



Templated fabrication of hierarchically porous Fe–Ti bimetallic solid superacid for efficient photochemical oxidation of azo dyes under visible light



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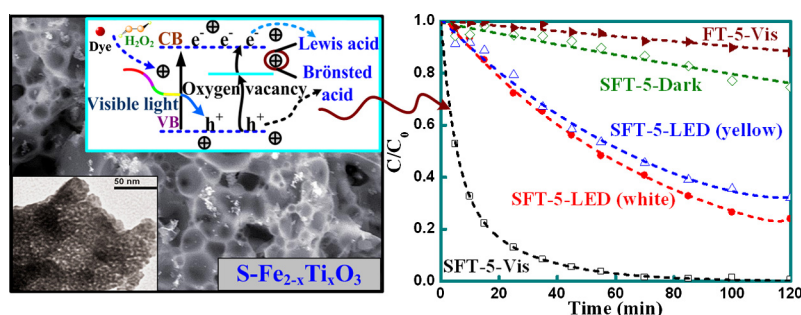
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HIGHLIGHTS

- Hierarchically porous S–Fe_{2–x}Ti_xO₃ was prepared by citric acid templated method.
- Cooperative effect of titanium and sulfate created lots of Lewis acid sites.
- Fe–Ti bimetallic solid superacid widened the pH range to 10.0 in Fenton reaction.
- Light with wavelength 450–595 nm had significant effect on activity of S–Fe_{2–x}Ti_xO₃.
- Favorable synergetic effect of acid sites and photo improved catalytic activity.

GRAPHICAL ABSTRACT



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ABSTRACT

A new hierarchically porous solid superacid SO₄²⁻/Fe_{2–x}Ti_xO₃ was prepared by way of facile citric acid templates and sulfuric acid impregnating strategy. The prepared catalyst exhibited high activity and stability for activation of H₂O₂ as higher than 90% of organic dyes were decomposed in 30 min at neutral pH under visible light irradiation. UV–vis spectrum and ion chromatography were used to investigate the degradation pathway of dyes. By characterizations, it was found that incorporation of titanium and sulfur had a significant effect on properties and structure of the solid. Large numbers of strong Lewis acid sites were produced on the surface due to cooperative effect of Ti and S, which made significant contributions toward high activity in strong alkaline condition (pH 10.0). Meanwhile, the transition metal doping and oxygen vacancies generation can narrow the band gap of the catalyst and efficiently enhance visible light photocatalytic performance. It was also observed that high catalytic activity can hardly be achieved if acid functionalization or light irradiation was applied individually. This was clearly evidenced that the synergetic effect of acid sites and photo-induced electrons transfer played a crucial role in Fenton reaction, which may be attributed to that the appearance of acid sites (Lewis and Brønsted acidic center) was favorable for the separation of photo-induced electrons and holes and suppressed charge recombination.

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1. Introduction

Wet hydrogen peroxide catalytic oxidation (WHPCO), as a practical, inexpensive, and green chemical process, is greatly needed to be used for remediation of a wide range of toxic and recalcitrant

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Nomenclature

BJH	Barrett, Joyner and Halenda	$k_{\text{H}_2\text{O}_2}$	rate constants of H_2O_2 decomposition (min^{-1})
C	concentration of dye solution (mg L^{-1})	LED	light-emitting diode
C_0	initial dye concentrations of first-order reaction (mg L^{-1})	SF	sulfated iron oxide
C_{10} and C_{20}	initial dye concentrations of two independent first-order reactions (mg L^{-1})	SFT-5	sulfated iron–titanium (5:1, molar ratio) biometallic oxide
CB	conduction band	t	time (min)
FT-5	iron–titanium (5:1, molar ratio) biometallic oxide	VB	valence band
k	rate coefficient of the pseudofirst order reaction (min^{-1})	WHPCO	wet hydrogen peroxide catalytic oxidation
k_1 and k_2	rate constants of two independent first-order reactions (min^{-1})		

organic pollutants presented in water and soil [1–5]. Homogeneous Fenton-type catalysts based on ferrous salts (Fenton's reagent) are currently used for the commercial industrial application of WHPCO due to its general applicability [6,7]. Unfortunately, the catalysts available today for homogeneous Fenton are far from ideal, such as very narrow operating pH range (2–3), separation for ferric hydroxide sludge, and high expenditure in labor and reagents [8]. To overcome these drawbacks, some efforts have been devoted to develop different strategies to enhance the wide applicability of homogeneous Fenton reaction [9]. Investigations into the heterogeneous Fenton catalysis are guiding us towards a highly promising alternative [10,11]. So far, different iron oxides and iron ions supported solid as heterogeneous catalysts for Fenton reaction have been a topic of much interest, such as $\text{MO-Fe}_2\text{O}_3$ (M: Fe, Co, Cu, Mn), Fe/resin, $\text{Fe}_2\text{O}_3/\text{silica}$, and $\text{Fe}_2\text{O}_3/\text{clay}$ [12–17]. Most heterogeneous Fenton catalysts show a high activity at nearly neutral pH under UV light irradiation, but an important remaining challenge is how to keep the same excellent performance in further widened alkaline condition and enhance the solar energy utilization to reduce the expense. Thus, it is significant to develop methods for the chemical modification of surface property and introduction of highly active sites. Recently, many attempts also refer to the interplay between activity and the acid prosperity of supports [18,19], but as yet little work has been done on enhancing Fenton catalytic oxidation and widening pH working range in the case of surface acid sites of solid.

In this context, we explore a new avenue for applying the environmental friendly and cost-effective Fe-based solid superacid ($\text{SO}_4^{2-}/\text{Fe}_{2-x}\text{Ti}_x\text{O}_3$) heterogeneous catalysts in Fenton process under visible light irradiation, which is chosen because of the following rationales: (1) solid acid catalysts always play an essential role in numerous applications for organic synthesis and transformation, such as alkylation, esterification, isomerization and rearrangement. Especially, $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$, substituting for the current liquid acids and halogen-based solid acid, are of the greatest interest in green catalysts, which have exhibited high thermostability, superacidic property and high catalytic activity [20,21]. So, we believe that the strong acid sites of the sulfated biometallic oxide should play an important role in Fenton reaction, which may not only provide better adsorption centers for H_2O_2 molecules and be active towards their decomposition, but also effectively overcome the dependence of pH; (2) TiO_2 as the n-type semiconductors have received the greatest interest in recent photocatalysis due to their multi-functional properties [22]. Evidence is presented suggesting that the incorporation of transition metal Ti into the Fe-based nanocatalysts can exhibit excellent photoactivity for H_2O_2 decomposition, which involves an electron transfer from the nanoparticles to H_2O_2 molecules.

Based on this new idea, the new porous solid superacid $\text{SO}_4^{2-}/\text{Fe}_{2-x}\text{Ti}_x\text{O}_3$ was prepared by citric acid templates and sulfuric acid impregnating method for the first time. More details in the possi-

bility of facilitating the heterogeneous Fenton process to make use of solid superacid under visible light were investigated in our work. Attempts have been made to characterize the properties and structure of solid superacid after incorporation of Ti and S, and deduce the structure–activity relationship in solid acid catalysts and the effect of light irradiation on performance enhanced. We believe that the method described in this paper provides an effective route to rational design of porous Fenton catalyst for applications; and the more important is that we try to propose a new opinion for assistance of catalytic reactions by the synergetic effect of acid sites and light irradiation.

2. Experimental

2.1. Synthesis and characterization of porous sulfated biometallic oxide

The pathway used to fabricate $\text{SO}_4^{2-}/\text{Fe}_{2-x}\text{Ti}_x\text{O}_3$ (SFT-5) is similar to our previous work [23]. More details in the preparation of solid acid are presented in Supporting Information. In order to further investigate the effect of sulfur and titanium species doped on the property, structure and performance of the catalyst, no sulfated Fe–Ti biometallic oxides and pure sulfated iron oxide was prepared similar to synthesis of SFT-5 and was denoted as FT-5 and SF, respectively. Characterizations of the prepared nanoparticles are described in Supporting Information.

2.2. Catalytic experiments

The catalytic oxidation experiments were carried out in a double glass cylindrical jacket reactor (2 L), equipped with magnetic stirrer, heating jacket, and condenser. In a typical run, 1.5 L of 100 mg L^{-1} reactive brilliant red X-3B aqueous solution and a known amount of a catalyst were transferred into the reactor. The initial pH value of the dye solution was adjusted to the required value with NaOH and H_2SO_4 solution. The suspension containing catalysts and dye was continuously stirred in the dark for 30 min at a mild temperature (25 °C) to achieve adsorption equilibrium. Prior to starting Fenton reaction, a certain amount of hydrogen peroxide (30 wt%) was added into the reaction solution after the lamp was turned on. A 200 W halogen lamp (purchased from Beijing Lighting Research Institute), emitting radiation between 350 nm and 450 nm and having a maximum emission wavelength at 420 nm, was positioned parallel to the tube at the center. To further eliminate the UV wavelength of the light during the reaction, the lamp was soaked into the 2 M NaNO_3 solution. Photo-induced catalytic experiments were carried out using different light-emitting diode (LED) lamp (OptiLED, SP-E27) as light resource with light irradiation intensity of 15 W. Light wavelength of photo irradiation was controlled by selecting three types of LED lights with wavelengths range 450–465 nm (white LED), 580–595 nm (yellow LED), and 615–650 nm (red LED) in our experiment.

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