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博 士 論 文 概 要
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論 文 題 目
Dissertation Title

Synthesis of Nonprecious Metal Borides with Mesoporous Architecture and Their Applications

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Mesoporous materials at the mesoscale of 2 to 50 nm have attracted a great deal of attention due to their high porosity, large specific surface area, tunable pore size, and varieties of the framework. Especially, mesoporous metal-based materials offer the prospect of a wide range of applications due to their fascinating physicochemical properties, including high electrical conductivity and high thermodynamic stability, which cannot be achieved with siliceous mesoporous materials. Although many efforts have been developed to prepare precious metal-based materials such as Pt, Pd, Rh and Ir, their high price and scarce reserve severely hinder their widespread application. Compared to these precious metals, earth-abundant transition-metal-based (*e.g.*, Fe, Co, Ni and Cu) materials with a much lower price and unique properties have emerged as highly promising. However, unlike precious metals that can be easily reduced by moderately reducing agents such as ascorbic acid, the chemical reduction of nonprecious metal ions is more difficult due to their low redox potential. This means that nonprecious metals usually require stronger reducing agents such as sodium borohydride and/or dimethylamine borane. Such drastic reaction tends to release large amounts of H_2, making the mesoporous structure more difficult to be constructed. Therefore, controlling the chemical reduction conditions to synthesize compounds consisting of nonprecious metals or their alloys with mesoporous architecture is a challenging but necessary step to obtain sustainable systems for depositing them.

Another strategy to regulate properties of earth-abundant metals is the combination with other elements. For example, many efforts have proved that alloying the earth-abundant metals with non-metal/metalloid elements such as sulfur (S), nitrogen (N), boron (B), phosphorus (P) is an effective strategy for tuning physicochemical properties and local atomic structures of active sites and improving their performance in a variety of applications. In my thesis, I focus on the preparation of transition metal borides (TMBs) with mesoporous architecture such as nickel–boron (Ni–B), nickel–cobalt–boron (Ni–Co–B), and nickel–iron–boron (Ni–Fe–B). The typical metal–metalloid bonds (M–B) in TMBs are often strongly combined with metal–metal (M–M) and metalloid−metalloid bonds (B–B). This provides TMBs with unique properties, such as the amorphization due to boron incorporation and the effective charge transfer between metal and boron, causing abundant variation in metal active centers.

In **Chapter 1**, I introduce the recent development of mesoporous TMBs (meso-TMBs) and their applications. It begins with a brief introduction to current synthesis strategies to meso-TMBs. I then emphasis the formation mechanisms for diverse mesoporous structures of meso-TMBs and the structure-performance relationship. After that, I focus on several applications of meso-TMBs and highlight boron's ability to facilitate performances. Finally, based on the current studies, a perspective on the current challenges and opportunities is proposed.

Chapter 2 describes a method to prepare open mesoporous amorphous Ni–B alloys for the first time. The successful synthesis of the mesoporous Ni–B is driven by the self-assembly of copolymer micelles (PEO-*b*-PMMA) and dual reducing agents. In the selective hydrogenation of benzyl cyanide to *β*-phenylethylamine, the as-prepared mesoporous Ni–B alloy spheres exhibit excellent intrinsic activity, nearly four times greater than non-porous Ni–B alloy spheres. The outstanding activity of the catalyst for selective hydrogenation can be attributed to the synergistic effects of the amorphous alloyed Ni–B with the open porous structure, which not only increases surface area but also provides more effective active sites for hydrogen adsorption due to the homogenous dispersity of Ni and B atoms.

Chapter 3 extends the self-assembly of copolymer method to the preparation of bimetallic boride alloys. I have described the synthesis of well-defined open mesoporous Ni–B. It is necessary to expand the compositions to bimetallic metal borides, *i.e.*, Ni–Co–B, to exploring the alloying effects. However, different physicochemical properties of Ni and Co force us to control the reduction system more precisely. In addition, strong reducing agents (dimethylamine borane and sodium borohydride) tend to cause gas bubbles that are stabilized by the surfactant. Here, I develop a controllable strategy to synthesize the mesoporous nickel−cobalt boron (NiCoB) amorphous alloy spheres (AASs) with adjustable compositions by using a soft template-directed assembly approach. The use of tetrabutylphosphonium bromide (Bu_4PBr) is beneficial to generate well-defined mesopores because it both moderates the reduction rate by decreasing the reducibility of M^{2+} species and prevents the generation of soap bubbles. The mesoporous $Ni_{10.0}Co_{74.5}B_{15.5}$ AASs generate the highest catalytic performance for the hydrolytic dehydrogenation of ammonia borane. Its high performance is attributed to the combination of optimal synergistic effects between Ni, Co, and B as well as the high surface area and the good mass transport efficiency. This work describes a systematic approach for the design and synthesis of mesoporous bimetallic borides as efficient catalysts.

Chapter 4 furthers the doped second metal and nonmetal simultaneously into the mesoporous nickel borides. Although the above studies successfully synthesized Ni/Co-based borides, the deposition of Fe ions in the Ni/Co components is more difficult and complicated because the dissolved Fe species can easily form hydroxides and the Fe species also tend to form unstable green rust. Moreover, an addition of heteroatoms such as P to the meso-TMBs system to tune the properties and preparation of meso-TMBs with desired pore size is still promising, but has not been reported yet. In this chapter, a well-defined phosphorus- and boron-doped NiFe alloy mesoporous nanospheres (NiFeB–P MNs) with adjustable Ni/Fe ratio and large pore size are synthesized *via* a soft-templated chemical reduction strategy followed by a phosphine steam phosphidation process. The NiFeB-P MNs as deposited exhibit a low OER overpotential of 252 mV at 10 mA cm^{-2}, significantly smaller than that of B-doped NiFe mesoporous nanospheres (274 mV) and commercial RuO_2 (269 mV) in alkaline electrolyte. This work highlights the practicality of designing mesoporous architecture of non-noble metals and the importance of further incorporating P to adjust the electronic structure of metal–B-based alloy and enhance the intrinsic activity of the catalyst.

The large open pores and accessible surfaces in meso-TMBs are desired for immobilization or adsorption of guest bulky molecules. **Chapter 5** develops a self-template confinement assembly strategy for the synthesis of a new large open mesoporous CoFeB, which can serve as an ideal scaffold for well-dispersed deposition of Au nanoparticles (~3.1 nm) through galvanic replacement reaction (GRR). The simple GRR allows us to deposit Au, which enables us to control the size and content without the use of additional reducing agents. The mesoporous Au-CoFeB possesses combined properties of the superparamagnetism of CoFeB and bio-favorable of Au. The Au-CoFeB is employed as dispersible nanovehicles for isolating *p*53 autoantibody from the patient samples with the limit of detection of 0.006 U/mL, which is around 50-times lower than the conventional *p*53-ELISA kit.

In addition to the above presented soft-templating methods, **Chapter 6** introduces a method to prepare two-dimensional (2D) mesoporous metal borides based on heterostructure engineering. An efficient 2D heterostructure consisting of amorphous nickel boron oxide and crystalline mesoporous iridium is designed for water splitting, named as Ni–B_i/meso-Ir. Benefiting from well-defined 2D heterostructures and strong interfacial coupling, the Ni–B_i/meso-Ir as prepared possesses abundant catalytically active heterointerfaces and boosts the exposure of active sites. The electronic state of the iridium sites is tuned favorably by hybridizing the mesoporous Ir with Ni–B_i layers. Consequently, the Ni–B_i/meso-Ir heterostructures show superior and stable electrochemical performance toward overall water splitting.

In the last **Chapter 7**, I summarize the thesis and describe future prospects.

My thesis highlights the significant of introduction of mesoporous architecture in TMBs, which is a powerful pathway to increase the accessible active sites and consequently improve the performances. It is necessary to further expand their application areas by adjusting the mesoporous structures and compositions.

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○ Paper	Microwave One-Pot Synthesis of CNT-Supported Amorphous Ni–P Alloy Nanoparticles with Enhanced Hydrogenation Performance. *Journal of Materials Chemistry A*, 10 (2022) 6560-6568. **Yunqing Kang**, Haoran Du, Bo Jiang, Hui Li, Yanna Guo, Mohammed A Amin, Yoshiyuki Sugahara, Toru Asahi, Hexing Li, Yusuke Yamauchi.
○ Paper	Heterostructuring Mesoporous 2D Iridium Nanosheets with Amorphous Nickel Boron Oxide Layers to Improve Electrolytic Water Splitting, *Small Methods*, 5 (2021) 2100679. **Yunqing Kang**, Bo Jiang, Victor Malgras, Yanna Guo, Ovidiu Cretu, Koji Kimoto, Aditya Ashok, Zhe Wan, Hexing Li, Yoshiyuki Sugahara, Yusuke Yamauchi, Toru Asahi.
○ Paper	Amorphous Alloy Architectures in Pore Walls: Mesoporous Amorphous NiCoB Alloy Spheres with Controlled Compositions via a Chemical Reduction. *ACS nano*, 14 (2020) 17224-17232. **Yunqing Kang**, Bo Jiang, Juanjuan Yang, Zhe Wan, Jongbeom Na, Qian Li, Hexing Li, Joel Henzie, Yoshio Sakka, Yusuke Yamauchi, Toru Asahi.
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