Full Length Article

Oxygen vacancies in TiO$_2$/SnO$_x$ coatings prepared by ball milling followed by calcination and their influence on the photocatalytic activity

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A R T I C L E    I N F O

Keywords:
TiO$_2$/SnO$_x$
Photocatalyst
Coatings
Oxygen vacancy
Cs-corrected STEM

A B S T R A C T

We prepared TiO$_2$/SnO$_x$ ($x=1$, 2) composite coatings through ball milling followed by calcination. The composite coatings were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), spherical aberration corrected scanning transmission microscopy (Cs-corrected STEM), X-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance (EPR) and other techniques. Bulk oxygen vacancies in the form of vacancy clusters rather than individual sites were directly observed by Cs-corrected STEM. With an increase in the calcination temperature from 873 K to 1073 K or holding time from five hours to ten hours, the concentration of bulk defects also increased. On the other hand, the photocatalytic activity of the as-prepared samples for degrading MB dye increased with the concentration increase of bulk defects. Sample 973 K-10 h showed the best photocatalytic activity whether under the irradiation of UV light or visible light. With a further increase in the concentration of bulk oxygen vacancies, the photocatalytic activity decreased, although surface Ti$^{3+}$ defects appeared. In other words, a moderate concentration of bulk defects could benefit the enhancement of the photocatalytic activity of the as-prepared samples. Ball milling followed by calcination is an effective method to introduce defects such as oxygen vacancies.

1. Introduction

Since Chen et al. [1] discovered the significant role of defects including Ti$^{3+}$ and oxygen vacancies in the photocatalytic performance enhancement of titanias in 2011, many studies have tried to introduce oxygen vacancies into the microstructure of photocatalysts and thereby improve their photocatalytic activity under visible light. The main methods to introduce oxygen vacancies include hydrogen thermal treatment [1–3], high-energy particle bombardment [4–6], ion doping [7–9], reduction reaction [10–12], and oxygen depleted thermal treatment [13–15]. Until now, we have demonstrated that the oxygen vacancies can greatly affect the electronic structure [16–18], charge transport [19], and surface properties [20] of photocatalysts. Specifically, they could form a donor level below the conduction band of semiconductors and therefore extend the light absorption range [21]. Furthermore, they can greatly increase the visible light-responsive photocatalytic activity [21,22]. On the other hand, some researchers found that the influence of oxygen vacancies on photocatalytic activity depends on their locations. The oxygen vacancies located on the surface acting as charge trapping centers as well as adsorption sites could prevent the recombination of photogenerated electron-hole pairs [2,23]. However, bulk oxygen vacancies are believed to serve as charge carrier traps when electron-hole pairs recombine [24,25]. The influence of oxygen vacancies on photocatalytic activity and relevant mechanism are rather complicated and need more intensive investigation.

Generally, oxygen vacancies are characterized by electron paramagnetic resonance (EPR) [26,27] and transmission electron microscopy (TEM) [23,28,29]. If oxygen vacancies are located at the surface of photocatalysts, we could observe them with scanning tunneling microscopy (STM) [30,31]. However, people have not observed clear
images of bulk oxygen vacancies of photocatalysts to the best of our knowledge. With the development of transmission electron microscopy, the spherical aberration-corrected scanning transmission electron microscope (Cs-corrected STEM) appeared, which made it possible to directly observe bulk oxygen vacancies and obtain their clear images.

In this work, we introduce oxygen vacancies into the lattice of TiO2 photocatalyst coatings with ball milling followed by thermal oxidation. At the same time, we also observe the bulk oxygen vacancies with a Cs-corrected STEM and obtain their clear images with atomic resolution. Furthermore, we also discuss the relationship between bulk oxygen vacancies and the photocatalytic activity.

2. Experimental

2.1. Preparation of TiO2/SnOx composite coatings

The mixture of Ti powder with an average diameter of 50 μm (purity: 99.1%, Osaka Titanium Technologies, Japan) and Sn powder with an average diameter of 30 μm (purity: 99.8%, Fukuda, Japan) was used as the coating material. Meanwhile, Al2O3 balls with an average diameter of one millimeter (purity: 98.5%, Nikkato, Japan) used as the matrix materials.

We used a planetary ball mill (Pulverisette 6, Fritsch, Germany) to carry out the ball milling. Ti powder (26.8 g), 13.2 g of Sn powder and 60.0 g of Al2O3 balls were charged into a bowl made of alumina (volume: 250 ml). Ball milling was then initiated with a revolution speed of 480 rpm. Second, the Al2O3 balls coated with Ti/Sn composite coatings were calcined in a muffle furnace in the air at 873 K, 973 K and 1073 K for five hours (Fig. 1b), we can see the intensive diffraction peaks of anatase TiO2 (101) and rutile TiO2 (110). This result indicates that a small amount of SnO2 and rutile TiO2 also formed during the annealing. Furthermore, weak peaks of rutile TiO2 also formed during the annealing. However, peaks of SnO2 were not observed. This finding indicates that the main product is rutile TiO2, while the amount of SnO2 and SnO decreased in the detection depth of X-rays from the surface. At the same time, it can be noted that some metallic Ti was reserved. From the above results, we concluded that TiO2/SnOx (x = 1 and/or 2) composite coatings could be prepared by ball milling followed by calcination.

The surface morphologies of the as-prepared TiO2/SnOx composite coatings are presented in Fig. 2. We can see that fine crystalline grains with irregular shapes formed during the calcination. With an increase in the calcination temperature from 873 K to 1073 K, the average grain size increased from approximately 300 nm to two microns. The cross-section images of the as-prepared TiO2/SnOx composite coatings are shown in Fig. 3. The thickness of these composite coatings varied from 20 to 30 μm. The gray and white areas correspond to TiO2/SnOx and Sn, respectively. We also note that the oxidation of Sn/SnOx proceeded from the outer layer to the inner layer.

Fig. 4 shows the TEM images of sample 873 K-10 h. In Fig. 4a, the coarse crystal grains on the surface and fine grains in the bulk of the composite coatings could be observed. Combined with the elemental mapping (Fig. S1), we could confirm that the coarse grains are mainly TiO2 and a small amount of SnO2 on the other hand, the fine grains are confirmed to be Ti/Sn composites (Fig. 4b). With an increase in magnification times (Fig. 4c and d), we found massive disorder in the lattice of rutile TiO2. This result indicates that defects or lattice distortion were introduced into the lattice. We also confirm the lattice distortion from the microdiffraction peak shift of rutile TiO2 (1 1 0).

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.apsusc.2018.10.071.
Fig. 2. SEM images of the morphologies of the as-prepared samples: (a) 873 K-10 h, (b) 973 K-5 h, (c) 973 K-10 h and (d) 1073 K-10 h.

Fig. 3. SEM images of the cross-section microstructures of the as-prepared samples: (a) 873 K-10 h, (b) 973 K-5 h, (c) 973 K-10 h and (d) 1073 K-10 h.
Fig. 5 shows the atomic-resolution STEM images of sample 873 K-10 h. From Fig. 5a, we could gauge that the interplanar distances are 0.248, 0.324 and 0.205 nm. These values are consistent with those of the crystal planes (1 0 1), (1 1 0) and (2 1 0) of rutile TiO₂, respectively. Therefore, we could safely affirm that the crystal phase is rutile TiO₂. On the other hand, we conducted the analysis on the oxygen vacancies, as shown in Fig. 5b–d. In Fig. 5b, we measured the heights of the corresponding oxygen atom columns, which are surrounded by square frames. As a result, we found that the heights of some oxygen atom columns were smaller than others. The height decrease means that some oxygen atoms were lost in the corresponding sites. In other words, oxygen vacancies indeed formed in the lattice of rutile TiO₂. From the height change of oxygen atom columns, the amounts of oxygen vacancies in different crystal planes in the same family of crystal planes vary. From Fig. 5c and d, we also confirm the existence of oxygen vacancies in the lattice of rutile TiO₂ since the loss of oxygen atoms in the lattice of rutile TiO₂ makes the difference degrees of brightness of the points corresponding to the atom columns. We also note that oxygen vacancies exist in the form of clusters rather than discontinuous individual sites as surrounded by the dot-dash line (Fig. 5c) or square frames (Fig. 5d).

The optical absorption spectra of the as-prepared samples are illustrated in Fig. 6. We can see that the absorption thresholds of samples 973 K-5 h, 973 K-10 h and 1073 K-10 h vary, from 420 nm to 450 nm; at the same time, the threshold of sample 873 K-10 h extends to nearly 500 nm. On the other hand, samples 873 K-10 h, 973 K-5 h and 973 K-10 h intensely absorb visible light and even infrared rays. This could be extremely helpful to enhance the visible-light-responsive photocatalytic activity.

Fig. 7 shows the XPS spectra of the as-prepared TiO₂/SnOₓ composite coatings. In Fig. 7a, the Ti2p₃/₂ peak of the samples 873 K-10 h, 973 K-5 h and 973 K-10 h is centered at 458.3 eV, and the peaks were highly symmetrical, which indicates the absolute coordination of Ti⁴⁺ [32–34]. However, that of the sample 1073 K-10 h can be divided into two at 458.9 eV and 457.8 eV. The two peaks correspond to the binding energies of Ti⁴⁺ [35] and Ti³⁺ [36,37], respectively. This means that TiO₂ accompanied with the Ti₂O₃ formed in the calcination at 1073 K with holding for ten hours. Fig. 2S (in the supplemental materials) shows the XPS spectra of O₁S. The intensive peaks within 527.7–530.2 eV are present due to the O²⁻ oxygen species of TiO₂. With an increase in the calcination temperature, the XPS peaks of O₁S shifted to greater binding energies, thus indicating the formation of oxygen vacancies [38–40]. At the same time, the XPS peak intensity of O₁S also increased, which indicates an increase in the defect concentration.

The oxidation conditions of metallic Sn were also investigated with
the results shown in Fig. 7b. For samples 873 K-10 h, 973 K-5 h and 973 K-10 h, the Sn3d peaks were centered at a binding energy of 486.3 eV, which corresponds to tetragonal SnO [41,42]. However, for sample 1073 K-10 h, the Sn3d peak was located at 486.9 eV, which corresponds to rutile-type SnO2 [41,42]. At the same time, the asymmetric peak also included a low peak at 486.3 eV. This finding indicates the peak at 486.9 eV corresponds to SnO2 and SnO. From the above results, we can conclude that the surface layer of the composite coatings mainly consists of rutile TiO2 and SnO for the samples prepared at 873 and 973 K; however, rutile TiO2, SnO2 and SnO became the main crystal phases of the surface layer of the composite coatings when the calcination temperature was increased to 1073 K. This conclusion is also consistent with that represented in the XRD patterns.

The EPR signals of the as-prepared samples are also recorded as shown in Fig. 8 to study the crystal defects including Ti3+ and oxygen vacancies. After being calcined at 873 K and holding for ten hours, the sample exhibited an EPR signal at g = 1.9845. It is reported that the signals at g = 1.94–1.99 correspond to Ti3+ [43,44]. On the other hand, Ti3+ in the surface layer of the TiO2/SnOx composite coatings was not detected by XPS (Fig. 7). Therefore, we can affirm that bulk Ti3+ was formed in sample 873 K-10 h. When the calcination temperature was increased to 973 K, the EPR signals appeared at g = 1.9998, 1.9992, 1.9865 and 1.9722. In addition to bulk Ti3+, oxygen vacancies were also confirmed since Zhangetal. [45] reported that the EPR signal of g = 1.99 corresponds to oxygen vacancies of TiO2. Therefore, we could confirm that bulk Ti3+ and oxygen vacancies were also confirmed since Zhang et al. [45] reported that the EPR signal of g = 1.99 corresponds to oxygen vacancies of TiO2. Therefore, we could confirm that the samples 973 K-5 h and 973 K-10 h contain bulk oxygen vacancies and bulk Ti3+. We also note that the intensities of the EPR signals increased with an increase in the calcination temperature or holding time. This observation indicates that the concentration of bulk defects increases with increases in the
calcination temperature or holding time. This result is highly consistent with that obtained in XPS measurements (Fig. 7). With a further increase in the calcination temperature to 1073 K, the signals were located at \( g = 1.9995, 2.0063 \) and 2.0093. The EPR signal at \( g = 2.0093 \) should reasonably correspond to the superoxide radical anions, and other researchers [46–48] have proven as such. In addition, the signal at \( g = 2.0063 \) is attributed to the electrons trapped on oxygen vacancies, which has been confirmed in published works [16,26,49]. From the above results, we can draw a conclusion that bulk defects including Ti\(^{3+}\) and/or oxygen vacancies formed in rutile TiO\(_2\) and the defect amounts increased with an increase in the calcination temperature or holding time.

The photocatalytic degradation of MB dye in aqueous solution under the irradiation of UV or visible light is shown in Fig. 9. Under the irradiation of UV light, sample 873 K-10 h shows the highest photocatalytic activity in the first round and the MB concentration decreased to below 70% of the original concentration within six hours. However, sample 973 K-10 h shows the best photocatalytic performance in the second and third rounds, and the MB concentration decreased to below 70% of the initial concentration. On the other hand, sample 973 K-10 h shows the best photocatalytic performance under the irradiation of visible light. Therefore, we believe that sample 973 K-10 h has the best photocatalytic activity whether under UV light or visible light irradiation.

The photocatalytic activity of TiO\(_2\) photocatalyst coatings depends on various factors including pollutant adsorption on the photocatalyst, absorption properties, contact area, crystal phase, surface morphology, and others. We found that the photocatalytic activity of all the as-prepared TiO\(_2\)/SnO\(_x\) composite coatings is not as high as that of nanosized photocatalysis particles in published works. This should be ascribed to the small specific area of no more than one m\(^2\) g\(^{-1}\). Among the as-prepared samples, sample 1073 K-10 h shows the lowest photocatalytic activity. Although Ti\(^{3+}\) defects were formed in the surface of the composite coatings (Fig. 7a), numerous bulk defects including oxygen vacancies and/or Ti\(^{3+}\) ions serving as electron capture centers [20,21] accelerate the recombination of photogenerated electron-hole pairs. The photocatalytic activity of TiO\(_2\)/SnO\(_x\) composite coatings increases with the increase of the calcination temperature from 873 K to 973 K or with an increase in the calcination time from five to ten hours (Fig. 9). We also note that the bulk defect concentration increased with the increase in the calcination temperature. Sample 973 K-10 h shows the greatest photocatalytic activity, which corresponds to moderate bulk oxygen vacancies. In other words, a proper amount of bulk defects is beneficial to enhance the photocatalytic activity of TiO\(_2\)/SnO\(_x\) composite coatings whether under UV light or visible light. This deduction is contradictory to the conclusion that bulk defects decrease the photocatalytic activity of photocatalysts in other works [20,21]. On the other hand, our conclusion agrees with that published by Wang [50]. He believed that both bulk defects and surface defects could enhance the photocatalytic activity.

4. Conclusions

TiO\(_2\)/SnO\(_x\) composite coatings were prepared by ball milling followed by calcination. Direct observation with Cs-corrected STEM
confirmed the formation of bulk oxygen vacancies in the form of cluster rather than individual site in rutile TiO$_2$. With an increase in the calcination temperature or holding time, bulk defects including oxygen vacancies and/or Ti$^{3+}$ also increased. Although surface Ti$^{3+}$ defects formed, sample 1073 K-10 h showed the lowest photocatalytic activity, which should be ascribed to the great bulk defect concentration. With a moderate concentration of bulk defects, sample 973 K-10 h showed the best photocatalytic activity under their radiation of UV light or visible light. A moderate concentration of bulk oxygen vacancies should be helpful in enhancing the photocatalytic activity.

**Acknowledgements**

The National Nature Science Foundation of China (No. 51404170) and the Scientific Research Foundation of Tianjin University of Science & Technology (No. 10220) financially supported this work. All the authors have no competing interests to declare.

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