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Efficient photoelectrocatalytic CO₂ reduction by cobalt complexes at silicon electrode

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ABSTRACT

Two homogeneous photoelectrocatalytic systems composed of simple polypyridyl Co complexes [Co(tpy)₂](PF₆)₂ and [Co(bpy)₃](PF₆)₂ as electrocatalysts and a Si wafer as the photoelectrode were used for combined photoelectrochemical reduction of CO₂ to CO. A high photocurrent density of 1.4 mA/cm² was observed for the system with the [Co(tpy)₂](PF₆)₂ catalyst and a photovoltage of 400 mV was generated. Faradaic efficiencies of CO were optimized to 83% and 94% for the [Co(tpy)₂](PF₆)₂ and [Co(bpy)₃](PF₆)₂ complexes, respectively, in acetonitrile solution with 10% methanol (volume fraction, same below) as a protic additive. Addition of 2% water volume fraction induced a large amount of non-specific H₂ evolution by the Si photoelectrode.

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Utilizing abundant solar energy to drive carbon dioxide (CO₂) reduction is a promising method to convert renewable energy to value-added chemicals [1,2]. Integrating molecular electrocatalysts with semiconductor photoabsorbers is an attractive approach to obtain efficient photoelectrochemical (PEC) systems for CO₂ conversion. Over the past three decades, molecular electrocatalysts based on precious metals have been commonly investigated because of their high selectivity and efficiency [3–11]. Only a few earth-abundant metal-based molecular electrocatalysts, such as iron, cobalt (Co), nickel, and manganese (Mn) complexes, have been investigated [12–19]. Semiconductor materials based on metal oxides, chalcogenides, and silicon (Si) are able to efficiently separate photogenerated charges, thus enhancing photoelectric conversion efficiency and reaction kinetics [3,7,11,16,17,20]. Incorporation of noble metal electrocatalysts into semiconductor PEC systems has

been mostly investigated for homogeneous and heterogeneous CO₂ catalytic reduction systems [3,5,7,11]. In contrast, PEC systems composed of non-precious metal complexes and semiconductor photoabsorbers have rarely been reported. Very recently, Reisner et al. [21] constructed mesoporous titanium dioxide functionalized with Mn complex for highly efficient CO₂ reduction in acetonitrile (MeCN); using this system, a turnover number of 112 was obtained at an overpotential of 420 mV. Fabre et al. [16] reported that a Si nanowire photocathode could effectively enhance the energy conversion efficiency of Mn carbonyl bipyridyl electrocatalysts for selective CO₂ reduction. Wang and co-workers [17] constructed a conjugated Co complex and Si photoelectrocatalytic system and investigated the effects of water and material morphology on its performance.

Herein, we demonstrate a hybrid PEC system combining a Si

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photoelectrode and Co complex electrocatalysts [22] for CO₂ reduction to carbon monoxide (CO). Adding a small amount of a proton source can greatly improve catalytic selectivity, which may shed light on enhancing the performance of CO₂ catalytic reduction systems.

To examine the electrochemical properties of the Co complex electrocatalysts (Scheme 1), cyclic voltammetry (CV) was carried out in dry MeCN solution using a glassy carbon working electrode. For complex **1**, two reduction waves were observed at peak potentials of −0.58 and −1.59 V vs. NHE under argon (Ar), as shown in Fig. 1. Wave I at peak potential of −0.58 V is assigned to reduction of Co^{II} to Co^I, and wave II at peak potential of −1.59 V is assigned to ligand-based reduction. When the

Scheme 1. Structures of [Co(tpy)₂](PF₆)₂ (catalyst **1**) and [Co(bpy)₃](PF₆)₂ (catalyst **2**).

electrolyte was saturated with CO₂, wave I remained the same, but the current of wave II increased by ca. three-fold, suggest-

Fig. 1. CVs of 1 mmol/L of catalyst **1** (a) and catalyst **2** (b) in MeCN + 0.1 mol/L Bu₄NPF₆ at a glassy carbon electrode under Ar and CO₂. Reference electrode: Ag/AgCl; counter electrode: platinum (Pt) wire; scan rate: 50 mV/s.

Fig. 2. CVs of 1 mmol/L of catalyst **1** (a, c) and catalyst **2** (b, d) in MeCN + 0.1 mol/L Bu₄NPF₆ at a glassy carbon electrode with added water under Ar (a, c) and CO₂ (b, d). Reference electrode: Ag/AgCl; counter electrode: Pt wire; scan rate: 50 mV/s.

ing the onset of electrocatalytic activity of **1** toward CO₂. Similarly, complex **2** displayed two reduction waves at potential of −0.67 and −1.49 V under Ar, and the current of the latter wave was enhanced ca. two-fold under CO₂.

The effect of addition of water as a proton source on the electrocatalytic activity of the catalysts was investigated (Fig. 2). When 0.8%–1.6% water was added under Ar, wave I and II of **1** were essentially unchanged. Conversely, under CO₂, the catalytic current of wave II increased by 50% compared with that in dry MeCN, thus indicating that adding water is advantageous for electrocatalysis. For catalyst **2** under CO₂, the catalytic current of wave II also increased with water addition, although enhancement was not as large as that of catalyst **1**, indicating that catalyst **1** is a more efficient electrocatalyst than **2**.

The electrochemical properties of the Co complexes were further investigated by varying the scan rate of CVs. CVs of **1** at

various scan rates were plotted with the current normalized by dividing the original current by the square root of scan rate. Under Ar, the normalized currents of both wave I and II overlapped at various scan rates, suggesting that the currents of wave I and II are diffusional with no catalysis (Fig. 3(a)). Under CO₂, normalized currents of wave II at lower scan rates are higher than those at higher scan rates, confirming that the process under wave II is electrocatalytically active toward CO₂ (Fig. 3(b)).

When 0.8% water was added to **1** under Ar, the normalized currents still overlapped with each other at different rates, suggesting that **1** did not actively catalyze hydrogen (H₂) evolution (Fig. 3(c), (e)). Under CO₂, adding water increased the catalytic current, suggesting that the catalysis is accelerated in the presence of water (Fig. 3(d), (f)). Catalyst **2** demonstrated similar behavior under both dry and wet conditions (Fig. S2). The

Fig. 3. CVs with current normalized of 1 mmol/L of catalyst **1** in MeCN + 0.1 mol/L Bu₄NPF₆ at a glassy carbon electrode under saturated Ar (a) without water and with (c) 0.8% water and (e) 1.6% water. The same system under 0.1 MPa of saturated CO₂ (b) without water and with (d) 0.8% v/v water and (f) 1.6% v/v water. Reference electrode: Ag/AgCl, counter electrode: Pt wire, scan rate: 10–200 mV/s.

Fig. 4. Product distribution after controlled potential electrolyses with 1 mmol/L of (a) catalyst **1** or (b) catalyst **2** in MeCN + 0.1 mol/L Bu₄NPF₆ at a glassy carbon working electrode. Reference electrode: Ag/AgCl; counter electrode: Pt wire.

above results suggest that adding a small quantity of water is advantageous to enhance catalytic current. Although the mechanism of this effect of water is unclear, it is possible that water may protonate the transient metal carboxylate species and thus promote CO formation.

The product selectivity of catalyst **1** (Fig. 4(a)) and **2** (Fig. 4(b)) was investigated under dry and wet conditions by controlled potential electrolysis measurements. After electrolysis at -1.5 V (vs. NHE), the Faradaic efficiency of CO increased from 79% under dry conditions to 90% with 2% added water for catalyst **1**. In contrast, adding water to catalyst **2** increased H₂ evolution and lowered the CO production efficiency from 95% under dry conditions to 67% with 2% added water.

Semiconductor Si is capable of improving photoelectric conversion efficiency [16]. Therefore, PEC reduction of CO₂ was performed in MeCN solutions of **1** and **2** using a silicon planar photocathode (SiPL). Comparing the CVs under dark and light conditions revealed that a photovoltage of about 400 mV was generated and the photocatalytic current of wave II for **1** and **2** was enhanced under saturated CO₂ (Fig. 5).

Vertically aligned Si nanowire arrays (Fig. S1) were also used to evaluate the photoelectrocatalytic performance of the catalysts because of their excellent charge separation and photoelectric conversion effect [16]. CVs of 1 mmol/L of catalyst **1** in MeCN + 0.1 mol/L Bu₄NPF₆ at the Si nanowire electrode under CO₂ indicated that a photovoltage of about 600 mV was generated (Fig. 6). Although the photovoltage of the Si nanowire electrode is larger than that of SiPL, which is preferable to lower the overpotential, non-specific H₂ evolution occurred markedly at the nanowire photoelectrode even in formally dry MeCN solution; thus, the Si nanowire electrode was not used for further study.

As was reported, protic additive could overcome the mass transfer limitation of interface between electrode and electrolyte [3]. To test this protic additive effect, 2%-10% methanol was added to catalyst solution. As was illustrated, after 10% methanol was added in catalyst solution, the photocurrent was obviously enhanced and the onset potential positively shifted for ca. 200 mV, indicating catalytic enhancement effect of protic additive (Fig. 7).

Fig. 5. CVs of 1 mmol/L of (a) catalyst **1** and (b) catalyst **2** in MeCN + 0.1 mol/L Bu₄NPF₆ at SiPL under Ar and CO₂. Reference electrode: Ag/AgCl; counter electrode: Pt wire; scan rate: 50 mV/s.

Fig. 6. CVs of 1 mmol/L of (a) catalyst **1** and (b) catalyst **2** in MeCN + 0.1 mol/L Bu₄NPF₆ under CO₂ at a Si nanowire electrode. Reference electrode: Ag/AgCl; counter electrode: Pt wire; scan rate: 50 mV/s.

Fig. 7. CVs of a solution of 1 mmol/L of (a) catalyst **1** and (b) catalyst **2** in MeCN + 0.1 mol/L Bu₄NPF₆ with 10% methanol (1) or without methanol (2) as a protic additive under CO₂ at SiPL. Reference electrode: Ag/AgCl; counter electrode: Pt wire; scan rate: 50 mV/s.

Fig. 8. Photostability of SiPL in a solution of 1 mmol/L of catalyst **1** in MeCN + 0.1 mol/L Bu₄NPF₆ under CO₂. Reference electrode: Ag/AgCl; counter electrode: Pt wire.

Chronoamperometry and chopped light analysis were performed to evaluate the photoelectrode stability in this system. A solution of 1 mmol/L of catalyst **1** in MeCN + 0.1 mol/L

Bu₄NPF₆ at SiPL under CO₂ was tested. During 14 h of electrolysis at -1.4 V, the current decayed by less than 30% (Fig. 8). Chopped light experiments indicated that the current increased linearly with the applied potential, and the photocurrent varied instantaneously with illumination, further confirming the outstanding photoelectric response and stability of the electrode (Fig. 9).

Methanol was also added to the PEC system as an alternative proton source to water. When 10% methanol was added to an MeCN solution of **1** during photoelectrolysis at -1.6 V, the steady-state current increased by ca. 2.3 fold relative to that in pure MeCN (Fig. 10(a)). Similar current enhancement was observed for **2** (Fig. 10(b)). The selectivity for CO increased with the addition of methanol (Fig. 11). After CPE at -1.5 V (vs. NHE) with added methanol under white light, the Faradaic efficiency of CO production by **1** rose from 49% to 83% (Fig. 11(a) and (b)) and that by **2** increased from 60% to 94% (Fig. 11(c) and (d)), while the Faradaic efficiencies of H₂ and methane (CH₄) production decreased. When no catalyst was added with 10% methanol under CO₂, the Faradaic efficiency of CO formation

Fig. 9. Chopped light response of SiPL in a solution of 1 mmol/L of catalyst **1** in MeCN + 0.1 mol/L Bu₄NPF₆ under CO₂. Inset: SiPL without catalyst. Reference electrode: Ag/AgCl; counter electrode: Pt wire. Thorlab LED light, wavelength 400–1100 nm.

Fig. 10. Chronoamperometry of 1 mmol/L of (a) catalyst **1** and (b) catalyst **2** in MeCN + 0.1 mol/L Bu₄NPF₆ with 10% methanol (1) as a protic additive or without methanol (2) under CO₂ at SiPL. Reference electrode: Ag/AgCl; counter electrode: Pt wire. Thorlab LED light source, wavelength 400–1100 nm.

Fig. 11. Product distribution after CPE using 1 mmol/L of catalyst **1** (a) without and (b) with 10% methanol in MeCN + 0.1 mol/L Bu₄NPF₆ at SiPL. Product distribution after CPE using 1 mmol/L of catalyst **2** (c) without and (d) with 10% methanol in MeCN + 0.1 mol/L Bu₄NPF₆ at SiPL. Applied potential: -1.5 V (vs. NHE); reference electrode: Ag/AgCl; counter electrode: Pt wire. Thorlab LED light source, wavelength 400–1100 nm.

after bulk electrolysis was 14%; the rest being H₂ and a trace amount of CH₄. Also, after adding 2% water, because of the competitive H₂ evolution reaction, Faradaic efficiencies for CO production lowered to 42% (Fig. S3). These results suggest that methanol is a superior proton source over water for PEC re-

duction of CO₂ to maximize CO selectivity.

In summary, two homogeneous photoelectrocatalytic systems composed of cobalt terpyridine and bipyridine complexes and a Si photoelectrode were investigated for efficient and selective CO₂ reduction. The system consisted of readily prepared

Graphical Abstract

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Efficient photoelectrocatalytic CO₂ reduction by cobalt complexes at silicon electrode

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A photoelectrochemical system based on earth-abundant materials for reducing CO₂ to CO is reported. The electrocatalysts are simple cobalt polypyridyl complexes that demonstrate high CO selectivity. Adding methanol as a proton source promotes CO formation.

complexes containing earth-abundant elements. Si as a photo-absorber was critical to lower the overpotential and increase catalytic current. Faradaic efficiencies for CO production reached 83% for the cobalt terpyridine complex and 94% for the cobalt bipyridine complex in MeCN solution with added methanol; adding methanol increased CO selectivity. A photovoltage of approximately 400 mV was generated and the photocurrent was stable during bulk electrolysis. This system is cost-effective and environmentally friendly, revealing a design to realize more efficient catalysts for CO₂ reduction.

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钴联吡啶配合物在硅电极表面高效光电催化二氧化碳还原反应

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摘要: 光驱动二氧化碳还原实现可再生能源转化近年来引起普遍关注. 利用小分子金属配合物电催化剂和吸光半导体材料构建的光电催化体系兼具电催化剂的高选择性和光电极的高光电转化效率等优点, 在能源催化领域的应用日益广泛. 已有将贵金属配合物催化剂用于光电催化二氧化碳还原的研究报道, 但催化剂成本较高且制备方法不简便, 在规模化实际应用中受到局限. 基于早期的研究报道, 我们发现非贵金属多联吡啶铁钴镍配合物在乙腈电解质中能高选择性电催化还原二氧化碳. 结合半导体材料的特异性电荷分离性能从而将光能高效转化为电能驱动催化反应进行, 我们选择廉价且易于制备的多联吡啶钴配合物催化剂, 利用半导体硅晶片光电极, 实现了均相体系二氧化碳的高效光电催化还原. 我们采用

电化学循环伏安法和恒电位电解法分别研究了催化剂在干燥和加水电解质环境中的催化还原行为,并且进一步研究了微量质子源的加入对半导体界面催化过程的影响,从而提出一种能改善半导体光电催化体系选择性的新方法。

首先我们构建了电化学三电极体系,研究了在暗环境下三联吡啶钴和二连吡啶钴这两种配合物催化还原二氧化碳的电流密度和电解产物分布情况。由循环伏安曲线发现,这两种配合物都有两组催化还原峰,第二个基于吡啶配体还原的峰具有明显的催化特性。少量水的加入能进一步增加催化电流强度,而三联吡啶钴配合物的催化增强效果更加显著。在变扫速条件下将电流密度对扫速平方根进行归一化处理,发现无论在干燥环境还是少量加水环境下,两种催化剂的归一化电流密度均随扫速降低而明显增强,证明了催化剂具有电催化特性。推测水的催化增强作用可能与质子化电催化过程活性中间体有关。恒电位电解结果说明电催化产物以一氧化碳为主。基于上述研究,我们构建了光电化学三电极体系,以单晶硅片为工作电极,研究了在光照环境下这两种配合物催化还原二氧化碳的电流密度和电解产物分布情况。研究发现,催化剂对二氧化碳仍具有催化活性,光电压为400 mV。不同于硅线电极加水导致产氢,改用少量甲醇做质子源后,光电流强度进一步增强,竞争性产氢受到了抑制,从而使一氧化碳的法拉第效率得到显著提高,分别优化为94%和83%,并且光电流在14 h内保持稳定。推测甲醇质子源的催化增强作用可能是与改变光电极液接界面传质动力学过程有关。

关键词: 光电催化体系; 分子电催化剂; 二氧化碳还原; 一氧化碳; 联吡啶配合物

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