Title	Plasmonic Cu-based Catalysts Towards Solar-driven Production of Hydrogen and Value-added Products from Alcohol [an abstract of dissertation and a summary of dissertation review]
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Citation	北海道大学. 博士(理学) 甲第14693号
Issue Date	2021-09-24
Doc URL	http://hdl.handle.net/2115/83131
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Type	theses (doctoral - abstract and summary of review)
Additional Information	There are other files related to this item in HUSCAP. Check the above URL.
File Information	LUO_SHUNQIN_abstract.pdf (論文内容の要旨)

学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　　博士（理学）　　氏名　ルオ シュンチン

学 位 論 文 題 名

Plasmonic Cu-based Catalysts Towards Solar-driven Production of Hydrogen and Value-added Products from Alcohol

（Cu 基プラズモニック金属触媒による光誘起アルコールの脱水素反応に関する研究）

Exploring new catalytic technologies for sustainable and highly-efficient H_2 production from renewable H_2 sources has attracted considerable attention. Due to the relatively high gravimetric H_2 content and easy availability from biomass fermentation, alcohols have been regarded as promising H_2 carriers. Cu-based materials, featuring good selectivity towards C-H bond activation and low price, are generally used for alcohol dehydrogenation. Nevertheless, the conventional alcohol dehydrogenation reactions suffer from intense energy consumption and unsatisfactory activity. In this thesis, the object is to introduce solar-energy as new form of stimulus, which could excite hot carriers from rational designed plasmonic Cu nanostructures for targeted activating specific chemical bonds of the reactants, initiating the alcohol dehydrogenation. Various strategies (i.e., modulating the size or composition of pristine Cu nanoparticle) were applied to improve the light harvesting and regulate the charge transfer pathway of plasmonic Cu towards highly-efficient solar-driven H_2 production from alcohol and thus to deepen the understanding of corresponding mechanism of plasmon-mediated reactant activation.

In chapter 1, a general background about solar-driven hydrogen production reaction and the fundamentals of plasmon-mediated photocatalytic processes (including plasmonic photocatalysis at room temperature, photothermal catalysis at high reaction temperature, and plasmonic photothermal catalysis where hot carrier activation and photothermal heating act in concert) were introduced. Then, the recent development of hydrogen production reaction driven by plasmon-mediated photocatalysis was summarized, with special attention given to the design concepts and reaction mechanisms of the catalysts.

In chapter 2, plasmonic Cu nanoparticles with different size distribution were developed for methanol self-coupling reaction to produce H_2 and methyl formate with the assistance of light energy. The results revealed that under purely thermocatalytic condition, the catalytic activity decreased with the increasing diameter of Cu nanoparticles; while in the photo-assisted thermocatalytic reaction, the optimized Cu catalysts with an average diameter of 34.8 nm exhibited the best photo-enhanced catalytic activity among other Cu samples. With the assistance of visible light, the apparent activation energy for methanol self-coupling over optimized Cu sample was reduced by 43% compared with purely thermocatalytic conditions, and the reaction activity was 14.4 time higher than that of thermocatalytic reaction rate at reaction temperature of 140 °C. Mechanistic investigations indicated that due to the effective visible light harvesting, the optimized plasmonic Cu could induce strong local electric fields and excite larger amounts of hot carriers, which played dominant role in activating the intermediate species and reducing the activation energies. The modulated plasmonic effect, together with the optimized thermocatalytic activity, rendered the optimal Cu nanoparticles a H_2 production activity of 4318 μmol g^{-1} min^{-1} with a high solar-to-energy efficiency of 3.6% during the solar-driven methanol self-coupling process.

In chapter 3, an efficient solar-driven ethanol dehydrogenation process was achieved using a low-cost Ni-Cu bimetallic catalyst for the high-yield and selective production of H_2 and acetaldehyde. Under the irradiation of focused simulated solar light, 176.6 mmol $g_{catalyst}^{-1}$ h^{-1} of H_2 production rate with a high solar-to-fuel conversion efficiency (3.8%) was achieved without additional thermal energy input. Mechanistic investigations revealed that photothermal heating and hot carrier generation over Ni-Cu catalysts took responsibilities for the high activity. Hot electrons generated from Cu nanoparticles could migrate to Ni atoms, which simultaneously favored the separation of charge carriers and the activation of adsorbates.

In chapter 4, in order to achieve highly efficient solar-driven methanol steam reforming (MSR) without additional thermal energy input, a low-cost plasmonic ZnCu alloy catalyst composed of Cu nanoparticles with surface-deposited Zn atoms was reported. An unprecedentedly high H_2 production rate of 328 mmol $g_{catalyst}^{-1}$ h^{-1} with a solar energy conversion efficiency of 1.2% under 7.9 Suns irradiation was obtained, which substantially exceeds the reported conventional photocatalytic MSR. Experimental results and theoretical calculations suggested that Zn atoms act not only as the catalytic sites for water reduction with lower activation energy, but also as the charge transfer channel, pumping hot electrons into water molecules and subsequently resulting in the formation of electron-deficient Cu for methanol activation. The interplay of dual active sites, together with photothermal heating, endowed the ZnCu catalysts with excellent capacity for activating both the water and methanol molecules, ultimately delivering a high H_2 production rate.

In chapter 5, an overall summary of this dissertation was presented. This thesis carried out a systematic study on Cu-based plasmonic nanoparticles for efficient solar-driven alcohol reforming reaction for the production of H_2 and other high value-added products without additional thermal energy input. Various strategies have been employed to improve the catalytic activity through modulating the optical response and regulating the charge transfer pathway, such as modulating the size or composition of pristine Cu nanoparticle. With the assistance of photo-induced hot carriers, a higher reaction rate and lower apparent activation energy can be achieved. This thesis revealed that the morphology and structure of plasmonic nanoparticle were of significance in determining the optical response and charge transfer pathway, which could ultimately control the catalytic property. The findings in this study deepened the understanding of the interaction between hot carriers and surface reactants, and provided a potential strategy for initiating efficient H_2 production and various other energy-demanding industrial reactions through designing plasmonic nanostructures.