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# Enhancement of photocatalytic activity of $CaTiO_3$ through $HNO_3$ acidification

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ABSTRACT

$CaTiO_3$ synthesized by the hydrothermal method was treated to improve its photocatalytic activity using the $HNO_3$ acidification. Changes of morphology, structure, and composition of the acidified $CaTiO_3$ were investigated through various means such as XRD, SEM, BET, FTIR, Raman spectra, XPS, and UV–vis DRS. The results show that the enhancement of $HNO_3$ acidification led to the increase of substitutional N (O–Ti–N) compared to interstitial N (Ti–O–N and Ti–N–O) in the $CaTiO_3$ lattice. The apparent first-order reaction constant ($k_{obs}$) of methylene blue over the acidified $CaTiO_3$ at pH 2 was the largest and increased by 1.0 times than that over the not-acidified $CaTiO_3$, indicating that the acidified $CaTiO_3$ at pH 2 has the best photocatalytic performance among as-prepared samples. A negatively linear relationship between $k_{obs}$ and $|1 - N_{O-Ti-N}/N_{Ti-O-N+Ti-N-O}|$ suggests that the improvement of photocatalytic activity of $CaTiO_3$ by $HNO_3$ acidification depends on synergistic effects of substitutional and interstitial N in $CaTiO_3$ lattice.

## 1. Introduction

The perovskite-type oxides with a structural formula of $ABO_3$ (A is a rare or alkaline earth metal and B is a first row transition metal) have excellent properties with wide applications in electronics, ceramics, superconductor, nonlinear optics, and catalysis [1–4]. $CaTiO_3$ is well known as one of the most important perovskites and has attracted more and more focus in the last decade. It can be prepared by many methods such as solid state [5–7], co-precipitation [8], mechanochemical [9], sol–gel [10–12], hydrothermal [13–16], and solvothermal methods [17,18]. Among these methods, hydrothermal or solvothermal routes for $CaTiO_3$ have become the popular methods because they can exactly control crystal growth, achieve novel crystal morphologies, and optimize physicochemical properties [14]. Hydrothermal or solvothermal methods generally involved the facile reactions of titanium alkoxides or $TiO_2$, calcium salt, mineralizers, and water or organic solvent in a Teflon-lined stainless steel vessel at 100–220 °C [13–18].

Based on the hydrothermal method, rod-like and cubic-shaped $CaTiO_3$ particles were successfully synthesized by changing temperature and Ti-sources such as $TiO_2$ and titanium-triethanolamine [13]. Three-dimension aggregated prisms, butterfly-like dendrites, and cross cubic shapes $CaTiO_3$ particles were prepared by controlling NaOH concentration during the hydrothermal process [14]. Single-crystalline hollow $CaTiO_3$ cubes can be produced through introducing 5% water during the solvothermal process [18]. Spherical, cubic, and rectangular $CaTiO_3$ particles can be obtained with varying content (1.25–5%) and addition order of water in the solvothermal process [17].

It has been widely reported that $CaTiO_3$ exhibits a superior photocatalytic performance in the removal of some organic and inorganic pollutants and the photolysis of water to hydrogen and oxygen [19–23]. The photodegradation percentage of methyl orange can reach to 96% using $CaTiO_3$ under ultraviolet light irradiation [12]. 98.4% of As(III) was oxidized to As(V) by photo-generated holes over fern-like $CaTiO_3$ nanoparticles [19]. Hydrogen production rate of 0.34 μmol/min was achieved with Pt-loaded $CaTiO_3$ as photocatalyst to decompose water [7]. $CaTiO_3$ shapes can affect its photocatalytic activity. Compared to flower-like and prism-like $CaTiO_3$, butterfly-like dendrites $CaTiO_3$ showed better photocatalytic activity to degrade rhodamine B [14]. Rectangular $CaTiO_3$ had higher activity than cubic and spherical ones for photocatalytic degradation of methylene blue [17].

Because of its wide band gap energy (3.5 eV), $CaTiO_3$ was photoactive only in ultraviolet light region. Recently, the metal

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doping has been made to enhance the photocatalytic activity of $CaTiO_3$. For example, the photocatalytic activity of Ag-La codoped $CaTiO_3$ for hydrogen evolution increased dramatically than that of $CaTiO_3$ when the doping amount was 3 mol% [10]. Compared to $CaTiO_3$, $CaTi_{1-x}Cu_xO_3$ ($0.1 \leq x \leq 0.04$) exhibited a higher activity for the photocatalytic decomposition of water to oxygen and hydrogen [11]. $Pt/CaTi_{0.9}Fe_{0.1}O_3$ had a certain activity while $Pt/CaTiO_3$ was inactive under visible light for photocatalytic generation of hydrogen from methanol–water solution [21]. Our previous study found that the doping of Fe in $CaTiO_3$ can promote the photocatalytic degradation of methylene blue [5].

In this study, $CaTiO_3$ synthesized using the hydrothermal method was modified to enhance its photocatalytic activity by $HNO_3$ acidification. The changes in the structures, compositions, and properties of the modified $CaTiO_3$ were detailedly characterized using various means including X-ray diffractometer (XRD), scanning electron microscope (SEM), specific surface area analysis, Fourier transform infrared spectrometer (FTIR), Raman spectrometer, X-ray photoelectron spectroscopy (XPS), and UV–vis diffuse reflection spectra (UV–vis DRS). The photocatalytic activity of $CaTiO_3$ was evaluated through the degradation of methylene blue (MB) under irradiation. Effects of $HNO_3$ acidification on the photocatalytic activity of $CaTiO_3$ were also discussed.

## 2. Experimental

### *2.1. $CaTiO_3$ synthesis*

$CaTiO_3$ particles were synthesized by the hydrothermal method. In a typical process, solid $Ca(NO_3)_2 \cdot 4H_2O$ (2.362 g) was dissolved by water in the Teflon-lined stainless steel vessel. Tetrabutyl titanate (3.4 mL) was dropwise added into the solution under vigorous stirring. The molar ratio of Ca to Ti was 1.0. Then, solid NaOH (0.8 g) was introduced as the mineralization reagent. The mixture was continuously stirred at ambient temperature for 1.0 h. Subsequently, the hydrothermal treatment was carried out for 24 h at 200 °C. After cooling, the precipitates were recovered by the filtration, washed several times with ethanol, diluted acetic acid, and deionized water, and dried for 12 h at 80 °C.

### *2.2. $HNO_3$ acidification of $CaTiO_3$*

The pH value of 20 mL deionized water was adjusted to 4 and 2, respectively, or the $HNO_3$ concentration in 20 mL deionized water was adjusted to 2 mol/L using $HNO_3$. These water solutions containing $HNO_3$ were used to modify $CaTiO_3$. After the addition of $CaTiO_3$ (0.2 g), the corresponding acidic solution was continuously stirred to evaporate water at 50 °C. The sample was further dried for 24 h at 80 °C and then was calcined for 3 h at 500 °C. Thus, the acidified $CaTiO_3$ by $HNO_3$ at pH 4, pH 2, and $HNO_3$ concentration of 2 mol/L was obtained. As a comparison, the not-acidified $CaTiO_3$ was also likewise treated without the addition of $HNO_3$.

### *2.3. $CaTiO_3$ characterizations*

X-ray diffractometer (XRD, X'Pert Pro, PANalytical) with Cu Kα radiation at 40 kV and 40 mA was used to analyze crystal structures of $CaTiO_3$. A surface area & pore size analyzer (NOVA 1200e, Quantachrome) was employed to measure specific surface areas of $CaTiO_3$ by $N_2$ adsorption/desorption at 77 K. Specific surface areas were determined by applying the Brunauer–Emmett–Teller (BET) method to the adsorption isotherm in the partial pressure range of 0.05–0.35. Scanning electron microscope (SEM, SSX-550, SHIMADZU) was used to observe micro morphologies of $CaTiO_3$. Fourier transform infrared spectrometer (FTIR, Thermo Nicolet-380) was adopted to investigate functional groups of $CaTiO_3$ with KBr as a pelletizing medium. A UV resonance Raman spectrometer (UVR DLPC-DL-03) was used to obtain Raman spectra of $CaTiO_3$. The exciting radiation was a continuous diode pumped solid state (DPSS) laser beam (325 nm), and the source power output was 60 mW. A surface analysis system (ESCALAB 250, Thermo Fisher Scientific) with an Al Kα radiation was employed to record X-ray photoelectron spectroscopy (XPS) of $CaTiO_3$. The UV–vis diffuse reflection spectra (UV–vis DRS) of $CaTiO_3$ was recorded by a diffuse reflectance UV–vis spectrophotometer (2550, SHIMADZU) with $BaSO_4$ as the reflectance standard.

### *2.4. Photocatalytic activity test*

The photocatalytic activity of $CaTiO_3$ was measured by decomposing MB in an aqueous solution under the irradiation of 500 W Xe lamp. During a typical MB removal experiment, $CaTiO_3$ (0.1 g) was dispersed into aqueous solution (200 mL) with initial MB concentration of 10 mg/L. Before irradiation, the aqueous suspension was magnetically stirred for 1.0 h to reach an adsorption/desorption equilibrium of MB on $CaTiO_3$ in the dark. Subsequently, the lamp was turned on and the photocatalytic

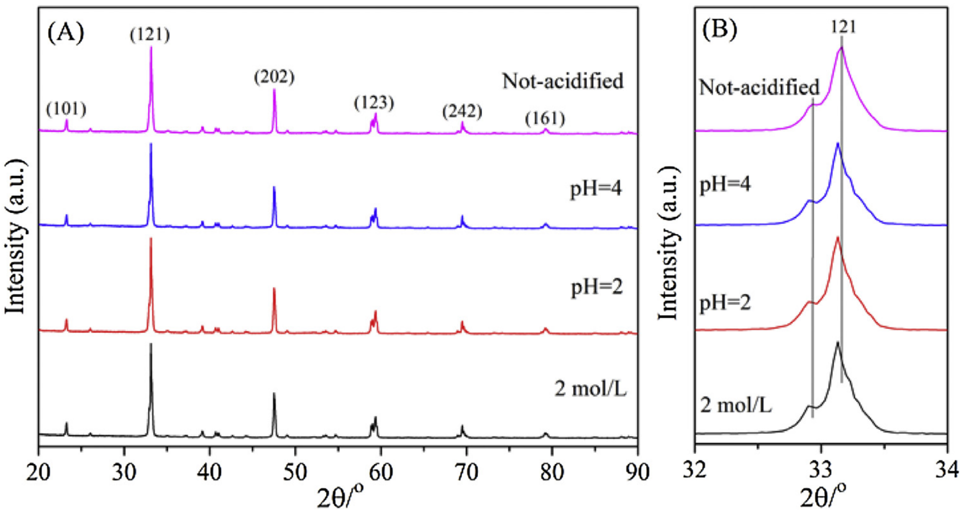

**Fig. 1.** XRD patterns of not-acidified and acidified $CaTiO_3$.