**Design of Plasmonic Catalysts Utilizing Nanostructures**

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This review describes the design of nanostructured plasmonic catalysts, such as nanoparticles and nanosheet morphologies, that strongly absorb visible light over a wide range of the solar spectrum due to localized surface plasmon resonance (LSPR) and application to enhanced hydrogen evolution. A new method for the synthesis of Ag nanoparticles, with color dependent on the particle size and morphology, combined microwave heating and the use of mesoporous silica materials. Further combination with Pd nanoparticles significantly enhanced the catalytic activities for hydrogen production from ammonia borane (NH3BH3) compared with the inherent Ag catalysts under both dark and visible-light irradiation conditions. We also describe the synergistic catalysis activities of plasmonic Au(core)-Pd(shell) nanoparticles supported on amine-functionalized metal-organic frameworks (MOFs) for boosting room-temperature hydrogen production from formic acid (HCOOH) under visible light irradiation. Our search for plasmonic materials based on earth abundant elements found that reduced molybdenum oxide (HxMoO3–y) nanosheet with oxygen defects and doped hydrogen displayed intense absorption in a wide range from the visible to the near-infrared region. This unique plasmonic HxMoO3–y nanosheet can enhance dehydrogenation from ammonia borane under visible light irradiation.

**Keywords**
Plasmonic catalyst, Hydrogen carrier, Silver nanoparticle, Reduced molybdenum oxide nanosheet

1. Introduction

Metal nanoparticles, such as Au and Ag, absorb visible and infrared light in specific regions resulting in visible colors such as red and yellow, so have been used for stained glass in churches since ancient times. Irradiation of light with a specific wavelength on such metal nanoparticles causes collective vibration of the surface free electrons, which is called “Localized Surface Plasmon Resonance (LSPR)”. LSPR results in partial perturbation of the charge density on the metal surface, with consequent changes in the electron density, electron transfer, surface electric field, and surface light quantity. Variations in the composition, shape, and size of the plasmonic material allows us to control the effective light wavelength (in the visible light to near-infrared light range) and light absorption intensity of the LSPR. The resultant LPSR-induced changes in the surface charge of the metal are expected to improve the catalytic properties. Consequently, LSPR-induced fields may evoke or enhance catalytic activities through mechanisms based on electric near-field, strong light-field, or electron transfer in contrast to the conventional mechanisms of thermal catalysts utilizing thermal energy and semiconductor photocatalysts utilizing light energy, with the possibility of creating a new concept of catalytic reaction processes based on plasmonic materials. However, compared with other approaches such as sensors and light emitting devices, the application of plasmonic materials in catalysis has rarely been reported.

Recently, photocatalytic systems based on the LSPR of Au and Ag nanoparticles have been mainly studied. These applications of LSPR for photocatalysis can be classified into several categories according to the differences in their reaction mechanisms (Fig. 1). Plasmon-induced electron transfer i) and plasmonic enhancement of light absorption ii) involve the plasmonic nanoparticles functioning as so-called dye sensitizers which increase the activity of semiconductor photocatalysts.

Catalytic reactions proceed on the surface of the cat-
alyst, so improvement of catalytic activity should result from the change in surface electron density induced by LSPR. Therefore, other possible mechanisms are direct activation of the reaction substrate on a plasmonic nanoparticle catalyst iii) and activation of the substrate by a composite catalyst with plasmonic nanoparticles and catalytic active metal nanoparticles iv). These hybrid materials can be recognized as a new type of catalyst that combines the properties of both metal catalysts and photocatalysts.

This review paper focuses on the design of plasmonic catalysts using the mechanisms of iii) and iv) and outlines the plasmonic catalysts we have developed recently. Specific Ag nanoparticles prepared in the pores of mesoporous silica using microwave heating, hybrid materials with metal-organic frameworks (MOFs) and plasmonic Au@Pd core-shell nanoparticles, and reduced molybdenum oxide (H\text{\textsubscript{1-x}}MoO\text{\textsubscript{3–y}}) nanosheet with oxygen defects and hydrogen doping were developed as efficient photocatalysts for hydrogen production from hydrogen carrier molecules such as ammonia borane and formic acid.

2. Plasmonic Catalysts Confined within Porous Support Materials

2.1. Color-controlled Ag Nanoparticles and Nanorods Confined within Mesopores

Metal nanoparticles with a uniform particle size distribution can be synthesized using heating induced by microwave irradiation. Combination of the size control using microwave heating and shape control using the meso-size cavities of mesoporous silica allows the synthesis of Ag nanoparticles with the specific size and color appropriate for the catalytic reaction and the light environment.

Color-controlled spherical Ag nanoparticles (NPs) and nanorods can be synthesized within the mesoporous structure of SBA-15 by the alcohol reduction method in the absence or presence of surface-modifying organic ligands\textsuperscript{15)–17). For example, Ag catalyst \textit{I} (Ag: 1 wt%) was synthesized by irradiating a 1-hexanol suspension of SBA-15 powder, an aqueous solution of AgNO\textsubscript{3} and sodium laurate (Lau; CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{10}COONa) with microwaves (500 W, 2.45 GHz) under an Ar atmosphere for 3 min. We employed microwave dielectric induction heating for the preparation of monodispersed metal NPs because energy-efficient microwave irradiation allows rapid and uniform internal heating\textsuperscript{18).}

Nanosized Ag particles were successfully deposited within the well-ordered mesoporous channel structure of SBA-15. Spherical Ag NPs with mean diameter of 3.9 nm and narrow size distribution were observed in Ag catalyst \textit{I} (yellow) (Fig. 2(a)). In contrast, Ag nanorods were observed parallel to the SBA-15 mesopores in the Ag samples prepared in the absence of Lau ligand. The aspect ratio of the Ag nanorods increased from 2.8 to 6.1 with increasing microwave irradiation.

![Fig. 1 Schematic Illustration of Different Types of Plasmonic Catalysts](image-url)
time from 3 min (Ag catalyst 2 (red)) to 5 min (Ag catalyst 3 (blue)) (Fig. 2(b)-2(c)). The mean distance perpendicular to these Ag nanorods was ca. 8 nm, in close agreement with the pore size of SBA-15. These Ag catalysts possessed characteristic colors due to the LSPR of the Ag nanostructures; Ag catalyst 1 (yellow), 2 (red), and 3 (blue). The intensity and wavelength of LSPR absorption reflected the UV-vis spectrum. Ag catalyst 1 (yellow) exhibited an intense absorption band at around 410 nm owing to the LSPR absorption of spherical Ag NPs. In contrast, Ag catalysts 2 (red) and 3 (blue) exhibited two absorption peaks in the visible and infrared regions corresponding to the transverse mode perpendicular to the Ag nanorods and longitudinal mode along the long axis of the Ag nanorods, respectively.

The smaller yellow Ag NPs of Ag catalyst 1 exhibited higher catalytic activities for the dehydrogenation of ammonia borane (NH$_3$BH$_3$, AB) under dark conditions. AB is a leading candidate for hydrogen storage materials because of its low molecular weight (30.87 g mol$^{-1}$), high theoretical hydrogen gravimetric capacity (19.6 wt%), and high stability in solid form at room temperature$^{19}$). The catalytic activity decreased in the order of Ag catalyst 1 (yellow) > 2 (red) > 3 (blue), which corresponds with the increase in Ag NP size. These results suggest that catalytic H$_2$ production from AB under dark conditions occurred on the exposed surface Ag atoms of the NPs, in accordance with the fact that smaller Ag NPs possess a larger number of surface atoms as well as more low coordination metal sites i.e. vertices and edges. However, catalytic performance under light irradiation ($\lambda>420$ nm, 320 mW cm$^{-2}$) was significantly dependent on the color of the Ag catalysts, and increased in the following order: 1 (1.24) < 2 (2.12) < 3 (2.48) (values are the rate of increase). Therefore, larger Ag NPs, especially blue Ag nanorods, achieved maximum enhancement of activity (Fig. 3(A)). The order of increasing catalytic performance is in close agreement with the order of absorption intensity due to the Ag-LSPR under light irradiation of more than 420 nm. Similar trends in the LSPR-enhanced catalytic activity were observed in the tandem reaction consisting of dehydrogenation of AB and hydrogenation of 4-nitrophenol.

Initial H$_2$ production activity using Ag catalyst 3 (blue) under dark conditions at 30 °C was 0.46 µmol min$^{-1}$, which was slightly higher than 0.32 µmol min$^{-1}$ under dark conditions at room temperature (25 °C), but significantly lower than 0.80 µmol min$^{-1}$ under light ir-
radiation. We also found that increasing rates of catalytic activity per irradiation intensity showed a good relationship with the Kubelka-Munk (KM) function intensity derived from Ag-LSPR calculated by UV-vis measurement at the irradiation wavelength (Fig. 3(B)). These results confirm the negligible contribution of temperature in the enhanced catalytic activity, and suggest that the increased catalytic performance under light irradiation is exclusively dependent on the particle color derived from Ag-LSPR.

Addition of NaHCO₃, a positive charge scavenger, to a suspension of Ag catalyst significantly retarded the reaction rate under light irradiation. This indicates that dehydrogenation of NH₃BH₃ is activated by the transitory deficient site of the electron population of Ag NPs, which is produced by the charge separation derived from the Ag-LSPR plasma oscillation. After dissociation of the B-N bonds, the generated positive NH₃ might react with photoelectrons from the hydrolysis (NH₃ + e⁻ + H₂O → NH₄OH), whereas hydroge- nation of the negative BH₃ spontaneously occurs on the h⁺ site (BH₃ + h⁺ + 2H₂ → HBO₂ + 3H₂).

2.2. Bimetallic M/Ag-based Plasmonic Photocatalyst Confined within Mesopores

Improvement of the catalytic activity was attempted by combination of plasmonic Ag nanorod (Ag catalyst 3 (blue)) with Pd NPs by a simple LSPR-assisted deposition method under visible light irradiation. The resultant catalysts were named Pd/Ag SBA-15. Figure 4 shows the high resolution transmission electron microscopy (HR-TEM) image and elemental mapping of uniformly deposited Pd NPs on the surface of Ag nanorods for Pd/Ag SBA-15. The aspect ratio of Ag nanorods showed no significant change after the deposition of Pd NPs. Energy dispersive X-ray spectroscopy (EDS) mapping unveiled uniform dispersion of very small Pd NPs onto the Ag nanorods. The shapes of the Pd K-edge X-ray absorption near edge structure (XANES) and Fourier transform-extended X-ray absorption fine structure (FT-EXAFS) spectra of Pd/Ag catalysts resembled those of PdO, confirming the metallic state of the Pd NPs. The Pd-Pd distance in the Pd/Ag catalysts was shorter than that of pure Pd foil, suggesting the presence of Pd-Ag heteroatomic bonding.

All bimetallic NPs showed higher catalytic activities and significant enhancement effects for the AB dehydrogenation reaction under both dark and light irradiation conditions. A similar trend with that of monometallic nanostructures was observed under visible light irradiation. The dependence of the catalytic performance over Pd/Ag catalysts on wavelength using monochromatic light was also explored, showing increased catalytic activities with the LSPR absorption intensities of Ag NPs. This finding further confirmed the key role of particle color in the catalytic activity.

The Pd/Ag bimetallic plasmonic catalysts were further applicable to the Suzuki-Miyaura coupling reaction with enhanced catalytic activity under visible light irradiation. The effects of plasmonic Au and Pd/Au nanostructures were investigated in this reaction, and absorption and catalytic activities compared with Ag and Pd/Ag nanocatalysts. The LSPR absorption peak of Ag, Pd/Ag and Au, Pd/Au catalysts displayed characteristic absorptions at approximately 400 nm and 520 nm, respectively. The spherical Pd/Ag and Pd/Au nanostructures had average particle sizes of 4.2 nm and 4.9 nm, respectively. Pd/Ag catalysts were active in the AB dehydrogenation reaction (Fig. 5(A)), whereas Pd/Au catalysts exhibited superior catalytic activity in the Suzuki-Miyaura coupling reaction of iodobenzene and phenylboronic acid in the presence of potassium carbonate as a base and ethanol as a solvent (Fig. 5 (B)).

A plausible mechanism of the plasmonic reactions using bimetallic catalysts under light irradiation conditions involves accumulation of the energetic electrons generated by resonant excitation of the plasmonic metals in the lowest unoccupied molecular orbital (LUMO) of the reactant molecules through the Pd NPs, which leads to weakening of the bonds. This mechanism is supported by the considerably higher work
function values of Pd (5.0 eV) than those of Ag (4.3 eV) and Au (4.7 eV). Therefore, the lower Fermi level of Pd compared to Ag and Au makes the electron transfer process quite feasible.

Several bimetallic combinations of catalytically active metals, such as Pd, Co, Ni, and Ru, with Ag NPs were also explored\(^{22}\). The choice of the second metal is based on the work function value, with Fermi energy levels lower than that of Ag. This characteristic enables efficient charge transfer from Ag to the second metal under visible light irradiation. These bimetallic plasmonic catalysts displayed excellent catalytic activities and visible light enhancements in the dehydrogenation of AB and reduction of nitrophenol using AB as a hydrogen source.

This study employed pure SBA-15 as a support material. In another strategy, an Ag-based plasmonic catalyst was supported on Ti-containing mesoporous sili-

cad\(^{23,24}\). X-ray photoelectron spectroscopy (XPS) analysis confirmed that the binding energies of Ag shifted towards lower values by the incorporation of isolated and tetrahedrally coordinated single-site Ti-oxide moieties. This shift confirms the possible interactions of Ti-oxide and Ag by electron-transfer from the Ti-oxide moieties to Ag to generate electron-rich Ag species, which ultimately enhances the catalytic reaction. We also reported the synthesis of Au NPs immobilized on morphologically-controlled TiO\(_2\) support, nanorod, nanotube, and microporous materials\(^{25}\). Au/TiO\(_2\) nanorod catalyst displayed the superior performance of 33 % yield in aerobic alcohol oxidation in the absence of light and 55 % yield of benzaldehyde with an external quantum efficiency of 3.4 % under visible light irradiation (\(\lambda > 420\) nm) at 373 K for 4 h.

2.3. Core-shell Plasmonic Catalysts Loaded on MOFs

Integration of plasmonic materials with metal-organic frameworks (MOFs) may be very effective\(^{26,27}\). The large surface area of MOFs can prevent the aggregation of plasmonic materials, which will further facilitate the diffusion and migration of reagents. The semiconducting property of MOFs can promote the transportation of photogenerated charges, leading to enhanced photocatalytic performance.

We have designed plasmonic Au(core)_Pd(shell) NPs loaded on titanium-doped zirconium based amine-functionalized MOFs (UiO-66(Ti\(_x\)Zr\(_{100-x}\))) (named Au@Pd/MOFs), in which Au NPs were first deposited by NaBH\(_4\) reduction, followed by photo-deposition of Pd using a Xe lamp to form core-shell Au@Pd NPs\(^{28}\). High-angle annular dark field scanning transmission electron microscope (HAADF-STEM) and energy dispersive X-ray fluorescence spectrometer (EDX)-line scanning clearly showed core-shell Au@Pd NPs with a mean size of 7.3 nm deposited on the MOFs without significant aggregation (Fig. 6(a)), as predicted with the large surface area of MOFs preventing aggregation of the metal NPs and the semiconducting property transferring the photogenerated charges to the surface of the Au NP. X-ray diffraction (XRD) detected no additional new reflection in the MOFs doped with Ti ions, indicating that doping of Ti ions within the UiO-66 framework did not change the framework structure and no new phase containing Ti was formed. In contrast, the absorption edge of MOFs displayed a slight red shift after doping with Ti ions compared with the sample without Ti doping. Thus, the Au@Pd/MOFs strongly absorb visible light over a wide range due to the LSPR effect of Au and the chromophore on the linker of MOFs.

The activity of Au@Pd/MOFs was evaluated for the dehydrogenation of formic acid (FA) under both dark and visible light irradiation conditions. Formic acid (FA, HCOOH) is recognized as one of the most promis-
ing hydrogen carriers for fuel cells in terms of simplicity, nontoxicity, and high hydrogen content (4.4 wt%). A promising strategy for the enhancement of catalytic activity and selectivity of supported Pd catalysts is to modify the electronic properties and geometric structure of Pd NPs through alloying or forming a core-shell structure with other metals.

The $H_2$ amount generated by FA dehydrogenation over Au@Pd/MOFs was significantly increased under visible light irradiation, compared to under dark conditions (Fig. 6(b)). Au@Pd/UiO-66(Zr55Ti45) produced the largest amount of $H_2$. No significant reaction occurred over Au/UiO-66(Zr85Ti15) without Pd, and little reaction was observed over Pd/UiO-66(Zr55Ti45) under dark conditions, suggesting that the reaction is driven by the Pd NPs. Higher amount of Ti doping enhanced the activity, presumably because Ti-doping both induced electron-rich metal NPs and enhanced visible light absorption of MOFs as well as the plasmonic absorption efficiency of core Au. The visible-light enhanced $H_2$ production rate of the optimum Au@Pd/UiO-66(Zr55Ti45) approached 42,000 mL h$^{-1}$ g$^{-1}$ (Pd) with corresponding TOF of 200 h$^{-1}$, and the catalyst could be recycled three times with slight decrease in catalytic activity, suggesting considerable stability in FA dehydrogenation.

The synergistic effect between plasmonic Au@Pd NPs and photoactive MOFs was investigated with reactions using monochromatic light ($\lambda = 400$ nm or 480 nm) and an LED lamp ($\lambda = 530$ nm) as the light source. The greatest enhancement was observed using monochromatic light ($\lambda = 400$ nm), possibly explained by a linker-to-cluster charge-transfer mechanism (LCCT), in which the incident light ($\lambda = 400$ nm) is absorbed by the organic linker, and photo-excited electrons are transferred from the linker to cluster. The photo-excited electrons are finally gathered on the surface of the Au@Pd metal of Au@Pd NP loaded MOFs, which leads to the generation of active electron-rich Pd species. Considerable enhancement was also observed under LED lamp ($\lambda = 530$ nm) irradiation, possibly ascribed to the increase in electron density of the Pd species by the positive LSPR effect of Au. Electron-rich Pd can greatly promote dissociation of the C–H bond as evidenced by a kinetic isotope study (KIE) using HCOOH and DCOOH. The KIE study using HCOOH and HCOOD also suggested that the weakly basic-NH$_2$ groups within the framework of MOFs have positive effects on the O–H bond cleavage. Therefore, the electron-rich Pd species generated by the activation of MOFs and plasmonic Au@Pd NPs under light irradiation as well as the weakly basic-NH$_2$ groups can promote the rate-determining step (C–H bond dissociation) and O–H bond dissociation, respectively. The synergetic effects of the weakly basic-NH$_2$, LSPR effect, and optically responsive MOFs for improving $H_2$ production from FA are illustrated in Fig. 6(c).

This study suggests that MOFs can serve as a platform to design novel photocatalysts by combination with other active catalysts for various reactions under light irradiation.
3. Non-noble Metal-based Plasmonic Catalysts

3.1. Reduced Molybdenum Oxide Nanosheet Plasmonic Catalyst

Surface Plasmon Resonance (SPR) occurs in both noble metal-based plasmonic catalysts (e.g., Ag and Au) and some metal oxides containing abundant dopant elements. MoO$_3$ and WO$_3$ are important n-type transition metal oxide semiconductors. Interestingly, doping of hydrogen atoms into these oxide matrices is known to yield a class of H$_x$MoO$_3$ and H$_x$WO$_3$ materials, which are generally called hydrogen molybdenum bronze and hydrogen tungsten bronze, respectively. These materials have high carrier density and electrical conductivity, so exhibit strong light absorption due to SPR in the visible to near infrared region, and have recently been applied to photoelectrodes and sensors as inexpensive alternatives to precious metal-based plasmonic nanoparticles. We prepared H$_x$MoO$_3$ nanosheets by reacting metal Mo powder with H$_2$O$_2$ in ethanol solution and subsequent solvothermal treatment. The as-prepared H$_x$MoO$_3$ nanosheets were intense blue (Fig. 7(a)), and displayed strong visible light absorption with an SPR peak at around 680 nm (Fig. 7(b)). In contrast, the commercial MoO$_3$ sample exhibited only UV-light response, with the absorption edge at around 400 nm corresponding to the wide band gap of ca. 3.1 eV. The H$_x$MoO$_3$ nanosheets were 200 nm to 1 μm in length and ca. 20-30 nm in thickness (Fig. 7(c) and 7(d)).

Experimental parameters (i.e., solvothermal temperatures, H$_2$O$_2$ volumes added, and solvents) were important in determining the phase structures and plasmonic resonances of the produced H$_x$MoO$_3$. The blue material was obtained using alcohols as solvents, suggesting that the alcohols acted as reductants during the solvothermal synthesis to incorporate hydrogen atoms into the MoO$_3$ matrix. XPS verified that Mo$^{5+}$ cations accounted for 77.3 % of total Mo species, revealing the presence of abundant delocalized d-electrons which sustain the plasmonic absorption.

The plasmonic H$_x$MoO$_3$ nanosheets acted as a highly efficient catalyst for ammonia borane (NH$_3$BH$_3$, AB) dehydrogenation. As mentioned above, noble metal nanoparticles (e.g., Pd, Ru, Rh, Pt) are conventionally used as catalysts for this reaction, but earth-abundant catalysts with low cost and high efficiency are desirable for practical applications. The as-obtained plasmonic H$_x$MoO$_3$ nanosheets outperformed commercial pristine MoO$_3$ under both dark and visible light irradiation conditions (Fig. 7(e)). Notably, the catalytic activity was dramatically improved by 4 times using the plasmonic H$_x$MoO$_3$ nanosheets under visible light irradiation, which exceeded that of the plasmonic Ag/SBA-15 catalyst mentioned above. The control experiments showed that the plasmonic effect accounted for ca. 77 % of the catalytic enhancement (Fig. 7(f)).

This study clearly demonstrated that plasmonic doped semiconductors can also be used as efficient visible light-driven photocatalysts, and allow potential utilization of earth-abundant elements instead of noble metals. We also synthesized high-surface-area H$_x$MoO$_3$ nanosheets using the polymer-templated self-assembly approach, and H$_x$MoO$_3$ NPs via a simple aqueous solution-based route under ambient synthetic conditions, which also showed intense visible light plasmonic absorption with SPR peaks in the visible light range. This SPR-induced strong light absorption allowed both H$_x$MoO$_3$ materials to achieve enhanced H$_2$ production rate in NH$_3$BH$_3$ dehydrogenation under visible light irradiation.
coupling Pd NPs and plasmonic H$_x$MoO$_3$. The plasmonic Pd/H$_x$MoO$_3$ hybrid was synthesized through a solution-processed impregnation of Pd precursor and the subsequent chemical reduction with NaBH$_4$, resulting in Pd NPs of about 10 nm loaded on micro-sized H$_x$MoO$_3$ plates (Fig. 8(a)). The as-synthesized Pd/H$_x$MoO$_3$ hybrid showed strong visible light response, with a prominent SPR peak at around 640 nm (Fig. 8(b)), whereas pristine MoO$_3$ exhibited light absorption in the UV region only. The plasmonic Pd/H$_x$MoO$_3$ hybrid exhibited dramatic enhancement in NH$_3$BH$_3$ dehydrogenation, with the wavelength-dependent activity enhancement under various LED (i.e., blue light 470 nm, green light 530 nm and red light 650 nm) irradiation (Fig. 8(c), 8(d)). Additionally, the plasmonic Pd/H$_x$MoO$_3$ hybrid also showed enhanced catalytic activity for the Suzuki-Miyaura coupling reactions under visible light. We also reported that hybridization of H$_x$MoO$_3$ and H$_x$WO$_3$ can enforce SPR-derived light absorption in the visible light region. The plasmonic Mo$_{1-x}$W$_x$O$_{3-y}$ synthesized under the optimized conditions by the solvothermal method showed dramatic enhancement of the dehydrogenation activity from NH$_3$BH$_3$ under visible light irradiation, which outperformed monometallic counterparts of H$_x$MoO$_3$ or H$_x$WO$_3$ owing to the enhanced light absorption ability. Moreover, further coupling of plasmonic Mo$_{1-x}$W$_x$O$_y$ with Pd NPs could greatly improve the catalytic activity towards NH$_3$BH$_3$ dehydrogenation under visible light irradiation. These findings verified that coupling of plasmonic doped semiconductor support and catalytic metal NPs could lead to highly efficient heterogeneous catalysis.

To obtain hydrogen-doped semiconductor plasmonic materials, we recently adopted an H-spillover approach. The chemisorbed hydrogen molecules dissociate on metal NPs (e.g., Pd, Pt) to produce reactive hydrogen atoms, which migrate to the surface and further diffuse into the bulk of the MoO$_3$ supports, leading to reduction of MoO$_3$ (Fig. 9(a)). Pd/MoO$_3$ reduced with H$_2$ at room temperature (Pd/MoO$_3$ H$_2$-RT) exhibited strong optical absorption in the visible regime, with an SPR peak at approximately 565 nm (Fig. 9(b)). At the same time, orthorhombic MoO$_3$ was converted into monoclinic H$_{1.68}$MoO$_3$ (Fig. 9(c)). Tunable plasmon resonances could be observed through variation of the stoichiometric compositions (Fig. 9(b)), which depend on the reduction temperature, metal species, and characteristics and size of the metal oxide supports in the H$_2$ reduction process.

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**Fig. 8 (a) TEM Image of Pd/H$_x$MoO$_3$ Hybrid and (inset) Particle Size Distribution of Pd NPs, (b) UV/vis-NIR Diffuse Reflectance Spectra of the Pd/H$_x$MoO$_3$ Hybrid and Pristine MoO$_3$, (c) Time Course of H$_2$ Generation over the Pd/H$_x$MoO$_3$ Catalyst under Blue, Green, and Red LED Illumination Together with Dark Condition in Dehydrogenation of Ammonia Borane (NH$_3$BH$_3$), (d) Increased H$_2$ Yield Rate as a Function of the Wavelength of LED Irradiation over Pd/H$_x$MoO$_3$ Catalyst**

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The as-prepared Pd/H\textsubscript{MoO\textsubscript{3}} was used as plasmonic catalyst for \(p\)-nitrophenol reduction to \(p\)-aminophenol using NH\textsubscript{3}BH\textsubscript{3} as a reductant. The plasmonic H\textsubscript{MoO\textsubscript{3}} support boosted Pd-catalyzed reduction of \(p\)-nitrophenol under exposure to visible light compared to the dark conditions. Therefore, a plasmonic Ru/H\textsubscript{MoO\textsubscript{3}} hybrid was also prepared via the H-spillover process on Ru NPs\textsuperscript{39}. The plasmonic Ru/H\textsubscript{MoO\textsubscript{3}} hybrid showed superior catalytic activity in the photocatalytic reduction of \(p\)-nitrophenol with H\textsubscript{2} in contrast to the dark conditions, in which H\textsubscript{MoO\textsubscript{3}} acted as electron-donor centers and Ru NPs acted as active centers for the hydrogenation reaction. Furthermore, based on the synergistic effect of bimetallic NPs, RuPd NPs immobilized on the plasmonic H\textsubscript{MoO\textsubscript{3}}, support were also prepared, which exhibited further enhancement of catalytic activity for \(p\)-nitrophenol reduction with H\textsubscript{2} under visible light irradiation\textsuperscript{40}. The as-synthesized plasmonic bimetallic RuPd/H\textsubscript{MoO\textsubscript{3}} hybrid could completely hydrogenation of \(p\)-nitrophenol within 5 min, which was superior to the Ru/H\textsubscript{MoO\textsubscript{3}} and Pd/H\textsubscript{MoO\textsubscript{3}} hybrids with single metallic NPs. These results demonstrate that hydrogen-doped molybdenum oxide can be used as an efficient and stable plasmonic platform for metal NP catalysts.

H\textsubscript{2} reduction at higher temperature allows a dehydration reaction to occur and oxygen-deficient molybdenum oxide (H\textsubscript{3}MoO\textsubscript{3.5}) containing oxygen defects (V\textsubscript{O}) is formed\textsuperscript{38}. These abundant defects form more active sites for reactions in the molybdenum oxide compared to the pristine counterpart, and could be promising for heterogeneous catalysis. We have recently found that plasmonic Pt/H\textsubscript{MoO\textsubscript{3}} hybrid showed highly enhanced catalytic activity towards deoxygenation of sulfoxides under 1 atm H\textsubscript{2} at room temperature with and even without visible light irradiation\textsuperscript{38}. The Pt/H\textsubscript{MoO\textsubscript{3-y}} hybrid was prepared through a solution-processed impregnation of Pt precursor and subsequent H\textsubscript{2} reduction at controlled temperatures. Reduction of \(\alpha\text{-MoO\textsubscript{3}}\) containing Pt precursor under H\textsubscript{2} flow causes dissociated H atoms to be intercalated into the MoO\textsubscript{3} matrix, resulting in transformation from orthorhombic MoO\textsubscript{3} into monoclinic H\textsubscript{0.9}MoO\textsubscript{3}. The Mo 3d XPS spectrum suggested the formation of low-valence Mo species (Mo\textsuperscript{5+}, Mo\textsuperscript{4+}, and Mo\textsuperscript{3+}), and the O 1s XPS spectrum suggested increased number of surface hydroxyl groups after H\textsubscript{2} reduction, confirming the formation of hydrogen-doped molybdenum oxide. Thermogravimetric analysis revealed that oxygen vacancies were introduced as the H\textsubscript{2} reduction temperature increased to 200 °C. After H\textsubscript{2} reduction, the Pt/H\textsubscript{MoO\textsubscript{3-y}} hybrid exhibited strong absorption in the visible to near-infrared spectroscopy (NIR) region with an intense SPR peak at around 556 nm reflecting the increased concentration of free electrons donated by hydrogen atoms, whereas unreduced Pt/MoO\textsubscript{3} only shows absorption below 400 nm. As the H\textsubscript{2} reduction temperature increased, a blue shift of the plasmonic wavelength from 564 to 556 nm and intensification of SPR peak were also observed (Fig. 10(a)).

Pt/H\textsubscript{MoO\textsubscript{3-y}} hybrid exhibited the highest catalytic activity of various catalysts for the deoxygenation of diphenyl sulfoxide under 1 atm H\textsubscript{2} at ambient temperature and pressure, affording diphenyl sulfide in >99 % yield within 7 h of reaction (Fig. 10(b)). Comprehensive analyses using XRD, XPS and electron spin resonance (ESR) revealed that the oxygen vacancies formed during H\textsubscript{2} reduction acted as active centers for deoxygenation of sulfoxide to produce sulfide. The proposed reaction pathway for the deoxygenation of sulfoxide over Pt/H\textsubscript{MoO\textsubscript{3-y}} hybrid involves four steps of H\textsubscript{2} dissociation on Pt NPs, H-spillover to form an oxygen vacancy, adsorption of sulfoxide on the oxygen vacancy, and final deoxygenation to complete the reaction cycle (Fig. 10(c)), in which the massive oxygen vacancies and the reversible redox property of Mo atoms in H\textsubscript{4}MoO\textsubscript{3-4} are important. The catalyst achieved high activity and selectivity for conversion of various sulfoxides to the corresponding sulfides under mild reaction conditions.

Intriguingly, significant improvement of catalytic efficiency was found for Pt/H\textsubscript{MoO\textsubscript{3-y}} hybrid under visible light, with a 2-fold faster reaction rate relative to the dark conditions (Fig. 10(c)). Such plasmonic enhancement of activity was not found for non-plasmonic catalysts of Pt/SiO\textsubscript{2}, Pt/WO\textsubscript{3}, and Pt/MoO\textsubscript{2} under visible light. Furthermore, the wavelength-dependency of the catalytic activity was in good agreement with the
light absorption intensity (Fig. 10(d)), indicating that the activity enhancement is driven by the plasmonic effect of hydrogen molybdenum bronze. This result demonstrated that hydrogen-doped plasmonic molybdenum oxide can be used as a light-harvesting platform in heterogeneous catalysis, which may promote various selective organic transformations under solar irradiation.

4. Conclusion

During the last several years, we have developed heterogeneous catalytic systems based on the LSPR of Au, Ag nanoparticles, combined with research on reduced-type molybdenum oxide ($H_xMoO_3-y$) nanosheets with plasmonic features. Development of plasmonic materials utilizing base elements (not including precious metals) and application to catalysis utilizing light as an energy source are very important for elemental strategy and green chemistry. We synthesized Ag nanoparticles and reduced molybdenum oxide nanosheets which showed strong LSPR under light irradiation at wavelengths ranging from visible to near infrared, and reported that these plasmonic catalysts promoted hydrogen formation from potential hydrogen carrier molecules. Noble metal and base metal plasmonic materials differ in material design and characterization methodology, but also share many common features in the LSPR-induced working mechanism. Several examples of base metal plasmonic catalysts have been reported, such as reduced type tungsten oxide, aluminum metal, hydrogen-doped nickel oxide etc., in addition to reduced molybdenum oxide, but studies are not extensive. We have not yet shown that such base metal plasmonic materials with earth abundant elements truly function as plasmonic materials equivalent to Au and Ag, or whether the working mechanisms are different. Upgrade of inexpensive base metal plasmonic materials into catalyst materials for practical applications requires further research by rigorous investigation of physicochemical properties and photochemical characteristics through multiple approaches to establish the fundamental characteristics of these materials.

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### 要旨

ナノ構造体を活用するプラズモン触媒の設計

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本総説では、局在表面プラズモン共鳴により可視光照射下で機能するナノ粒子やナノシートなどナノ構造制御したプラズモン触媒の設計、および高効率水素生成反応への応用に関して述べる。マイクロ波加熱とメモビラスシリカの細孔構造を利用して、形状・サイズ・色を制御したプラズモンAuAgナノ粒子触媒を合成する。さらに、Pdなどの活性サイトを融合することで、光照射下でのアンモニアボラントからの水素生成応答に高活性を示す。また、金属有機構体（MOF）とプラズモンAuPdコアシェルナノ粒子を融合させた触媒は、可視光照射により酸化からの水素生成反応を促進する。一方で、酸化元素を利用したプラズモン材料の探索においては、構造内の酸素欠損や水素を導入した還元型モリブデン酸化物（H2MoOx)が可視光を照射することで酸素および水素発生を促進する可能性がある。