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High-surface-area plasmonic MoO_{3-x}: rational synthesis and enhanced ammonia borane dehydrogenation activity

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The well-crystallized, high-surface-area plasmonic $MOO_{3\cdot x}$ was synthesized by combining evaporation induced selfassembly (EISA) process and the following hydrogen reduction in certain temperature. The intrinsic anisotropic crystal growth process of tiny MOO_3 nuclei to MOO_3 nanosheets was successfully inhibited. Detailed characterization by means of XRD, TEM, N₂ physisorption, and XPS measurements revealed that the synthesized $MOO_{3\cdot x}$ not only showed a strong localized surface plasmon resonance (LSPR) upon incident light but also had a relatively large specific surface area. The specific surface area (S_{BET}) of $MOO_{3\cdot x}$ post-reduced at 200 °C was 30.0 m²/g, which was 22.7 and 9.1 times higher than those of commercially available MOO_3 and our previously reported $MOO_{3\cdot x}$ nanosheets, respectively. We also demonstrate that such semiconductor with a large surface area could be used as a highly efficient catalyst that dramatically enhance the dehydrogenation activity from ammonia borane (NH₃BH₃; AB) under visible light irradiation.

Introduction

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Localized surface plasmon resonances (LSPRs) typically originate from nanostructures of noble metals leading to enhanced and geometrically tuneable absorption and scattering.¹ The overwhelming majority of research achievements of LSPRs have been focused on noble metals, such as Au and Ag, as they are stable under several conditions, have high charge carrier densities and exhibit apparent LSPRs from the ultraviolet (UV) region to the near infrared (NIR).^{2,3} However, it is difficult to get the desired plasmonic noble metals because plasmonic frequencies of noble metals are extremely relied on their shapes and size.⁴ Moreover, the amount of noble metals on the earth is scare and they usually have high resistive loss, which greatly limits their practical application.⁵ Thus, the exploration of the qualified candidates is a challenging task.

LSPRs are not primarily confined to the noble metals, but happen in conducting metal oxides.^{6,7} Some heavily doped semiconductor nanocrystals with appreciable free carrier densities, including copper chalcogenides, indium tin oxides (ITO), and transition-metal oxides have attracted more and

reported that the high energy of the WO_{2.83} LSPR has high charge carrier density of N = 6.3×10^{21} cm^{-3.2} Our group has already synthesized plasmonic molybdenum oxide nanosheets by a facile non-aqueous procedure without using any surfacecapping agents, which displayed strong LSPR under visible light irradiation.^{3,10} However, heavily doped semiconductor oxides, such as WO_{3-x} and MoO_{3-x}, usually exhibit very small specific surface area, which frequently results in relatively low catalytic activities.^{11,12} Some researchers have already reported importance of increasing in specific surface area of plasmonic transition-metal oxides. Zhao and co-workers successfully prepared highly ordered mesoporous WO₃ with a large surface area by using self-made template (amphiphilic poly (ethylene oxide)-b-polystyrene (PEO-b-PS) diblock copolymers) as a structure-directing agent.^{13,14} However, it is still a challenge to synthesize heavily doped transition-metal oxides with a strong LSPR and large surface area at the same time, especially for MoO_{3-x} .^{11,12,15} Take MoO_3 nanosheets ($S_{BET} = 3.3 \text{ m}^2/\text{g}$) as an example, the intrinsic anisotropic crystal growth tends to result in the preferential formation of 2D MoO₃ nanosheet,¹⁶⁻¹⁸ because the crystal structure plays a crucial role in determining the morphology of the samples and the layered crystal structure of orthorhombic MoO₃ is composed of MoO₆ octahedra by sharing edges and corners.¹⁹ Therefore, it is of great difficulty, but important to exploit the synthetic methodology for fabrication of plsamonic MoO_{3-x} with large specific surface area.

more concern recently.^{8,9} For example, Alivisatos's group

Herein, we report MoO_{3-x} nanostructures with relatively high surface area of 30.0 m²/g and a strong LSPRs in visible

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region by combining evaporation induced self-assembly (EISA) process²⁰⁻³⁰ and the following hydrogen reduction at a certain temperature. In this study, F127 was used as an organic template, which efficiently inhibited intrinsic growth process of tiny MoO₃ nuclei to MoO₃ nanosheets as illustrated in Scheme 1. It was found that the experimental parameters, such as hydrogen reduction temperature, were found to play a crucial role in LSPRs response intensity of MoO_{3-x} from the visible region to the NIR. Eventually, it was further certified that such hydrogen-reduced MoO_{3-x} showed greatly improved activity in the hydrogen (H_2) production from ammonia borane (NH₃BH₃; AB) compared with MoO_{3-x} nanosheets (S_{BET} = 3.3m²/g) and commercial MoO₃ (S_{BET} = 1.3 m²/g), which may provide a new strategy for highly efficient dehydrogenation from hydrogen storage materials. To the best of our knowledge, this should be the first report that definitely improves specific surface area of plasmonic MoO_{3-x}.

Experimental Section

Chemicals

Molybdenum metal powder, hydrogen peroxide (H₂O₂, 30 wt%), nitric acid (HNO₃, 69.2 wt%), acetic acid (CH₃COOH), ethanol, Pluronic F127 (PEO₁₀₆ PPO₇₀PEO₁₀₆, Mw = 12600 g mol⁻¹), were purchased from Nacalai Tesque Inc. Commercial MoO₃ was purchased from Wako Pure Chemical Industries. Ammonia borane (NH₃BH₃) was obtained from Sigma-Aldrich Co. All chemical reagents were used without any further purification.

Catalyst Synthesis

Synthesis of Plasmonic MoO_{3-x}-T

The well-crystallized, high-surface-area MoO_{3-x} was synthesized by EISA process and the following hydrogen reduction at a certain temperature. In a typical synthetic procedure, 2 mmol molybdenum metal powder was added to a flask (100 mL) containing 15 ml ethanol under magnetically stirred. Then 3 mL of H₂O₂ was injected and continued stirring for 30 min to acquire the transparent yellow solution (solution A). Next, 2.0 g of Pluronic F127 was added into 10.0 mL of ethanol at 40 °C to obtain a colorless solution with vigorous stirring. After that, 4.5 mL HNO₃ and 2.4 g CH₃COOH were added to the above solution dropwise (solution B). In the subsequent steps, solution A was added into solution B with vigorous stirring at 40 °C for 2 h to get a transparent yellow solution. This solution was cast in petri dish to form a thin gel layer and then aged at 40 $^{\circ}$ C for 24 h and 100 $^{\circ}$ C for another 24 h. The resulting film was calcined at 400 °C for 4 h in air with a heating rate of 1 °C/min to obtain MoO₃. Finally, hydrogen reduction of MoO_3 was carried out with pure H_2 gas at ambient pressure (1 bar). The products obtained at different reduction temperature (100 $^{\circ}$ C, 200 $^{\circ}$ C, and 300 $^{\circ}$ C) for 1 h with 5 $^{\circ}$ C/min of heating rate were defined as MoO_{3-x}-T (T means the reduction temperature).

Catalyst Characterizations

The X-ray diffraction (XRD) patterns were recorded using a Rigaku Ultima IV diffractometer with Cu k α radiation (λ =

1.5406 Å). Transmission electron microscopy (TEM) images were measured with a Hitachi H-800 electrola34677686666 equipped with an energy dispersive X-ray detector operated at 200 kV. UV-Vis-NIR diffuse reflectance spectra were collected on a Shimadzu UV 2600 recording spectrophotometer equipped with an integrating sphere at room temperature. The reference was BaSO₄ and the absorption spectra were obtained using the Kubelka-Munk function. XPS measurements were carried out using a Shimadzu ESCA 3200 photoelectron spectrometer with Mg k α radiation, and C 1s (284.6 eV) was used to calibrate the peak positions of the elements. Nitrogen adsorption measurements (BET) were performed using BEL SORP-max system (MicrotracBEL Corp.) at -196 °C. Samples were degassed under vacuum at 200 °C for 24 h prior to data collection. Thermogravimetric (TG) analysis was acquired on a Bruker TG-DTA2010SA system from room temperature to 800 °C at a heating rate of 10 °C/min under air flow.

Catalytic Activity Measurements

The catalytic performances of the molybdenum oxide nanostructures were measured by dehydrogenation of NH₃BH₃ in aqueous suspensions at room temperature (25 °C). Typically, MoO_{3-x}-T sample (20 mg) was suspended in 5 mL distilled water in a test tube. 200 µL of NH₃BH₃ (0.1 M, 20 µmol) solution was injected into the above solution through a rubber septum after bubbling with Argon gas for 30 min. The reaction was conducted with magnetically stirred in the dark condition and under visible light irradiation ($\lambda > 420$ nm) with cutoff filter. The amount of H₂ in gas phase was determined by a Shimadzu GC-8A gas chromatograph with MS-5A column by TCD detector.

Results and discussion

Route 1 and Route 2 in Scheme 1 show the designed synthetic routes of our previously reported MoO_{3-x} nanosheets and MoO_{3-x}-T developed in this study, respectively. Firstly, pure Mo powder was added to the ethanol solution containing 3 mL of H₂O₂ (30 wt%). The Mo powder was dissolved and present as a transparent yellow solution after magnetic stirring for 30 min. In this process, the solution-soluble precursor compound MoO₂(OH)(OOH) could form easily.^{31,32} In the subsequent growth stage, tiny MoO₃ nuclei was generated by dehydration of the dissolved yellow Mo-complex. The crystal structure plays a very important role in determining the morphology of the sample.17-19



Scheme 1. Schematic illustration for the plausible formation process of $MoO_{3,x}$ nanosheets (Route 1) and high-surface-area MoO_{3-x}-T (Route 2).



Figure 1. (a) Wide-angle XRD patterns of MOO_{3-x} -T samples hydrogen-treated at different temperatures and commercial MOO_3 . (b) Magnified XRD patterns of assynthesized MOO_3 and MOO_{3-x} -200 °C corresponding to the diffraction peaks of (040), (060), and (002) in Figure 1a.

Table 1. Lattice constants calculated by XRD d	ata
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Sample	Interplane distance (Å)			Lattice	e consta	nts (Å)
	d ₍₀₆₀₎	d ₍₀₀₂₎	d ₍₂₀₀₎	а	b	С
as-synthesized MoO ₃	2.32	1.84	1.98	3.96	13.9	3.69
MoO _{3-x} -200 °C	2.33	1.86	1.99	3.97	14.0	3.72

Because of the layered crystal structure of orthorhombic MoO_3 composed of MoO_6 octahedra by sharing edges and corners, the intrinsic anisotropic crystal growth led to the preferential formation of 2 D MoO_{3-x} nanosheets with very small specific area under solvothermal treatments at a certain temperature (Route 1).^{2,3} In order to prevent the unfavorable Route 1 and increase surface area of plasmonic MoO_{3-x} , we designed the Route 2. It is widely accepted that surfactants can efficiently control the crystal growth rate and crystal habit of a variety of materials.^{20,21} F127 was used as a surfactant to control growth process of MoO_3 nuclei to modify the final size of MoO_{3-x} during EISA process. Possible process is as follow,

polyether polyol chemical structure of F127 might effectively bind with dissolved Mo complex or MoO_3^{-1} were first by reducing the interaction between nucleus and then efficiently inhibiting the crystal growth of MoO_{3-x} (Route 2).²¹⁻²³

According to TG/DTA analysis of (Figure S1b), the mass of F127 decreases to 0 wt% from 100 wt% after temperature increased to 400 °C. So surfactant was completely removed by calcination at 400 °C for 4 h. As shown in Figure S1a, the mass of MoO_{3-x} -200 °C doesn't have any change with the increasing of temperature (from 0 °C to 700 °C), which means that catalyst is successfully prepared without any impurity.

XRD patterns of commercial MoO₃, as-synthesized MoO₃, MoO_{3-x}-100 °C and MoO_{3-x}-200 °C are shown in Figure 1a, which clearly show that all samples consist of orthorhombic MoO₃ phase (JCPDS NO.5-0508). The three-dimensional structure framework of MoO_{3-x} -T (100 °C and 200 °C) was retained to a large extent in MoO₃, which demonstrates that hydrogen reduction did not destroy the pristine crystal structure. When hydrogen reduction is performed at 300 °C, the intensity of some characteristic peaks of MoO₃ was significantly weakened, which is presumably because orthorhombic phase of MoO_{3-x} has been transformed into amorphous MoO2.5 Figure 1b is the magnified patterns corresponding to the diffraction peaks of (040), (060), and (002) in Figure 1(a), respectively. Careful comparison between two patterns indicates that the 20 values decrease to a certain degree from as-synthesized MoO₃ to MoO_{3-x}-200 $^{\circ}$ C. According to Bragg Formula 2 dsin θ = λ , the smaller 2 θ value means larger interplane distance (d value).³³ Therefore, MoO_{3-x}-200 °C shows larger distance (d values) between crystalline planes of (004), (060), and (002) compared with as-synthesized MoO₃, indicating that the lattice unit expands after hydrogen atom are inserted into MoO₃, as reflected on the calculated lattice constants that are listed in Table 1.

As shown in Figure S2a, N₂ adsorption-desorption isotherms did not apparently show type IV isotherms according to the IUPAC classification, which is closely related to the capillary condensation taking place in mesoporous solids. Meanwhile, Figure S2b shows the corresponding pore size distribution curves, which is calculated from the BJH method by using the adsorption branches. As shown in Figure S2b, the pore size of as-synthesized MoO₃ and MoO_{3-x}-T (100 °C, 200 °C, and 300 °C) is about 2.18 nm, 2.13 nm, 2.18 nm, and 2.13 nm, respectively, which fall within the scope of mesoporous. Structural parameters containing specific surface area (S_{BET}), pore diameter (d), pore volume, are shown in Table 2. Specific surface area and pore diameter of as-synthesized MoO₃ and MoO_{3-x}-T display similar volumes, indicating that sample structures were not destroyed after hydrogen reduction process. The specific surface areas of as-synthesized MoO₃ and MoO_{3-x}-T are larger than commercial MoO₃ and MoO_{3-x} nanosheets in Figure S2c (Route 1), and the resulted SBET is much higher than those of reported work.^{3,5,7,8,16, 32,33}

TEM images of hydrogen-treated MOO_{3-x} -T samples at different temperatures are shown in Figure 2. MOO_{3-x} synthesized via Route 1 is composed of smooth 2D nanosheets (Figure 2a), which was deemed to be related to the intrinsic growth of MOO_3 nuclei because of its layered crystal structure.^{31,32} As shown in Figure 2b-e, as-synthesized MOO_3 and MOO_{3-x} -T synthesized via Route 2 are also made up of nanosheets, but the nanosheets size of these samples is much smaller than that of our previously reported plasmonic MOO_{3-x}

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nanosheets in Figure 2a. This should be the main reason for increasing the specific surface area of as-synthesized MoO_3 and MoO_{3-x} , which is consistent with Route 2 of Scheme 1. Meantime, it is clearly found that the surface of as-synthesized MoO_3 and MoO_{3-x} -T (red circle in Figure 2b-e) become more rough than the smooth surface of MoO_{3-x} nanosheets (white circle in Figure 2a), which is also beneficial to improve surface area.

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Table 2. Structural parameters of commercial MoO_{3} , as-synthesized MoO_3 and MoO_{3-x^-} T samples hydrogen-treated at different temperatures.

Samples	Specific surface area (m²/g)	Pore diameter (nm)	Pore volume (cm ³ /g)
Commercial	1.32	-	0.002
MoO ₃			
as-synthesized	25.1	2.18	0.040
MoO ₃			
MoO _{3-x} -100 °C	27.7	2.13	0.065
MoO _{3-x} -200 °C	30.0	2.18	0.067
MoO _{3-x} -300 °C	27.4	2.13	0.066



Figure 2. TEM images of different samples: (a) $MoO_{3\star}$ nanosheets, (b) as-synthesized MoO_3 , (c) $MoO_{3\star}$ -100 °C, (d) $MoO_{3\star}$ -200 °C, (e) $MoO_{3\star}$ -300 °C.



Figure 3. UV/Vis-NIR diffuse reflectance spectra of different samples. (a) Commercial $MoO_{3,v}$ (b) as-synthesized $MoO_{3,v}$ -100 °C, (d) $MoO_{3,v}$ -200 °C, and (e) $MoO_{3,v}$ -300 °C.



Figure 4. Mo 3d XPS spectra of commercial MoO₃, as-synthesized MoO₃ and MoO_{3-x}-T samples.

Table 3. Mo chemical state of different samples determined by XPS data.						
Samples	Mo ⁶⁺	Mo ⁵⁺	Mo ⁴⁺	Mo average state		
Commercial MoO ₃	100%	0%	0%	6.00		
as-synthesized	97.3%	2.70%	0%	5.97		
MoO ₃						
MoO _{3-x} -100 °C	93.1%	6.90%	0%	5.93		
MoO _{3-x} -200 °C	90.5%	9.50%	0%	5.91		
MoO _{3-x} -300 °C	92.5%	0%	7.5%	5.85		

Figure 3 shows the UV/Vis-NIR spectra of commercial MoO₃, as-synthesized MoO₃ and MoO_{3-x}-T. Three strong absorption peaks located at approximately 623 nm, 756 nm, and 920 nm connected with LSPRs are clearly observed in the spectra of MoO_{3-x}-T (T = 300 °C, 200 °C, and 100 °C). With the decrease of reduction temperature, plasmonic wavelength of MoO_{3-x}-T shifts to longer wavelength due to the decrease of free electrons concentration.⁵ As-synthesized MoO₃ shows a weak absorption peak at 953 nm associated with the reduction ability of polyhydric alcohols structure of F127 or ethanol during the preparation process. On the contrary, commercial MoO₃ doesn't exhibit any absorption peak in visible light range and only show a peak in UV-light range with the absorption edge at about 400 nm, which corresponds to its wide band gap (ca. 3.1 eV).

In order to investigate the chemical state of Mo in the plasmonic MoO_{3-x} -T, X-ray photoelectron spectroscopy (XPS) measurement were implemented. Mo 3d XPS core spectra of commercial MoO_3 , as-synthesized MoO_3 and MoO_{3-x} -T are displayed in the Figure 4. For the commercial MoO_3 , only Mo^{6+} is detected and two peaks (236.15 and 233.05 eV) are assigned to the $3d_{3/2}$ and $3d_{5/2}$ of Mo^{6+} , respectively. On the contrary, the binding energies of as-synthesized MoO_3 and MoO_{3-x} -T shift to the lower energy position with the increase of

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reduction temperature compared with commercial MoO₃. According to Table 3, Mo⁵⁺ cation ratio increases gradually in the as-synthesized MoO₃, MoO_{3-x}-100 °C and MoO_{3-x}-200 °C, and the average Mo oxidation states of as-synthesized MoO₃, MoO_{3-x}-100 °C and MoO_{3-x}-200 °C are determined to be 5.97, 5.93 and 5.91, respectively. Mo⁴⁺ state emerges for only MoO_{3-x}-300 °C because of phase transformation at 300 °C, which is consistent with XRD spectra.^{3,5}

Ammonia-borane (NH_3BH_3 ; AB) has emerged as a candidate of hydrogen storage materials because of its low molecular weight (30.87 g mol⁻¹), nontoxicity, high stability in solid form under ambient conditions and higher theoretical hydrogen gravimetric capacity (19.6 wt%). The hydrolysis of AB can be attained under mild reaction condition with suitable catalysts, as illustrated in Equation 1.

$$NH_{3}BH_{3} + 2 H_{2}O \xrightarrow{Catalyst} NH_{4}^{+} + BO_{2}^{-} + 3H_{2}$$
(1)

Recently, many noble metal nanostructures, such as Pd, Au, Ru and Rh, have been already demonstrated to exhibit high activity for dehydrogenation of AB solutions.34-36 Considering application, we firstly investigated the practical dehydrogenation activities of samples in the dark condition. As shown in Figure 5a, it is easy to obtain H₂ over as-synthesized MoO_3 and MoO_{3-x} -T (100 °C, 200 °C). Initial reaction rates of as-synthesized MoO_3 and $MoO_{3\text{-}x}\text{-}T$ (100 $^{\circ}\text{C}\text{,}$ 200 $^{\circ}\text{C}\text{)}$ with relatively large surface area was 1.70, 2.11 and 2.21 $\mu mol/min,$ respectively. This was much faster than the rate of commercial MoO₃ (0.440 µmol/min).

Almost 45.8, 57.5, and 65.6 mol% conversion of AB was obtained by MoO₃ and MoO_{3-x}-T (100 °C, 200 1C) after reaction for 60 min. The highest H₂ production activity is due to the largest surface area and relatively strong LSPRs. In contrary, only 30.5 mol% conversion of AB was yielded by commercial MoO₃. Interestingly, when the dehydrogenation reaction was carried out under visible light irradiation (Figure 5b), productive rate of hydrogen was dramatically improved. MoO_{3-v}-200 °C could give 64.7 mol% conversion of AB in the first 10 min, whose initial reaction rate (3.88 µmol/min) was 4.21 times higher that of commercial MoO_3 (0.92 μ mol/min). After reaction for 60 min, MoO_{3-x}-100 °C and MoO_{3-x}-200 °C each obtained almost 92.9, 100 mol% conversion of AB, which were also much higher than commercial MoO₃. For assynthesized MoO₃ and commercial MoO₃ sample, they could response slightly to visible light due to in situ partial reduction of MoO₃ by H₂ produced from AB. Comparing commercial MoO_3 (S_{BET} = 1.32 m²/g) with MoO_{3-x} -T (100 °C, 200 °C), having a strong LSPRs and a large specific surface area were beneficial to product hydrogen from AB. The larger surface area of MoO₃₋ -T (100 °C, 200 °C) usually means the more oxygen vacancy, which is beneficial to increase the dehydrogenation performance of AB. Despite of its strong LSPR peak in the visible range and a relatively large surface area, MoO_{3-x}-300 °C did not show good hydrogen production activity both in the dark and under visible light irradiation because of phase transition from MoO_{3-x} to amorphous MoO_2 at around 300 °C.





Figure 5. Time course of H₂ evolution from AB at room temperature for different samples: (a) in dark and (b) under visible light irradiation ($\lambda > 420$ nm). 100 mol% conversion of 200 μ L of NH₃BH₃ (0.1 M, 20 μ mol) could generate 60 μ mol of hydrogen.

Figure 6. (a) The comparison of H₂ evolution from NH₃BH₃ aqueous solution at room temperature over MoO_{3-x}-200 °C sample under different visible light irradiation (λ > 420 nm and λ > 450 nm) using Y45 cutoff filter (AGC Asahi Glass Co., Ltd., Japan). (b) Wavelength-dependent initial H₂ yield rate enhancement of MoO_{3-x}-200 °C samples upon irradiation by LED light. (blue light λ = 470 nm, 33.3 mW cm⁻², green light λ = 530 nm, 17.0 mW cm⁻², red light λ = 650 nm, 23.5 mW cm⁻²).

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Scheme 2. Proposed reaction mechanism of hydrolysis of aqueous AB solution over plasmonic MoO_{3-x}-T under visible light.



Figure 7. (a) The five recycling experiments for NH₃BH₃ dehydrogenation under visible light irradiation. (b) XRD patterns, (c) UV-Vis-NIR diffuse reflectance spectra and (d) N₂ adsorption-desorption isotherms of fresh prepared and reused MoO_{3-x}-200 °C samples after the recycling NH₃BH₃ dehydrogenation experiments.

Our previously reported MOO_{3-x} nanosheets have more Mo^{5+} cations (22.7% of the total Mo) and a lower absorption peak position (680 nm associated with LSPR)³ in comparison with the MOO_{3-x} -200 °C developed in this study (9.5% of Mo^{5+} and absorption peak position at 756 nm). Nevertheless, the MoO_{3-x} -200 °C (100 mol% conversion of AB at 60 min) exhibited a higher dehydrogenation activity than the conventional MOO_{3-x} nanosheets (75.4 mol% conversion under the identical conditions) owing to its high surface area.

In order to exclude the possible effect of band-gap excitation on the photocatalytic activity of MoO_{3-x}-T, dehydrogenation experiment of AB was carried out under visible-light irradiation with a longer wavelength ($\lambda > 450$ nm) (Figure 6a). Compared to activity under the irradiation with $\lambda >$ 420 nm (60.0 μ mol), 53.7 μ mol of H₂ was yielded for MoO_{3-x}-200 °C under the irradiation with λ > 450 nm, indicating that the contribution by LSPR is greater than that given by bandgap excitation. By using LED lamp (λ = 470, 530, and 650 nm), the wavelength-dependence for H₂ production enhancement was also surveyed (Figure 6b). The enhancement of dehydrogenation rate was in line with the light absorption of MoO_{3-x}-200 °C, indicating that the enhancement of reaction activity can be attributed to the LSPRs effect of MoO_{3-x} -200 $^{\circ}C.^{37}$ Red LED light irradiation (λ = 650 nm) was achieved the maximum performance and its initial H₂ production rate (2.91

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μmol/min) was 1.32 times higher than that in the dark condition.

NaHCO₃ (as a positive charge scavenger), 2-propanol (as hydroxyl radicals (.OH) scavengers), NaNO₃ and Na₂S₂O₈ (as negative charge scavengers) were added to the suspension of MoO_{3-x}-200 °C sample in the dark and under visible light irradiation condition for dehydrogenation of NH₃BH₃ to investigate whether H₂ production was connected with the strong light-harvesting property of $MoO_{2,v}$ -200 °C induced by LSPR. As shown in Figure S3, catalytic activity was dramatically decreased in the dark and under visible light in the presence of NaHCO₃ and 2-propanol. MoO_{3-x}-200 $^{\circ}$ C could be excited by visible light irradiation and generate electron-hole, and then HCO_3^{-} and 2-proponol can easily react with a positive charge and .OH, respectively. So the catalytic performance of samples was greatly retarded under visible light condition. However, catalytic activity has only decreased marginally (7.30 µmol or 10.0 µmol) after adding NaNO₃ or Na₂S₂O₈ under visible light condition, which means only a small of electrons participate in dehydrogenation reaction of AB. The reasons for the nonstoichiometric ratio of the dehydrogenation activity of AB after adding NaHCO₃, NaNO₃ and Na₂S₂O₈ or what kinds of roles the electrons play are not clear at present. Additional studies on the detailed mechanism of dehydrogenation of AB with MoO_{3-x}-T and our previously reported MoO_{3-x} nanosheets are underway in this laboratory.

It has been reported that a plausible mechanism for catalytic dehydrogenation reaction of AB involves the following three steps: (1) an activated complex species forms between the metal particle surface and AB, (2) the B-N bond is dissociated after attack by a H₂O molecule, and (3) the resulting BH₃ intermediate hydrolyzes to produce H₂ along with the formation of a BO_2^{-1} ion.³⁸⁻³⁹ According to above study, we point out the possible dehydrogenation mechanism of AB molecules (Scheme 2). Firstly, MoO_{3-x}-T effectively adsorbs of AB molecule because of its large surface area to form MoO_{3-x}-T-AB complex species. Then, plasmonic MoO_{3-x}-T can be excited due to the strong LSPRs under visible light irradiation and generate electron-hole pairs. Meanwhile, a new band below the bottom of the original conduction band may be formed due to the presence of defective sites (Mo⁵⁺ center and oxygen vacancies), which decreases recombination of the photogenerated electrons and holes.⁷ From the difference of catalytic activity after adding NaHCO₃ (2.49 µmol of H₂) and 2propanol (22.35 µmol of H₂) (as shown in Figure S3), Holes as main active species can react with absorbed AB directly, on the other hand, holes can also react with the absorbed H₂O to generate hydroxyl radicals (OH), which will further interact with absorbed AB. Meanwhile, a small amount of electrons might gather on the surface of catalyst and react with dissolved oxygen molecules to produce the superoxide anions (O_2) (secondary-reaction).⁴⁰ Subsequently, not only H₂O molecule but also photogenerated OH and O2 attack the MoO_{3-x}-T-AB complex species to dissociate the B-N bond. Finally, the formed BH₃ will hydrolyze to generate H₂ and form a BO_2^{-1} ion.

The catalytic stability of MoO_{3-x} -200 °C was also inspected by repeated use. MoO_{3-x} -200 °C still showed a similar catalytic activity over five repeated cycle (Figure 7a). Furthermore, the structure, optical stability and surface adsorption capacity of MoO_{3-x} -200 °C was further ascertained by XRD spectra, UV/Vis-NIR diffuse spectra and N₂ adsorption-desorption isotherms

(Figure 7(b-d)) even after recycling experiment, which means high potential application prospect of plasmonic MoO_{3-x} -T with efficient and stable property.

Conclusions

In summary, plasmonic MOO_{3-x} -T was successfully obtained by EISA approach and the following hydrogen reduction in certain temperature. The prepared MOO_{3-x} with high specific surface area exhibits strong LSPR in the visible region, which can be tuned by varying the experimental parameter. Under visible light irradiation, such plasmonic MOO_{3-x} -T showed higher H₂ evolution from NH₃BH₃ solutions compared with the MOO_{3-x} nanosheet catalyst obtained by the conventional approach because of larger specific surface area. A relatively high NH₃BH₃ dehydrogenation activity was achieved under visible light irradiation, which exceeded the MOO_{3-x} nanosheet catalyst. This study offers a promising strategy in exploring stable and efficient plasmonic semiconductor photocatalysts with a large surface area for saving hydrogen evolution problems of new energy resources and energy carriers.

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Graphical abstract



Plasmonic MoO_{3-x} with high surface area efficiently enhances ammonia borane dehydrogenation activity.