



Photo- and thermo-coupled electrocatalysis in carbon dioxide and methane conversion

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With the large-reserve discovery and exploitation of shale gas and natural gas hydrate all over the world, the production of liquid fuels and basic chemicals by replacing petroleum with abundant shale gas and natural gas hydrate has become the focus of research and development in academia and industry. CO₂ and CH₄, as the main composition of shale gas and natural gas hydrate, are extremely stable and chemically inert, and thus selective activation and conversion of the two molecules remain grand challenges since the desired high-value products are more reactive than CO₂ and CH₄. Attributed to anthropogenic activities, billion tons of CO₂ and CH₄ are directly exhausted per year, and therefore, it is necessary to open up new routes to utilize the small molecular resource (Fig. 1).

Electrocatalysis at mild conditions has been recognized as a promising and alternative route for conversion of CO₂ and CH₄. However, the electrocatalytic conversion process still suffers from poor selectivity, low reaction rate and insufficient energy conversion efficiency. To overcome the above challenges, external energy input such as solar and thermal energy is expected to promote electrochemical activation of CO₂ and CH₄, and accelerate the reaction at the electrochemical interface. The key challenges and possible opportunities for photo- and thermo-coupled electrocatalysis in CO₂ and CH₄ conversion are discussed here.

PHOTO-COUPLED ELECTROCATALYSIS IN CO₂ AND CH₄ CONVERSION

Compared with electron utilization above 80% *via* electrocatalysis, photocatalysis usually shows much lower photon utilization below 5%, indicating that most of solar energy is lost (Fig. 2a and b). In the past decade, a series of studies about heterogeneous photocatalysts, photo-

catalytic systems and reactor design show a feasible route to convert CO₂ and CH₄. However, the low yield is still a significant challenge in photocatalysis [2,3]. Accordingly, extensive reports propose that external bias input can significantly facilitate the electron-hole separation, and thus photocatalytic activity (Figs 2c and 3a) [4]. Furthermore, a series of studies have reported that the solar-driven electrocatalytic CO₂ reduction provides a new possibility to meet the above-mentioned challenges in photocatalysis (Fig. 2d). In this system, the photovoltaic (PV) component can convert solar energy directly into electric energy. Meanwhile, the electrochemical cell (EC) accepts the electricity for hydrocarbon and oxygen production. The coupling of the PV and electrocatalytic devices can help us to make more use of solar energy in large-scale application. Although the PV system transforms the solar use-pattern, it does not alter the electrocatalytic nature. Therefore, whether the light field could directly promote the activation and conversion of CO₂

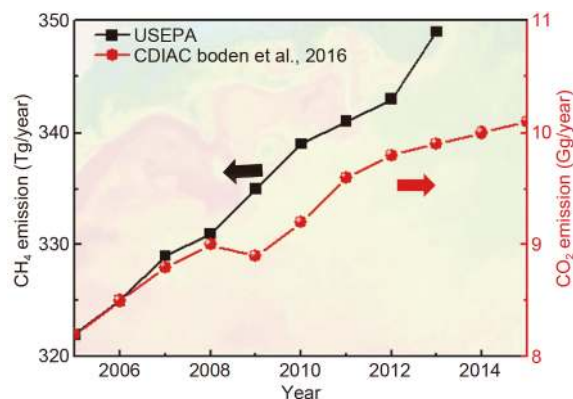


Figure 1 Emissions of CO₂ and CH₄ from anthropogenic sources. For CH₄, emission data (black curve) are plotted from USEPA inventory. For CO₂, emission data (red curve) are plotted from CDIAC [1].

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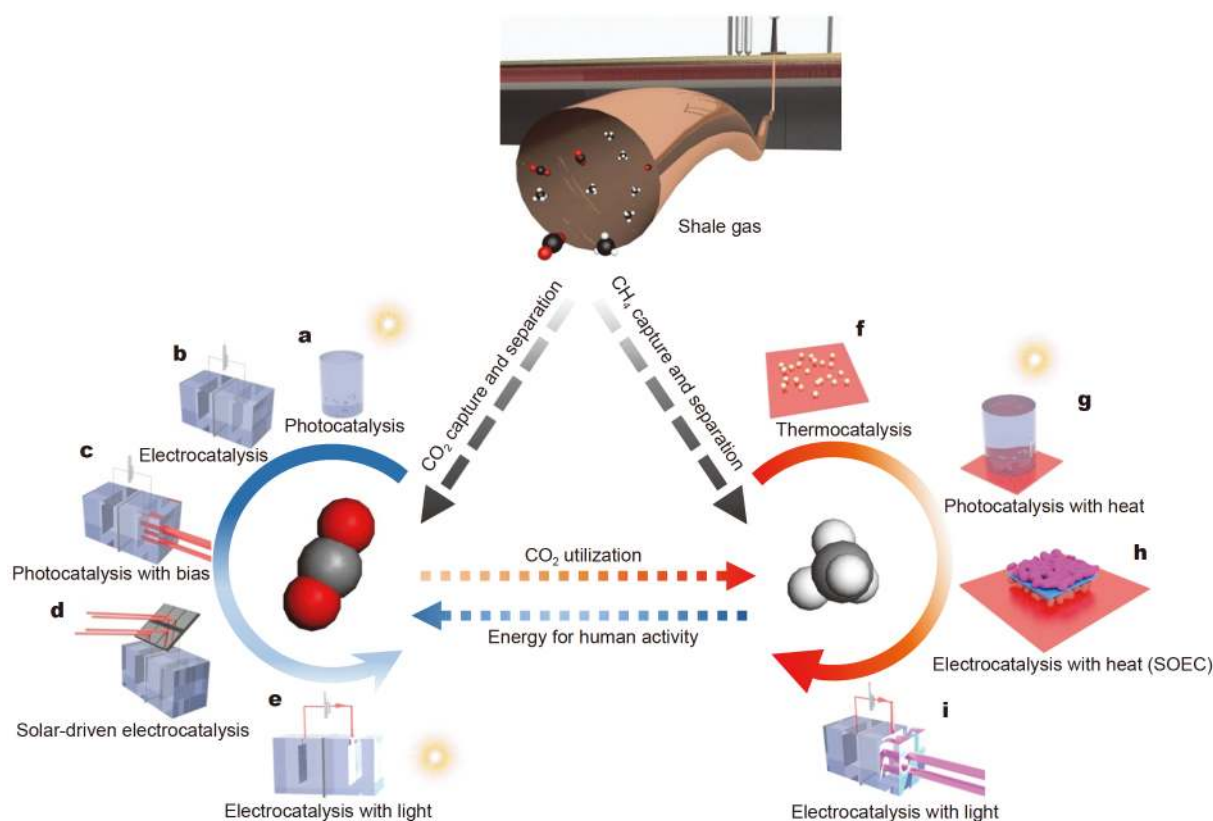


Figure 2 Schematic of photo- and thermo-coupled catalysis in CO_2 and CH_4 conversion. The schematic shows electrocatalysis, photocatalysis, photoelectrocatalysis and other promising photo/thermo-coupled catalysis in CO_2 (left side) and CH_4 (right side) conversion.

and CH_4 on specific electrocatalysts seems to be neglected but meaningful point.

The central challenge to activate CO_2 and CH_4 is their low molecular reactivities, which usually require high overpotential or high temperature for initial bond dissociation. When light field is introduced into traditional electrocatalysis, the electronic property of specific electrocatalysts will be easily interfered, such as electron transfer, band-bending, Fermi level and desorption energy of intermediate, and all of these factors will distinctly alter the intrinsic catalytic pathway and performance. Compared with single electrocatalysis, light-coupled electrocatalysis exhibits great potential for small molecules activation at low overpotential with high energy efficiency.

Additionally, the development of photo-coupled electrocatalysts can also play a vital role in this field (Fig. 2e). As previously reported, the catalysts possess two general features, high electrocatalytic activity for CO_2 and photosensitized structure. We must stress that it usually consists of three components, including photosensitizer as light harvester, semiconductor as electron mediator and metal component as CO_2 activator (Fig. 3b) [5].

Recently, Huang *et al.* [6] reported a semiconductor/metal-complex hybrid photoelectrocatalyst. According to this study, light-induced upward band-bending of Co_3O_4 /carbon aerogel (CA) lifted the Fermi level, which derived CO_2 reduction reaction (CO_2RR) at a relatively low onset potential of $-0.45\text{ V vs. normal hydrogen electrode (NHE)}$, positive shift of 160 mV than thermodynamic redox potential. Another heterostructured electrode was also applied for light-coupled electrochemical reduction of CO_2 in 2015 by decorating metallic Cu nanoparticles on the Co_3O_4 nanotube arrays (NTs) [7]. The current transformation efficiency of Cu- Co_3O_4 NTs electrode reaches a maximum of 62.9% at -0.89 V while it increases to 77.5% at -0.87 V under visible light, indicating that light field can assist to lower the electrochemical barrier and promote the electrode kinetics. It is worth mentioning that these hybrid structures not only increase the difficulty of synthesis, but also lower the interior stability.

Therefore, it is urgent to precisely design and synthesize the catalytic structure at the atomic scale, yet there are few reports for us to discuss. Metal-porphyrin and metal-phthalocyanine complexes are used as single-atom

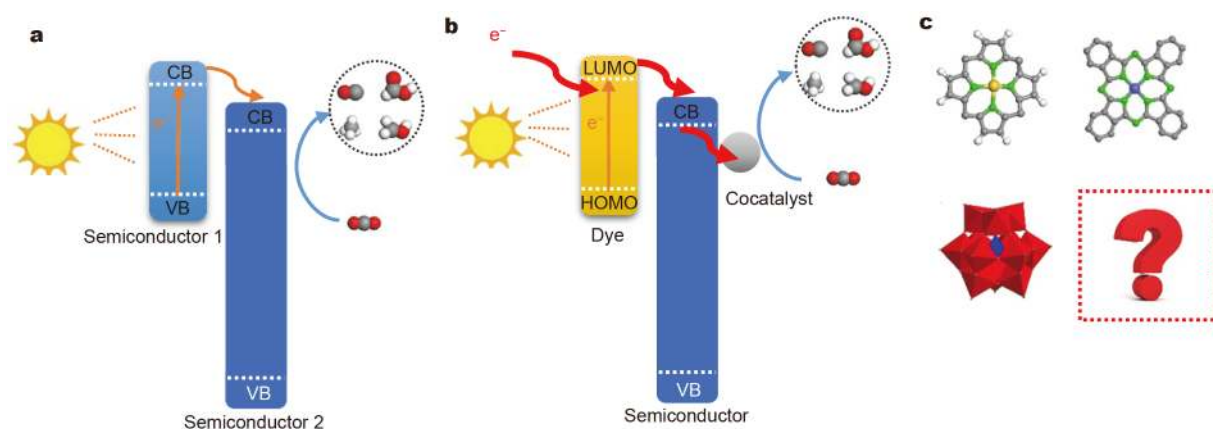


Figure 3 Schematic mechanism for the photoelectrochemical reduction of CO_2 . (a) Electron transfer on hybrid photocatalyst. (b) CO_2 reduction on photo-coupled electrocatalyst. (c) Promising photo-coupled electrocatalyst, for example, metal-porphyrin, metal-phthalocyanine, metal-polyacid complex and other catalysts.

catalysts in electrocatalysis as well as photosensitizers in photocatalysis, which meet the requirements for “photo-coupled electrocatalyst” (Fig. 3c). Furthermore, their electronic performance is susceptible to conjugative perturbation of 18π aromatic macrocycle, and hence rational external fine-tuning (light field) may drastically alter the electronic structure of catalytic site. It is expected that more and more well-designed catalysts, such as single atom catalysts, nanocluster catalysts (polyacids) and nanocrystalline catalysts will be designed and applied in this field.

CH_4 is another important carbon source consisting of around 90% shale gas. And the stable symmetrical structure and high C–H bond energy (434 kJ mol^{-1}) make it difficult to activate at mild temperature, particularly at room temperature (Fig. 2f). Recently, Xie *et al.* [8] successfully used photoenergy to drive CH_4 oxidation reaction on $\text{FeO}_x/\text{TiO}_2$ at room temperature. Therefore, it is reasonable to anticipate a possible alternative route by employing photoenergy instead of thermal energy, to achieve electrocatalytic conversion of CH_4 at low temperature (Fig. 2i). According to previous reports, the Pt group metals have been used as anode for electro-oxidation of CH_4 due to their high intrinsic activity. Through integrating atom-, cluster- or nanoparticle-sized Pt-based materials with photosensitive materials (for example, TiO_2 , MoO_3 , WO_3 and CdS), a synergistic effect is highly expected to promote CH_4 conversion.

THERMO-COUPLED ELECTROCATALYSIS IN CO_2 AND CH_4 CONVERSION

Electrochemical oxidation of CH_4 has been investigated for several decades, and electro-generated oxygen-con-

taining species activate CH_4 to produce methanol, ethylene, etc. [9]. However, over-oxidation is difficult to be inhibited and a considerable amount of CO_2 is inevitable in the final products. Based on the type of electrolyte materials, the operation temperature of electrolyzer can be varied between room temperature and 850°C . At a temperature lower than 300°C , methanol is produced with a considerable selectivity but a poor yield. At 800°C or higher temperature, solid oxide electrolysis cell (SOEC) has been investigated to electrochemically convert CH_4 into C_2H_4 with much increased conversion and selectivity (Fig. 2h) [10,11]. Since the operation temperature of SOEC is similar to that in thermocatalysis, it is possible that both direct electro-oxidation and thermo-oxidation by electrochemically evolved oxygen at the anode of SOEC would occur simultaneously.

Non-oxidative electrochemical dehydrogenation using SOEC with proton-conducting electrolyte membrane is proposed as a promising strategy to convert CH_4 to C2+ chemicals at intermediate temperature ($300\text{--}600^\circ\text{C}$). At the SOEC anode, the protons are split from CH_4 and transport across the electrolyte membrane to generate H_2 at the cathode, while the remaining methyl group, either a radical, a cation, or an anion combines together to produce C2+ chemicals. The separate production of C2+ chemicals and H_2 could increase the conversion efficiency, which simultaneously generate H_2 and chemicals. The process would be potentially economical and environmentally friendly.

Electrochemical CO_2 reduction reaction pathway is complex, and the product selectivity is low, especially for C2+ chemicals due to difficult C–C coupling. The widely-investigated CO_2RR is in aqueous electrolyte, and major

advancement has been achieved in recent years. Ethylene with a maximum Faradaic efficiency of 70% has been obtained over Cu catalysts [12]; however, the current density and energy efficiency are still required to be greatly improved. At intermediate and high temperatures (450–850°C), molten salt CO₂ capture and electrochemical transformation (MSCC-ET) process has shown promising applications in advanced functional carbon materials [13]. An apparent advantage for MSCC-ET process not only has no poisoning effect of NO₂ and SO₂ on the electrode catalysts, but also can produce S/N-doped carbon materials, which show high performance in super-capacitors, lithium ions batteries, fuel cells and catalysis.

SOEC is another promising device for efficient CO₂RR with several advantages, such as high Faradaic efficiency, current density and energy efficiency. A commercial SOEC system using oxygen-ion conducting yttria-stabilized zirconia (YSZ) as the electrolyte membrane has been demonstrated in 2016 for small-scale and high-purity (99.95%–99.999%) CO production by Haldor Topsoe Corp. Recently, using an SOEC with proton conducting electrolyte membrane BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-δ}, CH₄ was produced with a Faradaic efficiency of ~60%, and the selectivity can be further improved to ~100% when using a Ni/CeO₂ catalyst to promote the methanation of syngas and CO₂ hydrogenation [14].

SOEC also provides a reaction platform to simultaneously convert CO₂ and CH₄ into chemicals *via* thermo-coupled electrocatalysis, which has been demonstrated in SOEC with oxygen-ion conducting electrolyte membrane. An ideal strategy to convert CO₂ and CH₄ into high-value C₂₊ chemicals is SOEC with proton-conducting electrolyte membrane at intermediate temperatures (300–600°C). However, CO₂ is prone to react with the electrolyte materials and decrease the proton conductivity. A feasible way is to decrease CO₂ concentration in the fed gas and match the consumption of CO₂ during the CO₂RR, which is also of practical significance to eliminate the carbon dioxide enrichment step. The other challenge is to promote the C–C coupling and improve the selectivity of C₂₊ chemicals derived from CO₂ and CH₄ conversion while inhibiting carbon deposition. Thus, developing CO₂-tolerant proton-conducting electrolyte and highly selective catalysts as well as constructing robust electrochemical interfaces is vital to promote practical applications of SOEC in the near future.

CONCLUSION AND PERSPECTIVE

The catalytic conversion of CO₂ and CH₄ requires huge

energy input. The electrocatalysis can be powered by renewable electricity, which is abundant and cheap. In order to achieve considerable reaction conversion and rate, electrocatalysis should also be coupled with the photo- and thermo-catalysis. The synergistic effect between CH₄/CO₂ activation and photo/thermal field is expected to promote a high catalytic performance and make the catalytic conversion more economically viable.

Furthermore, the combination of *in situ/operando* spectroscopy and microscopy techniques, such as X-ray diffraction, X-ray absorption spectroscopy, ambient-pressure X-ray photoelectron spectroscopy, etc, and theoretical calculations are urgently needed to provide new insights into the coupling catalytic reaction mechanism. The atomic understanding of photo- and thermo-coupled catalytic conversion of CO₂ and CH₄ would help to develop active catalytic materials and efficient catalytic processes.

Apart from the fundamental research, many efforts are urgently needed to push forward the potential industrial applications. The scale-up design and assembly of catalytic reactor are vital to demonstrate the advantages of coupling catalysis. The activity and selectivity toward desired products as well as the energy efficiency and durability should simultaneously meet the requirements of industrial applications.

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Author contributions Wang X proposed and guided the project. Yang D and Wang G wrote the paper. Wang X and Wang G revised the manuscript. All authors joined the discussion and gave useful suggestions.

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



Deren Yang is currently a PhD candidate in inorganic chemistry under the supervision of Prof. Xun Wang at Tsinghua University. His research interests include the design, synthesis and application of novel catalysts for photocoupled electrocatalysis.



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光/热耦合电催化活化二氧化碳和甲烷分子

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摘要 新型催化方法的研究有助于实现二氧化碳和甲烷等小分子资源的高效利用, 从而优化目前的碳循环工艺. 二氧化碳和甲烷分子具有较高的键能, 所以它们均为最稳定的分子之一. 在过去十年, 如何实现二氧化碳和甲烷分子的活化一直是世界难题. 传统热催化通常使用化石燃料作为能源进行小分子活化, 不仅效率低, 同时会伴随着大量的二氧化碳生成. 最近几年, 一系列具有应用前景的催化方法逐步被研究验证. 本文不仅系统性地介绍了光/热耦合电催化在二氧化碳和甲烷等小分子催化转化中的应用, 而且对新型光/热耦合电催化剂的设计合成进行了展望.