

## REACTIVITY OF THE PHOTOEXCITED STATES OF CARBON MATERIALS WITH DIFFERENT STRUCTURAL FEATURES

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### Introduction

Understanding the photochemical activity of different carbon materials has become an interesting topic with new perspectives in the field of metal-free photoactive materials for energy conversion, environmental remediation, and sensing applications<sup>1,2</sup>. Due to the inherent complexity of certain carbon-based systems (e.g., amorphous and nanoporous carbons), the underlying mechanisms governing the carbon photoinduced reactions and the fate of the photoexcited states of the carbon atoms are still not well-understood. Following this idea, we have investigated the reactivity of the charge carriers photogenerated upon irradiation of various carbon materials with different chemical composition, porosity and structural order. The nature of the transient species formed upon irradiation of aqueous suspensions of nanoporous carbons was evaluated by photoluminescence assays at various temperatures and in different solvents. The lifetime of the transient species detected was further explored using time-resolved absorption spectroscopy. Finally, their ability to generate reactive oxygen species (including superoxide anion and hydroxyl radicals) was investigated using paramagnetic resonance spectroscopy.

### Materials and Methods

A series of nanoporous carbons obtained from various precursors (e.g., coal, lignocellulosic waste, polymer-derived, polysaccharides) and activation procedures (e.g. physical and chemical activation) were selected. Photoluminescence studies were recorded for suspensions of the nanoporous carbons at various loadings in solvents of different polarity. The experiments were recorded at ambient and cryogenic temperature. Laser flash photolysis experiments were carried for laser excitation at 266 and 355 nm in an instrument (Edinburgh Analytical LP900) equipped with a 450 W xenon lamp. Aliquots of the carbon suspensions contained in standard 1 cm path length quartz fluorescence cuvettes were excited and stirred between each laser shot; 10 laser-shots were average to obtain the transient absorption decays. Solutions were monitored for laser-induced decomposition by UV-vis absorption spectroscopy, in the presence of scavengers. Standard exponential decay routines were used to analyze the decays of the transient and obtain the lifetimes of the excited species. The formation of reactive oxygen species upon irradiation of the carbons suspensions was investigated by Electronic Spin Resonance spectroscopy, using 5,5-dimethylpyrroline-N-oxide (DMPO) as spin trapping<sup>3</sup>.

## Results and Discussion

Addressing the luminescence characteristics of carbon materials is a challenging task due to the strong light absorption of the carbon matrix itself. As a result, the phenomenon of photoluminescence has only been demonstrated for certain members of the carbon family with high electron mobility and a high degree of transparency, namely graphene-derivatives, carbon nanotubes and carbon quantum dots. Besides the high absorption, photoluminescence measurements in solid state materials are often masked by Raman scattering contributions, making data recording and interpretation a great challenge. In this study we have optimized the experimental conditions for exploring the photoluminescence of nanoporous carbons to minimize the contributions that might hinder the determination of such optical features. We have observed that the polarity of the solvent and the temperature of the analysis greatly influence the light emission spectra of the studied carbons, otherwise characterized by a weak intensity. The excitation and emission spectra of the carbons at room temperature allowed to discriminate the Raman scattering from the emission and absorption peaks, in the range of 200-700 nm. Further flash photolysis measurements confirmed the formation of short and long-lived transient species in the nanosecond scale, attributed to various excited states similar to those described for graphene-derivatives<sup>4</sup>. The surface chemistry of the nanoporous carbons played an important role in the emission characteristics, which is attributed to the presence of chromophore moieties with activity in the UV and/or visible range. Charge transfer states were highly reactive in the presence of electron scavengers, with fast transient absorption decays following exponential trends with decay constants between 35-50 ns (depending on the excitation wavelength). This was further confirmed by electronic spin resonance spectroscopy<sup>3</sup>.

## Conclusions

By using time-resolved absorption, photoluminescence paramagnetic resonance spectroscopies we have recorded the absorption and emission spectra of a series of nanoporous carbons with varied porous features, structural properties and surface chemistry. The irradiation of suspensions of the nanoporous carbons in various solvents gave rise to the formation of various types of excitons showing different light emission properties and reactivity in the presence of scavengers. The occurrence of intramolecular and/or intermolecular charge transfer reactions depended on the illumination conditions and the characteristics of the carbon materials.

## Acknowledgments

This study is supported by the European Research Council through a ERC Consolidator Grant (648161-PHOROSOL).

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