Synthesis and Characterization of a Graphene-based Composite Photocatalyst Applied to the Photoinactivation of Microorganisms

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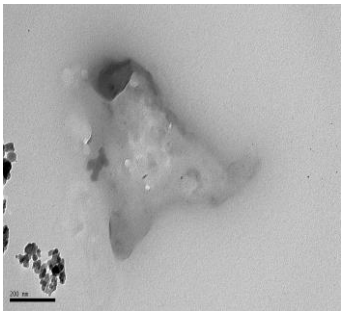

A novel composite photocatalyst prepared from graphene and commercial TiO_2 P25 exhibits enhanced photocatalytic activity. This composite presents increased efficiency for the Methylene Blue degradation and NO deep oxidation under ultraviolet (UV) radiation. The composite band gap, obtained from the reflectance spectrum, was of 2.95 eV, indicating that it absorbs both UV and visible light. The novel composite photocatalyst showed promising photoinactivation activity. Under visible light, the viability loss of the reference bacterial strain *Escherichia coli* DSM 1103 was two times higher than with the TiO_2 P25.

Introduction

In the 1970s and 1980s, the majority of work carried out on photoelectrochemistry field was applied to solar energy conversion systems to produce clean fuels. The most studied process was the splitting of water by solar energy for hydrogen production. Since then, it was also found that photocatalysis could be applied to decompose organic compounds and thus remarkable efforts have been made for using it in environmental applications. Actually, earth is nowadays facing severe environmental problems, as the greenhouse effect and acid rains caused by emissions of sulfur dioxide and nitrogen oxide, which react with water molecules in the atmosphere to produce acids [1].

Even though the environmental applications are probably nowadays the main focus of the photocatalysis research, microorganisms' photoinactivation is also catching attention within the scientific community. In fact, there is an alarming increase in the number of hospital-acquired infections, also known as nosocomial infections [2]. This increase is caused by an uncontrolled use of substances that promote the propagation of antibiotic resistance, strongly motivated by a lack of adequate legislation [3]. Nosocomial infections, besides causing concern for public health, also lead to high costs for the national health services. For example in the United Kingdom, the European Union country with the highest number of nosocomial infections, the health costs rise to 1200 million euros per year [4]. Therefore, the infectious diseases seem to be again a real threat with new emergent pathogens or new antibiotic resistance strains appearing almost daily. Moreover, the exponential increase in the movement of people across countries, oceans and continents is also intensively contributing to it. In the last decade many studies reported photocatalysis use for disinfection purposes; especially the antimicrobial application of titanium dioxide has been widely discussed in many reviews and research papers [5, 6].

The pioneer work developed by Fujishima *et al.* [7], describing water splitting with a TiO_2 photoelectrode, got the attention of several research groups working on this field and rapidly TiO_2 (anatase form) became the most used semiconductor for photocatalysis. Upon excitation with photons presenting energy higher than its band gap energy *(ca.* 3.2 eV), an electron is injected from the valence to the conduction band, generating an electron-hole pair in the conduction and valence bands respectively – Eq. (1). The strong oxidation potential of the photogenerated valence band holes in anatase TiO_2 (E_{VB} = +3.0 V *vs*. Normal Hydrogen Electrode (NHE), originates the formation of hydroxyl radicals ($OH^{\bullet}$) when in contact with water – Eq. (2). The reduction potential of anatase TiO_2 conduction band electrons is of *ca.* -0.2 V, and reduces O_2 to produce superoxide radical ($O_2^{\bullet-}$) – Eq.(3).

$$\text{Semiconductor} \xrightarrow{h\nu} e^-_{CB} + h^+_{VB} \quad (1)$$

$$\text{Semiconductor}(h^+_{VB}) + H_2O_{ads} \rightarrow \text{Semiconductor} + HO^{\bullet}_{ads} + H^+ \quad (2)$$

$$\text{Semiconductor}(e^-_{CB}) + O_{2ads} \rightarrow \text{Semiconductor} + O_2^{\bullet-} \quad (3)$$

The improvement of titanium dioxide photocatalytic activity can be achieved mainly by: i) avoiding the recombination of photogenerated electrons/holes; and ii) narrowing the

semiconductor band gap (E_g). While the first permits to efficiently generate higher quantities of free radicals, the later allows the photocatalyst to absorb a larger fraction of the solar spectrum.

For decreasing the e^-/h^+ recombination at the photocatalyst, several studies suggest the use of carbon-based supports such as carbon nanotubes (CNTs), fullerene or graphene being this last the most promising one. These materials have the ability to receive and store electrons and then preventing the recombination. Graphene has stimulated the research curiosity since its discovery in 2004 [8] due to its geometric planar single-layer carbon sheet and its physicochemical properties, including high mobility of charge carriers, high mechanical strength, excellent thermal conductivity and high surface area [9]. In most of the cases, partially oxidized graphene, named graphene oxide (GO), is used instead of pure graphene (G) due its tunable optical, conductive and chemical properties. Actually, graphene oxide can be regarded as graphene functionalized with carboxylic acid, hydroxyl and epoxide groups and thus its properties can be adjusted via chemical modification. Actually, the number of functional groups and the amount of oxygen in these groups, in the limit, allows changing graphene oxide properties from conductive to isolator. GO can bind easily to metal oxide particles, such as TiO_2, through oxygen functionalized groups [10].

Materials and Methods

In this work a composite photocatalyst was produced based on the work of *Zhang et al.* [11], from commercial P25 and graphene oxide, produced according to the Hummers method [12]. The methylene blue degradation trials were conducted according to the standard ISO 10678, 2010 and the NO deep oxidation values were obtained based on standard ISO 22197. The microorganism photoinactivation trials were conducted using the reference strain *Escherichia coli* DSM 1103 according with ISO 27447: 2009.

Results and Discussion

The produced composite photocatalyst was tested for methylene blue degradation and NO photo-abatement and the obtained results were compared to the commercial P25.

Regarding the methylene blue degradation under UV radiation it was possible to observe an increase in the activity of the composite photocatalyst when compared with the commercial P25 (Figure 1).

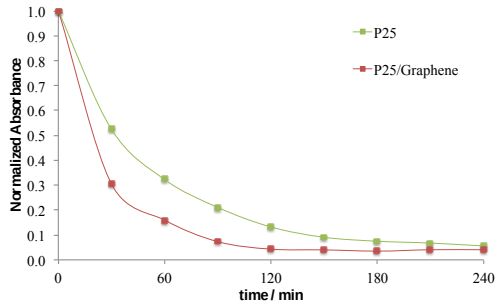

Figure 1. Normalized absorbance values for methylene blue degradation during 240 minutes (lines were added to improve the readability).

The observed higher photocatalytic activity may be ascribed to a higher conductivity of graphene, which leads to a decrease in e^-/h^+ recombination. This will be further studied by electrochemical impedance spectroscopy technique. Moreover, the bandgaps of the composite and P25 photocatalysts were calculated from the diffuse reflectance spectra (Figure 2). The bandgap of the composite photocatalyst was 2.95 eV, whilst the values obtained for commercial P25 were of 3.03 eV and 3.16 eV, corresponding to the two different crystalline forms of titanium dioxide. This decrease in the bandgap may be attributed to some doping of TiO_2 by the carbon molecules of graphene [11].

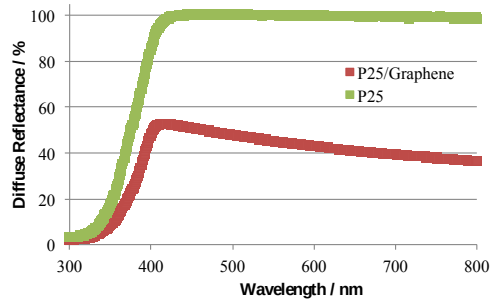

Figure 2. Diffuse reflectance spectra of P25 and P25/Graphene composite

NO deep oxidation test was also conducted under the influence of UV radiation. This test runs during 150 hours to evaluate the photocatalysts stability (Figure 3).

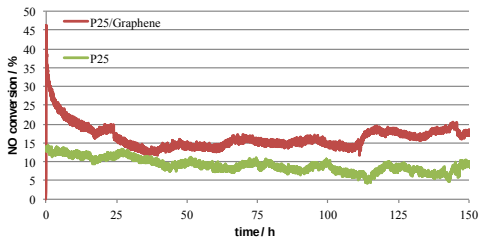

Figure 3. NO conversion for P25 and P25/Graphene composite during 150 hours.

The new composite photocatalyst presented higher initial and steady state NO conversion than P25. Furthermore, after the first 24 hours, the composite showed good stability throughout the 150 hours of test.

Finally, the photoinactivation activity of the composite photocatalyst was assessed. Under UV radiation, the viability loss values of the reference strain *E. coli* DSM 1103 were similar for the composite and P25. In opposition, under visible light the composite photocatalyst permitted to achieve 2 times higher viability loss values. Despite these promising results, improvements are necessary, since viability losses under visible light are low (average 28.54 %) when compared with UV radiation (average 99.98 %).

Table 1. *E. coli* DSM 1103 viability loss values in percentage under different photocatalytic conditions.

	Dark Conditions	UV Light	Visible light
Without photocatalyst	-	50.82 ± 2.54	-
P25	5.69 ± 3.44	99.98 ± 0.00	14.34 ± 0.61
P25/ Graphene	8.44 ± 0.67	99.98 ± 0.00	28.54 ± 1.78

Conclusion

The produced composite photocatalyst presented better results for methylene blue and NO oxidation under UV radiation when compared with P25. Additionally, regarding photoinactivation trials, the new composite photocatalyst exhibited higher activity under visible light against the reference strain tested than the commercial P25. Further developments in photoinactivation under visible light using TiO_2/Graphene composites are expected not only from the optimization of this material but also from the use of suitable co-catalysts.

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