



Sulfate radicals generation and refractory pollutants removal on defective facet-tailored TiO₂ with reduced matrix effects



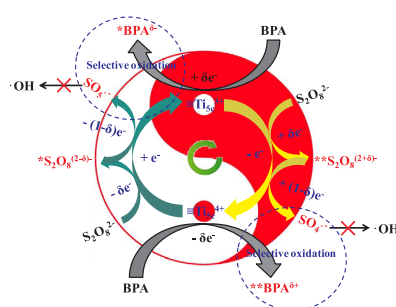
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HIGHLIGHTS

- A simple strategy was proposed to refine persulfate-based Fenton-like system.
- Titanium-based Fenton-like system was designed and estimated with two typical pollutants.
- {0 0 1}-TiO_{2-x}/PDS Fenton-like system exhibited good capacity and stability with much reduced matrix effects.
- The $\cdot\text{SO}_4^{\cdot-}$ -mediated mechanisms were elucidated and clearly presented.

GRAPHICAL ABSTRACT



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ABSTRACT

Sulfate radical (SO₄^{·-}) based oxidation is an efficient and selective strategy for environmental decontamination. Herein, we confirmed, for the first time, that the fine modulation on semiconducting TiO₂ was able to improve the redox-cycling capability for heterogeneous peroxydisulfate (PDS, S₂O₈²⁻) activation and radicals generation. PDS activation by defective TiO_{2-x} exposed by high-energy {0 0 1} polar facets was a superior Fenton-like catalytic system for rhodamine B (RhB) and bisphenol A (BPA) degradation, with good activity and selectivity under neutral pH. By radical inhibiting tests with two different scavengers, fluorescence measurements with terephthalic acid and electron paramagnetic resonance (EPR) technique, only the SO₄^{·-} was identified to be the main reactive species from PDS activation on defective TiO_{2-x} for pollutants degradation. Compared to the reported TiO_{2-x}/H₂O₂ system, the proposed TiO_{2-x}/PDS system exhibited much lower water matrix effects in the presence of four typical anions, natural organic matters and real surface water for target pollutants degradation. The selective SO₄^{·-}-mediated TiO_{2-x}/PDS catalytic system in natural water matrix and the no toxicity of catalytic material were of considerable interest for practical environmental applications with highly complex chemistry. Our findings elucidated a new strategy for efficient and selective PDS activation based on the defect-related chemistry, which can degrade environmental contaminants and remedy contaminated soil based on sulfate components with much reduced matrix effects.

1. Introduction

Advanced oxidation processes are promising strategies to decontaminate environmental pollutants from water and wastewater [1–3].

The mediated reactive radicals are mainly $\cdot\text{OH}$ and SO₄^{·-}. Compared to $\cdot\text{OH}$ (E⁰ = 1.8–2.7 V), SO₄^{·-} has a higher oxidative potential (E⁰ = 2.5–3.1 V) within a wider pH range for pollutants decontamination [4,5]. Moreover, $\cdot\text{OH}$ can react non-selectively with environmental

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pollutants and thus suffers from strong water matrix effects for practical applications, while $\text{SO}_4^{\cdot-}$ has a highly selective oxidation capacity for unsaturated chemical bonds and aromatic constituents, and thus possess a longer life time (30.0–40.0 μs) for a higher decontamination efficiency for refractory pollutants over a wide pH range [4,5]. $\text{SO}_4^{\cdot-}$ has a preference for electron transfer reactions as opposed to $\cdot\text{OH}$, which is more likely to participate in hydrogen abstraction and/or addition reactions [4,5]. Thus, $\text{SO}_4^{\cdot-}$ is selective which prefers to react with the aromatic ring, while $\cdot\text{OH}$ is non-selective which reacts with both aromatic ring and aliphatic chain in comparison [1–5]. In addition, handling of $\text{S}_2\text{O}_8^{2-}$ is much easier than H_2O_2 , and also exhibits a better stability and shows a limited loss in use at a low cost. These advantages make $\text{SO}_4^{\cdot-}$ -mediated oxidation more promising for site clean-up applications.

The non-selective $\cdot\text{OH}$ and selective $\text{SO}_4^{\cdot-}$ can be both produced via persulfate activation (peroxydisulfate (PDS, $\text{S}_2\text{O}_8^{2-}$) and peroxymonosulfate (PMS, HSO_5^-) and their specific contributions to Fenton-like catalysis are highly dependent on the given reaction conditions [6–11], thus how to improve the selective generation of preferred $\text{SO}_4^{\cdot-}$ and reduce environmental matrix effects are of considerable interest for practical applications of heterogeneous Fenton-like catalysis with highly complex chemistry. In principle, during persulfate activation, $\text{SO}_4^{\cdot-}$ is first generated from PDS and PMS decomposition on catalyst surface, then the as-generated selective $\text{SO}_4^{\cdot-}$ can either decontaminate environmental pollutants directly (k1) or react with water molecules and/or hydroxyl groups on solid catalyst to form the secondary non-selective $\cdot\text{OH}$ for pollutants degradation indirectly (k2) [12–20]. As a result, how to effectively regulate the reaction balance between k_1 and k_2 is of considerable interest for the dominant reactive species as well as the overall decontamination properties in persulfate-based Fenton-like catalytic systems [18–20]. Apparently, the surface chemistry of heterogeneous Fenton-like catalyst can play a governing role in modulating the reaction balance between k_1 and k_2 [21–28]. In details, if we could enhance the reaction potential between $\text{SO}_4^{\cdot-}$ and pollutants (k1) or inhibit the reaction potential between $\text{SO}_4^{\cdot-}$ and water molecules and/or hydroxyl groups (k2) on catalyst surface by finely regulating their specific surface chemistry and thus preferred surface interactions with pollutants and oxidants, then the selective $\text{SO}_4^{\cdot-}$ -mediated oxidation pathway should be anticipated with much reduced matrix effects for practical environmental decontaminations.

TiO_2 is the most studied transition metal oxide with high industrial importance due to its outstanding environmental compatibility, earth abundance, easy preparation and low cost [29]. However, it is not an efficient catalyst without high-energy UV irradiation [29]. Self-structural modifications with reductive $\equiv\text{Ti(III)}$ and/or oxygen vacancies can provide an highly important chance aided by the defect-related chemistry [30–33]. The defect-engineered TiO_2 with finely modified atomic configuration can bring about much improved properties including structural, electronic, optical, dissociative adsorption and catalytic activity, as well as a high anti-oxidation performance and a good catalytic stability [34–37]. In our previous work, the high-energy $\{001\}$ -engineered TiO_{2-x} with finely tuned crystal shape, exposed facet and oxygen-stoichiometry is proven to efficiently activate H_2O_2 for non-selective $\cdot\text{OH}$ -mediated pollutants degradation with strong matrix effects [29]. Due to the defective atomic and electronic structures with a higher density of atomic steps, edges and kinks of low-coordinate surface atoms with a large number dangling bonds [38–46], the strong surface interactions between TiO_{2-x} and pollutants might be well regulated to favor the reaction potential between $\text{SO}_4^{\cdot-}$ and pollutants with largely reduced energy barriers (k1), and thus inhibit the reaction potential between $\text{SO}_4^{\cdot-}$ and water molecules and/or hydroxyl groups (k2) on solid catalyst surface. The strong surface interactions between as-generated $\text{SO}_4^{\cdot-}$ and adsorbed pollutants might thermodynamically dissociate pollutants and dynamically accelerate degradation on TiO_{2-x} , thus the as-generated $\text{SO}_4^{\cdot-}$ could be

selectively consumed mainly by activated pollutants (k1) but not by water and/or hydroxyl groups to generate secondary non-selective $\cdot\text{OH}$ (k2). Then, a selective and preferred $\text{SO}_4^{\cdot-}$ -mediated TiO_{2-x} /PDS Fenton-like catalytic system could be developed for efficient pollutants decontamination with much reduced environmental matrix effects.

Herein, we originally focused on the defect-centered catalytic performance and mechanisms of defective TiO_{2-x} single crystals (SCs) exposed by high-energy $\{001\}$ polar facets to activate PDS for refractory pollutants degradation. The effects of main parameters, radical scavengers and different water matrix on TiO_{2-x} /PDS catalytic system were systematically investigated. The main reactive species from PDS activation for pollutants degradation were identified by different measurements, and the possible heterogeneous Fenton-like catalytic mechanism on defective TiO_{2-x} was comprehensively explored and clearly presented. This study dedicates to a novel and selective PDS activation strategy based on defect-related chemistry for Fenton-like catalysis with reduced matrix effects in environmental decontamination.

2. Materials and methods

2.1. Preparation of defective TiO_{2-x} and pristine reference

The defective TiO_{2-x} SCs dominantly exposed by high-energy $\{001\}$ polar facets, $\{001\}$ - TiO_{2-x} , were prepared by the thermal treatment of TiO_2 SCs, $\{001\}$ - TiO_2 , at 400 °C for 5.0 h in H_2 atmosphere (5.0 vol% H_2 + 95.0 vol% Ar) (Figs. S1 and S2) [29]. Polycrystalline TiO_2 nano-particles dominantly exposed by low-energy $\{101\}$ non-polar facets ($\{101\}$ - TiO_2 , mean particle size of ca. 25 nm, anatase/rutile = 80:20, Brunauer-Emmett-Teller (BET) surface area of ca. 50 m^2/g , exposed percentage of high-energy $\{001\}$ facets less than 5.0%) were commercially purchased for the reference (Degussa Co, Germany, Degussa P25) (Fig. S3).

2.2. RhB and BPA degradation tests in TiO_{2-x} /PDS system

Heterogeneous Fenton-like degradation tests were carried out in a 150-mL beaker containing 100 mL of organic solution at 20.0 ± 2.0 °C. Rhodamine B (RhB) and bisphenol A (BPA) were used as target pollutants, respectively. In a typical procedure, adding 0.10 g L^{-1} catalyst, $\{001\}$ - TiO_{2-x} , $\{001\}$ - TiO_2 or $\{101\}$ - TiO_2 , into 100 mL of 5.0–20.0 mg L^{-1} organic solution with or without adjusting pH condition by 1.0 M HCl or NaOH aqueous solution, then the Fenton-like reaction was initiated by further adding PDS oxidant, 3.0–10.0 mM, into catalytic system. A 2.0 mL of reaction solution was regularly sampled, filtered and immediately analyzed. For comparison, the heterogeneous PDS activation tests using $\{001\}$ - TiO_2 and $\{101\}$ - TiO_2 were also conducted under the same testing conditions as references. All experiments were carried out in triplicate, and the average values and standard deviations were presented. For 5-run cyclic tests, the $\{001\}$ - TiO_{2-x} catalyst was regularly obtained by micro-filtration after each run and thoroughly washed with distilled water several times to remove surface organic matters, then drying at 60 °C for 3.0 h before reuse.

3. Results and discussion

3.1. Degradation of typical azo dye in TiO_{2-x} /PDS system

The morphology- and defect-tailored TiO_{2-x} with high-energy $\{001\}$ polar facets and surface and sub-surface oxygen vacancies exhibited good heterogeneous Fenton-like activity for RhB degradation in the presence of PDS oxidant (Figs. 1 and S4). Neither TiO_{2-x} nor PDS exhibited a satisfactory capacity to remove RhB alone (Figs. 1a and S4a). The Langmuir-Hinshelwood first-order reaction rate constants for TiO_{2-x} /PDS, PDS and TiO_{2-x} systems were calculated to be 0.83, 0.08

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