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博士論文審査報告書

論　文　題　目
Thesis Theme

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

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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, these features effectively exploited the plethora of technology in terms of catalysis, sensing, adsorption, separation, optical imaging, phototherapy and energy conversion/storage devices. Recently, tremendous efforts have been focused on the synthesis of mesoporous metal oxides, aiming to control porosity, in addition to, intrinsic nanostructure and morphology. Despite these achievements in fabrication of mesoporous metal oxides, technical challenges in terms of intensive multistep procedures, high temperature and pressure conditions and time-consuming make 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 reports 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 are 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 broadly highlights the previous routes of synthesis of mesoporous metal oxides and their potential applications in the environmental remediation and energy storage devices. The fabrication avenues underlying the formation of mesoporous metal oxides are presented with special emphases on the recent progress in these fabrication approaches. Moreover, the 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 based the transformation and removal of organic contaminants from wastewater. This study focused on the fabrication of NiO nanoparticles (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 phenol contaminants. The NiO NPL showed higher catalytic activity toward the oxidation of organic contaminants than that of NiO NF and NS or even Fe_3O_4 NPs. However, the NiO NFs are enabled the high-gradient magnetic separation of organic contaminants from aquatic life, leading to wastewater management and supply. 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. This study may lead to possible potential of separation of single protein from pathogens. In general, the size-selective adsorption and removal of proteins that have different shapes, sizes, functions, and properties into mesostructured alumina and aluminosilica monoliths are previously reported. However, the clogging pores with large-molecular-weight proteins, particularly at high feed concentration, during the size-selective encapsulation assays 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 adsorbents of hemo-proteins, particularly haemoglobin (Hb), among various biological molecules. The NiO NFs showed higher adsorption capacity of Hb (~ 50 g/g) than that of NiO NSs and NPLs or even superparamagnetic Fe_3O_4 NPs. The key 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 real application, such approach may open a new avenue of magnetic separation of single proteins, leading to controlled biochemical applications.

In Chapter 5, the efficient sequestering and detection of toxic metal ions form environment using mesoporous metal oxides is are discussed. Simple, inexpensive, rapid responsive and portable sensors are highly recommended for monitoring of toxic metal ions. In this work, the mesoporous alumina and aluminosilica composites are used as selective optical sensing system for lead, copper, zinc and cadmium ions in environment. These sensitive, low cost, naked-eye sensors could be designed by the immobilization of chromophore molecules into mesocage cavities and surfaces of mesoporous alumina and aluminosilica monoliths. These new classes of optical cage sensors exhibited long-term stability of signaling and recognition functionalities, leading to 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. A unique feature of the core/multi-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 simultaneous detection and sequestering of toxic ions with a minimum sample manipulation, reasonable selectivity and sensitivity of Pb^{2+} ions from blood without use of reference devices.

Chapter 6 describes the 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), are synthesized in large-scale production, and low-cost manufacturing via microwave-assisted synthesis approach. The mesoporous NiO NPLs show superior electrochemical performance due to their unique morphology, size, and mesopore size distribution that enhances the diffusion of electrolyte through porous network "superhighways". These features induce high capacitance and recyclability of NiO NPLs more than that of NiO NFs and NiO NSs. This approach demonstrates the potential of free-standing NiO NPL electrodes for developing high-performance pseudocapacitors.

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

In summary, the thesis focused on the porous metal oxides in terms of fabrication, characterization and wide-range applications in catalysis, adsorbent, sensor and energy saving devices. This work explores how controlled porous surfaces of metal oxides nanostructures can play a key role in the performance of these applications. This work might open new avenues in real applications of related research. Indeed, this research merits awarding a Doctor of Science degree from Waseda University.

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