

## 学位論文題名

## Synthesis and formation mechanism analysis of mesoporous carbon nitrides prepared by using N rich precursors and their sensing and photocatalytic applications

（高窒素含有前駆体を用いたメソポア  $\text{CN}_x$  の合成とその合成機構の解析  
ならびにセンサー、光触媒への応用）

## 学位論文内容の要旨

As a result of rapid industrial development and population growth, two important issues are of prime focus for the scientific society: first is increased global energy demand and second is environmental protection. In first challenge, the search for clean and sustainable energy source such as hydrogen becomes important. Visible light driven photocatalysis is a potentially feasible way to produce clean hydrogen from water. For this purpose, photocatalyst materials with unique properties such as narrow band gap, high specific surface area, stability, crystallinity and so on, is highly desirable. So far, various inorganic semiconductors and molecular assemblies have been proposed and developed for  $\text{H}_2$  production from water. However, most of the catalysts are suffering with poor visible light absorption, low surface area, poor crystallinity, instability or toxicity. Therefore, the fabrication of cheap and novel catalysts with unique physical and chemical properties to produce  $\text{H}_2$  under visible light irradiation is highly anticipated. In the second challenge; the problems related to the environmental monitoring, especially highly selective and sensitive detection of harmful gases are important issues. So far, semiconducting metal oxides have been used as solid state gas sensor for the detection of toxic gases and vapors. However, the major disadvantage is the operation at elevated temperatures which can damage the materials that are made up of films and contacts. It is the cause of poor reliability. Hence the development of an easy method and a novel material for the room temperature sensing of harmful chemicals is highly desirable.

Carbon nitride could be the potential candidate to achieve aforementioned challenges because of its interesting physical and chemical properties such as inbuilt basic functionalities, thermal stability, optical and electronic properties. In addition, introducing the mesoporosity can increase the access to more number of active sites, capture more photons due to light scattering effect inside the pores and shorten the path length for the charge carriers to the surface of the photocatalyst due to thin walls. At present, preparation of  $\text{MCN}_x$  has been limited to the use of non-cyclic precursors like ethylenediamine, carbon tetrachloride, dicyanamide, and aminoguanidine. However, the synthesis mechanism of  $\text{MCN}_x$  materials prepared from aforementioned precursors is unclear and it becomes very important to understand the synthesis process of  $\text{MCN}_x$  in order to develop the materials for specific applications such as photocatalysis and sensing. In **chapter 1**, research history of N doped carbon,  $\text{C}_3\text{N}_4$ , and  $\text{MCN}_x$  materials together with above mentioned important points were summarized.

In **chapter 2**, synthesis of mesoporous silica templates which were used for the fabrication of  $\text{MCN}_x$  materials were briefly explained. Synthesis techniques and characterization methods were also presented in chapter 2. In **chapter 3**, synthesis and characterization of two  $\text{MCN}_x$  materials were presented. In the first part, N containing mesoporous carbons (NMC-G-x) with excellent textural properties and inbuilt basic functionalities were successfully fabricated from gelatin by nanocasting technique. In the second part, 3-Amino-1, 2, 4-triazine (ATN) was employed as a single source precursor to fabricate well ordered high N containing MCN materials ( $\text{MCN-ATN-x}$ ). Formation mechanisms of NMC-G and  $\text{MCN-ATN}$  were investigated for the first time through kinetic simulation by using non-parametric kinetic (NPK) method. The simulation study showed that gelatin-silica and ATN-silica composite followed reaction order kinetic model. Gelatin-silica composite showed highest activation energy among all the cases studied in this work. Also, simulation results showed that mesoporous silica significantly affects the rate of chemical reaction depending on the interaction with the precursor inserted inside the porous structure. Based on the simulation results, the reaction schemes

were proposed for the formation of NMC-G and MCN-ATN. The performance of NMC-G and MCN-ATN were tested for the sensing of harmful chemicals by using quartz crystal microbalance (QCM). NMC-G material showed high selectivity and sensitivity for the acidic compounds. Temperature programmed desorption (TPD) of CO<sub>2</sub> suggests that basicity of the NMC-G sample is 0.185mmol of CO<sub>2</sub>.g<sup>-1</sup>.

In order to achieve high nitrogen content in the MCN<sub>x</sub> materials, N rich, cyclic inexpensive single molecular CN precursors such as 3-Amino 1,2,4 triazole (3-AT) and 5 Amino-1H-triazole (5ATZ) were used for the fabrication of MCN-TZL and MCN-TT, respectively. The synthesis and characterization of the obtained materials were presented in **chapter 4**. Materials exhibits well ordered mesoporosity. QCM measurements showed that MCN-TT produced largest frequency shift (1925 Hz) for the acidic compounds. The reasons are high surface area and large density of basic sites (0.32mmol of CO<sub>2</sub>.g<sup>-1</sup>) detected on the surface of MCN-TT. In order to verify the role of basic sites in selective sensing of acidic compounds, urea was added in-situ along with 3AT during preparation of MCN-TZL. Although having less surface area (220m<sup>2</sup>.g<sup>-1</sup>), the obtained material (MCN-TU) displayed large frequency shift (1200 Hz) for the acidic compounds as compared with MCN-TZL (850 Hz). As expected, TPD profiles showed improved density of basic sites (0.20mmol of CO<sub>2</sub>.g<sup>-1</sup>) as compared with MCN-TZL (0.14mmol of CO<sub>2</sub>.g<sup>-1</sup>). From the kinetic simulation results, it was found that formation of MCN-TZL follows one dimensional (1D) diffusion model. The diffusion of the advancing reaction interface is controlled in 1 dimension which controls necessary orientations of the reactant molecules and causes chain extension. Short range order arises through parallel alignment of sufficiently regular chains where the repeating units in the adjacent chains are in appropriate crystallographic orientation. From wide angle XRD patterns, it was noticed that the crystallinity of MCN-TZL is improved as compared with NMC-G, MCN-ATN and MCN-TT. Based on the simulation results, the reaction scheme is proposed for the formation of MCN-TZL inside the porous silica. Activation energy obtained for 3AT-silica is the lowest among all cases studied in this work. In contrast, formation of MCN-TT follows reaction order model with n=4 and requires large activation energy. This indicates that the complex, multistep chemical reaction and bulk evaporation are more dominant than surface process. Based on simulation results, the reaction scheme is proposed for MCN-TT formation.

In order to improve the photocatalytic activity of the MCN<sub>x</sub> materials, new synthesis route for the preparation of metal oxide loaded mesoporous carbon nitrides have been introduced. In this method, metal oxide loaded SBA-15 was prepared first and then used as a sacrificial template to produce metal oxide loaded MCN<sub>x</sub> materials by simple nanocasting method. By this method, uniform distribution of SnO<sub>2</sub>, TiO<sub>2</sub> or ZrO<sub>2</sub> nanoparticles inside the porous framework of narrow band gap carbon nitride materials was achieved. The results are presented in **chapter 5**. Photocatalytic H<sub>2</sub> evolution experiments were performed on obtained materials. MCN-TU-Sn-R5 showed highest rate of H<sub>2</sub> evolution (220μmol.h<sup>-1</sup>) with good stability. H<sub>2</sub> evolution rate is higher than its pure counterpart (MCN-TU). The reason behind large activity of MCN-TU-Sn-R5 is the efficient charge transfer through SnO<sub>2</sub> nanoparticles which leads to low recombination rate. In addition, the performance of MCN-TZL, MCN-TT and MCN-TU were tested for the photocatalytic H<sub>2</sub> evolution under visible light irradiation. MCN-TZL showed highest H<sub>2</sub> evolution rate (267μmol.h<sup>-1</sup>). The high activity of MCN-TZL can be attributed to the narrow band gap energy (2.2eV), improved crystallinity, high surface area and low recombination rate. It can be concluded that controlled temperature, chemistry of the CN precursor, silica template, and quantity of precursor used for filling mesochannels of template are the key points in obtaining well ordered mesoporous CN<sub>x</sub> material with a high N content. It has been demonstrated that the crystalline fraction of the MCN<sub>x</sub> materials which is of significant importance in many applications can be improved by selecting the correct precursor and silica combination.

# 学位論文審査の要旨

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### Synthesis and formation mechanism analysis of mesoporous carbon nitrides prepared by using N rich precursors and their sensing and photocatalytic applications

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近年、触媒担体や放射性物質吸着分離剤などへの応用の観点から、高比表面積と大きな空孔容積を有するメソポア材料に関する研究開発が盛んに行われている。従来のメソポア材料に関する研究は、その応用の観点から、高比表面積と大きな空孔容積を持つメソポア材料の合成条件最適化と、その触媒反応への応用が中心であったが、表面における選択的吸着特性や、高い触媒反応活性を生み出す、メソポア化合物の生成反応機構を検討し、高比表面積と大きな空孔容積を有するメソポア材料を作製するために用いられるテンプレート（鋳型）の役割に関する、詳細な検討を行うことは、ほとんどなされておらず、こうした、反応機構解析や、テンプレートの役割に関する解析を基にした、メソポア材料の機能設計に関する研究は、未開拓分野であり、今後の発展が大いに期待される分野である。

本学位論文では、こうした学術的背景をもとに、4種類の窒素含有量の異なる炭窒化物( $CN_x$ )前駆体と、高比表面積を有するシリカテンプレートとの組み合わせをもとに、非晶質材料、低結晶性材料やナノ結晶化材料の反応機構解析のための、熱分析データを用いた反応機構解析手法である、ノンパラメトリック速度論解析法(non-parametric kinetic (NPK) method)を活用し、メソポアシリカ内における  $CN_x$  化合物生成機構に関する検討を行った。

こうした反応機構解析結果をもとに、作製した  $CN_x$  化合物の中から、表面の選択的吸着反応を設計するうえで、有望と思われる  $CN_x$  化合物を選定し、水晶共振子マイクロバランス(Quartz Crystal Microbalance: QCM)を用いて、有機物に対する選択的表面吸着特性を評価した結果、選択的表面吸着能を増大させることが可能であることを見出した。

また、このメソポア  $CN_x$  化合物に、遷移金属酸化物を担持した試料を用いて、遷移金属酸化物担持メソポア  $CN_x$  化合物の紫外可視吸収スペクトルの測定解析結果をもとに、水の分解による水素製造用可視光励起光触媒への応用の可能性についても検討を行い、高い量子収率と、優れた水素発生活性を確認するなどの成果を得、これらの結果を整理して、学位論文としてまとめた。

さらに、得られた新規メソポア化合物のキャラクタリゼーションとして、電子エネルギー損失分光(Electron Energy Loss Spectroscopy: EELS)法と制限視野電子回折法を用いて、バルク内における分子構造特有の炭素周囲における窒素の配位状態の解析や結晶相の同定を行い、あわせて赤外吸収分光(Infrared Absorption Spectrometry: IR)法とX線光電子分光(X-ray Photoemission Spectroscopy: XPS)法を用いて表面・界面の特徴を検討した結果を基に、

主として非晶質材料からなるメソポア化合物中に生成した結晶質  $\text{CN}_x$  化合物の構造の特徴を明らかにした。

上述の反応機構解析結果及び、生成物のキャラクタリゼーション結果をもとに、従来は、十分にその反応機構が検討されていなかった、シリカハードテンプレート法を用いた  $\text{CN}_x$  化合物生成機構を明らかにした点が特に優れている。 $\text{CN}_x$  前駆体を用いたメソポア  $\text{CN}_x$  化合物生成反応は、その合成過程において、 $\text{CN}_x$  前駆体が昇華または熱分解しやすく、十分な窒素含有量をもつ  $\text{CN}_x$  化合物の合成を行うことが、従来は難しい状況にあったが、熱伝導率の小さいシリカを鋳型に用いて、さらに大きな細孔構造を有するメソポア構造内に、最も小さい熱伝導率をもつ空気を閉じ込めることで、遅い  $\text{CN}_x$  化合物生成速度を改善することに成功し、あわせて窒素含有量の多い、新規メソポア  $\text{CN}_x$  化合物の合成に成功したことは、今後のハードテンプレート法による機能性メソポア材料設計分野の発展に大きな成果を残したといえる。また、本研究成果は、表面選択的吸着特性や、光触媒反応活性の設計以外にも活用可能であることから、今後、多くのメソポア材料の機能設計を行うメソポア材料科学分野に、有意義な設計指針を与えたともいえる。

よって、本論文は、北海道大学博士（理学）の学位を授与される資格があるものと認める。