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Data Article

Data on the convenient fabrication of carbon doped WO_{3-x} ultrathin nanosheets for photocatalytic aerobic oxidation of amines at room temperature

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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 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).

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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 spectrometer 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: $Na_2WO_4 \cdot 2H_2O$ (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_3CN (5 mL), LED lamp ($\lambda > 400$ 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}-UNSs. Table 2 shows the use of elemental analysis to study carbon content of CD-WO_{3-x}-UNSs. Fig. 5 shows that the effects of different reaction conditions: the Span60 was replaced by anhydrous ethanol. Fig. 6 shows detection of H_2O_2 as the byproduct using a DPD/POD method to study the reaction process. Table 3 displays catalytical performance

Table 1
The effects of different reaction conditions by changes in sulfuric acid and the amount of water on the products.

	VH_2O/mL	VH_2SO_4/mL	Product
1	17	3	No pure product
2	15	5	WO_3
3	13	7	WO_3
4	10	10	WO_{3-x}
5	11	9	WO_{3-x}
6	7	13	WO_{3-x}
7	5	15	WO_{3-x}
8	3	17	No pure product

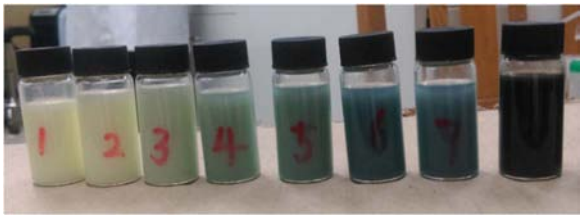


Fig. 1. The photos of the products obtained under different reaction conditions.

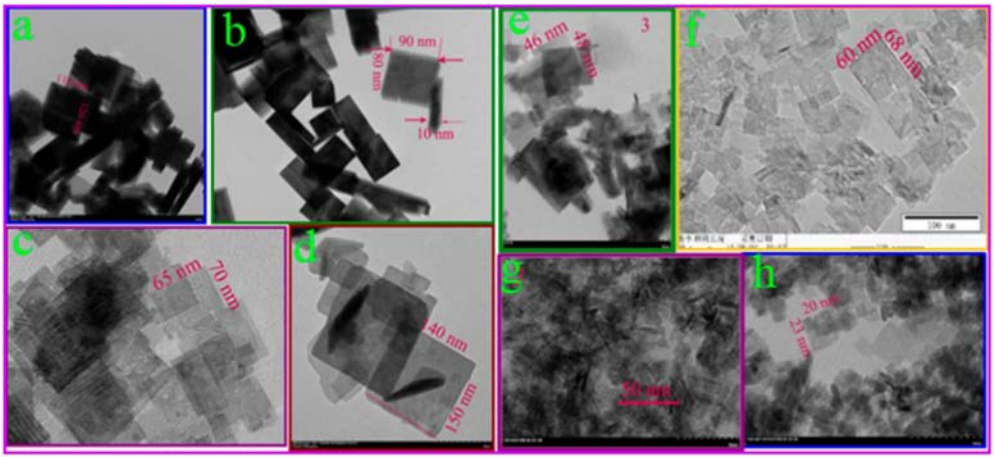


Fig. 2. TEM images of the products obtained under different reaction conditions.

of CD-WO_{3-x}-UNSs under different conditions. Scheme 1 shows the Reactions DPD Reacting with H_2O_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 $Na_2WO_4 \cdot 2H_2O$ 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.

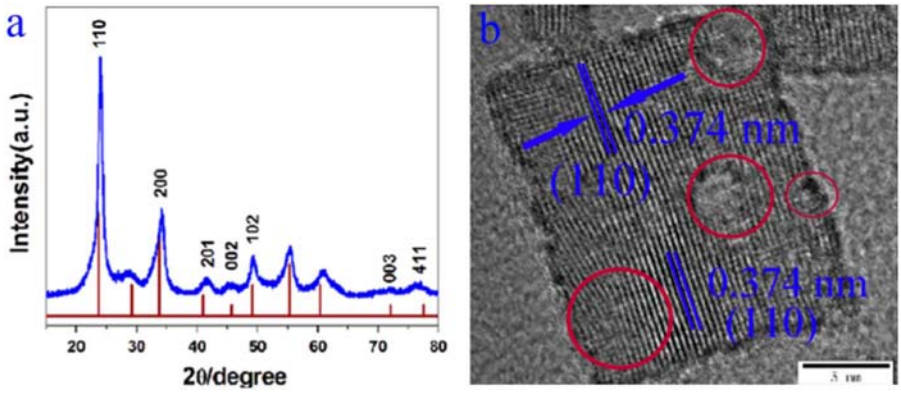


Fig. 3. (a) XRD pattern,(b)TEM image show the crystallographic defects of carbon doped WO_{3-x} ultrathin nanosheets.

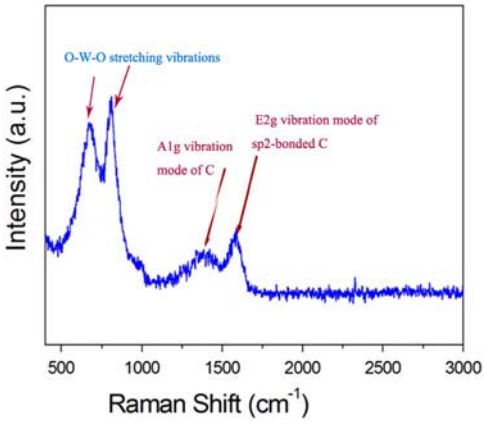


Fig. 4. Raman spectrum of CD-WO_{3-x}-UNs.

Table 2
Elemental analysis data of CD-WO_{3-x}-UNSs.

N	0.04%
C	2.08%
H	0.395%
S	0.059%

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

$$NaWO_4 \bullet 2H_2O + H_2O + H_2SO_4 + CH_3CH_2OH \xrightarrow{160^{\circ}C6h} WO_{3-x}/C$$

2 mmol	8 mL	10mL	2 mL	a
2	5	10	5	b
2	20	20	10	c

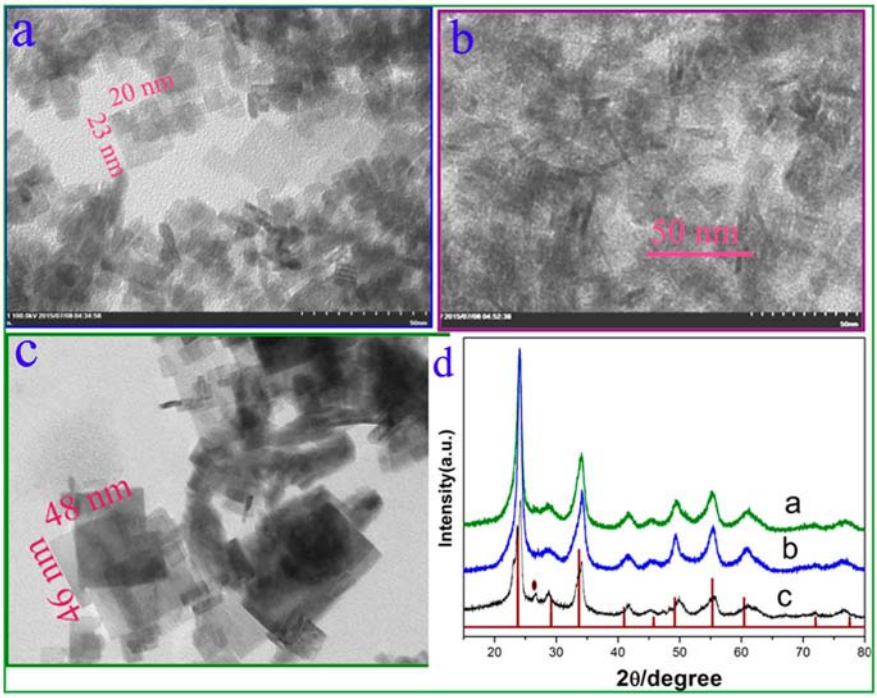


Fig. 5. The effects of different reaction conditions: the Span 60 was replaced by anhydrous ethanol.

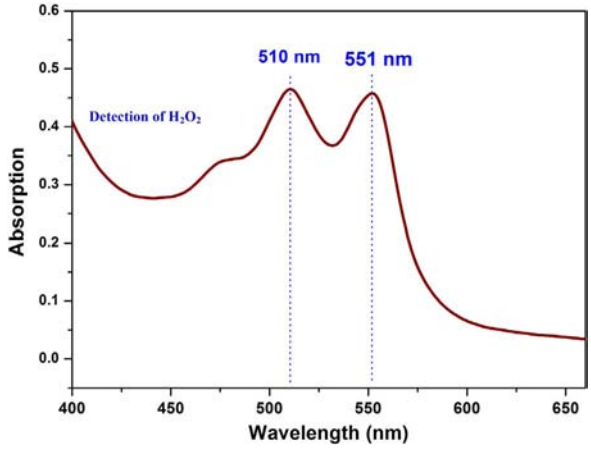
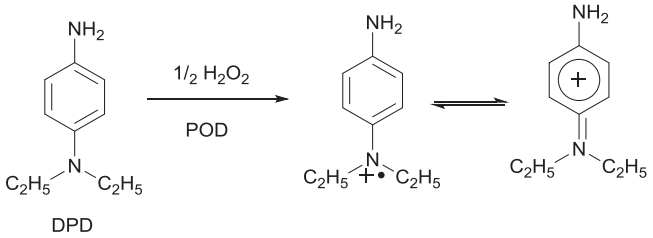


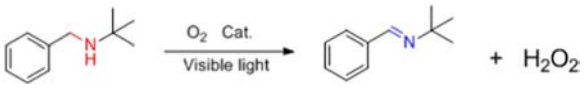
Fig. 6. Detection of H_2O_2 for the solution after the light-driven catalytic aerobic oxidation of *N-t*-butylbenzylamine using a DPD/POD method.

Table 3
Catalytical performance of CD-WO_{3-x}-UNSs under different atmosphere, 1 mmol scale, catalyst 50 mg, CH_3CN as solvent, reaction time 6 h.

Reaction condition	O_2	Air	O_2+TEOA	O_2+BQ	N_2
Conversion	43%	26%	9%	6%	4%



Scheme 1. Reactions DPD Reacting with H_2O_2 catalyzed by POD.



Scheme 2. Possible mechanism for photocatalytic aerobic oxidation of amines.

not show the diffraction peak of carbon [1]. 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]. Fig. 4 shows the Raman spectrum of the CD-WO_{3-x}-UNSs.The result indicates the successful formation of carbon doped WO_{3-x} material. The weak peat 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, the carbon content in this product is 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_2O_2). We assume H_2O_2 may be generated during the process of photocatalytic aerobic oxidation of amines. Production of H_2O_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_2O) and POD (10 mg in 2 mL of H_2O) were firstly prepared, and the solutions were stored in dark at below 278 K before used. Then the CH_3CN solution obtained after the light-driven catalytic aerobic oxidation of amine was dilution with 15 mL of H_2O, 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_2O 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 Varien Cary 60 spectrophotometer.

Scheme 1 shows the Reactions DPD Reacting with H_2O_2 catalyzed by POD. As a peroxidase, the POD well recognizes H_2O_2; hence this method exhibits excellent selectivity for H_2O_2.The radical cation ($DPD\cdot+$) produced from the oxidation of two DPD molecules exhibits two absorption maxima at 510 and 551 nm. In our reaction system, the H_2O_2 intermediate has been observed based on these two absorption maxima in Fig. 6. The concentrations of H_2O_2 in different catalytic systems are basically consistent with the conversion of the substrate, indicating that H_2O_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 $O_2\bullet-$ 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 photoproduct 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. Photoproduct holes, $O_2\bullet-$ generating from O_2 play key roles for the light-driven catalytic aerobic oxidation, as well as H_2O_2 can be detected during the reaction process. Base these facts possible mechanism was proposed, as shown in Scheme 2.

Acknowledgments

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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.

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