Coating-free TiO$_2$@β-SiC alveolar foams as ready-to-use composite photocatalyst with tunable adsorption properties for water treatment

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Coating-free TiO$_2$@β-SiC photocatalytic composite foams gathering within a ready-to-use shell/core alveolar media, the photocatalytically active TiO$_2$ phase and the β-SiC foam structure, have been prepared through a multi-step Shape Memory Synthesis (SMS) replica method. They have been elaborated following a sequential two-step carburization approach, in which an external TiC skin was synthesized at the surface of a β-SiC skeleton foam obtained from a pre-shaped polyurethane foam during a first carburization step. The adsorption behavior of the shell/core TiO$_2$@β-SiC composite foams towards the Diuron pollutant in water was tuned by submitting the carbide foams to a final calcination treatment within the 550–700°C temperature range. The controlled calcination step allowed (i) the selective oxidation of the TiC shell into a TiO$_2$ crystallite shell thanks to the β-SiC resistance to oxidation and (ii) the amount of residual unreacted carbon within the foams to be tuned. The lowest the calcination temperature, the highest the adsorption profile of the composites. The ready-to-use TiO$_2$@β-SiC composite foams were active in the degradation of the Diuron pesticide, without any further post-synthesis immobilization or synthesis process at the foam surface. They displayed a good reusability with test cycles and benefitted from an enhanced stability in terms of titania release to water.

** Introduction

In wastewater treatment, photocatalysis is one of the advanced oxidation processes that have demonstrated its ability to degrade and mineralize biorecalcitrant refractory compounds that cannot be eliminated by conventional treatments, or at least to degrade them into readily biodegradable compounds. Although photocatalysis is usually carried out at the lab scale with nanoparticle suspensions for taking advantage of a maximum irradiated and exposed surface for optimizing the degradation activity, the necessary implementation of time-consuming and costly nano-filtration recovery steps for separating the powdery photocatalyst from the treated water, as well as safety issues related to its handling, make the process less viable for real applications and with a less secure environment for recycling and handling.

Therefore, in parallel to the implementation of approaches based on the advanced design of nanomaterials for enhancing the activity of powdery photocatalysts, strategies dealing with the immobilization of photocatalysts – and more globally with the elaboration of macroscopic photocatalytic structures – are investigated for designing powder-free wastewater treatment processes allowing the photocatalysts to operate in a continuous mode. In this frame, among cellular monolithic solids, metallic and ceramic open-cell alveolar solid foams gained recently important interest for use as photocatalyst support in water treatment for taking advantage of an static mixer effect inside the reactor and of a better light transmission than honeycomb- or square-channel monoliths. In addition, their open structure enables the photocatalyst to operate at ultra-low pressure drop.

Among ceramic foams, medium surface area self-bonded β-SiC foams gained a strong interest thanks to a high thermal and chemical stability that allow them to be submitted to a wide range of severe conditions during the photocatalyst immobilization step, the reaction itself or thermal/chemical regeneration steps (if required). Further, the β-SiC foam surface is composed of a thin amorphous nanolayer exposing a high density of oxygenated surface groups favoring the anchorage of photocatalysts.

Binderless β-SiC alveolar foams have been already efficiently used as TiO$_2$ support in water treatment. However, the preparation of the foam supported TiO$_2$ photocatalysts requires immobilizing or synthesizing TiO$_2$ onto the β-SiC support as a separated post-synthesis process, so that the TiO$_2$/β-SiC foams can suffer detrimental stability problems that could provoke a release of photocatalyst to the water. The resistance of the catalyst–support interface towards strains derived from particle to particle and particle–fluid mechanical interactions in the reactor environment, remains indeed an essential quality...
criteria for a good support, in order to avoid release of photocatalyst particles from the support.

This work aimed at elaborating TiO$_2$@β-SiC photocatalytic composite foams that gather the TiO$_2$ photocatalyst and the β-SiC alveolar foam within a ready-to-use (coating-free) photocatalytic media, that consequently does not require the implementation of any post-synthesis immobilization or synthesis process at the foam surface. They were elaborated through a sequential multi-step carburization synthesis approach derived from the single carburization Shape Memory Synthesis (SMS) replica method developed by SICAT Catalyst for synthesizing pure self-bonded porous β-SiC foams from a pre-shaped polyurethane foam. Further, we aimed at controlling the adsorption properties of the ready-to-use TiO$_2$@β-SiC composite foams towards the pollutant in water.

Diuron (C$_8$H$_{15}$Cl$_2$N$_2$O, 3-(3,4-dichlorophenyl)-1,1-dimethylurea), one of the most used contact herbicides from the family of substituted phenyureas, has been taken as model substrate to degrade for evaluating the liquid phase photocatalytic activity of the TiO$_2$@β-SiC composite foams under simulated solar light. Diuron is known to be degraded by photocatalysis via a well-admitted multi-pathway degradation route, involving mainly hydroxyl OH$^-$ radicals as active species and, consisting first in the attack of the alkyl function or in the chlorine substitution, followed by hydroxylation steps leading to the formation of acetic, formic and oxalic acid as last short-chain acid reaction intermediates.

**Experimental part**

**Synthesis of the TiO$_2$@β-SiC photocatalytic composite foams**

Alveolar shell/core TiO$_2$@β-SiC composite foams with medium surface area were jointly developed at ICPEES and at the SICAT company (Strasbourg, France) according to a sequential multistep carburization SMS method, adapted from the single carburization SMS method owned by SICAT for synthesizing self-bonded porous β-SiC foams from a pre-shaped polyurethane foam. This two-step carburization SMS replica approach schematized in Fig. 1 implements a sequential carburization strategy, in which a second carburization of the foam is performed at the surface of a β-SiC skeleton obtained during a first carburization step:

1. first, a pre-shaped precursor polyurethane foam was impregnated/infiltrated with a phenolic resin containing micronized (< 20 μm) metallic Si and carbon black powder.
2. the shaped green body obtained was dried overnight at 120°C and subsequently submitted to a first carburization reactive step under Ar atmosphere for 1 h at 1360°C. During the thermal treatment, the polyurethane was pyrolyzed giving almost no carbon yield, whereas the high carbon yield resin was pyrolyzed into amorphous carbon binding the carbon black and the Si powders together. Above 1000°C, the carbon skeleton was subsequently attacked by SiO vapors formed by reaction between Si and the residual traces of oxygen, whereas CO was allowed to carburize the metallic Si, yielding to the formation of β-SiC according to (1).

\[ \text{SiO}_2 + 2\text{C} \rightarrow \text{SiC} + \text{CO} \]

(1)

3. the β-SiC skeleton foam was further impregnated by a Aerioxide® TiO$_2$ P25 ethanolic suspension at 15 g/L by dipping the foam 50 times to get a 20 wt.% TiO$_2$ content (with intermediate rinsing steps with ethanol solution). The impregnated β-SiC skeleton foam was dried at 100°C for 12 h. The impregnated β-SiC skeleton foam was dried at 100°C for 12 h. The wt.% loading of TiO$_2$ resulted from a preliminary study reported as Supporting Information S1.

4. the foam was further submitted to a second reactive carburization step at 1360°C for 1 h under Ar atmosphere.

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**Figure 1.** Schematic diagram of the sequential two-step carburization SMS replica synthesis of the shell/core TiO$_2$@β-SiC composite foams.
for forming a TiC shell using residual unreacted carbon, according to (2).

$$\text{TiO}_2\text{(s)} + 3\text{C}_2\text{(s)} \rightarrow \text{TiC}_2\text{(s)} + 2\text{CO}_2\text{(g)}$$  \hspace{1cm} (2)

5. Finally, a thermal treatment in air was performed at temperatures between 550°C and 700°C for producing the final shell/core TiO$_2$@β-SiC composite foams through the selective oxidation of the TiC skin into TiO$_2$.

A reference β-SiC foam supported TiO$_2$ catalyst with 15 wt.% of TiO$_2$ has been prepared via the classical deposition method consisting in successive dippings of the foam into a 15 g/L TiO$_2$ P25 ethanolic suspension, with intermediate rinsing steps with ethanol solution, drying at 100°C and final calcination treatment at 380°C. Prior deposition, the bare β-SiC foam was decarboned for 2 h at 700°C in air for removing residual unreacted carbon species by combustion. The TiO$_2$ content of 15 wt.% relative to the total foam weight, was previously optimized $^{13}$ and determined by weighing the TiO$_2$@β-SiC foam.

**Evaluation of the photocatalytic efficiency**

The experiments were carried out within an Suntest XLS+ reaction chamber (Atlas Material Testing Technology BV, Gelnhausen, Germany) equipped with a Xenon arc lamp of 1700 W adjustable power and a Solar ID65 filter to limit the UV radiation at 300 nm for simulating solar exposition according to ICH Q1B guidelines. The runs were performed with simulated solar light at 250 Wm$^{-2}$ (300–800 nm), which corresponds to an average solar radiation in a summer day in southern Europe (Fig. S2). The reaction volume was 100 mL and the starting concentration of diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) 10 mgL$^{-1}$. At each time interval, 5 mL of solution has been sampled and then filtered through 0.20 µm porosity filter to remove the photocatalyst powder if any, before the concentration of Diuron has been determined by UV-Visible spectrophotometry (Cary100 scan Varian) by monitoring the disappearance of the main absorption peak at $\lambda$=248 nm, and Total Organic Carbon measurements were performed using a Shimadzu TOC-L analyzer to determine the organic carbon load.

**Stability test of the photocatalytic composite foams**

The stability test protocol is a two-step protocol consisting first in subjecting the foam to the reaction conditions and constraints of a photocatalytic test in pure distilled water. After 12 h under stirring with an applied irradiance of 60 W/m$^2$, the foam was removed from the reactor before 4-chlorophenol as model substrate to degrade was added at 20 mg/L to the solution potentially containing the TiO$_2$ nanoparticles released from the foam. A photocatalytic test is subsequently performed following the same reaction conditions and protocol than in the case of the Diuron substrate.

**Characterisation techniques**

X-ray diffraction (XRD) patterns were recorded on a D8 Advance Bruker diffractometer in a θ/θ mode and using the Kα$_1$ radiation of a Cu anticathode ($\lambda$ = 1.5406Å).

The surface area measurements have been carried out on a Micrometrics Tristar 3000 using N$_2$ as adsorbent at −196°C with a prior outgassing at 200°C overnight to desorb the impurities or moisture. The Brunauer-Emmett-Teller (BET) specific surface area has been calculated from the N$_2$ adsorption isotherm.

Scanning electron microscopy (SEM) was performed in secondary electron mode on JEOL JSM-6700 F FEG microscope.

Thermogravimetric analysis (TGA) was carried out on a 20% (v/v) O$_2$/N$_2$ mixture at a 40 mL/min flow rate at a 10°C/min heating rate in the 25-900°C range with a Q5000TA analyzer.

X-ray photoelectron spectroscopy (XPS) characterization was performed on a ThermoVGMultilabESCA3000.

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**Table 1. Main physico-chemical properties of the TiO$_2$@β-SiC composite foams.**

|                  | β-SiC  | TiO$_2$@β-SiC-550 | TiO$_2$@β-SiC-600 | TiO$_2$@β-SiC-700 |
|------------------|--------|-------------------|-------------------|-------------------|
| TiO$_2$ crystallized phases (anatase/rutile) | -      | 97:3              | 65:35             | 63:37             |
| TiO$_2$ mean crystallite size (anatase/rutile) (nm)$^a$ | -      | 11/-              | 12/10             | 12/11             |
| S$_\text{BET}$ surface area (m$^2$/g) | 25     | 48                | 38                | 35                |
| Residual carbon content (wt. %)$^b$ | 0      | 4                 | 0.5               | 0                 |
| Mean cell size (φ) (µm) | 5400 ± 700 | 5000± 600 | 5100± 500 | 5200± 400 |
| Window size (a) (µm) | 2300 ± 575 | 2300± 300 | 2500± 500 | 2400± 400 |
| Bridge diameter (ds) (µm) | 575 ± 80 | 510± 30 | 545± 50 | 530± 20 |
| Open porosity$^c$ | 0.91± 0.05 | 0.94± 0.05 | 0.94± 0.05 | 0.94± 0.05 |
| Geometrical specific surface area (m$^{-1}$)$^d$ | 620 ± 200 | 460 ± 200 | 440 ± 200 | 453 ± 200 |

$^a$ determined from the XRD analysis by applying the Scherrer equation to the (101) and (110) peaks of anatase and rutile, respectively, with the classical assumption of spherical crystallites; $^b$ the residual unreacted carbon content was determined by TGA analysis by evaluating the weight loss observed between 500°C and 800°C; $^c$ measured by water displacement; $^d$ derived from the model developed by Edouard and coll. using the open porosity and the mean strut diameter $^{31,32}$.
spectrometer (Al Kα anode at hλ = 1486.6 eV). The energy shift due to electrostatic charging was subtracted using the adventitious sp2 carbon C 1s band at 284.6 eV.

Results and discussion
Characterization of the TiO$_2$@β-SiC composite foams
The main physico-chemical properties of the TiO$_2$@β-SiC composite foams are shown in Table 1. The schematic diagram of the sequential two-step carburization SMS replica synthesis shows optical images of the pre-shaped alveolar polyurethane precursor and of the composite foam at different steps of the replica synthesis process (Fig. 1). It evidenced that the original macrostructural features of the alveolar foams were retained throughout the multi-step sequential carburization SMS replica process, going from the pre-shaped polyurethane foam to the ready-to-use TiO$_2$@β-SiC composite foam (Table 1). Notably, both the alveolar open-cell structure and the cell size of the foam were maintained during each carburization step and the final calcination treatment.

Similary to the reference β-SiC foams, the TiO$_2$@β-SiC composite foams can be manufactured with adjustable shapes suitable for being adapted to the reactor geometry, and they have been prepared as 5 cm (d.) x 2 cm (h.) disks. The TiO$_2$@β-SiC composite foams and the reference β-SiC foam displayed globally similar macroscopic features in terms of characteristic parameters, with a cell size of 5200 ± 400 µm, a window size of 2380 ± 400 µm and a strut diameter at 540 ± 50µm, so that they exhibited a similar open porosity of ca. 0.91-0.94, and a similar geometrical surface area in the 440-620 m$^{-2}$ range. One can thus stress that the reference TiO$_2$/β-SiC foam and the newly developed TiO$_2$@β-SiC composite foams show a similar light transmission profile through the foams.

Figure 2. XRD patterns of the β-SiC-based foams at different steps of the synthesis protocol. (A) the bare alveolar β-SiC foam obtained through the classical SMS replica method, the C-rich β-SiC foam after the 1st carburization step and the shell/core TiC@β-SiC composite foam after the 2nd carburization step; (B) the TiO$_2$-β-SiC composite foams after calcination at 550°C, 600°C and 700°C. (*) most intense diffraction peak of crystallized SiO$_2$ (JCPDS card 65-0466).

The XRD patterns of the composite foams at different steps of the replica SMS are shown in Fig. 2A-B. They all exhibited the diffraction lines corresponding to the (111), (200), (202), (311) and (222) planes of the β-SiC polymorph in the fcc structure, that are similar to those of both the reference β-SiC foam and the β-SiC foam after the first carburization steps (labelled as C-rich β-SiC foam considering the presence of residual unreacted carbon species, see later Fig. 4A). After the 2nd carburization step at 1360°C, the pattern revealed the TiC@β-SiC nature of the composite foam, with the diffraction lines corresponding to the (111), (200), (220), (311) and (222) planes of TiC in a fcc structure. The TiC@β-SiC composite foam contained as well a small amount of crystallized SiO$_2$, evidenced by the presence of an additional peak at 22.0° characteristic of the diffraction of the (101) planes of crystallized SiO$_2$. This could result from the inhomogeneity of the carbon distribution within the shaped infiltrated body – due to the inhomogeneity either of the foam coating or within the infiltration slurry –, that could lead to the existence of carbon-poor zones during the foam carburization, and therefore to local deficits in reductive carbon compared to the silicon species. The TiC@β-SiC composite foam can be considered as a shell/core foam, since the 2nd carburization reaction occurred between the unreacted carbon species of the C-rich β-SiC foam and the TiO$_2$ exclusively located at the skeleton foam surface.

The XRD patterns of the composite foams after calcination shown in Fig 2B evidenced the selective oxidation of the TiC phase into TiO$_2$, thanks to the β-SiC resistance to oxidation, with the characteristic most intense peaks at 25.3° and 27.1° corresponding to the diffraction of the (101) and (110) planes of anatase (JCPDS card 21-1272) and rutile (JCPDS card 21-1276), respectively. At 550°C, the TiO$_2$@β-SiC composite foams had an anatase:rutile ratio of 97:3, that decreased to 65:35 and 63:37 at 600°C and 700°C, respectively. Although the rutile content increased with increasing the calcination temperature, it remained lower than that of TiO$_2$-β-SiC composite powders, that increased up to 70% when calcined at 600°C.
whereas β-SiC can act as a thermal regulator to disperse the heat issued from the TiC oxidation thanks to its high thermal conductivity, the continuous aspect of the self-bonded (i.e. binder-less) foams is known to improve the heat transfer through the whole matrix. This explained as well that the calcination temperature did not impact on the TiO$_2$ mean crystallite size, with a mean size around 11 nm.

The TiO$_2$@β-SiC composite foams had a higher surface area within the 35-48 m$^2$/g range when compared to that of the reference β-SiC foam at 25 m$^2$/g. This probably resulted from the presence in the foams of residual unreacted carbon with adsorption properties. Indeed, increasing the calcination temperature from 550°C to 700°C caused a decrease in the surface area of the composites, attributed to the combustion of the residual carbon. At 700°C, the surface area might be explained by the possible formation of voids and cracks during the TiC to TiO$_2$ oxidation, as reported in the case of TiO$_2$-β-SiC composite powder systems.

The heterogeneous nature of the TiO$_2$@β-SiC composite foam surface compared to the surface of the bare β-SiC foam was evidenced in the SEM images of Fig. 3. Further, the shell/core nature of the TiO$_2$@β-SiC composite foams was confirmed on the cross-section SEM images of a broken foam bridge, showing the existence of a thin skin located at the surface of a β-SiC core. EDS analysis carried out on the foam core revealed the absence of any titanium atoms, confirming its pure β-SiC nature, whereas both titanium and silicon elements were observed during the EDS analysis of the external skin, due to analysis depth in SEM (not shown).

TEM images of the TiO$_2$@β-SiC composite foam calcined at 550°C shown in Figure 4A evidenced the proximity of both β-SiC and anatase TiO$_2$ crystallites in the photocatalyst, with interplanar spacings of 2.5 Å and 3.5 Å consistent with the (111) and (101) planes of β-SiC and anatase TiO$_2$ phases, respectively. In addition, Figure 4B shows the residual presence of turbostratic carbon in the sample calcined at 550°C.
Dark adsorption experiments
The amount of residual unreacted carbon in the carbon-rich β-SiC skeleton foam after the 1st carburization step and in the TiO$_2$@β-SiC composite foams after calcination was determined by TGA experiments (Fig. 5A). The TGA profiles showed that the carbon-rich β-SiC skeleton foam contained 8 wt.% of excess carbon, whereas the calcination step applied to the TiC@β-SiC composite after the 2nd carburization of the foam for obtaining TiO$_2$ from TiC directly influenced the amount of residual unreacted carbon remaining within the TiO$_2$@β-SiC foams. A final calcination in air at 700°C was necessary for removing completely the residual carbon by combustion, whereas the TiO$_2$@β-SiC composite foams calcined at 550°C and 600°C contained about 4 wt.% and 0.5 wt.% of unreacted carbon (Table 1). The small weight gain above 800°C corresponded to the high temperature surface oxidation of SiC into SiO$_2$ as usually observed for SiC prepared via the SMS replica method. The evolution of the Diuron concentration during the dark adsorption period on the TiO$_2$@β-SiC composite foams calcined at temperatures in the 550-700°C range is shown in Fig. 5B for a 10 mg/L initial Diuron concentration and in Fig. S4 over a large range of concentrations (5, 10 and 20 mg/L). The adsorption properties of the composite foams were strongly influenced by the final calcination temperature, in agreement with the TGA profiles. Indeed, no significant adsorption of Diuron was obtained on the composite foams calcined at 700°C, while about 20% and 80% adsorption of Diuron was achieved on the composite foams calcined at 550°C and 600°C for a 10 mg/L initial Diuron concentration. Further, the influence of the amount of residual unreacted carbon in the composite on the adsorption profile was evidenced independently of the initial Diuron concentration (Fig. S4). The highest the amount of residual unreacted carbon in the composite foam, the highest the specific surface area developed by the foam and consequently the highest the adsorption profile, and the highest the Diuron amount removed by adsorption whatever the initial concentration.

So, the selection of the final calcination temperature (550-700°C range) appeared as an easy way to vary the amount of residual un-combusted carbon from 0 to 4 wt.%, and consequently, to tune the adsorption properties of the TiO$_2$@β-SiC composite foams, as materialized in Fig. 5C.

Photocatalytic runs
Fig. 6A shows that the TiO$_2$@β-SiC composite foams were active for degrading Diuron under solar light, whatever their adsorption properties, i.e. whatever the remaining diuron concentration to be removed after the adsorption step – 10, 8 or 2 mg/L for foams calcined at 700°C, 600°C and 550°C, respectively. The higher the adsorption capacity, the faster the reduction of the diuron concentration in water. However, the kinetic rate constants were not compared to that achieved on the TiO$_2$@β-SiC composite foam calcined at 700°C, due to far different initial concentrations of Diuron to be degraded. Calcined at 700 °C, the composite foam exhibited a lower activity in terms of Diuron degradation than the reference TiO$_2$/β-SiC foam prepared via impregnation and stabilization of TiO$_2$ on a conventional β-SiC foam, with an apparent kinetic constant of $3 \times 10^{-3}$ min$^{-1}$ vs. $14 \times 10^{-3}$ min$^{-1}$, respectively.
was evaluated by studying its ability to be reused, as well as by submitting the foam to a stability test procedure. First, the photocatalytic foam displayed a good reusability when performing several sequential runs, with apparent kinetic rate constants for Diuron degradation calculated in average as $2.9 \times 10^{-3} \text{ min}^{-1} \pm 0.1 \times 10^{-3} \text{ min}^{-1}$, respectively (Fig. 6C). Further, the implementation of the stability test procedure evidenced the superior stability of the TiO$_2$@β-SiC composite foam when compared to the TiO$_2$ supported β-SiC foam counterpart (Fig. 7). Indeed, after the first stirring treatment with the composite foams in pure water under UV-A, no 4-chlorophenol degradation was observed, whereas a degradation of 30% was obtained after of 150 min test in the case of the TiO$_2$/β-SiC foam. Although it cannot be ruled out that the TiO$_2$ nanoparticles potentially released from the composite foam displayed a lower photocatalytic activity than the TiO$_2$ P25 released from its supported counterpart, the amount of TiO$_2$ released from the supported photocatalyst has been estimated at 0.06 g/L using a calibration curve (Fig. S2), while by contrast remaining lower than 0.001 g/L in the case of the composite foam.

By contrast, the superiority of the reference TiO$_2$/β-SiC foam over the TiO$_2$@β-SiC composite foam was less pronounced in terms of TOC removal, with a kinetic constant of $12 \times 10^{-3}$ mg/Lmin$^{-1}$ vs. $9 \times 10^{-3}$ mg/Lmin$^{-1}$, respectively (Fig. 6B). This behavior might result from an enhanced degradation of the reaction intermediates on the composite foam compared to the reference foam counterpart.

Several groups evidenced that the Diuron degradation pathways were not affected when TiO$_2$ was associated to fibers and SiO$_2$ binder, or to Pt $^{19,27}$. Matos et al. also showed that associating TiO$_2$ with carbonized adsorbers did not modify the reaction mechanism and similar reaction intermediates were observed using phenol, 4-chlorophenol and 2,4-dichlorophenoxyacetic acid as model pollutants to degrade, when compared to bare TiO$_2$ (even if the product distribution might differ in some cases) $^{28,29}$. We thus proposed that the mechanism for the diuron photocatalytic degradation was not impacted by the adsorption properties of the TiO$_2$@β-SiC composite foams.

Finally, the stability of the TiO$_2$@β-SiC-700 composite foam was evaluated by studying its ability to be reused, as well as by The superior stability of the TiO$_2$@β-SiC composite foam was proposed to result from the existence of Ti-O-Si cross linking bonds between the external TiO$_2$ shell and the surface of the β-SiC skeleton core. Indeed, while the Ti$_{2p}$ orbital XPS spectra of the composite foam shows the typical Ti $2p_{3/2}$-Ti $2p_{1/2}$ doublet located at 458.3 eV and 464.0 eV with a spin-orbit splitting of 5.7 eV, ascribed to Ti$^{4+}$ (Ti-O) surface species in TiO$_2$ observed in the case of bulk TiO$_2$ powder and of the β-SiC foam supported TiO$_2$ counterpart, a higher energy contribution was observed and assigned to Ti-O-Si bonds in agreement with the literature (Fig. 8) $^{30-32}$. 

![Figure 6](image6.png)

(A) Diuron photodegradation kinetic and (B) mineralization kinetic obtained on the TiO$_2$@β-SiC composite foams. Comparison with a reference TiO$_2$(15wt.%)/β-SiC foam photocatalyst ; (C) Diuron photodegradation kinetics observed on the TiO$_2$@β-SiC-700 composite foam with consecutive runs.

![Figure 7](image7.png)

4-Chlorophenol photocatalytic degradation kinetics obtained during the stability test. Reaction conditions : [4-CP]$_0$ = 20 mg/L; T=25°C; UV-A irradiance of 60 W m$^{-2}$.
Figure 8. Ti 2p orbital XPS spectra recorded on the TiO$_2$@β-SiC composite foams, in comparison to the β-SiC supported TiO$_2$ photocatalyst counterpart and a reference TiO$_2$ powder (Aeroxide© P25 from Evonik).

**Conclusions**

Coating-free TiO$_2$@β-SiC photocatalytic composite foams have been synthesized through a sequential multi-step SMS replica method, in which an external TiO$_2$ layer was formed by the selective oxidation of an external TiC skin obtained by carburization of a TiO$_2$ coating at the surface of a β-SiC skeleton foam synthesized from a pre-shaped polymer foam during a first carburization step. This ready-to-use shell/core alveolar media exposed as irradiated surface the TiO$_2$ photocatalyst while the macroscopic structure was provided by the β-SiC alveolar foam, so that no post-synthesis immobilization or synthesis process of the active phase onto the foam support was necessary. Further, applying a final calcination treatment to the carbide foams (550-700°C) allowed the amount of residual unreacted carbon within the active shell/core TiO$_2$@β-SiC composite foams to be tuned, and consequently their adsorption behavior towards the Diuron pollutant in water to be tuned. The lowest the calcination temperature, the highest the adsorption profile of the composites. The ready-to-use TiO$_2$@β-SiC composite foams were active in the degradation of the Diuron pesticide in water, although remaining less efficient that the reference β-SiC supported foam TiO$_2$ photocatalyst counterpart. However, they displayed a good reusability with test cycles and benefitted from an enhanced stability in terms of titania release to water.

**Conflicts of interest**

There are no conflicts to declare.

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