



Heterogeneous activation of H_2O_2 by defect-engineered TiO_2-x single crystals for refractory pollutants degradation: A Fenton-like mechanism



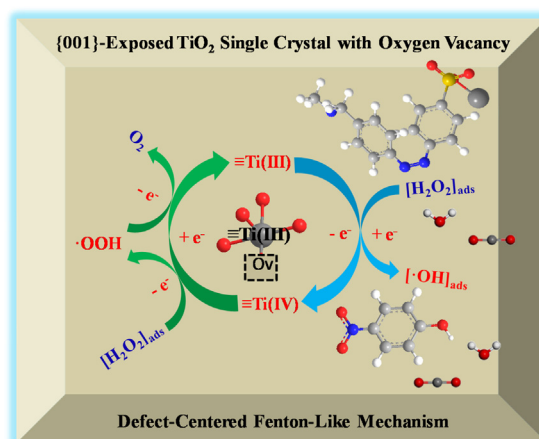
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HIGHLIGHTS

- Facet- and defect-engineered TiO_2 is proposed for water treatment as Fenton-like catalyst.
- The $\equiv\text{Ti(III)}$ center serves as lattice shuttle for electron transfer in H_2O_2 activation.
- TiO_2 is promising due to low cost, high abundance, no toxicity and stable performance.

GRAPHICAL ABSTRACT



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ABSTRACT

The heterogeneous catalyst plays a key role in Fenton-like reaction for advanced oxidation of refractory pollutants in water treatment. Titanium dioxide (TiO_2) is a typical semiconductor with high industrial importance due to its earth abundance, low cost and no toxicity. In this work, it is found that TiO_2 can heterogeneously activate hydrogen peroxide (H_2O_2 , $E^\circ = 1.78 \text{ eV}$), a common chemical oxidant, to efficiently generate highly-powerful hydroxyl radical, $\cdot\text{OH}$ ($E^\circ = 2.80 \text{ eV}$), for advanced water treatment, when its crystal shape, exposed facet and oxygen-stoichiometry are finely tuned. The defect-engineered TiO_2 single crystals exposed by high-energy $\{001\}$ facets exhibited an excellent Fenton-like activity and stability for degrading typical refractory organic pollutants such as methyl orange and *p*-nitrophenol. Its defect-centered Fenton-like superiority is mainly attributed to the crystal oxygen-vacancy, single-crystalline structure and exposed polar $\{001\}$ facet. Our findings could provide new chance to utilize TiO_2 for Fenton-like technology, and develop novel heterogeneous catalyst for advanced water treatment.

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1. Introduction

As an efficient exhaustive oxidation process for advanced water treatment, Fenton and Fenton-like systems have gained more and

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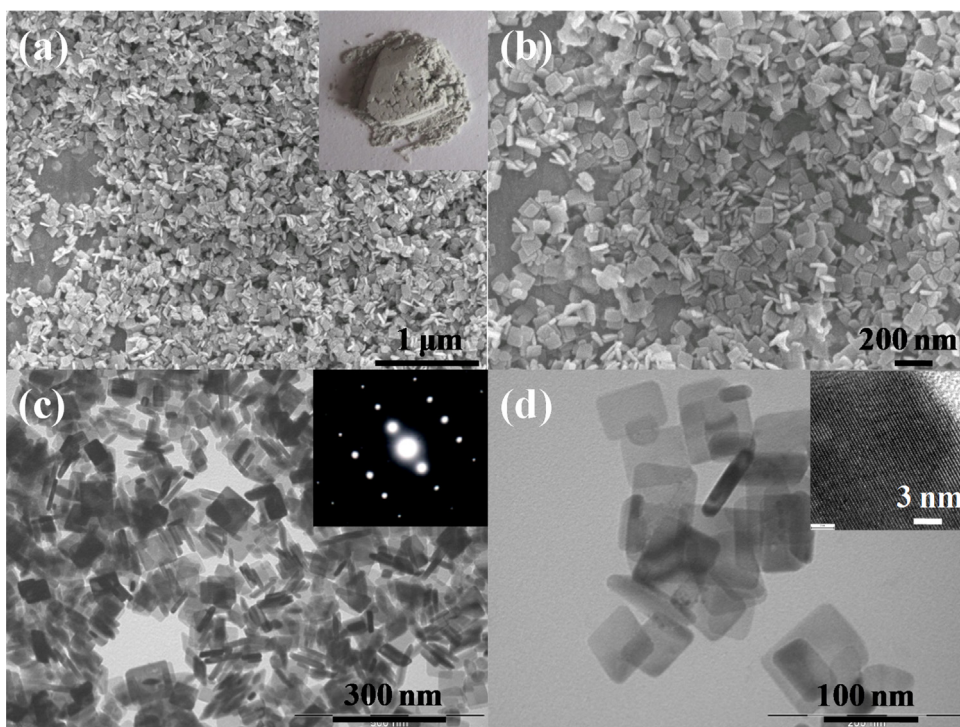


Fig. 1. (a, b) SEM and (c, d) TEM images of the defect-engineered TiO_{2-x} SCs, the insets of (a), (c) and (d) were the digital image, SAED diffraction pattern and HRTEM images of the defective sample.

more interest [1–3]. Although H_2O_2 is a strong chemical oxidant with the E^0 of 1.78 eV, it alone is not effective for refractory and persistent pollutants at reasonable dosage [1]. Reductive activation of H_2O_2 under acidic conditions by transition metal ions, especially Fe^{2+} , ozone or UV light to generate highly powerful hydroxyl radicals with the E^0 of 2.80 eV can substantially increase its oxidative capacity [4]. However, the conventional homogeneous Fenton and its combined systems using Fe^{2+} severely suffer from limited pH range, large iron sludge, poor regeneration kinetic and low activity, in addition to the secondary pollution from successive iron of usually $50\text{--}80\text{ mg L}^{-1}$ [3,5].

Solid catalyst plays a governing role in heterogeneous Fenton process. First of all, the iron-mediated H_2O_2 activation for $\bullet\text{OH}$ generation has been extensively studied, a variety of catalytic iron species, such as metal oxides (e.g., FeOOH , Fe_2O_3 and Fe_3O_4) and zero-valent metal (Fe^0), have been exploited for chemical, photochemical, sonochemical and electrochemical activation pathways [6–11]. However, the strict acidic condition to prevent iron precipitation and the poor stability during redox cycling still remains the main challenges for iron-based heterogeneous Fenton systems [3]. Thus, some alternative iron-free heterogeneous catalysts have been developed for advanced water treatment [12–21]. In principle, the elements with multiple redox states, such as chromium, cerium, copper, cobalt, manganese and ruthenium, all direct activate H_2O_2 into $\bullet\text{OH}$ through the Fenton-like pathways [3], but the H_2O_2 activation mechanism is very specific to the nature of the catalyst and critically depends on its composition.

TiO_2 , an important semiconductor material, has been widely used for efficient photocatalytic water treatment [22]. However, due to its low conductivity and poor reactivity, TiO_2 is not recognized as an efficient heterogeneous catalyst without light irradiation, and the usage of TiO_2 in dark for catalytic pollutants degradation is very limited [23]. Considering its unique benefits, it would be of considerable interest if we could significantly improve the performance of TiO_2 for activating H_2O_2 to generated $\bullet\text{OH}$ for advanced water treatment, using a simple strategy. It is well

known that many parameters, such as shape, crystal structure and exposed facets, significantly influence the physico-chemical and catalytic properties of TiO_2 [24–27]. In our previous work, an anodic TiO_2 with high performance and good stability was successfully developed for electrochemical water treatment, aided by shape-controlled single crystalline and high-energy polar $\{001\}$ facet [28]. The higher catalytic activity of high-index $\{001\}$ facet than low-index $\{101\}$ facet should be mainly attributed to a higher density of atomic steps, edges and kinks of low-coordinate surface atoms with a large number of dangling bonds. Thus, shape- and facet-engineering of TiO_2 is of considerable interests for its catalytic properties.

Self-structural modifications of TiO_2 by reductive Ti^{3+} and/or oxygen vacancies provide another promising chance for catalytic applications with the help of defect-related chemistry [29–32]. Compared to the pristine crystal, the defect-engineered analogue with deliberately-modified atomic structure can bring about improved properties including structural, electronic, optical, dissociative adsorption and catalytic activity. For example, the non-stoichiometric reduction of TiO_2 can substantially increase the donor density and electric conductivity as well as reduce charge transfer resistance by narrowing band gap usually below 2.0 eV, since the Ti^{3+} species can thermodynamically serve as electric donors and the electrons of which could hop to the conduction band (or adjacent Ti^{4+} sites) [33]. Also, the self-doped Ti^{3+} could significantly induce enhancement of oxygen and water adsorption as well as the catalytic activity on TiO_2 surface [34]. The defective oxygen vacancies are believed to be responsible for the catalytic activities of hydrogenated TiO_2 in dark [34]. Moreover, the defective self-doped TiO_{2-x} has exhibited high anti-oxidation performance and good catalytic stability in many processes. For example, TiO_{2-x} intrinsically remained its original color after exposing to air for even more than one year; also, the TiO_{2-x} did not exhibit any obvious activity decrease in strong oxidative photocatalysis, and the defective Ti^{3+} and oxygen vacancy can remain efficiently [29–32]. Thus,

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