

CHRONOAMPEROMETRIC RESPONSE OF NANOPOROUS CARBONS UNDER UV-VIS IRRADIATION

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Introduction

Since the first evidence of the ability of semiconductor-free nanoporous carbon materials to absorb photons and convert them into chemical reactions, several approaches have been focused on the study of the light/carbon material interactions due to the new potential applications of these materials in various disciplines related to light harvesting and applied photochemistry in nanoconfined systems^{1,2}. However, despite the interest raised by the topic and the developments achieved over the last years, the exact mechanisms and origin of this photoactivity remains yet unknown.

The aim of this work is to clarify the behavior of nanoporous carbons electrodes when they are exposed to light, exploring their ability to photocatalyze the oxidation of water and the extent of surface photocorrosion due to the long-term light exposure.

Materials and Methods

A series of nanoporous carbon materials with varied textural and chemical properties (low and high surface functionalization) were selected as photoanodes³. For the preparation of the photoanodes a slurry of the nanoporous carbon, polyvinylidene difluoride as binder and a carbon black conductive additive (ratio 85:10:5) in N-methyl-2-pyrrolidone was coated on a 1 cm² Ti foil collector. The electrodes were dried in air at 120 °C before usage. A standard three-compartment cell with an optically flat quartz window on the side and consisting of the nanoporous carbon photoanode as working electrode, a graphite rod as counter electrode, and a saturated Ag/AgCl as reference electrode were used. Illumination was carried out using a solar simulator and various LED with controlled wavelengths. The photoanodes were immersed in 20 mL of an aqueous electrolyte (0.1 M Na₂SO₄, pH adjusted to 2) and purged with N₂ before the illumination. The transient photocurrents of the carbon photoanode under on/off illumination were recorded at constant potentials between 0 and +1.5 V vs. Ag/AgCl, in a potentiostat (Biologic). Dark current equilibrium at the bias potential was allowed before the irradiation. The O₂ concentration in the electrochemical cell was measured using an oxygen sensor immersed in the electrolyte.

Results and Discussion

The irradiation of the nanoporous carbon photoanodes under different conditions provoked the generation of a photocurrent associated to the water splitting reaction (Figure 1). For all the carbons, the transient photocurrent curves upon on/off illumination presented a square-shaped profile, with a prompt initial rise followed by smooth fall until a steady-state regime was achieved; the anodic photocurrent retracted to original values once the illumination was turned off. The photocurrent response was stable and reproducible during several on/off short cycles (ca. 120 s of illumination). Since water molecules are the only scavengers in the reaction medium, the anodic photocurrent corresponds to the oxidation of water upon irradiation of the carbon photoanodes; this was also corroborated by measuring the O₂ concentration in the electrolyte using a sensor.

Important differences were obtained in the chronoamperometric response of the studied nanoporous carbon electrodes, in terms of shape and current intensity of transient photocurrent, pointing out the

strong dependence of the photoelectrochemical response with the nature of the carbon material, thus different mechanisms have been postulated and discussed considering the characteristics of the used carbon material, indicating the high influence of the nature of the carbon in its photoresponse. Following this, after the photoelectrochemical processes we observed the occurrence of photocorrosion reactions on highly functionalized carbons, especially under long illumination periods, giving rise to the consumption of the carbons' photoactive sites and to charge transfer limitations, therefore we have explored the issue of photocorrosion after long term light exposure³.

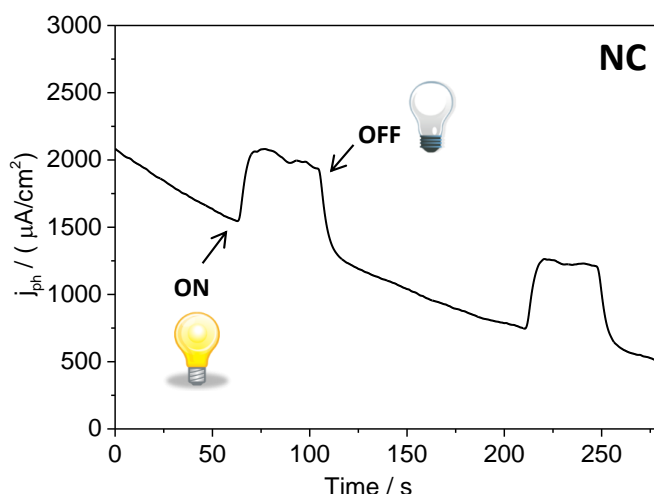


Figure 1. Chronoamperometric response of nanoporous carbon photoanode (NC) upon on/off illumination of simulated solar light irradiation at 1 V vs Ag/AgCl.

Conclusions

In this work, we have explore the origin of the photocurrent generation after the exposure of carbon electrodes under different irradiation conditions, furthermore we have study the photocorrosion phenomenon observed in nanoporous carbon photoanodes upon long-term exposure light exploring the changes in the chemical and textural composition of the irradiated materials. Our results revel the influence of the nature of the carbon material used as photoanode on its photoresponse under various conditions of irradiation, as well as on its photocorrosion showing different pathway mechanisms depending on the nature of the material.

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References

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