Defect-meditated efficient catalytic activity toward *p*-nitrophenol reduction: A case study of nitrogen doped calcium niobate system

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HIGHLIGHTS

- Nitrogen doped $Ca_2Nb_2O_7$ was found to be an efficient and green noble-metal-free catalyst toward catalytic reduction of *p*-nitrophenol.
- Defective nitrogen and oxygen species were found to play synergetic roles in the reduction of *p*-nitrophenol.
- Nitrogen doped $Ca_2Nb_2O_7$ showed photo-synergistic promotion effects toward *p*-nitrophenol reduction under UV light irradiation.

GRAPHICAL ABSTRACT

A series of nitrogen doped $Ca_2Nb_2O_7$ was successfully prepared via ion-exchange method, which was found to be an efficient and green noble-metal-free catalyst toward catalytic reduction of *p*-nitrophenol.
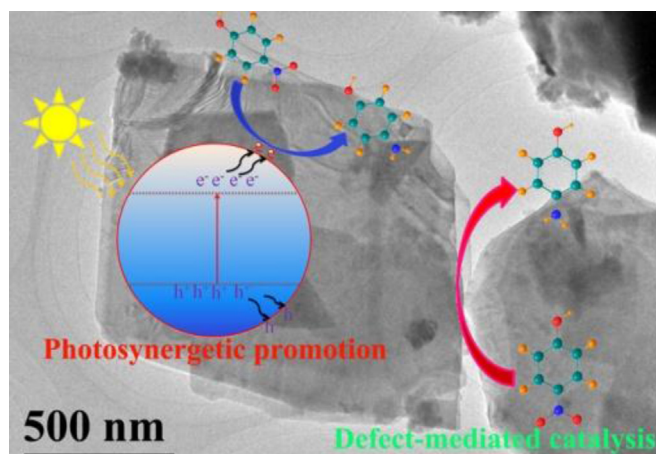
ABSTRACT

This work reported on the synthesis of a series of nitrogen doped $Ca_2Nb_2O_7$ with tunable nitrogen content that were found to be efficient and green noble-metal-free catalysts toward catalytic reduction of *p*-nitrophenol. XPS and ESR results indicated that the introduction of nitrogen in $Ca_2Nb_2O_7$ gave rise to a large number of defective nitrogen and oxygen species. Defective nitrogen and oxygen species were found to play synergetic roles in the reduction of *p*-nitrophenol. The underlying mechanism is completely different from those reported for metallic nanoparticles. Moreover, the more negative conduction band edge potential enabled nitrogen doped $Ca_2Nb_2O_7$ to show photo-synergistic effects that could accelerate the reduction rate toward *p*-nitrophenol under UV light irradiation. This work may provide a strategy for tuning the catalytic performance by modulating the chemical composition, electronic structure as well as surface defect chemistry.

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1. Introduction

Nitrobenzenes are generally generated as by-products that are the most frequent pollutants present in wastewaters causing

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environmental problems [1]. Numerous studies have been devoted to their removal via adsorption, photocatalytic degradation as well as chemical transformation [2,3]. In particular, the chemical transformation of nitrobenzenes via a catalytic reduction process to fabricate the corresponding aminobenzenes provides an efficient way to eliminate nitroaromatic pollutants for the reason that anilines are very important intermediates for industry to produce highly valuable products including dyestuffs, agricultural chemicals, antipyretic drugs, and so on [4,5]. Among nitrobenzenes, the *p*-nitrophenol is regarded as the most common contaminant that shows excellent chemical and biological stability. Therefore, the choice of suitable catalyst and reducing agent plays critical roles in this transformation because it determines the reaction conditions, efficiency, and selectivity of this conversion reaction.

Till now, a great number of investigations have been conducted to construct free or immobilized catalytic systems for the conversion of *p*-nitrophenol by using commercially available NaBH$_4$ as reducing agent. For instance, metallic nanoparticles (Ag, Au, Pd, etc.) exhibit superior catalytic activity toward the reduction of *p*-nitrophenol and can be greatly enhanced by depositing on different supports such as CeO$_2$, SBA-15, and boron nitride [6–9]. However, most of these investigations concerned on metallic nanoparticles, especially the noble metal nanoparticles. From the view point of unprecedented commercial applications and green chemistry principles, the exploration of novel and highly active catalytic systems is urgently essential, which may bring opportunities for catalyzing many electron transfer reaction.

Niobates of general formula A$_2$B$_2$O$_7$ are important inorganic materials showing potential applications in many fields, such as ionic conductors, photocatalysts, and luminescent host materials [10–12]. Among them, Ca$_2$Nb$_2$O$_7$ represents a typical pyrochlore structure, which shows a close structural link to many materials, such as Ca$_2$Ta$_2$O$_7$, Sn$_2$Nb$_2$O$_7$, and Cd$_2$Nb$_2$O$_7$. Consequently, an experimental identification of structure and defect chemistry of Ca$_2$Nb$_2$O$_7$ is advantageous for tuning its catalytic activities and other pyrochlore materials. However, Ca$_2$Nb$_2$O$_7$ with either cubic phase or orthorhombic phase is inactive to the reduction of *p*-nitrophenol to *p*-aminophenol. It is well-accepted that the catalytic performance of inorganic materials is governed by the nature of defective centers, which is related to the chemical composition, structure as well as surface features [13]. By tuning the defective structure of TaO$_x$N$_y$ nanoparticles, it is found that surface defective nitrogen species and oxygen vacancies played critical roles in the reduction of *p*-nitrophenol because the introduction of nitrogen species in oxide nanoparticles shows some advantages in yielding noble metal like electronic structures, enhanced conductivity, and band structure changes [14].

In this work, a series of nitrogen doped Ca$_2$Nb$_2$O$_7$ with tunable nitrogen content was synthesized via an ion exchange method with an aim of exploring the impact of surface nitrogen species and its relevance defective structure on the catalytic performance toward *p*-nitrophenol reduction.

2. Experimental

2.1. Sample preparation

All chemical were of analytical grade and were used without further purification. The typical synthetic procedure of nitrogen doped Ca$_2$Nb$_2$O$_7$ is briefly described as follows: For the first step, K$_4$Nb$_6$O$_{17}$ was obtained by using K$_2$CO$_3$, KCl, and Nb$_2$O$_5$ as regents according to previous literature. 1 mmol of K$_4$Nb$_6$O$_{17}$ and given amount of CaCl$_2$ were fully mixed in an agate mortar where the initial molar ratio of Ca/Nb was fixed to be 1–4. Then the mixture was transferred into a corundum crucible and calcined in a flow of

mixed gas with NH$_3$ and N$_2$ with the volume ratio of 2 at 800 °C for 4 h. After cooling to room temperature, the samples were washed with hydrochloric acid and distilled water for several times and dried at 80 °C for 3 h. The samples were named as NC-1, NC-2, NC-3, and NC-4 with an increase of initial molar ratio of Ca/Nb.

For comparison, the undoped Ca$_2$Nb$_2$O$_7$ was also prepared. Briefly, 1 mmol of K$_4$Nb$_6$O$_{17}$ and 2 mmol of CaCl$_2$ were fully mixed in an agate mortar and transferred into a corundum crucible and calcined in a flow of N$_2$ at 800 °C for 4 h. After cooling to room temperature, the samples were washed with hydrochloric acid and distilled water for several times and dried at 80 °C for 3 h. The as-prepared undoped Ca$_2$Nb$_2$O$_7$ sample was named as NC-0.

2.2. Sample characterization

Phase purities of all samples were characterized by X-ray diffraction (XRD) on D8 Advance Bruker X-ray diffractometer using a copper target. Morphologies of the samples were determined using scanning electron microscopy (SEM) on a S-4800 apparatus working at 10 kV and transmission electron microscopy (TEM) on a DHG-9240B FEI apparatus with an acceleration voltage of 200 kV. UV–visible diffuse spectra of the samples were measured using Lambda 750s UV/vis spectrometer. The presence of nitrogen species in samples was confirmed by energy dispersive X-ray energy spectroscopy and X-ray photoelectron spectroscopy (XPS). Energy dispersive X-ray energy spectroscopy was performed on Hitachi S-4800. XPS analyses were carried out on an ESCALab220i-XL with a monochromatic Al Kα and charge neutralizer. The deconvolution software program was provided by Kratos. This software is the standard program used and is accepted as reference in the field. All the binding energies were referenced to the C 1s peak at 285 eV. Powder samples were prepared by deposition of catalyst on carbon type stuck to sample holder. The powder samples were analyzed with very large spot of a dimension 0.3 mm × 0.7 mm. Electron spin resonance (ESR) spectra of all samples were obtained on a Brüker ER200-SRC apparatus. A frequency of about 9.06 GHz was used for a dual-purpose cavity operation. The magnetic field of 0.2 mT was modulated at 100 kHz. A microwave power of about 1 mW was employed. Other parameters for the apparatus were set at: sweep width of 250 mT, center field of 250 mT, sweep time of 2.0 min, and accumulated 5 times. All measurements were performed at room temperature in air without vacuum-pumping.

2.3. Catalytic reactivity test

The catalytic activity of nitrogen doped Ca$_2$Nb$_2$O$_7$ samples was examined by choosing the reduction of 4-nitrophenol in water with an excess of NaBH$_4$ as a model reaction. In a typical experiment, aqueous solutions of 4-nitrophenol (0.01 M, 0.6 mL) and NaBH$_4$ (0.5 M, 4 mL) were mixed with 50 mL water in a 100 mL flask with stirring in a dark chamber. A sample of Ca$_2$Nb$_2$O$_7$ catalyst was dispersed in water in advance. The net weight of the catalyst in the reaction solution was 0.3 mg, and the reaction temperature was also controlled to be 25 °C by air-conditioner. At given intervals, 5 mL of the suspensions was extracted and immediately dropped in a quartz cuvette. UV–vis absorption spectra of the suspensions were measured with a UVIKON XL/XS Spectrometer. The catalytic reduction efficiency of *p*-nitrophenol was calculated according to the following equation [15]:

$$\text{Remaining fraction of } p-\text{nitrophenol} = \frac{C}{C_0} \times 100\%$$

where C and C_0 are the *p*-nitrophenol concentration at time t and the initial concentration of *p*-nitrophenol, respectively.

The photo-synergetic experiment was carried similar to that in the dark chamber. In brief, aqueous solutions of 4-nitrophenol