Supplementary material

Exploitation of Sb P-doped C$_3$N$_4$ and peroxidase immobilized on epoxidized linseed oil films for pollutants removal.

E. Gaggero[(1)], M. Paturel[(2)], F. Cristaudo[(1)], R. Sesia[(3)], M. Sangermano [(3)], P. Calza* [(1)], T. Ohno[(4)]

(1) Department of Chemistry, University of Turin, Via Pietro Giuria 5, 10126 Turin, Italy

(2) Ecole Polytech Montpellier, France

(3) Department of Applied Science and Technology, Polytechnic of Turin, Corso Duca degli Abruzzi 24, 10129 Turin, Italy

(4) Department of Applied Chemistry, Faculty of Engineering, Kyushu Institute of Technology, 1-1 Sensuicho, Tobata, Kitakyushu, Japan

1. Synthesis of Sb(x) P-doped C$_3$N$_4$ materials

The synthesis of bare C$_3$N$_4$ was performed as follows: 10 g of melamine was heated in N$_2$ atmosphere for 2h in a closed ceramic crucible up to 520 °C at 3 °C min^{-1}, and then it was cooled down obtaining bulk graphitic carbon nitride.

Phosphorous doped C$_3$N$_4$ materials were prepared by adding slowly 2g of NH$_4$(H$_2$PO$_4$) to an aqueous suspension containing melamine (10 g). The final suspension was stirred at room temperature for 1 h and then heated at 50 °C until complete dryness. The obtained powder (A) was calcinated with the same temperature programme described above. Sb(x) P-doped C$_3$N$_4$ materials, where x indicates Sb mmols, were prepared by wet chemical method synthesis. X mmol of NaSbF$_6$ were dissolved in 120 mL of EtOH (x= 0.5 and 1) and the flask was kept in an ultrasound bath for 60 minutes at 60°C. Then, 4 g of (A) were added and maintained in ultrasound bath for 60 minutes at 60°C. The solvent was then removed by rotatory evaporation and a white powder was obtained. The powder was transferred into a tube furnace and calcinated under N$_2$ atmosphere at 560 °C for 4h.

2. Materials characterization

The crystalline phases of the synthetized photocatalysts were characterized by a powder X–ray diffraction (XRD) instrument (MiniFlex II, Rigaku Co.) with CuKα (λ=1.5418 Å) radiation (cathode voltage: 30 kV, current: 15 mA) and are shown in Figure S1. They reveal the presence of graphitic C_3N_4 phase only for pristine and modified samples, showing that the precursors are entirely condensed, and no crystalline phosphate impurities are present. The intensity of the diffraction maxima measured in Sb(x) P-doped materials is lower than in pristine sample and it decreases especially with samples with a higher amount of antimony.
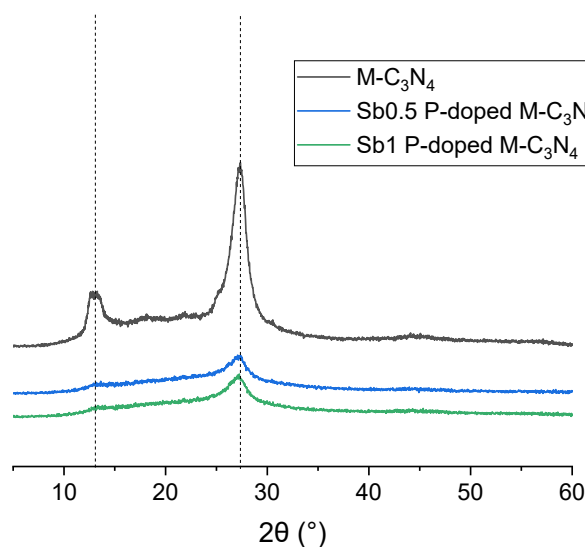

Figure S1. XRD patterns of prepared samples

UV–vis diffuse reflectance spectroscopy (UV-DRS) was executed using a UV/VIS/NIR spectrometer UV-2600 (Shimadzu Co.) and the band gap were calculated, by processing the Kubelka-Munk function of the spectra, through the Tauc plot method (Tab. S1).

Table S1. Band gap (eV) established for different synthesized materials.

SAMPLE	BAND GAP (EV)
Sb0.5 P-doped M-C$_3$N$_4$	2.65
Sb1 P-doped M-C$_3$N$_4$	2.63

Morphological analyses were performed with FEG-SEM TESCAN model S9000G, Schottky-type FEG source, theoretical resolution in In-Beam SE (Ultra High Resolution) mode: 0.7 nm at 15 keV. Point microanalysis and element distribution maps were obtained with energy dispersive spectrometer (EDS) for X-ray microanalysis, OXFORD EDS Ultim Max detector and AZTEC Software. The samples were deposited on special aluminium stubs to which double-sided carbon tape was applied in advance to facilitate conductivity and subsequently samples were subjected to metallization with a thin layer of chromium (5 nm).
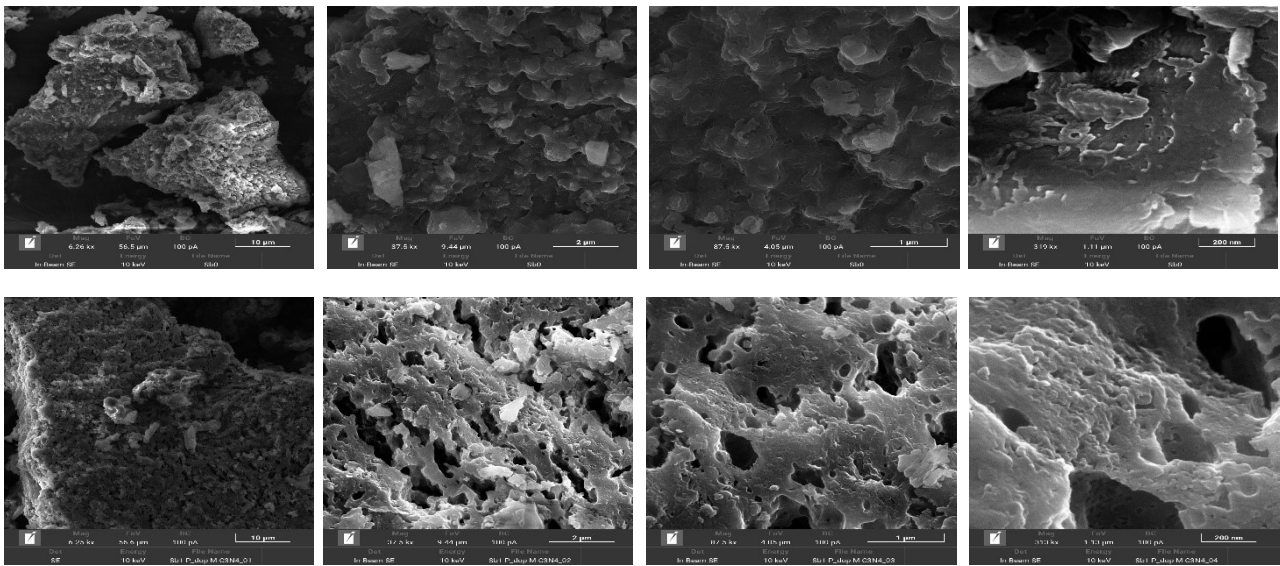
Figure S2. FEG-SEM images: (top) Sb0.5 P-doped C_3N_4 10 μm, bottom) Sb1 P-doped C_3N_4 1 μm.

Energy dispersive spectroscopy (EDS) and element mapping analyses were utilized to provide additional confirmation of the compositions and the spatial distribution of elements in the materials.

As shown in Figure S3, the EDS results indicates that the main compositions of the sample are C, N, O P, Sb and Na, the latter deriving from the precursor used for the synthesis of antimony-containing materials, namely $NaSbF_6$.
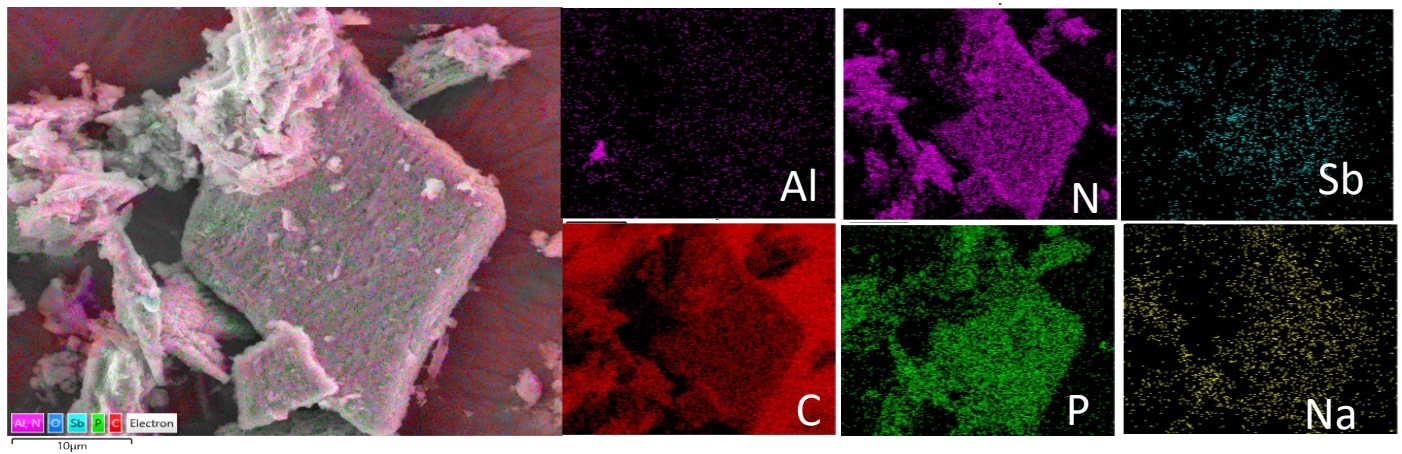
Figure S3. EDS map and elemental spectrum of Sb1 P-doped C_3N_4.

Elemental mapping reveals that N and C elements are the mainly components and evidences a homogeneous distribution of P and Sb throughout the sample, indicating the successful incorporation of P into the structure of C_3N_4 and the uniform dispersion of antimony throughout the sample.

Water matrix features are collected in Table S2.

Table S2. Main parameters, elements and organic compounds measured in the fish farm

General parameter	Value	Elements	Value, mg/l	Organic pollutants	Value, µg/L
Hardness	109	Ca	37.43	Geosmin	0,12
pH	7.76	K	15.78	2-phenylethylamine	1,121
TOC	12.6 mg/l	Mg	3.82	Carbamazepine	0,0375
		Na	378.55	Diclofenac	0,0040
		Fe	0,011	Paracetamol	0,113
		Zn	0,007	Phenazone	0,0231
				Propanil	0,019

3. *Epoxidized linseed oil (ELO) film preparation and characterization*

Mold were obtained with a rectangular shape as shown in Fig. S4.
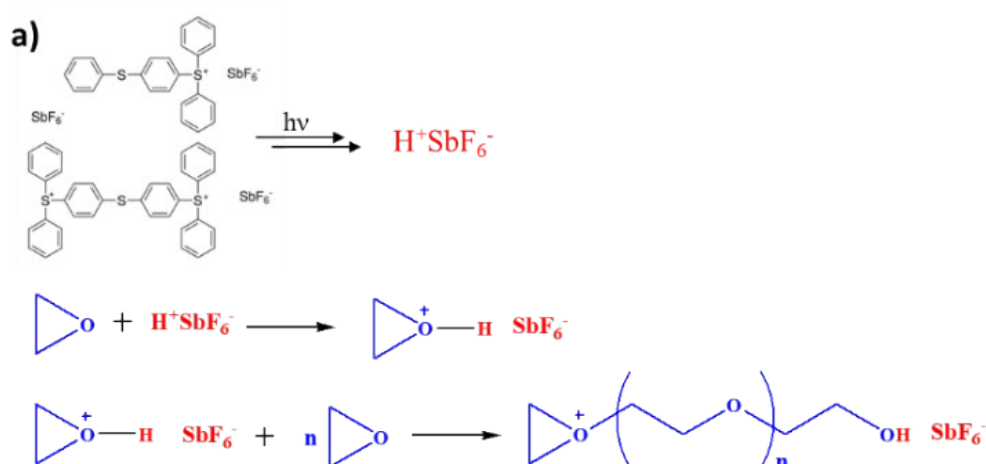
Figure S4. **a)** Schematic photo-crosslinking mechanism under UV light irradiation the cationic photoinitiator produces the Brønsted acid $H^+SbF_6^-$, which opens the epoxy rings and thus allows the cationic ring-opening polymerization of ELO; bottom) ELO multilayer film.

The percentage of conversion as a function of irradiation time in Figure S5.
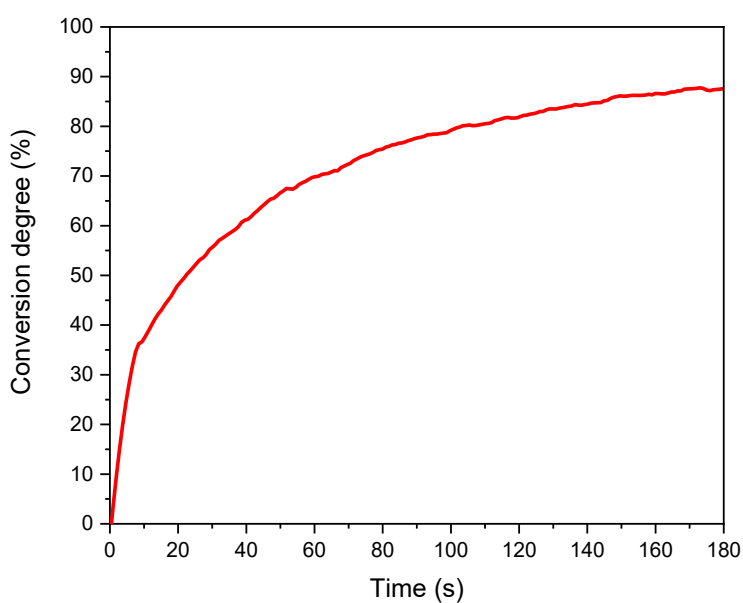

Figure S5. Conversion degree of epoxidized linseed oil.

4. Pollutants removal

The degradation of carbamazepine in the presence of Sb(0.5) and Sb(1) is reported in Figure S6.
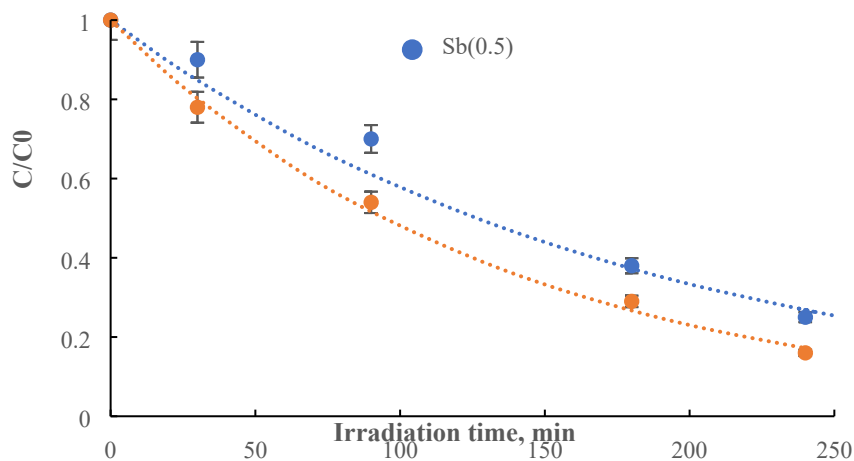
Figure S6. Degradation of carbamazepine in the present of a film with 1.5% of Sb(0.5) and Sb(1).

Toxicity tests:

Table S3. Toxicity predictions for DCP and its transformation products using ECOSAR software.

NAME	Acute toxicity (mg/L) ($EC_{(50)}$/$LC_{(50)}$)			Chronic toxicity (mg/L) (ChV)		
	Fish	Daphnid	Green algae	Fish	Daphnid	Green algae
2,4-Dichlorophenol	6,24	3,88	8,13	0,671	0,489	1,46
1,4-Benzoquinone	0,095	0,738	0,047	0,0091	4,87	0,011
Hydroquinone	7,73	25,3	0,962	11	3,2	7,7
Phenol	22,7	9,64	34,4	2,61	0,969	4,53

Reuse experiments show the capacity of the film to be used for several cycles.
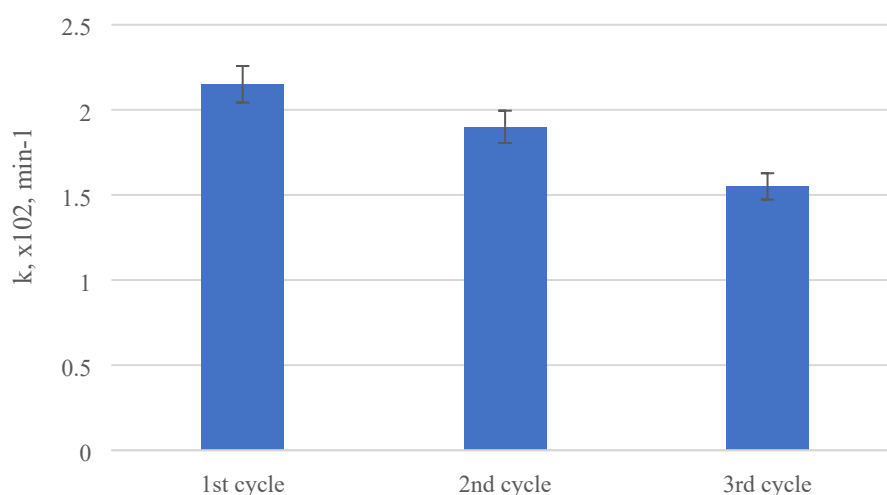

Figure S7. Kinetic constant values obtained in the experiments performed using the Sb(1) multilayer film in the presence of DCP.