



Title	Structural design and electronic state control of carbon-based catalysts for hydrogen evolution reaction
Author(s)	Yang, Xinran
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Abstract of Thesis

Name (Xinran Yang)	
Title	Structural design and electronic state control of carbon-based catalysts for hydrogen evolution reaction (水素発生反応における炭素系触媒の構造設計と電子状態制御)
Abstract of Thesis The intrinsic HER activity of most carbon-based catalysts remains significantly lower than that of platinum. To address this limitation, two main strategies have been explored in this essay: morphological engineering and electronic structure modulation. Structural designing aims to increase the density and accessibility of active sites, thereby enhancing the number of reactions per unit time. Electronic regulation, on the other hand, focuses on optimizing the intrinsic activity of active sites by tuning their electronic properties, improving intermediate adsorption energies, and thus lowering kinetic barriers. Specifically, I have synthesized transition-metal/heteroatom-doped carbon and metal-free carbon with special morphology for HER. Chapters 3 to 5 developed morphological control strategies for synthesizing transition metal-based carbon materials, aiming at limiting the migration kinetics of metal species at high temperatures. In Chapter 3, carbon coating and alloy reduction modification were simultaneously applied to layered double hydroxide (LDH) materials through chemical vapor deposition (CVD), which significantly improves the conductivity of the catalysts. Meanwhile, the layered structural characteristics of LDHs precursors are able to be preserved. In addition, the chemical etching effect of different molybdenum source reagents on LDHs precursors was systematically studied. In Chapter 4, the chelation effect of phytic acid on transition metal elements was used to effectively limit the aggregation of CoP particles in the product. The size of CoP particles in the prepared product is only 25 nm, demonstrating excellent HER activity. In Chapter 5, CoP nanoparticles with an average particle size of 19nm were successfully anchored on a carbon substrate through the spatial confinement effect of ion exchange resin and the molecular bridging effect of phytic acid. This catalyst exhibits comparable performance to Pt-based catalysts, while significantly reducing preparation costs. In addition, I studied the migration mechanism of S atoms after the decomposition of sulfonic acid groups and explored the feasibility of using SO₂ as a doping sulfur source. In Chapters 6 and 7, ultra-thin carbon nanosheets with high specific surface area were developed. I studied the synergistic enhancement mechanism of N and P dual-doped systems. In Chapter 6, ultra-thin N,P co-doped carbon nanosheets were synthesized by precisely adjusting the precursor concentration and utilizing the self-activation effect of phytic acid to enhance the exposure of active sites. Subsequently, the precursor ratio and carbonization temperature were further optimized to obtain products with customized N and P doping types and content gradients. Through DFT calculations, the synergistic doping mechanism was elucidated, and a model of C₃PO and N dopants was constructed for the first time. In Chapter 7, I studied the influence of precursor types on N and P dopants in the final product. The conjugation between imidazole ring and phytic acid was utilized to increase the content of graphite N in the product. In addition, by protonating the imidazole ring with phosphate groups, the content of C₃PO structure in the product was increased. The prepared catalyst exhibits excellent HER activity.	

論文審査の結果の要旨及び担当者

氏 名 (Xinran Yang)			
	(職)	氏 名	
論文審査担当者	主 査	教 授	西山 憲和
	副 査	教 授	水垣 共雄
	副 査	教 授	北河 康隆
	副 査	助 教	三宅 浩史
論文審査の結果の要旨 炭素系水素発生反応（HER）触媒は、資源制約および高コストといった課題を有する白金系触媒の代替材料として注目されているが、多くの場合、その本質的活性は白金に比べて依然として低い。この要因として、炭素材料中に存在する活性点構造の多様性や反応機構の複雑性に加え、形態的要因および電子構造因子が複雑に影響し合う点が挙げられる。そのため、これら各因子と触媒活性との相関関係は未だ十分に解明されておらず、高性能触媒の合理的設計を困難にしている。炭素系HER触媒の高性能化に向けては、これらの関係を体系的に明らかにし、明確な設計指針を構築することが不可欠である。 学位申請者は、形態制御および電子構造制御という二つの観点から炭素系HER触媒の精密設計を行い、各特性が触媒活性に及ぼす影響を詳細に検討した。第3章～5章においては、遷移金属/炭素系触媒の開発に取り組んだ。主に高温処理時の金属種の凝集挙動に着目し、種々の新規合成戦略を提案した。その結果、ナノサイズ金属リン化合物粒子の高分散固定化に成功し、白金系触媒に匹敵するHER性能を実現した。さらに、第6章、7章では、金属フリー炭素触媒の開発を行った。NおよびP共ドーピングによる電子構造制御に注目し、前駆体分子設計および炭素化条件の精密制御を通じて活性点構造の最適化を達成した。第一原理計算を併用することで、共ドーピングによる相乗効果を理論的に解明するとともに、新規なC₃P₀構造を含む活性点モデルを提案した点は、本研究の独創性を示す重要な成果である。 本研究成果は学術論文として公表され、炭素系HER触媒の設計指針を体系化するとともに、非貴金属触媒による水素エネルギー変換技術の発展に大きく貢献するものである。以上より、本論文は学術的および工学的価値の双方において高く評価され、博士（工学）の学位論文として十分に価値あるものと認められる。			