Data Article

Data on the convenient fabrication of carbon doped $\text{WO}_3-x$ ultrathin nanosheets for photocatalytic aerobic oxidation of amines at room temperature

Keyan Bao¹, Ping Ni¹, Shaojie Zhang, Zixiang Zhang, Kailong Zhang, Liangbiao Wang, LiXia Sun, Zhiguo Hou*, Yitai Qian, Quanfa Zhou, Wutao Mao*

Resource Environment & Clean Energy Laboratory, School of Chemical and Environmental Engineering, Jiangsu University of Technology, Changzhou 213001, China

Article info

Article history:
Received 20 November 2018
Received in revised form 18 December 2018
Accepted 18 December 2018

Keywords:
Ultrathin nano-sheet
Photocatalytic activity
Aerobic oxidation

Abstract

The oxidation of amines to imines is an important chemical transformation. In this article, we report original data on the synthesis of carbon doped $\text{WO}_3-x$ ultrathin nanosheets via an acid-assisted one-pot process, which exhibit excellent photocatalytic activity in the aerobic oxidation of amines to corresponding imines under visible light irradiation at room temperature. The composition, microstructure, morphology, photocatalytic activity of the corresponding samples and possible mechanism are included here.

The data are related to "Oxide Defect Engineering Enables to Couple Solar Energy into Oxygen Activation" (Zhang et al., 2016). © 2019 Published by Elsevier Inc. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
Specifications table

| Subject area                     | Chemical engineering, Environmental engineering, Materials chemistry |
|----------------------------------|---------------------------------------------------------------------|
| More specific subject area       | Advanced oxidation processes of amines to imines                    |
| Type of data                     | Tables, figures                                                     |
| How data was acquired            | XRD (using Bruker D8), TEM and HRTEM (JEOL JEM-2010), UV–vis–NIR    |
|                                  | diffuse reflectance spectra were recorded in the spectral region of  |
|                                  | 250–2500 nm with a Shimadzu SolidSpec-3700 spectrophotometer. Raman  |
|                                  | spectra were obtained using a PerkinElmer Raman Station 400 spect-  |
|                                  | rometer with a 514 nm laser as the excitation source.               |
| Data format                      | Raw and analyzed data                                               |
| Experimental factors             | Synthesis of carbon doped WO$_{3-x}$ ultrathin nanosheets:           |
|                                  | Na$_2$WO$_4$·2H$_2$O (1.65 g, 5 mmol), deionized water (50 mL),   |
|                                  | Span 60 (0.5 g), sulfuric acid (50 mL), 160 °C for 5.0 h.           |
|                                  | General procedure for the oxidation of amines: 50 mg of catalysts,   |
|                                  | 25 mL quartz Schlenk tube, O$_2$ balloon, amines (0.5 mmol), CH$_3$CN |
|                                  | (5 mL), LED lamp (λ > 400 nm, 0.5 W cm$^{-2}$).                    |
| Experimental features            | The designed experiments included the optimization of synthesis      |
|                                  | processes, comparison on the photocatalytic activity               |
| Data source location             | Changzhou, Jiangsu, China.                                         |
| Data accessibility               | Data are included in this article                                  |
| Related research article         | N. Zhang, X. Li, H. Ye, S. Chen, H. Ju, D. Liu, Y. Lin, W. Ye, C. Wang, Q. Xu, J. Zhu, L. Song, J. Jiang, Y. Xiong, Oxide defect engineering enables to couple solar energy into oxygen activation, J. Am. Chem. Soc., 138, 2016, 8928–8937 [1]. |

Value of the data

- The data on the synthesis processes optimization of the carbon doped WO$_{3-x}$ ultrathin nanosheets could give an insight into the formation of oxygen-vacancies, carbon doped, 2D nanocomposition.
- The data on the photocatalytic activity of the present nanocomposite could give an insight into the chemical transformation for oxidation of amines to imines.
- The data set can be used by researchers interested in developing new composite photocatalysts and understanding the mechanism of carbon doped WO$_{3-x}$ 2D nanosheets.

1. Data

This brief article describes the facile acid-assisted one-pot synthesis processes, microstructure, morphology, and photocatalytic activity of the carbon doped WO$_{3-x}$ ultrathin nanosheets (CD-WO$_{3-x}$-UNs). Table 1 shows the effects of different reaction conditions by changes in sulfuric acid and the amount of water on the products. Fig. 1 shows the photos of the products obtained under different reaction conditions. Fig. 2 shows the TEM images of the products obtained under different reaction conditions. Fig. 3 shows the characterization of CD-WO$_{3-x}$-UNs by XRD and TEM. Fig. 4 shows the Raman spectrum of the CD-WO$_{3-x}$-UNs. Table 2 shows the use of elemental analysis to study carbon content of CD-WO$_{3-x}$-UNs. Fig. 5 shows that the effects of different reaction conditions: the Span60 was replaced by anhydrous ethanol. Fig. 6 shows detection of H$_2$O$_2$ as the byproduct using a DPD/POD method to study the reaction process. Table 3 displays catalytical performance...
of CD-WO$_{3-x}$-UNSs under different conditions. Scheme 1 shows the Reactions DPD Reacting with H$_2$O$_2$ catalyzed by POD. Scheme 2 indicates possible mechanism for photocatalytic aerobic oxidation of amines.

2. Experimental design, materials and methods

CD-WO$_{3-x}$-UNSs were obtained by 1.65 g of Na$_2$WO$_4$·2H$_2$O and 0.5 g of Span 60 were dissolved in 50 mL deionized water under stirring. After 20 min, concentrated sulfuric acid (50 mL) was added drop by drop. The reaction mixture was heated at 160 °C for 5.0 h using an oil bath. Then the sample was washed with deionized water and ethanol for several times.
2.1. Data study

We found that the amount of concentrated sulfuric acid, in other words the concentration of sulfuric acid in the reaction system, is of vital importance for the generation of oxygen defects. Table 1 shows the effects of different reaction conditions by changes in sulfuric acid and the amount of water on the products. Fig. 1 shows the photos of the products obtained under different reaction conditions. Fig. 2 shows the TEM images of the products obtained under different reaction conditions. The amount of sulfuric acid in the reaction process is very important, decreases the amount of sulfuric acid, only WO$_3$ or no pure products were obtained. When the sulfuric acid and water were 10 mL respectively, the product named CD-WO$_{3-x}$-UNs had the best morphology and performance. Fig. 3 shows the characterization of CD-WO$_{3-x}$-UNs by XRD and TEM. The XRD pattern can be indexed as the tetragonal phase of WO$_{3-x}$ (JCPDS PDF No. 53-0434). Carbon content is relatively small, and the crystallinity is not good, XRD does
Fig. 5. The effects of different reaction conditions: the Span 60 was replaced by anhydrous ethanol.

Fig. 6. Detection of H$_2$O$_2$ for the solution after the light-driven catalytic aerobic oxidation of $N$-t-butylbenzylamine using a DPD/POD method.
The lattice fringes are discontinuous, and some are distorted, as shown in Fig. 3b. This indicates the presence of crystallographic defects in the WO$_3$–x/C nanosheets [2]. The Raman spectrum of the CD-WO$_3$–x/UNSs shows the successful formation of carbon doped WO$_3$–x material. The weak peak at 1353 cm$^{-1}$ is attributed to the A$_{1g}$ vibration mode of carbon atoms. The peak at 1590 cm$^{-1}$ corresponds to the E$_{2g}$ vibration mode of sp$^2$-bonded carbon atoms [3,4]. Table 2 elemental analysis proves the successful doping of carbon in the sample, with a carbon content of about 2.08%. Fig. 5 shows that the carbon doped WO$_3$–x composite nanomaterials can also be obtained by using anhydrous ethanol as carbon source, but the morphologies of the obtained samples are not very uniform. When the amount of ethanol increased to 10 mL, the characteristic peak of carbon was displayed in XRD. The small diffraction peak marked with star at 26.6° can be indexed as (003) diffraction of carbon (JCPDS PDF No. 26-1079) [5].

We also study the mechanism of light-driven catalytic aerobic oxidation by detection the generation of hydrogen peroxide (H$_2$O$_2$). We assume H$_2$O$_2$ may be generated during the process of photocatalytic aerobic oxidation of amines. Production of H$_2$O$_2$ was detected by a reported N,N-diethyl-p-phenylenediamine(DPD)/horseradish peroxidase (POD) method [6]. Briefly, the aqueous solutions of 100 mg of DPD (100 mg in 10 mL of H$_2$O) and POD (10 mg in 2 mL of H$_2$O) were firstly prepared, and the solutions were stored in dark at below 278 K before used. Then the CH$_3$CN solution obtained after the light-driven catalytic aerobic oxidation of amine was dilution with 15 mL of H$_2$O, and the mixture was further extracted with ethyl acetate (EtOAc, 10 mL*3) to remove the organic compounds. Then 0.5 mL of aqueous solution and 0.5 mL of PBS buffer (pH = 7.4) were added into 4 mL of H$_2$O followed by a 10-s shake. After adding 20 μL of DPD and 20 μL of POD solution, the UV–vis spectra of the sample were collected using an Agilent Cary 60 spectrophotometer.

Scheme 1 shows the Reactions DPD Reacting with H$_2$O$_2$ catalyzed by POD. As a peroxidase, the POD well recognizes H$_2$O$_2$; hence this method exhibits excellent selectivity for H$_2$O$_2$. The radical cation (DPD·+) produced from the oxidation of two DPD molecules exhibits two absorption maxima at 510 and 551 nm. In our reaction system, the H$_2$O$_2$ intermediate has been observed based on these two absorption maxima in Fig. 6. The concentrations of H$_2$O$_2$ in different catalytic systems are basically consistent with the conversion of the substrate, indicating that H$_2$O$_2$ may be the byproduct with main product.
In order to determine the role of O$_2$, different atmosphere such as air and N$_2$ was used to replace O$_2$ respectively, while keeping all the other conditions exactly the same. In order to determine O$_2$•− as active species are involved in the reaction process, additional 1.0 mmol benzoquinone (BQ) was added into the reaction tube before light irradiation, while keeping all the other conditions exactly the same. In order to determine photoproduction holes are involved in the reaction process, additional 1.0 mmol triethanolamine (TEOA) was added into the reaction tube before light irradiation, while keeping all the other conditions exactly the same. Please see Table 3. Photoproduction holes, O$_2$•− generating from O$_2$ play key roles for the light-driven catalytic aerobic oxidation, as well as H$_2$O$_2$ can be detected during the reaction process. Base these facts possible mechanism was proposed, as shown in Scheme 2.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. U1404505), the Natural Science Foundation of Jiangsu Province (Grants No. BK20181046), the Program for Innovative Talent in Henan University (No. 16HASTIT010), Postgraduate Research & Practice Innovation Program of Jiangsu Province (SJX18-1010, SJX18-0994, SJX18-1009).

Transparency document. Supporting information

Transparency data associated with this article can be found in the online version at https://doi.org/10.1016/j.dib.2018.12.062.

References

[1] N. Zhang, X. Li, H. Ye, S. Chen, H. Ju, D. Liu, Y. Lin, W. Ye, C. Wang, Q. Xu, J. Zhu, L. Song, J. Jiang, Y. Xiong, Oxide defect engineering enables to couple solar energy into oxygen activation, J. Am. Chem. Soc. 138 (2016) 8928–8937.
[2] F. Lei, Y. Sun, K. Liu, S. Gao, L. Liang, B. Pan, Y. Xie, Oxygen vacancies confined in ultrathin indium oxide porous sheets for promoted visible-light water splitting, J. Am. Chem. Soc. 136 (2014) 6826–6829.
[3] K.Y. Bao, S.J. Zhang, P. Ni, K.L. Zhang, W.T. Mao, Q.F. Zhou, Y.T. Qian, Convenient fabrication of carbon doped WO$_3$–x ultrathin nanosheets for photocatalytic aerobic oxidation of amines, Catal. Today (2019), https://doi.org/10.1016/j.cattod.2018.11.013 (In press).
[4] J. Yan, T. Wang, G. Wu, W. Dai, N. Guan, L. Li, J. Gong, Tungsten oxide single crystal nanosheets for enhanced multichannel solar light harvesting, Adv. Mater. 27 (2015) 1580–1586.
[5] K.Y. Bao, W.T. Mao, G.Y. Liu, L.Q. Ye, H.Q. Xie, S.F. Ji, D. Wang, C. Chen, Y.D. Li, Preparation and electrochemical characterization of ultrathin WO$_3$–x/C nanosheets as anode materials in lithium ion batteries, Nano Res. 10 (2017) 1903–1911.
[6] X. Lang, H. Ji, C. Chen, W. Ma, J. Zhao, Selective formation of imines by aerobic photocatalytic oxidation of amines on TiO$_2$, Angew. Chem. Int. Ed. 50 (2011) 3934–3937.