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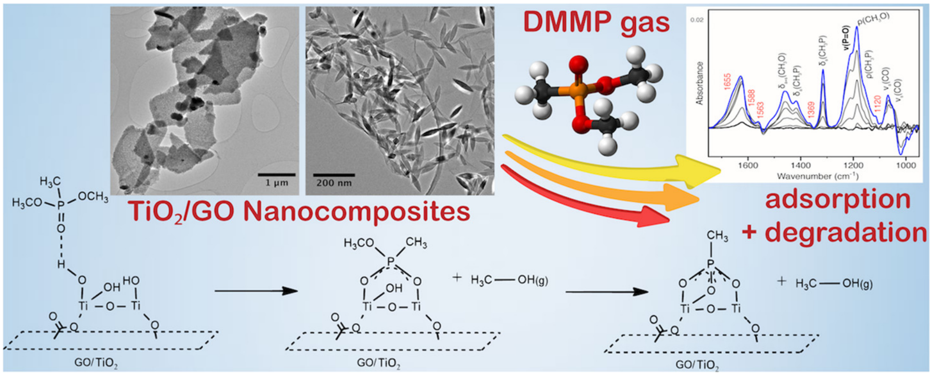
Chemical warfare agent simulant DMMP reactive adsorption on TiO_2/graphene oxide composites prepared via titanium peroxo-complex or urea precipitation

Jiří Henych[a,*], Václav Štengl[a], Andreas Mattsson[b], Jakub Tolasz[a], Lars Österlund[b]

[a] Materials Chemistry Department, Institute of Inorganic Chemistry, Czech Academy of Sciences, Husinec-Řež 1001, 250 68 Řež, Czech Republic
[b] Department of Engineering Sciences, The Ångström Laboratory, Uppsala University, P.O. Box 534, SE-751 21 Uppsala, Sweden

GRAPHICAL ABSTRACT



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ABSTRACT

Two water-based methods were used to produce TiO_2/graphene oxide (GO) nanocomposites with 1 and 2 wt.% GO. Both procedures exclude the use of organometallic precursors, as well as the high-pressure and high-temperature treatments, which facilitate pure and energy efficient synthesis amenable for larger scale synthesis. Nanocomposites with narrow (< 10 nm) and long spindle-like (< 100 nm) TiO_2 nanoparticles supported on GO flakes were obtained (TiO_2/GO), and their properties for reactive destruction of the organophosphorus simile chemical warfare agent (CWA) dimethyl methylphosphonate (DMMP) were investigated by in situ DRIFTS spectroscopy. Both synthesis procedures yielded highly reactive nanocomposites with markedly different properties compared to similarly prepared pure TiO_2 nanoparticles. GO also induced morphology and texture changes, which were observed to have a significant impact on the adsorption and reactivity of the nanocomposites, and which were strongly related to synthesis procedure. In particular, the reduction state of GO, as measured by Raman spectroscopy, was observed to play a major role for the reactivity of the TiO_2/GO nanocomposites.

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* Corresponding author.
E-mail address: henych@iic.cas.cz (J. Henych).

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1. Introduction

Organophosphates (OP) belong to a class of chemicals that may be very toxic depending on the functional groups that are attached to the central P atom, and can induce severe health effects; environmental pollution, as well as being of national safety concerns as chemical warfare agents (CWA). Many CWAs, but also herbicides and insecticides, are based on esters of phosphoric acid and cause acute and chronic effects to humans [1,2] and animals [3]. These compounds are stable and easily dispersed and can enter the body either via skin contact or by respiration where they affect the transmission of nerve impulses through binding to acetylcholine esterase causing muscular paralysis [1,2]. CWAs based on OP are suspected of being used in recent civilian attacks in Syria, and due to existing stockpiles around the world they represent a considerable threat to global security [4]. Consequently, it is not surprising that a variety of inorganic and polymeric materials, including metal oxides [5,6] and hydroxides [7], zeolites [8], or more recently, polyoxometalates [9], or metal-organic frameworks [10,11], are examined in order to deactivate toxic OP.

Due to the toxicity of CWAs, simile agents such as dimethyl methylphosphonate (DMMP) are used in laboratory tests to study basic properties of OP decontamination materials and processes. In the late ‘90 s and early 2000s, several research groups extensively studied the interaction of DMMP with nanosized metal oxides (e.g. MgO [12], Al_2O_3 [13], TiO_2 [14–16], CeO_2 [17], iron oxides [13,17]). We [18] and others [13–17], have previously studied the interaction of DMMP with metal oxides surfaces at various temperatures, humidity, and OP surface coverages. It was concluded that DMMP adsorbs on the metal oxide surfaces in two steps. First, adsorption occurs via interaction of the phosphoryl oxygen through the P═O group with isolated surface hydroxyls and via Lewis acid sites, and second, hydrolysis of the DMMP molecule takes place by cleavage of the P—OCH_3 groups which produces OCH_3 groups bonded to the surface metal atom and strongly adsorbed phosphonate species. [13–18]

Pioneering detoxification studies have mainly used commercially available single metal oxides, most commonly TiO_2 [16,19–21]. But in order to increase process efficiency, doped TiO_2 with metal/non-metal ions [22,23], or various (nano)composites [24], have been employed recently. In particular, combinations of metal oxides or hydroxides with low-dimensional materials appear very promising. Readily available, non-toxic carbon materials such as nanotubes [25], graphene [25,26], or graphene oxide (GO) [24,27] are among the most studied systems. Cost-effective and reliable synthesis of these intriguing materials in large quantities remains however challenging. Our group has previously reported two undemanding methods suitable for large-scale synthesis of TiO_2-based nanocomposites [28,29], which are further exploited in this study.

To elucidate the interaction of OP with the composites surface and its degradation mechanism, chromatographic methods such as nuclear magnetic resonance and FTIR spectroscopy have shown to be very useful. Especially, in situ DRIFT spectroscopy allows for mechanistic studies of adsorption kinetics and surface chemical reactions, on the vapour/solid interfaces of nanoporous materials in a controlled environment (temperature and reactant concentration) [30].

Here, in situ DRIFT spectroscopy was employed to study adsorption and surface degradation of DMMP on GO/TiO_2 composites prepared by two water-based methods. Both synthesis procedures exclude organometallic titanium precursors or organic solvents, and proceed at ambient pressure and temperature up to 100 °C without the use of any laborious equipment (such as an autoclave), and can thus be considered as environment-friendly and suitable for industrial scale synthesis. The materials were characterized with focus on the physicochemical properties of GO in the catalysts. Our results revealed different behaviors of the GO nanocomposites that are strongly dependent on the preparation route. In particular, the redox state of the GO markedly influences the reactivity of the GO/TiO_2 nanocomposites.

2. Materials and methods

2.1. Graphene oxide (GO) synthesis

GO was prepared by a slight modification of our original procedure based on high-power ultrasonication of natural graphite, which we previously employed to synthesize low-dimensional materials such as graphene [31] or MoS_2 [32] nanosheets. A more detailed procedure of the GO synthesis is given in the electronic supplementary material (ESM).

2.2. Preparation of TiO_2/GO composites: urea method

TiO_2/GO composites were prepared by a precipitation method that utilizes titanium oxysulfate ($TiOSO_4$) as titanium source and urea as precipitating agent. The details of this low-cost synthesis method have been reported elsewhere [29,33], and in this work some important improvements, detailed below, have been used in order to achieve a higher GO concentration and dispersion of the composites.

In detail, 1 g of $TiOSO_4$ was dissolved in 200 ml distilled water (35 °C) acidified with 1 mL of H_2SO_4. A certain amount of GO (1 or 2 wt.% of the theoretical yield of TiO_2) was dispersed in 1 L of distilled water by bath sonication (1 h, 300 W) and mixed with the $TiOSO_4$ solution, followed by dissolving 10 g of urea in the solution. The obtained brownish pellucid liquid was heated to 90 °C and kept for 6 h under vigorous stirring. The slow thermal decomposition of urea leads to a gradual pH increase which in turn induces homogeneous precipitation of TiO_2 on the dispersed GO sheets in the solution. The obtained brown-greyish precipitate was washed with water by decantation several times until the conductivity of the solution was less then 100 mS/m. The solution was filtered and air-dried thus yielding dry powders of the GO/TiO_2 nanocomposite.

2.3. Preparation of TiO_2/GO composites: Ti peroxo-complex method

The process is based on preparation of water-soluble Ti peroxo-complex from titanium oxysulfate and its refluxing under ambient pressure for 36 h without the use of an autoclave [34]. This process was successfully used by our group for preparation of TiO_2/graphene composites [28]. Contrary to the original procedure, easily water-dispersed GO was used in this work, which led to the substantial higher dispersion of GO sheets in the composites.

In detail, 1 g of $TiOSO_4$ was dissolved in 200 ml water (35 °C) and 10 ml of NH_4OH/water solution (1:1) was added dropwise under vigorous stirring. The resulting white precipitate was washed with water by decantation until the conductivity of the solution was < 100 mS/m. The water was filtered off and the precipitate was dissolved by addition of 5 ml 30% H_2O_2 in a beaker immersed in an ice bath. The clear yellow/orange solution was then mixed with GO solution (1 or 2 wt.% of the theoretical TiO_2 yield; dispersed in 500 ml water and sonicated in a 300 W ultrasonic bath for 1 h), and then transferred into a round-bottom flask and refluxed at 100 °C for 36 h. The resulting dark grey precipitate was then filtered and air-dried. The samples prepared by the peroxo-complex route were denoted with “P”, and similarly “U” is used for samples prepared using the urea route.

2.4. Characterization methods

Structural analysis of the samples was performed using a Bruker D2 diffractometer equipped with a conventional X-ray tube (Cu $K_{\alpha I}$ (1.5418 Å) radiation, 30 kV, 10 mA) and a LYNXEYE 1-dimensional detector.

The structure and morphology were investigated using FEI Nova NanoSEM 450 scanning electron microscope (SEM) and a FEI Talos F200X high-resolution transmission electron microscope (HRTEM).

The surface area and porosity were obtained from low-temperature