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Supplementary Information

The methanolysis and heterogeneous photocatalysis combined action in the decomposition of chemical warfare agents

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1. Experimental Section

1.1. Materials

The following chemicals were used in this study: sodium methoxide (25 wt. % in methanol), $La(OTf)_3$ (99.999%), $HAuCl_4 \bullet 3H_2O$ (99.999%), sodium hydroxide (99.99%), anhydrous methanol (99.9%), and N-ethylmorpholine (99%), all being purchased from Sigma-Aldrich and used as received. Titanium dioxide in anatase phase was purchased from Fluka. All the CWAs used in this study, namely: sarin (GB), VX, soman (GD) and yperite (HD or sulfur mustard), were freshly prepared by trained CBRN (chemical, biological, radiological and nuclear) defence personnel following several synthetic procedures typically employed in these cases.

Catalyst preparation

The catalyst has been prepared according to a synthetic procedure previously reported in ref. [1]. Thus, a stock solution of $La(OTf)_3$ and sodium methoxide has been prepared to a concentration of 50 mM in anhydrous methanol. Before performing the reactions, the working solution was adjusted by dropping N-ethylmorpholine until a pH value of 9.14 was reached. It has to be underlined that the pH measurement was performed under non-aqueous conditions (anhydrous methanol). The N-ethylmorpholine is acting as a non-inhibitory buffering agent and its used do not affect the rate of the catalysed methanolysis.

Photocatalysts preparation

The Au/TiO_2 photocatalysts have been prepared using the deposition-precipitation method by following a synthetic procedure previously reported in ref. [2]. In summary, the 0.5, 1 and 1.5 wt. % Au/TiO_2 samples were obtained by adding 1 g of TiO_2 anatase support to a 100 mL aqueous solution containing 10, 20 and 30 mg, respectively of $HAuCl_4 \bullet 3H_2O$ previously adjusted at pH~8.5 with a 0.2 M NaOH solution. To get a better deposition of the gold nanoparticles, the formed slurries were heated at 80 °C for at least 5 h and under vigorous stirring. After this step, the slurries were cooled down to room temperature and the solid samples were filtered and thoroughly washed with deionized water until the elimination of chloride had occurred. Later on, the samples were dried under vacuum at 80 °C for 48 h.

1.2. Photocatalysts characterization

The amount of gold deposited on the TiO_2 surface has been determined by using an ICP-OES Optima 9300 spectrophotometer from Perkin Elmer. The nominal values were found to be 0.35, 0.9 and 1.3 wt. %, respectively. The solid samples have been further investigated by UV-Vis spectroscopy (PerkinElmer Lambda 950 spectrophotometer equipped with an integration sphere of 150 mm diameter). The spectra have been recorded in the range of 200–800 nm by using $BaSO_4$ as baseline. Structural, morphological and surface properties of the samples were analysed by Powder X-ray diffraction (PXRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The PXRD measurements were performed by using a Bruker-AXS D8 Advance diffractometer equipped with a one-dimensional detector (LynxEye type) using Cu-Kα radiation (0.1541 nm). Scanning electron micrographs of the samples were taken with a scanning electron microscope model Vega II LMU from Tescan, equipped with a spectrometer of energy dispersion of X-ray (EDX) Bruker Quantax 200, at the following operational parameters: accelerating voltage 30 kV, measuring time 1200 s, working distance around 10.5 mm, counting rate 0.4 kcps. The XPS measurements were performed in a surface science cluster (Specs), using Al $K\alpha_1$ radiation (1486.74 eV) produced by a monochromatized (Al/Mg Kα) X-ray source operating on a total power of 300 W (12.5 kV x 24 mA), on a routine base pressure of 2×10^{-8} Pa. Photoelectrons are recorded by using a Phoibos 150 hemispherical energy analyser operated in fixed analyser transmission mode with a pass energy of 20 eV. Additionally, an electron flood gun operating at 1 eV electron energy and 0.1 mA current is used to avoid sample charging during measurements. The above parameters were optimized in order to obtain the C 1s peak of the adventitious carbon contamination of the sample at 284.60 ± 0.05 eV.

Figure S1 presents the DR-UV-Vis spectra of the Au/TiO_2 prepared series together with the undoped TiO_2. The undoped TiO_2 sample presents a typical absorption threshold in the UV region at around 370 nm, which corresponds to a bandgap of 3.2 eV. The DR-UV-Vis spectra of the Au/TiO_2 samples revealed the presents of an absorption band at around 550 nm which is typical to this type of materials, this absorption being caused by surface plasmon vibrations induced by the gold nanoparticles. The presence of this absorption band induces the photoactivity of these materials under visible light irradiation.[2,3]

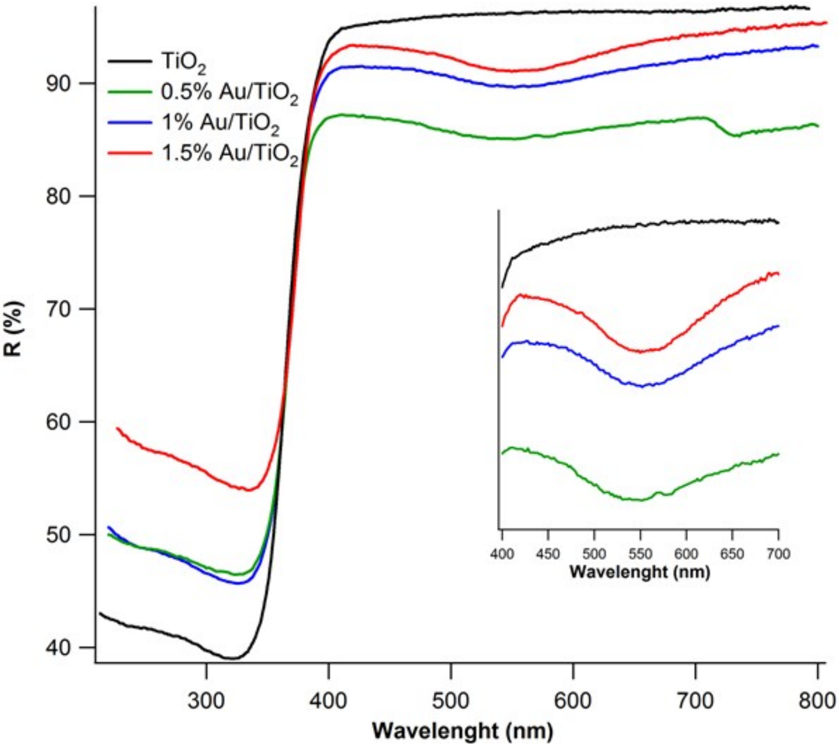

Figure S1. The diffuse reflectance UV-Vis spectra of the Au/TiO_2 photocatalysts. The inset represents an expansion of the region 400–700 nm of the spectra.

All the Au/TiO_2 samples were characterized by X-ray diffraction and the XRD patterns are presented in Figure S2. As it can be observed, besides the typical diffraction lines associated to crystalline TiO_2 anatase phase (JCPDS 21-1272) no other diffraction lines were detected, suggesting that gold particles are very well dispersed on the surface of titania.

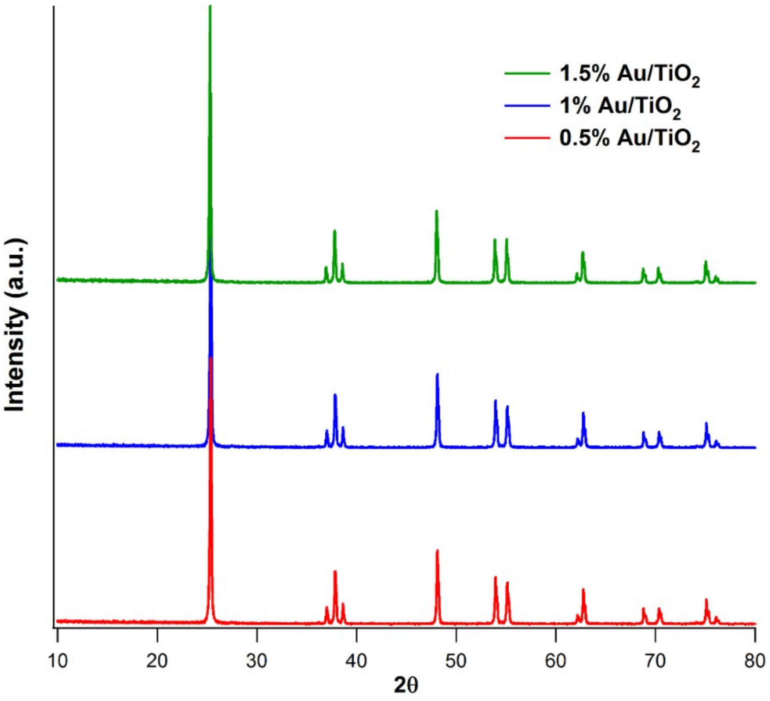

Figure S2. X-ray diffraction patterns of the Au/TiO_2 photocatalysts.

The scanning electron microscopy images of the samples are presented in Figure S3. The EDX mapping of the surface reveal that the Au nanoparticles (coded in red color) are well dispersed on the surface of TiO_2, which is in good agreement with the XRD data.

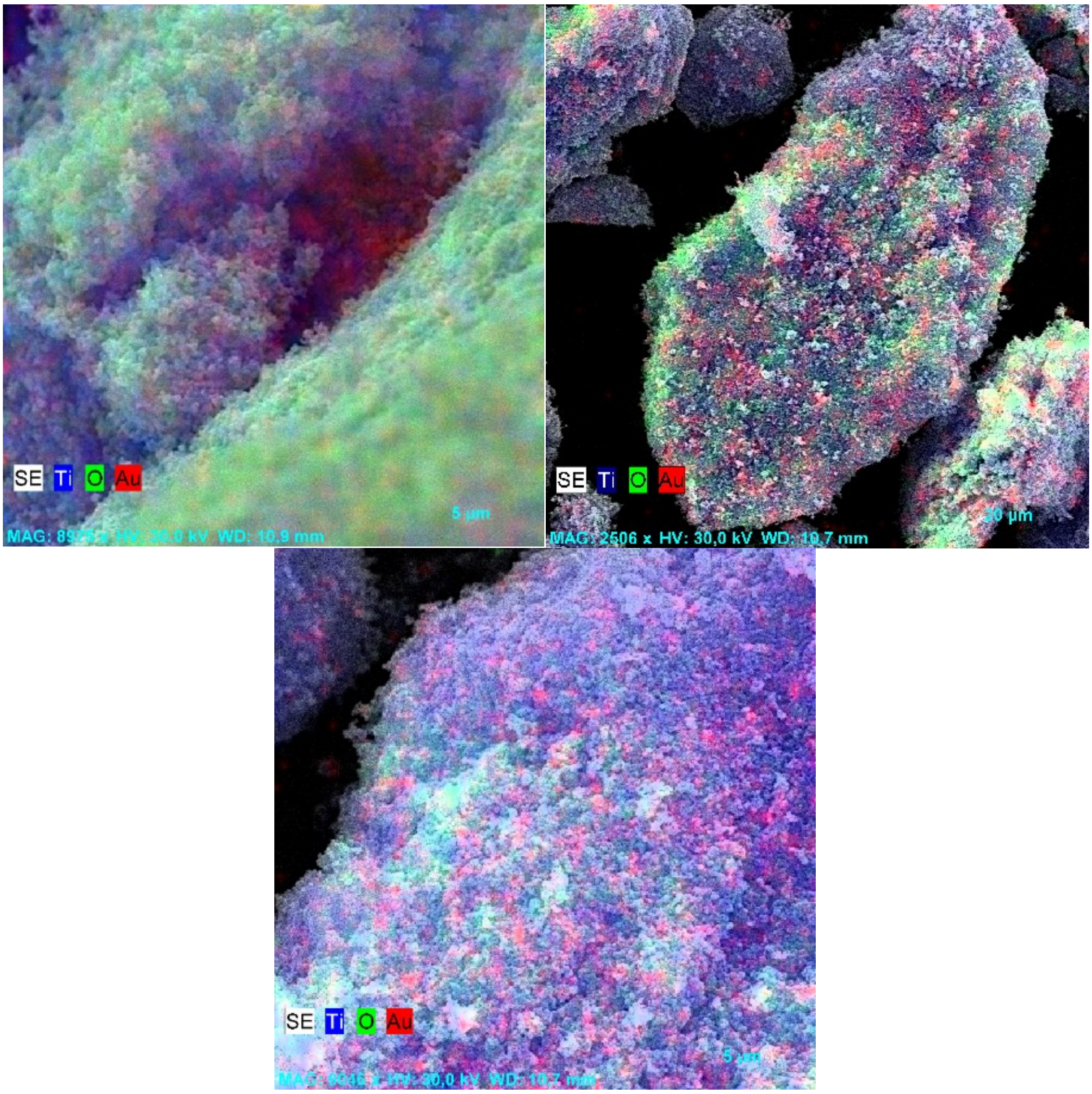

Figure S3. SEM micrographs of the 0.5 (left side), 1 (right side), and 1.5 wt. % (bottom) Au/TiO_2 photocatalysts.

The Au 4f region from the XP spectra of the most active Au/TiO_2 materials in the series (1 and 1.5 wt. %) are depicted in Figure S4. As can be observed, the Au 4f spectra present a major component with an Au $4f_{7/2}$ signal centered at around 83.2 eV, which correspond to the metallic state, and other two secondary components with signals centered at around 85.0 eV and 86.6 eV that could be assigned to higher oxidation states, such as Au^+ and Au^{3+}, respectively. The atomic ratio between these components are presented in Table S1.

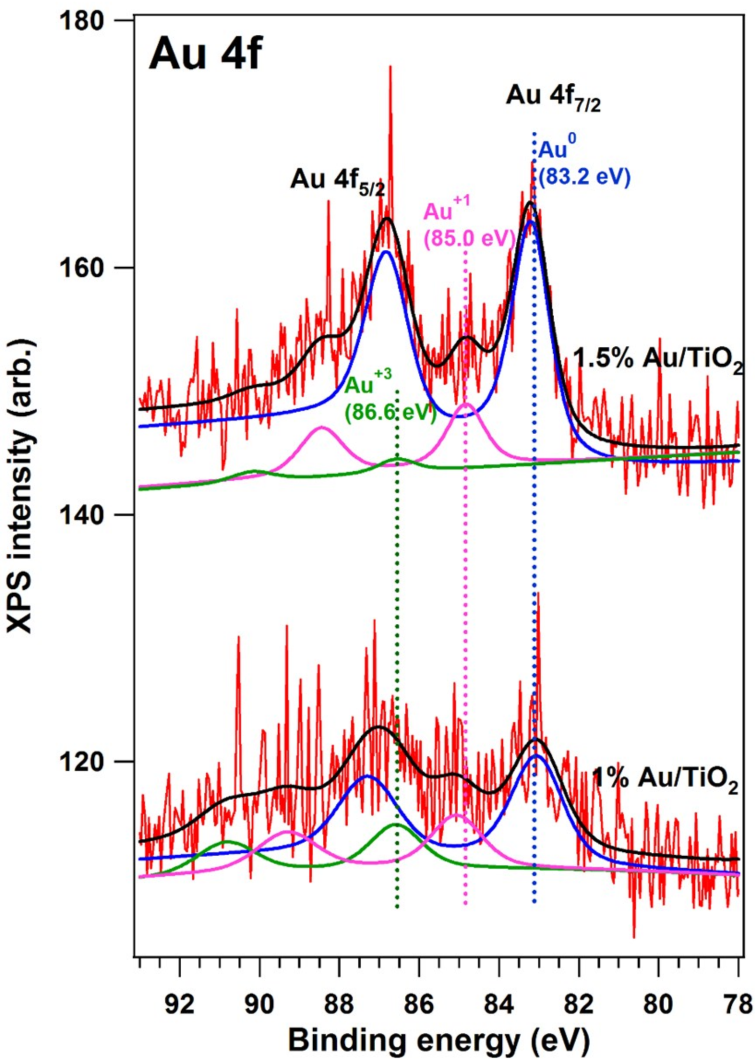

Figure S4. XP spectra of 1 and 1.5 wt. % Au/TiO_2 photocatalysts in the Au 4f region.

Table S1. XPS data of the Au/TiO_2 materials.

Sample	1 wt. % Au/TiO_2			1.5 wt. % Au/TiO_2		
Au $4f_{7/2}$ BE (eV)	83.2 (Au^0)	85.0 (Au$^+$)	86.6 (Au^{3+})	83.2 (Au^0)	85.0 (Au$^+$)	86.6 (Au^{3+})
Au^0/Au^{3+} [a]	2.38			16.77		
Au^0/Au$^+$	2.01			3.66		
Au$^+$/Au^{3+}	1.18			4.58		

[a] Atomic ratio

1.3. Decomposition tests

The real CWA used in this study comprises organic compounds which hold in their structure P=O, P–O, P–F, P–S, and C–S bonds, like sarin, soman, VX, and yperite. The molecular structures of these toxic organic compounds are presented in Figure S5.

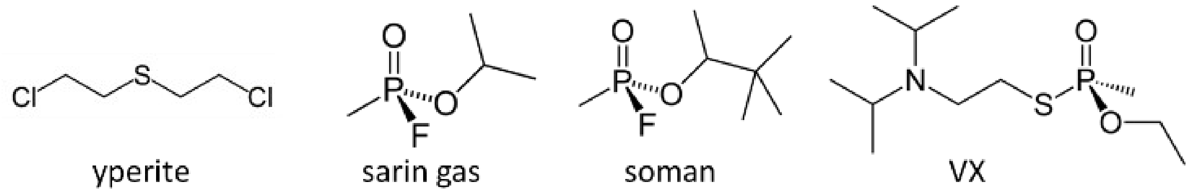

Figure S5. Molecular structure images of the targeted CWAs.

All reactions were performed by trained personnel using safety procedures in a closed system (in the case of all nerve agents) or in a hood (in the case of yperite), under good ventilation. The decomposition of real CWA has been performed under visible light irradiation and, in all cases, the distance between the irradiation source and the catalytic/photocatalytic bed was 50 cm and the temperature monitored at the reaction site was around 25 °C. No evaporation of the CWA was highlighted during the course of the reaction. The evolution of the reaction was followed by extracting the suspension with dichloromethane after 1 minute or 5, 20, 30 and 90 minutes (in the case of yperite) of visible light irradiation (300W Xe arc lamp equipped with an UV cutoff filter), concentrating the resulting extracts and analysing them by using a gas chromatograph coupled with a mass spectrometer, only after silylation with BSTFA (N,O-bis(trimethylsilyl)trifluoroacetamide and TMCS (trimethylchlorosilane) at 60 °C for 30 minutes. The GC/MS equipment used in this study was a Trace GC Ultra DSQ II from Thermo Scientific equipped with TR-5MS column and MS Quadrupole detector. Helium was used as carrier gas. For shorter reaction times (<30 min) a carbon mass balance of 98% was obtained, while for longer reaction times (>30 min) a 90-95% carbon mass balance was determined, due to the formation of gaseous byproducts.

Catalytic test

The decomposition reaction of the chosen CWA was realized by putting in contact 5 µL of toxic compound with 200 µL of decontamination solution (10^{-5} moles of catalyst) onto a 1 cm^2 poly(methyl methacrylate) (PMMA) plate. Before performing the catalytic reaction different blank experiments (in the absence of the catalyst) were conducted. No catalytic reactions were highlighted as the toxic compound was quantitatively recovered.

Photocatalytic test

The photocatalytic decomposition of the chosen CWAs was realized by covering a surface of 1 cm^2 of PMMA with 10 mg of photocatalyst and the addition of 5 µL of toxic compound. The phocatalytic performances of the Au/TiO_2 materials are presented in Table S2. In the case of the yperite decomposition, supplementary procedures have been made in order to differentiate between the photocatalytic process and the yperite physisorption on the surface of the solid material. For instance, prior to the starting of the degradation process, several adsorption experiments have been carried out. Thereby, solutions in hexane containing yperite were kept in contact with the solid photocatalyst and maintained under dark conditions for at least 20 minutes. These experiments proved that in all cases a molecular chemisorption of the yperite onto Au/TiO_2 surface took place with almost no degradation, and the amounts adsorbed on the solid can be quantitatively recovered by percolation.

Table S2. The photocatalytic performances of the investigated materials.

Substrate	Decomposition yield [%][a]			
	TiO_2	0.5 wt. % Au/TiO_2	1 wt. % Au/TiO_2	1.5 wt. % Au/TiO_2
Yperite	0	1	2	6
Soman	0	2	3	7
Sarin	0	3	5	9
VX	0	3	5	9

[a] The decontamination rate was calculated as the percentage of the toxic compound consumed from the initial quantity after performing the reaction under visible light irradiation in the presence of different Au/TiO_2 photocatalysts. The time of exposure was 1 minute in all cases.

Caution: *The manipulation of any type of CWAs might cause severe injuries and/or death and is strictly regulated under Chemical Weapons Conventions agreements and its production, storage and use require special authorization. Therefore, all reactions were performed by trained personal using safety procedures in a closed system or in a hood under good ventilation*.

2. References

1. R. E. Lewis, A. A. Neverov and R. S. Brown, *Org. Biomol. Chem.*, 2005, **3**, 4082-4088.
2. S. Neatu, B. Cojocaru, V. I. Parvulescu, V. Somoghi, M. Alvaro and H. Garcia, *J. Mater. Chem.*, 2010, **20**, 4050–4054.
3. Z. Lou, Z. Wang, B. Huang and Y. Dai, *ChemCatChem*, 2014, **6**, 2456–2476.