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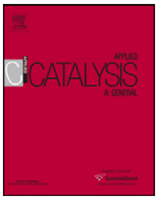

Self-decontaminating layer-by-layer functionalized textiles based on WO_3-modified titanate nanotubes. Application to the solar photocatalytic removal of chemical warfare agents

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ABSTRACT

Self-decontaminating photocatalytic textiles functionalized by the layer-by-layer approach with high aspect ratio WO_3-modified titanate nanotubes have been developed and successfully used under solar light illumination for the photocatalytic degradation of organophosphorous and organosulfide chemical weapon agents. This multilayer building method, unlike both dipping and spray techniques, has been efficiently applied to textile substrates using polyethyleneimine as counter polyelectrolyte for homogeneously functionalizing textiles by a thin layer of a dense network of entangled WO_3-modified titanate nanotubes, and preparing self-decontaminating photocatalytic textiles highly efficient toward the removal under solar light of the yperite blister live agent and of dimethylmethylphosphonate as neurotoxic agent simulant. Solar light responsive high surface WO_3-modified titanate nanotubes were synthesized by hydro-thermally treating TiO_2 powder, with tungstate salt impregnation prior to the final calcination step.

1. Introduction

Attacks occurring both on the battlefield and in civilian areas have demonstrated the high occurrence of casualties, and have materialized the increase of the threat from chemical warfare agents (CWA) over the past century. Exposure to lethal doses can lead to collapse within seconds and even death within 10 min after a single deep inhalation or contact. Hence a need for efficient protection technologies and for post-use decontamination procedures on exposed and thus contaminated materials is required for human beings as well as for equipments. Passive protection technologies, e.g. barriers, permselective membranes, filtration or adsorbents, although they could be efficient, led to maintain an important surface toxicity, and such technologies required thus to further set post-use decontamination, in addition to well-known restrictive drawbacks specific to each technology. Therefore, active protection, i.e. with simultaneous degradation of the agent, should be preferred.

Of the current methods investigated or used, all present significant drawbacks: either they cannot be directly applied on the battlefield or they do not lead to destruction of the toxic agent but rather only to an adsorption or a skin barrier protection effect. By contrast, photocatalytic materials could be efficiently applied over textiles or paints for designing self-decontaminating materials with active protection resulting from their chemical (as well as biological) agent degradation properties under UV-A or solar illumination. It could thus be possible to envisage protecting clothes that would be not only based on impermeable or semi-permeable barrier protection layers but also on a permeable adsorptive protective over-garment, acting actively as a direct destructive layer toward toxic chemicals. Indeed, photocatalysis has been successfully used for degrading organosulfur compounds such as diethylsulfide (DES), acting as a simulant for the live yperite CWA (blister agent, also known as mustard gas), as well as for degrading organophosphorous compounds such as dimethylmethylphosphonate (DMMP), acting as a simulant for live neurotoxic organophosphorous CWA (such as Soman, sarin, tabun and VX) [1–6]. It should be mentioned that photocatalysis has also already been applied, even if scarcely, on live CWA such as mustard gas [6–8]. In parallel to that, investigation on the photocatalytic oxi-

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dation of nauseous organosulfides such as dimethylsulfides has also been performed [9,10].

Since the discovery of carbon nanotubes, extensive research on the synthesis of nanotubes made of materials other than carbon, and especially of oxides like MoO_3, WO_3, VO_x, ... as well as TiO_2, has been reported [11–13]. Nanoscale 1D TiO_2 structures, including materials derived from TiO_2, have been studied in recent years for applications in high effect photovoltaic cells [14,15], gas sensors or UV blockers. Such high aspect ratio TiO_2 nanostructures have started recently to attract much attention for targeting promising applications in photocatalytic environmental technology [16–22], owning to a unique tubular structure with a large surface-to-volume ratio resulting in a larger surface area available in comparison to nanoparticles, to possible size confinement in radial direction, to enhanced electron transfer through the tubular structure and globally to reduced photogenerated charge recombination rates [23–25]. Thus, the high adsorption capacity as well as efficient charge separation yielding to reduce the photo-electron and -hole recombination should have determinant roles in photocatalytic reactions [26]. Within this trend, the development of high aspect ratio TiO_2 with high activity focused on solar applications has become one of the main challenges concerning this material within this area. For instance, the search for new TiO_2-based photocatalysts has already pointed out the positive influence of adding WO_3 to TiO_2, with regard to the oxide loading, for liquid and gas phase photocatalytic oxidation reactions [27–31]. Recently, Xiao et al. have prepared WO_3/titanate nanotube composites with enhanced photocatalytic properties, evidenced in the case of the liquid phase Rhodamine B degradation [20].

The electrostatic layer-by-layer (LbL) self-assembly method has received a growing interest and has been proved a well-established approach to build composite or function-specific multilayer assemblies such as multilayer thin films on planar substrates. The layer-by-layer self-assembly of polyelectrolytes was rigorously investigated and rationalized by the group of Decher [32,33]. This method consisted in the building of multilayer thin films through electrostatic interactions, by the alternate deposition of polyanions and polycations on the surface of a substrate, previously either negatively or positively charged. This by layer-by-layer self-assembly has been extended to other charged systems, such as globular proteins [34], organic molecules [35], mineral as well as metallic nanoparticles [36,37] and semiconductors [38], including titanate nanotubes [16,17,39–41]. Amongst numerous anchorage techniques [42–47], the LbL deposition method was already successfully applied for functionalizing textile fibers by photocatalytic materials [6,48].

The aim of this paper is thus to report on the preparation of self-decontaminating layer-by-layer functionalized textiles based on WO_3-modified titanate nanotubes with application to the photocatalytic removal under solar light illumination of the DMMP organophosphonate as live organophosphorous CWA simulant, and directly of the live yperite organosulfide CWA.

2. Experimental

2.1. Photocatalyst preparation

Titanate nanotubes (TiNTs) were synthesized by the hydrothermal treatment of a TiO_2 powder in a 10 M concentrated NaOH solution at 130 °C [23]. In a typical synthesis, 1 g of TiO_2 P25 from Degussa-Evonik) was added to 50 mL of solution in a Teflon autoclave, stirred for 1 h, and digested at 130 °C for 24 h. After the hydrothermal treatment, the white powder obtained was rinsed with distilled water, vacuum filtered and further washed with 1 M HCl. The material was rinsed with distilled water until neutral pH and finally overnight dried at 110 °C (H-TiNT).

The dried H-TiNT sample was impregnated with an ethanol/deionized water (25/75, vol.%) solution of $(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$ ammonium paratungstate pentahydrate, further dried at 110 °C for 2 h, before final calcination was performed in air at 380 °C for 2 h (WO_3-TiNT).

2.2. Preparation of the functionalized photocatalytic textile

Coton/polyamide (50/50) military textile samples were provided by the DGA. Prior to any photocatalytic material deposition, they were first cleaned with a commercially available detergent. The surface of the textile was then hydroxylated by submitting the textile to a 0.5 M KOH solution treatment [49], rinsed with distilled water, dried at ambient temperature for 15 h and further at 100 °C for 1 h. The as-prepared textiles were finally maintained inside Ziploc© bags, especially for protecting them against excessive humidity capture and storage.

The deposition method by dipping consisted in immersing the textile for 30 min under orbital stirring in an ethanolic/aqueous (50/50, vol.%) suspension of the nanomaterials at 10 g/L, previously mechanically stirred for 24 h and ultrasonicated for 20 min. The textile was subsequently pressed under a rubber roll for mechanically forcing the suspension to impregnate the textile and then the nanoparticles to be in contact with the fibers, before being rinsed with distilled water for removing the excess nanoparticles. This step can be repeated several times if necessary. Finally, the textile was dried at ambient temperature for 15 h and further at 100 °C for 1 h.

The spray deposition method was based on the pulverization of the suspension containing the photocatalytic material onto the textile target, using a commercial spray gun, known as High Volume Low Pressure (HVLP) device. The nanomaterial suspension was the ethanolic/aqueous (50/50, vol.%) suspension at 1 g/L, previously mechanically stirred for 15 h and ultrasonicated for 20 min. The target–spray distance was set at 10–20 cm (with a pulverization nozzle diameter of 0.5 mm and pressurized air at about four bar) and the crossed-layers spray technique was used. After spraying, the textile was rinsed with distilled water for removing the excess nanoparticles. Each vaporization/rinsing cycle was followed by a drying at ambient temperature for 15 min and a further drying at 100 °C for 1 h.

Layer-by-layer deposition was performed by the alternate spray onto the textile substrate target of, either a cationic polyethylenimine (PEI^+) solution (8 g/L) or the ethanol/water (50/50, vol.%) suspension of WO_3-TiNTs at 1 g/L, rectified at pH = 9. This sequence was repeated until the number of layers was attained. After deposition of each layer (PEI^+ or WO_3-TiNTs), the substrate was rinsed three times with pure water. One should note that after the deposition of the first polyelectrolyte layer, a compression step using a rubber roll was performed for mechanically increasing the contact with the textile. The final textile loaded with the photocatalyst was finally dried at 90 °C.

2.3. Characterization techniques

X-ray diffraction (XRD) measurements were carried out on a D8 Advance Bruker diffractometer, in a $\theta/2\theta$ mode and using the $K\alpha_1$ radiation of Cu at 1.5406 Å.

Scanning electron microscopy (SEM) was carried out on a Jeol JSM-6700F working at 1–10 kV, equipped with a CCD camera. The sample was previously coated with carbon and then deposited on a standard holder for observation.

The surface area and porosimetry measurements were carried out on an ASAP2010 Micromeritics using N_2 as adsorbant at liq-