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Photocatalytic performance of TiO₂ nanocrystals with/without oxygen defects

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ABSTRACT

To investigate the role of oxygen defects on the photocatalytic activity of TiO₂, the TiO₂ nanocrystals with/without oxygen defects are successfully synthesized by the hydrothermal and sol-gel methods, respectively. The as-prepared TiO₂ nanocrystals with defects are light blue and the absorption edge of light is towards the visible light region (~420 nm). Raman and X-ray photoelectron spectroscopy (XPS) measurements all confirm that the concentration of oxygen vacancies in the TiO₂ synthesized by the sol-gel method is less than that synthesized through the hydrothermal route. The introduction of oxygen defects contributes to a new state in the band gap that narrows the band gap, which is the reason for the extension of light absorption into the visible light region. The photocurrent results confirm that this band-gap narrowing enhances the photocurrent response under simulated solar light irradiation. The TiO₂ with oxygen defects shows a higher photocatalytic activity for decomposition of a methylene blue solution compared with that of the perfect TiO₂ sample. The photocatalytic mechanism is discussed based on the density functional theory calculations and photoluminescence spectroscopy measurements.

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1. Introduction

Since Fujishima et al. [1] observed the phenomenon of photocatalytic water splitting on TiO₂ electrodes in 1972, semiconductor photocatalysis has received much attention. Recently, many semiconductors have been used as photocatalysts. TiO₂ is one of the most important photocatalysts, because of its low cost, non-toxicity, high stability and relatively high photo-

catalytic activity. However, the large band gap of TiO₂ seriously restricts its application in photocatalysis because it can only absorb ultraviolet light, and the energy of ultraviolet light only constitutes for a small fraction of sunlight (~4%), while the visible light constitutes for a large fraction of sunlight (~45%). Therefore, it is significant to enhance the visible light response for TiO₂ photocatalysts [2–6]. Recently, many attempts have been made to enhance the visible light response for photoca-

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talysis, such as doping with metals/non-metals [7–11], depositing noble metals [12–14], constructing heterojunctions [15–22], working with photosensitizers [23], and coupling with carbon materials [24–27]. Among the above methods, impurity doping is a useful method to enhance the visible light adsorption for TiO_2 [28–31]. However, doping will usually effect the thermal and crystal stability and increase the recombination of photogenerated carriers because of the dopant-induced trap levels in the energy band for e^-h^+ pairs.

Compared with doping metals/non-metals, Ti^{3+} defects or oxygen vacancies are kinds of self-doping that preserve the intrinsic TiO_2 structure, and is an efficient way to enhance the photocatalytic performance [32–34]. The oxygen defect can enhance the visible light response and improve the photocatalytic activity, which has been confirmed for many materials, such as ZnO [35,36], C_3N_4 [37–39], CeO_2 [40], CsTaWO_6 [41], MoS_2 [42], $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ [43], and WO_3 [44]. The defect mediated synthesis of these materials usually involves annealing in a reducing atmosphere or under high vacuum at high temperature [45]. These methods usually suffer from some drawbacks, such as requiring complicated facilities or a high energy consumption. Hence, the challenge remains to find a simple and useful method to prepare TiO_2 with an oxygen vacancy. Furthermore, only minimal systematic investigations exist where the mechanism of how oxygen vacancies effect the photocatalytic performance of TiO_2 has been studied.

In this work, to explore how oxygen defects influence the photocatalytic activity of TiO_2 , the TiO_2 nanocrystals with/without defects are prepared by the hydrothermal and sol-gel methods, respectively. The TiO_2 obtained from the hydrothermal method shows a dramatically increased photocatalytic activity owing to the formed bulk defects. However, the perfect TiO_2 shows a slightly lower photocatalytic activity. The mechanism of how the oxygen defects effect the photocatalytic performance of TiO_2 is further studied by density functional theory (DFT) calculation and photoluminescence (PL) spectroscopy. It is hoped that this work will provide new insight for controlling crystal defects to improve the photocatalytic performance.

2. Experimental

2.1. Material synthesis

For the synthesis of anatase TiO_2 (A- TiO_2) nanocrystals with defects, the hydrothermal method was used. First, TiCl_4 (0.35 mL) was added to distilled water (20 mL), then HF (1 mL) was added to the above reaction solution and stirred for 10 min. Second, the above reaction solution was transferred to a 30 mL autoclave and maintained at 180 °C for 12 h. Finally, the as-prepared samples were washed several times with distilled water and ethanol, respectively, then dried in a vacuum oven at 70 °C for 6 h. For the synthesis of perfect A- TiO_2 nanocrystals, the sol-gel method was used. First, TiCl_4 (2 mL) was added to ethanol (15 mL) and stirred for 10 min. The solution was gelatinized for 5 d to form a sol-gel. Second, the sol-gel solution was vaporized at 80 °C. The dry-gel precursor was calcined at

400 °C for 5 h in air.

2.2. Characterization

The crystalline structures of the as-prepared samples were investigated by X-ray diffraction (XRD) using a Bruker (D5005) X-ray diffractometer equipped with graphite monochromatized $\text{Cu } K_\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) was measured using a Sigma Probe X-ray photoelectron spectrometer (ThermoVG, U. K.) with a source of $\text{Al } K_\alpha$ radiation (1486 eV). The Raman spectrometer (Bruker SEN-TERA 200 LX model) employed a solid-state laser with an excitation wavelength of 532 nm. Field emission scanning electron microscopy (FESEM) images were obtained using a scanning electron microscope (Hitachi S-4800). The absorption spectra of the as-prepared samples were recorded using ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS) using a Jasco V670 spectrometer, with BaSO_4 as a reference.

2.3. Photocatalytic performance test

The photocatalysis performance was studied in a cylindrical borosilicate glass reactor vessel with a volume of 500 mL. A 150 W sodium vapor lamp (OSRAM Vialox NAV-TS Super 150 W) was used as the light source. The photocatalyst (0.10 g) was added to an aqueous MB solution (250 mL). Before irradiation with simulated solar light, the above reaction solution was stirred in the dark for 30 min to maintain the adsorption equilibrium between the dye and TiO_2 particles. The photocatalytic performance was analyzed by using a UV-Vis spectrophotometer (Perkin-Elmer Lambda 45) and the concentration of MB was monitored at 664 nm.

The photoelectrochemical property was measured by a conventional three-electrode system. The ITO glass stuck to the as-prepared TiO_2 samples was used as the working electrode, a Pt wire as the counter electrode and a calomel electrode as the reference electrode. An Na_2SO_4 aqueous solution (0.1 mol/L) was used as the electrolyte. The photocatalysts (5 mg) were added into ethanol (1 mL) to make an homogeneous slurry and then was coated onto 2 cm × 4 cm ITO glass for use as an electrode. EIS Nyquist plots were obtained with an amplitude of 5 mV for the frequency range from 10^5 to 1 Hz at a bias voltage of 0.34 V.

2.4. Theoretical calculations

All the calculations were performed with the Vienna Ab initio simulation package (VASP) [46,47], based on the DFT method and the generalized gradient approximation adopting the functional of Perdew et al. (GGA-PW91) [48]. The electron-ion interaction was described by the projector augmented-wave (PAW) method [49,50], and for a plane wave basis set where a cutoff energy of 400 eV was used. The lab model was used to simulate the catalyst surface, and the (101) surface of A- TiO_2 was selected in this work, because the (101) facet is the most stable facet among all of the A- TiO_2 exposed facets [51]. The surfaces were modeled by a periodical array of six atomic

layers and separated by 15 Å of a vacuum region. A $p(2 \times 2)$ for A-TiO₂ (101) was considered. The top three atom layers of A-TiO₂ (101) were allowed to relax in the calculation, whereas the bottom atom layers of the slab were fixed. The Brillouin-zone integrations were performed using a $2 \times 2 \times 1$ Monkhorst-Pack grid, which has been tested and shown to be a reasonable k-points grid [52]. The structural optimization was performed with a termination criterion of 0.05 eV/Å for the atomic forces.

3. Results and discussion

3.1. Structure

The phase and structure of TiO₂ nanocrystals with/without defects were studied by XRD measurement. As depicted in Fig. 1(a), both samples exhibited diffraction peaks, which could be indexed to the anatase phase (JCPDS No. 21-1272). Although the difference in the synthesis method was obvious, the crystalline structures of the two as-prepared A-TiO₂ nanocrystals were almost the same with the anatase phase well preserved. The diffraction peaks were broadened, which indicated that the synthesized TiO₂ crystals were small. The average crystallite sizes of the as-synthesized A-TiO₂ samples were calculated, using the Scherrer equation from the diffraction peak of the A-TiO₂ (101) facet, to be 10 and 8 nm for the hydrothermal and sol-gel methods, respectively.

Raman spectroscopy was also used to study the crystalline structure of the as-prepared samples, as shown in Fig. 1(b). From the Raman spectrum, it was clear that there were three Brillouin zones located at 396, 517 and 636 cm⁻¹, which corresponded to B_{1g}, A_{1g} and E_g, respectively. This result was in agreement with the Raman peaks of A-TiO₂ [53]. Thus, both the Raman and XRD analyses confirmed that the as-synthesized samples by the two different methods were in the anatase phase.

3.2. Morphology

Fig. 2(a) and (b) show the SEM images of TiO₂ nanocrystals prepared by the sol-gel and hydrothermal methods, respectively, both of which showed a morphology of small nanoparticles. However, the diameter of TiO₂ nanocrystals synthesized

Fig. 2. SEM and HR-TEM images of the as-prepared TiO₂ samples by the sol-gel method (a, c) and by the hydrothermal method (b, d).

by the sol-gel method (8 nm) was smaller than that synthesized by the hydrothermal method (10 nm). To confirm the morphology of the as-prepared TiO₂ nanoparticles, a TEM measurement was performed. Fig. 2(c) and 2(d) show the high-resolution TEM images of the as-prepared TiO₂ samples, where, again, the diameter of the nanocrystal was approximately 8 nm for the TiO₂ prepared by the sol-gel method and approximately 10 nm for the TiO₂ prepared by the hydrothermal method. Additionally, the crystallite size from the TEM result was consistent with that calculated from the XRD analyses (Fig. 1(a)). From the high-resolution TEM images, the lattice spacing was ~0.241 nm, which corresponded to the (101) planes of A-TiO₂. This indicated that the exposed crystal facets were (101) facets, and the (101) facet was indeed the most stable facet among the A-TiO₂ surfaces because of its low surface energy [54].

3.3. XPS

XPS measurements were employed to investigate the composition and chemical states of the as-synthesized TiO₂ samples (Fig. 3). The binding energy of 284.42 eV was corrected with C 1s. The survey XPS spectra showed that the characteristic

Fig. 1. (a) XRD patterns and (b) Raman spectra of the as-prepared TiO₂ samples.

Fig. 3. XPS spectra of defect and perfect TiO₂. (a, d) Survey scan; (b, e) Ti 2p spectra; (c, f) O spectra.

peaks of Ti, O and C elements were in the binding energy range of 0–700 eV. The emerged C peak was attributed to the carbon supporting film on the TEM grid. The peaks of both samples having binding energies of 458.3 and 464.4 eV corresponded to 2p_{3/2} and 2p_{1/2} of the Ti atom, which verified the identical existence state of Ti⁴⁺ in both TiO₂ samples [55], that is, there were no obvious differences for the XPS spectra of Ti 2p for the two TiO₂ samples. Based on the Gaussian curve fitting, the O 1s XPS spectra was separated into two peaks, at 529.7 and 531.7 eV, and these peaks were assigned to O²⁻ species in the crystal lattice (O_L) and oxygen vacancies (O_V), respectively [56–58]. The signals of oxygen species observed at 531.7 eV could be assigned to either surface hydroxyl groups (Ti-OH), H₂O, or oxygen defects on the TiO₂ surface. However, because of the high vacuum in the XPS system, the Ti-OH and H₂O could easily be desorbed and removed, thus the signal could be assigned to oxygen defects. From the XPS results, the O_V (531.7 eV) of O 1s showed a higher intensity for the sample prepared by the sol-gel method (Fig. 3), which indicated that the sample pre-

pared by the hydrothermal method had a higher density of surface oxygen defects. The more the surface oxygen defects, the more the trapping of photoinduced electrons and holes, and the better the photocatalytic performance.

3.4. Optical property

The optical adsorption of the TiO₂ nanocrystals with/without oxygen defects was studied using the UV-Vis DRS measurements. In Fig. 4(a), both of the samples showed a strong UV absorption, owing to the intrinsic band gap of A-TiO₂ [59]. The absorption edge of the A-TiO₂ with defects exhibited an enhanced visible light response compared with the A-TiO₂ without defects. The optical absorption calculation was conducted according to the equation $ah\nu = A(h\nu - E_g)^{n/2}$, where α , ν , E_g and A are the absorption coefficient, the light frequency, the band gap and a constant, respectively [60]. The band gaps were 2.88 and 3.03 eV for the TiO₂ nanocrystals with/without oxygen defects, respectively (Fig. 4(b)), where it was clearly shown

Fig. 4. UV-Vis DRS spectra (a) and the plot of the transformed Kubelka-Munk function versus the energy of the light absorbed (b) for the TiO₂ samples with/without defects.

Fig. 5. Degradation curves (a) and kinetic curves (b) of MB catalyzed by the as-prepared TiO_2 photocatalysts.

that the oxygen defect contributed to the enhancement of the visible light adsorption of TiO_2 . The ability of visible light absorption was also reflected by their physical light-blue appearance, which possibly arose from the formation of V_O sites [61–63].

3.5. Photocatalytic performance

The photocatalytic performance of the above two TiO_2 samples was examined by the photodegradation of an MB aqueous solution under simulated solar light irradiation. Fig. 5 shows the decrease in C/C_0 , that is, the MB concentration ratio, when photocatalysts were added into the reaction solution under simulated solar light irradiation. The photocatalytic performance of the two TiO_2 samples was different for the degradation of MB. After irradiation for 1 h, the fraction of decomposed MB was approximately 20% and almost 100% for the TiO_2 nanocrystals with/without oxygen defects, respectively (Fig. 5(a)). Obviously, the TiO_2 samples with defects showed a higher photocatalytic activity compared with the TiO_2 samples without defects. Fig. 5(b) shows the apparent reaction rate constant (k) for MB degradation, which was extracted from the first hour reaction data. From the fitted kinetic constants, the rate constant for the degradation of MB for the TiO_2 nanocrystals with defects was almost 10 times faster than that for the perfect TiO_2 nanocrystals. This could be explained by the more defects on TiO_2 surface, the more active positions that could be provided at the exposed facets. Another reason was the enhanced light adsorption of this sample. Hence, the photocatalytic performance of TiO_2 nanocrystals could be enhanced by controlling the crystal defects through different synthesis methods.

3.6. Photocurrent

The photocatalytic performance of photocatalysts is largely affected by the separation efficiency of their photogenerated e^- – h^+ pairs. Fig. 6 shows that the photocurrent densities of as-prepared A- TiO_2 samples under simulated sunlight irradiation. The as-prepared TiO_2 nanocrystals with defects displayed highly reproducible on-off cycles for many times. The photocurrent value dropped to zero as the light was switched off, and

the photocurrent restarted again as soon as the light was switched on. The A- TiO_2 crystal with defects had a higher photocurrent density ($8.3 \mu\text{A}/\text{cm}^2$) than that of the A- TiO_2 crystal without defect ($1.2 \mu\text{A}/\text{cm}^2$). The higher photocurrent value was a result of the higher separation efficiency of the photo-generated e^- – h^+ pair in the TiO_2 nanocrystals with defects. The higher separation efficiency of the photogenerated e^- – h^+ pair for the TiO_2 nanocrystals with defects agreed well with its higher photocatalytic activity for the degradation of an MB solution.

3.7. PL spectroscopy

PL spectra of the as-prepared TiO_2 samples with/without defect excited by light with a wavelength of 350 nm are shown in Fig. 7(a). A strong broad peak at 415 nm was observed for both A- TiO_2 samples. Furthermore, multiple PL signals could be observed in the visible region and the center was at 475 nm, which was related to the traps on surface oxygen defects, and was consistent with the literature reports [64]. This intensity change of PL signals was consistent with the light absorption increases for the TiO_2 with defects compared with the TiO_2 without defects, and the mechanism of the PL emission is shown in Fig. 7(b). This PL result further supported the XPS and Raman results, that is, the existence of oxygen defects in A- TiO_2 as prepared by the hydrothermal method play an important role in photocatalysis.

Fig. 6. Photocurrent response of the as-prepared TiO_2 samples.

Fig. 7. (a) PL spectra of the as-prepared TiO_2 samples with/without defects; (b) Mechanism of photoluminescence for the A- TiO_2 with an oxygen vacancy.

3.8. DFT calculation

To further understand the role of oxygen defects on the performance of TiO_2 photocatalysts, a slab model was built for simulating the catalyst surface, and DFT calculations were used to study the electronic structure. An oxygen defect was created by removing one oxygen atom from the clean A- TiO_2 (101) surface, because the (101) surface was the most stable facet among the A- TiO_2 exposed surfaces. The optimized structures of A- TiO_2 (101) surfaces with/without defects are shown in Fig. 8(a) and (b). From the optimized structures, an oxygen vacancy contributed a small structural change for the A- TiO_2 (101) surface, while the band structure was substantially changed. From the electronic density of states (DOS) results (Fig. 8(c) and (d)),

it could be seen that a new state appeared below the conduction band, which resulted in the narrowing of the band gap from 2.30 to 2.00 eV. This narrowed band gap contributed to expanding the range of light absorption and lowering the excitation energy for electron activation, which increased the charge carrier density. This was further confirmed by the photocatalytic and photocurrent experimental results.

3.9. Photocatalytic mechanism

Fig. 9 shows the proposed photocatalytic mechanism of the as-prepared TiO_2 nanocrystals with/without oxygen defects in the photocatalytic process. As an electron and hole trap, oxygen vacancies play a key role in photocatalytic degradation through inhibition of the e^-h^+ pair recombination. The PL band cen-

Fig. 8. Optimized geometries of the A- TiO_2 (101) surface without (a) and with (b) oxygen vacancies. The calculated density of states of the A- TiO_2 (101) surface without (c) and with (d) an oxygen vacancy.

Fig. 9. Photocatalytic mechanism for an oxygen defect in TiO₂ under simulated sunlight irradiation.

tered at 475 nm agreed well with the fluorescence emission of oxygen vacancies [65]. This result also agreed well with the band gap based value determined from the DFT calculation. Under simulated solar radiation, the excited electrons were captured by oxygen vacancies on the surface of TiO₂ and reacted with O₂²⁻ to produce superoxide O₂^{·-}. The photogenerated holes from the valence band reacted with OH⁻ to produce ·OH radicals. With the emergence of oxygen vacancies, the decrease of the fluorescence intensity corresponded to the reduction of recombination or internal consumption of the e⁻-h⁺ pair, which was beneficial for the enhancement of the photocatalytic efficiency. Thus, oxygen vacancies act as electron traps. The direct excitation of electrons from the valence band to the level of the oxygen vacancy by visible light irradiation is shown in Fig. 9. The photogenerated electrons then joined the redox reaction for the photocatalytic decomposition of the MB dye.

4. Conclusions

In this work, both A-TiO₂ nanocrystals with/without oxygen defects have been successfully synthesized by the hydrothermal and sol-gel methods, respectively. The obtained TiO₂ with defects exhibits a light blue color, and has enhanced visible light absorption. Both Raman and XPS results confirm that the concentration of oxygen vacancies in the TiO₂ prepared by the sol-gel method is less than that in the TiO₂ prepared by the hydrothermal method. The introduction of oxygen defects contributes to the band gap narrowing and enhancement of the

visible light response of the TiO₂ with defects, which is confirmed by the photocurrent measurement. The as-prepared TiO₂ sample with defects also shows an improved performance for the photocatalytic decomposition of an MB solution. Based on the DFT calculations and photoluminescence spectroscopy results, the mechanism of enhancing the photocatalytic performance can be attributed to the introduction of a doping state in the band gap through the introduction of an oxygen vacancy into TiO₂.

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Graphical Abstract

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TiO₂ nanocrystals with/without oxygen defects have been successfully synthesized by the hydrothermal and sol-gel methods, respectively. The obtained TiO₂ with defects exhibits an enhanced photocatalytic performance.

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无缺陷和氧缺陷二氧化钛的光催化活性

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摘要: 随着全球工业的发展, 大量有机污染物排放到水中, 已经威胁到人类健康. 自1972年Fujishima和Honda发现TiO₂半导体材料可在光照下分解水以来, 光催化技术作为一种新型污水处理方法引起广泛重视. 近几十年来, 光催化已被广泛研究, 已成为水体净化领域最有前途的方法之一. TiO₂光催化剂由于具有无毒、耐腐蚀、高稳定和低成本等特点, 在光催化领域

受到广泛关注,是最具有开发前景的光催化材料之一。然而, TiO_2 的禁带较宽,只能吸收仅占太阳光4%的紫外光部分,这严重限制了 TiO_2 光催化材料对太阳光的有效应用。最新研究结果表明,适量缺陷的存在可以拓展 TiO_2 对可见光的响应,从而通过提高其对太阳光的利用效率来有效提升 TiO_2 的光催化活性。因此,研究半导体缺陷与其光催化剂性能的关系,对于提升光催化污染物降解性能具有重要意义。

本工作采用水热法和溶胶-凝胶法分别制备了具有氧缺陷的和无缺陷的 TiO_2 ,用于研究氧缺陷对 TiO_2 光催化活性的影响。所制备的氧缺陷 TiO_2 纳米材料为浅蓝色,光的吸收波长向可见光区($\sim 420\text{ nm}$)拓展。拉曼光谱和X射线光电子能谱(XPS)测试均证明溶胶-凝胶法制备的 TiO_2 中氧空缺位的浓度低于水热合成 TiO_2 的氧空缺位浓度。光化学测试结果表明,氧缺陷 TiO_2 在模拟太阳光下的光电流响应增强,这是由于氧缺陷的引入导致能带隙内出现了新的电子态,使得禁带宽度变窄。在光降解亚甲基蓝(MB)的实验中,氧缺陷 TiO_2 材料表现出更高的光催化活性。根据密度泛函理论(DFT)计算和荧光光谱测试结果,讨论了氧缺陷 TiO_2 的光催化机理。

关键词: 二氧化钛; 缺陷; 光学性质; 光催化活性; 密度泛函理论计算

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