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RESEARCH ARTICLE

Pyrolytic formation and photoactivity of reactive oxygen species in a SiO₂/carbon nanocomposite from kraft lignin

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Abstract

SiO₂ and carbon produced by kraft lignin pyrolyzed at 600°C can generate stable reactive oxygen species (ROS) by reaction with atmospheric oxygen. In this study, we systematically investigate the photochemistry of peroxy radicals in carbon-supported silica (PCS) and assess its effects on the methylene blue (MB) photodegradation. Characterization revealed that the higher ROS generation ability of SiO₂/carbon under UV light irradiation was attributed to its abundant photoactive surface-oxygenated functional groups.

Keywords

ROS, photochemistry, methylene blue, degradation, UV

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Approval Status

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Any reports and responses or comments on the article can be found at the end of the article.		

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Introduction

Consistent access to clean water has come into focus this millennium due to high pollution; a reduced amount of drinkable water could be the next challenge for the future due to overpopulation¹⁻³. The application of photocatalytic technology using semiconductors to solve the environmental problems, like the degradation of organic effluents have been received much attention⁴⁻⁸. Heterogeneous photocatalysis using semiconductors is an interesting method falling into advance oxidation processes (AOPs)⁹⁻¹¹ that can produce highly reactive species containing oxygen (ROS). In fact, with this method is possible to produce oxidizing molecules like hydrogen peroxide and singlet oxygen (¹O₂) together with radicals like hydroxyl radical (OH[•]) and superoxide radical anion ([•]O₂⁻)¹²⁻¹³. These reactants can decompose organic pollutants in wastewater giving harmless compounds¹⁴.

Recently, N. Chen *et al.* reported that reactive oxygen species generation in hydrochar and photochemistry of Sulfadimidine degradation in water¹⁵. Y. Chen *et al.* reported the photo degradation of tetracycline in aqueous solution under simulated sunlight irradiation through the singlet oxygen¹⁶. Li *et al.* reported that the degradation of ibuprofen by UV-visible light irradiation included direct photolysis and self-sensitization via ROS¹⁷. Wang *et al.* reported that when a simpler molecule without visible-light absorption is degraded, the Fe-hydroxyl complexes still promote the generation of ROS and thus accelerate degradation, although the pathway of electron transfer, and the mechanism of photocatalysis was not completely understood¹⁸.

In literature are present many methods for photoassisted AOPs like photo-electrochemical cells composed by an anode made with boron-doped diamond and cathode in carbon nanotubes; with this system, a model azo dye was depleted¹⁹. Also exfoliated graphene, decorated with titanium dioxide and nanoparticles, is effective for photo-catalytic water treatment^{20,21}.

In our current scenario, stable peroxy radicals in carbon-supported silica (PCS) are prepared from cheap starting materials. The method used is the pyrolysis under vacuum of kraft lignin deposited onto silica. Vacuum pyrolysis produced defective carbon bearing carbon radicals. These radicals are quickly transformed into peroxy radicals by reaction with oxygen molecules present in the atmosphere.

Methods

The materials and methods to produce PCS using high-vacuum pyrolysis are clearly explained and characterized previously²². In brief, kraft lignin was absorbed onto silica and pyrolyzed under vacuum at 600 °C. For the kinetic data analysis, linear quadratic fitting and other kinetic fitting (reaction order checking) were performed by using Origin v6.0.

Degradation of MB dye procedures and analyses

100-ml of air-equilibrated 10⁻⁶ M solutions of MB (Sigma Aldrich, India) in water containing 100 mg (1 mg/ml) of neat SiO₂ or PCS were poured in quartz cylindrical reactors (90 mm diameter x 25 mm height). Solutions were magnetically stirred in the dark for 10 min before irradiation and kept under stirring during the experiment. The light source consisted of two 15-W

phosphor-coated lamps (center of emission, 366 nm). Aliquots (4 ml) were withdrawn at 5-min intervals (for a total of 10-12 samples) during the irradiation until the disappearance of the color. Solids were removed by syringe filtration with a 0.4-μm pore size, and the filtrates immediately examined by UV-visible absorption spectroscopy in 1-cm quartz cuvettes using a JASCO V-630 UV-visible spectrophotometer. The absorbance was normalized by dividing the absorbance at 668 nm of the sample (A) with the absorbance of the initial solution (A₀).

Results and discussion

Degradation of MB

To assess the respective photocatalytic activity of PCS and of neat SiO₂, we carried out competitive experiments with MB (Figure 1). PCS did not react with MB, in fact, solutions left for 24 hours in the dark does not show a decrease of MB concentration. Nonetheless, under dark conditions the dye was absorbed by PCS to a nearly tenfold greater extent than with pristine SiO₂ (dark region between -10 and 0 min, Figure 1b).

Normally photocatalysts produce radicals able to degrade organics but in the case of PCS the catalyst already possesses reactive radicals.

Simple mechanism of established photocatalysts in MB

The net effect of PCS on the photodegradation of MB is a threefold increase in the kinetics of photodegradation (Table 1). Without the assistance of an active photocatalyst, the only reaction mechanism that is applicable is the generation of singlet oxygen by sensitization (Equation 2) via the excited state of the dye. The singlet oxygen can react with MB, giving rise to photobleaching (Equation 3).

With PCS, MB is strongly absorbed onto the pyrolytic carbon present on the catalyst surface. Moreover, pyrolytic carbon possesses a high concentration of peroxy radicals. The enhancement on the reaction kinetic could be due to a local increase of concentration of dye and active oxygen. Since the oxygen is reversibly absorbed on the carbon giving peroxy radicals²², the surface of the catalyst is never depleted due to the presence of oxygen in solution.

In fact, in these conditions, we can have, together with Equation 1–Equation 3, a possible reaction of the excited state of the reactant with peroxy radicals or adsorbed oxygen on PCS (Equation 4).

The peroxy radicals are reversibly formed by capture of atmospheric oxygen due to the presence of highly active pyrolytic carbon on PCS:

Figure 1. Normalized spectral intensity of the 668 nm band of methylene blue (MB) during (a) the UV-irradiation of the MB/SiO₂ suspension at 366 nm at different time intervals, and (b) the same process for the MB/peroxyl radicals in carbon-supported silica (PCS) suspensions under otherwise identical conditions. The region between -10 and 0 min refers to the extent of adsorption of the MB dye under dark conditions. It shows the first-order kinetics of the photodegradation of the MB dye by MB/PCS. 3 repeats performed.

Table 1. Extent of adsorption and first-order kinetics of photodegradation of methylene blue (MB) (1.0 μM) on pristine SiO₂ and on SiO₂/graphene in aqueous media under ambient atmospheric conditions and under UV irradiation at 366 nm.

Dye	k (min ⁻¹)		Adsorption, %	
	SiO ₂	PCS	SiO ₂	PCS
MB	0.027 ± 0.005	0.092 ± 0.006	24	91

Another possibility is the transfer of energy (or sensitization) of the excited state of the absorbed dye directly to the defective pyrolytic carbon, giving rise to formation of ROS. All these mechanism lead to an enhancement on the degradation of MB.

Dataset 1. Raw data for the article 'Pyrolytic formation and photoactivity of reactive oxygen species in a SiO₂/carbon nanocomposite from kraft lignin' are presented

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Conclusion

This study has shown that silica can be coated successfully with pyrolytic carbon obtained from inexpensive waste materials, such as kraft lignin and silica. The pyrolytic process performed at

600°C did not affect the crystalline state of silica when it was coated with carbon. The photocatalytic activity was measured against pristine SiO₂ through an examination of the kinetics of degradation of MB by UV-vis spectroscopy. Under UV light irradiation, the degradation was threefold greater for the MB-PCS compared with MB-silica.

Data availability

Dataset 1: Raw data for the article 'Pyrolytic formation and photoactivity of reactive oxygen species in a SiO₂/carbon nanocomposite from kraft lignin' are presented, [10.5256/f1000research.16080.d218907](https://doi.org/10.5256/f1000research.16080.d218907)²³

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Stefano Crespi

Institute for Organic Chemistry, University of Regensburg, Regensburg, Germany

Vadivel and Malaichamy report on the activity of stable peroxy radical species generated on carbon-supported silica after pyrolysis of kraft lignin deposited onto SiO₂. The synthetic method applied is crucial to generating carbon radicals on the surface of the catalyst. These species can react with oxygen, readily forming stable ROS on the catalyst itself.

The photocatalytic activity of these peroxidic reactants is tested against the photobleaching of methylene blue, providing a complete analysis of the results obtained.

The article herein presented has a structured scholar presentation that is based on the authors' previous work. The literature cited is coherent and adequate with the topic.

As minor comments, the authors should pay attention to the citation of some of the references that got mixed up in the version presented, e.g. Y. Chen in the text (ref 16) is stated correctly, however it is wrong in the reference section, where names and surnames are cited incorrectly.

To improve the readability, please write "Methylene Blue" in its full extent along with "MB" the first time it appears in the main body of the article, because the extended name is present only in the abstract.

The study is based on the experience and methodology that the authors have recently published on Kraft lignin and its pyrolysis. Being experts in the field, they have devised a carefully planned work in all its aspects, comprising the synthetic, photochemical and analytical part.

The authors provide the reader with a schematic, yet very precise method section. It is highly appreciated the author's attention in giving detailed information on the specifics of all the instruments used, e.g. explicitly reporting the wavelength used for the irradiation (366 nm) when in several reports only generic data is given to the reader.

All the data are repeated and checked three times. The average and the standard deviation is

furnished in the text. The statistical interpretation of the data is adequate to the problem treated.

The very low deviation found in the measures testifies the reproducibility of the method, which is remarkable, given the complex matrix analysed. All the data are accurately reported in a spreadsheet furnished as supplementary file to the article.

The conclusions of the work are drawn in a schematic yet elegant way, summing up a nice work that is fully supported by the experimental evidence.

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: I am currently working in photochemistry, photocatalysis, and elucidation of reaction mechanisms on the ground and excited state.

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard.

Reviewer Report 05 October 2018

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Simone Lazzaroni

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This manuscript is focused on the application of supported stable peroxy radicals for the photo-degradation of organic materials. In this work the authors systematically investigated the photochemistry of peroxy radicals in carbon-supported silica (PCS) and then they evaluated the effects of PCS on the methylene blue photodegradation as a model for a generic organic effluent. The manuscript is clearly written with few errors (e.g. "N. Chen *et al.*" and "Y. Chen *et al.*" refer to the same reference article). However, the authors have extracted some interesting data that well supports the discussion and the appropriate conclusions. Furthermore, problems such as overpopulation and the lack of drinking water are unfortunately a plague that afflicts our entire planet. I encourage the authors to continue with their research, thus contributing to increase the impact of their study.

Competing Interests: No competing interests were disclosed.

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard.

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