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Macroscopic carbon nanofibers for use as photocatalyst support

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Abstract

To reduce the drawbacks related to the use of powders or immobilized catalysts in gas- and liquid-phase applications, a new material for the use as photocatalyst support was obtained by chemical vapor decomposition at 700 °C of an ethane–hydrogen mixture over a woven glass microfiber supported nickel catalyst, consequently leading to carbon nanofibers with macroscopic shaping, consisting in woven glass microfibers supporting a dense network of entangled 40 nm diameter carbon nanofibers. This material could be directly used after synthesis without any subsequent purification treatment due to the high yield and totally selective carbon nanofiber production. This shape memory design results in the direct use of the carbon nanofiber–woven glass microfiber composite as support without any post-synthesis shaping. The presence of hydrophilic oxygenated groups located at the outer surface of the carbon nanofibers allowed the sol–gel preparation of a woven glass microfiber–carbon nanofiber supported TiO_2 (20 wt.%) catalyst, using tetraisopropoxide as precursor. This new photocatalyst was totally stable under UV irradiation.

Keywords: Photocatalysis; Catalyst support; Carbon nanofiber; Morphology; Microstructure

1. Introduction

Development and application of the gas- and liquid-phase photocatalytic oxidation at room temperature for the removal of volatile organic compounds in air and organic pollutants in water have been increasing in the past decades [1–4]. The main advantage of photocatalysis over other oxidation treatments results from the replacement of the conventional thermal heating by the direct absorption of light at room temperature for supplying energy, allowing total mineralisation of pollutants to be obtained at room temperature. This light activation requires the use of semiconductor materials with adequate band gaps as catalysts. Among the generally used semiconductors, titanium dioxide (TiO_2) is up to now the most attractive and efficient one, i.e., a high photocatalytic efficiency due to its high quantum yield, its stability towards photocorrosion, its insolubility in water, its low toxicity and low costs. Its band gap energy of 3.2 eV requires photoexcitation with wavelengths less than about 385 nm, i.e., a near-UV illumination. Extensive reviews summarized the reaction mechanisms and the electron/hole generation processes involved in photocatalytic reactions [1–5].

However, their powder form makes them difficult to use (i) in slurry reactors due to restricting post-reaction separation processes for suspended powders and problematic diffusion limitations, and (ii) in fixed bed reactors because of the pressure drop. In addition to that, the use of a fluffy powder leads in both cases to difficulty of handling. In order to overcome such restricting drawbacks, a promising way is to immobilize them on solid substrates. However, heterogeneous phase reactors using immobilized powder may be limited by mass transfer due to the relatively lower external mass transfer area available for mass transfer per unit mass of catalyst. Mass transfer limitation could then be reduced by using glass microfibers for a direct support of semiconductor films [6,7]. Recently, Jitianu et al. have

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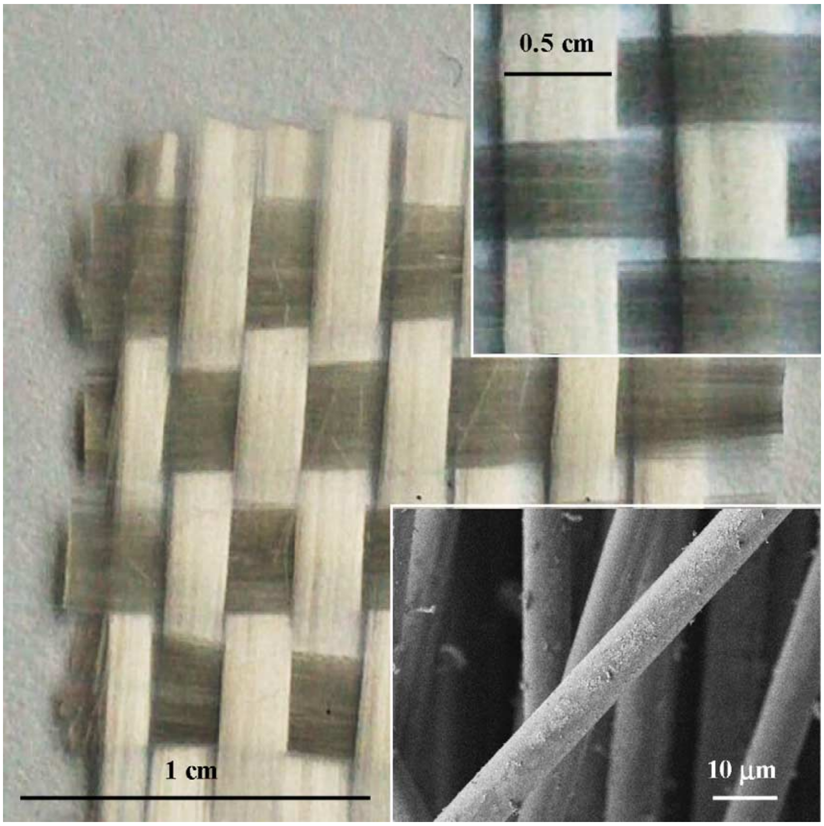

Fig. 1. Optical and scanning electron microscopy (inset down) images of the starting woven glass microfibers, showing glass microfibers with a mean diameter of 10 μm.

reported the synthesis of carbon nanotubes coated with TiO_2 nanoparticles or a continuous TiO_2 thin film for a potential use as photocatalysts in liquid-phase applications [8]. This highly interesting new material should lead to a decrease in mass transfer phenomena problems, but remains up to now in a powder form with the restricting drawbacks cited above.

Following the trend to avoid the restricting drawbacks of semiconductor powders, the aim of this article is to report the synthesis and characterization of a new carbon-based material for use as support material for photocatalytically active phase, carbon nanofibers with a macroscopic shaping. The solution proposed is to support the photocatalytic material on a new macroscopic support made of woven glass microfibers supporting carbon nanofibers, which combines the properties of the macroscopic woven glass microfiber host structure and the advantages of the carbon nanofibers, i.e., a high external surface area which significantly reduces mass transfer limitations and thus decreases the liquid reactant diffusion for liquid-phase processes and allows higher space velocity gas-phase processes to be performed. The characterization of this macroscopic carbon nanofiber material at different steps of the synthesis process was performed by means of powder X-ray diffraction (XRD), specific surface area measurements, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS).

2. Experimental section

2.1. Material synthesis

The host macroscopic structure for the growth of carbon nanofibers was very low surface area (lower than 1 m^2/g) and non-porous woven glass microfibers, with a mean diameter of about 10 μm supplied by Sinto (Aubagne, France). Fig. 1 shows a 2 cm × 2 cm cut piece of the starting woven glass microfibers. Deposition of nickel (1 wt.%) was performed by wet impregnation of the woven glass microfibers with a nickel nitrate $Ni(NO_3)_2 \cdot 6H_2O$ (Merck) ethanolic solution (0.9 mL of ethanol at 0.19 mol/L of nickel for 0.5 g of woven glass microfiber support). Evaporation of the solvent was performed overnight at room temperature before the solid was dried overnight at 110 °C and further calcined in static air at 350 °C for 2 h to form the corresponding nickel oxide. After reduction of the catalyst at 400 °C under pure hydrogen flow for 2 h in order to obtain metallic nickel supported particles, the carbon nanofiber synthesis was performed by the catalytic chemical vapor decomposition (CCVD) of a mixture of ethane and hydrogen (1:5 molar ratio and a total flow rate of 120 $cm^3 min^{-1}$) at 700 °C for 1 h using 0.5 g of starting Ni/glass microfiber catalyst.

TiO_2 supported on the carbon nanofiber–woven glass microfiber composite was elaborated by means of a conventional sol–gel precipitation process using titanium tetraisopropoxyde (Ti(OiPr)$_4$, i.e., TIP supplied by Aldrich, >97 vol.%) as reported by Colon et al. [9]. The composite material (0.5 g) was first impregnated with ethanol (0.5 mL) before adding dropwise TIP (0.5 mL) until the saturation of the material. This could be considered as an incipient wetness impregnation and all accessible carbon surface sites were wetted by the ethanol/TIP mixture. A volume of water equal to that of ethanol was then added dropwise to the material, kept at pH 9 by dropping 0.3 mL of a 30 vol.% ammonia aqueous solution. The gel was directly formed on the composite material by drying at room temperature and further overnight drying at 110 °C. The material was finally calcined in static air at 420 °C (heating rate of 2 °C/min) to obtain crystalline TiO_2. The exact amount of TiO_2 (expressed in wt.%) was determined both by atomic absorption spectroscopy (AAS) performed at the Service Central d'Analyse of the CNRS (Vernaison, France) and by comparing the weight of the composite supported TiO_2 material after calcination at 420 °C to that of the bare material.

2.2. Characterization techniques

Structural characterization was done by powder XRD measurements with a long time scan (10 s) and small steps (0.02° 2θ) carried out with a Siemens Diffractometer Model D-5000, using the Cu Kα radiation. The mean crystallite size, i.e., the average size of the coherently diffracting domains, was determined from the Scherrer equation with the normal assumption of spherical crystallites using the XRD peak width at half-maximum peak, corrected from the instrument broadening.

The surface area measurements were performed on a Coulter SA-3100 porosimeter using N_2 as adsorbant at LN_2. Before measurement, the sample was evacuated at 300 °C for 3 h in order to desorb the impurities and water adsorbed on its surface. The specific surface area of the sample was calculated from the N_2 adsorption isotherm using the B.E.T. method, and the micropore surface area was derived from the *t*-plot method reported by de Boer [10].

SEM, using a Jeol microscope Model JSM6700F operating with an accelerating voltage of 3 kV, was used to provide information on the morphology of the materials.

Microstructure of the materials was observed by TEM, carried out in a Topcon Model EM200B instrument operating at 200 kV.

XPS technique provided insight on the surface nature of materials and was performed at 12 kV and 20 mA (pass energy of 20 eV) in a static UHV chamber equipped with a VG CLAM analyzer, using Mg Kα source (1253.6 eV).

2.3. Photocatalytic device and validity experiment

The validity of the woven glass microfiber supported carbon nanofiber material for use as photocatalyst support

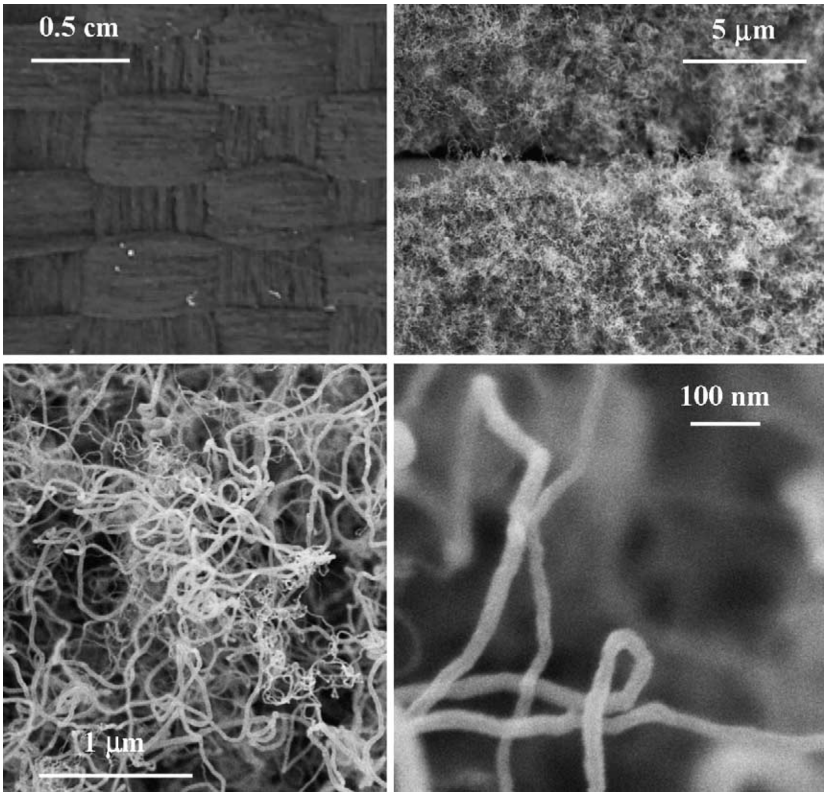

Fig. 2. Optical and scanning electron microscopy images of the woven glass microfiber supported carbon nanofiber material after 1 h of synthesis.

was checked by submitting the TiO_2/composite photocatalyst to 200 mL/min airflow at room temperature under UV irradiation. The air stream flows between the internal (quartz) and the external (Pyrex) concentric tubes, set 4 mm apart, of a single pass cylindrical concentric Pyrex/quartz tubular photoreactor, i.e., an annular reactor (300 mm length) previously described [11]. Illumination is provided by 8 W black light tube with a spectral peak at around 350 nm, located inside the inner tube of the photoreactor (35 mm diameter). The photocatalytic material was rolled between the internal and external tubes. The outlet stream was analyzed by a thermal conductivity dectector (microGC M200H HP microchomatograph) equipped for H_2O and CO_2 quantification (1 ppm of CO_2 accuracy). Relative humidity of 100% was defined as the saturated vapor pressure of water at 25 °C, which corresponded to about 24 Torr (about 3% relative to the total atmospheric pressure).

3. Results and discussion

Optical and SEM observations of the material after 1 h of CCVD with the mixture of hydrogen and ethane on the woven glass microfiber supported nickel catalyst are shown in Fig. 2. A weight increase of 87 wt.% was obtained for 1 h of growth. Fig. 2 shows that the glass microfibers were coated after growth by a thick layer (about 1 μm) of a dense entangled carbon nanofiber network. Very few parts of glass microfibers remained uncovered after reaction as it could be seen on a statistical sample of SEM images. The TEM image of Fig. 3 shows the well-known herringbone or "Chinese-hat" structure of the carbon nanofibers, with stacked graphene sheets forming a close angle exposing prismatic planes at the outer surfaces and sometimes connected at the middle of the nanofibers. They had a mean diameter of about 40 nm with lengths up to several micrometers. It should be mentioned that the metal loading was chosen to be low enough to have a negligible effect in further use and high enough to obtain a high yield to carbon nanofibers. Both SEM and TEM techniques revealed the total selectivity towards nanofiber formation, since no amorphous carbon, onion-like carbon or nanoparticles were detected in good agreement with the literature, which highlighted the advantages in terms of nanofiber selectivity for the CCVD of hydrocarbons [12–15]. In addition to that, the high purity obtained and the carbon nanofiber yield could allow the material to be directly used as support without any subsequent purification treatments.

The gross morphology of the woven glass microfibers was completely retained after the carbon nanofiber coverage process (Figs. 1 and 2a) leading to the concept of shape memory design (SMD), in which the macrostructural features of an appropriate woven glass microfiber preform determined the macroscopic shape of the resulting carbon nanofiber-based support, i.e., the macroscopic carbon nanofibers. The SMD method results in the direct use of the carbon nanofiber–woven glass microfiber composite as support without any post-synthesis shaping. This evidenced the advantage and the efficiency of the SMD method in the obtainment of photocatalyst support materials, especially designed for further uses in photocatalytic reactors with specific geometry.

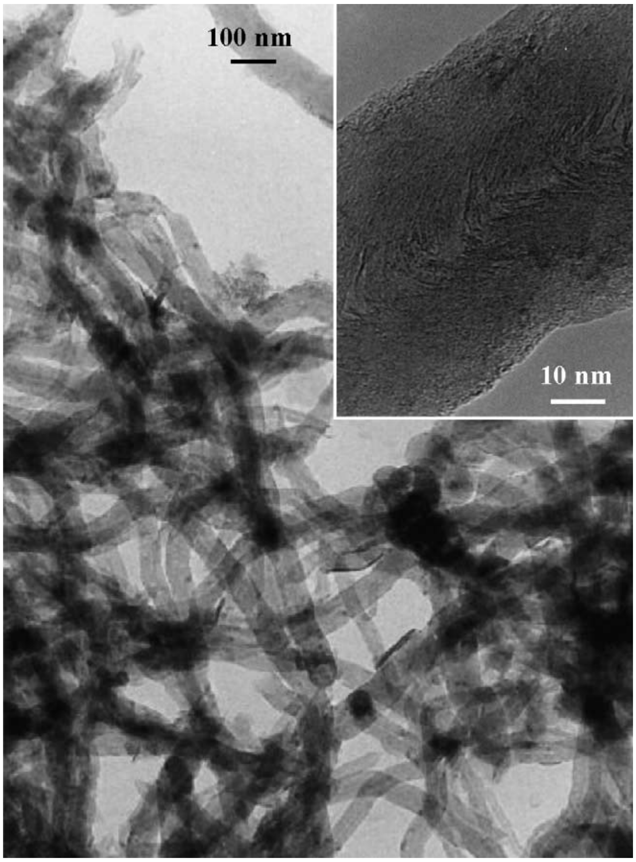

Fig. 3. Transmission electron microscopy image of the carbon nanofibers supported on the glass microfiber, evidencing the "Chinese-hat" structure.

The carbon nanofiber synthesis led to a strong increase in the surface area of the material, from lower than 1 up to 75 m^2/g and 115 m^2/g for the composite after 1 and 2 h of growth, respectively, without any additional porosity. The material could thus be considered as a high external surface area material, with a specific surface area given by the prismatic planes of carbon exposed at the outer surface of the nanofibers. It could be seen as a sponge with no closed porosity. The large void volume between each carbon nanofiber allowed the increase in the number of adsorption sites for nitrogen molecules. It should be noted that the surface area was lower than that of pure carbon nanofibers [16–18], because of the remaining very low surface area glass microfibers located in the core of the composite. The large void volume between each glass microfiber and between each carbon nanofiber inside the dense network surrounding the microfiber, evidenced by SEM characterization, means that large amounts of gas and liquid can pass through the material and both reactants and products can

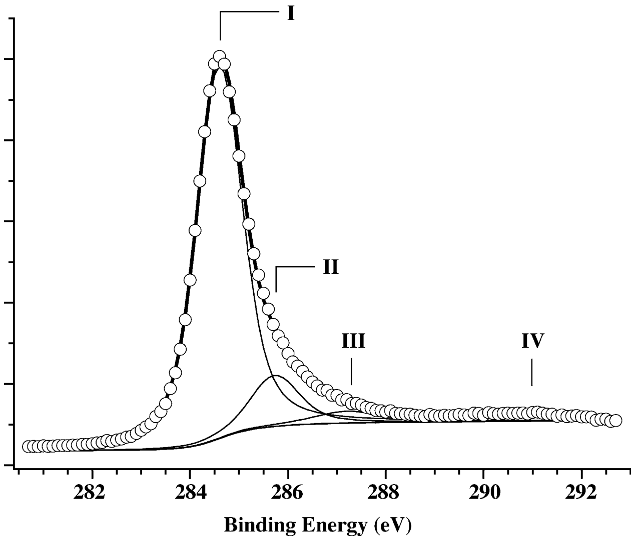

Fig. 4. C 1s X-ray photoemission spectroscopy spectrum obtained on the carbon nanofiber–woven glass microfiber composite material. The C 1s peak of graphite has been taken as energy reference at 284.6 eV according to the literature [19]. (○) Experimental points and (—) fitted curve. Contributions: (I) graphitic sp^2 carbon, (II) phenol groups, (III) carbonyl groups and (IV) plasmon peak.

diffuse inside the material following a 3D diffusion mode, as in a monolith-like structure.

The material displayed a good mechanical stability, neither carbon nanofiber loss nor soot formation having been observed after sonication (weight loss lower than 2 wt.%). This behavior could avoid the formation of fines during handling and processing of the material. This could be attributed to the bridging of the structure, neighboured microfibers, which were initially separated in the bare host structure, having been interwoven during the synthesis by means of the growing entangled carbon nanofiber web-like network.

Fig. 4 shows the C 1s XPS spectrum of the composite material. Due to the large shift sensitivity, the carbon C 1s range is commonly used in almost all applications in order to analyze oxygen functional groups on carbon materials. In addition to that, the O 1s signal is disturbed by (i) the glass (i.e., silica) microfibers located below the carbon nanofiber network and (ii) the presence of a film of molecular water which is not removed in UHV at low temperature, thus creating a large O 1s signal which overrides many structures in the oxygen functional group spectrum [19]. The broadening of the C 1s signal could be attributed to the presence of surface oxygen groups, with single and multiple carbon–oxygen bonds. Four contributions could be assigned, corresponding to graphitic sp^2 carbon (at 284.6 eV) together with phenols and carbonyl oxygenated groups, at 285.8 and 287.2 eV, respectively, and the graphite surface plasmon peak at about 291 eV, in close agreement with the literature [18–22]. The low-intensity surface plasmon component was a good indication for the average graphitic nature of the nanofibers with an extended π-electron conduction band system, as the $\pi \rightarrow \pi^*$ transition can be interpreted as a fingerprinting tool of the graphite surface quality. The surface of sp^2-hybridized carbon materials, heterogeneous in nature, is made of faces of graphene sheets and edges of such layers, the carbon atoms in the interior of the graphene sheets being less reactive than the atoms located at the edge sites. Oxygenated surface groups are thus preferentially located on the edges, giving also hydrophilic properties to the material.

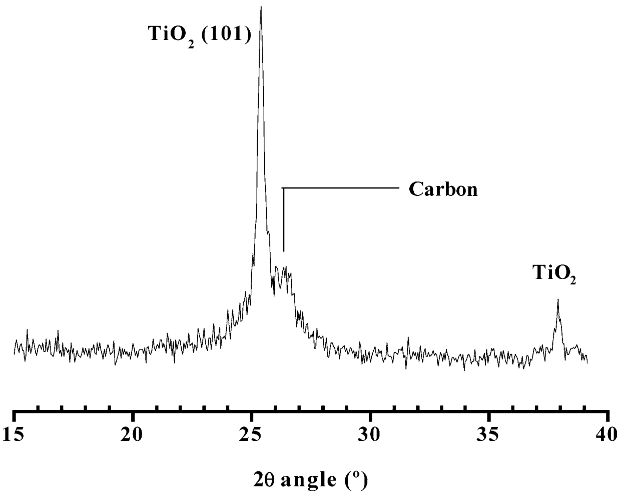

Fig. 5. X-ray diffraction pattern of the carbon nanofiber–woven glass microfiber composite material coated with TiO_2 nanoparticles (20 wt.%).

A woven glass microfiber–carbon nanofiber supported TiO_2 (20 wt.%) catalyst was obtained after calcination at 420 °C. A selected area of the XRD pattern of the material is shown in Fig. 5, and exhibited the main diffraction peak (101) corresponding to TiO_2 crystallized in the anatase structure (JCPDS File No. 21–1272) together with the main broad peak of graphitic carbon. The TiO_2 nanoparticles had an average particle size derived from the XRD peak broadening measurement of about 25 nm. Fig. 6 shows SEM images of woven glass microfiber–carbon nanofiber supported TiO_2 material, and evidenced the efficiency of the sol–gel method for supporting TiO_2 onto the composite material. In addition, no modification of the support material morphology could be observed, the carbon nanofiber-based support remaining stable towards oxidation in air up to 600 °C. It should be noted that even when the TiO_2 particles were not directly located on the carbon nanofibers, they had diameters ranging from 50 to 500 nm and remained located on a single microfiber, no larger particles having been observed. The easy anchorage of the supported phases on the carbon nanofiber–woven glass microfiber composite support could be helped by the presence of the hydrophilic surface groups, as compared to what is generally reported for the low reactivity basal planes of other sp^2 carbon structures such as multi-walled nanotubes. It should be noted that the easy deposition of homogeneously dispersed TiO_2 nanoparticles onto this new support by a conventional sol–gel method is a

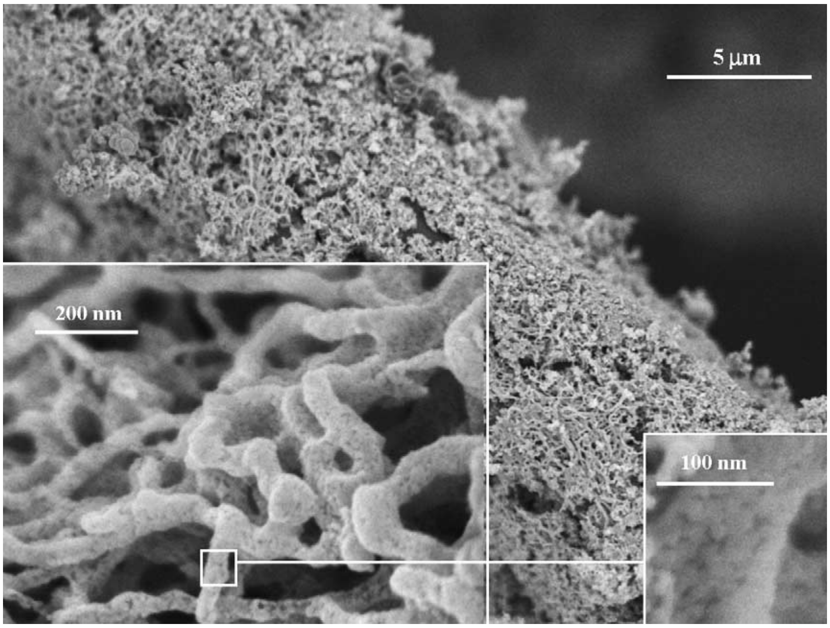

Fig. 6. Scanning electron microscopy images of the carbon nanofiber–woven glass microfiber composite material coated with TiO_2 nanoparticles (20 wt.%).

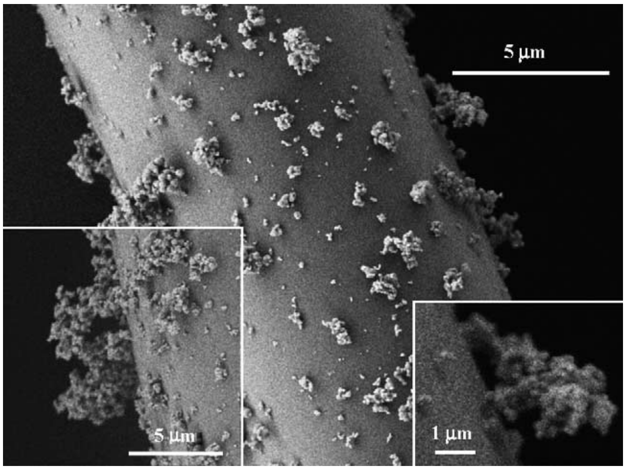

Fig. 7. Scanning electron microscopy image of the TiO_2 (10 wt.%)/glass microfibers material obtained by the same sol–gel method as used for the carbon nanofiber–woven glass microfiber composite.

great advantage as compared to restricting processes required when bare glass microfibers are used as support for TiO_2 nanoparticles or thin film. Indeed, performing the same sol–gel method on glass microfibers led to a highly inhomogeneous deposit of TiO_2 domains on the support (10 wt.% of TiO_2), as shown by SEM image (Fig. 7). Moreover, the TiO_2/glass microfiber material showed a very low anchorage of TiO_2, i.e., a low mechanical resistance, a decrease in the TiO_2 amount from 10 to 0.4 wt.% having been observed after 1 h sonication treatment. Contrarily, the anchorage of TiO_2 particles at the carbon nanofiber surface was strong enough to resist the sonication mechanical resistance testing, 1 h sonication leading to a decrease in the TiO_2 content from 20 to 18 wt.%.

The validity of the woven glass microfiber supported carbon nanofiber material for use as photocatalyst support was checked by submitting the TiO_2/composite photocatalyst to 200 mL/min airflow at room temperature under UV irradiation. It was noteworthy that whatever the relative humidity of the inlet airflow (from 0 to 90%), no CO_2 was detected in the outlet stream. The stability of the material under UV irradiation was essential to put forward for validating it as photocatalyst support.

4. Conclusion

The synthesis of macroscopic carbon nanofibers for use as photocatalytic support, made of woven glass microfibers supporting carbon nanofibers, was performed by a catalytic chemical vapor decomposition process on a woven glass microfiber supported nickel catalyst. Each woven glass microfiber was coated after growth by a dense network of entangled herringbone-like carbon nanofibers. This new material could be used as photocatalyst support without any subsequent purification treatments. The non-porous open structure with high external surface of the material, together with the hydrophilic properties given by the oxygenated functional groups located at the carbon nanofiber surface allowed easy anchorage of TiO_2 nanoparticles by a sol–gel synthesis method. The procedure could be extended to other photocatalysts, coupled-semiconductor systems or chemically modified TiO_2, as the mainly used precursor salts interacts with the oxygenated surface groups. The stability under UV light illumination of the photocatalyst allowed the macroscopic carbon nanofiber material to be validated for potential use as photocatalyst support.

This new photocatalyst support is more generally a promising way for designing minimum mass transfer limitation catalysts within the trend to avoid the restricting drawbacks of photocatalytic powders. Its macroscopic form hinders troubles of handling when compared to fluffy powders. Its use in liquid-phase processes could lead to a decrease in the liquid reactant diffusion, whereas higher space velocity processes could be performed for gas-phase applications.

Acknowledgments

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