Graduate School of Advanced Science and Engineering,
Waseda University

博士論文概要
Doctor Thesis Synopsis

論文題目
Thesis Theme

Surface Chemical Reactions of Mesoporous Metal Oxides for Environmental and Energy Systems

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Research in the field of porous nanomaterials has expanded tremendously over the last two decades due to its potential to revolutionize environmental, energy, and biological research. Among the porous nanostructures materials, the mesoporous metal oxides have attracted much attention and shown great potentials, due to outstanding properties, including high surface areas, arranged mono-dispersed mesopore space, tunable pore sizes, alternative pore shapes, and uniform nanosized frameworks, that can be effectively exploited in a plethora of technology in terms of catalysis, sensing, adsorption, separation, optical imaging, phototherapy and energy conversion/storage devices. Recently, tremendous efforts have been directed toward the synthesis of mesoporous metal oxides, aiming to control porosity in addition to intrinsic nanostructure and morphology. Template-assisted methods have been established as convenient approaches to fabricate various mesoporous metal oxides nanoparticles (NPs). Either organic or inorganic templates are used; however, the mesoporous structures tend to collapse during the removal of these templates. Despite these significant achievements in fabrication of mesoporous metal oxides, technical challenges in terms of intensive multistep procedures, high temperature and pressure conditions and time-consuming that making these procedures non-economic for scale up production. Therefore, the development of a simple and economic method for high yield synthesis of mesoporous metal oxide nanostructures with defined and ordered pore architectures is still a challenge. Thus, this Ph.D. research work focused on simple and eco-friendly fabrication approaches of various mesoporous metal oxides targeting environmental remediation based monitoring, sensing, and decontamination, in addition to possible applications in the energy storage. Detailed studies were provided to achieve these potential applications of mesoporous metal oxides, as follows;

- ❖ Catalytic hand-safe chemical transformation of organic contaminants.
- ❖ Nanomagnet selective adsorption and removal of biological molecules.
- ❖ Sequestering and optical detection of toxic metal ions.
- ❖ Development of pseudocapacitors for efficient energy storage devices

Chapter 1 provides broadly covered the general routes of synthesis of mesoporous metal oxides and their potential applications in the environmental remediation and energy storage devices. The previous fabrication procedures underlying the formation of mesoporous metal oxides are presented with special emphases on the recent progress in fabrication approaches. Moreover, the significant key factors controlling the performance of mesoporous metal oxides in various applications such as catalysis, adsorption, sensing and energy storage devices are also summarized.

Chapter 2 summarizes the experimental details, synthetic methods, and techniques used for fabrications and characterization of the porous metal oxides.

In **Chapter 3**, the development of a sustainable catalyst could potentially provide a long-term solution to industrial health-risk processes, especially in the environmental cleanup systems for the transformation and removal of organic contaminants from wastewater. Establishing a proper design for a highly efficient and long-term reusable catalyst is one of the crucial environmental issues. The nickel oxide (NiO) is a prosperous, affordable, abundant, environment-friendly material, and has a stable band gap. Thus, the study focused on the fabrication of NiO NPs with hexagonal nanoplatelet (NPL), nanoflower (NF), and nanosphere (NS)-like morphology with mesopore cavities via a simple hydrothermal method. Significantly, the controlled size, shape and pore cavity of the NiO NPs are key factors in the catalytic transformation of organic contaminants such as *o*-aminophenols and *o*-aminothiophenols. The NiO NPL showed higher catalytic activity toward the oxidation of organic contaminants than that of NiO NF and NiO NS or even Fe_3O_4 NPs. However, the NiO NFs are capable of the high-gradient magnetic separation of organic contaminants from aquatic life which might help in wastewater management and supply. Despite, the reducibility and reversibility of the catalyst are still a challenge. The NiO nanocatalyst retained its texture, morphology, and magnetic properties in terms of reactivity with fast chemical transformation even after multiple cycles. In addition, this study may provide guidelines for mesoporous NiO NPs optimization as an effective catalyst for the transformation and removal of organic contaminants from wastewater.

Chapter 4 discusses the role of mesoporous metal oxide features for selective adsorption of biological molecules, leading to possible potential of separation of single protein from pathogens. The size-selective adsorption and removal of proteins that have different shapes, sizes, functions, and properties into mesostructured alumina and aluminosilica monoliths are reported. However, the clogging pores with large-molecular-weight proteins, particularly at high feed concentration, during the size-selective encapsulation assays (i.e., dead-term adsorption) still remain challenge. Therefore, the fabrication of selective protein supercaptors that didn't impede by the physical shape of the protein, its 3-D hydrodynamic dimensions, clogging effect with high retentate, and uniformly-sized pore of adsorbents is a key requirement in successful protein encapsulation and uptake. Sequentially, the adsorption of proteins onto magnetic mesoporous NiO and Fe_3O_4 NPs is also studied. Interestingly, the mesoporous NiO and Fe_3O_4 NPs can act as nanomagnet-selective adsorbent of hemo-proteins, particularly haemoglobin (Hb), among various biological molecules. The NiO NFs showed higher loading capacity of Hb (~ 50 g/g) than that of NiO NSs and NiO NPLs or even superparamagnetic Fe_3O_4 NPs. The key to this achievement is that mesoporous NiO nanomagnet supercaptors show exceptional encapsulation and selective separation of high concentration of Hb from human blood. In this induced-fit separation model, the morphology, crystal size and shape and magnetic properties of NiO NPs, in addition to the heme group distributions, and protein-carrier binding energy playing a key role in broadening the controlled immobilization affinity and selectivity of hemeproteins. In addition, the thermodynamics, kinetics and theoretical studies were carried out to investigate the optimal performance of protein adsorption. In real application, such approach opens a new avenue of magnetic separation of single proteins regardless size- and shape of proteins which is impressive in biochemical processing applications.

In **Chapter 5**, the efficient sequestering and detection of toxic metal ions form environment using mesoporous metal oxides is discussed. Simple, inexpensive, rapid responsive and portable sensors are highly recommended for monitoring of toxic metal ions. In recent development, the mesoporous alumina and aluminosilica composites used as selective optical sensing system due to the use of "low-tech" spectroscopic instrumentation to detect relevant metal ions such as lead, mercury, copper, zinc and cadmium ions in environment. Highly sensitive, low cost, naked-eye sensors were designed by the immobilization of chromophore molecules into mesocage cavities and surfaces of mesoporous monoliths. These new classes of optical cage sensors exhibited long-term stability of signaling and recognition functionalities that in general provided high sensitivity, selectivity, reusability, and fast kinetic detection and quantification of various metal ions.

In order to apply the developed nanosensors in medical applications, a novel optical multi-shell nanosphere sensor is fabricated. This sensor enables selective recognition, unrestrained accessibility, monitoring, and removal of Pb^{2+} ions from human blood (i.e. red blood cells, RBCs). A unique feature of the core/double-shell sensor design is the capacious hollow cage shell structure that can encapsulate numerous different types of functional groups and protect the immobilized probe to maintain electron acceptor and donor strength. Indeed, such optical sensors offer a possibility of simultaneous detection and sequestering of toxic ions with a minimum sample manipulation, reasonable selectivity and improved sensitivity of Pb^{2+} ions from RBCs without using any reference devices.

Chapter 6 describes future prospects of mesoporous NiO NPs in the development of pseudocapacitors for efficient energy storage applications. The mesoporous NiO NPs with controlled morphologies, including nanoflakes (NFs), nanoslices (NSs), and nanoplatelets (NPLs), were synthesized in a large-scale production, and low-cost manufacturing via microwave-assisted synthesis approach. The mesoporous NiO NPLs showed superior electrochemical performance due to their unique morphology, size, and mesopore size distribution that enhance the diffusion of electrolyte through porous network “superhighways”. These characteristics induce high capacitance and excellent recyclability of NiO NPLs more than NiO NFs and NiO NSs. This approach demonstrates the potential of free-standing NiO NPL electrodes for developing high-performance pseudocapacitors.

In **Chapter 7**, presents general conclusion of suggested synthesis approaches and potential applications of fabricated mesoporous metal oxides that depicted in this dissertation. Finally, this research guidelines show evidence of the applicability of developed metal oxides as a key to the future development of high-grade environmental chemistry and energy.

早稲田大学　博士（理学）　学位申請　研究業績書

(List of research achievements for application of doctorate (Dr. of Science), Waseda University)

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(1) Paper

○ **1.** Mesoporous NiO nanomagnets as catalysts and separators of chemical agents
Applied Catalysis B: Environmental, 2012, 127, 1-10. (Oct. 30, 2012)
Mohamed Khairy, Sherif A. El-Safty, Mohamed Ismael, Hiroshi Kawarada

○ **2.** Mesoporous NiO nanosheets for the catalytic conversion of organic contaminates
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Mohamed Khairy, Sherif A El-Safty

○ **3.** Green Chemical Transformation of phenolic pollutants using mesoporous NiO nanocrystals with sheet-like morphology,
Recent Research in Nanotechnology 2012, 215-219. (Published at Camridge, UK)
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○ **4.** Mesoporous nanomagnet supercaptors for selective heme-proteins from human cells.
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○ **5.** Selective encapsulation of hemo-proteins using mesoporous metal oxide nanoparticles.
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(2) Cover pages	***1.*** Mesoporous nanomagnet supercaptors for selective heme-proteins from human cells. ***Chemical Communications,*** 2012, 48, 10790-10790. DOI: 10.1039/C2CC90368G **Mohamed Khairy**, Sherif A. El-Safty, Mohamed Ismael *2.* Mesoporous NiO nanosheets for the catalytic conversion of organic contaminates. ***Current Catalysis***, 2012, 2 (1) DOI: 10.2174/2211544711302010001 **Mohamed Khairy**, Sherif A. El-Safty ***3.*** Optical mesosensors for monitoring and removal of ultra-trace concentration of Zn(II) and Cu(II) ions from water. ***Analyst***, 2012, 137, 5442-5442, DOI: 10.1039/C2AN90097A Sherif A. El-Safty, Mohamed A. Shenashen, Mohamed Ismael, **Mohamed Khairy,** Md. R. Awual

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(3) Presentation	**1.** Water Treatment from Phenolic Pollutants by Chemical Transformation Process Using Mesoporous NiO Mosaics. 8th International Mesostructured Materials Symposium (IMMS-8, IMMS2013), Awaji Island, Hyogo, Japan. (May, 20, 2013) **Mohamed Khairy**, Sherif A. El-Safty, and Mohamed Shenashen **2.** Mesoporous NiO Nanocrystals as Sustainable catalyst for chemical conversion of organic pollutants. The 4th NIMS (MANA)-Waseda International Symposium PP. 26. (Mar. 11, 2013) **Mohamed Khairy**, Sherif A. El-Safty **3.** Optical mesosensor for water monitoring and removal of ultra-trace concentration of Zn(II) and Cu(II) ions from water. The 4th NIMS (MANA)-Waseda International Symposium, PP. 24.(Mar. 11, 2013) Mohamed Shenashen, **Mohamed Khairy**, Emad A. Elshehy and Sherif A. El-Safty **4.** Water Treatment through Chemical Transformation and Removal Based on Mesoporous Nickel Oxide Nanocrystals. 3rd International Conference on Advanced Materials Research (ICAMR 2013), Dubi, 2013.(Jan. 19, 2013) **Mohamed Khairy**, Sherif A.　El-Safty **5.** Green Chemical Transformation of phenolic pollutants using mesoporous NiO nanocrystals with sheet-like morphology. 4th WSEAS International Conference on Nanotechnology at Cambridge, UK (NANOTECHNOLOGY 2012). (Feb. 22, 2012) **Mohamed Khairy,** Sherif A. El-Safty, Mohamed Ismael, Mohamed A. Shenashen **6.** Mesoporous nickel oxide nanocrystal mosaics as catalysts for chemical transformation and removal of organic pollutants, The Fifth Saudi Science Conference (SSC5, 2012), Umm Al-Qura University. Makkah, Saudi Arabia. (Apr. 16, 2012) **Mohamed Khairy**, Sherif A. El-Safty, Mohamed Ismael, Mohamed A. Shenashen. **7.** 3D Mesocaptor Aluminosilica Monoliths for Visual Removal of Heavy Metals from Water. IUMRS-International Conference on Electronic Materials (IUMRS-ICEM 2012) 2012 Yokohama, Japan (Sep. 23, 2012) **Mohamed Khairy**, Sherif A. El-Safty, Mohamed A. Shenashen.. **8.** Mesoporous NiO Nanocrystal Mosaics as Catalysts for Chemical Transformation and Removal of Organic Pollutants. ZMPC 2012: International Symposium on Zeolites and Microporous Crystals, Hiroshima, Japan, P074. (July 28, 2012) **Mohamed Khairy,**　Mohamed Ismael, Sherif A. El-Safty, **9.** Mesoporous Nickel oxide with Nanocrystals Sheet-like Morphology as Effective catalysts of Organic Pollutants. The 3rd NIMS (MANA)-Waseda International Symposium, PP. 20. (Nov. 3, 2011) **Mohamed Khairy**, Mohamed Ismael, Sherif A. El Safty