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Synergic effects of Cu_xO electron transfer co-catalyst and valence band edge control over TiO_2 for efficient visible-light photocatalysis

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ABSTRACT

Bandgap engineering by doping and co-catalyst loading are two primary approaches to designing efficient photocatalysts by promoting visible-light absorption and charge separation, respectively. Shifting of the TiO_2 conduction band edge is frequently applied to increase visible-light absorption but also lowers the reductive properties of photo-excited electrons. Herein, we report a visible-light-driven photocatalyst based on valence band edge control induced by oxygen excess defects and modification with a Cu_xO electron transfer co-catalyst. The Cu_xO grafted oxygen-rich TiO_2 microspheres were prepared by ultrasonic spray pyrolysis of the peroxotitanate precursor followed by a wet chemical impregnated treatment. We found that oxygen excess defects in TiO_2 shifted the valence band maximum upward and improved the visible-light absorption. The Cu_xO grafted onto the surface acted as a co-catalyst that efficiently reduced oxygen molecules to active intermediates (i.e., $\text{O}_2^{\cdot-}$ radical and H_2O_2), thus consuming the photo-generated electrons. Consequently, the Cu_xO grafted oxygen-rich TiO_2 microspheres achieved a photocatalytic activity respectively 8.6, 13.0 and 11.0 as times high as those of oxygen-rich TiO_2 , normal TiO_2 and Cu_xO grafted TiO_2 , for degradation of gaseous acetaldehyde under visible-light irradiation. Our results suggest that high visible-light photocatalytic efficiency can be achieved by combining oxygen excess defects to improve visible-light absorption together with a Cu_xO electron transfer co-catalyst. These findings provide a new approach to developing efficient heterojunction photocatalysts.

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1. Introduction

Semiconductor oxides, in particular TiO_2 , possess excellent activity and stability for photocatalytic applications, but are limited by rapid charge recombination and the requirement for UV light irradiation [1–8]. Co-catalysts are known to provide electrons/holes trap sites, which can promote charge transfer, and inhibit charge recombination [9–12]. Noble metals are

effective and commonly used co-catalysts; however, the use of these materials is limited by their costliness and scarcity [13–15]. Recently, noble-metal-free materials, such as transition metals, transition metal sulfides and oxides, and carbon-based materials have been widely studied as co-catalysts for degradation of toxic-substances, water splitting, and CO_2 conversion [16–20]. Therein, transition metal oxides (e.g., Co-, Ni-, Cu-, and Fe- oxides) are promising co-catalysts owing to

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their earth-abundant nature, low-toxicity, and highly efficient charge transfer properties [21–29]. These co-catalysts can also render TiO_2 sensitive to visible-light, albeit weakly, by introducing a pathway for photoinduced interfacial charge transfer [30]. Based on the surface modification by electron transfer co-catalysts and conduction band edge control by donor defects, it is possible to simultaneously realize electron transfer and visible-light response from TiO_2 [31–33]. Hashimoto et al. [31] obtained efficiency visible-light TiO_2 photocatalysts by combining a metal oxide nanocluster co-catalyst with conduction band edge control over TiO_2 . We also studied the synergistic effects of the Fe-species co-catalyst and surface oxygen vacancy defects on TiO_2 photocatalysts under visible light irradiation [32]. However, this strategy is potentially limited by the decreased reduction ability of electrons at donor defect sites and the difficulty of achieving one-electron reduction of absorbed oxygen molecules to superoxide radicals.

Oxygen defects are intrinsic and fundamental defects in TiO_2 (and other semiconductor oxides) for bandgap engineering and modifying photoelectric properties [34–37]. In addition to the use of oxygen-deficient defects in TiO_2 for conduction band edge control, oxygen excess defects also offer a way to improve visible-light absorption through valence band edge control, because TiO_2 has a sufficiently high photo-oxidizing capacity [38–42]. Etacheri et al. [38] reported that oxygen-rich TiO_2 features a higher valence band maximum (VBM), high temperature stability, and enhanced visible-light photocatalytic activity. Tan et al. [39] also verified that oxygen-rich TiO_2 had high photo-activity towards CO_2 reduction under visible-light irradiation. Wang et al. [40] fabricated oxygen-rich TiO_2 nanoparticles with Ti vacancies, which exhibited p-type conduction characteristics and a shifted valence band (VB) edge. Moreover, oxygen-rich TiO_2 is highly stable owing to the large energy of formation of oxygen excess defects [41]. Therefore, it is hypothesized that, combining co-catalysts to improve electron transfer and raising the valence band edge by the introduction of oxygen excess defects for visible-light absorption is a potential strategy to enhance the photocatalytic activity of TiO_2 .

To date, the main strategies for obtaining oxygen-rich TiO_2 have been limited to calcination of peroxo-titania xerogels or solvothermal methods [38–41]. There is a need to develop simple and high-yield strategies for the fabrication of oxygen-rich TiO_2 with favorable particle dispersions and large surface areas. Ultrasonic spray pyrolysis (USP) is a powerful and easy-to-operate method for producing microspheres [43–45]. With the use of USP, microspheres become stacked with a large amount of small nano-grains, which exhibit a porous structure with a well-dispersed and homogeneous composition distribution [46–48]. Moreover, co-catalysts are more uniformly supported on the microspheres owing to their porous structure. Herein, we combine a Cu_xO co-catalyst with TiO_2 microspheres containing oxygen excess defects by USP of a peroxo titanate precursor followed by a wet chemical impregnation treatment. The oxygen excess defects shifted the valence band maximum of the TiO_2 upward and improved the visible-light absorption. The Cu_xO acted as an electron transfer co-catalyst, inducing multi-electron reduction of the oxygen

molecule, thus promoting charge separation. In this way, the combination of oxygen excess defects and the Cu_xO co-catalyst promoted the photocatalytic activity of TiO_2 microspheres for degradation of gaseous acetaldehyde under visible light irradiation.

2. Experimental

2.1. Preparation of normal and oxygen-rich TiO_2 microspheres

The USP method was used to prepare normal and oxygen-rich TiO_2 microspheres. Fig. 1 shows a schematic representation of the fabrication procedure. For the normal TiO_2 microspheres, 7.9 mL of TiCl_4 (99.9%) was gently injected into 500 mL ice water to obtain a transparent aqueous solution, then, 50 mL of $\text{NH}_3\cdot\text{H}_2\text{O}$ (25 wt%) was added and a white precipitate was formed. This white precipitate was a titanate precursor (TP), which was washed well with deionized water to remove Cl^- and NH_4^+ . The TP aqueous solution was atomized by an ultrasonic nebulizer, and the mist passed through an 800 °C quartz tube, resulting in the formation of white normal TiO_2 microspheres (named as TP- TiO_2) from the electrostatic collecting device. For the oxygen-rich TiO_2 microspheres, 100 mL of H_2O_2 (30 wt%) was dissolved into the TP aqueous solution to obtain a peroxo titanate precursor (PTP). The oxygen-rich TiO_2 microspheres (denoted as PTP- TiO_2) were also obtained by ultrasonic spray pyrolysis of the PTP aqueous solution with the same USP process used to produce the TP- TiO_2 microspheres. The PTP- TiO_2 microspheres were calcined at 500 °C under an air atmosphere. The freshly prepared PTP- TiO_2 microspheres and those calcined for 10 and 60 min are denoted as PTP- TiO_2 -Fresh, PTP- TiO_2 -10 min, and PTP- TiO_2 -60 min, respectively. In comparison, the normal TP- TiO_2 sample was only calcined at 500 °C for 60 min.

2.2. Loading Cu_xO co-catalyst on TP- TiO_2 and PTP- TiO_2 microspheres

The Cu_xO was deposited on the surface of the TP- TiO_2 -60 min and PTP- TiO_2 -60 min microspheres by a wet chemical impregnated route. The samples were dispersed into CuCl_2 aqueous solution (mass fraction of Cu compared with TiO_2 was 0.1 wt%) and the mixture was stirred at 90 °C for 1 h. The sus-

Fig. 1. Synthesis procedure of the oxygen-rich TiO_2 and Cu_xO -grafted oxygen-rich TiO_2 microspheres.

pension was washed with distilled water and dried at 110 °C for 24 h. Afterwards, the Cu_xO-TP-TiO₂ and Cu_xO-PTP-TiO₂ microspheres were obtained. We also prepared 0.25-, 0.5-, and 1 wt% Cu_xO-grafted PTP-TiO₂-60 min microspheres by the same approach.

2.3. Characterization

The morphology of the samples were studied with a scanning electron microscope (SEM; FEI Quanta250 instrument), transmission electron microscope (TEM; JEOL JEM-2100 instrument). Inductively coupled optical emission spectrometry (ICP-OES; Leeman, Plodigy ICP) measurement was conducted to determine Cu content. The samples were digested by 10-mL of nitric acid (68%), 10-mL of nitric acid (37%) and 5-mL of hydrofluoric acid (40%) at 150 °C for 3 h. The obtained solution was diluted and fed into the ICP-OES and the RF power was set to 1200 W with a plasma gas flow rate of 15 L min⁻¹. The N₂ adsorption-desorption isotherms was measured in a micromeritics ASAP 2020 analyzer at -196 °C. Brunauer-Emmett-Teller (BET) specific surface area, pore volumes (VP), and pore diameters (DP) of the samples were evaluated from the adsorption branches of the nitrogen isotherms based on the BET and Barrett-Joyner-Halenda (BJH) model). X-ray diffraction (XRD; Rigaku, D/max-2500 X-ray diffractometer) was measured at a scan rate of 1°/min in steps of 0.002°. The lattice parameters of the samples were calculated with Unitcell software. Unitcell is a program which refines lattice parameters from powder diffraction data by a non-linear least squares method. Fourier transform infrared (FTIR) spectra were recorded using a Nicolet Magna 560 FTIR spectrometer. X-ray photoelectron spectroscopy (XPS) experiments were performed on a VGESCA LAB MKII instrument with an Mg K_α ADES ($h\nu = 1253.6$ eV) source. UV-vis diffuse reflectance (DR) spectra of the samples were collected on a PerkinElmer UV WinLab spectrophotometer, and BaSO₄ was used as a reference.

2.4. Photocatalytic measurements

The photocatalytic activity was evaluated in a 500-mL gas-tight top-irradiation-type reaction vessel with an quartz window and contained with the synthetic air (O₂/N₂, 20:80, vol/vol) under ambient conditions, allowing for visible, simulated solar, and UV light irradiation. The target volatile organic compound (VOC) was 200 ppm of the acetaldehyde gas. Samples of catalyst (100 mg) were spread over a 2 cm² area for irradiation in the presence of the target pollutant gas and kept in the dark for 30 min. A 150 W xenon lamp (Hayashi LA-410) was used to simulate solar irradiation (100 mW/cm²), with a 400-nm long-pass and 380-nm short-pass filters for visible-light (100 mW/cm², $\lambda > 400$ nm) and UV light (3 mW/cm², $\lambda < 380$ nm) irradiation, respectively. The acetaldehyde gas and the evolved CO₂ were analyzed by a gas chromatograph (Shimadzu, GC-2014C). The photostability of the Cu_xO-grafted PTP-TiO₂ microspheres was evaluated through five cycles of gaseous acetaldehyde degradation under visible-light irradiation.

2.5. Luminol chemiluminescence (CL) probe method

The formation of O₂⁻ and H₂O₂ of the as-synthesized samples was monitored by with a luminol CL probe during photocatalytic reactions under visible-light (100 mW/cm², $\lambda > 400$ nm) irradiation. The CL intensity of luminol was detected with fluorescence spectrophotometer (Jobin Yvon FL3). Typically, 20 mg of photocatalyst was dispersed in an ethanol/water mixture (1:9, vol/vol; 20 mL, pH = 3.0). After ultrasonication (10 min) and O₂ bubbling (10 min), the solution was irradiated by visible-light and continuously stirred. Every 2 h, 1 mL of sample was extracted and filtered for detection. The luminol (7 mmol/L, 98%), peroxidase (1 mg/mL, POD, horseradish), and sodium phosphate buffer (pH = 8.0) were prepared for the following detection.

Measurements of O₂⁻

Immediately after visible-light irradiation, 1 mL of filtered sample, 0.95 mL of phosphate buffer, and 0.05 mL of luminol were mixed and stirred for 10 s. The CL intensity of the luminol excitation at 310 nm and emission at 425 nm were detected with the fluorescence spectrophotometer and used to calculate the concentration of O₂⁻ generated during irradiation.

Measurements of H₂O₂

A 1-mL portion of filtered sample was extracted and stored in the dark for 30 min after irradiation because the O₂⁻ disappeared within 30 min of its formation. Then 0.05-mL of luminol (7 mmol/L) was added. The sample was again stored for 10 min in dark. A 0.05-mL portion of the POD and 0.9 mL of phosphate buffer were then injected into the sample and stirred for 10 s. The CL intensity of the luminol, corresponding to the amount of H₂O₂, was then detected by the fluorescence spectrophotometer.

Calibration of the CL intensity

A 1-mL portion of the sample solution (ethanol/water mixture, 1/9 vol/vol, pH = 3.0), 0.05 mL of H₂O₂ (0, 20, 100, 200 mmol/L), 0.05 mL of luminol (7 mmol/L), 0.05 mL of POD (1 mg/mL), and 0.9 mL of phosphate buffer (pH = 8.0) were mixed and stirred for 10 min. Then, the CL intensity of the samples was detected with a fluorescence spectrophotometer. The observed CL intensity was plotted as the function of the concentration of H₂O₂. The resulting CL intensity corresponded to the concentrations of O₂⁻ and H₂O₂.

3. Results and discussion

USP with the PTP and TP precursors was used to fabricate PTP-TiO₂ and normal TP-TiO₂ microspheres, respectively. Fig. 2(a) shows an SEM image of the PTP-TiO₂-60 min microspheres. The microspheres were spherical with a diameter of 200–2000 nm. The TP-TiO₂ microspheres had a similar morphology to that of the PTP-TiO₂-60 min microspheres. Fig. 2(b) shows that the as-synthesized microspheres were porous and compactly stacked with numerous small nanoparticles, as previously reported [42,48]. The crystal form of the PTP-TiO₂-60 min was assigned to anatase TiO₂ according to the high-resolution TEM (HRTEM) images, shown in Fig. 2(c) [49, 50]. We selected four different concentrations of Cu_xO for

Fig. 2. SEM (a), TEM (b), HRTEM (c) images of PTP-TiO₂-60 min microspheres; HRTEM (d) and TEM (e) images of the Cu₂O-PTP-TiO₂ microspheres; (f–h) TEM-EDS mapping of the O, Ti, and Cu elements in Cu₂O-PTP-TiO₂ microspheres.

grafting onto the surface of PTP-TiO₂-60 min. ICP-OES elemental analysis indicates that the weight fractions of Cu relative to TiO₂ were 0.035 wt%, 0.067 wt%, 0.152 wt%, and 0.545 wt%. The measured values were smaller than the starting stoichiometric ratios (0.05 wt%, 0.1 wt%, 0.25 wt%, and 1 wt%). Among these Cu_xO ratios, we mainly discussed the Cu_xO-PTP-TiO₂ with 0.1 wt% of Cu in the following. And, we denote the Cu_xO-PTP-TiO₂ sample as containing 0.1 wt% of the Cu_xO. According to the HRTEM image shown in Fig. 2(d), a small amount of Cu_xO clusters were observed on the surface of the Cu_xO-PTP-TiO₂ microspheres. Energy dispersive X-ray elemental (EDS) mapping obtained by TEM (Figs. 2(e)–(h)) confirmed the presence and even dispersion of Cu over the Cu_xO-PTP-TiO₂ microspheres. This feature is desirable for achieving the full potential of the co-catalyst.

In addition, the BET specific surface area and porous structure of the PTP-TiO₂-60 min and Cu_xO-PTP-TiO₂ were confirmed by nitrogen adsorption-desorption isotherms. The specific surface areas of PTP-TiO₂-60 min and Cu_xO-PTP-TiO₂ were found to be 19.8185 and 22.3678 m²/g, respectively. The N₂ adsorption-desorption isotherms in Fig. 3 were type IV of the Brunauer-Deming-Deming-Teller (BDDT) classification, indicating the existence of mesopores in both PTP-TiO₂-60 min and Cu_xO-PTP-TiO₂ microspheres [51]. The pore size distributions were calculated by the Barrett-Joyner-Halenda (BJH) method and are shown in the inset of Fig. 3. Both PTP-TiO₂-60 min and Cu_xO-PTP-TiO₂ exhibited a pore size distribution in the range of 1–10 nm centered at approximately 5 nm.

Fig. 4(a) shows XRD patterns of the TP-TiO₂, PTP-TiO₂, and Cu_xO-PTP-TiO₂ microspheres. The PTP-TiO₂-Fresh without calcination was amorphous. After annealing at 500 °C for 10 min, the PTP-TiO₂-10 min exhibited anatase crystallinity. As the annealing time was extended, anatase peaks of the PTP-TiO₂-60 min become sharper, and traces of rutile (4.2%) become visible. The XRD patterns showed no obvious differences among the Cu_xO-PTP-TiO₂ and PTP-TiO₂-60 min samples. We believe these similarities could be attributed to the very low Cu_xO content and its high dispersion. However, the normal TP-TiO₂-60 min exhibited only an anatase phase. A slight rutile phase in

PTP-TiO₂-60 min suggested the promotion of a phase transformation from anatase to rutile phase induced by H₂O₂ [52]. The diffraction peaks of PTP-TiO₂ shifted to lower angles compared with those of normal TP-TiO₂, as shown in Fig. 4(b) indicating lattice expansion. The lattice parameters of the PTP-TiO₂ samples were calculated with the Unitcell software, and are listed in Table 1. Lattice expansion of the PTP-TiO₂ samples was proposed to explain the formation of oxygen-excess defects in the TiO₂ lattice sites through pyrolysis of the PTP precursor.

Fig. 5 shows FTIR spectra of the samples. The obvious peak at 905 cm⁻¹ in the PTP xerogel was assigned to the stretching vibration of Ti-O-O bonds (peroxo-species) [53,54]. The FTIR spectra of the as-synthesized microspheres only exhibited vibrations of O-H (absorbed water) and O-Ti-O (TiO₂ lattice) groups [55]. Because the PTP-TiO₂ microspheres were prepared from pyrolysis of the PTP precursor, peroxo-species (oxygen excess defects) might remain in the PTP-TiO₂ at concentrations below the detection limits of FTIR spectroscopy. The lattice expansion of PTP-TiO₂ was induced by oxygen excess defects in agreement with the XRD analysis.

Fig. 3. N₂ adsorption-desorption isotherms of the PTP-TiO₂-60 min and Cu₂O-PTP-TiO₂ microspheres. Inset shows the size pore distribution curves.

Fig. 4. (a) XRD patterns of the PTP-TiO₂ (PTP-TiO₂-Fresh, PTP-TiO₂-10 min, and PTP-TiO₂-60 min), TP-TiO₂, and Cu_xO-PTP-TiO₂ microspheres. (b) Magnified XRD patterns of the (101) and (200) planes of the anatase TiO₂.

XPS was used to investigate the surface chemical compositions and elemental binding states of the samples. Fig. 6(a) shows the O 1s spectra. For TP-TiO₂, the O 1s signal could be fitted by two peaks at 529.35 and 531.45 eV, corresponding to lattice oxygen (O-Ti) and absorbed H₂O (O-H), respectively [56,57]. For PTP-TiO₂-Fresh, PTP-TiO₂-10 min, PTP-TiO₂-60 min, and Cu_xO-PTP-TiO₂, the O 1s peak could be fitted by three dominant peaks. The peak positions are listed in Table 2. In addition to the O-Ti and O-H absorption bands, another peak was located around 532.8 eV, which was defined as the O-O absorption band deriving from peroxo-species [58,59]. The ratios of O_(O-O)/total O (excepting absorbed O-H) were calculated to 34.1%, 20.2%, 11.6%, and 11.4% for the PTP-TiO₂-Fresh, PTP-TiO₂-10 min, PTP-TiO₂-60 min, and Cu_xO-PTP-TiO₂, respectively. These results indicate that the content of peroxo-species progressively decreased with prolonged annealing time.

Fig. 6(b) shows the high-resolution of Ti 2p spectra of the samples. For TP-TiO₂, the binding energy peaks at 458.16 and 463.91 eV corresponded to the Ti 2p_{3/2} and Ti 2p_{1/2} for the Ti⁴⁺ in anatase [60]. For PTP-TiO₂-Fresh, PTP-TiO₂-10 min, PTP-TiO₂-60 min, and Cu_xO-PTP-TiO₂ microspheres, the Ti 2p_{3/2} and Ti 2p_{1/2} were fitted by two pairs of peaks. The two peaks located around 458.3 and 464.1 eV were assigned to Ti 2p_{3/2} and Ti 2p_{1/2} of lattice Ti-O bonds. Another pair of peaks around 459.5 and 465.1 eV were assigned to Ti 2p_{3/2} and Ti

2p_{1/2} of surface Ti-O-O (Ti-peroxo-species) bond [61]. The ratios of Ti-O-O/total Ti were estimated to be 34.6%, 20.1%, 10.6%, and 11.5% for PTP-TiO₂-Fresh, PTP-TiO₂-10 min, PTP-TiO₂-60 min, and Cu_xO-PTP-TiO₂ microspheres, respectively. These ratios were similar to those of O_(O-O)/lattice O. Therefore, the content of the peroxo-species decreased as the annealing time of the PTP-TiO₂ microspheres was prolonged. The Ti 2p and O_{O-Ti} 1s peaks of the PTP-TiO₂ also shifted to lower binding energy after longer annealing times owing to the lower concentration of peroxo-species. The peroxo-species in PTP-TiO₂ microspheres caused partial electron transfer from neighboring Ti to peroxo groups and a decrease of the electron

Fig. 5. FT-IR spectra of PTP, TP-TiO₂, PTP-TiO₂ (PTP-TiO₂-Fresh, PTP-TiO₂-10 min, and PTP-TiO₂-60 min) samples. Peaks at 1627 and 574 cm⁻¹ are attributed to vibrations of the O-H group (absorbed water and O-Ti-O (TiO₂ lattice)), respectively. The peak at 1403 cm⁻¹ of the peroxo titanate precursor is attributed to the absorbed NH₃ from ammonium hydroxide in the preparation process.

Table 1

Lattice parameters of the PTP-TiO₂-10 min, PTP-TiO₂-60 min, and TP-TiO₂ samples.

Composition	a (Å)	c (Å)	Cell Vol (Å ³)
PTP-TiO ₂ -10 min	3.786	9.510	136.317
PTP-TiO ₂ -60 min	3.785	9.507	136.188
TP-TiO ₂	3.782	9.487	135.679

Fig. 6. O 1s (a), and Ti 2p (b) core level of the as prepared microspheres; (c) Cu 2p XPS spectra for the samples; (d) Valence band XPS spectra of the samples. (All peak maxima were calibrated to C 1s at 284.6 eV).

density on Ti, resulting in an increase of the Ti–O binding energy [38]. In addition, the atomic ratios of O/Ti were determined to be 2.78, 2.38, 2.20, 2.20, and 1.77 for the PTP-TiO₂-Fresh, PTP-TiO₂-10 min, PTP-TiO₂-60 min, and Cu_xO-PTP-TiO₂ and TP-TiO₂, respectively, which again illustrates the oxygen-rich nature of PTP-TiO₂ and that the content of peroxo-species decreased with prolonged annealing time.

The Cu_xO-PTP-TiO₂ and PTP-TiO₂-60 min samples had similar O 1s and Ti 2p spectra. The proportion of the peroxo-species of Cu_xO-PTP-TiO₂ was consistent with that of PTP-TiO₂-60 min. After incorporating the Cu_xO co-catalyst, Cu 2p_{3/2} and Cu 2p_{1/2} peaks appeared in the XPS measurements located at 931.97 and 951.46 eV, as shown in Fig. 6(c), which could be assigned to the binding energies of Cu²⁺ [62,63]. Together with the TEM results, we verified that Cu_xO was successfully grafted onto the surface of the TiO₂ microspheres.

The VBM of the PTP-TiO₂-10 min, PTP-TiO₂-60 min, Cu_xO-PTP-TiO₂ and TP-TiO₂ samples respectively appeared at 1.3, 2.0, 2.0, and 2.2 eV, as shown in Fig. 6(d). The VBM of the PTP-TiO₂-60 min exhibited a 0.2-eV upward shift compared with that of TP-TiO₂, which corresponded to the presence of oxygen excess defects. The PTP-TiO₂-10 min, with more oxygen excess defects than the PTP-TiO₂-60 min, exhibited the greatest

upward shift of the VBM. The Cu_xO-PTP-TiO₂ had a similar VBM to that of PTP-TiO₂-60 min, as the Cu_xO had no influence on the peroxo-species.

Fig. 7(a) displays the UV-vis diffuse reflectance spectra (DRS) of the microspheres. The Tauc plot constructed from the transformed Kubelka-Munk spectra of $(\alpha h\nu)^{1/2}$ versus energy of light ($h\nu$) gave indirect bandgaps at 3.20 eV for the TP-TiO₂, 3.02 and 3.05 eV for the PTP-TiO₂-10 min and PTP-TiO₂-60 min, respectively. The PTP-TiO₂-10 min and PTP-TiO₂-60 min catalysts showed distinct visible-light absorption profiles. The PTP-TiO₂-10 min possessed a larger shoulder and greater visible-light absorption, which could be attributed to more oxygen excess defects and a disordered structure, i.e., a large number of structural defects and non-crystalline regions. Incidentally, a mechanical mixture of TiO₂ with the same rutile/anatase proportion to that of PTP-TiO₂-60 min presented with the same optical absorption spectrum to that of pure anatase owing to the trace rutile content. Thus, we excluded the possibility of the bandgap narrowing of the PTP-TiO₂-60 min microspheres deriving from the existence of a rutile phase. The visible-light response and lower bandgap energy of PTP-TiO₂ compared with that of TP-TiO₂ could be attributed to the presence of oxygen excess defects.

Table 2

XPS results for the prepared microspheres.

Sample	PTP-TiO ₂ -Fresh	PTP-TiO ₂ -10 min	PTP-TiO ₂ -60 min	Cu _x O-PTP-TiO ₂	TP-TiO ₂
Ti _{2p3/2} (eV)	458.63	458.54	458.17	458.24	458.16
Ti _{2p1/2} (eV)	464.30	464.28	463.86	463.90	463.91
Ti _{2p3/2} -O (eV)	459.80	459.52	459.06	458.99	—
Ti _{2p1/2} -O (eV)	465.66	465.05	464.74	464.75	—
O _{1s} (eV)	530.33	529.87	529.41	529.53	529.35
O _H 1s (eV)	531.22	531.20	531.25	531.22	531.48
O _O 1s (eV)	533.05	532.61	532.70	532.80	—
O-O/total O ^a	34.1%	20.2%	11.6%	11.4%	—
Ti-O-O/total Ti ^b	34.6%	20.1%	10.6%	11.5%	—
O/Ti ^c	2.78	2.38	2.20	2.20	1.77

^a O-O (peroxo band) concentration ratios relative to the total O (sum of the O-O and O-Ti band). ^b Ti-O-O (Ti-peroxo band) concentration ratios relative to the total Ti. ^c Total O (sum of the O-O and O-Ti band) and total Ti (sum of the Ti-O and Ti-O-O band) atomic ratio.

Fig. 7. (a) UV-vis DRS and Tauc plot (inset) of the PTP-TiO₂-10 min, PTP-TiO₂-60 min, and TP-TiO₂; (b) UV-vis DRS and Tauc plot (inset) of the PTP-TiO₂-60 min, and Cu_xO-PTP-TiO₂.

Simultaneously, the Cu_xO co-catalysts (0.05 wt%, 0.1 wt%, 0.25 wt%, and 1 wt%) were also grafted onto the PTP-TiO₂-60 min microspheres and the corresponding UV-vis DRS are shown in Fig. 7(b). All the Cu_xO-PTP-TiO₂ samples had a similar bandgap to that of the PTP-TiO₂-60 min. The visible-light absorption simultaneously increased as the amount of the Cu_xO co-catalysts was increased. The increase of the visible-light absorption band from 400 to 500 nm corresponded to direct interfacial charge transfer (IFCT) from the VB of TiO₂ to the Cu_xO co-catalyst. This feature will likely be beneficial for photocatalytic performance. The absorption band from 600 nm to the near infrared region was attributed to the intrinsic excitation band of Cu_xO and *d-d* transitions of Cu(II) species.

The photocatalytic activities of the prepared microspheres were monitored by measuring the decomposition of gaseous acetaldehyde under visible-light irradiation ($\lambda > 400$ nm, 100 mW/cm²). The gaseous acetaldehyde was a kind of indoor VOC pollutant which could be completely decomposed to CO₂ and water by a photocatalyst. The degradation of acetaldehyde under visible-light irradiation could be fitted by a pseudo-first-order kinetic equation for all the microspheres and acetaldehyde was decomposed to the intermediate CH₃COOH and finally to CO₂, as shown by the photocatalytic acetaldehyde

degradation curves in Fig. 8 and the photocatalytic mechanism in Fig. 9.

The TP-TiO₂ presented weak visible-light photocatalytic activity for acetaldehyde degradation and negligible CO₂ generation owing to its poor visible-light response (Fig. 8). The Cu_xO alone showed no obvious enhancement in terms of visible-light photocatalytic activity owing to its poor absorption of visible-light. The PTP-TiO₂-10 min and PTP-TiO₂-60 min microspheres both exhibit enhanced visible-light photocatalytic activity. The PTP-TiO₂-10 min microspheres possessed incomplete anatase crystallinity, which is unfavorable for photocatalytic activity, despite the structure having more oxygen excess defects. The PTP-TiO₂-60 min microspheres showed increased photocatalytic activity with a rate constant $k = 0.117$ h⁻¹, which was 1.5 times as high as that of TP-TiO₂. Herein, oxygen excess defects induced a slight improvement in the photocatalytic activity of the PTP-TiO₂ microspheres owing to the extension of the visible-light absorption by shifting the VBM of TiO₂ upward, as indicated by our UV-vis DRS and XPS results.

The grafting of Cu_xO onto the surface of PTP-TiO₂-60 min markedly increased the photocatalytic activity of TiO₂ under visible-light irradiation, as shown in Fig. 8. Among the Cu_xO-PTP-TiO₂ microspheres, the Cu_xO-PTP-TiO₂ with 0.1 wt%

Fig. 8. Photocatalytic acetaldehyde degradation curves (a), degradation kinetic curves (b), and generation of CO₂ curves (c) for the TP-TiO₂, Cu₂O-TP-TiO₂, PTP-TiO₂, and Cu₂O-PTP-TiO₂ microspheres under visible-light irradiation.

Fig. 10. Photocatalytic acetaldehyde degradation curves and generation of CO₂ curves for the PTP-TiO₂-60 min and Cu₂O-PTP-TiO₂ microspheres under (a) simulated solar light irradiation and (b) UV light (350–400 nm) irradiation, and (c) kinetic degradation curves of acetaldehyde for the two samples under simulated solar light and UV light irradiation.

co-catalyst exhibited the fastest rates of photocatalytic degradation of acetaldehyde and CO₂ evolution. The k value for acetaldehyde degradation of the Cu₂O-PTP-TiO₂ microspheres was 1.006 h⁻¹, which was respectively 8.6, 11.0, and 13.0 times as high as those of PTP-TiO₂-60 min, Cu₂O-TP-TiO₂, and TP-TiO₂ microspheres according to Fig. 8(b).

Fig. 9. Schematic diagram illustrating the energy-level structure and photocatalytic mechanism of the Cu₂O-PTP-TiO₂ microspheres.

Furthermore, the Cu₂O-TP-TiO₂ microspheres exhibited an acetaldehyde degradation rate 4.6 and 2.7 times as high as that of the PTP-TiO₂-60 min microspheres under irradiation by simulated solar light ($\lambda \approx 350\text{--}700$ nm, 100 mW/cm²) and that under UV light ($\lambda \approx 350\text{--}380$ nm, 3 mW/cm²), respectively (Fig. 10). However, the increased reaction rates of Cu₂O-PTP-TiO₂ compared with those of PTP-TiO₂-60 min followed the order: visible-light (8.6 times) > solar light (4.6 times) > UV light (2.7 times). The superior photo-activity of the Cu₂O-PTP-TiO₂ microspheres under visible light irradiation was attributed to synergic effects of the oxygen excess defects and the Cu₂O co-catalyst. Under simulated solar light or UV light irradiation, the effects of the increased visible-light absorption induced by oxygen-excess defects was slight. Furthermore, the good stability of the Cu₂O-PTP-TiO₂ was confirmed by the same rate of photocatalytic degradation of acetaldehyde and generation of CO₂ over five cycles of the experiments in Fig. 11 under visible-light irradiation.

The luminol CL probe method was used to detect H₂O₂ and O₂⁻ and investigate the reaction mechanism of the samples during visible light irradiation. (Fig. 12) [64–67]. The TP-TiO₂ and Cu₂O-TP-TiO₂ produced negligible amounts of O₂⁻ or H₂O₂

owing to their inferior visible-light response. For the PTP-TiO₂-60 min (PTP-TiO₂ for convenience) and Cu_xO-PTP-TiO₂ samples, the amounts of O₂^{•−} and H₂O₂ detected increased as the irradiation period increased. After 8 h of irradiation, the concentrations of O₂^{•−} were 0.72 and 1.27 mmol/L, and the concentrations of H₂O₂ were 0.63 and 1.13 mmol/L for PTP-TiO₂ and Cu_xO-PTP-TiO₂, respectively. The O₂^{•−} and H₂O₂ generation rate decreased as time progressed, owing to the spontaneously decay of O₂^{•−} and photo-decomposition of the H₂O₂ [68]. Thus, the higher O₂^{•−} and H₂O₂ generation rate during the photocatalytic reaction supports the finding of high photocatalytic activity for the Cu_xO-PTP-TiO₂ microspheres.

The Cu_xO-PTP-TiO₂ microspheres exhibited optimal photocatalytic performance for acetaldehyde degradation under visible-light irradiation with rate constants respectively 8.6, 11.0, and 13.0 times as high as those of oxygen-rich TiO₂, Cu_xO-TiO₂, and normal TiO₂. The oxygen excess defects shifted the VBM upward without decreasing the reducing ability of electrons and was beneficial for the visible-light photocatalytic activity.

Upon visible-light excitation, electrons in the VBM transferred to the Cu_xO co-catalysts through two routes: inter-band transition (VBM→CBM→Cu_xO) and interfacial charge transfer (IFCT, VBM→Cu_xO), as shown in Fig. 8. The electrons transformed Cu²⁺ to Cu⁺, which efficiently reduced oxygen molecules via a multielectron reduction process which led to the reformation of Cu²⁺. Therefore, the Cu_xO promoted the separation of charge carriers and formed more of the photocatalytically active species, O₂^{•−} and H₂O₂. The holes generated in the higher VBM maintained sufficient oxidation power to decompose acetaldehyde. Upon simulated solar and UV light excitation, the Cu_xO-PTP-TiO₂ microspheres also exhibited higher photocatalytic activity than PTP-TiO₂-60 min; however, the degree of activity improvement was lower than that under visible-light irradiation. This further demonstrates the important role of visible-light absorption induced by the oxygen-excess defects. Therefore, we conclude that synergic effects of oxygen excess defects and Cu_xO co-catalyst contributed to the high photocatalytic performance of Cu_xO-PTP-TiO₂ microspheres under visi-

Fig. 11. Cycling tests of the Cu_xO-PTP-TiO₂ microspheres for gaseous acetaldehyde degradation under visible-light irradiation (100 mW/cm², $\lambda > 400$ nm). (a) Photocatalytic acetaldehyde degradation; (b) CO₂ generation.

Fig. 12. Concentration of O₂^{•−} (a) and H₂O₂ (b) as a function of the duration of the visible-light irradiation for PTP-TiO₂-60 min, Cu_xO-PTP-TiO₂, TP-TiO₂, and Cu_xO-TP-TiO₂ samples.

Graphical Abstract

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Synergic effects of Cu_xO electron transfer co-catalyst and valence band edge control over TiO₂ for efficient visible-light photocatalysisLina Kong, Xintong Zhang *, Changhua Wang, Fangxu Wan, Lan Li *
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The Cu_xO grafted oxygen-rich TiO₂ microspheres possessed efficient visible-light photocatalytic activity, where oxygen excess defects improved visible-light absorption and Cu_xO promoted the reduction of oxygen to O₂⁻ and H₂O₂, thus facilitating charge separation.

ble-light irradiation.

4. Conclusions

Cu_xO-grafted oxygen-rich TiO₂ microspheres were synthesized by ultrasonic spray pyrolysis of a peroxo titanate precursor followed by wet chemical impregnation techniques. The Cu_xO grafted oxygen-rich TiO₂ exhibited excellent photocatalytic performance and photo-stability for gaseous acetaldehyde degradation under visible-, solar-, and UV-light irradiation. The oxygen-rich defects shifted the VBM upward and extended the optical absorption edge of TiO₂ into the visible-light region. The Cu_xO co-catalyst served as electron-trapping centers and efficiently reduced adsorbed O₂ to O₂⁻ and H₂O₂, therefore increasing the separation of charge carriers. Thus, oxygen excess defects and the Cu_xO co-catalyst increased the photocatalytic activity of TiO₂. The present work represents a general strategy for developing other heterojunction photocatalysts for energy- and environmental-related applications.

References

- [1] A. Fujishima, X. T. Zhang, D. A. Tryk, *Surf. Sci. Rep.*, **2008**, 63, 515–582.
- [2] L. Liu, X. B. Chen, *Chem. Rev.*, **2014**, 114, 9890–9918.
- [3] A. Fujishima, X. T. Zhang, *C. R. Chimie*, **2006**, 9, 750–760.
- [4] J. X. Low, B. Cheng, J. G. Yu, *Appl. Surf. Sci.*, **2017**, 392, 658–686.
- [5] M. C. Wen, S. S. Zhang, W. R. Dai, G. S. Li, D. Q. Zhang, *Chin. J. Catal.*, **2015**, 36, 2095–2102.
- [6] M. H. N. Assadi, D. A. H. Hanaor, *Appl. Surf. Sci.*, **2016**, 387, 682–689.
- [7] J. X. Low, J. G. Yu, S. Wageh, A. A. Al-Ghamdi, *Adv. Mater.*, **2017**, 29, 1601694.
- [8] J. Q. Wen, X. Li, W. Liu, Y. P. Fang, J. Xie, Y. H. Xu, *Chin. J. Catal.*, **2015**, 36, 2049–2070.
- [9] Z. Wang, W. W. Wu, Q. Xu, G. D. Li, S. H. Liu, X. F. Jia, Y. Qin, Z. L. Wang, *Nano Energy*, **2017**, 38, 518–525.
- [10] W. T. Bi, X. G. Li, L. Zhang, T. Jin, L. D. Zhang, Q. Zhang, Y. Luo, C. Z. Wu, Y. Xie, *Nat. Commun.*, **2015**, 6, 8647.
- [11] Q. Wang, T. Hisatomi, Q. X. Jia, H. Tokudome, M. Zhong, C. Z. Wang, Z. H. Pan, T. Takata, M. Nakabayashi, N. Shibata, Y. B. Li, I. D. Sharp, A. Kudo, T. Yamada, K. Domen, *Nat. Mater.*, **2016**, 15, 611–615.
- [12] X. F. Wang, T. Y. Li, R. Yu, H. G. Yu, J. G. Yu, *J. Mater. Chem. A*, **2016**, 4, 8682–8689.
- [13] X. P. Han, J. N. Lü, L. Tian, L. R. Kong, X. M. Lu, Y. Mei, J. W. Wang, X. X. Fan, *Chin. J. Catal.*, **2017**, 38, 83–91.
- [14] N. T. Nguyen, M. Altomare, J. E. Yoo, N. Taccardi, P. Schmuki, *Adv. Energy Mater.*, **2016**, 6, 1501926(1–7).
- [15] X. F. Wang, R. Yu, K. Wang, G. Q. Yang, H. G. Yu, *Chin. J. Catal.*, **2015**, 36, 2211–2218.
- [16] C. Yang, B. Zhao, R. Gao, S. Y. Yao, P. Zhai, S. W. Li, J. Yu, Y. L. Hou, D. Ma, *ACS Catal.*, **2017**, 7, 5661–5667.
- [17] J. Wang, B. Li, J. Z. Chen, N. Li, J. F. Zheng, J. H. Zhao, Z. P. Zhu, *Appl. Surf. Sci.*, **2012**, 259, 118–123.
- [18] S. W. Zhang, H. C. Yang, H. H. Gao, R. Y. Cao, J. Z. Huang, X. J. Xu, *ACS Appl. Mater. Interfaces*, **2017**, 9, 23635–23646.
- [19] J. Q. Wen, J. Xie, Z. H. Yang, R. C. Shen, H. Y. Li, X. Y. Luo, X. B. Chen, X. Li, *ACS Sustainable Chem. Eng.*, **2017**, 5, 2224–2236.
- [20] H. G. Yu, P. Xiao, P. Wang, J. G. Yu, *Appl. Catal. B*, **2016**, 193, 217–225.
- [21] Z. Y. Mao, J. J. Chen, Y. F. Yang, D. J. Wang, L. J. Bie, B. D. Fahlman, *ACS Appl. Mater. Interfaces*, **2017**, 9, 12427–12435.
- [22] W. L. Ong, S. W. L. Ng, C. Zhang, M. H. Hong, G. W. Ho, *J. Mater. Chem. A*, **2016**, 4, 13307–13315.
- [23] L. L. Zhu, M. H. Hong, G. W. Ho, *Nano Energy*, **2015**, 11, 28–37.
- [24] M. Miyauchi, H. Irie, M. Liu, X. Q. Qiu, H. G. Yu, K. Sunada, K. Hashi-

- imoto, *J. Phys. Chem. Lett.*, **2016**, 7, 75–84.
- [25] Y. X. Liu, Z. L. Wang, W. X. Huang, *Appl. Surf. Sci.*, **2016**, 389, 760–767.
- [26] Q. Q. Hu, J. Q. Huang, G. J. Li, Y. B. Jiang, H. Lan, W. Guo, Y. G. Cao, *Appl. Surf. Sci.*, **2016**, 382, 170–177.
- [27] Q. Q. Hu, J. Q. Huang, G. J. Li, J. Chen, Z. J. Zhang, Z. H. Deng, Y. B. Jiang, W. Guo, Y. G. Cao, *Appl. Surf. Sci.*, **2016**, 369, 201–206.
- [28] R. Michal, E. Dworniczek, M. Caplovicova, O. Monfort, P. Lianos, L. Caplovic, G. Plesch, *Appl. Surf. Sci.*, **2016**, 371, 538–546.
- [29] Y. F. Li, W. P. Zhang, X. Shen, P. F. Peng, L. B. Xiong, Y. Yu, *Chin. J. Catal.*, **2015**, 36, 2229–2236.
- [30] M. Liu, X. Q. Qiu, M. Miyauchi, K. Hashimoto, *Chem. Mater.*, **2011**, 23, 5282–5286.
- [31] M. Liu, X. Q. Qiu, M. Miyauchi, K. Hashimoto, *J. Am. Chem. Soc.*, **2013**, 135, 10064–10072.
- [32] L. N. Kong, C. H. Wang, F. X. Wan, H. Zheng, X. T. Zhang, *Appl. Surf. Sci.*, **2017**, 396, 26–35.
- [33] L. Q. Yang, J. F. Huang, L. Shi, L. Y. Cao, W. Zhou, K. Chang, X. G. Meng, G. G. Liu, Y. N. Jie, J. H. Ye, *Nano Energy*, **2017**, 36, 331–340.
- [34] X. B. Chen, L. Liu, P. Y. Yu, S. S. Mao, *Science*, **2011**, 331, 746–750.
- [35] A. Sinhamahapatra, J. P. Jeon, J. S. Yu, *Energy Environ. Sci.*, **2015**, 8, 3539–3544.
- [36] X. Y. Pan, M. Q. Yang, X. Z. Fu, N. Zhang, Y. J. Xu, *Nanoscale*, **2013**, 5, 3601–3614.
- [37] L. N. Kong, Z. Q. Jiang, C. H. Wang, F. X. Wan, Y. Y. Li, L. Z. Wu, J. F. Zhi, X. T. Zhang, S. J. Chen, Y. C. Liu, *ACS Appl. Mater. Interfaces*, **2015**, 7, 7752–7758.
- [38] V. Etacheri, M. K. Seery, S. J. Hinder, S. C. Pillai, *Adv. Funct. Mater.*, **2011**, 21, 3744–3752.
- [39] L. L. Tan, W. J. Ong, S. P. Chai, B. T. Goh, A. R. Mohamed, *Appl. Catal. B*, **2015**, 179, 160–170.
- [40] S. B. Wang, L. Pan, J. J. Song, W. B. Mi, J. J. Zou, L. Wang, X. W. Zhang, *J. Am. Chem. Soc.*, **2015**, 137, 2975–2983.
- [41] H. Pan, *J. Mater. Sci.*, **2015**, 50, 4324–4329.
- [42] L. N. Kong, C. H. Wang, H. Zheng, X. T. Zhang, Y. C. Liu, *J. Phys. Chem. C*, **2015**, 119, 16623–16632.
- [43] D. S. Jung, T. H. Hwang, J. H. Lee, H. Y. Koo, R. A. Shakoar, R. Kahraman, Y. N. Jo, M. Park, J. W. Choi, *Nano Lett.*, **2014**, 14, 4418–4425.
- [44] W. J. Wang, T. W. Ng, W. K. Ho, J. H. Huang, S. J. Liang, T. C. An, G. Y. Li, J. C. Yu, P. K. Wong, *Appl. Catal. B*, **2013**, 129, 482–490.
- [45] Y. N. Ko, S. B. Park, K. Y. Jung, Y. C. Kang, *Nano Lett.*, **2013**, 13, 5462–5466.
- [46] Y. H. Cho, Y. N. Ko, Y. C. Kang, I. D. Kim, J. H. Lee, *Sensors Actuat. B*, **2014**, 195, 189–196.
- [47] J. K. Yang, X. T. Zhang, H. Liu, C. H. Wang, S. P. Liu, P. P. Sun, L. L. Wang, Y. C. Liu, *Catal. Today*, **2013**, 201, 195–202.
- [48] J. K. Yang, X. T. Zhang, C. H. Wang, P. P. Sun, L. L. Wang, B. Xia, Y. C. Liu, *Solid State Sci.*, **2012**, 14, 139–144.
- [49] Q. L. Xu, J. G. Yu, J. Zhang, J. F. Zhang, G. Liu, *Chem. Commun.*, **2015**, 51, 7950–7953.
- [50] Y. X. Liu, Z. L. Wang, W. X. Huang, *Appl. Surf. Sci.*, **2016**, 389, 760–767.
- [51] M. S. Akple, J. X. Liu, Z. Y. Qin, S. Wageh, A. A. Al-Ghamdi, J. G. Yu, S. W. Liu, *Chin. J. Catal.*, **2015**, 36, 2127–2134.
- [52] Y. Zhang, L. Z. Wu, Q. H. Zeng, J. F. Zhi, *J. Phys. Chem. C*, **2008**, 112, 16457–16462.
- [53] M. Ilkaeva, I. Krivtsov, V. Avdin, S. A. Khainakov, J. R. García, *Colloids Surf. A*, **2014**, 456, 120–128.
- [54] R. Nakamura, A. Imanishi, K. Murakoshi, Y. Nakato, *J. Am. Chem. Soc.*, **2003**, 125, 7443–7450.
- [55] W. Z. Fang, M. Y. Xing, J. L. Zhang, *Appl. Catal. B*, **2014**, 160–161, 240–246.
- [56] K. Li, S. M. Gao, Q. Y. Wang, H. Xu, Z. Y. Wang, B. B. Huang, Y. Dai, J. Lu, *ACS Appl. Mater. Interfaces*, **2015**, 7, 9023–9030.
- [57] W. Ho, *Chin. J. Catal.*, **2015**, 36, 2109–2118.
- [58] S. Z. Hu, F. Y. Li, Z. P. Fan, J. Zhang, *Asia J. Chem.*, **2013**, 25, 9169–9173.
- [59] F. Bonino, A. Damin, G. Ricchiardi, M. Ricci, G. Spano, R. D. Aloisio, A. Zecchina, C. Lamberti, C. Prestipino, S. Bordiga, *J. Phys. Chem. B*, **2004**, 108, 3573–3583.
- [60] Y. Zhang, Z. Y. Zhao, J. R. Chen, L. Cheng, J. Chang, W. C. Sheng, C. Y. Hu, S. S. Cao, *Appl. Catal. B*, **2015**, 165, 715–722.
- [61] J. Zou, J. C. Gao, Y. Wang, *J. Photoch. Photobiol. A*, **2009**, 202, 128–135.
- [62] X. Q. Qiu, M. Miyauchi, K. Sunada, M. Minoshima, M. Liu, Y. Lu, D. Li, Y. Shimodaira, Y. Hosogi, Y. Kuroda, K. Hashimoto, *ACS Nano*, **2012**, 6, 1609–1618.
- [63] H. B. Feng, Y. P. Li, D. M. Luo, G. R. Tan, J. B. Jiang, H. M. Yuan, S. J. Peng, D. Qian, *Chin. J. Catal.*, **2016**, 37, 855–862.
- [64] A. Naldoni, M. Allieta, S. Santangelo, M. Marelli, F. Fabbri, S. Cappelli, C. L. Bianchi, R. Psaro, V. Dal Santo, *J. Am. Chem. Soc.*, **2012**, 134, 7600–7603.
- [65] Y. Nosaka, S. Takahashi, H. Sakamoto, A. Y. Nosaka, *J. Phys. Chem. C*, **2011**, 115, 21283–21290.
- [66] T. Hirakawa, Y. Nosaka, *J. Phys. Chem. C*, **2008**, 112, 15818–15823.
- [67] M. C. Ramos, M. C. Torijas, A. N. Díaz, *Sensor. Actuat. B*, **2001**, 73, 71–75.
- [68] D. Tsukamoto, A. Shiro, Y. Shiraishi, Y. Sugano, S. Ichikawa, S. Tanaka, T. Hirai, *ACS Catal.*, **2012**, 2, 599–603.

基于Cu_xO电子转移助剂及TiO₂价带边调控的协同效应驱动可见光催化

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摘要: TiO₂基光催化剂迈向实际应用的关键在于更加有效地分离电荷和拓宽光吸收范围至可见光区域. 通过负载助剂促进光生电荷分离以及掺杂调控能带、提高可见光吸收是实现高性能光催化剂的两个重要途径. 在众多助剂中, 廉价、无毒且催化性能优异的过渡金属氧化物(如Co-, Ni-, Cu- 和Fe-氧化物)助剂在光催化降解污染物、水分解、CO₂还原等领域尤其引人关注. 而氧缺陷作为氧化物的固有缺陷, 可实现TiO₂的能带调控, 提升可见光吸收性能. 其中, 常见的缺氧缺陷是通过导带边调控来拓宽可见光吸收范围, 但其光生电子还原能力降低. 因TiO₂价带空穴具有足够强的氧化能力, 本文拟通过在

TiO₂中引入富氧缺陷调控价带边及负载电子转移助催化剂的途径研制高效可见响应型光催化剂。

本文利用超声喷雾热解过氧钛酸和湿化学浸渍法制备了Cu_xO负载富氧型TiO₂微球。采用扫描电子显微镜(SEM), 透射电子显微镜(TEM), N₂吸附-脱附等温曲线, X射线衍射(XRD), X射线光电子能谱(XPS), 紫外可见漫反射光谱(UV-Vis-DRS)等手段对Cu_xO负载富氧型TiO₂微球的结构特征和光谱吸收性质进行系统研究。SEM, TEM和N₂吸附/脱附等温曲线结果表明, Cu_xO负载富氧型TiO₂微球是纳米颗粒紧凑堆叠的介孔微球, 直径为200–2000 nm, Cu元素高度均匀分散于微球上。XRD和XPS分析表明, 富氧缺陷TiO₂微球相比参照TiO₂微球具有更大的晶格参数, 同时晶体中具有大量的过氧物种(Ti-O-O), 证明了过氧缺陷的存在。UV-Vis-DRS和XPS的价带谱验证, 富氧缺陷使得TiO₂价带项上移, 提高了可见光吸收性能。鲁米诺化学发光(CL)探针实验进一步证明, 表面负载的Cu_xO助剂将表面吸附氧高效还原为活性氧物种(O₂^{•-}和H₂O₂), 提高了光生电子利用率。因此, Cu_xO负载富氧型TiO₂微球表现出更快的可见光催化降解乙醛速率, 分别为富氧型TiO₂、非富氧型TiO₂和Cu_xO-TiO₂的8.6、13.0和11.0倍。并且, Cu_xO负载富氧型TiO₂微球在可见光催化降解乙醛的五次循环实验中, 活性基本保持不变。Cu_xO负载富氧型TiO₂微球在模拟太阳光和UV光辐照下光催化降解乙醛速率相比富氧型TiO₂微球也大幅提升, 分别提升4.6和2.7倍。Cu_xO负载富氧型TiO₂微球光催化性能增强归因于富氧缺陷和Cu_xO电子转移助催化剂的协同作用。其中, 富氧缺陷使得TiO₂价带边上移, 拓宽可见光吸收范围, Cu_xO电子转移助剂引入界面电荷转移和多电子氧还原过程, 加速光生电子利用率, 促进光生电荷分离。该策略也为开发其他高效异质结光催化剂提供参考。

关键词: 可见光催化; TiO₂; Cu_xO助催化剂; 富氧缺陷; 介孔微球

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