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In Situ Detoxification of Venomous Agent X Surrogate Profenofos by Doped Titanium Dioxide Nanoparticles under Illumination at the UV and Visible Ranges

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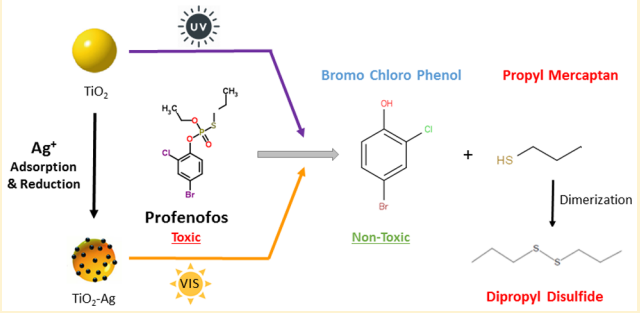
Supporting Information

ABSTRACT: The photocatalytic activity of titanium dioxide (TiO_2) due to the generation of reactive oxygen species (ROS) under UV excitation is often used for the decontamination of toxic hazardous materials and self-cleaning processes. However, the large band gap of TiO_2 limits the activity to the UV region. This limitation can be overcome by metal doping, which results in extending TiO_2 activity into the visible range (vis). This paper describes the preparation and characterization of several TiO_2 forms and their modifications for enhanced photocatalytic activity in the UV/vis range. In order to advance this concept for environmental decontamination, the degradation of the organophosphorus pesticide and chemical warfare agent, profenofos (PF), was tested. Fast and full degradation of PF was achieved using either TiO_2 in the near-UV (365 nm) or Ag-doped TiO_2 (TiO_2−Ag) in the UV and vis ranges (400−550 nm). The degradation products were identified chromatographically using GC/MS and HPLC, while the detoxification effect was determined electrochemically using an acetylcholinesterase biosensor. In view of our results, we suggest that TiO_2−Ag may be implemented as an additive in surface coatings to allow in situ green self-cleaning.



1. INTRODUCTION

Organophosphates are common acetylcholinesterase (AChE) inhibitors, used as pesticides in the agricultural industry, as well as chemical warfare agents for military applications.[1] In the case of environmental contamination with these materials, urgent remediation is required. The current decontamination methods, such as bleaching powders and decontamination foams and solution, are often insufficient due to the needed storage, transport, and material disposable.[2] This limitation can be overcome by metal oxides such as ZiO_2,[3] CaO,[4] and TiO_2[5] as in situ decontaminating agents.

The photocatalytic activity of TiO_2 has been widely applied in the decontamination processes, particularly in self-cleaning, odor removal, degradation of toxic materials, and bacteria annihilation.[6] TiO_2 is particularly suitable for this purpose due to its high photoreactivity, high chemical and physical stabilities, low toxicity, and commercial availability at relatively low cost compared to other photocatalytic metal oxides.[7] The large band gap of TiO_2 requires excitation in the UV region.[8] Upon UV illumination, excited TiO_2 produces reactive oxygen species (ROS),[9] which play an important role in the photocatalytic reaction mechanism.[10] When TiO_2 absorbs photons with energies higher than its band gap, electrons are excited from the valence band into the unoccupied conduction band, which leads to the creation of positively charged holes in the valence band.[11] Excited-state electrons and holes react with water and O_2 molecules that are innately present on metal oxides. Depending on the exact conditions, the holes, $OH^{\bullet}$ radicals, O_2^{-}, H_2O_2, and O_2 play an important role in the photocatalytic reaction mechanism.[10]

One of the goals for improvement of the performance of TiO_2 nanomaterials is to enhance their photoreactivity applicability by shifting their optical reactivity toward the vis range due to the fact that only a small fraction (3−5%) of sunlight radiation falls within the UVA range, usually utilized for photodegradation.[12] Commonly used methods are bulk[10] and surface[13] modifications, which involve either introduction of impurities into the crystal lattice or adsorption of metal species to the surface of the catalyst, leading to the decrease in the band gap of the catalyst, TiO_2.[14] Surface modification may also facilitate the attachment to the carrier of other photon-capturing molecules, increasing its photoreactivity.[13]

This research is focused on the study and characterization of TiO_2 as a photocatalyst for decontamination of toxic hazards, producing nontoxic products that pose no threat to humans or the environment. Profenofos (PF) is an organophosphorus pesticide that acts by inhibition of AChE activity[15] and often serves as a nerve gas model.[2,16] In this work, a fast degradation

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of PF was achieved using TiO_2 in the near-UV range (365 nm). The same positive results were obtained after surface modification of TiO_2 by transition metal deposition with silver atoms (TiO_2−Ag) under illumination at the more desirable vis scale (400−550 nm).

2. EXPERIMENTAL SECTION

2.1. Materials. All chemicals and carriers were of analytical grade and purchased from Sigma-Aldrich (St. Louise, MO), unless otherwise specified.

2.2. Methods. *2.2.1. Catalyst Preparation.* The preparation of Ag-doped titania samples (TiO_2−Ag) was according to ref 17. Briefly, 0.2 g of TiO_2 was dispersed in 100 mL of distilled water and sonicated for 5 min followed by the addition of 0.0425 g of $AgNO_3$. The solution was mixed, adjusting the pH to 10 with NH_4OH (30% in water). For wet-impregnation reduction, 9.4 mg of sodium borohydride ($NaBH_4$) in 10 mL of distilled water was added, and the solution was mixed for 30 min. The precipitate was collected by centrifugation and dried overnight at 50 °C in a dry oven.

2.2.2. X-ray Diffraction (XRD). The X-ray diffraction (XRD) data was acquired using a laboratory standard D8 Advance X-ray diffractometer in Bragg−Brentano geometry (supplied by Bruker AXS, Germany) equipped with a Cu Kα source and LynxEye detector. The following XRD setting parameters were used: range between 10 and 70 with a step size of 0.05, 0.5 s per step, sample rotation of 60 rpm.

2.2.3. X-ray Fluorescence (XRF). Chemical analysis was done using a Thermo Scientific NITON energy-dispersive X-ray fluorescence (EDXRF) analyzer, model XL3t XRF. The XL3t XRF analyzer, a hand-held device, was mounted in the laboratory configuration to quantify the presence of elements in the standard analytical range (from sulfur S16 to uranium U92) and additional light elements (magnesium Mg12, aluminum Al13, silicon Si14, and phosphorus P15 via helium purge) in road dust. The detection limits for all analyses were based on a 130 s total analysis time in a regular Cu/Zn mining mode.

2.2.4. Diffuse Reflectance UV/Vis. For the evaluation of photophysical properties, diffuse reflectance UV/vis spectra were recorded in the diffuse reflectance mode (R) using a Thermo Scientific Evolution 300 spectrometer equipped with a DRA-EV-300 Integrating Sphere with $BaSO_4$ as a standard.

2.2.5. Scanning Electron Microscopy (SEM). Scanning electron microscopy (SEM) analyses were performed using two methods: (A) environmental scanning electron microscopy (ESEM, FEG, FEI Quanta 200) and (B) high-resolution scanning electron microscopy (HR-SEM, Ziess Ultra-Plus FEG HR-SEM). Both were equipped with EDX (energy-dispersive X-ray), SE (secondary electron), and BSE (backscattered electron) detectors. The powdered sample was dispersed in ethanol, and the suspension was treated in an ultrasonic bath for 3 min. The suspension was then applied as a droplet on an adhesive C slice without additional coating.

2.2.6. Transmission Electron Microscopy (TEM). Transmission electron micrographs (TEMs) were obtained using a JEOL JEM 2100 at 200 kV, in TEM and STEM mode. The powdered sample was dispersed in ethanol, and the suspension was treated in an ultrasonic bath for 3 min. The suspension was then applied as a droplet on a copper grid without additional coating.

2.3. Illumination. *2.3.1. Near-UV Range.* UVA exposures at 365 nm (Philips F15T8/BL 15 W lamp, Amsterdam, The Netherlands) were used for 0−150 min at a distance of 35 cm from the samples, equivalent to 2.7 J/cm^2. The radiation flow was 1.5 mW/cm^2 as determined by UVA light meter type YK-37UVSD, (Radiometer, Copenhagen, Denmark).

2.3.2. Vis Range. A vis light source (Philips 15WT8/Daylight lamp, Amsterdam, The Netherlands) was used for 0−150 min at a distance of 35 cm from the samples. The samples were covered by a UV filter (clean-room filter), which absorbed radiation under 550 nm.

2.4. Photodegradation. *2.4.1. Cytochrome C Reduction Assay.* Cytochrome C (Cyt C) reduction assay was carried out in 24 well plates, each containing 2 mL of oxidized Cyt C solution (0.1 mM Cyt C in PBS buffer, pH 7.4) and 0−0.8 mg of anatase nanoparticles (A-NPs), stirred with a micro magnetic bar. The wells were exposed to a light source for up to 30 min. Dark conditions in the control wells were obtained by covering the wells with aluminum foil. Samples (1 mL) were withdrawn, and the A-NPs were sedimented by centrifugation (Heraeus, Thermo Fisher Scientific, Waltham, MA) at 17 800g for 15 min. Optical densities of the supernatants (0.5 mL) were determined at 450 and 550 nm using a Genesys 10S UV/vis spectrometer (Thermo Fisher, Waltham, MA, USA) to follow Fe^{3+}Cyt C reduction to Fe^{2+}Cyt C, and a reference value of 23.65 OD at 550 nm for 1 mM reduced Cyt C was used.[18] A 24 well plate was placed on a magnetic stirrer and under UV, filtered vis light, or dark conditions. Because Cyt C absorbs radiation in the UV region, the experimental setup included a UV filter that is usually used for covering the well plate (clean-room filter).

Constant agitation of the solution was ensured by a magnetic stirrer placed in each well. The plate was irradiated for 30 min, and every 5 min, 0.5 mL samples were transferred to Eppendorf vials, which were centrifuged at 15000 rpm for 15 min in order to separate the catalyst. The supernatants from each vial (0.5 mL) were diluted two-fold with PBS and examined by a UV/vis spectrometer (Thermo, Genesys 10S) in the wavelength range of 200−800 nm.

2.4.2. PF Degradation. Stock solutions of 12 ppm PF were prepared: 5 μL of PF analytical standard in 1.0 mL of acetonitrile (HPLC grade). Then, 0.25 mL of this solution was dissolved in 500 mL of distilled water. Glass vials (20 mL) placed on a magnetic stirrer and under (35 cm below) a UV/vis light source or dark conditions wereused. Each vial contained 10 mL of PF stock solution (12 ppm PF in distilled water) and 3.75 mg of the catalyst (TiO_2, TiO_2−Ag). Constant agitation of the solution was ensured by an orbital stirrer at 300 rpm. The PF degradation was sampled for 0−250 min, withdrawing 1.0 mL aliquots every 30 min. The samples were centrifuged at 15000 rpm in order to separate the catalyst form the PF solution and were used for the GC/MS and HPLC analyses.

2.5. GC/MS Analysis. The samples from section 2.2.1 were extracted in hexane 1:1, and 50 μL of the hexane extract was injected into the GC/MS (PerkinElmer Clarus 680 GC coupled to an MS detector Clarus 600T in electron ionization (EI, 70 eV) mode). The GC/MS oven was fitted with an HP 5 column (Agilent 30 m × 0.25 mm × 0.25 μm). The chromatographic conditions were as follows: oven temperature 40 °C (for 4.1 min), increased to 290 °C at 15 °C/min; run time 20.77 min; injector temperature 70 °C for 2.5 min, increased to 300 °C at 99 deg/min; detector temperature 200 °C; injector split ratio 1:250 until 2.5 min and after a splitless mode. The samples were first analyzed in SCAN mode in order

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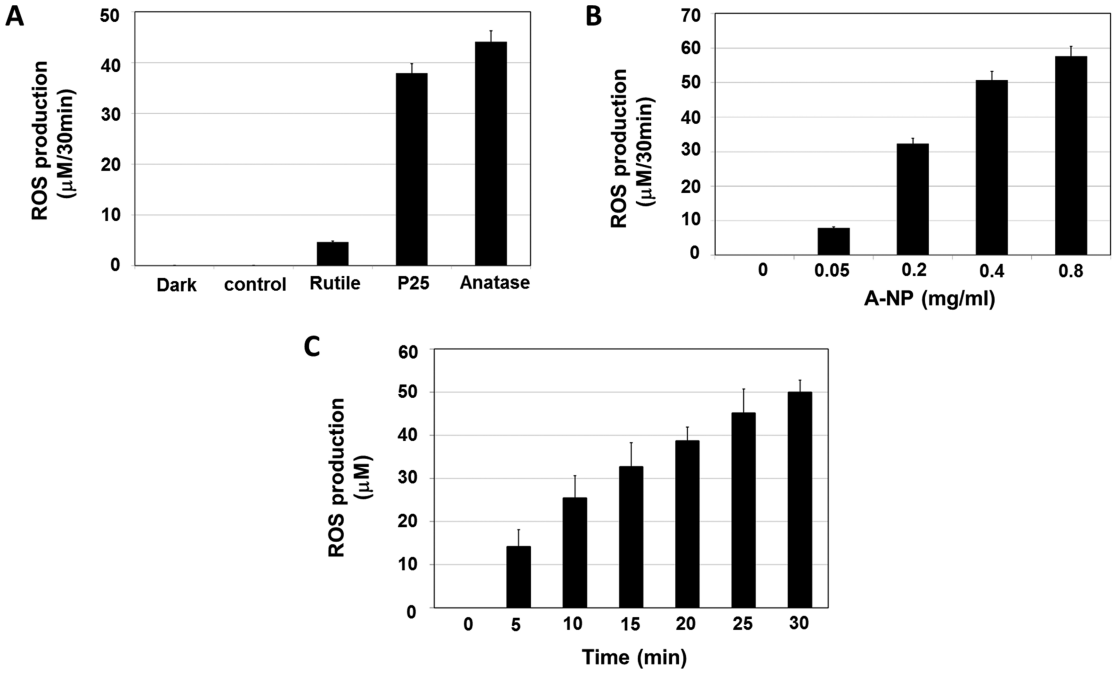

Figure 1. Photocatalytic activity of TiO_2 forms and platforms upon UVA illumination as determined by the Cyt C assay. (A) ROS production by different TiO_2 structures after 30 min. (B) ROS production by different amounts of A-NPs after 30 min of measuring. (C) Time dependence of ROS production by a constant amount of A-NPs (0.4 mg/mL). Experiments were repeated three times.

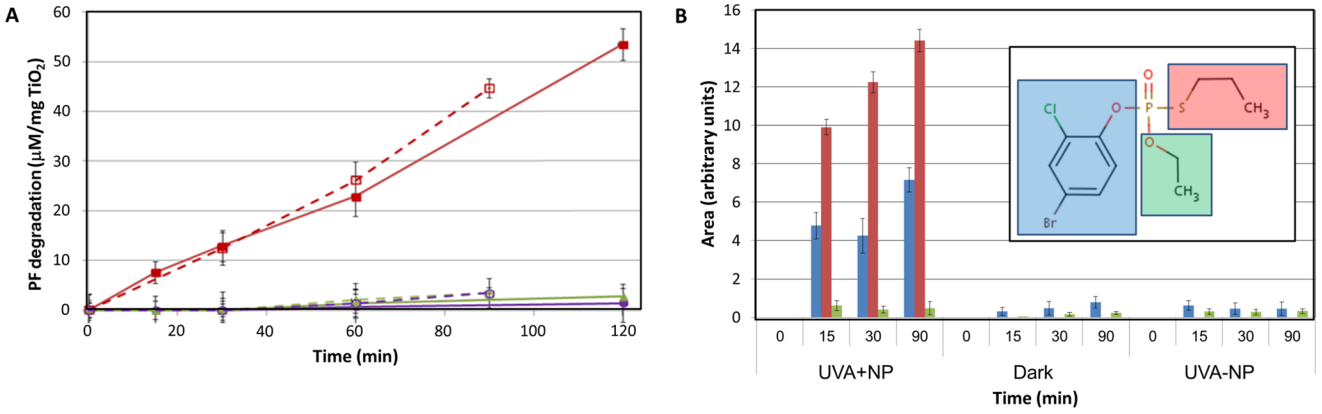

Figure 2. PF degradation by A-NP illumination. (A) Toxicity measured by inhibition of AChE activity (solid line) and degradation of PF measured by GC/MS (dashed line) under UV illumination (red lines) or in the absence of illumination (blue lines). The reaction with no TiO_2 particles is shown in green. (B) GC/MS analysis of the reaction products of PF degradation: BCP, blue; DPDS, red; and acetic acid, green.

to select the retention time and the ion for PF and 4-bromo-2-chlorophenol (BCP). A single-ion monitoring function (SIM) was used; Table S1 depicts the retention time and selected ion for each compound.

2.6. HPLC Analysis. The samples from section 2.2.1 were analyzed using an Alliance waters 2690 high-performance liquid chromatograph (HPLC) equipped with a PDA detector (Waters 996). Samples (100 μL) were injected onto a C18 Zorbax ODS column (5 μm × 25 cm × 0.46 cm) at a rate of 1 mL/min; the oven temperature was 30 °C, monitored at 220 nm. The mobile phase was an isocratic combination of acetonitrile (80%), water (19.9%), and 0.1% trifluoroacetic acid. Analytical curve: Stock solutions of 12 ppm PF and BCP were prepared (Figure S1). These stock solutions were used to prepare working solutions at 2, 4, 6, 8, 10, and 12 ppm for each compound. Next, 100 μL samples were analyzed by HPLC, as described above.

2.7. Statistical Analysis. All data are expressed as means ± standard error of the mean. Significant differences were assessed by the *P* value.

3. RESULTS

3.1. Anatase Structure of TiO_2 NPs as the Most Photoreactive Form. In this section, we aimed to study the physicochemical properties and photocatalytic activity of TiO_2 in order to define the optimal forms that possess the highest surface area and ROS activity of the TiO_2 matrixes. For that, several types of TiO_2 (anatase, rutile, amorphous) at the nanosize scale were examined by the Cyt C reduction assay (described in the Experimental Section) and were used to assess the ROS production of the different TiO_2 preparations (A-NP, R-NP, P-25) upon UVA illumination. As shown in Figure 1A, the most active form of TiO_2 is the A-NP, as expected from the high surface area, small particle size, high

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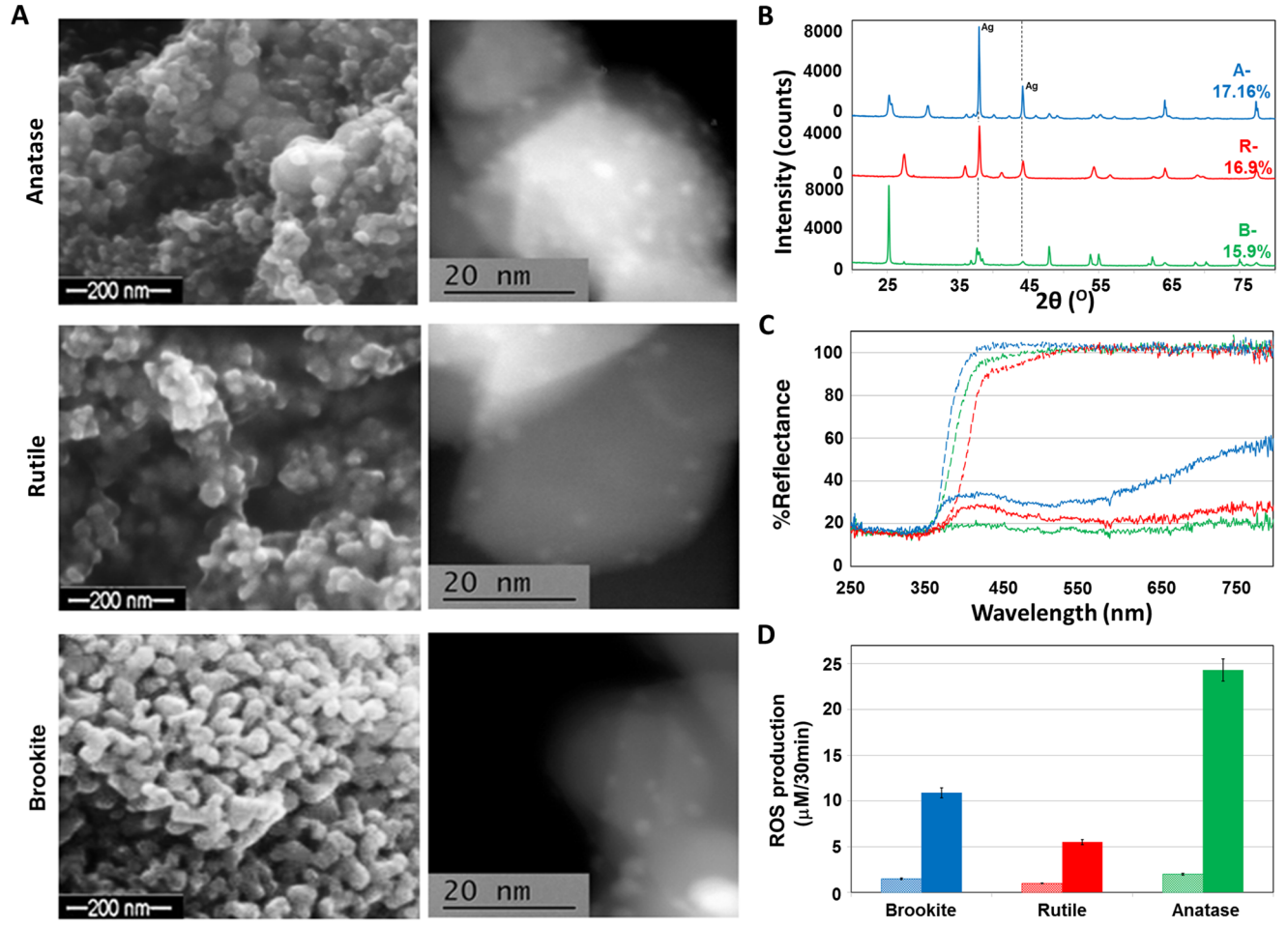

Figure 3. TiO_2–Ag characterization. (A) ESEM micrograph of Ag–TiO_2, anatase (upper), rutile (middle), and brookite (lower). (B) XRD analysis of the TiO_2- NPs shown in Figure 2A. (C) % Reflectance of TiO_2 forms, anatase (blue), rutile (red), and brookite (green), before (upper curve) and after (lower curve) modification with Ag. (D) Photoreactivity in the vis range of TiO_2 forms before and after modification with Ag.

permeability, high surface ratio, and retention.[19] Illumination under UVA without Ti NPs showed negligible photolysis.

Next, we set to measure the ROS generation by A-NPs using the Cyt C reduction assay under the same illumination conditions. Optimization of the A-NP concentration in the ROS generation assay for 30 min is shown in Figure 1B. On the basis of these experiments, 0.4 mg/mL of A-NPs was chosen to study the rate of ROS production over time (Figure 1C).

3.2. Detoxification of PF Using A-NPs under UVA illlumination. Next, we set to examine A-NPs' application for detoxification of hazardous materials. As a model, we used PF, an organophosphorus pesticide that inhibits AChE activity and is extremely toxic to living animals.[20] A biosensor of AChE activity was used to determine the residual toxic effect following PF degradation. As demonstrated in Figure 2A, PF was rapidly degraded by A-NPs under UVA illumination, 45% within 90 min, as shown by both biosensor and GC/MS analysis of the degradation products. Figure 2B depicts the GC/MS analysis of PF degradation products, including the positions of degraded bonds. It can be seen that the main degradation products are 4-BCP, produced by cleavage of the P–O bond, and dipropyl disulfide (DPDS), which is a dimerized product of propyl mercaptan formed by cleavage of the P–S bond in PF.

3.3. TiO_2-Modified by Silver Atoms for Photocatalysis under Vis Illumination. Attempts to increase TiO_2 photocatalytic activity by surface atomic metal dispersion is under extensive investigation. This approach is expected not only to increase photocatalysis under UV but also to allow activation in the vis light range. Transition metal deposition on TiO_2 NPs of silver (Ag) atoms, in particular, has been reported before in the literature.[17] We adopted this method to prepare a derivative of TiO_2–Ag by modifications of A-NPs with Ag atoms.

Figure 3A shows different forms of the TiO_2 surface (anatase, rutile, and brookite) with atomic metal dispersion by Ag. The Ag clusters appear as white dots on the TiO_2 surface, as shown on the right side panels of this figure. This preparation contains about 16–17% Ag on the surface of the A-NPs, as determined by XRD (Figure 3B). Figure 3C shows the % reflectence of different forms of the TiO_2 surface before (upper curves) and after modification by Ag (lower curves). As expected, the modifications of TiO_2 with Ag led to the increase of absorbance (low reflectance) in the vis range, followed by an increase in photoreactivity in this range (Figure 3D) with all TiO_2 modified forms, mostly with the anatase form.

3.4. Detoxification of PF Using A-NPs–Ag under Vis Illumination. After it was established that the same results had been obtained with TiO_2–Ag under vis light (data not shown), the samples were injected into an HPLC, and the

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concentrations of BCP and PF were determined by comparing the peak area of the samples with the analytical curve. The kinetics of BCP accumulation was investigated under vis illumination conditions. As shown in Figure 4, only TiO_2−Ag

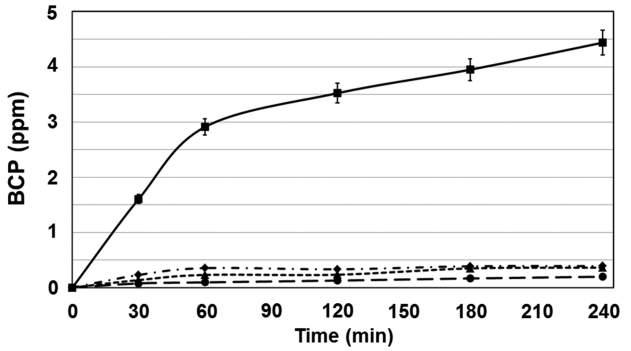

Figure 4. Kinetics of BCP accumulation under vis illumination using different catalysts. TiO_2−Ag (—■—),TiO_2 (–●–), Ag (- -▲- -), and non (· –◆– ·).

succeeded in generating ROS under vis light, while TiO_2 or Ag alone failed to do this. The kinetics profile is similar to that of radical generation, indicating that the degradation may be attributed to the presence of radicals, including ROS. Figure S2 depicts the photocatalytic activity of A-NPs−Ag under both illumination conditions, while the activity in the UV light region is much higher than that in the vis spectrum.

4. DISCUSSION

The photocatalytic activity of TiO_2 under UV illumination is a well-studied process[9] and has been applied in many self-cleaning systems.[6] In this work, we identified that A-NPs are the most photoreactive TiO_2 crystal structure form[10] with an optimized amount of 0.4 mg/mL leading to increasing ROS production with time upon UVA illumination, apparently resulting from the higher surface activity of anatase, compared to the rutile form.[21] Attempts to increase TiO_2 photocatalytic activity by metal doping, allowing activation in the vis light range due to band gap reduction,[13] are currently underway. Transitional metal deposition on TiO_2 NPs of Ag atoms, in particular, was reported earlier in the literature.[17] We adopted this method to prepare a derivative of Ag−TiO_2 by modifications of various TiO_2 forms with Ag atoms and revealed that A-NP is the most reactive form with optimization of 7.2% Ag concentration on the A-NP surface. To note, neither TiO_2 alone nor Ag^+ alone exhibits ROS production, which indicates that the enhancement of the photocatalytic activity is due to TiO_2−Ag and not to the Ag itself.

PF was used as a surrogate for nerve gas, venomous agent X (VX),[2,16] in order to demonstrate the ability of TiO_2 photodegradation of hazardous organic materials in situ under UV or vis illumination. Degradation processes by photocatalysis techniques were found to be efficient for many organics, including VX surrogates, in aqueous solutions[5,22] and in films,[23] but they require direct contact with the agent. An alternative ROS-generating technique is by vapor hydrogen peroxide or ozone, which requires storage, transport, unique equipment, and material disposable and may damage equipment.[24] Therefore, the application of TiO_2−Ag in the vis range is more suitable for outdoor green decontamination.

TiO_2−Ag was found to degrade PF in aqueous solutions by cleavage of the P−S and the P−O bonds within a few minutes under UV/vis illumination as well as A-NPs at the UV spectrum. The degradation products were first identified as BCP, formed by cleavage of the P−O bond in PF, and DPDS, a dimerized form of propyl mercaptan formed by P−S bond cleavage. As expected, the degradation of PF leads to its detoxification, as shown electrochemically with an AChE activity sensor. In the presence of hydroxyl radicals, PF loss is expected to proceed mainly through hydrogen abstraction, but the products identified here are different than those previously reported,[2,25] while biodegradation of PF using *Bacillus subtilis* resulted in similar degradation products.[26]

5. CONCLUSIONS

The goal of this research was to develop and characterize a photodegradation system for toxic hazardous organic materials in situ by TiO_2 and its derivatives. The decomposition of PF by several forms of TiO_2 via illumination in the UV range was studied. Reaction kinetics and products were identified as well as the detoxification effect. By modifying TiO_2 with Ag atoms, a doped complex of TiO_2−Ag was generated with the ability to produce ROS under vis light illumination as well, which led to fast and highly effective detoxification of PF.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.9b07492.

GC/MS data of the SIM-mode analyses, BCP kinetics accumulation using A-NPs−Ag under vis illumination conditions, and ROS production by A-NPs−Ag under different illumination conditions (PDF)

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

AChE - acetylcholinesterase
A-NP - anatase nanoparticle
BCP - 4-bromo-2-chlorophenol
Cyt C - cytochrome c
DPDS - dipropyl disulfide
EDS - energy dispersive spectroscopy
GC - gas chromatography
HPLC - high-performance liquid chromatography
HR-SEM - high-resolution scanning electron microscope
MS - mass spectrometry

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PF - profenofos
ROS - reactive oxygen species
TEM - transmission electron microscopy
TiO_2 - titanium dioxide
UV - ultraviolet
vis - visible
XRD - X-ray diffraction
XRF - X-ray fluorescence

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