



Electrochemical CO₂ Reduction Using Electrons Generated from Photoelectrocatalytic Phenol Oxidation

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Electrochemical CO₂ reduction (ECCO₂R) requires electrons, for example, from oxygen evolution reaction (OER). However, such a multiple-electron-involved reaction is complicated and kinetically slow, leading to high overpotential. Herein, OER is replaced with photoelectrocatalytic phenol oxidation reaction (PECPOR) that provides electrons for ECCO₂R. In an integrated cell, ECCO₂R is conducted on the cathode of Cu nanowires and PECPOR is performed on the anode of SnO₂ and Sb coated TiO₂ nanotubes. Significant improvement of ECCO₂R into CO and hydrocarbons is realized when PECPOR is conducted at a high current density. The use of this integrated system results in the reduction of the specific energy consumption by a factor of 51.33%, compared with the utilization of two half-cells for individual ECCO₂R and PECPOR. This study thus proposes a novel strategy to couple ECCO₂R with PECPOR and eventually to tackle the problems of environmental pollution and energy crisis.

1. Introduction

Electrochemical CO₂ reduction (ECCO₂R) using either homogenous or heterogeneous catalysts^[1–3] has been proved to be a promising strategy to convert this greenhouse gas into useful liquid fuels and value-added chemicals, enabling both renewable energy storage and a negative carbon cycle.^[4] To date, ECCO₂R is usually coupled with water oxidation in aqueous electrolytes where electrons for ECCO₂R are provided by oxygen evolution reaction (OER).^[5,6] However, the OER involves multiple electrons and is kinetically slow. High overpotential is thus always required. Replacing OER with new oxidation reactions to provide electrons for ECCO₂R is thus of great significance.

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Among various oxidation reactions to replace OER for ECCO₂R, oxidation of phenolic compounds is expected to be one promising option. Electrochemical phenol oxidation reaction (ECPOR) using boron-doped diamond (BDD) electrodes is expected to be one possible choice. This is because hydroxyl radicals are generated at high positive potentials (or current densities) on the BDD electrodes and further react or oxidize efficiently phenolic compounds into small organic molecules (e.g., CO₂) and water.^[7] A much better choice is to oxidize phenolic compounds using the photoelectrocatalysts like SnO₂ and Sb coated TiO₂ nanotubes (Sb/SnO₂-TiO₂ NTs) since these photoelectrocatalysts combine the features of electrocatalysts and photo-

catalysts.^[8] It has been shown that the consumed electric energy in these photoelectrocatalytic systems can be reduced due to the additional introduction of solar energy; the existence of synergistic effect between photocatalysts and electrocatalysts can lead to complete and rapid oxidation of pollutants to CO₂ and H₂O.^[9]

Herein, an integrated cell is constructed to investigate simultaneously ECCO₂R on a cathode and photoelectrocatalytic phenol oxidation reaction (PECPOR) on an anode. This is fully different from those reported where only individual ECCO₂R or PECPOR is studied.^[10–13] Its working principle is schematically shown in **Figure 1**. Such an integrated cell consists of the cathode of copper nanowires and the anode of Sb/SnO₂-TiO₂ NTs. The selection of copper nanowires as the cathode is because only on copper and related cathodes different reduction products such as CO and C1 (e.g., methane, formic acid, formaldehyde and methanol) and multicarbon products (e.g., C2 products),^[14,15] depending on the numbers (from 2 up to 12) of provided electrons, can be obtained. Through selecting a BDD anode as a reference for ECPOR, a suitable PECPOR on the anode of Sb/SnO₂-TiO₂ NTs that can replace OER for ECCO₂R is expected to be found.^[16–19] Some issues that have not been clarified up to date can also be revealed, such as the reaction kinetics and mechanisms of PECPOR, as well as the energy consumption of both reactions in such an integrated cell.

2. Results and Discussion

The anode of Sb/SnO₂-TiO₂ NTs and the cathode of copper nanowires were first characterized using different techniques. **Figure 2** shows the scanning electron microscopy (SEM) images of prepared Cu_xO and copper nanowires. Once thermal