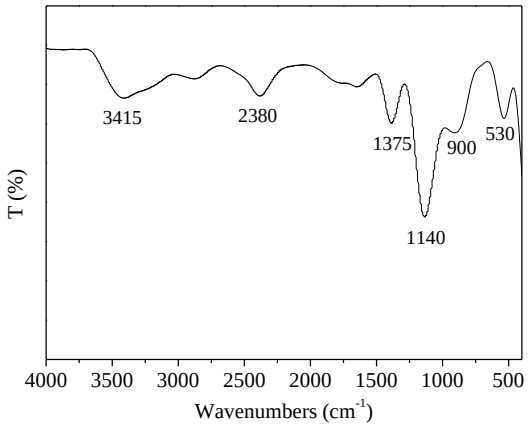


Figure.3 FT-IR spectrum of the as-prepared $ErMnO_3$ sample.

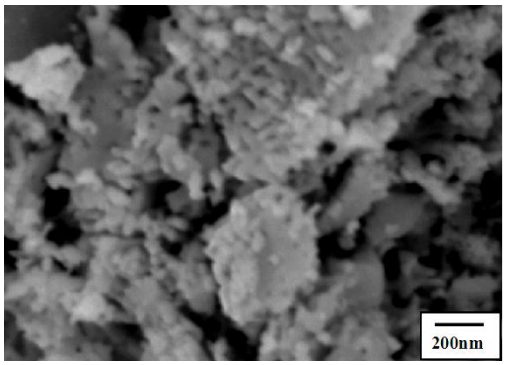


Figure.4 SEM image of the as-prepared $ErMnO_3$ Sample.

Figure.5 shows that photocatalytic degradation rate of methyl orange in the presence of $ErMnO_3$. From figure.5, when the illumination time was less than 60 min, the degradation rate of methyl orange increased rapidly along with the increase of illumination time. When the illumination time was more than 60 min, the degradation rate of methyl orange increased slowly along with the increase of illumination time. When the illumination time was equal to 120 min, the degradation rate of methyl orange has reached about 95%. This indicates that $ErMnO_3$ showed excellent photocatalytic activity for removal of methyl orange from simulated sewage under ultraviolet light conditions.

Figure.6 shows the kinetic curve of methyl orange degradation in presence of $ErMnO_3$. From figure.6, the degradation of methyl orange in presence $ErMnO_3$ sample was basically consistent with the first order kinetics, and its apparent rate constant is 0.022 min^{-1}.

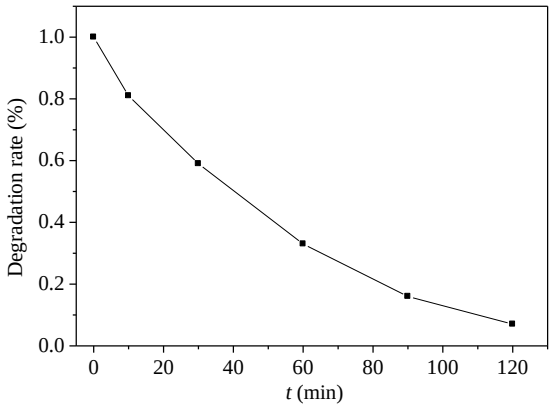


Figure.5 Photocatalytic degradation rate of methyl orange in the presence of $ErMnO_3$.

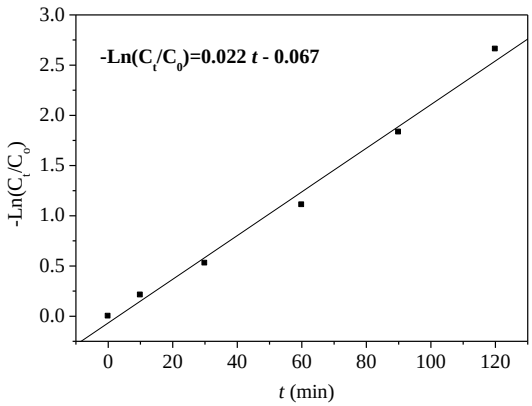


Figure.6 The kinetic curve of methyl orange degradation in presence of $ErMnO_3$.

4. Conclusions

The perovskite type $ErMnO_3$ sample was successfully prepared after calcination at 800 ℃ by sol-gel method using $Er(NO_3)_3$, manganese acetate, citric acid and urea as starting materials. XRD and SEM demonstrate synthesis of $ErMnO_3$ and an average grain size of 100 nm. $ErMnO_3$ shows excellent photocatalytic degradation activity for the simulated sewage methyl orange under ultraviolet light conditions. The degradation of methyl orange is basically consistent with first order kinetic model in presence $ErMnO_3$ sample, and its apparent rate constant is 0.022 min^{-1}. Therefore, $ErMnO_3$ is a kind of photocatalyst with foreground in sewage treatment.

Acknowledgements

The authors acknowledge the financial supports from National Training Programs of Innovation and Entrepreneurship for Undergraduates (No.201710347013) and General Project of Zhejiang Provincial Department of Education (Y201737320).

References

[1] Negi P, Dixit G, Agrawal H M and Srivastava R C. 2013 Structural, optical and magnetic properties of multiferroic $GdMnO_3$ nanoparticles. *Journal of Superconductivity & Novel Magnetism* **26** 1611-15.

[2] Standard E C, Stanislavchuk T, Sirenko A A, Lee N and Cheong S W. 2012 Magnons and crystal-field transitions in hexagonal $RMnO_3$ (R=Er, Tm, Yb, Lu) single crystals. *Physical Review B* **85** 2207-11.

[3] Lin-lin. 2010 Hexagonal and orthorhombic perovskite phases of $ErMnO_3$ and $TmMnO_3$ from hydrothermal systems. *Chemical Research in Chinese Universities* **26** 707-11.

[4] M Chandra Sekhar, K Padmavathi, J G Park and P Venugopal Reddy. 2003 Elastic behavior of $YMnO_3$ and $ErMnO_3$ manganites. *Modern Physics Letters B*. **17** 1119-25.

[5] Liu P, Cheng Z X, Du Y and Wang X L. 2010 Enhanced magnetic moment in $ErMnO_3$ by copper doping and negative magnetocapacitance effect. *Journal of Physics D: Applied Physics* **43** 325002-7.

[6] Romaguerabarcelay Y, Moreira J A, Almeida A, Tavares P B and Pérez D L C J. 2013 Structural, electrical and magnetic properties of magnetoelectric $GdMnO_3$ thin films prepared by sol-gel method. *Thin Solid Films* **564** 419-25.

[7] Kim Y T, Kim E S, Chae J H and Ryu J H. 2002 Ferroelectric properties of $ErMnO_3$ thin film prepared by sol-gel method. *Journal of the Korean Ceramic Society* **39** 829-34.

[8] Yan C H, Huang Y H, Wang Z M, Zhu T, Liao C S and Cheng F X. 2000 Microstructure and transport properties of sol-gel fabricated $La_{0.7}Sr_{0.3}MnO_3$ nanocrystalline films on Si(100) substrates. *Thin Solid Films* **366** 302-5.

[9] Tang P, Tong Y, Chen H, Cao F and Pan G. 2013 Microwave-assisted synthesis of nanoparticulate perovskite $LaFeO_3$ as a high active visible-light photocatalyst. *Current Applied Physics* **13** 340-43.

[10] Tang P, Hu Y, Lin T, Jiang Z and Tang C. 2014 Preparation of nanocrystalline $GdFeO_3$ by microwave method and its visible-light photocatalytic activity. *Integrated Ferroelectrics* **153** 73-8.