

The Preparation and Characterization of N-F-Sm-TiO₂ Sol and Its Photocatalytic Performance for 4-chlorophenol Degradation

Wen-tao Zhang

School of Environmental Science and Engineering
Nanchang University, Nanchang

Shui qing Quan

School of Environmental Science and Engineering
Nanchang University, Nanchang
quansq123456@126.com

Wen-fa Xie

School of Environmental Science and Engineering
Nanchang University, Nanchang

Donggen Huang

School of Environmental Science and Engineering
Nanchang University, Nanchang
dg Huang1017@163.com

Abstract—Anatase N, F and Sm codoped TiO₂ sol (N-F-Sm-TiO₂) catalysts were prepared by a modified sol-gel hydrothermal method, using tetra butyl titanate as precursor. The morphology, particle size and the present forms of F, N and Sm atoms of as-prepared N-F-Sm-TiO₂ sol were characterized by XRD、TEM、UV-Vis-DRS and XPS; The results showed that N-F-Sm-TiO₂ particles in sol were anatase structure and the average particle size was ca. 15.0 nm calculated from XRD after hydrothermal reaction at 130°C for 72 hours. It was also shown that fluorine and nitrogen atoms were adopted by TiO₂ sol particles with two forms, one was physically adsorbed on the surface of TiO₂, and the other was embedded into TiO₂ crystal lattice, and Sm did not incorporate into TiO₂ crystal lattice, existed in the form of Sm₂O₃ formed binary metal compound with TiO₂. It was found that the N-F-Sm-codoped TiO₂ sol particles showed strong visible-light absorption and high photocatalytic activity for 4-chlorophenol under irradiation by visible light (400-500nm). The high visible-light photocatalytic activity of the obtained N-F-Sm-codoped TiO₂ sol may result from the synergistic effect of nitrogen, fluorine and samarium co-doping.

Key words-titanium dioxide sol; photocatalyst; N, F and Sm co-doping; photodegradation; 4-chlorophenol

I. INTRODUCTION

Compared with powder state TiO₂ photocatalyst, TiO₂ sol catalyst has several advantages: (1) Better dispersion in water, final particle size with more uniform distribution and small particle itself; (2) High photocatalytic activity; (3) Easy coating on different supporting materials including those substrates with a poor thermal resistance such as some polymers, optical fibers, plastics, wood, porcelain, tile, and papers. Hereby, much attention has been focused on the anatase TiO₂ sol photocatalyst [1-2]. However, it is generally believed that most sol without high temperature treatment has an amorphous structure, and the amorphous TiO₂ has poor

photoactivity; In addition, the crystal phase of TiO₂ is also a critical factor and the anatase phase usually shows a better photoactivity than the rutile phase. On the other hand, Surface acidity and adsorption capacity are important factors that may influence the photocatalytic activity of TiO₂ for the photodegradation of environmental pollutant [3]. Therefore, it is very important how to prepare anatase multi-element doped TiO₂ sol catalyst on facile conditions.

There were many investigative reports on TiO₂ sol photocatalysts that related to the preparation, characterization, modification and application. Basing on the report of literatures, the preparation of TiO₂ sol photocatalyst had several methods, such as: dispersion of TiO₂ powder, sol-gel-thermal method, sol-gel-pepization method, gel-peptization method. Like TiO₂ powder photocatalyst, the doping of TiO₂ sol particles was an effective means to improve its photocatalytic activity, and the transition metals, rare earth metal ions [4], noble metals were the main doping elements. As we know, although anions doping TiO₂ powder catalysts had reported by many investigators [5], the preparation of anatase N-F-Sm-TiO₂ sol by sol-gel-hydrothermal method has not been reported.

In this paper, N, F and Sm ion co-doped TiO₂ sol (N-F-Sm-TiO₂) catalysts was fabricated by a modified sol-gel hydrothermal method, using tetra butyl titanate as precursor. The catalysts were characterized with XRD, TEM, UV-Vis-DRS, SPD and XPS. Possible mechanism of high visible-light photocatalytic activity of the N-F-Sm-codoped TiO₂ sol was discussed.

II. EXPERIMENTAL

A. Preparation of N-F-Sm-TiO₂ sol

Tetrabutyl titanate was used as a starting material, triethylamine as a nitrogen source, ammonium fluoride as a fluorine source, and samarium nitrate as a samarium source. All chemicals used in the experiments were of analytical reagent grade. Firstly, precursor tetrabutyl titanate (30 ml), 15

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ml ethanol and 5.0 ml acetic acid were put into a 250 ml flask with stirring for 60 minutes to form solution A; 5.0 ml triethylamine, ammonium fluoride (the atomic ratios of F to Ti was 0.03), 6ml ultrapure deionized water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$), 3.0 ml nitric acid, samarium nitrate (the atomic ratios of Sm to Ti were in the range of 0.001-0.08 and 85.0 ml ethanol were mixed stirring 10 minutes to form solution B. Secondly, solution B was added dropwise into solution A under vigorous stirring. After the completion of addition, slow stirring continued until the solution formed a transparent immobile gel. The gel was dispersed in water to form a sol mixture. Finally, the sol mixture was placed into a Teflon tube that was then placed in a 300 cm^3 stainless steel autoclave. The autoclave was heated in an oven and kept at 130°C for 72 h. After ultrasonic treatment, the obtained product formed uniform, stable and semitransparent sol. The acquired N-F-Sm-TiO₂ sol could maintain homogenous dispersion for quite a long time.

In addition, pure anatase TiO₂ sol, Sm-TiO₂, F-TiO₂ sol, N-TiO₂ sol and N-F-TiO₂ sol samples were also prepared in the same procedure.

B. Characterization

The phase constitution and crystallite size of the samples were determined by X-ray diffractometry (XD-3A, Shimadzu, Japan) using nickel filtered copper radiation ($\text{Cu K}\alpha$) at 30 kV, 30 mA over 2θ range of $10\sim 50^\circ$ according to the Scherrer equation using the FWHM data of phase after correcting the instrumental broadening. $D = 0.89 * \lambda / B * \cos \theta$, Where λ is the wavelength of the characteristic X-ray applied, B is the half-value width of anatase(101) peak obtained by XRD, and θ is the diffraction angle.

Morphology and size of the TiO₂ sol particles were also examined by electron microscopy (TEM). UV-Vis-DRS spectra of TiO₂ sol sample powders dried in a rotatory evaporator at 50°C and then dried in vacuum at 50°C for 64 hours were obtained for the dry-pressed disk samples using a UV-Visible spectrophotometer with an integrating sphere (UV-3010, HITACHI). Absorption spectra were referenced to BaSO₄.

X-ray photoelectron spectroscopy (XPS) measurements were performed with the PHI1600 Quantum ESCA Microprobe System, using the Mg K Line of a 300W Mg X-ray tube as a radiation source at 15 kV. All the binding energies were referred to the C 1s peak at 284.8 eV of the surface adventitious carbon. The N-F-Sm-TiO₂ sol sample dried in a rotatory evaporator at 50°C , and then dried in vacuum at 50°C for 72 hours, finally, pretreated under an O₂ flow at 320°C for 6 hour, in order to completely decompose and remove any possible precursor residues and organic contaminants.

C. Photocatalytic activity measurements

1) Experimental set-up

The schematic diagram of experimental system for 4-chlorophenol degradation is shown in Figure 1. The outside of cylindrical photoreactor made of glass with a diameter of 12 cm and a length of 60 cm was a cooling water sleeve to maintain stable reaction temperature. A 100 W tungsten

halogen lamp in conjunction with a light filter (wavelength: 400-500 nm), whose light intensity at 420 nm was 10.0 mW cm^{-2} , was used as light source, then the lamp was put into a quartz sleeve, and immersed within the photoreactor.

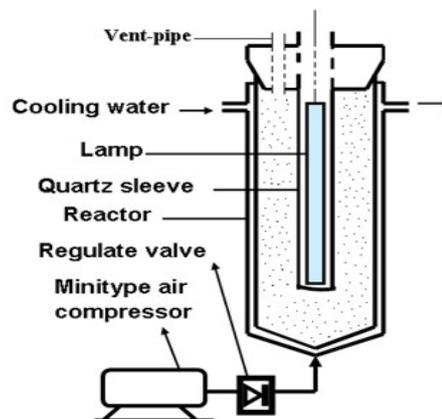


Figure1. The diagram of experimental setup for photocatalytic reaction

2) Analyses and procedures

Photocatalytic activity of N-F-Sm-TiO₂ sol was estimated by measuring the percentage decomposition of 4-chlorophenol in an aqueous solution. The concentration of 4-chlorophenol was 130 mg L^{-1} . The used amount of catalyst was 1.0 g TiO_2 per 100 ml of solution, the reactive liquid was aeration 15 min before the reaction, and the reaction time was 10~15 h. The mineralization of 4-chlorophenol was measured by determining the TOC (Liqui TOC, elemental, German) total organic carbon of reaction liquid. The degree of mineralization of reactant could be calculated as follows:

$$D_1 (\%) = 100 (\text{TOC}_0 - \text{TOC}) / \text{TOC}_0$$

Where C_0 and C is the concentration of liquid reaction before and after reaction respectively.

The degradation of 4-chlorophenol was measured by determining the concentration of 4-chlorophenol with HPLC(1100, Agilent, US). The degradation of 4-chlorophenol could be calculated as follows:

$$D_2 (\%) = 100(C_0 - C)/C_0$$

Where C_0 and C is the concentration of liquid reaction before and after reaction respectively.

III. RESULTS AND DISCUSSION

A. The particle morphology and size

Figure 2 shows the XRD patterns of Sm-TiO₂, F-TiO₂, N-TiO₂, N-F-TiO₂ and N-F-Sm-TiO₂ particles. It was found that all the TiO₂ particles had typical XRD patterns of anatase form. According to Scherrer's equation, the particles size of N-F-Sm-TiO₂ sol was 15.0 nm.

The testing results indicated that the Sm atom did not incorporate into the TiO₂ crystal lattice and that the Sm₂O₃ might form binary metal oxide with TiO₂. The ionic radii of Sm³⁺ is 0.108 nm, which is bigger than that of Ti⁴⁺ (0.068 nm), so it is impossible for Sm³⁺ ions to really enter the lattice of

TiO₂ structure on the testing condition of hydrothermal process(130 °C for 72 h).

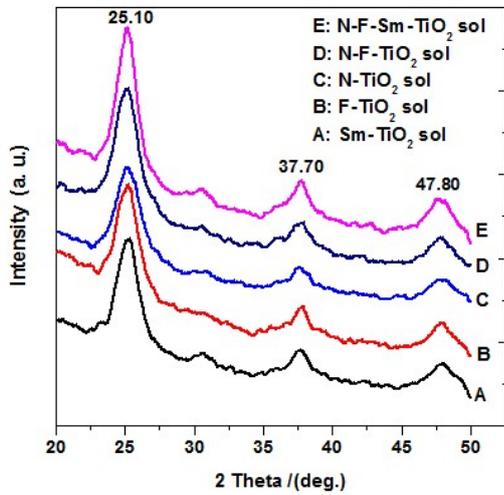


Figure 2 XRD patterns of TiO₂ sol

TEM micrograph shows that N-F-Sm-TiO₂ sol particles with spheroidal shape homogeneously distributed and the average size was about 15.0 nm (Figure 3).

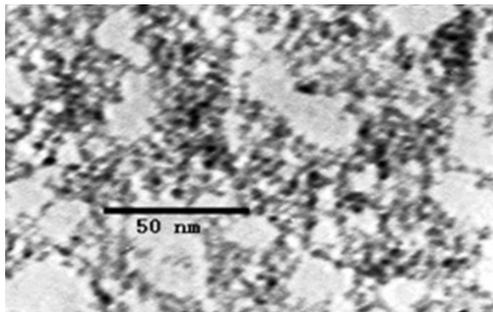


Figure3 TEM micrograph of N-F-Sm-TiO₂

B. UV-Vis absorption spectra

The absorption spectra of N-TiO₂ sol, F-TiO₂ sol, Sm-TiO₂ sol, N-F-TiO₂ sol and N-F-Sm-TiO₂ sol samples prepared by the sol-gel-hydrothermal method were shown in Figure 4. A new absorption shoulder peak was observed in the visible range of 400~550 nm apart from the fundamental absorption edge of TiO₂, which was located in the UV region at about 387nm, this indicated that the doped N atoms in TiO₂ particles could improve its visible-light absorption. Nitrogen doping led to a narrowing of the band gap by mixing the N_{2p} and O_{2p} states and consequently inducing visible-light absorption [6].

C. XPS analysis

Figure 5 presents the F1s XPS spectra of the N-F-Sm-TiO₂ sol sample powder pretreated under an O₂ flow at 320°C for 6 h. The F_{1s} region was composed of two contributions. One symmetrical peak adsorbed on the surface of TiO₂ sol particles. However, the small peak located at 688.0 eV was attributed to the F atoms doped in TiO₂, i.e., the substitute F atoms that occupied

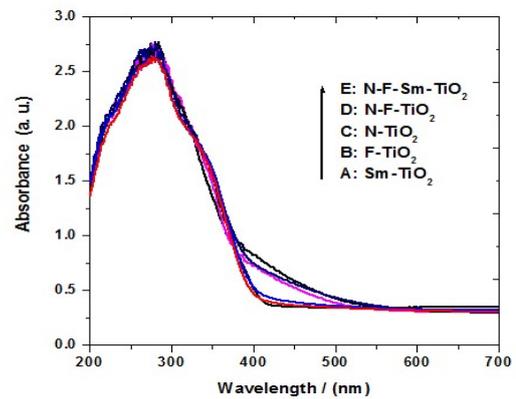


Figure 4 UV-Vis-DRS spectra of TiO₂ sol sample powders dried at 60 °C

Oxygen sites in the TiO₂ crystal lattice. It was reasonable to assume that the small peak was resulted from Ti-F bonds [5]. It indicated that F atoms were incorporated into the TiO₂ crystal lattice by the sol-gel-hydrothermal method.

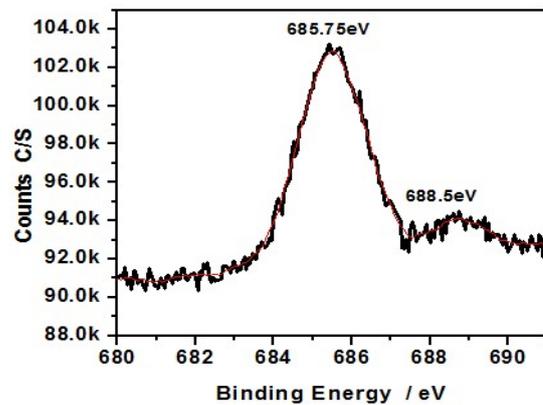


Figure 5 F1s XPS spectra of the N-F-Sm-TiO₂ sol sample

Figure 6 shows the N_{1s} XPS spectra of N-F-Sm-TiO₂ sol sample. A peak appeared at 400.1 eV, and was ascribed to the N atoms from adventitious N-N, N-H, O-N, or N-containing organic compounds adsorbed on the surface of TiO₂[6]. At around 396.0 eV, a small wide peak was observed, and was generally considered as the evidence for the presence of Ti-N bonds formed when the N atoms replaced the oxygen in the TiO₂ crystal lattice [6]. This analysis indicated that N atoms were incorporated into the TiO₂ crystal lattice by the modified hydrothermal processes.

Figure 7 shows the Sm_{3d} XPS spectra of N-F-Sm-TiO₂ sol sample. A peak appeared at 1082.96 eV (Sm_{3d5/2}), and was ascribed to the Sm atoms from Sm₂O₃. No evidence of other oxidation states of samarium was found. But the binding energy for Sm_{3d5/2} is 1083.4eV in Sm₂O₃ (Sm-O bonds), which is little different from Sm_{3d5/2} in Sm-N-TiO₂. This phenomenon indicated that the chemical environment surrounding samarium had changed. All results show that Sm did not incorporate into TiO₂ crystal lattice, existed in the form of Sm₂O₃, and might form binary metal compound with N-TiO₂.

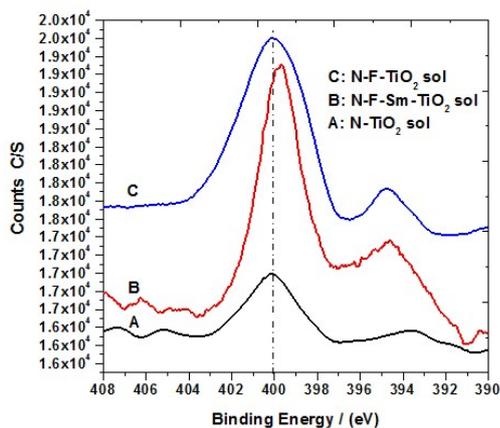


Figure 6 N_{1s} XPS spectra of N-F-Sm-TiO₂ sol

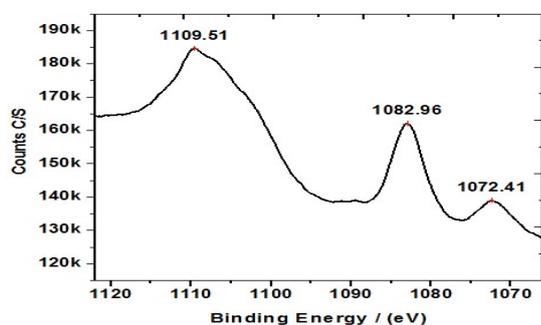


Figure 7 shows the Sm_{3d} XPS spectra of N-F-Sm-TiO₂ sol sample

D. Photocatalytic activity of N-F- Sm-TiO₂ sol

1) Effects of Sm/Ti atomic ratio in N-F- Sm-TiO₂ on the 4-chlorophenol degradation

As shown in Figure 8, the photocatalytic degradation of 4-chlorophenol by a series of N-F- Sm-TiO₂ (the ratio of Sm / Ti (at.)) = 0.001, 0.002, 0.003, 0.005, 0.007, 0.008, 0.010) samples were prepared by modified hydrothermal process at 130 °C photocatalytic activity of N-F- Sm-TiO₂ increased and reach the maximum at Sm : Ti = 0.005(at.). The increase in photocatalytic activity was ascribed to Sm³⁺ ion acts as electron traps and thus facilitated the charge separation.

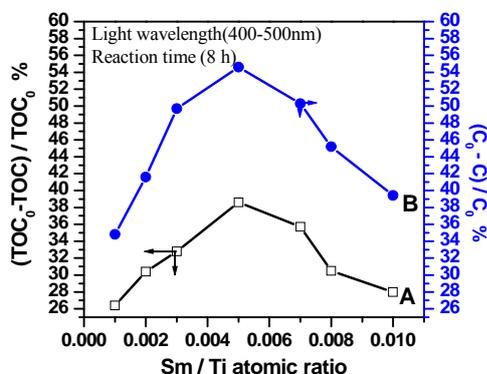


Fig. 8 Effects of Sm/Ti atomic ratio on photocatalytic activity of N-F-Sm-TiO₂

With the increase of further samarium concentration, when Sm : Ti (at.) was more than 0.005, the degradation percentage of 4-chlorophenol started to decrease, which means that more doping may convert the dopant from the trap center to the combination center of the electron and the hole, thereby resulting in a decrease in the photocatalytic ability of N-F-Sm-TiO₂.

2) Influence of N, F and Sm co-doping in TiO₂ on the 4-chlorophenol degradation

The photocatalytic activities of the Sm-TiO₂, F-TiO₂, N-TiO₂, N-F-TiO₂, and N-F-Sm-TiO₂ were evaluated by photodegradation of 4-chlorophenol, which was shown in Figure 9. The N-F-Sm-TiO₂ presented good activity for the degradation of 4-chlorophenol, the degradation rate could be up to 42.4% after photoreaction for 10 h; Under the same condition, the photodegradation rate of 4-chlorophenol degraded by Sm-TiO₂, F-TiO₂, N-TiO₂, was 0.5%, 1.2% and 16.7% respectively. The co-doping of nitrogen, fluoride and samarium could enhance its activity of catalyst significantly, and it was much higher than that of only Sm atoms doped TiO₂ or only nitrogen atoms doped TiO₂.

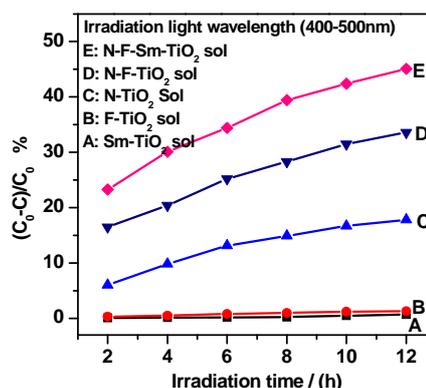


Figure 9 Photocatalytic activities of TiO₂ sol

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