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Article

Photoelectrocatalytic CO₂ reduction based on metalloporphyrin-modified TiO₂ photocathode

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ABSTRACT

The conversion of CO₂ and water to value-added chemicals under sunlight irradiation, especially by photoelectrocatalytic reduction process, is always a dream for human beings. A new artificial photosynthesis system composed of a metalloporphyrin-functionalized TiO₂ photocathode and BiVO₄ photoanode can efficiently transform CO₂ and water to methanol, which is accompanied by oxygen release. This photoelectrocatalytic system smoothly produces methanol at a rate of 55.5 μM h⁻¹ cm⁻², with 0.6 V being the membrane voltage in plants. The production of hydrogen can also be observed when the voltage is more than 0.75 V, due to photocatalysis. Our results evidently indicate that the molecules of metalloporphyrin attached onto the surface of anatase (TiO₂) behave as chlorophyll, NADP, and Calvin cycle in plant cells.

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1. Introduction

The over consumption of fossil fuels in our modern society has brought about a serious energy crisis and the global warming problem. Many scientists have therefore dedicated themselves to discovering new science and technology for storing solar energy in solar fuels through water splitting [1–4], photocatalytic CO₂ reduction [5–7], and electrocatalytic CO₂ reduction in water [8,9]. In this context, Wang's group [5] reported a new C/N material with an apparent quantum efficiency of 4.8%, and catalysts containing metal-N sites for electrochemical CO₂ reduction have been well documented by Bao et al. [8]. In fact, the plentiful solar energy is mainly stored by trees and grasses via natural photosynthesis, in which CO₂ and H₂O are converted to sugars, cellulose, etc. Recently, catalytic

CO₂ reduction has emerged as one of the hotspots in the interdisciplinary fields of environment, energy, catalysis, and materials [10–23]. To achieve efficient CO₂ reduction as in the case of photosynthesis in plant cells, three processes need to be considered [24,25]: CO₂ adsorption, quick reduction action, and product desorption. For the photoelectrocatalytic reduction of CO₂, a semiconductor with a suitable conduction band (CB) is the basic requirement for stably hosting the active photoelectrons.

Multi-electron transfer in semiconductor electrodes is a longstanding target because of the potential for application in solar-to-chemical energy conversion [26]. One of the major issues is that most semiconductors possessing a suitable band gap for solar energy absorption, such as Cu₂O [27,28] and CuFeO₂ [29], are thermodynamically unstable in aqueous solu-

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tions. Furthermore, the surfaces of some semiconductors are not catalytically active for multi-electron transfer reactions, especially for CO₂ reduction [30]. Therefore, appropriate cocatalysts are required [31,32].

Although TiO₂ nanoparticles have been intensively investigated in terms of their stability and economy, their performance in CO₂ reduction is poor, owing to the weak adsorption of CO₂ on the catalyst surfaces and inefficient harvesting of the solar radiation [33]. To enhance the absorption of sunlight, molecular porphyrin is commonly utilized in DSSC devices [34]. CO₂ adsorption can be realized by introducing ligands on the surfaces of photocathodes [35–37].

As is well known, porphyrin structures widely exist in nature, such as chlorophyll, hemoglobin, and vitamin B₁₂. Porphyrins have been extensively investigated in DSSCs as sensitizers owing to their brilliant light absorption ability [38–40]. Furthermore, metalloporphyrins have been increasingly applied to homogeneous and heterogeneous catalysis [41–46], including electrocatalytic CO₂ reduction [47,48]. Recently, Yang and his coworkers [49] developed an electrocatalytic system composed of covalent frameworks and cobalt metal that has been applied in CO₂ reduction to produce CO with high selectivity. Here, metalloporphyrins were anchored through covalent bonds onto the surface of TiO₂ as the solar absorber and catalyst to improve both the light absorption and efficiency of CO₂ reduction in an artificial photosynthesis (APS) cell (Fig. 1).

2. Experimental

2.1. General

Porphyrins and metalloporphyrins were prepared according to the methods reported in the literature [38,50], and named as TCPP (D1, *meso*-tetra-*p*-carboxyphenylporphyrin), CoTCPP (D2), NiTCPP (D3), CuTCPP (D4), and PdTCPP (D5). The FTO glass plates (15 Ω/cm²) used were purchased from Nippon Sheet Glass Co. Ltd.. ¹H NMR spectra were recorded on a Varian Mercury 300/400 spectrometer by using tetramethylsilane as an internal standard. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet NEXUS 670 instrument. UV-vis absorption spectra were obtained by using a UV-3600 spectrophotometer in absorption spectra of a 1 × 10^{−5} M (mol/L) solution of D1–D5. DMSO:EtOH = 1:10 at room temperature. Fluorescence spectra were obtained by using an

F-7000 fluorescence spectrophotometer. The lifetimes of the porphyrin derivatives were obtained with Edinburgh Instruments FS920. XRD patterns of the electrodes were recorded by using a Philips X'Pert Pro Super diffractometer with Cu K_α radiation (λ = 1.5406 Å). The SEM images and EDX maps were collected with MIRA3 XMU. TEM was carried out on a Tecnai F30 instrument.

2.2. Preparation of electrodes

The TiO₂/FTO electrodes were prepared by a spin coating method. A paste of TiO₂ was obtained by grinding a mixture (4.5 g P25, 0.2 mL Triton X-100, and 0.5 g polyethylene glycol 20000) with 10 mL pure water. The coated FTO glass plates were sintered at 500 °C for 1 h. The area of the TiO₂ film was about 1.5 × 1.5 cm², and the average weight was about 1.25 mg. These TiO₂/FTO electrodes were immersed in an aminopropyltriethoxysilane (APTES) ethanol solution (5%) and kept at 70 °C for 1 h. These amino-functionalized TiO₂/FTO electrodes (NH₂@TiO₂) were then placed in a 10 mL DMF solution for 24 h at room temperature, which contained 1 mM D1–D5, 2.5 mM dicyclohexylcarbodiimide, and 1 mg 4-dimethylaminopyridine. The electrodes were washed with pure water and dried at 50 °C in vacuum. The obtained porphyrin-modified electrodes were named as D1@TiO₂, D2@TiO₂, D3@TiO₂, D4@TiO₂, and D5@TiO₂.

After porphyrin modification of the electrodes, Pd nanoparticles were deposited onto the Dx@TiO₂ films by pulsed electrodeposition technique to yield Pd/Dx@TiO₂ electrodes.

The BiVO₄ electrodes were modified by using FeOOH and NiOOH according to the literature method [50].

2.3. Photoelectrochemical and electrochemical experiments

Cyclic voltammetry curves of the porphyrins D1–D5 (0.1 M DMSO) were obtained by using a CHI 660E instrument with the traditional three-electrode system by employing ferrocene as the standard. The working electrode, reference electrode, and counter electrode were a glassy C disk electrode, Ag/AgCl, and a Pt wire electrode, respectively. The linear sweep voltammetry (LSV) curves of the porphyrin-functionalized electrodes were recorded by using the same reference and counter electrodes in 0.1 M aqueous NaHCO₃ solution. The *j*-*t* curves of the cell were measured by using a two-electrode system, in which BiVO₄ served as both the reference and counter electrodes upon irradiation from a 300 W Xe lamp (PLS-SXE300). The incident light intensity was 100 mW/cm² and calibrated with a standard Si solar cell. The photovoltaic reduction of CO₂ was performed in a 100 mL aqueous NaHCO₃ solution (0.1 M) saturated with CO₂.

2.4. Artificial photosynthesis experiments

The APS cell of Dx@TiO₂||BiVO₄ was set up in a sealed quartz cell equipped with an external Si solar cell, and filled with 100 mL of the electrolyte, 0.1 M aqueous NaHCO₃ solution. The voltage of the Si solar cell was adjusted to −0.45 to −0.9 V to mimic the membrane voltage of plants, and the system was

Fig. 1. Schematic diagram of an APS cell for CO₂ reduction in water.

irradiated by using simulated sunlight with the light density of 100 mW/cm².

2.5. Analysis of products

The liquid products in the electrolyte were quantified by ¹H NMR (JNM-ECS400, JEOL) spectroscopy. 0.7 mL of the electrolyte was mixed with an internal standard solution of 0.035 mL deuterium water that contained dimethyl sulfoxide (10 mM) and phloroglucinol (50 mM). The ¹H spectra were obtained through water suppression technique [24]. The released gas products were detected by using a VARIAN CP-3380 gas chromatograph.

2.6. Isotopic labelling experiment

¹³CO₂ (Aldrich, 99%) was directly used for the isotopic labelling experiment to trace the C source by utilizing D1@TiO₂ as the photocathode. After purging the whole system with Ar gas for 30 min, 100 mL of 0.1 M NaHCO₃ was saturated with ¹³CO₂ gas in a sealed photoelectric cell.

3. Results and discussion

3.1. Characterization of porphyrin and metalloporphyrins

The UV-vis absorption spectra of TCPP (D1), CoTCPP (D2),

NiTCPP (D3), CuTCPP (D4), and PdTCPP (D5) are shown in Fig. 2a. Light absorption in these porphyrins occurs around 416 nm, which is assigned to the B band, and the several peaks observed in the range 500–700 nm are assigned to the Q bands of the porphyrin ring. These data, as well as the molar absorption coefficients, are listed in Table 1. Their ground-state oxidation potentials (E_{ox}) were determined by cyclic voltammetry (Fig. 2c) and assigned to their HOMO. The values of E_{ox} vary from 1.0 to 1.16 eV. The excitation energies ($E_{0-0} = E_{LUMO} - E_{HOMO}$) were determined to be 2.03 V for TCPP, 1.97 V for CoTCPP, 1.98 V for NiTCPP, 1.95 V for CuTCPP, and 2.01 V for PdTCPP. Therefore, their excited-state potentials (E_{S/S^*}) could be calculated from the normalized absorption and photoluminescence spectra ($E_{ox} - E_{0-0} = E_{S/S^*}$) [40], and were found to be higher than the potential for CO₂ reduction (−0.38 V for methanol). The energy-level diagrams of porphyrin, metalloporphyrins, and anatase (TiO₂) are presented in Fig. 2d.

3.2. Characterization of photocathodes

The morphologies of these photocathodes were obtained by SEM and TEM technologies and are presented in Fig. 3a and 3b, respectively. It can be seen that the TiO₂ nanoparticles are uniformly compacted onto the FTO plates and their surfaces are very flat. The APTES and porphyrin modification of the TiO₂ nanoparticles via covalent bond formation can be confirmed by the absorptions corresponding to the ν_{Si-O} stretching vibration

Fig. 2. Photophysical and electrochemical properties of porphyrins. (a) UV-vis spectra; (b) Photoluminescence spectra; (c) Cyclic voltammetry curve; (d) Calculated energy levels of the HOMO and LUMO.

Table 1

Photophysical and electrochemical properties of porphyrins.

Porphyrin	Absorption $\lambda_{\max}$ (nm) ($\epsilon/(10^3 \text{ M}^{-1} \text{ cm}^{-1})$)	Emission $\lambda_{\max}$ (nm)	E_{ox}^a (V vs. NHE)	$E_{\text{S/S}}^b$ (V vs. NHE)	E_{0-0}^c (V)
TCPP	417(273), 512(20), 547(12), 588(9), 645(6)	650	1.01	−1.02	2.03
CoTCPP	411(110), 532(16)	651	1.12	−0.85	1.97
NiTCPP	410(136), 526(16)	651	1.23	−0.75	1.98
CuTCPP	414(49), 540(8)	651	1.26	−0.69	1.95
PdTCPP	416(189), 516(19), 546(11), 588(8), 645(6)	650	1.16	−0.91	2.01

(1125 cm^{-1}) and $\nu_{\text{C}=\text{C}}$ vibration of the aryl ring (1539 cm^{-1}). On the other hand, the IR spectrum of D1@TiO₂ displays peaks in the region of 1705 to 1380 cm^{-1} , which are attributed to $\nu_{\text{C}=\text{O}}$

Fig. 3. (a) SEM image of TiO₂ electrode; (b) TEM image of TiO₂ nanoparticles; (c) FTIR spectra of the samples; (d) SEM image and elemental maps of Pd/D3@TiO₂ electrode.

and $\nu_{\text{C}-\text{N}}$ stretching vibrations (Fig. 3c). The elemental distribution map of Pd/D3@TiO₂ electrode is presented in Fig. 3d, in which the elements C, Pd, Ti, O, N, and Ni are well distributed on the surface of the electrode, which also confirmed the successful modification.

Compared with those of pure TiO₂ and APTES-modified TiO₂ (NH₂@TiO₂), the solid UV-vis absorbances of the D_x@TiO₂ photocathodes (Fig. 4a) are evidently enhanced in the range of visible light wavelengths. The band gap values can be obtained from these UV-vis data (Fig. 4b). Furthermore, the flat-band potentials of the photocathodes were determined from the Mott-Schottky (MS) plots; positive slopes in the linear region indicate that TiO₂ is an n-type semiconductor. Because the flat-band potential of the n-type semiconductor is close to the bottom edge of the CB, these flat-band potentials can also be considered as the CB potentials (Fig. 4c). These CB potentials of the photocathodes are in the range −0.65 to −0.79 V, that is, they are more negative than the potential (−0.62 V vs. SCE) required for the conversion of CO₂ to methanol. The valence band (VB) potentials of these photocathodes can be calculated and are shown in Fig. 4d. These results reveal that porphyrin molecules could shift the CB and VB potentials of the electrodes to more negative values and thus narrow their band gaps, so that they can harvest more visible light photons and have enough power to reduce CO₂ to methanol.

3.3. Characterization of the APS cells

In order to investigate the photoelectrocatalytic activities of the new cells, the LSV curves of the APS cells D_x@TiO₂||BiVO₄ were recorded on an electrochemical workstation at a scan rate of 100 mV/s in 0.1 M aqueous NaHCO₃ solution saturated with CO₂ (Fig. 5). The applied voltage varied from 0.0 to −1.0 V for this new APS system. We can clearly see that the zero current of the cell is observed at −0.43 V for D1@TiO₂, and positive current is measured between the voltages of 0.0 and −0.43 V, which indicate that oxidation reaction occurs at the working electrode; the negative current observed between −0.43 and −1.0 V suggests the occurrence of a reduction reaction at the working electrode. Therefore, the voltages of −0.45, −0.60, −0.75, and −0.90 V were chosen as the external voltages of the APS cell for CO₂ reduction.

3.4. Artificial photosynthesis of methanol

3.4.1. Effect of voltage on the new APS cells

In this new APS cell of D1@TiO₂||BiVO₄, when the voltage

Fig. 4. Photo and electrochemical properties of electrodes. (a) UV-vis spectra; (b) Band gap spectra; (c) Mott-Schottky (MS) plots; (d) Energy-level diagrams.

Fig. 5. LSV curves of $Dx@TiO_2||BiVO_4$ cells obtained in dark and light conditions.

was set to -0.45 V for the photocathode, the only methanol production could be obtained at a rate of $14 \mu M h^{-1} cm^{-2}$; when the voltage was set to -0.6 V, the formation rate of methanol increased to $51.2 \mu M h^{-1} cm^{-2}$ (Fig. 6). When the voltage crossed -0.75 V, hydrogen evolved, the amount of which could be determined and enhanced through an increase in the external voltage (Fig. 7). That is consistent with its LSV curve, in which the slope of the current evidently increases when the voltage is up to -0.75 V, due to the facilitation of the reaction

involving H_2 release, which competes against the decrease in CO_2 reduction (Fig. 8a). Therefore, -0.6 V was chosen as the best voltage for mimicking the membrane voltage of plants.

3.4.2. Effect of porphyrin on the new APS cells

The different photocathodes (D2–D5) were then assembled with $BiVO_4$ to form the new APS cells, which worked at -0.6 V under optimal conditions. The results are presented in Fig. 8b. The cell of $D3@TiO_2||BiVO_4$ with NiTCPP as the light harvester

Fig. 6. ^1H NMR spectrum of $\text{D1@TiO}_2||\text{BiVO}_4$ for 2 h APS experiment.

Fig. 7. GC spectra of $\text{D1@TiO}_2||\text{BiVO}_4$ for 2 h APS experiment at -0.75 V .

and catalyst showed the best performance towards CO_2 reduction at a rate of $55.5\text{ }\mu\text{M h}^{-1}\text{ cm}^{-2}$ and 0.92% light quantum efficiency, which are attributed to their better ability to capture protons. In contrast, the cells D2 , $\text{D4@TiO}_2||\text{BiVO}_4$ showed lower formation rates of methanol owing to the good oxidative properties of CoTCPP and CuTCPP . The cell $\text{D5@TiO}_2||\text{BiVO}_4$ also exhibited a lower formation rate of methanol owing to a higher polarization potential (0.64 V) of the photocathode (Fig. 5).

The stability and recyclability of electrodes are important factors in practice. A long-term test over 8 h was conducted for D3@TiO_2 photocathode by repeating the test every 2 h. The results are presented in Fig. 9. The catalytic activity diminished to half the original value because the porphyrin molecules serve as not only a catalyst but also a sensitizer in this APS cell.

3.4.3. Isotope labelling experiments

In order to trace the C source, $^{13}\text{CO}_2$ labelling experiments were carried out. After purging the whole system with Ar, $^{13}\text{CO}_2$ was bubbled into the electrolyte. The ^{13}C -labeled methanol was detected by using GC-MS (Fig. 10).

Fig. 8. (a) Formation rates of methanol when using $\text{D1@TiO}_2||\text{BiVO}_4$ cell under different bias potentials; (b) Formation rates of methanol when using various photocathodes at -0.6 V in 0.1 M NaHCO_3 .

3.5. Mechanism of the APS cells

On the basis of our experimental results, a possible mechanism has been proposed in Scheme 1. The electrons in the HOMO of porphyrin harvest photons and jump into the LUMO, then, the generated photoelectrons are quickly injected into the CB of TiO_2 and transferred to TCPPs, where they can be captured by the protons adsorbed on the metal and N atoms of the Lewis base center to produce H atoms. The CO_2 molecules activated by the N of the amide or the N of metalloporphyrin are then reduced immediately to methanol by these highly active H atoms, like in a Calvin cycle. When the electrons of OH^- groups are transferred to the BiVO_4 photoanode and then flow through an external circuit, O_2 would be released. The external elec-

Fig. 9. Stability tests for the electrode of D3@TiO_2 .

Fig. 10. GC-MS plot for liquid detection of $^{13}\text{CH}_3\text{OH}$ ($m/z = 33$).

trons fill the HOMOs of the porphyrin molecules under the action of voltage, thus mimicking the membrane voltage of leaves and completing the recovery of the porphyrin molecules. When the OH^- groups directly donate electrons to the HOMOs of porphyrin, the photocatalytic CO_2 reduction can proceed without involving the electrons of the external circuit, which results in a high quantum efficiency for this APS cell.

3.6. Comparison with the results reported in the literature

To better understand the advantages of our new APS system, the recently reported results for the use of metalloporphyrin as catalysts are summarized in Table 2. The formation rate of methanol could be changed to $8333 \mu\text{mol h}^{-1} \text{g}^{-1}$ in the case of an average weight of 1.25 mg of TiO_2 . This result is really superior to the results reported in the literature.

4. Conclusions

A new APS cell that consists of a photocathode of metalloporphyrin-functionalized TiO_2 and a modified BiVO_4 photoanode was designed for CO_2 reduction in water. This PEC system can mainly produce methanol at a high efficiency without using a sacrificing agent. The excellent results imply that the metalloporphyrin molecules covalently linked on the surface of anatase (TiO_2) could play the roles of chlorophyll, NADP, and Calvin cycle in the CO_2 reduction. The highest optical quantum efficiency of the conversion of CO_2 and water to methanol without any side-product by using nickel porphyrin-modified TiO_2 photocathode in D3@TiO_2 can be up to

Scheme 1. Proposed mechanism of a metalloporphyrin-based APS cell.

0.92%, which is about two times that of a plant cell. A new mechanism of APS was proposed, in which metalloporphyrins could behave as a sensitizer, light absorber, and catalyst. Accordingly, this new APS system obviously demonstrates the synergetic effect of electrocatalysis and photocatalysis, which leads to excellent APS performance of cells, thus providing a new way to enhance the light absorbance and improve the efficiency of PEC CO_2 reduction to value-added chemicals.

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Table 2

New APS result compared with the literature results.

Matrix	Porphyrin	Condition	Product	Rate ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	Selectivity (%)	Quantum efficiency (%)	Ref.
CNT	TPPCo	Electro	CO	—	>90	—	[51]
None	TPPZn	Photo	CO	—	>90	None	[52]
P25	TPPCu	Photo	CO	15.5	>90	None	[53]
			CH_4	2.3			
P25	ZnP_{CNPA}	Photo	CO	103	>90	None	[54]
None	TDHPPFe	Electro	CO	—	>90	—	[55]
P25	TPPNi	Photoelectro	CH_3OH	8333	100	0.92	This work

Graphical Abstract

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Metalloporphyrin molecules were covalently anchored to the surface of TiO₂ that mimic chlorophyll, NADP and Calvin cycle in CO₂ reduction, improving the efficiency of artificial photosynthesis cells to methanol in 0.92% quantum efficiency.

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卟啉修饰的光阴极用于光电催化二氧化碳还原

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摘要: 将二氧化碳有效地转化为高附加值化学品是人类的梦想, 尤其是通过光电催化实现该过程更加令人期待. 本文报道了一种新的人工光合成体系, 它是由金属卟啉配合物修饰的二氧化钛光阴极以及羟基氧化铁和羟基氧化镍修饰的钨酸铋光电阳极构成, 电解液是0.1 M碳酸氢钠水溶液. 该体系在有硅太阳能电池供电和一个标准太阳下工作. 在外加电压为−0.6 V时, 甲醇是光电池的唯一产物, 同时放出氧气; 生成甲醇的速率是55.5 $\mu\text{M h}^{-1} \text{cm}^{-2}$. 当外加电压大于−0.75 V时, 光电催化电池有氢气生成.

卟啉和金属卟啉按照文献合成并命名为Dx, 即D1 (*meso*-tetra-*p*-carboxyphenylporphyrin), D2 (CoTCPP), D3 (NiTCPP), D4 (CuTCPP), 和D5 (PdTCPP). 制备电极时, 首先将P25粉涂覆在FTO玻璃上, 然后经胺丙基三乙基硅烷(APTES)修饰, 再与Dx反应生成酰胺键, 从而实现卟啉染料与TiO₂半导体材料的共价键键合, 制备的系列电极记为Dx@TiO₂. 对卟啉和金属卟啉进行了紫外吸收、发射光谱(PL)、核磁共振和电化学循环伏安测试等检测, 以及简单的DFT计算. 对制备的光电阴极进行了红外光谱、固体紫外和电化学交流阻抗测试, 计算了电极的Mott-Schottky曲线, 得到了电极材料的平带电位, 对于n型半导体, 一般认为是近似的导带电位(CB). 所有电极的CB电位均高于−0.56 V, 高于甲醇生成需要的电位−0.38 V. 经过卟啉修饰的电极材料, 其能带结构发生了根本变化, 由TiO₂锐钛矿的3.2 eV降低到了2.37–2.73 eV. SEM及其元素分布彩色图表明所需元素都均匀分布在电极表面. 电化学线性伏安扫描图表明, 在光照条件下电流的提升是能带修饰和降低的结果. 最好的光阴极在光电还原电池D3@TiO₂/NaHCO₃/BiVO₄中, −0.6 V条件下, 一个标准太阳光照射2 h, 生成甲醇的光量子效率用500 nm光子估算为0.92%, 达到了自然界植物光合作用效率的2倍. 循环实验表明, 光阴极经过4次2 h照射后仍有约50%的催化效力, 性能的减弱主要来自卟啉作为光敏剂的消耗. 在这一新的光电催化二氧化碳还原系统中, 由于卟啉修饰的TiO₂半导体材料表面构筑了合适的3D结构空间、敏化剂和催化剂, 形成了对天然植物细胞和Calvin循环的有效模拟, 因而提高了人工光合成的效率. 同位素标记实验(¹³CO₂)证实了产物甲醇来自CO₂气体. 与文献报道的卟啉催化体系相比, 本文新催化体系的主要产物是甲醇而不是CO, 而且新催化体系的效率是文献报道的80–500倍.

关键词: 人工光合成; 二氧化碳还原; 光电催化; 金属卟啉配合物; 二氧化钛

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