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学位論文紹介
**Doctoral Thesis Introduction**

# Development of Active Photocatalysts for $CO_2$ Conversion by High-Pressure Torsion

## 高圧ねじりによる $CO_2$ 変換用活性光触媒の開発

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### 1. Introduction

$CO_2$ as a harmful gas generated by burning the fossil fuels, have led to environmental disasters in all over the universe. All attempts have focused on decreasing this component to minimize it's damaging effects. Photocatalytic $CO_2$ conversion or $CO_2$ photoreduction as an artificial photosynthesis is considered as the cleanest method to convert the $CO_2$ to other usable materials such as CO, $CH_4$, $CH_3OH$. Main drawback of these process is the low activity of photocatalysts and various strategies have been introduced to improve their efficiency. Doping with elements is the usual method but it faces with recombination of electrons and holes. It this work, high-pressure torsion (HPT) was utilized to enhance the photocatalytic activity for $CO_2$ conversion by four different strategies includes introducing the (i) high-pressure phases, (ii) strain and oxygen vacancies, (iii) high-entropy phases and (iv) high-entropy oxynitrides.

### 2. Strain and oxygen vacancy engineering of $BiVO_4$ photocatalyst

$BiVO_4$ is the typical photocatalyst for $CO_2$ conversion but it suffers from high recombination of electrons and holes and unappropriated position of conduction band. HPT method was used to solve these problems by simultaneous strain and oxygen vacancy engineering. After HPT process and introducing the oxygen vacancy and lattice strain, the light absorbance of $BiVO_4$ increased significantly in visible region and it's bandgap decreased. The electronic band structured aligned and recombination rate of electrons and holes suppressed effectively. The processed $BiVO_4$ using HPT showed higher photocatalytic activity compared to sample before HPT and same activity with P25 $TiO_2$ as benchmark photocatalyst.

### 3. $TiO_2$-II high-pressure phase as new photocatalyst

HPT was used to produce the $TiO_2$-II (columbite) as the high-pressure phase of $TiO_2$ and was examined for photocatalytic $CO_2$ conversion for the first time. The $TiO_2$-II phase was oxygen deficient and could adsorb the light higher than initial anatase phase. Bandgap of this new phase was decreased significantly and it had the optimized bandstructure compared to anatase. This new photocatalyst could generate the photocurrent much more than anatase and produce the CO from $CO_2$ under UV much better than initial anatase powder without adding any impurities.

### 4. Defective high-entropy oxide photocatalyst

High- entropy oxides (HEOs) are new and promising materials with five or than five elements for catalysis. In this regard, a HEO with composition of $TiZrNbTaHfO_{11}$ was produced using HPT and evaluated for $CO_2$ photoreduction for the first time. The synthesized HEO showed higher light absorbance compared with initial binary oxides. It showed an appropriate electronic band structure to support all $CO_2$ reduction reactions. The material could successfully generate the photocurrent and convert $CO_2$ to CO under UV irradiation without adding any co-catalyst. Activity of this HEO photocatalyst was higher than anatase $TiO_2$ and $BiVO_4$ and as high as P25 $TiO_2$ as benchmark photocatalyst.

### 5. Highly-efficient high-entropy oxynitride photocatalyst

Metal oxynitrides are promising photocatalyst for $CO_2$ conversion due to their low bandgap but their application for $CO_2$ conversion has been limited. By considering this issue and promising features of high-entropy ceramics, a high-entropy oxynitride (HEON) with composition of $TiZrNbTaHfO_6N_3$ was fabricated by HPT for photocatalytic $CO_2$ conversion. This material showed higher light absorbance, narrower bandgap, lower recombination rate of electrons and holes, higher $CO_2$ adsorption and finally higher photocatalytic activity for $CO_2$ conversion compared with corresponding HEO and P25 $TiO_2$ as benchmark photocatalyst.

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## List of Publications


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[2] S. Akrami, M. Watanabe, T. H. Ling, T. Ishihara, M. Arita, M. Fuji, K. Edalati, High-pressure $TiO_2$-II polymorph as an active photocatalyst for $CO_2$ to CO conversion, Appl. Catal. B 298 (2021) 120566.

[3] S. Akrami, Y. Murakami, M. Watanabe, T. Ishihara, M. Arita, M. Fuji, K. Edalati, Defective high-entropy oxide photocatalyst with high activity for $CO_2$ conversion, Appl. Catal. B 303 (2022) 120896.

[4] S. Akrami, P. Edalati, Y. Shundo, M. Watanabe, T. Ishihara, M. Fuji, K. Edalati, Significant $CO_2$ photoreduction on high-entropy oxynitride, Chem. Eng. J. 449 (2022) 137800.


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**Curriculum Vitae**

Saeid Akrami received his Bachelor degree in Chemical Engineering at Ferdowsi University of Mashhad, Iran in 2015 and then connived his education in the same university and received a Master degree in Chemical Engineering in 2019. He obtained his Doctoral degree in Applied Chemistry and Life Sciences in Nagoya Institute of Technology, Japan in 2023.