Solvothermal Synthesis of Strontium Titanate Based Materials Designed for Efficient Visible Light Photocatalysis

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URL	http://hdl.handle.net/10097/59063

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学 位 記 番 号	学術（環）博第１３９号
学位授与年月日	平成２３年３月２５日
学位授与の根拠法規	学位規則第４条第１項
研究科，専攻の名称	東北大学大学院環境科学研究科（博士課程）環境科学専攻
学 位 論 文 題 目	Solvothermal Synthesis of Strontium Titanate Based Materials Designed for Efficient Visible Light Photocatalysis（優れた可視光応答性光触媒として設計されたチタン酸ストロンチウム基物質のソルボサーマル反応合成）
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論 文 内 容 要 旨

Solvothermal Synthesis of Strontium Titanate Based Materials Designed for Efficient Visible Light Photocatalysis

Chapter 1. General introduction

The environmental problem and energy crisis, two main of global issues, will come soon on the earth. In order to establish the sustainability of human life in the future, the great efforts should be devoted from now. The sunlight energy utilizing approaches are very promising and good feasibility for solving the environmental problem and energy crisis. Visible light responsive photocatalysts, one of the semiconductor materials could be effectively used to convert the sun light energy into various applications such as disinfection of drinking water, antibacterial, persistent toxic compounds treatment, organic degradation and even hydrogen production. Visible-light-responsive photocatalysts are great beneficial because ~43% of the whole solar energy is visible light, while only ~4% is UV light. Therefore, the design and synthesis of a photocatalyst for the enhancement of the photocatalytic activity in visible light are a highlight works.

Generally, titanium dioxide is the most common photocatalyst, because it has a remarkable photocatalytic activity. Besides the titanium dioxide, the promising alternative photocatalyst materials, strontium titanate, also could be effectively used for the application in photocatalysis because of the excellent photocatalytic activity, high stability and non-toxicity. However, since strontium titanate is a wide gap semiconductor, it requires UV light to generate the photocatalytic activities. Development of visible light induced strontium titanate photocatalyst has a great potential to utilize the wider range of solar energy. Therefore, in this thesis, attention was concentrated mainly on the design and synthesis of strontium titanate based efficient visible-light photocatalysis for environmental clean-up.

Chapter 2. Solvothermal Synthesis of Designed Non-Stoichiometric $SrTiO_3$ for Efficient Visible-Light Photocatalysis

Non-Stoichiometric $SrTiO_3$ photocatalysts with variation of Sr/Ti atomic ratio to induce the defect crystals which have unique photocatalytic properties were realized. The nanoparticles of perovskite type $SrTiO_3$ with the particle size of 30-40 nm were successfully synthesized using microwave-assisted solvothermal reaction of $SrCl_2.6H_2O$ and $Ti(OC_3H_7)_4$ in KOH aqueous solutions. The photocatalytic activity was determined by $DeNO_x$ ability using LED (light emitting diode) lamps with the wavelengths of 627 nm (red), 530 nm (green), 445 nm (blue) and 390 nm (UV). The visible light responsive photocatalytic activity was generated by adding an excess amount of Sr. The photocatalytic activity in visible light could be enhanced by an increase in the Sr/Ti atomic ratio up to 2.0, indicating that the visible light responsive photocatalytic activity is due to the generation of a new band gap between the conduction band and valence band of $SrTiO_3$ by the formation of oxygen vacancy.

Chapter 3. Visible Light Photocatalytic Activity Induced by the Carboxyl Group Chemically Bonded on the Surface of $SrTiO_3$

$SrTiO_3$ nanoparticles were synthesized by a microwave-assisted solvothermal reaction of $SrCl_2.6H_2O$, $Ti(OC_3H_7)_4$ in KOH methanol-oleic acid solution. The nanoparticles of perovskite type $SrTiO_3$ with the particle size of 15-18 nm were successfully synthesized. The photocatalytic activity of $SrTiO_3$ (see Fig.1) under visible light (λ=530 nm) irradiation could be generated by modification of the surface with the carboxyl group (-COO) from oleic acid, which enabled the absorption of visible light.

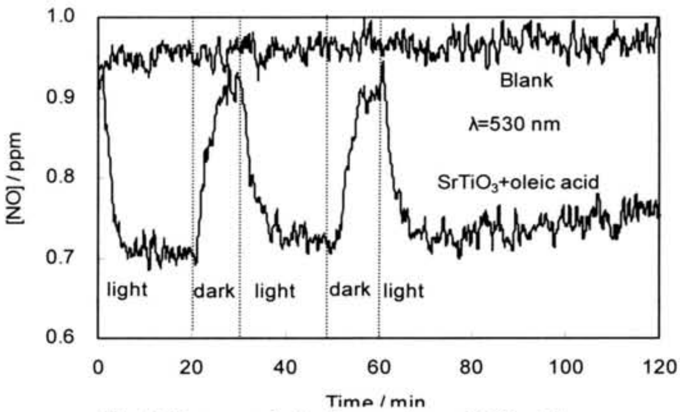

Fig.1 Photocatalytic destruction of NO with $SrTiO_3$-oleic acid at λ =530 nm (green light)

Chapter 4. Solvothermal Synthesis and Photocatalytic Properties of Chromium-Doped $SrTiO_3$ Nanoparticles

Chromium (Cr)-doped $SrTiO_3$ were synthesized by a microwave-assisted solvothermal reaction using $SrCl_2.6H_2O$ and $Ti(OC_3H_7)_4$ as starting materials in KOH methanol-oleic acid solution. The $Cr(NO_3)_3.6H_2O$ was used as a source of chromium doping. The nanoparticles of perovskite type Cr-doped $SrTiO_3$ with a particle size of 15-20 nm were successfully synthesized (Fig.2). Cr-doped $SrTiO_3$ showed photocatalytic activity even under red light irradiation (λ=627nm), indicating that the chromium ion has a significant role

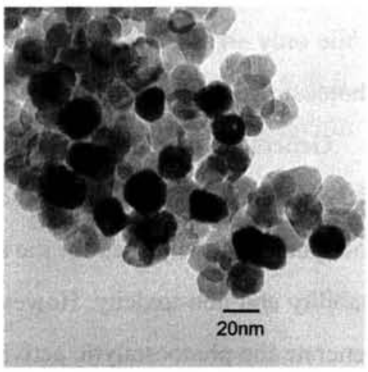

Fig.2 TEM Images of Cr doped $SrTiO_3$

in visible light photocatalytic activity. It can be seen that the photocatalytic activity of Cr-doped $SrTiO_3$ increased at first by doping Cr up to x=0.005 (Fig.3), then greatly decreased with an increase in Cr content. The decrease in the photocatalytic activity by doping with excess amounts of Cr^{3+} may be due to the increase in the amount of oxygen vacancies as $SrTi^{IV}_{1-2x}Cr^{III}_{2x}O_{3-x}\square_x$, ($\square$: vacancy), which becomes the recombination centers of photo-induce electrons and holes. The photocatalytic activity of Cr-doped $SrTiO_3$, increased by the calcinations up to 300°C due to an increase in the absorption in the visible region. The high photocatalytic activity of Cr-doped $SrTiO_3$ in the visible light region may be due to the narrowing of the band gap (2.14 eV).

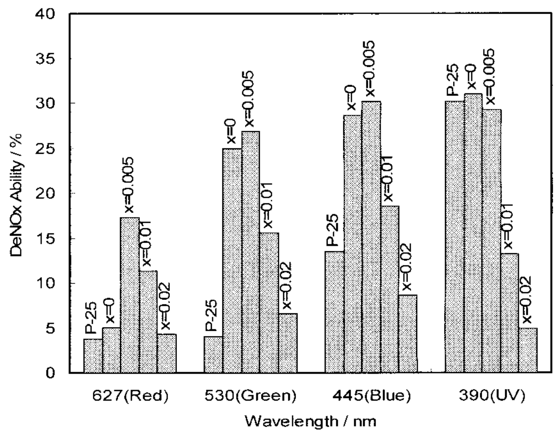

Fig. 3 Photocatalytic destruction of NO with $SrTi_{1-x}Cr_xO_3$ (x=0-0.020) and TiO_2 (P-25)

Chapter 5. Solvothermal Synthesis and Photocatalytic Properties of Nitrogen-doped $SrTiO_3$ Nanoparticle

Perovskite type nitrogen doped $SrTiO_3$ nanoparticles of 50-80 nm in diameter were successfully synthesized by the solvothermal reaction of $Ti(OC_3H_7)_4$, $SrCl_2.6H_2O$, and hexamethylenetetramine in KOH aqueous solution. Nitrogen doped $SrTiO_3$ showed excellent photocatalytic activity under both UV and visible light irradiation, i.e., the photocatalytic activity of N-doped $SrTiO_3$ for $DeNO_x$ reaction was greater than that of $SrTiO_3$ and commercial TiO_2 (Degussa P25) in both visible light region (>510nm) and UV light region (> 290 nm). The excellent visible light photocatalytic activity of this substance was caused by generating a new band gap corresponding to the Ti3d conduction band and N2p valence band that absorbs visible light.

Chapter 6. Solvothermal Synthesis of $SrTiO_3$-$LnTiO_2N$ Solid Solution and Their Visible Light Responsive Photocatalytic Properties

The $SrTiO_3$-$LnTiO_2N$ solid solution, $Sr_{1-x}La_xTiO_{3-y}N_y$, was synthesized by the solvothermal reactions in KOH aqueous solution using $Ti(OC_3H_7)_4$, $SrCl_2.6H_2O$, $La(NO_3)_3.6H_2O$ and hexamethylenetetramine as raw materials. The nano particles of perovskite type $Sr_{1-x}La_xTiO_{3-y}N_y$ (x= 0, 0.025, 0.05 and 0.1) were successfully synthesized by solvothermal method. The photocatalytic activity of $SrTiO_3$ for $DeNO_x$ ability in visible light region (>510nm) could be improved by co-doping of La^{3+} and N^{3-}. The high visible light photocatalytic activity of this substance may be due to generation of a new band gap that enables to absorb visible light. The powder with a smaller ratio of La content (x= 0.025) possessed excellent photocatalytic activity under visible light irradiation.

Ch apter 7. Solvothermal Synthesis and Photocatalytic Properties of Nitrogen and Metal (V) Co-Doped $SrTiO_3$

Regarding the $SrTiO_3$, M^{5+} and N^{3-} co-doping in $SrTiO_3$ as $SrTi^{4+}_{1-x}M^{5+}_xO^{2-}_{3-x}N^{3-}_x$ (M=Nb^{5+}, Ta^{5+}) is one of the potential methods to dope nitrogen ion without forming anion vacancy. The Nb^{5+} or Ta^{5+} can substitute Ti^{4+} in

$SrTiO_3$ without large lattice strain because of the similar ionic radius. Therefore, it is expected that co-doping of M^{5+} (M=Nb^{5+}or Ta^{5+}) and N^{3-} in $SrTiO_3$ decreases the band gap energy without forming lattice defect and lattice strain, and consequently, leads to generate high visible light photocatalytic activity. In this experiment, the $SrTi_{1-x}M_xO_{3-y}N_y$ (M=Nb,Ta) were synthesized using microwave assisted solvothermal method. The niobium and nitrogen co-doped $SrTiO_3$, $SrTi_{1-x}Nb_xO_{3-y}N_y$ (x= 0, 0.05, 0.1 and 0.2), were synthesized by the solvothermal reactions in KOH aqueous solutions using $Ti(OC_3H_7)_4$, $SrCl_2{\cdot}6H_2O$, $NbCl_5$ and hexamethylenetetramine as starting materials. The $SrNb_xTi_{1-x}O_{3-y}N_y$ showed the photocatalytic activity for oxidative destruction of NO_x under visible light irradiation. The photocatalytic activity changed depending on the amount of niobium and $SrTi_{1-x}Nb_xO_{3-y}N_y$ (x= 0.02) showed the highest photocatalytic activity under visible light irradiation.

The Nanoparticles of Ta and N co-doped $SrTiO_3$, $SrTi_{1-x}Ta_xO_{3-y}N_y$ (x= 0, 0.02, 0.05 and 0.1) were synthesized by solvothermal reactions in KOH and oleic acid mixed methanol solutions using $Ti(OC_3H_7)_4$, $SrCl_2\,6H_2O$, $TaCl_5$ and HMT (hexamethylenetetramine) as the starting materials. $SrTa_xTi_{1-x}O_{3-y}N_y$ showed excellent photocatalytic activity for the oxidative destruction of NO under visible light irradiation (λ>530 nm). The optimum Ta content was determined to be x=0.02-0.05

Chapter 8. Performance Comparison of Visible Light Responsive $SrTiO_3$ Prepared by Various Methods

The performances of visible light responsive $SrTiO_3$ based photocatalysts prepared by various methods are summarized in Fig.4. Most samples showed excellent activity under visible light irradiation of wavelength up to 530 nm, and Cr-doped $SrTiO_3$ showed the superior activity under red light (λ=627 nm) irradiation. The excellent photocatalytic activity of Cr-doped $SrTiO_3$ is caused by the narrowing the band gap to be 2.14 eV.

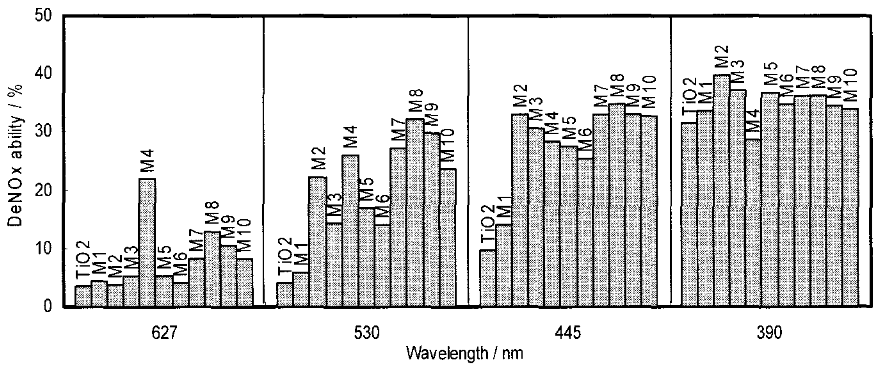

Fig.4 Photocatalytic activities of $SrTiO_3$ syntesized with different methods, M1=$SrTiO_3$, M2= non-stoichiometric $SrTiO_3$ (Sr/Ti = 1.25), M3=$SrTiO_3$-oleic acid, M4=Cr-$SrTiO_3$-oleic acid, M5=N-$SrTiO_3$, M6=La/N-$SrTiO_3$, M7=N-$SrTiO_3$, M8=La/N $SrTiO_3$, M9=Nb/N $SrTiO_3$, M10=Ta/N $SrTiO_3$-oleic acid. M5, M6=conventional solvothermal, M1-M4, M7-M10=microwave assisted solvothermal synthesis

Chapter 9. Summary and Conclusion

The photocatalytic activity of $SrTiO_3$ for $deNO_x$ ability in the visible light region could be enhanced by precisely controlling the chemical compositions and microstructures of non-stoichiometric $SrTiO_3$, carboxyl group chemically bonded $SrTiO_3$, Cr doped $SrTiO_3$, N doped $SrTiO_3$, La/N co-doped $SrTiO_3$, Nb/N co-doped $SrTiO_3$ and Ta/N codoped $SrTiO_3$. Chromium doped $SrTiO_3$ prepared in KOH methanol oleic acid solution, showed the superior photocatalytic activity under irradiation of visible light of λ=627 nm.

論文審査結果の要旨

光触媒反応は、セルフクリーニング、脱臭、抗菌、防曇等で既に実用化され、さらに環境浄化への利用が期待されている。しかし、現在利用されている酸化チタン光触媒は、紫外線しか利用できないため、太陽光や室内灯の主成分である可視光を利用可能な光触媒の開発が求められている。

本研究は、窒素ドープチタン酸ストロンチウムナノ粒子をソルボサーマル反応により合成する手法を開発し、環境浄化光触媒特性について系統的に調べた研究であり、全編9章よりなる。

第1章は緒論であり、光触媒反応機構、可視光応答性光触媒などに関する過去の研究を網羅し、その特徴を述べ、また、重要ながら未解明な事項を列挙し、その上で、本研究の目指す方向とその概要を述べている。

第2章では、ソルボサーマル反応によりSr/Ti原子比の異なるチタン酸ストロンチウムのナノ粒子を合成し、Sr過剰の格子欠陥導入チタン酸ストロンチウムが可視光応答性光触媒機能を有することを明らかにした。

第3章では、オレイン酸存在下でチタン酸ストロンチウムを合成し、表面に化学吸着されたカルボキシル基のダイポール効果により、可視光応答性光触媒機能を付与できることを見出した。

第4章では、固相法による直接合成が困難な Cr^{3+} ドープチタン酸ストロンチウムナノ粒子をソルボサーマル反応により合成し、得られたナノ粒子が優れた可視光応答性光触媒機能を有することを明らかにした。

第5章では、ソルボサーマル反応により窒素ドープチタン酸ストロンチウムナノ結晶を合成し、優れた可視光応答性光触媒機能を有することを明らかにした。

第6章では、ソルボサーマル反応により窒素とともに Sr^{2+} サイトに La^{3+} をドープしたチタン酸ストロンチウムナノ粒子を合成し、アニオン欠陥の減少により光触媒活性を向上できることを明らかにした。

第7章では、ソルボサーマル反応により窒素とともに Ti^{4+} サイトに Nb^{5+} や Ta^{5+} をドープしたチタン酸ストロンチウムナノ粒子を合成し、アニオン欠陥の減少により光触媒活性を向上できることを明らかにした。

第8章では、第2章から第7章において合成した各種可視光応答性チタン酸ストロンチウムの環境浄化光触媒活性を比較し、クロムドープチタン酸ストロンチウムが最も優れた特性を有することを明らかにした。

第9章は結論であり、各章の結言を要約している。

以上、要するに本論文は、クリーンで無尽蔵な太陽エネルギーを利用する環境浄化光触媒の開発を目的として、種々の可視光応答性チタン酸ストロンチウムの光触媒の合成法を開発するとともに、活性に及ぼす諸因子の影響について系統的に調べた研究であり、環境科学、物質科学の分野の発展に寄与するところ少なくない。

よって，本論文は博士(学術)の学位論文として合格と認める。