Hierarchical synthesis of corrugated photocatalytic TiO₂ microsphere architectures on natural pollen surfaces

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ABSTRACT

Biomaterials are challenging, yet vastly promising templates for engineering unusual inorganic materials with unprecedented surface and structural properties. In the current work, a novel biotemplate-based photocatalytic material was synthesized in the form of corrugated TiO₂ microspheres by utilizing a sol-gel methodology where Ambrosia trifida (Ab. Giant ragweed) pollen was exploited as the initial biological support surface. Hierarchically synthesized TiO₂ microspheres were structurally characterized in detail via SEM-EDX, Raman spectroscopy, XRD and BET techniques in order to shed light on the surface chemistry, crystal structure, chemical composition and morphology of these novel material architectures. Photocatalytic functionality of the synthesized materials was demonstrated both in gas phase as well as in liquid phase. Along these lines, air and water purification capabilities of the synthesized TiO₂ microspheres were established by performing photocatalytic oxidative NOx(g) storage and Rhodamine B(aq) degradation experiments; respectively. The synthetic approach presented herein offers new opportunities to design and create sophisticated functional materials that can be used in micro reactor systems, adsorbents, drug delivery systems, catalytic processes, and sensor technologies.

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1. Introduction

Hazardous chemicals arising from combustion of fossil fuels, such as sulphur dioxide, nitrogen oxides, mercury, as well as industrial waste material including organic dyes, and solvents are among the prominent contaminants contributing to the water, air and soil pollution; causing a wide variety of severe health and environmental problems [1–5]. Heterogeneous catalysis plays an important role in coping with the environmental pollution at the global scale. One of the most abundant renewable energy sources that can be exploited in heterogeneous catalysis applications in an environmentally friendly and economical manner is the solar energy. Thus, there exists an immense demand to develop novel photocatalytic materials using innovative synthetic methodologies [6–11].

A large variety of materials such as metal oxides, metal hydroxides, metal carbides, metal nitrides, carbon allotropes and their derivatives have been investigated in the literature as photocatalysts [12–18]. Among them, titanium dioxide (TiO₂) has received considerable attention since the successful generation of H₂ from water via electrochemical photolysis of water by Fujishima and Honda [19]. TiO₂ has been the most frequently utilized photocatalytic material due to its functional versatility in a wide range of processes such as energy storage/conversion, photocatalytic pollution abatement, and biotechnology [20–22].

It is well known that physical and chemical properties of materials such as shape, texture, particle size, porosity, specific surface area, crystallinity, electronic band gap, surface defects and surface functional groups directly influence the photocatalytic performance. Particularly, shape and surface structural properties of photocatalytic materials can be closely linked to the reactivity and selectivity of these systems [23–25]. One of the most efficient and simple approaches to prepare sophisticated surface structures on materials is templating. Natural/biological starting materials can be used as temporal support systems/sacrificial templates in order to create well-defined shapes, sizes and textures on surfaces. For instance, mesoporous hollow SnO₂ microfibers were prepared using natural kapok (Ceiba pentandra) fiber as a template and were found to be photocatalytically active in methylene blue dye degradation under UV irradiation [26]. In another study, fresh natural rose (Rosa hybrida L.) petals were used as a template to synthesize TiO₂ flakes exhibiting higher photocatalytic activity than the commercial Degussa P25 photocatalyst [27]. Also, cerium-doped TiO₂ mesoporous nanofibers were prepared by a single-pot synthesis method using collagen fiber...
biotemplates [28]. A variety of synthetic techniques have been developed to deposit the desired photocatalytic material on the surface of bio-templates including sputtering, sol-gel, electrochemical deposition, and chemical vapour deposition approaches. Using such synthetic methods, micro/nanostructures such as wires, tubes, rods or spheres can be fabricated preserving the original shape and size of the initial natural template. Pollen grains attract attention as versatile biotemplates due to their unique and sophisticated surface structures at the micro/nanoscale [7,29–33].

Thus, in the present study, a simple biotemplate assisted sol-gel route is presented in order to synthesize TiO$_2$ photocatalytic microspheres with unique surface morphologies, where Ambrosia trifida (Ab, Giant ragweed) pollen is used as the starting bio-substrate. Ab is selected as a biotemplate due to its unusual micron-sized surface morphology exhibiting conical nano-spikes. Upon detailed structural characterization of this novel material platform, photocatalytic functionality of these hierarchical systems under ultraviolet-A (UVA) irradiation is also demonstrated at two different interfaces namely, Rhodamine B (Rhb) photodegradation at the liquid/solid interface as well as the photocatalytic oxidative storage of NO$_x$(g) at the gas/solid interface; illustrating the catalytic versatility of this new family of materials.

2. Experimental

2.1. Materials

Ambrosia trifida (Ab, Giant ragweed) pollens were obtained from Bonapol a.s. Company (Czech Republic). Titanium (IV) isopropoxide (TIP, 97%), ethanol (99.8%), and Rhodamine B (Rhb, dye content ~95%) were purchased from Sigma-Aldrich (Germany). All chemicals were of analytical grade and used as received without any further treatment. Milli-Q ultra-pure deionized water (18.2 MΩ cm) was also used as a solvent.

2.2. Synthesis of biotemplated TiO$_2$ microspheres

Biotemplated TiO$_2$ microspheres were prepared using a method analogous to the one described in one of our previous reports [7]. Briefly, Ab pollens were washed with anhydrous ethanol to remove surface impurities and subsequently dried under ambient conditions for 48 h. Then, titanium (IV) isopropoxide (TIP, 4 mL) precursor was mixed with ethanol (2 mL) for a period of 10 min at room temperature. 100 mg clean Ab pollen (i.e., biotemplate) was added to the prepared precursor solution and the slurry was stirred vigorously for 30 min. After depositing precursor solution on the outer surface (i.e. exine) of the biotemplate, the mixture was filtered to remove the excess decantate. Coated sample was aged for 60 min under ambient conditions in order to allow for the hydrolysis and polycondensation reactions to proceed, forming an amorphous TiO$_2$ shell on the biotemplate surface. Then, calcination steps were executed in a muffle furnace at various temperatures varying within 400°C–900°C (for 2.5 h per calcination step) in air, where the sacrificial biotemplate was eliminated and the crystallization and ordering of the TiO$_2$ overlayer were achieved. Products obtained at the end of the synthesis protocol are named as AbTi-X, where X indicates the calcination temperature.

2.3. Characterization

Surface structure and morphology of the samples were investigated via a Carl-Zeiss Evo40 scanning electron microscope (SEM) with an accelerating voltage varying within 5–10 kV. For elemental analysis, energy dispersive X-ray (EDX) analysis of the powder samples dispersed on an electrically conductive carbon film was performed using an accelerating voltage of 10 kV.

Crystallographic changes on the samples after calcination were determined via XRD measurements performed using a Rigaku (Japan) X-ray diffractometer equipped with a Miniflex goniometer and a monochromated high-intensity CuKα radiation (λ = 1.5405 Å, 30 kV, 15 mA) source. XRD data were collected by scanning the 2θ range within 10–60° using a step size of 0.02° s$^{-1}$. Identification of the unknown phases in the powder XRD data were made by utilizing Powder Diffraction File (PDF) database maintained by the International Centre for Diffraction Data (ICDD).

Raman experiments were carried out using a LabRAM HR800 spectrometer (Horiba Jobin Yvon, Japan) equipped with a Nd:YAG laser (λ = 532.1 nm, 20 mW) and an integrated confocal Olympus BX41 microscope. The system was calibrated using the reference Si Raman shift at 520.7 cm$^{-1}$ by adjusting the zero-order position of the grating. Powder sample was evenly spread on a single crystal Si wafer and Raman spectra were recorded in the range of 100–1500 cm$^{-1}$ with a spectral resolution of 4 cm$^{-1}$ at room temperature.

The Brunauer–Emmett–Teller (BET) SSA measurements of the synthesized catalysts were determined by nitrogen adsorption-desorption isotherms using a Micromeritics Tristar 3000 surface area and pore size analyser. Prior to SSA analysis, all samples were outgassed in vacuum for 2 h at 150°C.

2.4. Liquid phase photocatalytic activity tests for the degradation of Rhb (aq)

Photocatalytic functionality of the biotemplated TiO$_2$ microspheres in liquid phase was demonstrated via Rhb (aq) dye degradation under UVA irradiation at room temperature. Rhb is a frequently used model pollutant for testing the photocatalytic activity of novel materials in water. Rhb degradation experiments were performed in a photocatalytic reactor equipped with an 8 W Sylvania UVA-lamp (FW8, T5, Black-light, 368 nm). A cooling fan was also installed inside the reactor for temperature regulation. Initially, a 48 mL aqueous solution of Rhb (10 mg L$^{-1}$) was prepared in dark and 25 mg of biotemplated TiO$_2$ microspheres were ultrasonically dispersed in this solution to form a suspension. Then, the sample container was placed at a specified position inside the photocatalytic reactor, where the distance between the light source and the suspension was fixed at 13 cm. Prior to UVA light irradiation, the suspension was magnetically stirred inside the reactor under dark conditions for 30 min in order to establish an adsorption-desorption equilibrium between the photocatalyst and Rhb (aq). Before the UVA light exposure, a 3 mL aliquot was extracted from the suspension under dark conditions and the concentration of this starting solution was designated as C$_0$. Identical amounts of samples were obtained during the UVA light irradiation after certain time intervals whose concentrations were denoted as C$_t$. After removing the photocatalyst from the extracted samples via centrifugation, Rhb concentration of the extracted solutions were determined using a UV–vis spectrophotometer (Cary 300, Agilent) with the help of a calibration curve utilizing the Rhb characteristic maximal absorption band at ca. 553 nm. The typical photon power density (irradiance) during the experiments was 7.4 W m$^{-2}$ which was measured by a photo radiometer (Delta Ohm, HD2302.0, Italy) equipped with a UVA probe (DeltaOhm, LP471 UVA). The photocatalytic dye degradation efficiency ($D_{off}$) of the photocatalysts was calculated according to following equation:

$$D_{off} (%) = \frac{C_0 - C_t}{C_0} \times 100$$  

where, $C_0$ is the initial Rhb concentration and $C_t$ is the Rhb concentration at a given time $t$.  


2.5. Gas phase photocatalytic activity tests for the removal of gaseous nitric oxide

In order to demonstrate the functional versatility of the synthesized biotemplated TiO$_2$ microspheres, in addition to the liquid phase photocatalytic tests, obtained materials were also used in photocatalytic oxidative storage of NO at the solid/gas interface. Photocatalytic removal of NO($g$) over biotemplated TiO$_2$ microspheres was performed at room temperature in a custom-made continuous photocatalytic flow reactor which was designed considering the ISO 22197-1: 2007 standard [8–10,34]. This photocatalytic reaction system was composed of a gas supply unit, a flat-bed photoreactor chamber housing the sample, a UVA illumination source and a chemiluminescent NOx analyser (Horiba APNA-370) for continuous inline monitoring of the NO, NO$_2$ and total NOx concentrations [8–10]. In the gas supply unit, NO (100 ppm NO in N$_2$ balance, Linde GmbH) was mixed with O$_2$ (99.998%, Linde GmbH) and N$_2$ (99.998%, Linde GmbH) at room temperature. The total gas flow rate in the reactor was kept at ca. 1.0 SLM (standard liters per minute) via mass flow controllers (MFCs, MKS, 1479A) by adjusting the flow rate of each gas (i.e. N$_2$ = 0.75 SLM, O$_2$ = 0.25 SLM, and NO = 0.01 SLM). The gas mixture was also passed through a water bubbler before the reactor for humidification and the relative humidity (RH) of the gas mixture was measured via a Hanna HI 9565 humidity analyzer at the sample position in the photocatalytic reactor at room temperature. RH was detected to be typically ca. 70% at room temperature during the measurements. Synthesized photocatalyst powder samples (250 mg) were gently pressed on a poly-methyl methacrylate (PMMA) sample holder (2 × 20 × 20 mm$^3$) to produce a smooth surface. In order to activate the photocatalysts and remove the initial surface contaminants, before the gas phase photocatalytic activity measurements, samples were exposed to UVA irradiation under ambient conditions for 18 h. Then, the sample was placed into the photocatalytic reactor, where a UVA lamp (Sylvania UV-lamp, black-light, FBW, TS, 368 nm) was placed above the reactor. Next, the gas mixture was fed to the photocatalytic reactor, where the gas feed swept the surface of the powder photocatalyst sample. After establishing the adsorption-desorption equilibrium inside the photocatalytic reactor, UVA illumination source was activated to initiate the photocatalytic reaction. Control experiments carried out in the absence of a photocatalyst (i.e. in the empty reactor under the UVA illumination) revealed no catalytic conversion. Photocatalytic conversion efficiency for NO and photocatalytic NO$_2$ production efficiency (ζ%) over TiO$_2$ microspheres were calculated as follows:

\[
\zeta = \frac{n_{\text{NO}_2\text{tot}} - n_{\text{NO}_2\text{pass}}}{n_{\text{photon}}} \times 100
\]

(2)

where, $n_{\text{NO}_2\text{tot}}$ is the decrease in the total number of moles of all gaseous NOx species and $n_{\text{NO}_2\text{pass}}$ is the number of moles of NO$_2$ generated in 60 min (i.e. over the course of a full photocatalytic NOx removal experiment). In this equation, $n_{\text{photon}}$ corresponds to the total number of moles of incident UVA photons impinging on the catalyst surface during the 60 min time interval. $n_{\text{photon}}$ was calculated by using the photon power density of the UVA lamp ($I = 7.4$ W m$^{-2}$), representative emission wavelength of the UVA lamp ($\lambda = 368$ nm), surface area of the sample holder that is exposed to the UVA irradiation ($S = 2$ cm $\times$ 2 cm $= 4$ cm$^2$), duration of the
Fig. 2. Schematic illustration of one of the possible synthetic routes leading to the formation of biotemplated TiO$_2$ microspheres: (i) coated Ab pollen, (ii) biotemplated TiO$_2$ microspheres after the removal of the Ab pollen by calcination.

photocatalytic test ($t = 3600$ s), Avogadro's number ($N_A$), Planck's constant ($h$), and the speed of light ($c$) as shown in Eq. (3) below:

$$n_{\text{photon}} = \frac{h c}{N_A h c}$$

(3)

3. Results and discussion

3.1. Structure and morphology

Surface elemental composition and the morphology of the uncoated Ab pollen grains were investigated using SEM and EDX techniques (Fig. 1a and b). Macroscopic structural components of the Ab pollens were also schematically described in Fig. 1c. As can be seen in Fig. 1c, Ab pollens are composed of two nested layers covering the living matter and protecting it against the external physical and chemical adverse effects [35,36]. The robust outer surface called exine (Fig. 1c) is composed of a highly crosslinked organic substance that can include fatty acids, phenylpropanoids, and phenolic sporopollens. The inner layer of the pollen (Fig. 1c) is called the intine and is primarily composed of cellulosic materials and polysaccharides [35,36]. In order to study the morphological and structural alterations occurring upon calcination, uncoated Ab pollen samples were investigated comparatively by SEM and EDX analysis before and after calcination (Fig. 1a–e). Fig. 1b shows that, uncoated Ab pollens have a spherical shape with an average pollen size of 23.5 ± 1.5 μm decorated with conical nano-spikes/thorns. After the calcination of the uncoated pollens at 800 °C, obvious structural and morphological changes were observed signifying visible geometric deformation (Fig. 1e). According to the EDX spectra given in Fig. 1a, while uncoated microspheres have a carbonaceous outermost layer exhibiting mainly C and O signals before calcination, upon calcination at 800 °C, pollens seem to lose their structural integrity and deform from their original shapes, revealing a variety of EDX signals corresponding to elements such C, O, Mg, P, S, K, and Ca (Figs. 1d and e). It is likely that during the calcination process, outer exine layer of the uncoated pollens is partially destroyed and the biological material inside the intine capsule, which may involve various minerals for vitality, diffuse to the surface at elevated temperatures, leading to the detection of the EDX elemental signals for C, O, Mg, P, S, K, and Ca (Figs. 1d and e).

In the current work, Ab pollens were selected as a biotemplate to direct the formation of biomorphic TiO$_2$ microspheres using the
sol-gel process. Fig. 2 provides one of the possible reaction pathways for the sol-gel synthetic route used herein. As illustrated in Fig. 2, after the alcoholysis reaction, metal alkoxide species are expected to bind to the naturally functionalized surface of the pollen template through condensation and hydrolysis reactions. Extent of the metal alkoxide deposition and the corresponding thickness of the ultimate TiO₂ overlayer were controlled by the composition/concentration of the precursor solution as well as the duration of the alcoholysis reaction. After the formation of the TiO₂ overlayer, calcination process leads to the formation of a bimorphic TiO₂ surface preserving most of the original shape, size, and morphology of the Ab biotemplate.

Fig. 3 shows the SEM image and the corresponding EDX spectrum of the TiOₓ deposited Ab pollens after hydrolysis and polycondensation reactions at room temperature (i.e. before calcination). SEM image reveals the formation of a homogenous/continuous TiOₓ overlayer preserving the characteristic microstructure of the nascent pollen surface. This is also evident by the EDX spectrum in Fig. 3, indicating a strong Ti signal overwhelming that of the other pre-existing elements on the surface such as Ca, S, K, and P.

Calcination was employed in order to convert amorphous TiOₓ coating on the Ab pollens into crystalline TiO₂ overlayers (Fig. 4). Low-magnification SEM image (Fig. 4a) shows that TiO₂ microcrystals are relatively well-dispersed rather than severely aggregated. While the calcination process induces the crystallization of the TiOₓ overlayer to TiO₂, it also leads to morphological modifications at the nanometer scale resulting in the formation of a spongy/porous and a corrugated network on the surface (Fig. 4b–d and f). Comparison of the bare Ab (Fig. 1b) or coated Ab pollens before calcination (AbTi-25, Fig. 3), with the ones obtained after calcination (e.g. 600 °C and 800 °C) suggests deformation of the sharp conical spikes (Fig. 4b–d and f), in addition to the shrinking of the pollens to a smaller average diameter of ca. 13 μm.

After calcination (Fig. 4e), P, K, and Ca signals originating from the biotemplate becomes discernible on the AbTi-600 and AbTi-800 surfaces. It can be seen in Figs. 4b and 4e that an aperture with an approximate diameter of 2.5 μm exists in the Ab pollen structure, from which the pollen tube extends at germination to fertilize the ovum. Thus, it is feasible that during the calcination process, the interior part of the pollen (i.e. intine and other biological living matter depicted in Fig. 1c) diffuses outbound through this aperture and spilled over on the TiO₂ surface at elevated temperatures.

Fig. 5a and b illustrate the phase changes occurring on the AbTi materials as a function of calcination temperature via XRD and Raman spectroscopy, respectively. It is apparent that the diffraction signals in Fig. 5a intensify and sharpen with increasing calcination temperatures suggesting ordering and crystallization of the TiO₂ overlayer on the AbTi surface. XRD patterns of the AbTi microspheres reveal predominantly anatase phase at calcination temperatures ≥600 °C, while two different ordered TiO₂ phases namely, anatase (ICDD No. 00-021-1272) and rutile (ICDD No. 00-021-1276) are visible for the calcination temperatures above 600 °C (Fig. 5a). Also, Fig. 6 depicts relative mass fraction of anatase and rutile phases for various samples calculated using the XRD data via Spurr and Myers approach [37]. It is clear that the anatase to rutile phase transition on the Ab surface starts to occur predominantly at T ≥ 800 °C. Rutile mass fraction increases drastically for T > 800 °C, while for the AbTi-900 sample, anatase and rutile phases reveal almost equal mass fractions.

Average crystallite sizes of the anatase and rutile phases were also calculated using the anatase (101) and rutile (110) diffraction signals via Scherrer equation [38,39] (Fig. 6). These results suggest that anatase and rutile domains have similar average crystallite sizes (ca. 20–30 nm) for AbTi-700 and AbTi-800 samples while they drastically diverge from each other for the AbTi-900 sample, where rutile crystallite size surpasses that of the anatase (ca. 47 nm for anatase and ca. 134 nm for rutile). Fig. 6 indicates that increasing calcination temperatures results in a monotonic increase in the crystalline sizes of anatase and rutile domains due to sintering.

Raman spectroscopic measurements were also performed in order to confirm the structural properties of the biotemplated TiO₂ microspheres. Fig. 5b displays the Raman spectra of the samples prepared by calcination of the coated AbTi samples at different temperatures. Characteristic anatase Raman scattering features at 147 cm⁻¹ (E₂g), 397 cm⁻¹ (B₁g), 515 cm⁻¹ (A₁g), and 641 cm⁻¹ (E₂g) are observed for all samples except the AbTi-400 sample. For the AbTi-900 sample, additional Raman peaks at 445 cm⁻¹ (E₂g) and 612 cm⁻¹ (A₁g) are visible which can be attributed to the rutile phase. In good accordance with the current XRD measurements (Fig. 5a), Raman data in Fig. 5b also indicate that the rutile content of the samples increases with increasing calcination temperatures. In addition to these signals, some of the Raman spectra in Fig. 5b also includes an additional feature at 484 cm⁻¹ (labelled “with the symbol *” in Fig. 5b) which can tentatively be attributed to complex temporal species generated during the calcination of the biopolymer matrix of the underlying Ambrosia template [7].

### 3.2. Photocatalytic activity of the biotemplated TiO₂ microspheres

Fig. 7a presents the photocatalytic RhB (aq) degradation studies performed under UV-A irradiation at room temperature by using biotemplated TiO₂ microspheres calcined at various temperatures. Fig. 7b shows a typical series of time-dependent UV–vis absorption spectra of the RhB(aq) containing the AbTi-800 sample obtained during the UVA irradiation. It is apparent that the characteristic RhB absorption band at 553 nm gradually decreases while the photocatalytic dye degradation reaction proceeds. After 120 min UVA light exposure, color originating from RhB dye is virtually disappears evident by the vanishing absorption signal at 553 nm. Note that the photocatalytic RhB (aq) degradation performance of the AbTi-400 sample is not reported in Fig. 7. This is due to the fact that such low calcination temperatures do not allow the complete removal of the biotemplate which in turn, leads to the formation of grains with low material density that can float on the top of the RhB (aq) solution preventing their homogenous mixing and uniform irradiation.

As a standard control experiment, measured decrease in RhB concentration of the RhB (aq) solution under UVA irradiation in the absence of a catalyst was also monitored in order to investigate the non-catalytic self photodegradation of the RhB dye (Fig. 7a). As can be seen in Fig. 7a, within 500–800 °C, increasing calcination temperature leads to a monotonic enhancement in the photocatalytic RhB (aq) degradation. However, calcination at higher temperatures such as 900 °C results in an attenuation of the photocatalytic RhB (aq) decomposition performance. Based on the structural characterization data provided in Fig. 6 and the liquid phase photocatalytic activity data given in Fig. 7, it can be realised that the optimum photocatalyst sample for RhB (aq) degradation (i.e. AbTi-800) is comprised of both anatase and rutile domains with a specific surface area of ca. 7–8 m²/g. It is also apparent that the monotonic increase in the photocatalytic RhB (aq) decomposition performance within 500–800 °C is concomitant to the increase in the crystallinity as well as the average size of the anatase domains, where the latter converges to ca. 30 nm for the AbTi-800 sample. Fig. 6 also suggests that the AbTi-800 sample is comprised of 94.9% anatase and 5.1% rutile by mass. On the other hand, at elevated calcination temperatures such as 900 °C, relative rutile mass fraction increases to values above the optimal value, leading to attenuation in the photocatalytic performance (Figs. 6 and 7). It is apparent that the optimum bio-templated photocatalyst studied in the current work for the RhB (aq) degradation processes possesses co-existing anatase and rutile domains functioning in a synergistic manner with
Fig. 4. SEM images of the biotemplated TiO₂ microspheres calcined for 2.5 h in air at (a) 800 °C (low magnification image, AbTi-800), (b) 600 °C (AbTi-600), and (c, d, and f) 800 °C (AbTi-800). Image (d) also emphasizes the SEM image showing the detailed morphology of the AbTi-800 pollen surface exhibiting a porous and a corrugated TiO₂ overlayer structure. (e) EDX spectra obtained from the circled regions labelled as 1, 2, 3 in (f).

Fig. 5. (a) XRD patterns and (b) the Raman spectra of the biotemplated TiO₂ microspheres calcined at 400, 500, 600, 700, 800, and 900 °C for 2.5 h in air after coating. “A” and “R” letters correspond to anatase and rutile phases, respectively (see text for details).
particular crystallite sizes and a unique mass fraction. This observation is in perfect agreement with former photocatalytic studies on other TiO$_2$-based systems in the literature [40–42]. It should be noted that the photocatalytic activity of AbTi systems are typically lower than that of a conventional benchmark catalyst such as Degussa P25 revealing% photonic efficiencies of 0.45 and 0.11 for NO$_2$(g) production and NOx storage; respectively. This can be attributed to the higher SSA of P25 (ca. 50 m$^2$/g).

After having demonstrated the photocatalytic water purification capabilities of the Ab-templated TiO$_2$ microspheres under UVA irradiation, we performed further studies in order to establish the photocatalytic activity of this new family of materials in photocatalytic air purification applications. Along these lines, photocatalytic NO(g) oxidation and storage experiments were carried out using a custom-made photocatalytic flow reactor under UVA irradiation [8–10]. Fig. 8 presents results of these gas phase photocatalytic activity tests. The resulting typical time-dependent concentration profiles for the photocatalytic NO oxidative storage experiment is also shown in the inset of Fig. 8. In the histograms of Fig. 8, percent photonic efficiency values for total NOx removal (blue bars) and NO$_2$ production (red bars) are shown. It is worth mentioning that an ideal photocatalyst for gas phase DeNOx applications should exhibit a high NOx(g) storage/removal efficiency as well as low NO$_2$(g) generation/release characteristics. Photocatalytic oxidative
storage of NO(g) includes oxidation steps [11,34,43,44] involving the formation of NO2(g), where the eventual storage of NOx species on the catalyst surface may occur in the form of chemisorbed NO, NO2/NO3−, N2O, and NO3−. Thus, maximizing the oxidative NOx storage at the solid state, while simultaneously minimizing the gas phase release of toxic NO2(g) requires optimization of the chemical, electronic and surface structure of the photocatalysts.

Along these lines, photocatalytic DeNOx performance of the synthesized AbTi photocatalysts were investigated as a function of the calcination temperature used in the synthetic protocol, in an attempt to monitor the structure-functionality relationships. Photocatalytic activity data presented in Fig. 8 can be analysed in the light of these arguments (Figs. 1–6). It is apparent that unlike the liquid phase RhB (aq) degradation results given in Fig. 7, suggesting AbTi-800 as the optimum catalyst in the liquid phase, Fig. 8 shows that AbTi-800 has limited photocatalytic NOx abatement capability in gas phase. This observation may suggest relatively different reaction mechanisms and involvement of dissimilar active sites for the photocatalytic liquid phase water purification processes as compared to the gas phase photocatalytic DeNOx processes occurring on the same catalyst surface.

The highest total photocatalytic gas phase activity can be assigned to the AbTi-600 catalyst given in Fig. 8 due to the fact that this catalyst reveals maximum NOx removal efficiency and maximum photocatalytic oxidation of NO(g) to NO2(g). On the other hand, AbTi-500 should not be identified as the photocatalyst of choice due to its high NO2(g) release to the atmosphere. Comparison of the AbTi-600 catalyst with AbTi-500 reveals that the AbTi-500 has a comparable NOx storage efficiency to that of the AbTi-600 catalyst, while exhibiting much lower NO2(g) release. Hence, AbTi-500 can be considered as the preferable catalyst in the series for gas phase photocatalytic DeNOx applications. It is likely that the gas phase photocatalytic oxidation of NO(g) requires the presence of ordered anatase domains, while prevention of the NO2(g) slip to the atmosphere requires a porous/high surface area catalyst that can optimize capture/adsorption/solid state storage of the generated NO2(g). This is consistent with the observation that the AbTi-400 catalyst obtained after a low-temperature calcination step has limited NOx removal efficiency as well as low NO2(g) production, due to the lack of ordered anatase domains and presence of small anatase particles and disordered (amorphous) domains. In other words, the main reason for the poor performance of AbTi-400 seems to be its limited photocatalytic oxidation capability rather than its lack of surface area for NOx storage. In contrast, for the catalysts calcined at T ≥ 700 °C, the main catalytic disadvantage could be shrinkage of the pollens at high temperatures (i.e., decrease in the available surface sites for adsorption and storage of oxidized NOx species) and decrease in the number of exposed active sites, which in turn hinder the storage of photocatalytically produced NO2 species, resulting in detrimental NO2 release to the atmosphere. Comparison of the liquid phase photocatalytic activity of AbTi systems with that of a benchmark catalyst (i.e. Degussa P25) reveals that the latter system has a higher photocatalytic activity, where 100% decolorization efficiency can be reached after ca. 70 min. This observation can be associated with the higher surface area of the latter system.

4. Conclusions

A novel biotemplate-based photocatalytic material platform was synthesized by utilizing Ambrosia trifida (Ab, Giant ragweed) pollen as the initial biological support surface. Structural characterization of the synthesized biotemplated TiO2 microspheres was performed using SEM-EDX, Raman spectroscopy, and XRD techniques. Photocatalytic functionality of the synthesized materials was demonstrated both in gas phase (via photocatalytic oxidative NOx storage) and in liquid phase (via photocatalytic Rhodamine B (aq) degradation) as a function of the calcination temperature used in the synthetic protocol. Optimum catalyst for RhB (aq) photocatalytic degradation in the liquid phase was found to be AbTi-800, while the optimum catalyst for gas phase photocatalytic oxidative NOx storage was AbTi-500; emphasizing different structural/functional requirements for different catalytic reactions occurring on the same catalytic surface. The synthetic approach presented herein offers new opportunities for obtaining advanced functional materials which can have potential prospective applications in micro reactor systems, adsorbents, drug delivery systems, catalytic processes, and sensor technologies.

Fig. 8. Photocatalytic NO(g) oxidation and storage performance results obtained via UVA irradiation at room temperature for biotemplated TiO2 microspheres initially calcined at various temperatures (inset shows the typical time-dependent concentration profiles for total NOx(g), NO(g), and NO2(g) over AbTi-600. (For interpretation of the references to colour in text, the reader is referred to the web version of this article.)
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