Creation of Mo active sites on indium oxide microrods for photocatalytic amino acid production

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ABSTRACT As an n-type semiconductor, In_2O_3 is considered a promising photocatalyst for producing amino acids using biomass derivatives as precursors. However, similar to other intrinsic semiconductors, In_2O_3 suffers from poor charge dynamics. Herein, we show the synthesis of Mo-doped In_2O_3 ($\text{Mo-In}_2\text{O}_3$) with a porous rod-shaped structure through a one-step solvothermal reaction followed by calcination. Under visible-light irradiation, $\text{Mo-In}_2\text{O}_3$ achieves a high conversion rate of 81% for the reaction that transforms lactic acid into alanine with a selectivity of 91%. Spectroscopic techniques and density functional theory calculations reveal that Mo doping introduces defect states slightly below the conduction band of In_2O_3 , which improves the separation of photogenerated electron-hole pairs. In addition, Mo atoms on the surface form extra adsorption and reaction centers that greatly enhance the reaction rate. This work provides insights into the development of transition metal-doped semiconductor photocatalysts to produce amino acids.

Keywords: photocatalysis, In_2O_3 , transition metal doping, charge transfer, organic synthesis

INTRODUCTION

Amino acids are organic compounds containing amino and carboxyl groups. They are not only regarded as the cornerstones of life but also widely used in the production of medicines, polymer materials, and pesticides [1–3]. The broad applications of amino acids in human activities necessitate efficient synthetic strategies [4–6]. However, as a traditional method, chemical synthesis suffers from many shortcomings, such as the use of toxic cyanide and harsh reaction conditions [7,8]. Therefore, heterogeneous catalysis has been explored. For example, Wang *et al.* [9] reported the direct conversion of lactic acid (LA) derived from lignocellulosic biomass into α -amino acids using ruthenium-containing nanoparticles supported by carbon nanotubes. In addition, Deng *et al.* [10] prepared $\text{Ru}_1\text{Ni}_7/\text{MgO}$ by wet impregnation, which was used to convert crude glycerol to LA via a two-step process. By contrast, the newly developed synthetic methods, which use biomass as the precursor, are more

advantageous. Nevertheless, harsh conditions are necessary to drive the reaction, including high temperature [11].

Recently, photocatalysis that uses semiconductors such as TiO_2 [12,13], CuO [14], C_3N_4 [15–18], ZnIn_2S_4 [19], and In_2O_3 [20,21] has witnessed great progress in the application of organic synthesis. This technology generates electrons and holes to induce redox reactions under mild conditions, making it suitable for the production of amino acids [22]. For example, Song *et al.* [23] reported the conversion of biomass-derived LA into an amino acid over CdS excited by visible-light illumination. In the photocatalytic production of amino acids, the design and synthesis of effective catalysts are considered a key challenge. In_2O_3 , which is an n-type semiconductor, has excellent stability and efficiency in organic synthesis involving small molecules and photocatalytic CO_2 reduction [20,21,24–27]. However, similar to most unmodified semiconductor photocatalysts, In_2O_3 suffers from low separation efficiency of photogenerated charge carriers [28].

Recent reports have shown that doping of photocatalysts with heteroatoms introduces defect energy levels, which can improve the charge distribution and catalytic activity [29,30]. For example, Guo *et al.* [31,32] demonstrated doping of CdS nanorods with P or Mo and its role in promoting charge separation and transfer. In addition, Liu *et al.* [33] doped $\alpha\text{-Fe}_2\text{O}_3$ with Pt^{2+} and created Schottky barriers, which could effectively hinder the recombination of photogenerated electrons and holes, thereby increasing their lifetime. To date, doping of semiconductors with transition metals has been regarded as a potential strategy to improve their photocatalytic efficiency through the following mechanisms: (1) modification of the local electronic environments [34–36], (2) improvement in the separation efficiency of charge carriers [37–39], and (3) creation of new active centers [40,41]. Despite these advantages, excessive doping can decrease photocatalytic performance because of the formation of charge recombination centers [37]. In addition, the introduction of heteroatoms as dopants will inevitably reduce the apparent band gap of the catalyst and reduce its redox ability [35]. Thus, selecting a suitable catalyst and doping method is important to enhance photocatalytic performance and explore the doping mechanism of photo-

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catalysis.

In this work, we demonstrate the synthesis of rod-shaped Mo-doped In_2O_3 (Mo- In_2O_3) using a metal-organic framework (MOF), MIL-68(In), as the structural template. Experiments and theoretical calculations reveal that Mo with an oxidation state of +5 is incorporated into the In_2O_3 lattice to substitute In^{3+} ions and form Mo–O–In bonds as new reactive sites. Moreover, the interaction between Mo and In atoms can regulate the charge distribution and facilitate the transfer and separation of photo-generated charge carriers. Mo doping introduces defect energy levels below the conduction band (CB) and creates localized electron-trapping centers, which not only improve the transfer of charge carriers, but also reduce the apparent band gap, thereby enhancing the ability of In_2O_3 to use visible light.

EXPERIMENTAL SECTION

Materials

Indium(III) nitrate hydrate ($\text{In}(\text{NO}_3)_3$), ammonium molybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$), and 1,4-dicarboxybenzene (PTA) were all obtained from Aladdin Industrial Corporation. All chemicals were of analytical grade and used as received without further purification. Deionized water was used in the following experiments.

Synthesis of In-MOF

$\text{In}(\text{NO}_3)_3$ (0.32 g) was dissolved in 25 mL of dimethylformamide (DMF) under sonication. After stirring for 30 min, 0.2 g of PTA was added under sonication, and then the mixture was further stirred for 20 min. Next, the mixture was transferred to a hydrothermal kettle and placed in an oven at 120°C for 3 h. The precipitate was collected by centrifugation and dried at 60°C in air.

Synthesis of In_2O_3

In-MOF was transferred to a muffle furnace and calcined in air at 500°C for 2 h.

Synthesis of bulk In_2O_3

Indium nitrate (1 mmol) was dissolved in 60 mL of deionized water. Subsequently, 3 mmol of urea was added; the mixture was further stirred for 30 min. Next, this mixture was transferred to a 100-mL Teflon-lined stainless-steel autoclave and then heated at 140°C for 10 h. The precipitate was collected by centrifugation and washed thrice with purified water and ethanol. Finally, it was calcined in air at 500°C for 2 h.

Synthesis of MOF-polyoxometalate (POM)

First, 0.1 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ was dispersed in 1.5 mL of deionized water under sonication. Next, 25 mL of DMF was added under stirring, and the mixture was further stirred for 5 min. Afterward, 0.32 g of $\text{In}(\text{NO}_3)_3$ was added under sonication, and then the mixture was stirred for 20 min. Finally, PTA was added, and the mixture was agitated continuously until a yellowish precipitate was formed. The precipitate was transferred to the Teflon-lined stainless-steel autoclave and kept at 120°C for 3 h.

Synthesis of Mo- In_2O_3

Dried MOF-POM was transferred to a muffle furnace and calcined in air at 500°C for 2 h.

Synthesis of Mo-doped In_2O_3

$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (0.1 g) and a certain amount of In-MOF were physically mixed in a mortar, and then the ground sample was calcined in air at 500°C for 2 h.

RESULTS AND DISCUSSION

Mo-doped In_2O_3 (Mo- In_2O_3) was prepared using MIL-68(In) as the indium source and the structural template and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ as the molybdenum source [42]. The precursors of MIL-68(In) and source of Mo were mixed to produce POM-MOF, which has the same rod-like structure as In-MOF (Fig. S1). The production of In_2O_3 and its doping with Mo were achieved simultaneously by calcining In-MOF at 500°C (Fig. 1a). At this temperature, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and POM-MOF were decomposed as verified by thermogravimetric analysis (Fig. S2). Scanning electron microscopy (SEM) images show that the In_2O_3 and Mo- In_2O_3 samples are composed of micro-sized hexagonal rods (Figs S3 and S4). The adsorption isotherms of Mo- In_2O_3 and In_2O_3 present a type H3 hysteresis loop (Fig. S5), which indicates the presence of mesopores formed *via* particle aggregation. The Brunauer-Emmett-Teller method was used to calculate the specific surface area, and the result shows that the doping has negligible effect (36.1 and 35.6 $\text{m}^2 \text{g}^{-1}$ for Mo- In_2O_3 and In_2O_3 , respectively) [43]. However, the average pore size is decreased after doping (Fig. S6). The rod-shaped structure of Mo- In_2O_3 was also observed using transmission electron microscopy (TEM). Moreover, the TEM image shows that the structure consists of tightly connected nanoparticles, which can improve the transfer of electrons and holes (Fig. 1b and Fig. S7) [44]. The high-resolution TEM image exhibits clear lattice fringes with a spacing of 0.29 nm corresponding to the (222) facet of cubic In_2O_3 (PDF#06-0416, Fig. 1c). Furthermore, individual Mo atoms are shown as bright spots in the high-angle annular dark-field (HAADF) image (Fig. 1d), indicating that Mo atoms have been doped into the crystal structure of In_2O_3 [45]. The Mo content was determined to be 0.47 wt% by inductively coupled plasma atomic emission spectrometry (Table S1). The Mo atoms are uniformly distributed in In_2O_3 as evidenced by elemental mapping (Fig. 1e–g) and energy-dispersive X-ray spectroscopy (EDS, Fig. S8). In addition, a small amount of carbon and nitrogen are found by EDS.

The cubic structure of In_2O_3 was further verified by X-ray diffraction (XRD). The most intense peak in the patterns of In_2O_3 and Mo- In_2O_3 is located at 30.5° (Fig. 2a) [42]. In addition, given the small amount of Mo, no additional peak was found in the pattern of Mo- In_2O_3 . However, given the difference in the radius of Mo and In ions, the XRD peaks of Mo- In_2O_3 were shifted compared with those of In_2O_3 (Fig. S9) [31]. Furthermore, the XRD patterns of In-MOF, POM-MOF, and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and the Fourier transform infrared spectra show that the addition of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ into the precursors of MIL-68(In), namely, $\text{In}(\text{NO}_3)_3$ and phthalic acid, did not hinder the formation of the MOF (Figs S10 and S11) [46]. Preservation of the crystal structure of In_2O_3 after Mo doping is evident by the Raman spectra of In_2O_3 and Mo- In_2O_3 , which present peaks at the same Raman shifts (Fig. S12) [47].

The chemical state and electronic structure of Mo- In_2O_3 were studied by X-ray photoelectron spectroscopy (XPS). The peaks at approximately 451.04 and 443.45 eV in the high-resolution XPS In 3d spectrum of Mo- In_2O_3 are attributed to the $3d_{3/2}$ and $3d_{5/2}$ electrons of In^{3+} , respectively (Fig. 2b) [48]. This pair of peaks is

Figure 1 (a) Schematic illustration of the synthesis of micro-sized Mo-In₂O₃ hexagonal rods. (b, c) TEM and (d) HAADF-scanning TEM (STEM) images of Mo-In₂O₃; (e–g) the corresponding elemental mappings for Mo-In₂O₃.

shifted to lower binding energies for Mo-In₂O₃, indicating the increase in the electron density around In atoms. The XPS O 1s spectra of In₂O₃ and Mo-In₂O₃ can be deconvoluted to two peaks (Fig. 2c), corresponding to the defect oxygen (O defect, larger binding energy) and lattice oxygen [49,50]. Apart from the increase in the electron density around In, the decrease in the binding energy for the lattice oxygen caused by Mo doping indicates an electron transfer from Mo to In through O (i.e., the formation of Mo–O–In bonds) [42,51,52]. The presence of Mo with an oxidation state of +5 is evidenced by the XPS Mo 3d spectrum that features two peaks located at 232.03 and 235.26 eV (Fig. 2d). These XPS results indicate that a portion of the In³⁺ ions have been replaced by Mo⁵⁺ ions [53].

The ultraviolet-visible (UV-vis) diffuse reflectance spectra indicate that In₂O₃ and Mo-In₂O₃ can absorb visible light (Fig. S13); however, doping of In₂O₃ with Mo decreases the apparent band gap determined by Tauc plots from 2.56 to 2.43 eV (Fig. 3a). The flat band potentials of Mo-In₂O₃ and In₂O₃ relative to the Ag/AgCl electrode reach −0.83 and −0.92 V by constructing Mott-Schottky plots at frequencies of 0.8, 1.0, and 1.2 kHz (Fig. 3b and Fig. S14) [25]. The shift of the flat band potential of In₂O₃ toward a less negative value after Mo doping has been ascribed to the formation of defect states in the band gap [39,54]. Considering that In₂O₃ is an n-type semiconductor, its Fermi level is close to the bottom of the CB. Hence, the potential of the CB minimum is approximated as the flat band potential. Consequently, the potentials of the valence band (VB)

maxima of In₂O₃ and Mo-In₂O₃ are 1.64 and 1.60 V (vs. the Ag/AgCl electrode), respectively [25]. Notably, the edges of the VB are also evident by XPS valence-band spectra (Fig. S15). As shown in the resultant band diagram (Fig. 3c), the introduction of Mo atoms in In₂O₃ reduces the apparent band gap and improves the ability of In₂O₃ to absorb visible light [55].

Density functional theory (DFT) calculations were conducted to investigate the electronic structure of the materials. The charge density distribution of In₂O₃ was obtained by subtracting the charge density of In and O atoms from the total charge density [56]. As expected, electrons are accumulated around the O atoms. However, the substitution of part of the In atoms by Mo atoms resulted in charge redistribution. Notably, electrons of Mo are strongly attracted by the surroundings (Fig. 3d, e). The projected density of states (PDOS) of pure In₂O₃ reveals that the valance band is primarily composed of O 2p orbitals, and the CB is composed of In d orbitals, which indicate that electrons of O are excited and then transferred to In [57]. The PDOS profile of Mo-In₂O₃ shows the presence of Mo d orbitals in the bandgap. In₂O₃ is an n-type semiconductor, and its Fermi level is located near the bottom of the CB [58]. The defect states close to the Fermi level caused by Mo doping may not only reduce the band gap to improve light absorption, but also serve as electron traps to inhibit electron-hole recombination (Fig. 3f and Fig. S16) [59]. Compared with In₂O₃, the d-band center of Mo-In₂O₃ moves up to larger energy, which improves electron transfer from Mo-In₂O₃ to LA [60].

Figure 2 (a) XRD patterns of In₂O₃ and Mo-In₂O₃. High-resolution XPS spectra of (b) O 1s, (c) In 3d, and (d) Mo 3d.

Figure 3 (a) Band gaps determined by Tauc plots of In₂O₃ and Mo-In₂O₃. (b) Mott-Schottky plots of Mo-In₂O₃ at various frequencies (pH = 7). (c) Band diagrams of In₂O₃ and Mo-In₂O₃. (d, e) Charge density isosurface of In₂O₃ and Mo-In₂O₃, in which accumulation and depletion are colored in cyan and yellow. (f) PDOS of In₂O₃ and Mo-In₂O₃.

Steady-state and transient-state photoluminescence (PL) spectroscopy was used to investigate the dynamics of photo-generated electrons and holes. The steady-state PL spectrum of In_2O_3 shows an emission peak at 435 nm, which is attributed to the radiative recombination of electrons and holes. By contrast, the PL peak of $\text{Mo-In}_2\text{O}_3$ is greatly weakened, indicating that the defect states below the CB of In_2O_3 serve as electron traps to inhibit electron-hole recombination (Fig. S17). Transient-state PL spectra of In_2O_3 and $\text{Mo-In}_2\text{O}_3$ indicate that Mo doping enhances charge transport as evidenced by the short lifetime of the charge carriers in $\text{Mo-In}_2\text{O}_3$ during relaxation (Fig. 4a). In addition, the radius of the semicircle in the Nyquist plot of $\text{Mo-In}_2\text{O}_3$ is smaller than that of In_2O_3 (Fig. 4b), thereby confirming the improvement in charge transfer because of the Mo doping [61,62]. This improvement in charge transfer was further verified by the strong photocurrent responses of $\text{Mo-In}_2\text{O}_3$ under intermittent light irradiation (Fig. 4c). The work function of In_2O_3 and $\text{Mo-In}_2\text{O}_3$ was determined by Kelvin probe force microscopy (Fig. 4d) [63–65]. Consequently, Mo doping reduces the work function of In_2O_3 , which is in agreement with the observation that the flat potential of In_2O_3 is more negative than that of $\text{Mo-In}_2\text{O}_3$.

$\text{Mo-In}_2\text{O}_3$ was used as a photocatalyst in converting LA into an amino acid (i.e., alanine) because of its good physicochemical properties. Control experiments (Table 1, entries 1–6) revealed that the reaction must be conducted at 50°C in a nitrogen atmosphere in the presence of ammonia to achieve the optimal conversion rate and selectivity, which was confirmed by gas

chromatography-mass spectrometry (GC-MS) (Fig. S18). In addition, the conversion rate increases with time, and it reaches the maximum at a reaction time of 4 h (Fig. S19). Furthermore, different amounts of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ were added during synthesis to determine the amount of Mo favorable for the reaction of LA (Table S2). Under the optimal reaction conditions and simulated sunlight irradiation, $\text{Mo-In}_2\text{O}_3$ achieved a high LA-to-alanine conversion rate of 81% with a selectivity of 91% (Table 1, entry 9). Therefore, $\text{Mo-In}_2\text{O}_3$ is an effective heterogeneous catalyst for this reaction (Table S3). By contrast, neither bulk In_2O_3 (Table 1, entry 7) nor hexagonal tubular In_2O_3 (Table 1, entry 8) can induce comparable conversion efficiency, which indicates the importance of doped Mo atoms and the neglectable effect of the morphology of In_2O_3 . The role of Mo doping is further supported by the low conversion rates of ground $\text{Mo-In}_2\text{O}_3$ (Table 1, entry 10) and the physical mixture of In_2O_3 and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (POM; Table 1, entry 11).

Apart from the conversion rate and selectivity, the reaction rate is also important. On the one hand, the reaction rate can be measured on the basis of LA conversion, and it is as high as $0.407 \text{ mmol h}^{-1}$ for $\text{Mo-In}_2\text{O}_3$, which is about 1.6 times that of In_2O_3 ($0.254 \text{ mmol h}^{-1}$, Fig. 5a). On the other hand, the reaction rate can be assessed on the basis of alanine production, which is 0.369 and $0.186 \text{ mmol h}^{-1}$ for $\text{Mo-In}_2\text{O}_3$ and In_2O_3 , respectively (Fig. 5b). In addition, the photocatalyst showed great stability during the reaction. As shown in Fig. 5c, after five reaction cycles (corresponding to a total reaction time of 20 h), the conversion rate and selectivity did not decrease significantly.

Figure 4 (a) Transient-state PL spectra; (b) Nyquist plots; (c) time-resolved photocurrent responses; (d) scanning Kelvin probe mappings (SKP) of In_2O_3 and $\text{Mo-In}_2\text{O}_3$.

Table 1 Experimental conditions and results of LA-to-alanine conversion

Entry	Catalyst	NH ₃ ·H ₂ O	Temperature (°C)	N ₂	Light	Scavenger	Conversion rate (%)	Selectivity (%)
1	—	+	50	+	+		0	0
2	Mo-In ₂ O ₃	+	50	+	—		15	37
3	Mo-In ₂ O ₃	+	—	+	+		29	25
4	Mo-In ₂ O ₃	+	50	—	+		13	21
5	Mo-In ₂ O ₃	—	50	+	+		0	0
6	Mo-In ₂ O ₃	—	50	—	+		0	0
7	In ₂ O ₃	+	50	+	+		35	45
8	In ₂ O ₃	+	50	+	+		34	36
9	Mo-In ₂ O ₃	+	50	+	+		81	91
10	Mo-In ₂ O ₃	+	50	+	+		30	52
11	In ₂ O ₃ + POM	+	50	+	+		13	43
12	Mo-In ₂ O ₃	+	50	+	+	C ₆ H ₅ NO ₂	20	47
13	Mo-In ₂ O ₃	+	50	+	+	IPA	45	38

Figure 5 Amounts of (a) LA converted and (b) alanine produced as a function of time for In₂O₃ and Mo-In₂O₃; (c) conversion rate and selectivity of five consecutive 4 h reactions; (d) mechanisms of the conversion of LA to alanine over Mo-In₂O₃.

Studies of the recycled Mo-In₂O₃ catalyst by using SEM and XRD indicate that the morphology and crystallinity are not altered (Figs S20 and S21).

Electron and hole scavengers were selectively added to the reaction system to determine the active species responsible for

LA-to-alanine conversion and understand the reaction mechanism. When nitrobenzene (an electron scavenger) was added, the conversion rate dropped from 81% to 20% (Table 1, entry 12). This result indicates the important role of photo-generated electrons in the reaction, although such electrons are

not involved in any change in the oxidation state. Similarly, the addition of isopropanol (IPA, a hole scavenger) also led to a decrease in the conversion rate from 81% to 45% (Table 1, entry 13). By combining these experimental results with previous reports, we propose a reaction mechanism (Fig. 5d). In brief, LA molecules adsorbed on Mo-In₂O₃ are first transformed to pyruvic acid after receiving holes from the photocatalyst. Next, the latter molecules react with NH₃, forming imine molecules. Finally, the imine is reduced to alanine by the photogenerated electrons in Mo-In₂O₃ [23].

CONCLUSIONS

Mo-In₂O₃ with a rod-like structure was synthesized by a simple solvothermal method, followed by pyrolysis using MIL-68(In) as the In source and the structural template and (NH₄)₆Mo₇O₂₄·4H₂O as the Mo source. Under visible-light irradiation, Mo-In₂O₃ effectively catalyzed the conversion of LA into alanine, reaching a conversion reaction rate of up to 0.407 mmol h⁻¹, which was about 1.6 times that of In₂O₃ (0.254 mmol h⁻¹). From the perspective of alanine production, the reaction rate of Mo-In₂O₃ (0.369 mmol h⁻¹) was about two times that of In₂O₃ (0.186 mmol h⁻¹) because of the good reaction selectivity of the former photocatalyst. The excellent photocatalytic performance of Mo-In₂O₃ was attributed to the enhancement in bulk and interfacial charge transfer as a result of Mo doping revealed by PL spectroscopy, electrochemical impedance spectroscopy, photocurrent spectroscopy, and DFT calculations. This work demonstrates the great potential of a well-developed technology for the synthesis of an amino acid, which may be used to develop more photocatalysts for the production of other amino acids.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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氧化铟表面构建Mo单原子活性位点用于光催化合成氨基酸

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摘要 In_2O_3 作为一种n型半导体,被认为是合成氨基酸最有前途的光催化剂之一,然而 In_2O_3 自身在光生电荷动力学方面存在不足.我们通过一步溶剂热和煅烧法合成了具有多孔棒状结构的Mo原子掺杂 In_2O_3 ($\text{Mo-In}_2\text{O}_3$).在可见光照射下,将 $\text{Mo-In}_2\text{O}_3$ 用于乳酸转化为丙氨酸的反应,实现了81%的转化率和91%的选择性.光谱技术和密度泛函理论计算表明,Mo原子引入了略低于 In_2O_3 导带的缺陷能级,改善了光生电子-空穴对的分离效率.此外, In_2O_3 表面上的Mo原子形成新的吸附和反应活性中心,可显著提高催化反应速率.本工作为开发过渡金属单原子修饰的半导体光催化剂应用于氨基酸生产提供了理论基础.