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Torben Seemann, Volker Zöllmer, Henning Kurz and Matthias Busse of IFAM, Judit Ménesi and Imre Dékány of the University of Szeged, Hungary, and André Richardt of the German Armed Forced Scientific Institute for Protection Technologies, explore the potential of reactive nano particles in chemical decontamination

BESIDES preventive measures, the decontamination of pollutants and warfare agents is one of the core competences of NBC defence. All substances have to be removed which makes it a challenging task.

Nano-scaled semiconductor materials such as ZnO, SnO and in particular TiO_2 are well known to show photo catalytic activity by absorbing UV-light. Electrons from the valence band are promoted to the conductive band where radicals will be produced and used to induce photochemical reactions. The aim of the current study is to investigate the potential of these reactive nano particles to degrade pollutants as well as warfare agents. In addition to the scientifically motivated questions, the aim is also to evaluate possible processing strategies to ensure a transfer from laboratory results to practical usages.

There are several challenges for using photo catalytic coatings. First of all, the rate of UV-light in sunlight is less than five per cent. Using doping materials such as Pt, Ag, or Pd, the activation energy may be lowered in order to use visible light for the activation of the photo catalyst. Secondly, the substances to be degraded have to connect on the reactive particles. So, on the one hand, the adsorption and desorption of the organic material and its degradation products must be optimised. On the other hand, the specific surface of the coating should be maximised. Nano porous coatings presented in this article provided corresponding properties. This project aims to define decontamination parameters, showing the possibility of removing warfare agents using similar but harmless substances, and to develop a concept to implement self-decontaminating coatings in technical devices.

In this understanding, a photo catalyst should have the following properties. In addition to known activities under UV-light irradiation, a useable photo catalyst for decontamination applications should also provide high photo catalytic activity at visible light irradiation, as the content of UV-light is lower than five per cent. It is evident to ensure a specific degradation of pollutants or warfare agents without decomposing the substrate surface. For this purpose, one has to ensure a very good contact of the reactive particles at the pollutants.

To evaluate these challenges with the current state-of-the-art technology, the degradation behaviours of the investigated different TiO_2-films are compared to that of commercial available Degussa TiO_2 P25.

Will nano particles mean the sunset of normal decontamination. All pictures ©DOD

The experiment

Chemical and physical approaches have been taken into account to tailor nano scaled photo catalytic materials for decontamination purposes. Nano scaled semiconductors have been produced as clay-composites, in special montmorillonite-composites, and doping of semiconducting materials has been performed to enhance the photo catalytic activity under sunlight conditions.

In a first approach, TiO_2-Ca-montmorillonite composites have been prepared by wet grinding in an agate mill. Positively charged TiO_2 nano-particles are bound to the surface of the negatively charged Montmorillonite layers via heterocoagulation. Clay minerals are used as adsorbent and support for the photo oxidation process. Aquatic solution of 0.5mM/l phenol was degraded by irradiation with UV-Vis light in suspensions of TiO_2 – clay composites.

In addition, the structural and photo catalytic properties of undoped and phosphate-doped TiO_2 have been investigated. Here, titanium isopropoxide was used as precursor of titanium dioxide. Photo catalytic properties were tested on gas-phase photo oxidation of ethanol at 25 degrees centigrade.

In addition, photo catalytic active TiO_2-layers with different structures have been prepared by physical vapour deposition methods, allowing them to tailor the structure of the photo catalytic materials on a nano-meter scale. Here, the photo catalytic active TiO_2-films have been prepared using a

titanium

sputtering technology. With this technique, the morphology can be directly influenced by the sputtering pressure, time and power.

This sputter process runs in a vacuum chamber which is filled with Ar-gas. By ionisation of the Ar-gas, Ar+-ions are accelerated towards the target material (cathode), where particles and clusters are sputtered-off and collected on a substrate surface. The structure and morphology strongly depend on the sputtering power, pressure and time. The structure and morphology themselves strongly influence the photo catalytic activity of the thin film layer.

To investigate the influence of sputtering parameters on the photo catalytic activity of thin TiO_2 layers, deposition of TiO_2 has been performed by sputtering TiO_2-target materials as well as sputtering metallic titanium under the presence of oxygen.

The morphology of the produced photo catalytic layers has been investigated by scanning-electron-microscopy (SEM) – images showing the morphology of sputtered thin TiO_2-films on Si-substrates on a micrometer scale. The nano-scaled structure of TiO_2-photocatalysts could be investigated by high-resolution transmission-electron-microscopy (HRTEM). The photo catalytic activities of the prepared structures were tested in gas-phase oxidation of ethanol, phenol and also toluene at 25 degrees centigrade.

Results

Significant photo degradation on TiO_2-clay composites was observed at 40-60 per cent TiO_2/Ca-montmorillonite compositions. A synergistic effect was detected at solid/liquid interfaces for degradation of phenol and at solid/gas interfaces in the recycling flow reactors for photo oxidation of ethanol and toluene vapors.

The observed rapid oxidation of ethanol on phosphate-doped titanium dioxide was probably due to coupling between titanium dioxide and titanium phosphate, which increases the efficiency of charge separation in semiconductive nano-sclaed materials.

HR-TEM analysis of sputtered thin TiO_2

Nano-activated titanium will draw its decontamination powers from UV rays films (<20nm) on carbon support mostly reveals aggregated nano particles with a typical diameter of about 3-10nm. To determine the photo catalytic activity of the TiO_2-layers, a photo reactor was filled with a contaminated fluid. Samples were irradiated under UV-light (360nm) for 120 minutes. Decomposition was measured with a spectrophotometer (Ocean 2000).

Photo catalytic thin films have been prepared with different sputtering parameters. The samples produced with higher sputtering pressures show higher specific photo catalytic activities. This can be explained with a higher porosity of the thin TiO_2 films.

After defining the decontamination parameters, possible materials were chosen for the photo catalytic degradation of various pollutants. The semiconductors were doped with metals, and subsequently the effects on the degradation rate and activation with sunlight were tested. Higher degradation rates were measured with Ag, Pt and Pd doped coatings, depending on the rate of those materials.

The substrate and its influence on the photo catalytic activity were investigated as well. In particular, Montmorillonite can increase the photo catalytic activity due to improved adsorption along with its high specific surface.

The results from the lab were transferred to technical issues. The coatings were produced with reactive sputtering where titanium is sputtered at an oxygen atmosphere. During the process, Ti and O_2 react to TiO_2. This technology offers the possibility to coat surfaces with a defined, thin, and uniform layer where doping materials may be introduced flexibly. Those coatings will be tested in a special photo reactor with optional UV and visible light irradiation.

The potential of reactive nano particles for the degradation of pollutants and warfare agents could be validated. After doping the materials the degradation rate was increased and the activation with visible light indicated. Using a semiconductor-clay-composite the photo degradation will be increased significantly, which can be traced back to a synergy effect between those materials. With the sputtering technique the photo reactive materials can be applied to technical surfaces allowing a very precise definition of the coating. In the future, the technical implementation of the composites and experiments regarding the visible light activation will be the focus of this project.

Activated nano particles may well unlock the secret of sensitive decontamination