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Article

Tunable localized surface plasmon resonances in $\text{MoO}_{3-x}\text{-TiO}_2$ nanocomposites with enhanced catalytic activity for CO_2 photoreduction under visible light

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ABSTRACT

The photocatalytic reduction of CO_2 with H_2O to fuels and chemicals using solar energy is one of the most attractive but highly difficult routes. Thus far, only a very limited number of photocatalysts has been reported to be capable of catalyzing the photocatalytic reduction of CO_2 under visible light. The utilization of the localized surface plasmon resonance (LSPR) phenomenon is an attractive strategy for developing visible-light photocatalysts. Herein, we have succeeded in synthesizing plasmonic $\text{MoO}_{3-x}\text{-TiO}_2$ nanocomposites with tunable LSPR by a simple solvothermal method. The well-structured nanocomposite containing two-dimensional (2D) molybdenum oxide (MoO_{3-x}) nanosheets and one-dimensional (1D) titanium oxide nanotubes ($\text{TiO}_2\text{-NT}$) showed LSPR absorption band in the visible-light region, and the incorporation of $\text{TiO}_2\text{-NT}$ significantly enhanced the LSPR absorption band. The $\text{MoO}_{3-x}\text{-TiO}_2\text{-NT}$ nanocomposite is promising for application in the photocatalytic reduction of CO_2 with H_2O under visible light irradiation.

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1. Introduction

With the rapid development of human society, the growing emission of CO_2 and the decline of fossil resources have stimulated research activities toward the production of fuels and chemicals from the utilization of CO_2 as a carbon source [1]. Among various CO_2 utilization options, the photocatalytic reduction of CO_2 with H_2O is one of the most attractive but highly difficult routes [2–9]. The efficiency of photocatalysis is determined by the light absorption efficiency of the catalyst, the separation efficiency of the photogenerated charges and the

reaction rate on the catalyst surface. The co-catalysts which can significantly promote the charges separation and surface reaction have been intensively investigated [10–14]. So far, only very limited photocatalysts have been reported to be capable of catalyzing the photocatalytic reduction of CO_2 under visible light [2–14]. Typical visible-light responsive semiconductors such as BiVO_4 or CdS either cannot work for CO_2 reduction due to the energy-band position or are not stable enough. UV light only take up 3% in the solar spectrum, while the visible light take up 44% [15]. Therefore, it is highly meaningful to develop a visible-light responsive catalyst to improve the utilization of

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solar energy, and build a highly efficient catalyst for CO₂ reduction.

The localized surface plasmon resonance (LSPR) is a near-field enhancement phenomenon, which is capable of harvesting light at the nanoscale with maximum optical absorption [16–24]. The utilization of the LSPR phenomenon is an attractive strategy to develop photocatalysts that can absorb visible light. The LSPR phenomenon of noble metals, such as Au, Ag, Pt, have been widely studied [16–21]. Despite the easy manipulation of LSPR, noble metals inevitably suffer from high cost, which prevents them from being used in large scale practical applications [16–21]. Besides noble metals that can cause the LSPR, several low cost transition metal oxides with lower-valent self-dopants such as MoO_{3-x} and WO_{3-x} can also show LSPR phenomenon, represent another class of important candidates to harvest visible light for photocatalysis [22–24].

Molybdenum oxide (MoO₃) is a low cost, nontoxic and environmentally benign transition metal oxide. As an n-type semiconducting material with the wide bandgap (~3.1 eV) renders MoO₃ only responsive to UV light [23]. As compared with stoichiometric MoO₃, the heavily lower-valent self-doped non-stoichiometric counterparts (MoO_{3-x}) have recently been revealed to display LSPR absorption in a wide spectral range [22–24]. Moreover, the plasmonic frequency is highly dependent on the shape and dopant concentration, as well as the surrounding medium [22–24]. The LSPR absorption region of MoO_{3-x} can adjust from visible-light to near-infrared (NIR) [22–24]. Through such LSPR absorption, it offers the resource of light, heat, and energetic electrons, which has manifested great prospects in efficient conversion of solar energy to trigger chemical reactions. Hence, the MoO_{3-x} has been used as photocatalyst for hydrogen evolution reaction [25–28], photothermal [29–31] and sensing materials [32,33]. In photocatalysis, single-component materials are usually could not meet the requirement due to their intrinsic features of weak light absorption or low catalytic efficiency. In contrast, the nanocomposites which integrate different components with diverse properties and exhibit synergistic effects [22,24]. For example, Au/TiO₂ showed outstanding plasmonic photocatalytic performance than Au [22,24]. Therefore, albeit with many challenges, it is intriguing and meaningful to develop facile approaches to prepare plasmonic MoO_{3-x}-based nanocomposites, which could be endowed with improved visible light harvesting and enhanced photocatalytic performances. To the best of our knowledge, there is no systematic study concerning photocatalytic reduction of CO₂ using plasmonic MoO_{3-x}-based nanocomposites photocatalyst.

Herein, we illustrate a facile access to synthesis plasmonic MoO_{3-x} and TiO₂ nanocomposites with tunable LSPR absorption in the visible-light region. The TiO₂ species in MoO_{3-x}-TiO₂ nanocomposites was found to play important roles in their optical response and the oxidation states of MoO_{3-x}. We further demonstrated that, comparing with MoO_{3-x} nanosheets, the MoO_{3-x}-TiO₂ nanocomposites displayed improved visible light harvesting and enhanced photocatalytic performances for CO₂ reduction under visible light. The present paper may open up a new prospective possibility for the design of plasmonic photo-

catalysts capable of photocatalytic reduction of CO₂ under visible light.

2. Experimental

2.1. Material synthesis

The synthesis of TiO₂-NT was performed according to the previously reported method [34,35]. In the preparation process, 0.2 g TiO₂-NP (Degussa P25) was added into 60 mL NaOH aqueous solution (10 mol/L) in a hydrothermal autoclave and kept at 200 °C for 48 h. The precipitate was filtered off, washed with distilled water until pH = 7, and finally dried at 400 °C for 4 h. MoO_{3-x} nanosheets and MoO_{3-x}-TiO₂ nanocomposites were prepared by solvothermal method. For the preparation of MoO_{3-x} nanosheets, 0.19 g (2 mmol) of Mo metal powder was added into 60 mL of ethanol, then 3.0 mL of hydrogen peroxide (H₂O₂, 30%) was introduced and magnetically stirred for about 1 h to obtain Mo complex precursor. The precursor was heated and maintained at 160 °C for 6 h. The precipitate was collected by centrifugation, rinsed with ethanol for 3 times and finally dried at vacuum. For the preparation of MoO_{3-x}-TiO₂ nanocomposites, 0.048 g (0.6 mmol) TiO₂ powder (TiO₂-NT or TiO₂-NP) was added into the above Mo complex precursor before solvothermal treatment, then the same solvothermal conditions and precipitate treating processes were used. The Mo/Ti molar ratio was 10/3 in the MoO_{3-x}-TiO₂ nanocomposites. MoO₃ was prepared by calcinating MoO_{3-x} nanosheets in air at 500 °C for 4 h.

2.2. Catalyst characterization

Transmission electron microscopy (TEM) and High resolution TEM (HRTEM) measurements were performed on a Philips Analytical FEI Tecnai 20 electron microscopy and were operated at an acceleration voltage of 200 kV. Atomic force microscopy AFM was performed with an Agilent 5500 ILM. X-ray diffraction (XRD) patterns were recorded on a Panalytical X'pert Pro diffractometer using Cu K_α radiation (40 kV, 30 mA). Diffuse reflectance UV-vis spectroscopic measurements were performed on Varian-Cary 5000 spectrophotometer equipped with a diffuse reflectance accessory. Electron spin resonance (ESR) spectroscopic measurements were performed at room temperature using a Bruker EMX-10/12 ESR spectrometer operated at X-band frequency. The parameters for ESR measurements were as follows: microwave frequency 9.8 GZ, microwave power 20 mW, modulation frequency 100 kHz, attenuator 10 dB. The XPS measurements were performed on a Quantum 2000 Scanning ESCA Microprobe (Physical Electronics) using Al K_α radiation (1846.6 eV) as the X-ray source.

2.3. Photocatalytic reaction

Photocatalytic reactions were carried out in a stainless-steel reactor (volume, 100 cm³) with a quartz window on the top of the reactor. The reactor design was reported in our previous paper [13]. The light source was a 300 W Xe lamp with a UV

Scheme 1. Schematic illustration for the fabrication of $\text{MoO}_{3-x}\text{-TiO}_2\text{-NT}$ nanocomposite.

cut-off filter ($\lambda = 420\text{--}780\text{ nm}$). The light intensity was 500 mW cm^{-2} . The photocatalytic reaction was performed in a gas-solid heterogeneous reaction mode. The powdery photocatalyst (10 mg) was placed on a glass catalyst holder in the upper region of the reactor. Distilled water with a volume of 4.0 cm^3 was pre-charged in the bottom of the reactor. The pressure of CO_2 was typically regulated at 0.2 MPa . The temperature of the reactor was kept at $50\text{ }^\circ\text{C}$. The reaction system was connected to an on-line gas chromatograph (GC) through valves. The products (CO , CH_4 , H_2) were analyzed by an Agilent Micro GC3000 (Micro GC) equipped with a Molecular Sieve 5A column and a high-sensitivity thermal conductivity detector (TCD). Liquid products such as CH_3OH , HCHO and HCOOH possibly formed and dissolved in water were also analyzed carefully by gas chromatography or high-performance liquid chromatography, but no such products were detected under our reaction conditions.

3. Results and discussion

In the present work, the MoO_{3-x} nanosheets and TiO_2 nanotubes nanocomposite ($\text{MoO}_{3-x}\text{-TiO}_2\text{-NT}$) was synthesized by a facile solvothermal method, which showed strong LSPR absorption in the visible-light region (Scheme 1). Firstly, pure Mo metal powder was added into an ethanol solution containing of

H_2O_2 . The Mo powder was dissolved by the oxidation of H_2O_2 and a transparent yellow solution was obtained. In this synthetic process, the solution-soluble precursor Mo complex compound $\text{MoO}_2(\text{OH})(\text{OOH})$ was formed easily [25,28]. The TiO_2 nanotubes ($\text{TiO}_2\text{-NT}$) was synthesized by a hydrothermal method, in which TiO_2 nanoparticles ($\text{TiO}_2\text{-NP}$) was treated chemically with NaOH aqueous solution for 48 h at $200\text{ }^\circ\text{C}$ (Scheme 1) [34,35]. Then, the obtained $\text{TiO}_2\text{-NT}$ was added into the above Mo complex precursor, and treated for 6 h at $160\text{ }^\circ\text{C}$ in a solvothermal condition to form the $\text{MoO}_{3-x}\text{-TiO}_2\text{-NT}$ nanocomposite (Scheme 1). Additionally, the $\text{MoO}_{3-x}\text{-TiO}_2\text{-NP}$ nanocomposite was also synthesized with the same method by replaced the $\text{TiO}_2\text{-NT}$ with $\text{TiO}_2\text{-NP}$. The pure MoO_{3-x} nanosheets was synthesized with similar method without adding of $\text{TiO}_2\text{-NT}$.

TEM and AFM images revealed that the obtained nanostructures of MoO_{3-x} showed sheet-like morphology with diameters from hundreds of nanometers to several micrometers (Fig. 1(a),(b)). The average thickness of these nanosheets was measured to be about 4.3 nm by AFM, corresponding to 3 fundamental MoO_6 octahedra double layers (Fig. 1(c)) [30,32]. The mean diameter of $\text{TiO}_2\text{-NT}$ was $\sim 8\text{ nm}$, and the length was about $100\text{--}200\text{ nm}$ (Fig. 1d). In the $\text{MoO}_{3-x}\text{-TiO}_2\text{-NT}$ nanocomposite, MoO_{3-x} maintained the nanosheet morphology and $\text{TiO}_2\text{-NT}$ is well dispersed on the MoO_{3-x} nanosheets, the 2D MoO_{3-x} nanosheets contacted well with 1D TiO_2 nanotubes (Fig. 1(e),(f)). For comparison, $\text{TiO}_2\text{-NP}$ with a diameter of $20\text{--}40\text{ nm}$ was also combined with MoO_{3-x} nanosheets to form the $\text{MoO}_{3-x}\text{-TiO}_2\text{-NP}$ nanocomposite (Fig. 1(g),(h)). From the XRD pattern (Fig. S1), no obvious phase structure changes were found between the MoO_{3-x} and $\text{MoO}_{3-x}\text{-TiO}_2$ nanocomposites.

Fig. 2 shows the diffuse reflectance UV-visible spectra of the as-prepared MoO_3 , MoO_{3-x} , $\text{MoO}_{3-x}\text{-TiO}_2\text{-NP}$ and $\text{MoO}_{3-x}\text{-TiO}_2\text{-NT}$. All samples have signal responses in the UV region ($200\text{--}400\text{ nm}$), which is determined by the bandgap of

Fig. 1. (a) TEM image of MoO_{3-x} ; (b) AFM image of MoO_{3-x} ; (c) The AFM-measured height profile of MoO_{3-x} for lines in b; (d) TEM image of $\text{TiO}_2\text{-NT}$; (e) TEM image of $\text{MoO}_{3-x}\text{-TiO}_2\text{-NT}$; (f) HRTEM image of $\text{MoO}_{3-x}\text{-TiO}_2\text{-NT}$; (g) TEM image of $\text{MoO}_{3-x}\text{-TiO}_2\text{-NP}$; (h) HRTEM image of $\text{MoO}_{3-x}\text{-TiO}_2\text{-NP}$.

Fig. 2. Diffuse reflectance UV-vis spectra of MoO_3 , MoO_{3-x} , $\text{MoO}_{3-x}\text{-TiO}_2\text{-NP}$ and $\text{MoO}_{3-x}\text{-TiO}_2\text{-NT}$.

MoO_3 (~ 3.1 eV). The MoO_{3-x} nanosheets displays a broad absorption over the entire visible wavelength range and its absorption peak is located at approximately 752 nm, showing a dramatic difference compared with that of MoO_3 . The strong absorption peak is associated with the LSPR effect. Moreover, the $\text{MoO}_{3-x}\text{-TiO}_2\text{-NP}$ and $\text{MoO}_{3-x}\text{-TiO}_2\text{-NT}$ nanocomposites display stronger optical response in the visible region than MoO_{3-x} , with a prominent LSPR absorption peak at approximately 710 and 670 nm, respectively. The dramatic difference lies in their optical response indicates that we succeeded in adjusting the LSPR absorption of the MoO_{3-x} by controlling the TiO_2 species in $\text{MoO}_{3-x}\text{-TiO}_2$ nanocomposites.

In order to investigate the reason for the change of optical response, ESR and X-ray photoelectron spectroscopy (XPS) characterizations were conducted to probe the difference in molybdenum oxidation states between plasmonic MoO_{3-x} nanosheets and $\text{MoO}_{3-x}\text{-TiO}_2$ nanocomposites. As seen in Fig. 3, the MoO_{3-x} nanosheets and $\text{MoO}_{3-x}\text{-TiO}_2$ nanocomposites show

Fig. 3. ESR analysis of MoO_3 , MoO_{3-x} , $\text{MoO}_{3-x}\text{-TiO}_2\text{-NP}$ and $\text{MoO}_{3-x}\text{-TiO}_2\text{-NT}$.

strong ESR signal at $g = 1.93$ and $g = 2.00$, which is a direct evidence for the existence of a single electron bringing from Mo^{5+} and oxygen vacancies in MoO_{3-x} , respectively [29,36]. No signal was observed for the MoO_3 sample. The signal intensity of Mo^{5+} increased in the following sequence: $\text{MoO}_3 < \text{MoO}_{3-x} < \text{MoO}_{3-x}\text{-TiO}_2\text{-NP} < \text{MoO}_{3-x}\text{-TiO}_2\text{-NT}$.

Furthermore, XPS analysis of Mo 3d spectra (Fig. 4) shows that MoO_{3-x} nanosheets and $\text{MoO}_{3-x}\text{-TiO}_2$ nanocomposites display two sets of doublets, one being ascribed to Mo^{6+} (236.2 and 233.0 eV corresponding to $3d_{3/2}$ and $3d_{5/2}$ of Mo^{6+}), the other to Mo^{5+} (234.9 and 231.8 eV corresponding to $3d_{3/2}$ and $3d_{5/2}$ of Mo^{5+}) [27,28]. The Mo^{5+} concentration increased in the following sequence: $\text{MoO}_3 < \text{MoO}_{3-x} < \text{MoO}_{3-x}\text{-TiO}_2\text{-NP} < \text{MoO}_{3-x}\text{-TiO}_2\text{-NT}$ (Fig. 4). This was consistent with the observation from ESR. By calculating the ratio of $3d_{3/2}$ peak area of Mo^{5+} to that of Mo^{6+} , the percentage of Mo^{5+} in Mo of MoO_{3-x} was found to be 7.4%. Only Mo^{6+} existed in the MoO_3 . The percentage of Mo^{5+} in Mo of $\text{MoO}_{3-x}\text{-TiO}_2\text{-NP}$ and $\text{MoO}_{3-x}\text{-TiO}_2\text{-NT}$ nanocomposites were 10% and 25%, respectively. Higher Mo^{5+} concentration means higher free carrier concentration in MoO_{3-x} , which can benefit to LSPR effect and increase visible light harvesting.

For a specific plasmonic system, the composite structure can affect the LSPR [37]. Here we give a simple estimation: before contact, the Fermi level of TiO_2 is $E_{f(\text{Ti})} = -0.23$ eV vs. NHE (pH = 7) and the Fermi level of MoO_{3-x} is $E_{f(\text{Mo})} = 1.04$ eV [38,39]. After contact, the electrons flow from TiO_2 to MoO_{3-x} and build up a new equilibrium state, then the Fermi level of TiO_2 is equalized to the Fermi level of MoO_{3-x} (Fig. 5). This process can increase the electron density of MoO_{3-x} , and enhance the LSPR effect of MoO_{3-x} [40,41]. Thus, $\text{MoO}_{3-x}\text{-TiO}_2$ nanocomposites show stronger and blueshift of LSPR absorption compared with MoO_{3-x} . Moreover, the contact between MoO_{3-x} and $\text{TiO}_2\text{-NP}$ was better than the contact between MoO_{3-x} and $\text{TiO}_2\text{-NT}$ (Fig. 1), which will benefit for the transfer of electrons from TiO_2 to MoO_{3-x} . This might be the main reason why $\text{MoO}_{3-x}\text{-TiO}_2\text{-NT}$ shows stronger LSPR absorption than $\text{MoO}_{3-x}\text{-TiO}_2\text{-NP}$.

Fig. 4. XPS spectra of MoO_3 , MoO_{3-x} , $\text{MoO}_{3-x}\text{-TiO}_2\text{-NP}$ and $\text{MoO}_{3-x}\text{-TiO}_2\text{-NT}$.

Fig. 5. Energy diagrams of the plasmonic MoO_{3-x}-TiO₂ materials in different states (before contact and after contact).

The photocatalytic results displayed in Table 1 suggest that the LSPR plays a key role in determining the catalytic activity. TiO₂-NP, TiO₂-NT and MoO₃ were inactive under visible light irradiation. MoO_{3-x} and MoO_{3-x}-TiO₂ nanocomposites showed very high selectivity for photocatalytic reduction of CO₂ and suppressed the production of H₂. MoO_{3-x}-TiO₂-NT produced a significantly larger amount of (CO + CH₄) than MoO_{3-x}. The correlation of the LSPR absorption with the catalytic activity (Table 1) suggests that the visible-light absorption ability is the activity-determining factor in our system. Further studies were performed with the MoO_{3-x}-TiO₂-NT catalyst. When the reaction was carried out under N₂ atmosphere instead of CO₂ atmosphere, almost no CH₄ and only trace CO were detected under N₂ atmosphere, confirming that CO and CH₄ were formed from CO₂ (Fig. 6). The control experiments with heating condition also confirmed that CO and CH₄ were formed from photocatalytic reduction of CO₂ (Fig. S2). Furthermore, the present MoO_{3-x}-TiO₂-NT nanocomposite was stable during the reaction (Fig. 6). The CO and CH₄ amounts increased nearly linearly within 12 h. After each 12 h, the reactor was degassed and CO₂ was re-introduced. No obvious deactivation was observed in the three recycling experiments.

4. Conclusions

We have succeeded in synthesizing the MoO_{3-x}-TiO₂-NT nanocomposite containing MoO_{3-x} nanosheets and TiO₂ nanotubes by a simple solvothermal method. The MoO_{3-x} nanosheets showed LSPR absorption band in the visible-light region and the incorporation of TiO₂-NT significantly enhanced the LSPR absorption band. The MoO_{3-x}-TiO₂-NT nanocomposite is a promising candidate for the photocatalytic reduction of CO₂ with H₂O under visible light. This work has expanded the

Fig. 6. Repeated uses of the MoO_{3-x}-TiO₂-NT catalyst for the photocatalytic reduction of CO₂ with H₂O vapour under CO₂ or N₂ atmosphere. Reaction conditions: catalyst 0.010 g, CO₂ or N₂ pressure 0.2 MPa, H₂O 4 mL, light source Xe lamp ($\lambda = 420\text{--}780\text{ nm}$). After each 12 h, the catalyst was degassed and CO₂ or N₂ was re-introduced into the reactor.

possibility of catalyst design using LSPR for the development of highly efficient visible-light responsive photocatalysts for photocatalytic reduction of CO₂.

References

- [1] G. Centi, E. A. Quadrelli, S. Perathoner, *Energy Environ. Sci.*, **2013**, 6, 1711–1731.
- [2] S. Xie, Q. Zhang, G. Liu, Y. Wang, *Chem. Commun.*, **2016**, 52, 35–59.
- [3] S. Liu, C. Han, Z. R. Tang, Y. J. Xu, *Mater. Horiz.*, **2016**, 3, 270–282.
- [4] J. L. White, M. F. Baruch, J. E. Pander III, Y. Hu, I. C. Fortmeyer, J. E. Park, T. Zhang, K. Liao, J. Gu, Y. Yan, T. W. Shaw, E. Abelev, A. B. Bocarsly, *Chem. Rev.*, **2015**, 115, 12888–12935.
- [5] M. Marszewski, S. Cao, J. Yu, M. Jaroniec, *Mater. Horiz.*, **2015**, 2, 261–278.
- [6] W. Tu, Y. Zhou, Z. Zou, *Adv. Mater.*, **2014**, 26, 4607–4626.
- [7] X. Li, J. Yu, M. Jaroniec, X. Chen, *Chem. Rev.*, **2019**, 119, 3962–4179.
- [8] L. Zhang, Z. Zhao, T. Wang, J. Gong, *Chem. Soc. Rev.*, **2018**, 47, 5423–5443.
- [9] H. Tong, S. Ouyang, Y. Bi, N. Umezawa, M. Oshikiri, J. Ye, *Adv. Mater.*, **2012**, 24, 229–251.
- [10] J. Yang, D. Wang, H. Han, C. Li, *Acc. Chem. Res.*, **2013**, 46, 1900–1909.
- [11] X. Chang, T. Wang, J. Gong, *Energy Environ. Sci.*, **2016**, 9, 2177–2196.
- [12] Q. Zhai, S. Xie, W. Fan, Q. Zhang, Y. Wang, W. Deng, Y. Wang, *Angew. Chem. Int. Ed.*, **2013**, 52, 5776–5779.
- [13] S. Xie, Y. Wang, Q. Zhang, W. Fan, W. Deng, Y. Wang, *Chem. Com-*

Table 1

Photocatalytic behaviors of the MoO_{3-x}-TiO₂ nanocomposites for the reduction of CO₂ under visible light.

Photocatalyst	Formation rate/ $\mu\text{mol g}^{-1}\text{ h}^{-1}$			LSPR peak and intensity ^a /nm (a.u.)	Mo ⁵⁺ /(Mo ⁵⁺ +Mo ⁶⁺) ^b /%
	CO	CH ₄	H ₂		
TiO ₂ -NP	0	0	0	—	—
TiO ₂ -NT	0	0	0	—	—
MoO ₃	0	0	0	—	0
MoO _{3-x}	2.8	0	0	752 (9.5)	0.074
MoO _{3-x} -TiO ₂ -NP	6.8	0	0	710 (12)	0.10
MoO _{3-x} -TiO ₂ -NT	12	0.91	0	670 (18)	0.25

Reaction conditions: catalyst 0.010 g, CO₂ pressure 0.2 MPa, H₂O 4.0 mL, light source Xe lamp ($\lambda = 420\text{--}780\text{ nm}$), irradiation time 4 h. ^a The data was collected from UV-vis spectra. ^b The data was calculated from the peak area of XPS spectra.

Graphical Abstract

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Tunable localized surface plasmon resonances in $\text{MoO}_{3-x}\text{-TiO}_2$ nanocomposites with enhanced catalytic activity for CO_2 photoreduction under visible light

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The MoO_{3-x} nanosheets shows localized surface plasmon resonance (LSPR) absorption band in visible-light region and the incorporation of TiO_2 nanotubes significantly improves the LSPR absorption and enhances photocatalytic performances for CO_2 reduction under visible light.

- mun.*, **2013**, 49, 2451–2453.
- [14] L. Yuan, S. F. Hung, Z. R. Tang, H. M. Chen, Y. Xiong, Y. J. Xu, *ACS Catal.*, **2019**, 9, 4824–4833.
- [15] D. M. Schultz, T. P. Yoon, *Science*, **2014**, 343, 1239176.
- [16] C. Clavero, *Nat. Photonics*, **2014**, 8, 95–103.
- [17] P. Zhang, T. Wang, J. Gong, *Adv. Mater.*, **2015**, 27, 5328–5342.
- [18] G. V. Naik, V. M. Shalae, A. Boltasseva, *Adv. Mater.*, **2013**, 25, 3264–3294.
- [19] N. Zhang, C. Han, Y. J. Xu, J. J. Foley IV, D. Zhang, J. Codrington, S. K. Gray, Y. Sun, *Nat. Photonics*, **2016**, 10, 473–482.
- [20] C. Han, Q. Quan, H. Chen, Y. Sun, Y. J. Xu, *Small*, **2017**, 13, 1602947.
- [21] C. Han, S. H. Li, Z. R. Tang, Y. J. Xu, *Chem. Sci.*, **2018**, 9, 8914–8922.
- [22] H. Cheng, K. Fuku, Y. Kuwahara, K. Mori, H. Yamashita, *J. Mater. Chem. A*, **2015**, 3, 5244–5258.
- [23] I. Kriegel, F. Scotognella, L. Manna, *Phys. Rep.*, **2017**, 674, 1–52.
- [24] Z. Lou, Z. Wang, B. Huang, Y. Dai, *ChemCatChem*, **2014**, 6, 2456–2476.
- [25] H. Cheng, T. Kamegawa, K. Mori, H. Yamashita, *Angew. Chem. Int. Ed.*, **2014**, 53, 2910–2914.
- [26] H. Cheng, X. Qian, Y. Kuwahara, K. Mori, H. Yamashita, *Adv. Mater.*, **2015**, 27, 4616–4621.
- [27] J. Shi, Y. Kuwahara, M. Wen, M. Navlani-García, K. Mori, T. An, H. Yamashita, *Chem. Asian J.*, **2016**, 11, 2377–2381.
- [28] H. Yin, Y. Kuwahara, K. Mori, H. Cheng, M. Wen, H. Yamashita, *J. Mater. Chem. A*, **2017**, 5, 8946–8953.
- [29] Q. Huang, S. Hu, J. Zhuang, X. Wang, *Chem. Eur. J.*, **2012**, 18, 15283–15287.
- [30] G. Song, J. Hao, C. Liang, T. Liu, M. Gao, L. Cheng, J. Hu, Z. Liu, *Angew. Chem. Int. Ed.*, **2016**, 55, 2122–2126.
- [31] J. Li, Y. Ye, L. Ye, F. Su, Z. Ma, J. Huang, H. Xie, D. E. Doronkin, A. Zimina, J.-D. Grunwaldt, Y. Zhou, *J. Mater. Chem. A*, **2019**, 7, 2821–2830.
- [32] M. M. Y. A. Alsaiif, K. Latham, M. R. Field, D. D. Yao, N. V. Medehkar, G. A. Beane, R. B. Kaner, S. P. Russo, J. Z. Ou, K. Kalantar-zadeh, *Adv. Mater.*, **2014**, 26, 3931–3937.
- [33] W. Liu, Q. Xu, W. Cui, C. Zhu, Y. Qi, *Angew. Chem. Int. Ed.*, **2017**, 56, 1600–1604.
- [34] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, *Langmuir*, **1998**, 14, 3160–3163.
- [35] X. Li, H. Liu, D. Luo, J. Li, Y. Huang, H. Li, Y. Fang, Y. Xu, L. Zhu, *Chem. Eng. J.*, **2012**, 180, 151–158.
- [36] X. N. Song, C. Y. Wang, W. K. Wang, X. Zhang, N. N. Hou, H. Q. Yu, *Adv. Mater. Interfaces*, **2016**, 3, 1500417.
- [37] X. Zhang, Y. L. Chen, R. S. Liu, D. P. Tsai, *Rep. Prog. Phys.*, **2013**, 76, 046401.
- [38] V. Subramanian, E. E. Wolf, P. V. Kamat, *J. Am. Chem. Soc.*, **2004**, 126, 4943–4950.
- [39] M. Vasilopoulou, A. M. Douvas, D. G. Georgiadou, L. C. Palilis, S. Kennou, L. Sygellou, A. Soultati, I. Kostis, G. Papadimitropoulos, D. Davazoglou, P. Argitis, *J. Am. Chem. Soc.*, **2012**, 134, 16178–16187.
- [40] C. Novo, A. M. Funston, P. Mulvaney, *Nat. Nanotechnol.*, **2008**, 3, 598–602.
- [41] C. Novo, A. M. Funston, A. K. Gooding, P. Mulvaney, *J. Am. Chem. Soc.*, **2009**, 131, 14664–14666.

局部表面等离子体共振可调的 $\text{MoO}_{3-x}\text{-TiO}_2$ 纳米复合物用于提高可见光下光催化还原 CO_2 的性能

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摘要: 利用太阳能光催化还原 CO_2 和 H_2O 到燃料和化学品是一条极具吸引力但又充满挑战性的转化途径。迄今为止, 只有非常有限的光催化剂已经被报道可以在可见光照射下光催化还原 CO_2 。局部表面等离子体共振(LSPR)现象可以被用作一种有效的开发可见光催化剂的策略。贵金属Au, Ag, Pt等的LSPR现象已经被较为广泛的研究, 并应用于光催化、光热、气

敏等多种领域。而低价态金属自掺杂的金属氧化物,如 MoO_{3-x} 和 WO_{3-x} ,也被证明具有LSPR现象,可用于开发更加廉价的可见光催化剂。本文通过简单的溶剂热法成功合成了低价态Mo自掺杂的 MoO_{3-x} 纳米片催化剂,并在合成过程中原位加入 TiO_2 纳米颗粒($\text{TiO}_2\text{-NP}$)和 TiO_2 纳米棒($\text{TiO}_2\text{-NT}$),构建了 $\text{MoO}_{3-x}\text{-TiO}_2$ 纳米复合物。电镜表征显示, $\text{MoO}_{3-x}\text{-TiO}_2\text{-NT}$ 纳米复合物中, MoO_{3-x} 纳米片和 TiO_2 纳米管的结合更为紧密。UV-vis光谱显示, TiO_2 的复合不仅可以增强 MoO_{3-x} 可见区的吸收强度,同时吸收峰的位置也发生了蓝移。XPS表征显示, TiO_2 复合后, MoO_{3-x} 中 Mo^{5+} 的比例明显增加,从而提高了 MoO_{3-x} 中自由电子的浓度,进而增强了LSPR现象和LSPR吸光能力,且 TiO_2 纳米管相对 TiO_2 纳米颗粒具有更好的促进效果。 MoO_{3-x} 纳米片具有在可见光照射下光催化还原 CO_2 的性能, CO 的生成速率为 $2.8 \mu\text{mol g}^{-1} \text{h}^{-1}$ 。复合 TiO_2 纳米颗粒后, $\text{MoO}_{3-x}\text{-TiO}_2\text{-NP}$ 纳米复合物上, CO 的生成速率提高到 $6.8 \mu\text{mol g}^{-1} \text{h}^{-1}$ 。当复合 TiO_2 纳米管时,光催化性能显著提高,在 $\text{MoO}_{3-x}\text{-TiO}_2\text{-NT}$ 纳米复合物上, CO 的生成速率可达 $12 \mu\text{mol g}^{-1} \text{h}^{-1}$,约为 MoO_{3-x} 纳米片的四倍,此外还可观测到 CH_4 的生成。当我们将反应气氛由 CO_2 替换成 N_2 后, CO 和 CH_4 的生成量几乎为零,证明 CO 和 CH_4 的生成主要来自 CO_2 的光催化还原。此外,我们还考察了 $\text{MoO}_{3-x}\text{-TiO}_2\text{-NT}$ 纳米复合物光催化还原 CO_2 的催化性能稳定性,以12 h反应时间为一个循环,经3个循环反应后,催化剂的活性基本保持不变,证明该催化剂具有较好的稳定性。综上,我们通过 MoO_{3-x} 纳米片和 TiO_2 复合的策略,增强了 MoO_{3-x} 纳米片的LSPR效应,提升了催化剂对可见光的吸收能力,进而提高了 $\text{MoO}_{3-x}\text{-TiO}_2\text{-NT}$ 纳米复合物光催化还原 CO_2 的性能。 $\text{MoO}_{3-x}\text{-TiO}_2\text{-NT}$ 纳米复合物是一种具有发展潜力的光催化还原 CO_2 的可见光催化剂,且该纳米复合物调变LSPR效应的策略还有望用于增强其他LSPR光催化材料的光催化性能。

关键词: 光催化; 二氧化碳; 可见光; 局部表面等离子体共振; $\text{MoO}_{3-x}\text{-TiO}_2$ 纳米复合物

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