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Tunable selectivity of radical generation over TiO_2 for photocatalysis

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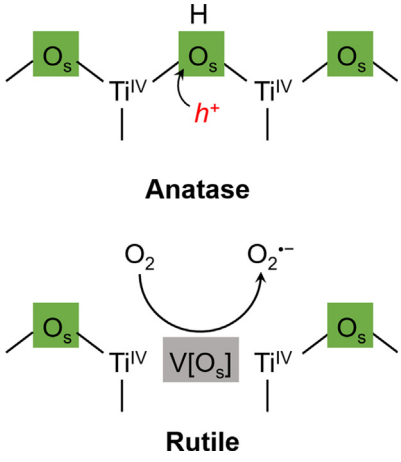
HIGHLIGHTS

- Modified TiO_2 photocatalysts exhibit tunable selectivity for radical generation.
- Anatase-rich TiO_2 shows preferential hole-mediated decomposition.
- Increasing ratio of rutile in TiO_2 favors superoxide facilitated dye degradation over hole.

GRAPHICAL ABSTRACT



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ABSTRACT

The realization of controllable radical generation through structural modification of photocatalyst is a challenging goal and is an important strategy for environmental remediation and noncomplete and selective photo-oxidation. Here, we control structural composition of TiO_2 through crystalline modification and use photocatalytic dye degradation as a model system to investigate photocatalytic details. Importantly, modified TiO_2 materials exhibit tunable mechanism pathway towards photocatalytic decomposing methylene blue (MB) monitored by radical trapping experiments. The anatase-rich TiO_2 heterojunction shows preferential hole-mediated decomposition pathway in comparison with superoxide and hydroxyl radicals. In contrast, increasing ratio of rutile in TiO_2 favors superoxide-facilitated MB decomposition over hole. The surface chemistry of specific surface atomic configuration is a key factor in tuning the capability of oxygen reduction and hole trapping, resulting in photocatalytic selectivity of radical generation towards photo-oxidation.

1. Introduction

With urbanization and industrialization, organic water pollutants such as toxic dyes are widely produced by the printing, food and texture industries all over the world, which has post significant risk on environment and human health. Photocatalysis is a promising solution to this environmental issue by using inex-

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haustible solar energy and abundant air as the oxidant, to achieve total mineralization of organic pollutants under ambient conditions. Understanding photocatalytic mechanism pathway is not only essential to the eco-environmental services, but also highly desirable for broader applications such as non-complete, selective and advanced photo-oxidation, which are important for degradation of targeted organic pollutants.

Since the pioneer work of John H. Carey in 1976 (Carey et al., 1976), intensive research efforts have focused on treatment of organic wastes and pollutants in atmospheric and aquatic environment, and significant progress has been made (Chen et al., 2010; Liu et al., 2010; Low et al., 2017; Schneider et al., 2014). Among the plentiful semiconductor photocatalysts, TiO_2 nanoparticles exhibit many desirable features including high reactivity, stability and non-toxicity when used to promote various significant photocatalytic reactions (Schneider et al., 2014). Under light excitation, electrons and holes produced by incident photons can interact with oxygen and water molecules to produce reactive radical species (e.g. ·OH, $O_2^{\cdot-}$) at TiO_2 surface, which promote organic compounds degradation. Extensive research efforts have demonstrated that efficient electron/hole (e^-/h^+) separation, large particle/solution interface area and an abundant amount of active sites leads to high photocatalytic efficiency (Low et al., 2017). Furthermore, many investigations have also been carried out to tune band gap of TiO_2 to visible light region by doping small amounts of metal or non-metal components. (Schneider et al., 2014) However, photoprocess on TiO_2 tend to generate highly oxidative radicals like ·OH that oxidize all organic species simultaneously, leading to poor photodegradation selectivity. (Liu et al., 2010) Thus, developing an approach to control radical species generation is highly desirable.

The general consensus in photocatalysis is that superoxide anion ($O_2^{\cdot-}$) is one of the most anticipated reactive oxygen species in organic pollutants degradation (Chen et al., 2010), since photogenerated electrons can easily transfer to adsorbed O_2 and organic degradation intermediates may also give their unpaired electrons to O_2. The degradation rates of dye pollutants increases with increasing amount of $O_2^{\cdot-}$ in photocatalytic system, evidenced by spin-trapping ESR technique and/or chemiluminescent probe luminol (Bedouhène et al., 2017; Wang et al., 2011). Photo-generated h^+ and ·OH also play important role in total mineralization of organics due to their high reactivity in chemical nature. Although effect of TiO_2 structural composition on photodegradation reactivity has been reported (Xu et al., 2015; Yan et al., 2013), investigation of mechanism pathway and selective radical generation is rather limited (Kakuma et al., 2015; Ndong et al., 2015). To date, the role of TiO_2 surface structure on details of photocatalytic reactivity remains ambiguous. Understanding such interfacial chemical process is also crucial towards development of solar cell, photocatalytic water splitting and solar CO_2 reduction (Wenderich and Mul, 2016).

As the active radical species are important to the function of photocatalysts and provide many essential eco-environmental services, a deeper understanding of relationship between interfacial atomic structure and radical species generation is significant. In present study, we therefore chose well-defined TiO_2 materials with tunable structural composition, to evaluate the impact of surface atomic structure on selectivity of active species, in order to access the potential of further application of photo-oxidation and to determine the underlying mechanisms.

2. Material and methods

2.1. Materials

TiO_2 (P25), methylene blue (MB) were purchased from Degussa, Tianjin East China Reagent company, respectively. *P*-benzoquinone (BQ), isopropyl alcohol (IPA), triethanolamine (TEOA) and nitrotetrazolium blue chloride (NBT) were bought from Aladdin Reagent Co. Ltd (Shanghai). All the chemicals are analytical reagents and were used as received.

2.2. Preparation of TiO_2 with various structural composition

The TiO_2 materials with tunable phase composition were prepared by a facile one-step aerobic heat treatment. In a typical experimental procedure, the P25 TiO_2 powder was heated in a ceramic tube reactor (diameter of 3 cm) to target temperatures (500, 600, 700, 1100 °C) with ramp rate of 15 °C min^{-1} and remaining for certain period of time in air. Consequently, TiO_2 materials with various phase composition were generated.

2.3. Characterization

X-ray diffraction patterns (XRD) were collected with a D8 Advance (Bruker, Germany) X-ray diffractometer using Cu Kα radiation (λ = 1.542 Å) and a 2θ scan rate of 2° min^{-1} over the 2θ range 20–85°. Transmission electron microscopy (TEM) and HRTEM images were obtained with a Tecnai G2 F20 STWIN (FEI US) field emission electron microscope operating at an accelerating voltage of 200 kV. Raman spectra were taken on a LabRAM Xplo RA (Horiba Jobin Yvon, France) Raman microscope with a wavelength of 514 nm. UV–vis spectra were collected using a UV-3600 (Shimadzu, Japan) spectrometer in diffuse reflection mode. The analysis range was 200–800 nm, and $BaSO_4$ was used as a baseline reflectance. After treatment in vacuum at °C for 2 h, Brunauer-Emmett-Teller (BET) nitrogen (N_2) adsorption/desorption was measured with a V-sorb2800P analyzer (Gold APP, China) and surface area was calculated with multi-point method. The ability of TiO_2 in generating $^1O_2$ was evaluated by using 1,3-Diphenylisobenzofuran (DPBF), a well-known $^1O_2$ monitor, through time-dependent spectrum absorption measurement. X-ray photoelectron spectra (XPS) were collected using a Kratos Ultra AXIS DLD XPS with a monochromated Al source.

2.4. Photocatalytic activity test

The photodegradation activities of TiO_2 were examined by the photodegradation of MB dye in aqueous solution. The experiments were carried out using BL-GHX photochemical reactor coupled with 500 W mercury lamp (Shanghai Billon, China) in open air and at room temperature without any light filter. In a typical degradation system: 50 mL of aqueous suspension of 18 mg L^{-1} MB and 10 mg TiO_2 sample was placed in a quartz reactor. Prior to photoreaction, the suspension was magnetically stirred in the dark for 30 min to ensure the establishment of desorption-adsorption equilibrium. During the photodegradation reaction, stirring was continued. At certain time intervals, ~5 mL suspensions were collected and centrifuged using a LD5-2B centrifuge (Beijing Jingli, China) at 3800 rpm for 5 min to separate TiO_2 sample and solution. The MB concentration changes were monitored by measuring the absorption intensity at its maximum absorbance wavelength (~660 nm for MB) using a TU-1810 UV–vis spectrophotometer (Beijing Persee, China).

2.5. Radical trapping and superoxide radical quantification experiments

For detecting the active species during photocatalytic reaction, hydroxyl radicals (·OH), superoxide anions ($O_2^{\cdot-}$), and holes (h^+) were investigated by adding 1.0 mM IPA (a quencher of ·OH), BQ (a quencher of $O_2^{\cdot-}$), and TEOA (a quencher of h^+), respectively (Ye et al., 2012). The rest part of experiment was identical to the