

Photoelectrochemical reduction of CO₂ on hybrid organic/inorganic photocathodes

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Introduction

Sunlight is undoubtedly one of the most valuable resources in the quest to find adequate solutions towards a diversified and sustainable energy supply. Given that CO₂ is a greenhouse gas, using sunlight to convert CO₂ to transportation fuel (such as methanol) represents a value-added approach to the simultaneous generation of alternative fuels and environmental remediation of carbon emissions from the continued use of conventional fuels. Photoelectrochemistry has been proven to be a useful avenue for solar water splitting; CO₂-reduction, however, is multi-electron in nature (e.g., 6 e⁻ to methanol) with considerable kinetic barriers to electron transfer. In these reactions photogenerated electrons are utilized to reduce CO₂ either directly at semiconductor/electrolyte interface, or indirectly, employing a redox mediator. Different p-type semiconductors (SCs), such as p-Si, CdTe, InP, GaAs, GaP, FeS₂, Cu₂O and CuFeO₂ have been studied in this manner. Due to kinetic constraints, however, it is required to use carefully designed electrode surfaces to accelerate e⁻ transfer rates to levels that make practical sense in terms of the required energy input. In this paper we present the use of hybrid semiconductor/conducting polymer photocathodes for the photoelectrochemical reduction of CO₂.

Experimental

Nanoporous films of polyaniline were grown on gold electrodes in a three-electrode electrochemical cell using a large Pt foil as counter-electrode and Ag/AgCl reference electrode respectively. Aqueous 0.5 M H₂SO₄ and 0.2 M aniline was used as the electrolyte. Both potentiostatic and dynamic polymerization methods were used to obtain PANI films with different morphologies. After the polymer films were grown, the electrodes were washed carefully, and transferred to an aqueous solution containing 0.4M cupric sulfate and 3M lactic acid. The bath pH was adjusted to 9 by addition of concentrated sodium hydroxide solution; the temperature of the bath was maintained at 60 °C. Subsequently cathodic electrodeposition of Cu₂O was performed at -0.2 V versus SHE for preselected time periods.

Both qualitative and quantitative aspects of PEC CO₂-reduction on the hybrid photocathode was assessed by linear-sweep photovoltammetry, photo-chronoamperometry, and by recording photoaction spectra. The photocurrent-potential profiles using a slow potential sweep in conjunction with interrupted irradiation were recorded both under N₂ and CO₂ atmosphere

Results and Discussion

Copper and its oxides have shown high *electrocatalytic* activity for CO₂ reduction, and we presented the efficient solar photoelectrosynthesis of methanol from CO₂ using hybrid CuO/Cu₂O

SC nanorod arrays recently.^[1,2] Long term stability of this oxide, however, remains a major drawback to be solved. In this paper we present examples for the electrosynthesis SC/CP composite materials,³ and their application in solar energy conversion, as photocathodes for PEC CO₂ reduction. Through careful control over the composition and morphology of these hybrid materials we aim to make improvements in: light absorption, interfaces (charge separation), and stability. A carefully designed sequential method will be presented, where the oxide component of the hybrid material is in situ generated in the presence of its polymeric counterpart. These methods result and in an intimate contact between the organic and inorganic components, both at the physical and electronic level (see Fig. 1) which is likely to contribute to an improved PEC performance. Also note that here we apply the reverse order to the generally employed strategies; because Cu₂O is prone to electrochemical oxidation at potentials where CPs could be electrogenerated.

In this paper particular emphasis will be given on the role of composition and morphology on the PEC performance. Structure property relationships will be shown, which may act as guidelines for the rational design of hybrid photocathodes.

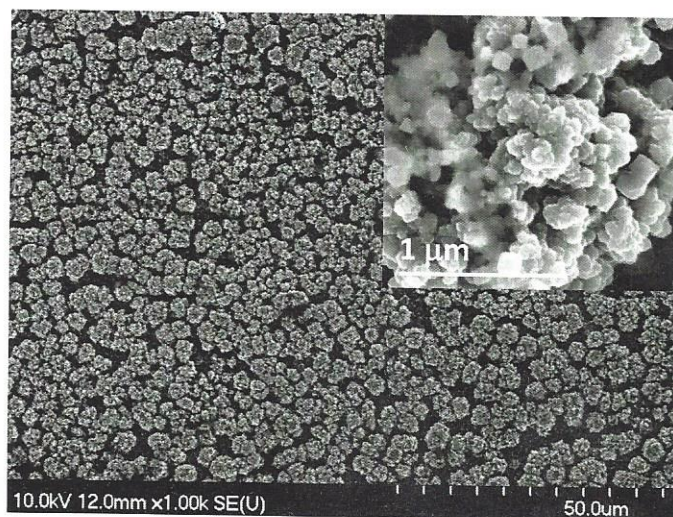
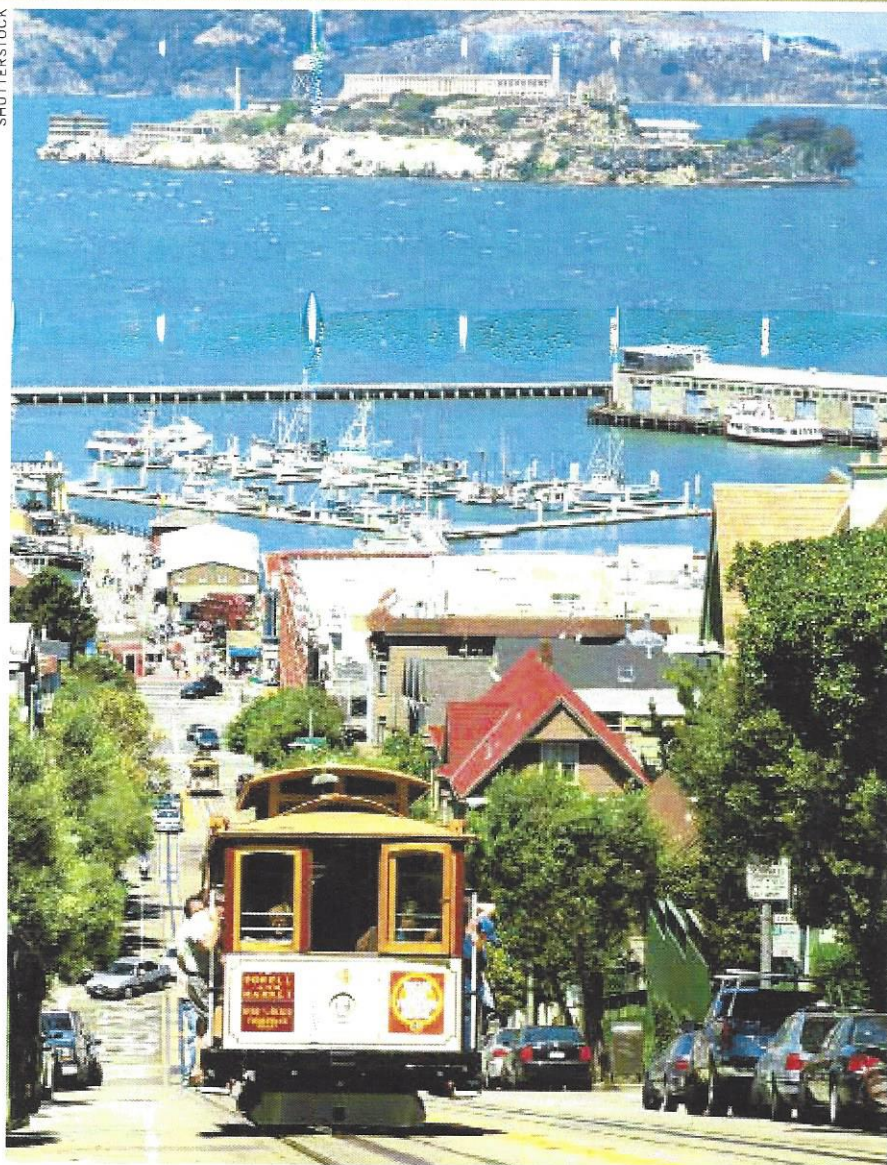


Figure 1. SEM image of a Cu₂O/PANI hybrid

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248TH ACS NATIONAL MEETING

SAN FRANCISCO, Aug. 10–14

“CHEMISTRY & GLOBAL STEWARDSHIP” will be the theme in San Francisco this August. Among symposia centered around that idea, the American Chemical Society Division of Environmental Chemistry will cel-

brate “100 Years of Scientific Contribution for a Safer & Sustainable Environment.” Other symposia will focus on reaching beyond the scientific community, such as “Communicating to the Public & the Role of Social Media” and “Global Stewardship by Increasing Climate Science Literacy.”

ACS President Tom Barton will host 29 technical divisions and nine committees in original programming over 1,013 half-

day oral sessions and 168 poster sessions, including Sci-Mix. More than 7,400 papers will be presented, and nearly 4,400 poster presentations will take place at the meeting.

In concert with the meeting theme, Barton will sponsor two presidential symposia. On Monday, Aug. 11, “‘Fracking’—Where Are We & Where Are We Going” will probe the science behind this suddenly central energy extraction technology—and its environmental implications. On Tuesday, Aug. 12, “Photocatalytic Conversion of Water to Hydrogen & Oxygen,” co-organized with Daniel G. Nocera of Harvard University, will explore the state of the art in solar-energy conversion.

Many education-focused programs for high school teachers, undergraduate and graduate students, postdocs, and chemical professionals will be offered. A range of professional development courses will be available; ACS Professional Education Short Courses have a separate registration and fee. For job seekers and employers, the career fair will provide opportunities for interviews (both on-site and online), one-on-one career assistance, and career-related workshops.

The exposition will feature more than 250 companies showcasing services, instruments, books, lab equipment, and much more in booths that number more than 350.—CRAIG BETTENHAUSEN

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