Application of S-doped TiO₂ photocatalysts in degradation of BTEX from synthetic surfaces

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Abstract. S-doped anatase TiO₂ (average grain size: 20 nm) was synthesized by a hydrothermal treatment, and the crystalline phase and morphology of the as-fabricated materials were characterized with XRD, TEM, and EDX. We investigated the catalytic reactions in a simulated environment (60 L environmental chambers) in tandem with TD-GC-MS determinations. Furthermore, the photocatalytic activity of S-doped TiO₂ was evaluated by monitoring the degradation of BTEX from synthetic surfaces, and maximum of 85% degradation rate exhibited for the S-doped TiO₂ under visible light after irradiation for 1 h.

1. Introduction

Volatile organic compounds such as BTEX (benzene, toluene, ethylbenzene, xylenes) are of particular interest in the field of air quality [1,2]. At present, the emissions of BTEX from synthetic surfaces catch social attention of the departments in China [3], and are key factors to outdoor emission sources. Synthetic surfaces are traditionally used for track and field exercise, and together with stable physical performance [4]. The United States Environmental Protection Agency believes that BTEX cause serious air pollution which endangers ecological environment [5]. Many researches have been conducted on the effects of BTEX on human health [6,7], and there is always a demand to degrade BTEX from air and synthetic surface samples since they are at a wide range of concentrations.

Catalytic degradations have been carried out under ultraviolet (UV) light sources because TiO₂ shows relatively high activity and chemical stability. Normally, solar light contains only about 4% of UV—this is a small amount compared to 45% of energy in the visible region, and the practical application of TiO₂ photocatalysts is restricted. The modification using nonmetal-doped TiO₂ is a promising technique [8-11], and has been applied to many investigations to achieve outstanding catalytic performance under visible light irradiation [12-15]. However, photodegradation of BTEX from synthetic surfaces during their application has received less attention. Thus, evaluation of visible light active catalysts for degradation of BTEX in a simulated environment has social benefits.

In this study, S-doped anatase TiO₂ was prepared using a hydrothermal process and post-calcination. The morphology and chemical composition of the S-doped TiO₂ were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), and energy dispersive X-ray (EDX), respectively. Simulated with environmental chambers, the BTEX were determined by thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS), and S-doped TiO₂ was used to degrade BTEX from synthetic surface under visible light. The photocatalytic activity of S-doped TiO₂ was investigated, and meaningful progress was made for the efficient degradation of BTEX.
2. Experimental section

2.1. Instruments and chemicals
The TD-GC-MS system consisted of a Thermo Scientific Trace 1300 gas chromatograph coupled to an ISQ mass spectrometer (USA), and a Markes International TD 100-xr thermal desorber (UK). Other main instruments included a Philips-FEI Tecnai G2 F30 S-Twin high-resolution transmission electron microscopy (Netherlands), a PNAlytical X' Pert Pro multi-function X-ray diffractometer (Netherlands), an Impact Scientific SC-10 multi-tube aging set (China), an AMAE EM-1500 intelligent air sampler (China), and a 60-L VHX environmental chamber (China).

99.9% purity TiCl₄, 99.0% purity thiourea, methanol and ethanol of chromatographic grade were purchased from the Macklin Biochemical (China). 1000 μg mL⁻¹ BTEX in methanol (benzene, toluene, ethylbenzene, m-xylene, p-xylene, styrene, o-xylene) were purchased from o2si smart solutions (USA), and water (resistivity of 18.2 MΩ cm) was prepared by a Millipore Milli-Q integral ultrapure water system (USA).

2.2. Preparation of S-doped TiO₂ and characterizations
To synthesize the photocatalyst powders, 200 mL 98% ethanol, 2.9 mL TiCl₄, and 8.0 g thiourea (as a sulfur source) were successively added to a beaker with stirring. The mixed solution (via ultrasonic treatment for 30 min) was obtained until to be completely dissolved. Next, the liquid was transferred to a 400 mL Teflon-lined hydrothermal reactor when stirred at 150 °C for 6 h. Precipitates were washed with ethanol and water, and then dried in an oven at 60 °C for 30 min. After that, the precursors were calcined in a muffle furnace at 500 °C for 3 h, resulting in S-doped TiO₂.

XRD analysis was carried out using Cu-Kα radiation (λ = 1.5406 Å) with a Cu X-ray tube operated at 40 kV. Jade software was used to measure the half maximum bandwidth (β) and diffraction angle (θ) of diffraction peak. Catalyst particles were scattered in ethanol by ultrasonic dispersion for 5 min, and then made into wafers of 3 mm in diameter. They were put on a copper mesh in TEM. The microstructure was observed under the accelerating voltage of 300 kV, and Digital Micrograph software was used to measure the lattice spacings.

2.3. Simulation conditions in environmental chambers
Environmental chamber methods are widely used due to reliable environmental simulations, which can be applied to the BTEX monitoring of chamber air. Simulation conditions in chambers and TD-GC-MS conditions are listed in Table 1 and Table 2. Capillary column was selected referring to the separability of BTEX, and a 7-level calibration curve was prepared with BTEX in a range of 0.1–1.0 μg in methanol solvent. The integral areas of chromatographic peaks were in good linear relation to the known amount of standards, and the correlation coefficients were 0.998 or above.

3. Results and discussion

3.1. Crystalline size, morphology and properties
S-doped TiO₂ nanoparticles fabricated by controllable hydrothermal steps appeared to be three-dimensional crystallines with partly aggregation (Figure 1A). The average grain size (L) of particles was counted as 20 nm (Figure 1B). It was similar to that of (101) diffraction peak’s θ (Figure 2B) calculated by Scherrer equation (Equation (1)). K is a constant related to crystalline shape. Because the particles were nonspherical (K = 0.94), for the low-angle diffraction lines of crystals, Lₐ was calculated to be 20.1 nm (Equation (2)). The lattice spacing was 3.5 Å corresponding to (101) crystal plane of high-resolution TEM observation (Figure 1C), which was regarded as the crystal plane of anatase phase.

\[
L = \frac{K\lambda}{\beta \cos \theta}
\]  

(1)
\[ L_n = \frac{k}{2\pi x \cos \theta} \tag{2} \]

**Table 1.** Simulation conditions in environmental chambers.

| Parameters                     | Conditions          |
|-------------------------------|---------------------|
| Atmospheric pressure          | 101.5 kPa           |
| Temperature                   | 50 ± 1 °C           |
| Relative humidity             | 40 ± 2%             |
| Surface air velocity          | 0.1 m s\(^{-1}\)    |
| Sampler sorbent               | Tenax-TA            |
| Air flow rate                 | 0.2 L min\(^{-1}\)  |
| Total sampling volume         | 6 L                 |
| Sample loading factor         | 0.4 m\(^2\) m\(^{-3}\) |
| Visible light wavelength      | 420 nm              |
| Irradiation energy            | 86.7 mW cm\(^{-2}\) |
| Irradiation time              | 1 h                 |

**Table 2.** TD-GC-MS analysis conditions.

| Variables | Conditions |
|-----------|------------|
| TD        | Tenax-TA activation: aged at 260 °C (30 min) |
|           | Cold trap temperature: -2 °C |
|           | Desorption disposal: 240 °C (10 min) |
|           | Column: DB-WAXMS (30 m × 0.25 mm × 0.25 µm) |
| GC        | Carrier gas: He (99.999%) of 1.0 mL min\(^{-1}\) flow rate |
|           | Temperature program: 60 °C (5 min) at a heating rate of 5 °C min\(^{-1}\)→150 °C (5 min) at a heating rate of 15 °C min\(^{-1}\)→240 °C (5 min) |
|           | Ionization mode: electron ion (EI) |
|           | Ionization energy: 70 eV |
| MS        | Mass-to-charge ratios (m/z) scan range: 40–300 amu |
|           | Transmission line temperature: 220 °C |
|           | Ion source temperature: 200 °C |
|           | Solvent delay: 2 min |

Figure 2A and 2B display the EDX spectrum of micro area elemental analysis and the XRD pattern of products. The chemical compositions were S, Ti and O, where Cu peak came from the copper mesh. Based on JCPDS No. 89-4921, it was clear that the crystal was anatase phase. The peaks at 25.3°, 37.9°, 48.1°, 54.1°, 55.0°, 62.8°, 68.9°, 70.3°, and 75.2° were assigned to the diffraction of (101), (004), (200), (105), (211), (204), (116), (220), and (215) crystal planes of the anatase phase, respectively.
3.2. Degradation of BTEX from synthetic surfaces under visible light irradiation

The synthetic surfaces were cut to 15 × 16 cm in size, and sealed with aluminum foil tape at both the artificial cutting edges and the bottom. After specimen preparation, the surfaces were placed in chambers for testing (LED lamp off). With no heating process of chambers, a porous nickel foam net (10 cm × 10 cm × 1.6 mm) with 25 pores per linear inch was used as a catalyst carrier. 0.3 g catalysts were mixed with 60 mL water using ultrasonic treatment for 5 min, and then attached to the nets with a sodium silicate binder. They were placed in the center of the chambers, and the reaction was started by illumination with a LED lamp at 420 nm wavelength (Figure 3). Anatase TiO₂ is considered to have a high photocatalytic activity based on the generation of hydroxyl radicals and trapped holes. The proposed photocatalytic mechanism is as follows: S dopant is incorporated to take the place of Ti or O in the lattice of TiO₂, resulting in bandgap narrowing in TiO₂ nanostructures. Hence, S-doped TiO₂ had been applied to degradation of BTEX from synthetic surfaces under visible light irradiation.

![Figure 1. TEM (A,B) and high-resolution TEM (C) images of S-doped TiO₂.](image-url)
Figure 2. EDX spectrum (A) and XRD pattern (B) of S-doped TiO$_2$.

Figure 3. Schematic of photodegradation of BTEX in environmental chambers.
All the samples were measured in triplicate. After reaction, the degradation rate of BTEX ($D$, %) is calculated by Equation (3):

$$D = \frac{\sum m_o - m_t}{m_o} \times 100\%$$  \hspace{1cm} (3)

where $m_o$ is the initial amount (μg) of BTEX, $m_t$ is the reactant amount of BTEX after irradiation, and $\sum m$ corresponds to the total integral area of chromatographic peak which is the summation of BTEX amounts.

We compared the photocatalytic activities of S-doped anatase and pure anatase by monitoring the degradation of BTEX as a function of irradiation time (Figure 4). Aliquots of 100 mL BTEX with a concentration of 20 μg mL$^{-1}$ were pipetted to quartz containers in chambers using different sequence numbers. The degradations of BTEX that emitted from methanol solvent were then carried out by nickel foam nets attached with two photocatalysts. Before reaction, BTEX emissions were contacted with catalysts for 30 min. Here, the $D$ of pure anatase was less than 16% in 50 min, while the $D$ of S-doped anatase was 70% after irradiation for 60 min. For the nonmetal-doped TiO$_2$, a maximum $D$ was achieved.

![Figure 4. Effect of irradiation time on photocatalytic performance of catalysts; error bars represent standard deviations ($n = 3$).](image)

To further evaluate BTEX emissions and degrade them from representative synthetic surfaces, enhancing the photocatalytic degradation over S-doped TiO$_2$ was illustrated. Results in Table 3 imply that the mean $D$ are examined (>79%), and they reach 85% which presents efficient removals of BTEX. Consequently, it demonstrated that the catalytic application of S-doped TiO$_2$ was reliable, and possessed practical applicability to degradation of BTEX emissions. These treatments with visible light active catalysts made significant progress in controlling BTEX produced from synthetic surfaces at low levels after irradiation for 1 h.
Table 3. Mean degradation rates of BTEX from synthetic surfaces.

| No. | $\sum m_0$ (µg, before photodegradation) | $\sum m_t$ (µg, catalyzed by 20 nm S-doped TiO$_2$) | $D$ (%) |
|-----|----------------------------------------|-----------------------------------------------|---------|
| 1   | 1.216                                  | 0.229                                         | 81.2    |
| 2   | 1.137                                  | 0.178                                         | 84.3    |
| 3   | 0.908                                  | 0.135                                         | 85.1    |
| 4   | 1.052                                  | 0.206                                         | 80.4    |
| 5   | 1.479                                  | 0.252                                         | 83.0    |
| 6   | 1.285                                  | 0.194                                         | 84.9    |
| 7   | 1.120                                  | 0.233                                         | 79.2    |
| 8   | 1.145                                  | 0.200                                         | 82.5    |
| 9   | 0.894                                  | 0.183                                         | 79.5    |
| 10  | 1.019                                  | 0.167                                         | 83.6    |

4. Conclusions
S-doped anatase TiO$_2$ with enhanced catalytic performance was prepared through a facile hydrothermal method. Subsequently, the photocatalytic activity of as-fabricated catalysts in environmental chambers was evaluated under visible light, and the mean $D$ increased up to maximum of ~85%. S-doped TiO$_2$ can be expected to be utilized for degradation of BTEX from synthetic surfaces and environmental remediation, and this application is not only appropriate for authorities to monitor corresponding pollutants but also a critical step for controlling BTEX emissions.

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