



# New carbon xerogel-TiO<sub>2</sub> composites with high performance as visible-light photocatalysts for dye mineralization

Esther Bailón-García<sup>a</sup>, Abdelhakim Elmouwahidi<sup>a</sup>, Miguel A. Álvarez<sup>b</sup>,  
Francisco Carrasco-Marín<sup>a</sup>, Agustín F. Pérez-Cadenas<sup>a</sup>, Francisco J. Maldonado-Hódar<sup>a,\*</sup>

<sup>a</sup> Research Group in Carbon Materials, Inorganic Chemistry Department, Faculty of Sciences, University of Granada, Campus Fuentenueva s/n, 18071 Granada, Spain

<sup>b</sup> Inorganic and Organic Chemistry Department, Faculty of Experimental Sciences, University of Jaén, Campus Las Lagunillas, 23071 Jaén, Spain

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## ABSTRACT

A series of carbon xerogels-TiO<sub>2</sub> samples was prepared by sol-gel synthesis, modifying the synthesis procedure to have carbon-TiO<sub>2</sub> composite or TiO<sub>2</sub>-coated materials. Textural, morphological and chemical properties were extensively characterized and correlated with the photocatalytic activity. In the case of composites, a homogeneous and highly mesoporous structure is formed, where the intimate contact between both phases allows a high and homogeneous dispersion of TiO<sub>2</sub> nanoparticles. During carbonization, the formation of oxygen vacancies is favoured, but the transition anatase to rutile is avoided by the carbon matrix. In the case of coated samples, microporous materials structured as microspheres were obtained, TiO<sub>2</sub> present a greater crystal size and some transformation to rutile. The synergetic role of carbon phase and the formation of oxygen vacancies in the TiO<sub>2</sub>-phase contribute to narrow the composite band gap in such a manner that all samples are active under visible radiation reaching the total mineralization of the pollutant and the elimination of the toxicity.

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## 1. Introduction

The increasing pollution level of water resources together with the appearance of new and more stable pollutant in solution (emerging pollutant) make necessary the development of new and more efficient protocols to deal with this new problem. Traditionally, environmental catalysis tries to respond adequately to this requirement, fitting or developing materials and processes for a progressively more industrialized society. A large battery of advanced oxidation processes (Fenton, ozonation, catalytic wet air oxidation (CWAO), etc) is being developed [1–3]. Between them, photocatalytic processes are very interesting, and sometimes are used in combination [4] with the previous ones (photoFenton, photoozonation, etc). Photocatalytic processes become especially interesting when are able to use the visible radiation, not only by the energy saving, but because in such a way can be easily used in developing countries.

It is well known that TiO<sub>2</sub> is the most extensively used photocatalyst. It has been regarded as an efficient photocatalyst for

degradation of organic pollutants from water due to its high stability, low cost and environmental friendliness [5,6]. However, UV-light is necessary to create the hole-electron pairs needed for the photocatalytic reaction which limits their use in environmental applications. Only 3–5% of UV in solar spectrum can be absorbed by pure TiO<sub>2</sub> due to its wide band gap (3.2 eV of anatase and 3.0 eV of rutile), which greatly restricts its photocatalytic applications in the visible-light range [7,8].

Therefore, to improve the efficiency of TiO<sub>2</sub> under solar (or visible) light is necessary to modify the material in order to facilitate the visible light absorption. Several approaches are made with this aim such as the introduction of doping agents or sensitizers to decrease the material band gap [9,10]. The introduction of metal doping agents into TiO<sub>2</sub> narrows the band gap by producing new hybrid states which confer significant visible light absorbance to TiO<sub>2</sub>. On the other hand, the improvement obtained using sensitizers is due to the direct absorption of visible light by the sensitizer and the release of electrons to TiO<sub>2</sub> in a redox process.

However, different problems were also detected. Metal doping shows thermal instability of doped TiO<sub>2</sub>, electron trapping by the metal centres decreasing the photocatalytic activity and high processing costs [11,12]. Alternatively, doping with non-metals such as N and S are used [13,14] being now the main drawbacks (i) the

\* Corresponding author.

E-mail address: [fjmalodon@ugr.es](mailto:fjmalodon@ugr.es) (F.J. Maldonado-Hódar).

difficulty to obtain N-doped TiO<sub>2</sub> with high nitrogen concentration; (ii) the formation of defects which can act as recombination centres for carriers [15]; and (iii) the decrease of N concentration at the surface layer after irradiation [16].

The synergetic effect of the addition of carbon materials to TiO<sub>2</sub> photocatalysts was initially presented using directly simple mixtures of both solids [17,18]. Although activated carbons were initially used to enhance the TiO<sub>2</sub> photocatalytic performance [19], nanocarbons including carbon nanotubes (CNT) [18], nanohorns, fullerenes and graphene [20,21] have been combined with TiO<sub>2</sub> by different approach for such objective. Carbon gels are a new type of nanocarbons [22] with high potential applications in catalysis due to their unique properties [23]. In spite that some carbon gels –TiO<sub>2</sub> composites were previously described [24], until our knowledge they have not been used today as photocatalysts.

The incorporation of carbon materials to the photocatalyst improve the TiO<sub>2</sub> photoactivity by different mechanism [25]: (i) carbon absorbs over a wide range of visible light producing band-gap tuning/photosensitization, (ii) minimisation of electron/hole recombination and (iii) promotion of the reactants adsorption. The higher porosity of carbon facilitates the titania dispersion and the adsorption of reactants, enhancing the active site number and the contact between reactants and catalysts [25]. Additionally, carbon is a good electron acceptor. Electron transfers to the carbon phase minimize the electron/hole recombination on the TiO<sub>2</sub>. Also the better dispersion of the semiconductor nanoparticles on the carbon phase reduce that recombination because mainly occurs at boundaries and defects [26]. Thus, if the particle size is reduced, the distance that the photogenerated electrons and holes need to travel through the surface reaction sites is reduced, thereby decreasing the recombination probability [27].

In this paper, new TiO<sub>2</sub>-carbon composites were prepared by a sol-gel process and the xerogels obtained were deeply characterized and tested in the degradation of organic pollutants under visible light. The photocatalytic activity of the composites was evaluated using Orange G (OG) as a target molecule, and the relationship of the photocatalytic activity with the physicochemical characteristics of composites was studied. The prepared new materials present a high performance for the complete mineralization of pollutants (OG) under visible light.

## 2. Experimental

### 2.1. Synthesis of TiO<sub>2</sub>-carbon xerogel composites

TiO<sub>2</sub>-carbon xerogel composites were prepared by sol-gel synthesis using resorcinol-formaldehyde and titanium isopropoxide (IV) as carbon and titanium oxide precursor, respectively, in the presence of a non-ionic surfactant (Span 80). In a typical synthesis procedure, Span 80 (S) was dissolved in 900 mL of *n*-heptane and heated at 70 °C under reflux and stirring (450 rpm). Then a mixture containing resorcinol (R), formaldehyde (F) and water (W) was added dropwise into the above solution. Immediately after this addition, the proper amount of titanium isopropoxide was added drop by drop to the mixture. The molar ratio of the mixture was R/F = 1/2, R/W = 1/14 and R/S = 4.5.

The formed gel was aged at 70 °C for 24 h under stirring, and after that the suspension was filtered and the obtained solid, which displays an intense orange color, was placed in acetone (5 days, changing acetone twice daily) to exchange water within the pores by acetone. This procedure reduces the collapse of porosity during the subsequent drying process [28]. Then, the gel was filtered again and dried by microwave heating under argon atmosphere in periods of 1 min at 300 W until constant weight using a Saivod MS-287W microwave oven, according to previous results [28]. Pyrolysis

of organic xerogel-titanium oxide composites to obtain the corresponding carbon xerogel-titanium oxide composites was carried out at 900 °C in a tubular furnace using a N<sub>2</sub> flow of 300 cm<sup>3</sup>/min, and a heating rate of 1 °C/min, in order to allow a soft removing of pyrolysis gases, and soaking time of 2 h at this temperature.

In this way, four TiO<sub>2</sub>-carbon xerogel composites were prepared with different amount of titanium oxide (tentatively 10, 20, 30, and 40 wt% in the carbonized materials) by fitting the alkoxide ratio (assuming a weight loss during carbonization of 50%). TiO<sub>2</sub>-carbon xerogel composites were referred as CTiX (X corresponding to the theoretical percentage of titanium oxide present in the carbonized composite, e.g. CTi40 should contain 40% wt. of TiO<sub>2</sub>).

In order to make a comparison, carbon spheres covered by TiO<sub>2</sub> were also synthesized. For that, the synthesis method was modified: the mixture of R, F and W was previously pre-gelled at 60 °C during the half of the time (2 h) needed to achieve the gel point. Then this pre-gelled mixture was added dropwise to a *n*-heptane solution containing Span 80 and maintained 1 h at 70 °C under reflux and stirring. This procedure permits the formation of organic xerogels structured in spheres which were finally coated with TiO<sub>2</sub> by adding dropwise to the reactor the proper amount of titanium isopropoxide to obtain a TiO<sub>2</sub> loading of 30 wt.%. After dry and carbonization, following the procedure previously described, this sample was referred as CTi30s2h.

A pure carbon xerogel (C100) prepared following the same sol-gel method used for CTi30s2h synthesis (but without Ti-alkoxide), P25 (from Degusa) and TiO<sub>2</sub> anatase (From Sigma-Aldrich) were used as reference materials.

### 2.2. Characterization

Textural characterization was carried out by N<sub>2</sub> and CO<sub>2</sub> adsorption at –196 °C and 0 °C, respectively, using a Quantachrome Autosorb-1 equipment. The BET and Dubinin–Radushkevich equations were applied to determine the apparent surface area (*S*<sub>BET</sub>) and the micropore volume (*W*<sub>0</sub>), the mean micropore width (*L*<sub>0</sub>) and the microporous surface (*S*<sub>mic</sub>), respectively. Furthermore, the DFT method was used to calculate the mesopore volume of the samples (*V*<sub>mes</sub>). Pore size distributions were also obtained by applying the DFT method [29–32]. The total pore volume was considered as the volume of N<sub>2</sub> adsorbed at P/P<sub>0</sub> = 0.95 [33]. The morphology of supports was studied by scanning electron microscopy (SEM) using a LEO (Carl Zeiss) GEMINI-1530 microscope.

The titanium oxide phase was determined by powder X-ray diffraction (XRD) pattern using a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation at a wavelength (λ) of 1.541 Å. The 2θ angles were scanned from 20 to 70°. The average crystallite sizes (*D*) were estimated by the Debye–Scherer equation,  $D = 0.95\lambda/\beta \cos \theta$ , where θ is the diffraction angle and β is the full width at half-maximum (fwhm). The fwhm was determined with an extrapolated baseline between the beginning (low-angle side) and the end (high-angle side) of a diffraction peak with the highest intensity.

Optical absorption spectra of samples were obtained on a double-beam UV–vis spectrophotometer (CARY 5E from VARIAN) equipped with a Praying Mantis diffuse reflectance accessory (DRS). The reflectance spectra were analyzed according to the Kubelka–Munk (KM) method in order to calculate the band gap (*E*<sub>g</sub>) of samples. The graphic representations (F(R)·hν)<sup>n</sup> versus *E* = hν were used to calculate *E*<sub>g</sub>; where F(R) is a function of the reflectance;  $F(R) = (1-R)^2/2R$ , *R* is the absolute reflectance of the sample layer and hν is the photon energy (eV), assuming also a value of *n* = ½ for an indirect allowed transition and *n* = 2 for a direct allowed transition. The *E*<sub>g</sub> value was obtained by extrapolating the slope to *a* = 0 according to the procedure used by López et al. [34].

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