

## INFLUENCE OF RAPID HEAT TREATMENT ON THE PHOTOCATALYTIC ACTIVITY AND STABILITY OF STRONTIUM TITANATES AGAINST A BROAD RANGE OF POLLUTANTS

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### Abstract

Strontium titanate (STO) photocatalysts were synthesized using a modified Pechini sol–gel method. These photocatalysts were then subjected to rapid calcination at various temperatures with short exposure times. The samples were characterized using a range of techniques, including X-ray diffractometry, scanning electron microscopy, diffuse reflectance spectroscopy, infrared spectroscopy, nitrogen adsorption–desorption measurements, and X-ray photoelectron spectroscopy. The photocatalytic activity of the samples was evaluated by testing their ability to oxidize phenol, oxalic acid, chlorophenol, glucose, and propanol under UV light irradiation. Notably, all the prepared samples exhibited higher photocatalytic activity compared to the commercial STO reference. Increasing the calcination temperature resulted in improved crystallinity and larger primary crystallite sizes, but it also led to reduced band gaps and specific surface areas. The enhanced photocatalytic activity observed in the most efficient samples was attributed to the presence of SrCO<sub>3</sub> on the surface of the catalyst. Importantly, the STO photocatalysts exhibited high stability, maintaining their crystalline composition even after exposure to chemicals with different functional groups. Reusability experiments showed that the photocatalytic activity increased over successive reuse cycles, for which further investigations will be carried out to identify the possible causes.

### Introduction

Strontium titanate (SrTiO<sub>3</sub>) is a perovskite-type photocatalyst featuring a 3.2 eV band gap, making it a favorable contender for applications in both water splitting [1, 2], and the photodegradation of organic contaminants [1-4]. The catalyst offers several benefits, including affordability, robust photocatalytic performance, resistance to photo corrosion, and non-toxic nature. However, the primary drawback of SrTiO<sub>3</sub> lies in its limited ability to harness solar energy, absorbing only a narrow portion (about 5%) due to its wide band gap. This wide band gap confines its utility for photocatalytic degradation when exposed to UV light [1-5]. Hence, the majority of research endeavors have centered on enhancing SrTiO<sub>3</sub> through methods like anion doping [6-8], introducing metal dopants [9, 10], creating oxygen deficiencies [11], depositing noble metals [12], crafting composites [13], or employing dye sensitization [14]. Various methods are employed for SrTiO<sub>3</sub> synthesis, including reverse microemulsion, carbon-free combustion, hydrothermal, polymeric precursor, and sol-gel techniques [15, 16]. Among these methods, the sol-gel approach has garnered research interest due to its simplicity and adaptability [16, 17]. The Pechini method, a sol-gel technique, is widely utilized to obtain highly pure oxides [18, 19]. However, perovskite preparation through sol-gel methods

necessitates a costly high-temperature calcination step [20]. The calcination temperature significantly impacts the physicochemical properties of photocatalysts, as demonstrated by Jia et al., who observed its strong influence on the stability and photocatalytic activity of doped SrTiO<sub>3</sub> photocatalysts [5]. Despite extensive research on sol-gel synthesis of SrTiO<sub>3</sub>, some aspects, such as the influence of calcination parameters on photoactivity, remain unclear. Calcination, while offering an effective and controllable means to crystallize amorphous materials, is often underexplored [17, 21, 22]. Employing unmodified, optimally calcined SrTiO<sub>3</sub> could yield more cost-effective catalysts while maintaining their relatively high photoactivity [17]. While research typically focuses on achieving maximum photocatalytic activity, it is equally important to develop stable photocatalysts for practical applications [23-26]. Notably, the stability of SrTiO<sub>3</sub> against pollutants with various functional groups has not been investigated to date.

In this study, unaltered SrTiO<sub>3</sub> photocatalysts were synthesized using a distinctive rapid heat treatment process at varying temperatures. The influence of this calcination technique on the characteristics of the specimens was thoroughly examined. We explored their photocatalytic efficiency in degrading phenol, chlorophenol, and oxalic acid under UV exposure and assessed their resilience against a range of compounds with different functional groups.

## **Experimental**

This study employed a modified Pechini sol-gel method, based on the previous research by Chen et al. [27] and Lu et al. [28]. This method involved dissolving Sr(NO<sub>3</sub>)<sub>2</sub> and citric acid in deionized water, adding titanium(IV) butoxide and ethylene glycol, and subjecting the solution to 4 hours of heating at 100 °C. The resulting amorphous product was collected and dried to obtain the xerogel. Calcination was carried out using a controlled air supply in a tube furnace, with materials labeled as "STO\_RHSE\_X" (strontium titanate; rapid heating, short exposure; and "X" corresponds to the different calcination temperatures).

Characterization of the catalysts involved various analytical techniques. X-ray diffraction (XRD) was used to measure crystallite sizes. Scanning electron microscopy (SEM) was used to obtain morphological insights, while nitrogen adsorption and the Brunauer-Emmett-Teller model were used to calculate specific surface areas. Optical properties were studied through diffuse reflectance (DR) spectroscopy, determining band gap energies from first-order derivative spectra. Thermal gravimetric (TG) analysis was carried out to determine the minimum calcination temperature. Fourier-transform infrared (IR) spectroscopy and X-ray photoelectron spectroscopy (XPS) were used to study the surface of the samples.

To evaluate photooxidation performance, the study used three pollutants (phenol, chlorophenol, and oxalic acid) under UV light in a temperature-controlled vessel. High-performance liquid chromatography (HPLC) quantified changes in pollutant concentrations. The study also examined the stability of RHSE samples against different functional groups by repeating XRD, IR, and SEM measurements after photocatalytic activity tests, expanding the evaluation to include propanol and glucose.

Following the characterization of material structure and the evaluation of photocatalytic activity and stability, we investigated the reusability of the STO\_RHSE samples. Three consecutive phenol degradation measurements were carried out for each sample, and the reusability measurement was repeated two additional times for the best-performing samples to investigate how further the photocatalytic activity can be increased and over how many cycles.

## Results and discussion

Following the synthesis, a pale yellow xerogel was obtained, and TG measurements indicated no mass loss beyond 600 °C. Consequently, calcination temperatures ranging from 600–1000 °C were used to prepare the RHSE STO samples. XRD patterns revealed characteristic reflections for SrTiO<sub>3</sub> and SrCO<sub>3</sub>. The primary crystallite sizes exhibited an increase, ranging from 14.7 to 39.2 nm, with the temperature rising from 600 to 1000 °C. Simultaneously, specific surface areas decreased from 54.5 to 2.1 m<sup>2</sup> g<sup>-1</sup>. As a matter of fact, the calculated primary crystallite sizes increased in line with the calcination temperature, and specific surface areas decreased with higher temperatures. SEM micrographs revealed polycrystalline samples with various shapes and sizes, forming aggregated structures. DRS results showed that the band gap values varied only within a narrow range (3.20–3.25 eV), with slight redshifts resulting from the higher calcination temperatures.

The XPS results could not reveal the reason for the superior activity of the best-performing sample (i.e., STO\_RHSE\_700). However, IR spectra indicated the presence of SrCO<sub>3</sub>, which was successfully related to the observed high photoactivity. Stability tests against various functional groups showed that RHSE samples were generally stable, with some changes observed after exposure to oxalic acid.

Photocatalytic activity assessments for phenol, chlorophenol, and oxalic acid indicated that our RHSE samples outperformed the commercial STO reference. RHSE STO samples displayed varying photocatalytic activity related to calcination temperature, with STO\_RHSE\_700 being the most efficient. The significant photocatalytic performance of STO\_RHSE\_700 can be rationalized by the existence of SrCO<sub>3</sub>, which is recognized for its role as a co-catalyst in SrTiO<sub>3</sub>/SrCO<sub>3</sub> configurations. SrCO<sub>3</sub> enhances the separation of charges by capturing photogenerated electrons found in the conduction band of SrTiO<sub>3</sub>. This capture process diminishes recombination rates, resulting in an overall enhancement of photoactivity [26, 29]. STO\_RHSE\_700 and STO\_RHSE\_800 photocatalysts, identified as the most efficient ones, were selected to evaluate the maximum number of cycles for which their activity in phenol degradation tests continues to increase. It was observed that the photoactivity gain of the catalysts decreased after the third cycle, suggesting that the catalysts are approaching their maximum activity levels for phenol degradation under the given experimental conditions. After the third cycle, the active sites on the surface of the catalysts may have become saturated with phenol or other intermediates, which can limit their ability to further degrade phenol. Based on XRD and SEM results, the crystalline composition and morphology of STO\_RHSE\_700 and STO\_RHSE\_800 did not change even after five cycles of exposure to phenol solution.

## Conclusion

The impact of RHSE treatment on STO photocatalysts was explored. As the temperature increased from 600 to 1000 °C, there was a noticeable growth in the primary crystallite sizes, spanning a range of 14.7 to 39.2 nm. At the same time, the specific surface areas experienced a decline, decreasing from 54.5 to 2.1 m<sup>2</sup> per gram. The morphology and band gap values remained largely unaffected, except for a slight redshift in the band gaps. The photocatalysts demonstrated high stability by retaining their crystalline composition even after exposure to compounds with various functional groups. Notably, the photocatalytic activities predominantly improved with lower calcination temperatures. The most effective sample, displaying enhanced performance against phenol, chlorophenol, and oxalic acid, was the one prepared at 700 °C calcination temperature. The superior photocatalytic activity was primarily attributed to the presence of SrCO<sub>3</sub>. The photocatalysts remained stable against compounds containing phenolic –OH, alcoholic –OH, –Cl, and –CHO functional groups, although minor changes were observed in their crystalline composition following exposure to relatively

concentrated oxalic acid (–COOH). Photoactivity enhancement was observed over the reusability cycles, which is most likely due to a surface-related phenomenon.

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