

NANOSTRUCTURED ELECTRODE ASSEMBLIES FOR (PHOTO)ELECTROCHEMICAL SOLAR FUEL GENERATION

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Given that CO₂ is a greenhouse gas, using the energy of sunlight to convert CO₂ to transportation fuels (such as methanol or methane) represents a value-added approach to the simultaneous generation of alternative fuels and environmental remediation of carbon emissions.¹ Electrochemistry and photoelectrochemistry have 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. It therefore requires the use of carefully designed electrode surfaces to accelerate e⁻ transfer rates to levels that make practical sense.

Carbon nanomaterials, especially carbon nanotubes and graphene (either alone, or as building blocks of organized 3-D superstructures), are attracting significant attention as large surface area electrode materials. In the first part of my talk I will focus on how to use such carbon-based materials for the **electrochemical reduction of CO₂**. Structure-property relationships will be shown, which may act as guidelines for the rational design of nanocarbon-based cathodes.

Subsequently, I will present the use of electrosynthetic (and photoelectrosynthetic) methods for preparing semiconductors on nanocarbon-modified electrode surfaces.^{2,3} Composites of nanocarbons with both inorganic and organic semiconductors represent an interesting class of new functional materials. Therefore, I will show how electrodeposition can be used to tune composition, crystal structure, and morphology of the nanocomposites for targeted applications.

Finally, selected examples will be given for how these electrosynthesized hybrid assemblies can be deployed in various **photoelectrochemical application schemes**, most importantly CO₂ conversion.³ I will present the controlled synthesis and photoelectrochemical behavior of Cu₂O/CNT⁴ and Cu₂O/graphene composites⁵. TiO₂/3D graphene nanocomposites were also obtained in a similar manner. This enhanced charge transport property for the hybrids resulted in a drastic increase in the photocurrents measured for the CO₂ reduction. In addition to this superior performance, long term photoelectrolysis measurements proved that the Cu₂O/nanocarbon hybrids were more stable than the oxide alone. Taking these observations together, as a whole a general model will be presented on the role of the nanocarbon scaffold.⁵

References

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