

Nanofiber Template-Induced Preparation of ZnO Nanocrystal and its Application in Photocatalysis

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Research Article

Keywords: ZnO Nanocrystal, Electrospinning, Nanofiber mat, Photocatalysis, Rhodamine B

Posted Date: July 20th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-691426/v1>

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Abstract

Traditional preparation of ZnO nanocrystal requires heating zinc acetate to a temperature over 350°C, whereas in this work, zinc acetate was first electrospun with PVDF to form a nanofiber, followed by thermal treatment at only 140°C to give nanocrystalline ZnO. The much lower temperature required in thermal treatment is attributed to the high reactivity of zinc acetate at nano dimension. The as-prepared ZnO-doped PVDF nanofiber mat shows excellent effect in the photocatalytic degradation of Rhodamine B, comparable to ZnO particle thermally treated at 600°C. Highly-oriented ZnO nanorods were obtained by further hydrothermal synthesis of the electrospun nanofiber mat, giving nanostructured ZnO of different morphologies well-aligned on the surface of organic nanofiber. Notably, the hydrothermal synthesis of the successful preparation of these nanostructured ZnO requires a processing temperature below 100°C at atmospheric pressure, showing great potential to be scaled up for vast manufacturing.

1. Introduction

Nanostructured materials possess unique properties because their constituent units are at a dimension comparable to the size of molecules. Nanofibers are flexible materials that are bendable and knotable, making them perfect candidates for wearable devices. Compared to pristine ZnO particle, the organic nanofiber composites loaded with nano ZnO are of great importance, with excellent optical, electrical, mechanical and chemical properties, enabling many potential applications in optoelectronic devices¹⁻³, sensors⁴, photocatalysts⁵⁻⁸, etc.

There are a few ways for the preparation of ZnO nanomaterials, such as gas-phase synthesis⁹⁻¹², solid-phase¹³ based synthesis and liquid-phase synthesis. Although these syntheses have succeeded in the preparation of nano ZnO with various morphologies, costly equipment with strict synthesis conditions, such as high temperature and high pressure, are often required. Moreover, obtaining organic nanofiber materials loaded with highly oriented ZnO is also challenging with these synthetic methods. In order to optimize the synthesis, in this work, electrospinning was employed to prepare nanofiber mat precursors, followed by low-temperature thermal treatment to give organic fibers with ZnO nanoparticles, and finally hydrothermal preparation, leading to highly ordered ZnO nanorods nanofiber mat. This cost-efficient approach requires very little on the equipment thus can be readily scaled up for mass production.

2. Experimental

2.1 Materials

Table 1
Summary of polymers, solvents and reagents used in the study

Name	Grade	Molecular weight (g/mol)	Supplier
Polyvinylidene fluoride (PVDF)	AR	400,000	J&K Chemical Ltd.
N,N-Dimethylformamide (DMF)	AR	73.09	Chinasun Specialty Products Co., Ltd.
Acetone	AR	58.08	Chinasun Specialty Products Co., Ltd.
Zinc Acetate (C ₄ H ₆ O ₄ Zn)	AR	183.48	Shanghai Aladdin Biochemical Technology Co., Ltd.
Hexamethylene Tetramine (C ₆ H ₁₂ N ₄)	AR	140.19	Sinopharm Chemical Reagent Co., Ltd.
Zinc Chloride (ZnCl ₂)	CP	136.30	Sinopharm Chemical Reagent Co., Ltd.
Rhodamine B	HPLC	479.01	Shanghai Aladdin Biochemical Technology Co., Ltd.
Ammonia (NH ₃ ·H ₂ O)	GR	17.03	Sinopharm Chemical Reagent Co., Ltd.

The materials used in this study are listed in Table 1. All materials were all used as received unless otherwise indicated. A polyvinylidene fluoride (PVDF) polymer with a molecular weight of 400,000 g/mol was used as the main constituent for electrospun nanofiber template. The relatively high molecular weight of the polymer ensures structural and thermal stability when subjected to heat treatment in the preparation of ZnO crystals.

2.2 Preparation and treatment of nanofiber

2.2.1 Preparation of PVDF/ Zn(Ac)₂ nanofiber membrane

PVDF particles and a mixed solvent of N-N dimethylformamide (DMF) and acetone were added in a beaker. The solution was heated and kept at 55°C. Anhydrous zinc acetate (Zn(Ac)₂) powder was added to the beaker when the PVDF particles were completely dissolved. The solution was stirred until a uniform dispersion solution was formed. PVDF/Zn(Ac)₂ nanofiber membranes were then prepared by electrospinning at a voltage of 15 kv and a receiving plate-to-spinning end distance of 12 cm.

2.2.2 Low temperature treatment for the preparation of ZnO-loaded PVDF nanofiber membrane

Experiment 1. The PVDF/Zn(Ac)₂ nanofiber membrane was thermally treated from 60°C to 200°C at an interval of 20°C for 24 h.

Experiment 2. The PVDF/Zn(Ac)₂ fiber membrane was thermally treated at 140°C for 1h, 12h, and 36h.

2.2.3 Preparation of PVDF/ZnO nanorods membrane

First, 60 mL of deionized water and desired amount of zinc chloride (ZnCl₂) powder was placed in a beaker and stirred for 10 min, then hexamethylenetetramine (HMTA) powder was added and stirred till complete dissolution. To this solution, a certain volume of ammonia solution was added, then ionized water was filled to make a total solution volume of 100 mL. Second, the PVDF/Zn(Ac)₂ nanofiber membranes thermally treated at 140°C were subjected to hydrothermal reaction to allow the growth of ZnO nanorods. Finally, the ZnO-loaded PVDF nanofiber membranes were rinsed several times with deionized water, and dried in a muffle furnace.

2.2.4 Factors affecting the growth of ZnO nanorods

The influence of the M(ZnCl₂:HMTA) molar ratio on the structure of ZnO nanorods was studied. Four M(ZnCl₂:HMTA) ratios were employed: 1:3, 1:2, 1:1 and 2:1. The 100 mL solution with 5 mL of ammonia was subject to hydrothermal reaction for 3 h.

The influence of hydrothermal temperature on the nanostructure of ZnO was investigated with a ZnCl₂:HMTA molar ratio of 1:1 at a total concentration of 0.1 M. The solution, with 5 mL of ammonia and a total volume of 100 mL, was subject to hydrothermal reaction at night different temperatures for 3 h.

Influence of volume of ammonia solution on the nanostructure of ZnO was studied. The solution with a growing solution concentration of 0.1 M and a ZnCl₂:HMTA molar ratio of 1:1 was filled with different volume of ammonia for a total solution volume of 100 mL. The solution was subject to hydrothermal reaction at 90°C for 3 h.

The nanostructure of ZnO prepared from different growing time was compared. The solution with a growing solution concentration of 0.1 M and a ZnCl₂:HMTA molar ratio of 1:1 was filled with 5 mL of ammonia to a total volume of 100 mL, followed by hydrothermal reaction at 90°C for different time.

The morphologies of ZnO prepared on nanofiber mat are pre-treated for 18 h at different temperature. The solution with a growing solution concentration of 0.1 M and a ZnCl₂:HMTA molar ratio of 1:1 was filled with 5 mL of ammonia to make a total volume of 100 mL, followed by hydrothermal reaction at 90°C for 3 h.

2.2.5 Photocatalytic investigation

To examine the effect of ZnO nanorods on photocatalytic degradation of Rhodamine B, two groups of experiment were carried out. The first group shows the comparison between the ZnO nanorod-loaded PVDF nanofiber membranes with different weights (1 g, 2 g and 3 g) and pristine ZnO powder (1 g) synthesized by hydrothermal method, whereas the second group shows the difference between the ZnO nanorod-loaded PVDF nanofiber membranes with the same weight (2 g) but different hydrothermal reaction time (1 h, 3 h and 5 h). Subsequently, the nanofiber membranes with the powder of these two

experiments are added to the rhodamine B solution with a concentration of 10 mg/L and a total volume of 30 mL.

3. Results & Discussion

Preparation of ZnO nanocrystal loaded on PVDF nanofiber mat

Solutions of inorganic salt are usually not suitable for electrospinning of nanofiber because they do not have appropriate concentration, viscosity and surface tension that are required by the technique for continuous long-range fibers. Instead, a PVDF solution pre-dissolved with zinc acetate ($\text{Zn}(\text{Ac})_2$) was successfully used for electrospinning, giving a PVDF/ $(\text{Zn}(\text{Ac})_2)$ nanofiber mat. Simple thermal treatment of the as-prepared nanofiber mat leads to nanocrystalline ZnO-loaded PVDF nanofiber. The influence of thermal treatment temperature on the morphology of ZnO was investigated from 80°C to 200°C. It was found that at 80°C, only few particulate ZnO was obtained, whereas from 100°C to 140°C, both the number and size of particulate ZnO increased with temperature. The fiber morphology is also well-maintained at 140°C, but starts to have cracks at 160°C where the fibrous structure starts to fail, and finally collapses at 200°C due to the melting of the polymer^{14,15}. The influence of duration time of thermal treatment on the morphology of ZnO nanocrystal was also investigated. The most number and largest size of crystals are obtained after 12 h of treatment. Further increase of thermal treatment time does not give any increase in the number and size of the crystals.

Preparation of ZnO nanorods loaded on PVDF nanofiber mat

The ZnO nanorods were prepared by hydrothermal synthesis of the ZnO nanocrystal-loaded PVDF nanofiber mat, thermally treated at 140°C, in a growth-promoting solution consisting ZnCl_2 , hexamethylenetetramine (HMTA) and ammonia. The growth of ZnO nanorods is a complex chemical reaction among ZnCl_2 (or ZnNO_3 and $\text{Zn}(\text{Ac})_2$), where OH^- , released by hydrolysis of HMTA and/or ionization of ammonia, first complexes with Zn^{2+} to give $[\text{Zn}(\text{NH}_3)_4]^{2+}$ or $[\text{Zn}(\text{OH})_4]^{2-}$, followed hydrothermal dehydration to give rise to the ZnO nanorods on the surface of nanofiber.

The concentration of the growth-promoting solution, proportion of ammonia, time and temperature of thermal synthesis, temperature of thermal treatment all have an influence on the growth of ZnO nanorods. The results show that the best orientation of the ZnO nanorods were obtained at a growth-promoting solution concentration of 0.1 M with ZnCl_2 :HMTA molar ratio of 1:1 and 5 mL of ammonia. ZnO nanorods with the smallest diameter are obtained at a hydrothermal temperature of 100°C, while well-dispersed and uniformly structured ZnO nanorods are achieved when the time of hydrothermal synthesis is 3 h. The nanofiber mat of PVDF/ $\text{Zn}(\text{Ac})_2$ without pre-thermal treatment mainly consists

interstacked ZnO crystals of film shape. In comparison, the one thermally treated at 140°C has well-defined nanorods that are aligned along the c axis.

Research on photocatalytic performance

To investigate the photocatalytic property of the ZnO nanorods, an organic dye, rhodamine B was selected as the target material. The ZnO nanorods synthesized by the polymer nanofiber mat template shows clearly better catalytic effect than the pristine ZnO nanorods powder, as evidenced by the larger photocatalytic degradation of rhodamine B under the catalysis of the ZnO nanorods-loaded nanofiber mat. The catalytic efficiency increases with the increase of ZnO nanorods amount. This may be because that the pristine ZnO nanorods powder may aggregates at the bottom of the solution, whereas the one formed on the nanofiber mat has much larger area that facilitates the light-absorbing efficiency. Besides, larger amount of ZnO nanorods also leads to larger area of nanofiber mat, which effectively increases the irradiation area, resulting in elevated photocatalytic degradation efficiency. The time duration of hydrothermal synthesis also affects the photocatalytic efficiency. The ZnO-doped nanofiber prepared with 3 h of hydrothermal synthesis exhibits the highest efficiency in the photocatalytic degradation of Rhodamine B, while shorter or longer hydrothermal treatment leads to lower efficiency. This is because that the nano ZnO hydrothermally prepared for 1 h only gives short nanorods with irregular structure that closely aligned at barely the surface of the fiber, and the one prepared for 3 h is too condensed to be exposed to light. Both products cannot provide optimal capturing surface that are essentially important for effective absorption of light.

4. Conclusion

In conclusion, we have shown that zinc acetate doped on electrospun nanofiber is a cost-efficient yet effective way of preparing ZnO nanocrystals and nanorods. The PVDF nanofiber mat acts as an excellent template for the in-situ growth of nano ZnO to give well-defined and uniformly-dispersed morphology. This brings advantages on the photocatalytic properties of the nano ZnO, as shown by the much improved photocatalytic degradation of Rhodamine B. The material design and synthesis in this work provides an alternative and useful approach for the efficient preparation of functional nanocrystals with controllable morphology and tunable properties that can be readily scaled up for vast production.

Declarations

Author Contributions

Mingyi Chen drafted the manuscript, analyzed the data and made the figures and tables.

Peng Liu carried out the synthesis, structural and morphological characterization.

Ji-Huan He oversaw the preparation and part of the characterization of the nanofibers.

Hsing-Lin Wang co-supervised the project and commented on the writing.

Xin Wang proposed the significance and supervised the writing as well as corrected the manuscript to a publishable level.

Rouxi Chen conceived the idea and oversaw the research.

Notes

The authors declare no competing financial interest.

Acknowledgement

The authors acknowledge support from Key-Area Research and Development Program of Guangdong Province (Grant No.2019B010941001), Natural Science Foundation of Guangdong Province China (Grant No.2018A0303100022) and China Postdoctoral Science Foundation Grant (Grant No. 2018M630949).

Appendix

Experimental details including materials, preparation and supplementary SEM, TEM, XRD images can be found in the Supporting Information.

References

1. Stafiniak, A. *et al.* Electrical Conduction of a Single Electrospun ZnO Nanofiber. *J. Am. Ceram. Soc.***97**, 1157-1163.<http://doi.org/10.1111/jace.12759>. (2014).
2. Tanveer, M., Habib, A. & Khan, M. B. Structural and optical properties of electrospun ZnO nanofibres applied to P3HT:PCBM organic photovoltaic devices. *J. Exp. Nanosci.***10**, 640-650.<http://doi.org/10.1080/17458080.2013.869841>. (2015).
3. Zhu, L. *et al.* Electrospun ZnO Nanofibers-Based Ultraviolet Detector with High Responsivity. *J. Am. Ceram. Soc.***96**.<http://doi.org/10.1111/jace.12483>. (2013).
4. Wang, W. *et al.* Zinc Oxide Nanofiber Gas Sensors Via Electrospinning. *J. Am. Ceram. Soc.***91**, 3817-3819.<http://doi.org/10.1111/j.1551-2916.2008.02765.x>. (2008).
5. Song, L., Jiang, Q., Du, P., Yang, Y. & Xiong, J. A facile synthesis of novel ZnO structures and their applications in photocatalysis. *Mater. Lett.***123**, 214-216.<http://doi.org/10.1016/j.matlet.2014.03.009>. (2014).
6. Senthamizhan, A., Balusamy, B., Aytac, Z. & Uyar, T. Grain boundary engineering in electrospun ZnO nanostructures as promising photocatalysts. *CrystEngComm***18**, 6341-6351.<http://doi.org/10.1039/C6CE00693K>. (2016).
7. Busuioc, C., Evangelidis, A., Enculescu, M. & Enculescu, I. Optical and photocatalytic properties of electrospun zno fibers. *Dig. J. Nanoma. Ter. Bios***10**, 957-965. (2015).

8. Li, J. *et al.* Electrospun dendritic ZnO nanofibers and its photocatalysis application. *J. Appl. Polym. Sci***132**.<http://doi.org/10.1002/app.41627>. (2014).
9. Gao, P.-X., Zhong, L. & Wang. Self-Assembled Nanowire–Nanoribbon Junction Arrays of ZnO. *J. Phys. Chem. B***106**.<http://doi.org/10.1021/jp0265485>. (2002).
10. Yang, P. *et al.* Controlled Growth of ZnO Nanowires and Their Optical Properties. *Adv. Funct. Mater.***12**.[http://doi.org/10.1002/1616-3028\(20020517\)12:53.0.CO;2-G](http://doi.org/10.1002/1616-3028(20020517)12:53.0.CO;2-G). (2002).
11. Lao, J. Y., Huang, J. Y., Wang, D. Z. & Ren, Z. F. Hierarchical oxide nanostructures. *J. Mater. Chem***14**, 770-773.<http://doi.org/10.1039/B311639E>. (2004).
12. Kong, X., Ding, Y., Yang, R. & Wang, Z. Single-Crystal Nanorings Formed by Epitaxial Self-Coiling of Polar Nanobelts. *Science (New York, N.Y.)***303**, 1348-1351.<http://doi.org/10.1126/science.1092356>. (2004).
13. Salavati-Niasari, M., Gholami-Daghian, M., Esmaeili-Zare, M. & Sangsefidi, F. S. Solid State Synthesis and Characterization of Zinc Oxide (ZnO) Microflakes by [Bis(acetylacetonato)zinc(II)] and Sodium Hydroxide at Room Temperature. *J. Cluster. Sci***24**, 1093-1101.<http://doi.org/10.1007/s10876-013-0600-5>. (2013).
14. Liu, Z., Maréchal, P. & Jérôme, R. Melting and crystallization of poly(vinylidene fluoride) blended with polyamide 6. *Polymer***38**, 5149-5153.[http://doi.org/https://doi.org/10.1016/S0032-3861\(97\)00047-5](http://doi.org/https://doi.org/10.1016/S0032-3861(97)00047-5). (1997).
15. Yang, J. *et al.* Effects of Crystallization Temperature of Poly(vinylidene fluoride) on Crystal Modification and Phase Transition of Poly(butylene adipate) in Their Blends: A Novel Approach for Polymorphic Control. *J. Phys. Chem. B***116**, 1265-1272.<http://doi.org/10.1021/jp209626x>. (2012).

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