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Enhancing the visible-light photocatalytic activity of TiO_2 by heat treatments in reducing environments

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ABSTRACT

Following a series of recent studies that demonstrated enhanced visible-light photocatalytic activities of TiO_2 by annealing in reducing atmospheres, a systematic investigation was conducted, in which TiO_2 nanoparticles were annealed in various controlled atmospheres with the estimated oxygen partial pressure being varied from $\sim 10^{-1}$ to $\sim 10^{-25}$ atm and presence of other species (Ar, H_2, N_2, vacuum or hydrocarbon); subsequently, photocatalytic activities were tested. The results suggest that the oxygen partial pressure during annealing is not the dominant controlling factor. Furthermore, the use of vacuum environments or the presence of hydrocarbon species during annealing is effective in enhancing the photocatalytic activity, but the presence of H_2 at a partial pressure of 0.05 atm does not show an appreciable beneficial effect. HRTEM suggested that the enhanced photocatalytic activity of vacuum-activated TiO_2 may be related to subnanometer-thick disordered surface layers.

1. Introduction

TiO_2 based photocatalysts are promising for applications in remediation of wastes, purification of water, and generation of solar hydrogen [1,2]. However, the wide band gap of TiO_2 (>3.0 eV) limits its photocatalytic efficiency in response to solar radiation because only UV light, which counts for ~5% of the solar spectrum, can be utilized [1]. Doping and other strategies have been used to improve the photocatalytic efficiency of TiO_2 in response to visible light [1,2].

In 2011 [3], Chen et al. reported an approach to make "disorder-engineered" TiO_2 by annealing anatase nanoparticles in a 20-bar H_2 atmosphere at 200 °C to form a nanometer-thick, disordered, surface phase (akin to those impurity-based, equilibrium, surface amorphous films [4]); consequently, a "black TiO_2" powder with enhanced efficiency for photocatalytic water splitting under the irradiation of solar light was obtained. Several other recent studies [5–9] also showed that annealing TiO_2 in reducing environments (*e.g.*, in a 1-bar hydrogen atomsphere [6] or with active carbon [7]) can enhance the visible-light adsorption and photocatalytic activities. In particular, Xing et al. developed a "vacuum-activated TiO_2" via annealing TiO_2 in a vacuum drying oven at approximately 200 °C to obtain a brownish powder with improved visible-light photocatalytic activities [8]. This work demonstrated that hydrogenation is not a necessary condition for improving visible-light adsorption and photocatalytic activity and suggesting that the reducing atmosphere during annealing may be a key factor in "activating" TiO_2.

These recent studies [3,5–9] collectively point us to a new direction of improving the visible-light adsorption and photocatalytic activity of TiO_2 nanoparticle by heat treatments in reducing environments. However, a systematical investigation of the effects of oxygen partial pressure and the presence/use of other species/environments (Ar, H_2, N_2, hydrocarbon species or vacuum) on activating TiO_2 has not been conducted, which motivated this study.

2. Experimental procedure

TiO_2 anatase powders (MTI, ~10 nm in size, 99.99% purity) and methyl orange (Alfa Aesar) were purchased. To systematically test the effects of oxygen partial pressure, TiO_2 nanoparticles were annealed in a tube furnace flowing dry air, Ar–2% O_2, Ar, N_2, and Ar–5% H_2, respectively, as well as in a separate vacuum furnace using a diffusion pump (with high vacuum; $\sim 10^{-6}$ Torr), at 200 or 450 °C isothermally. The specimens were also annealed in a vacuum drying oven (with rough vacuum; <25 Torr) at 200 °C, similar to the procedure used in the prior report [8].

The photocatalytic activities were evaluated by degradation of methyl orange in an aqueous solution under visible-light irradiation using a solar simulator (Abet Technologies; Model 10500) with a standard AM 1.5G solar spectrum equipped with a 420 nm cutoff filter. In a typical test, ~0.07 g of TiO_2 photocatalyst was added into 70 mL of an aqueous solution of methyl orange (5 mg/L). Photoreaction was performed in a water cooled jacket beaker,

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which was open to air. Prior to irradiation, the suspensions were magnetically stirred in a dark environment for 30 min to establish an adsorption–desorption equilibrium. After irradiation of visible light for a preset period (typically 1 h), 3 mL aliquot was sampled and filtered. UV–vis spectrophotometry (Agilent technologies, Cary 60) was used to determine the concentrations of methyl orange in the solution before (C_0) and after (C) irradiation at a maximum absorption band of 464 nm, and the C/C_0 ratio after 1 h irradiation is used to represent the photocatalytic activity. A calibration curve was used for concentration calculation (for background removal). The photocatalytic reactions were carried out at neutral pH conditions.

Fourier-transform infrared (FTIR) spectra of the samples were recorded using a Thermo-Nicolet Magna 550 FTIR spectrometer. For each sample, 16 scans at a resolution of 4 cm^{-1} were collected. A background spectrum was collected from the Diamond ATR window for the baseline correction. The surfaces of TiO_2 nanoparticles were characterized using a Hitachi 9500 high-resolution transmission electron microscope (HRTEM). HRTEM specimens were prepared by dispersing particles ultrasonically in isopropanol and placing a small amount of suspension onto holey carbon-coated Cu grids.

3. Results and discussion

Fig. 1 shows a photo comparing the color of TiO_2 powders annealed at 200 °C for 7 h in different atmospheres. The TiO_2 powder annealed in the vacuum oven exhibits a brownish color, similar to that reported in the prior study [8], and the powder annealed in high vacuum shows a (lighter) yellowish color; in comparison, pristine TiO_2 and TiO_2 annealed in all other gaseous atmospheres are white.

Fig. 2(a) summarizes the measured photocatalytic activity (C/C_0 ratios after 1 h irradiation) for 15 different powders annealed in dry air, Ar–2% O_2, Ar, N_2, Ar–5% H_2, rough vacuum, and high vacuum. The *x*-axis in Fig. 2(a) represents estimated oxygen partial pressures during the annealing for each case. A key observation is that visible-light photocatalytic activity of TiO_2 is not a simple function of the estimated oxygen partial pressure. Measured UV–vis spectra for the vacuum-activated TiO_2 are shown in Fig. 2(b) as an example, and Fig. 2(c) shows that C/C_0 decreases monotonically with increasing irradiation time as a result of photocatalytic degradation.

Fig. 2(a) shows that annealing in vacuum environments appears to be the most effective method to "activate" TiO_2. This result, along with the change of color shown in Fig. 1, is consistent with Xing et al.'s prior report [8]. Xing et al. [8] attributed the enhanced visible-light photocatalytic activity of vacuum modified TiO_2 to the formation of the associated oxygen vacancies (O_V^{2-}) and Ti^{3+} due to the partial reduction in vacuum. However, this theory would suggest a color change and increased activity for TiO_2 annealed in other reducing atmospheres such as in flowing Ar, N_2 or Ar–5% H_2; our results (Figs. 1 and 2a) showed that this is not true. This theory would also suggest that annealing high vacuum should be more effective in activating TiO_2, which is again inconsistent with the observations shown in Figs. 1 and 2(a). Furthermore, we annealed TiO_2 in Ar–2% O_2, where the oxygen partial pressure matches to that in our vacuum oven, but the resulted powder has virtually no visible-light photocatalytic activity (Fig. 2(a)). Thus, we conclude that while annealing in vacuum is proven effective for improving the visible-light photocatalytic activity of TiO_2, the vacuum activation of TiO_2 is not simply due to the formation of defects in reducing environments.

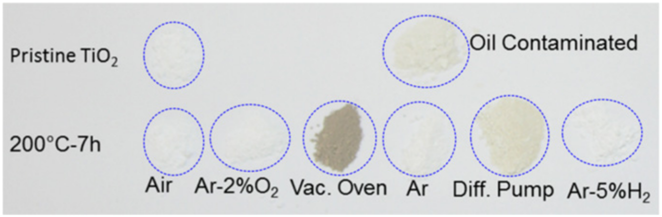

Fig. 1. A photo comparing the color of TiO_2 powders annealed at 200 °C for 7 h in different atmospheres as well as the pristine and "oil contaminated" TiO_2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

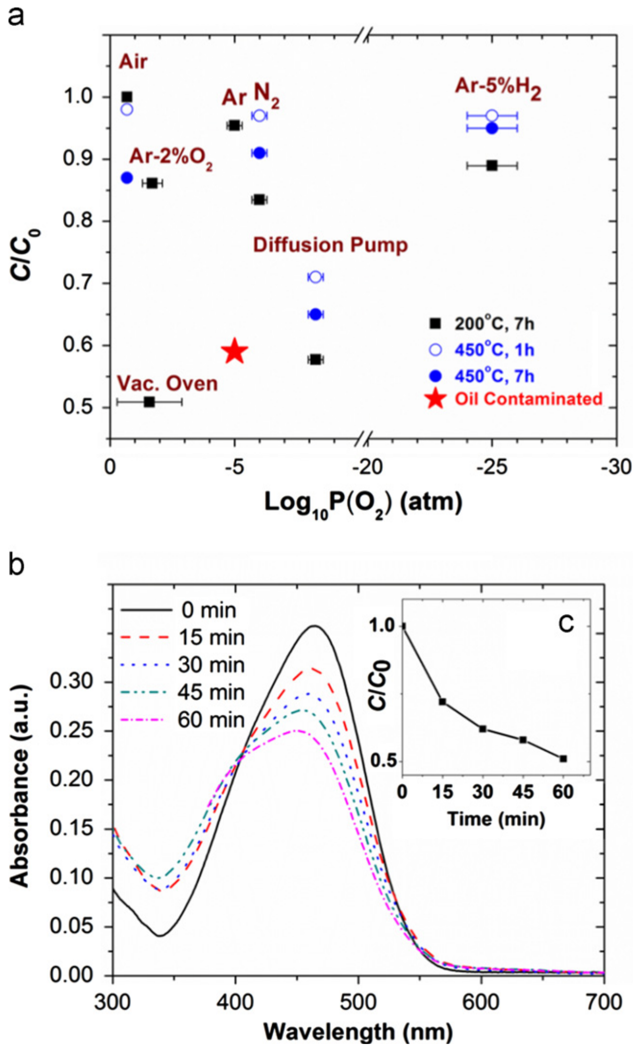

Fig. 2. (a) Measured visible-light photocatalytic activities of TiO_2 that annealed using 15 different conditions. The *x*-axis represents the estimated oxygen partial pressures of the atmospheres used in the heat treatments. (b) Representative UV–vis absorption spectra during photodegradation of methyl orange using the vacuum-activated TiO_2 and (c) the corresponding C/C_0 (after background removals) *vs.* time.

Furthermore, the current study shows that the annealing TiO_2 in H_2 (0.05 atm) or N_2 (1 atm) at 200 or 450 °C have little effects on improving photocatalytic activity of TiO_2 (Fig. 2(a)). However, we should note that this result does not exclude the possible beneficial effects of hydrogenation at higher pressure/H activity (*e.g.* in a 20-bar H_2 atomsphere [3]).

Notably, small peaks at 2800–2900 cm^{-1} that are associated with saturated C–H bonds are found in the FTIR spectra obtained from powders annealed in vacuum (Fig. 3(d)–(g)), but they are not present in spectra obtained from pristine TiO_2 and TiO_2 annealed in Ar or dry air (Fig. 3(a)–(c)). Noting that these C–H peaks were also evident for Xing et al.'s vacuum-activated TiO_2 [8]. This observation suggested possible (decomposed) hydrocarbon contamination, which is presumably coming from vacuum oils. It is known that carbon doping can enhance visible-light photocatalytic activity [10,11]. First-principle calculations also suggested that C–H co-doping are energetically favorite and can narrow the band gap of TiO_2 more effectively than C-doping itself [12]. To test the effects of oil contamination, we intentionally placed 4 drops of vacuum oil (Maxima C plus, from Fisher Scientific) in one TiO_2 specimen (~0.4 g) and annealed it in flowing Ar at 200 °C for 7 h. This oil-contaminated specimen exhibits enhanced photocatalytic activity that is comparable with the vacuum-activated TiO_2 (Fig. 2(a)). Nonetheless, this oil-contaminated specimen only shows yellowish color that is significantly lighter than that of the vacuum-activated TiO_2 (Fig. 1), although its FTIR spectrum exhibits a much stronger C–H peak (Fig. 3(h)). In our experiments, we pre-pumped the vacuum oven and closed the valve to maintain a low level of vacuum during the 7-hour annealing. Thus, the hydrocarbon contamination should be minor, which is consistent with the FTIR spectra (Fig. 3). In conclusion, the presence of (decomposed) hydrocarbon contamination during low-temperature annealing in reducing atmospheres appears to be effective to enhance the photocatalytic activity, but the observed color change and activation of TiO_2 via annealing in a vacuum oven cannot be fully explained by (decomposed) oil/hydrocarbon contamination. These discrepancies may be explained by the different types and amounts of oils presented/used or the different kinetic routes that the specimens were contaminated.

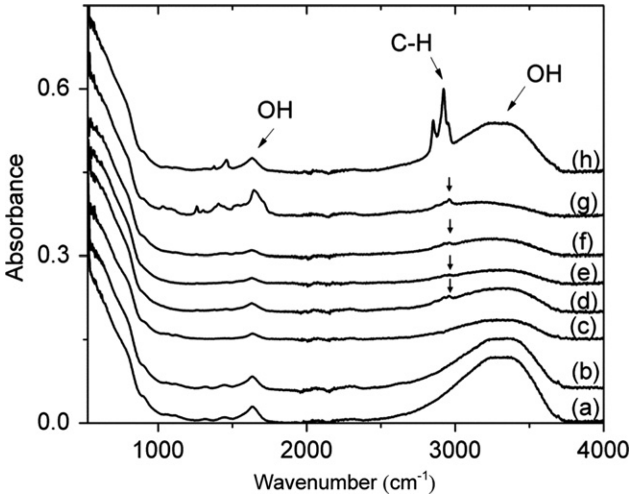

Fig. 3. FTIR spectra of (a) pristine TiO_2 as well as TiO_2 annealed in (b) Ar and (c) dry air at 200 °C for 7 h; in a tube furnace using a diffusion pump (d) at 450 °C for 7 h; (e) at 450 °C for 1 h and (f) at 200 °C for 7 h; (g) in an vacuum oven at 200 °C for 7 h; and (h) the "oil contaminated" TiO_2 annealed in Ar at 200 °C for 7 h.

As illustrated in HRTEM images in Fig. 4, the surfaces of vacuum-activated TiO_2 appear to be more disordered or "dirty" than the surfaces of the TiO_2 annealed in Ar–2% O_2 (with similar oxygen partial pressures). The surfaces of vacuum-activated TiO_2 look somewhat similar to those of disorder-engineered TiO_2 in the *Science* report [3]. However, it is not possible to determine whether these ultrathin disordered surface layers are hydrocarbon contaminations or disordered TiO_2 layers as claimed in the

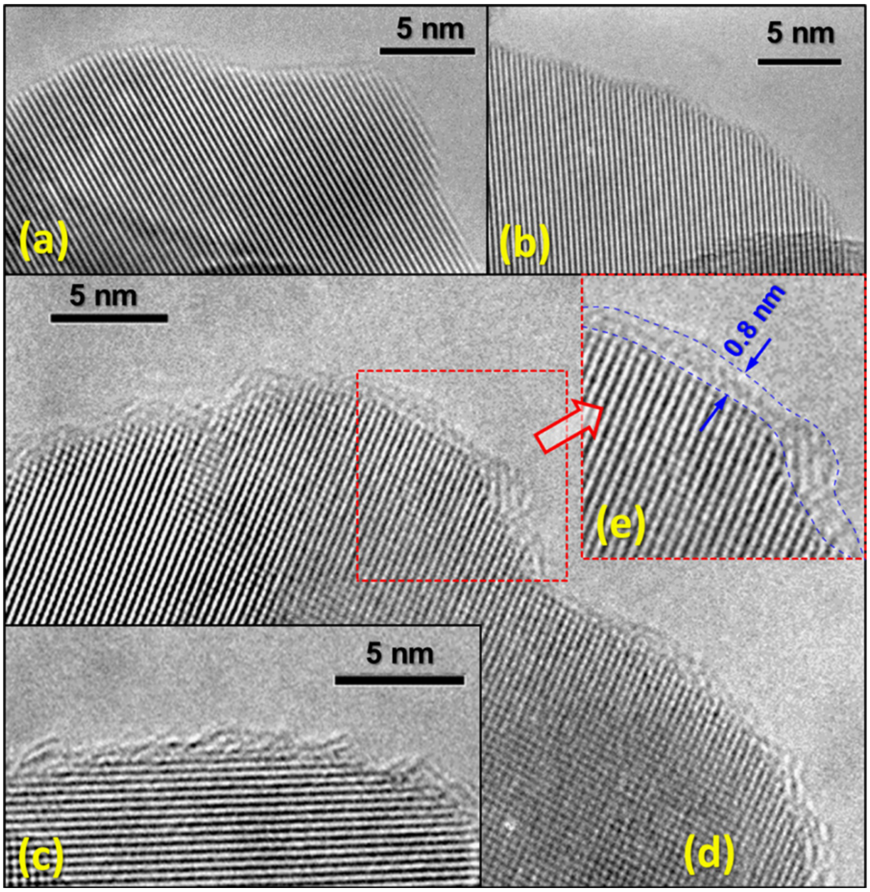

Fig. 4. Representative HRTEM micrographs of surfaces of TiO_2 annealed in (a and b) a tube furnace flowing Ar—2% O_2 gas and (c–e) in a vacuum oven, respectively, at 200 °C for 7 h.

prior study [3]. What we can conclude after examining a large number of surfaces is that the surfaces of vacuum-activated TiO_2 are more disordered or ‘‘dirty’’ on average. It is therefore inferred that these subnanometer-thick disordered surface layers may be related to the color change and enhanced visible-light photocatalytic activity of vacuum-activated TiO_2.

4. Conclusions

We have systematically investigated the effects of annealing environments on improving the visible-light photocatalytic activity of TiO_2 by using 15 different heat treatment conditions, in which estimated oxygen partial pressure varies from $\sim 10^{-1}$ to $\sim 10^{-25}$ atm. In contrast to the hypothesis that enhanced visible-light photocatalytic activity is due to the formation of defects in reducing atmospheres, this study showed that the oxygen partial pressure during annealing is not the dominant controlling factor. This study confirmed the effectiveness of the simple vacuum activation method, and suggested that the presence of minor hydrocarbon species during annealing may be a factor for enhancing the photocatalytic activity. Further HRTEM characterization suggested that subnanometer-thick disordered surface layers may relate to the color change and enhanced visible-light photocatalytic activity of vacuum-activated TiO_2. This study also showed that the presence of H_2 at a partial pressure of 0.05 atm during annealing at 200–450 °C does not show an appreciable beneficial effect, but it does not exclude the possible beneficial effects of hydrogenation at higher H_2 pressures.

Acknowledgment

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