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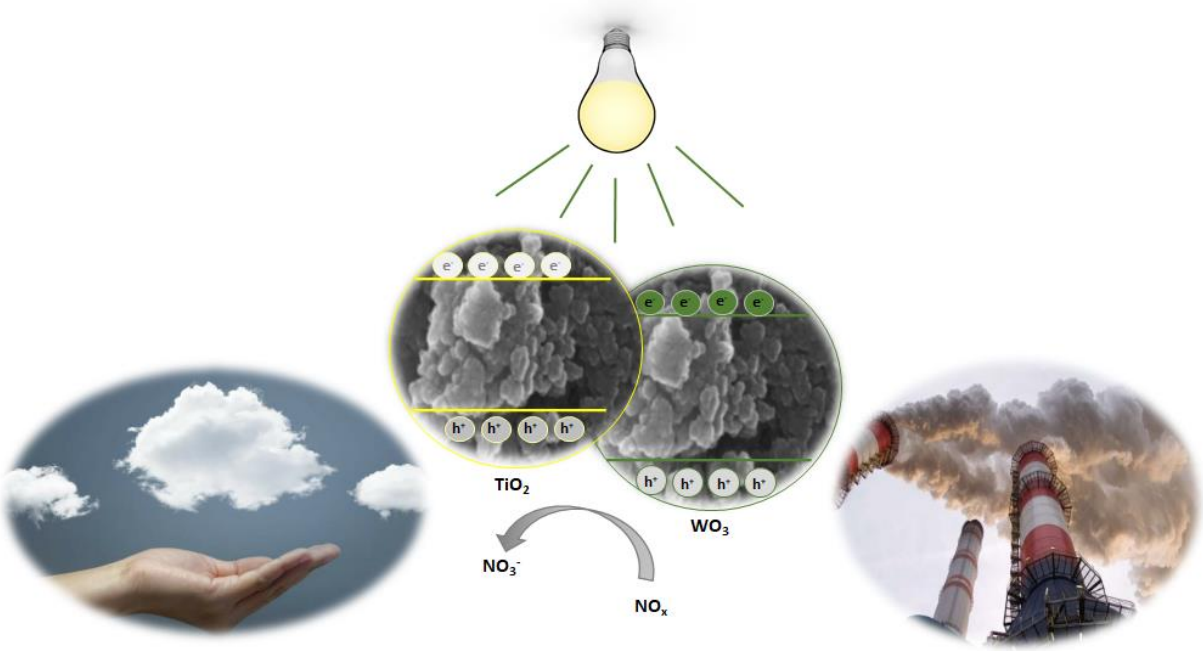
Tungsten trioxide and its TiO_2 mixed composites for the photocatalytic degradation of NO_x and bacteria (Escherichia coli) inactivation

E. Falletta, C.L. Bianchi, F. Morazzoni, A Polissi, F. Di Vincenzo, I. R. Bellobono



I novantanni del Prof. Bellobono: la sua ricerca e le nuove generazioni

Milano, 16 Novembre 2022

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Article

Tungsten Trioxide and Its TiO_2 Mixed Composites for the Photocatalytic Degradation of NO_x and Bacteria (*Escherichia coli*) Inactivation

Ermelinda Falletta [1], Claudia Letizia Bianchi [1], Franca Morazzoni [2,*], Alessandra Polissi [3], Flavia Di Vincenzo [3] and Ignazio Renato Bellobono [4]

* Correspondence: franca.morazzoni@unimib.it

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Abstract: The increased air pollution and its impact on the environment and human health in several countries have caused global concerns. Nitrogen oxides (NO_2 and NO) are principally emitted from industrial activities that strongly contribute to poor air quality. Among bacteria emanated from the fecal droppings of livestock, wildlife, and humans, *Escherichia coli* is the most abundant, and is often associated with the health risk of water. TiO_2/WO_3 heterostructures represent emerging systems for photocatalytic environmental remediation. However, the results reported in the literature are conflicting, depending on several parameters. In this work, WO_3 and a series of TiO_2/WO_3 composites were properly synthesized by an easy and fast method, abundantly characterized by several techniques, and used for NO_x degradation and *E. coli* inactivation under visible light irradiation. We demonstrated that the photoactivity of TiO_2/WO_3 composites towards NO_2 degradation under visible light is strongly related to the WO_3 content. The best performance was obtained by a WO_3 load of 20% that guarantees limited e^-/h^+ recombination. On the contrary, we showed that *E. coli* could not be degraded under visible irradiation of the TiO_2/WO_3 composites.

RESEARCH TOPICS…

Water recovery from industrial emissions

Green hydrogen production from nitrogen-rich pollutants

Smart materials for air pollutant abatement and odour control

Synthesis of advanced photocatalysts (TiO_2-free) active in the visible region for environmental remediation

Development of innovative sorbents for air and water decontamination

Development of floating materials for water remediation

Development of easily recoverable adsorptive photocatalysts for water remediation

NO_x *degradation*

MAIN SOURCES

- Anthropogenic and natural-

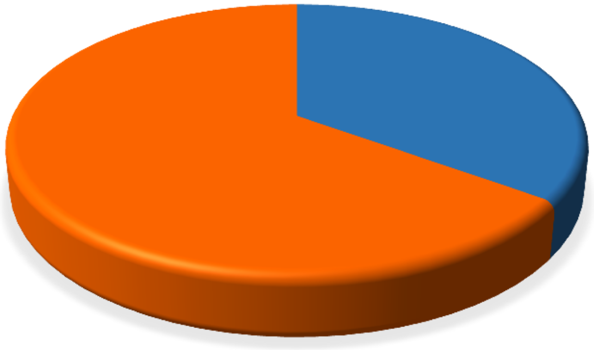
vehicular pollution

industries

agricolture

combustion

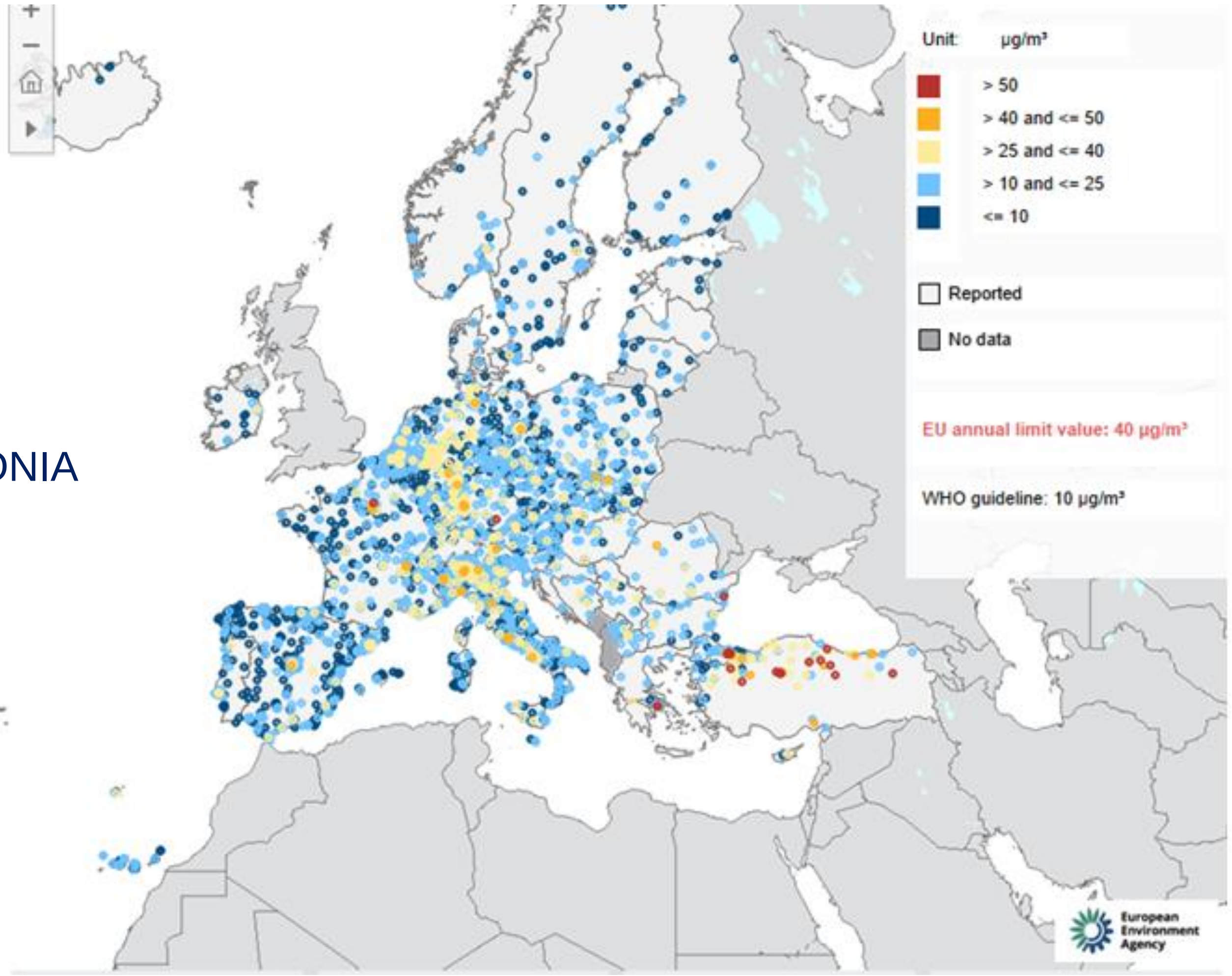
65% NITROGEN OXIDES (NOx) -NO, NO_2 and N_2O-



35% AMMONIA (NH_3)

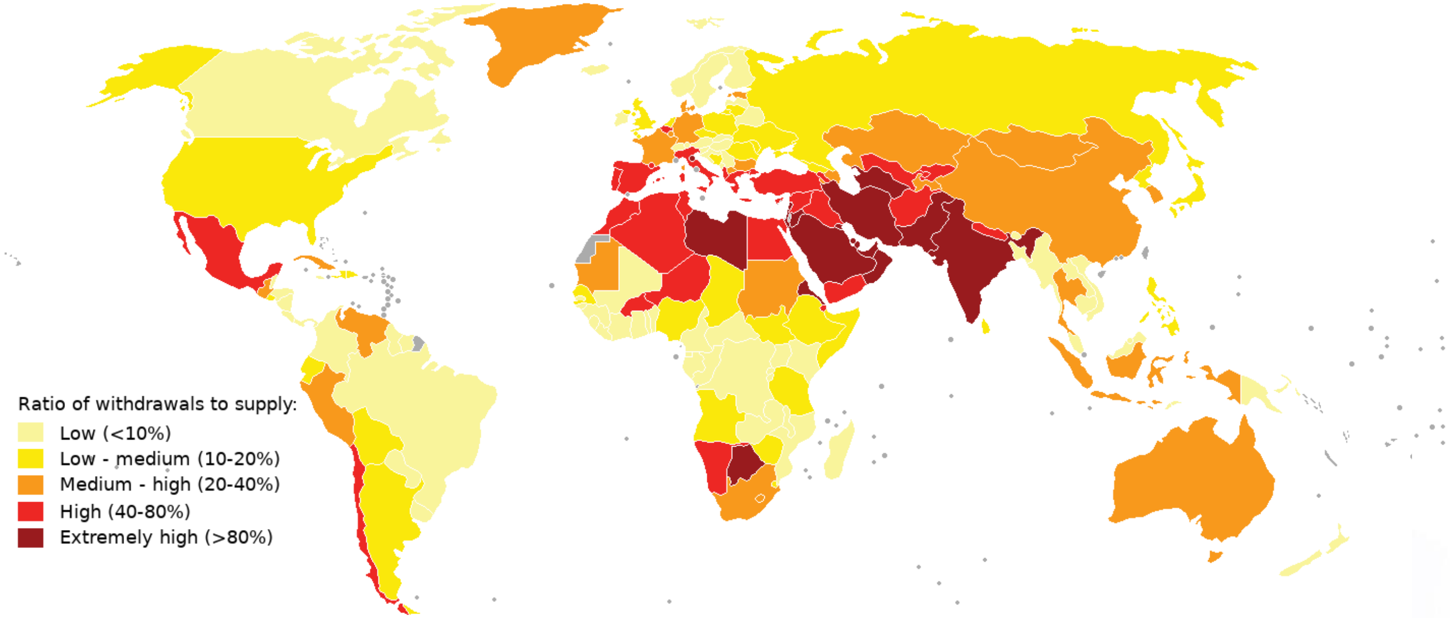
Different techniques have been developed:

- ✓ selective catalytic reduction (SCR)
- ✓ absorption, adsorption,
- ✓ electrical discharge processes
- ✓ photocatalysis
- ✓ etc.



Concentrations of NO_2 in 2020 and 2021 in relation to the EU annual limit value and the WHO annual guideline

Bacteria Infection: clean water and surfaces

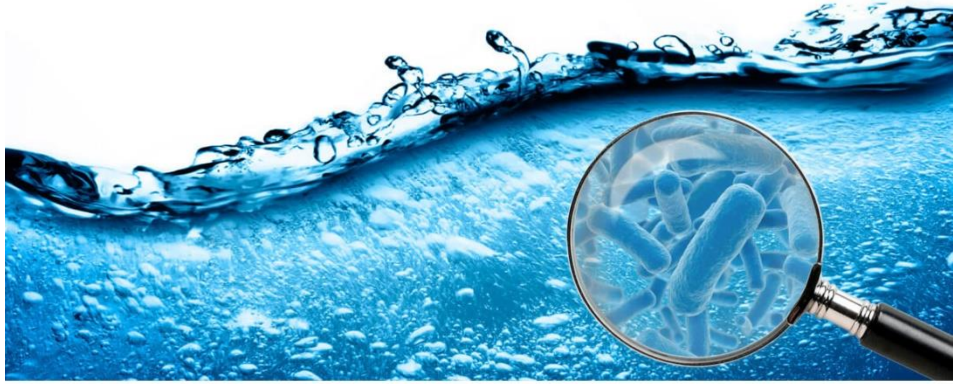


Water stress per country in 2019

$$\text{Water stress} = \frac{\text{water use}}{\text{water availability}}$$

771 million (1 in 10) people do **not** have **access** to safe **water**.
About **4 billion people**, representing nearly two-thirds of the world population, **experience severe water scarcity** during at least one month of the year.

By America's Charities on March 1, 2022



The traditional disinfection methods lead to chloro-organic disinfection by-products (DBPs) with carcinogenic and mutagenic effects.

Agenda 2030 for Sustainable Development

SUSTAINABLE DEVELOPMENT GOALS

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ScienceDi

Journal of Hazardous Materials 146 (2

Photocatalytic degradation
TiO$_2$-containing paint: A

Th. Maggos[a,*], J.G. Bartzis[b], M.

Applied Catalysis B: Environmental 253 (2019) 218–225

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

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Correlation preparation parameters/activity for microTiO$_2$ decorated with SilverNPs for NOx photodegradation under LED light

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Giuseppina Cerrato[a], Federico Galli[c], Daria C. Boffito[b], Lorenza Operti[a], Claudia L. Bianchi[c,*]

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Applied Catalysis B: Envir

Inhibition effect of SO$_2$
photodegradation of syn
at parts per billio

C.H. Ao[a], S.C. Lee

Chemical Engineering Journal 261 (2015) 76–82

Contents lists available at ScienceDirect

Chemical Engineering Journal

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Chemical Engineering Journal

Pigmentary TiO$_2$: A challenge for its use as photocatalyst in NO$_x$ air purification

CrossMark

Claudia L. Bianchi[a,b,*], Carlo Pirola[a,b], Federico Galli[a,b], Giuseppina Cerrato[c,d], Sara Morandi[c,d], Valentino Capucci[e]

Bonetta *et al. AMB Express* 2013, **3**:59
http://www.amb-express.com/content/3/1/59

ORIGINAL ARTICLE

Photocatalytic bacterial inactivat
surfaces

Silvia Bonetta[1], Sara Bonetta[2], Francesca Motta[1], Alberto Strini[3] and Elisab

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Applied Catalysis B: Environmental 76 (2007) 257–263

APPLIED CATALYSIS
B: ENVIRONMENTAL

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Photocatalytic inactivation of *Escherischia coli*
Effect of concentration of TiO_2 and microorganism, nature, and intensity of UV irradiation

A.K. Benabbou [a,b], Z. Derriche [a], C. Felix [d], P. Lejeune [c], C. Guillard [b,*]

Cement & Concrete Composites 36 (

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Nano-TiO_2-based architectural mortar for NO
inactivation: Influence of coating and weather

Ming-Zhi Guo, Tung-Chai Ling, Chi-Sun Poon *

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Applied Catalysis B: Environmental 44 (2003) 263–284

APPLIED CATALYSIS
B: ENVIRONMENTAL

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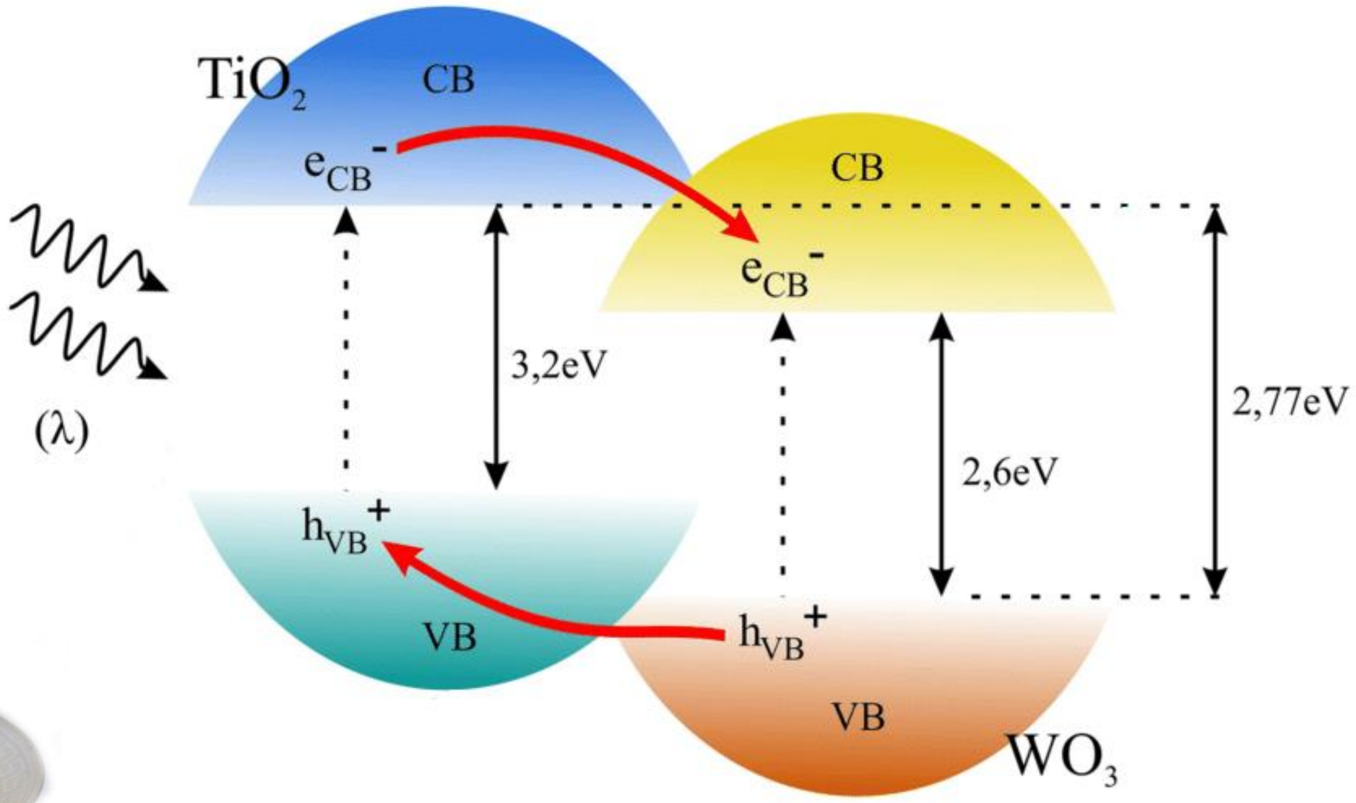
Photocatalytical inactivation of *E. coli*: effect of (continuous–intermittent) light intensity and of (suspended–fixed) TiO_2 concentration

A.G. Rincón, C. Pulgarin*

TiO_2 vs WO_3

- ✓ High availability
- ✓ Low costs
- ✓ High UV activity

- ✓ Poor activity under visible light irradiation
- ✓ Low adsorption of the pollutants
- ✓ High particles aggregation
- ✓ Poor thermal stability
- ✓ High electron/hole recombination rate
- ✓ Potential carcinogenic properties in nanoscale



WO_3

- ✓ high absorption of visible light
- ✓ nontoxic nature
- ✓ stability in oxidative and acidic conditions
- ✓ Low costs

- ✓ Photocorrosion
- ✓ unsuitable band gap structure for the reduction of molecular oxygen

Our approach

catalysts

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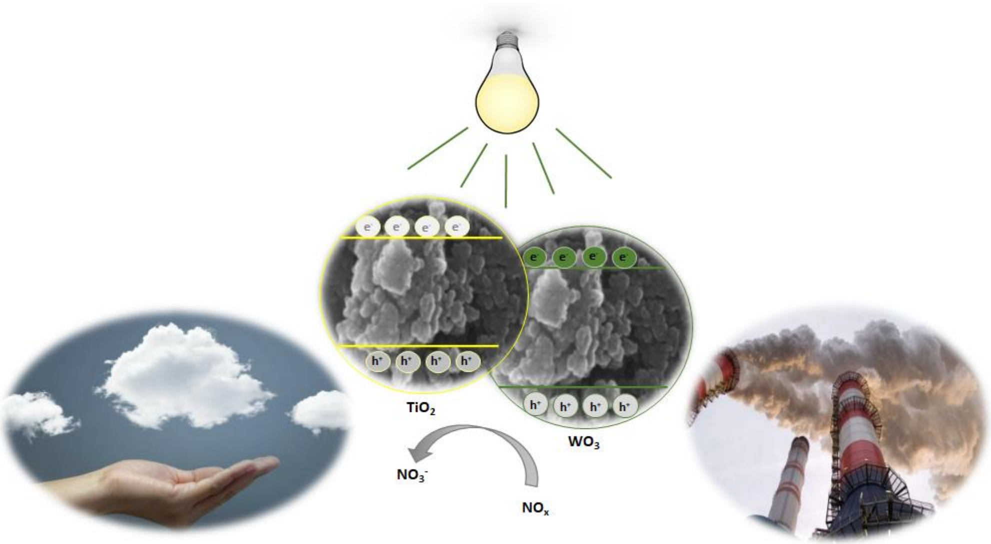
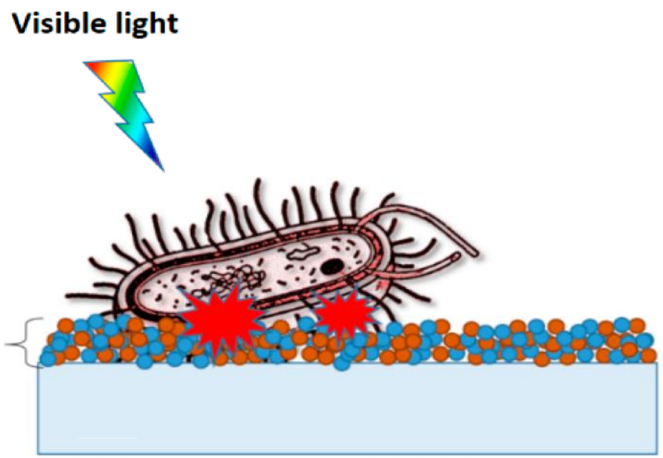
Article

Tungsten Trioxide and Its TiO_2 Mixed Composites for the Photocatalytic Degradation of NO_x and Bacteria (*Escherichia coli*) Inactivation

Ermelinda Falletta [1], Claudia Letizia Bianchi [1], Franca Morazzoni [2,*], Alessandra Polissi [3], Flavia Di Vincenzo [3] and Ignazio Renato Bellobono [4]

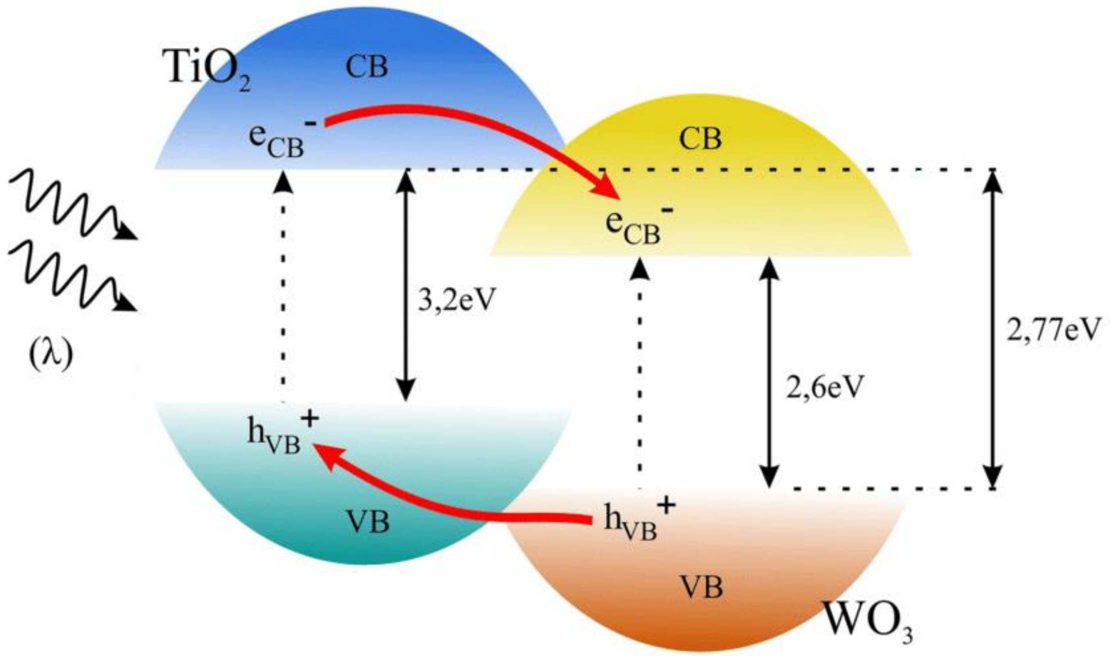
Catalysts **2022**, *12*, 822. https://doi.org/10.3390/catal12080822





The influence of WO_3 on TiO_2 photoactivity depends on several factors:

- ✓ crystal phase
- ✓ electrons accumulation ability of WO_3
- ✓ type of pollutants
- ✓ degradation pathways involved

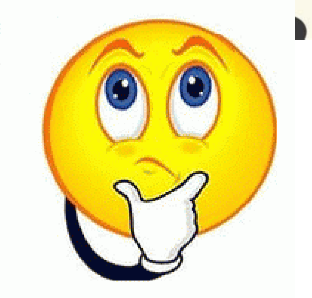


Conflicting results

Amorphous WO_x species, demonstrating that they are more active than the crystalline ones toward methylene blue degradation (*Appl. Surf. Sci. 2014, 313, 470–478*).

WO_3 with a polyhedral shape leads to 50% NO oxidation to NO_2 (*Ceram. Int. 2014, 40, 12123–12128).*

Photo-transformation of NO_2 into NO in the presence of N_2 on the surface of a WO_3 photocatalyst under UV/visible light irradiation (*Res. Chem. Intermed. 2017, 43, 7159–7169*).



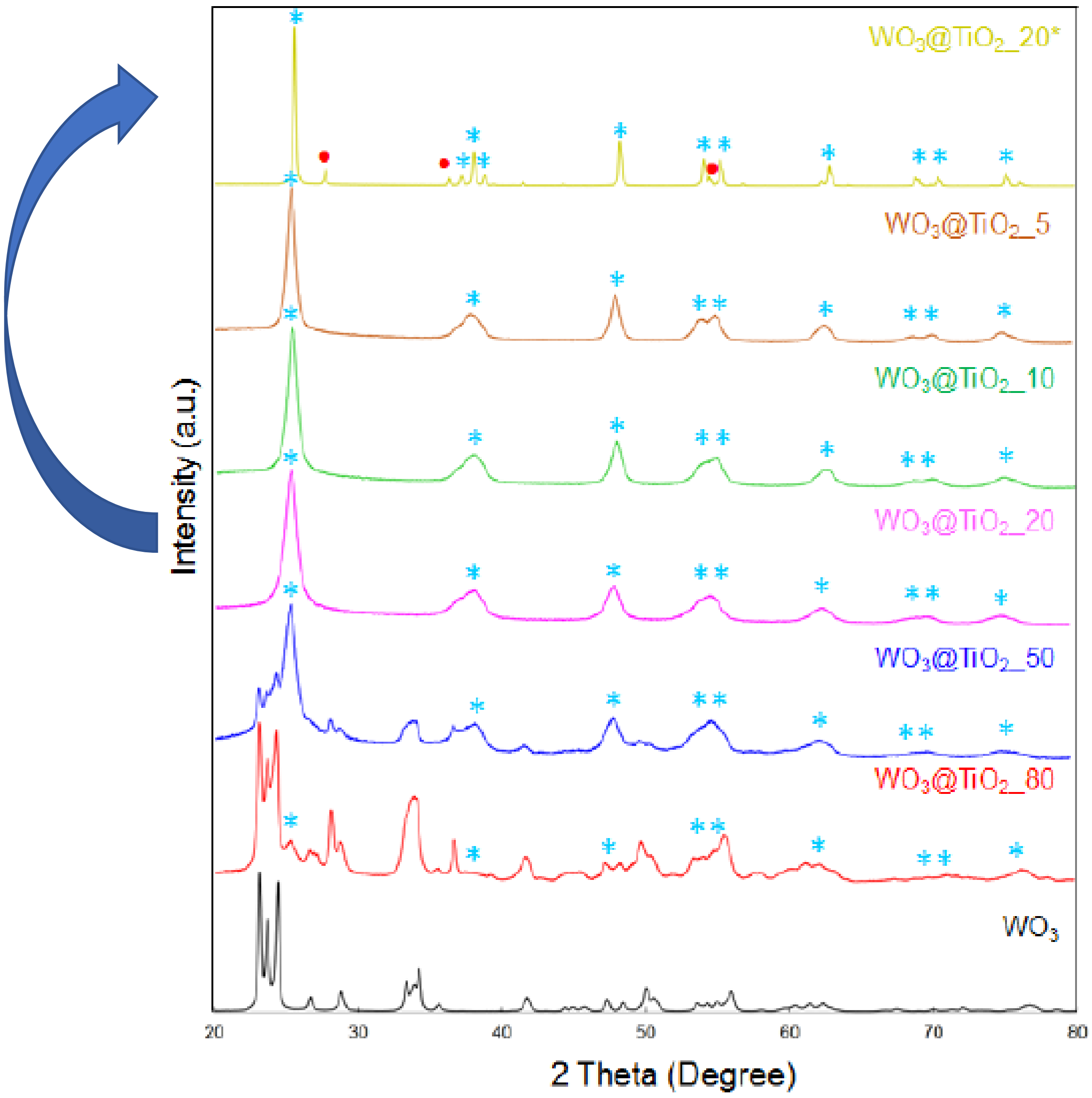
Decay of the photocatalytic activity of TiO_2/WO_3 heterostructures as a function of the W(VI) content (*Photochem. Photobiol. Sci. 2019, 18, 2469–2483*)

Our approach

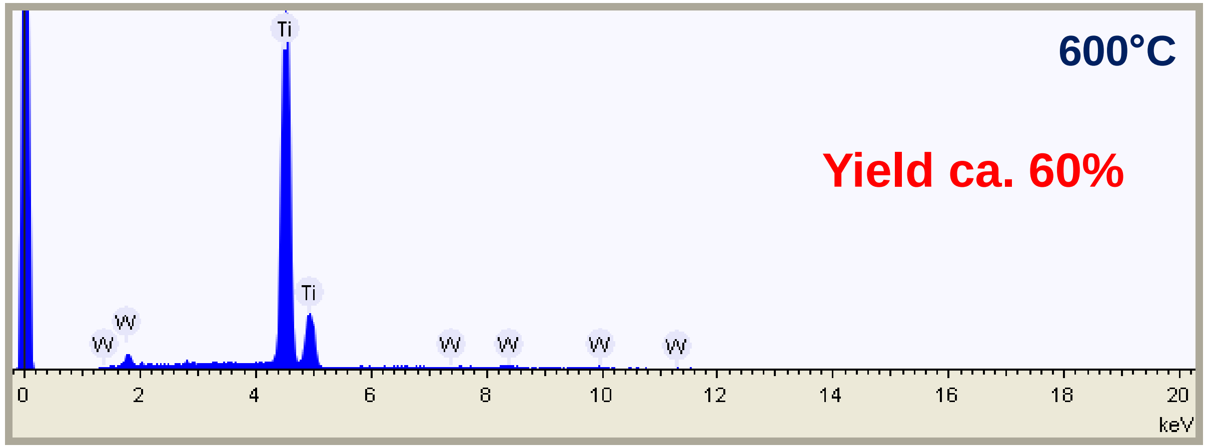
WO_3 and a series of TiO_2/WO_3 composites were synthesized by a fast and cost-effective chemical procedure and tested for the photodegradation of NO_x and the inactivation of *E. coli* under visible light irradiation.

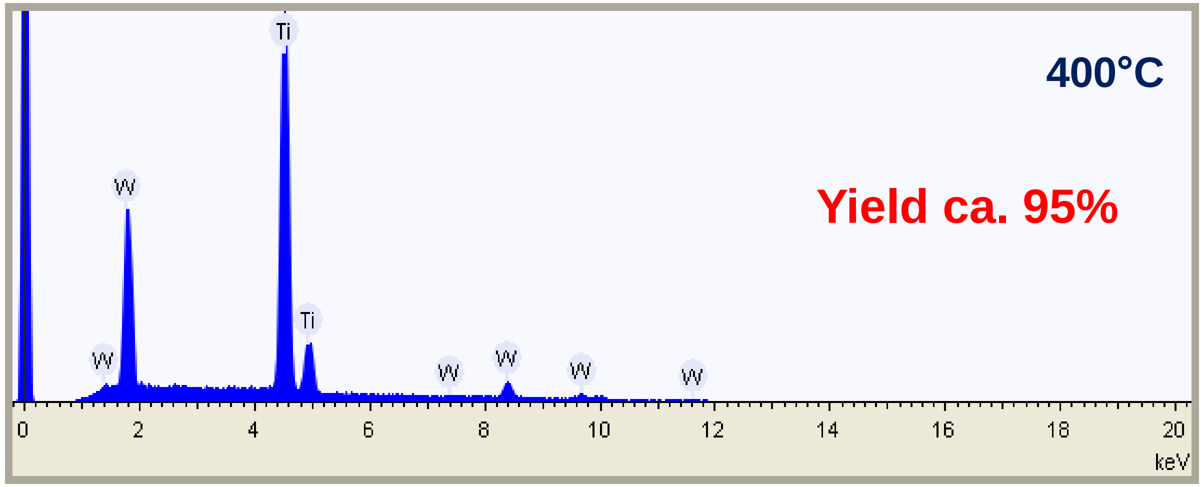
Sample	Band Gap (eV)	Specific Surface Area (m^2/g)	CBET	Vm (cm^3/g)	Mean Pore Diameter (nm)
WO_3	2.39	4.00	75.75	0.94	21.17
WO_3@TiO_2_80	2.63	42.78	123.22	9.92	8.6
WO_3@TiO_2_50	3.05	110.65	98.11	25.87	6.4
WO_3@TiO_2_20	3.14	179.78	75.50	43.26	6.0
WO_3@TiO_2_10	3.26	139.47	94.7	33.15	6.8
WO_3@TiO_2_5	3.20	111.08	112.87	31.29	9.1
TiO_2	3.29	318.00	84.48	75.50	4.70

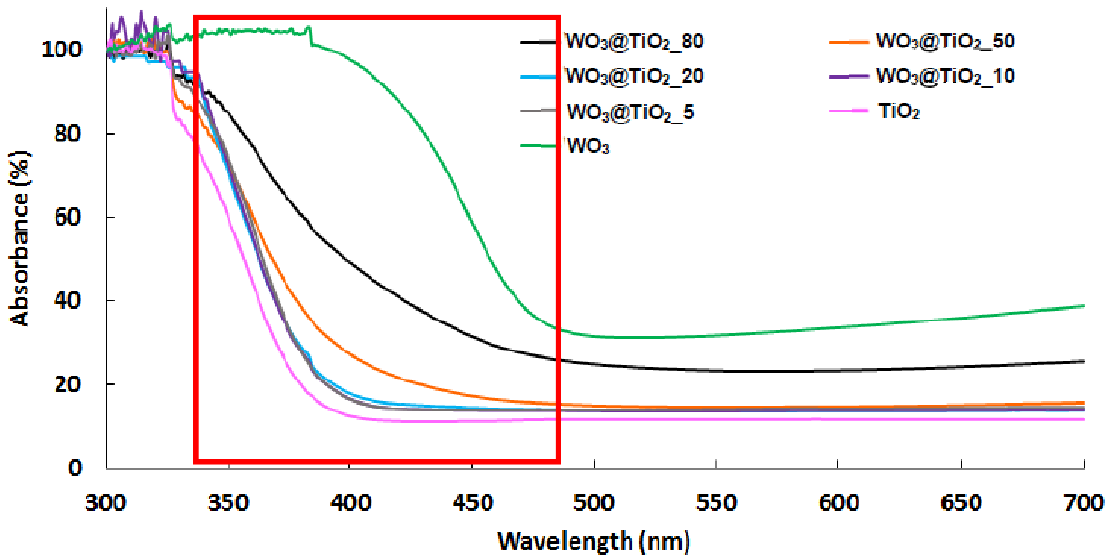
Chemosphere 182 (2017) 539-546

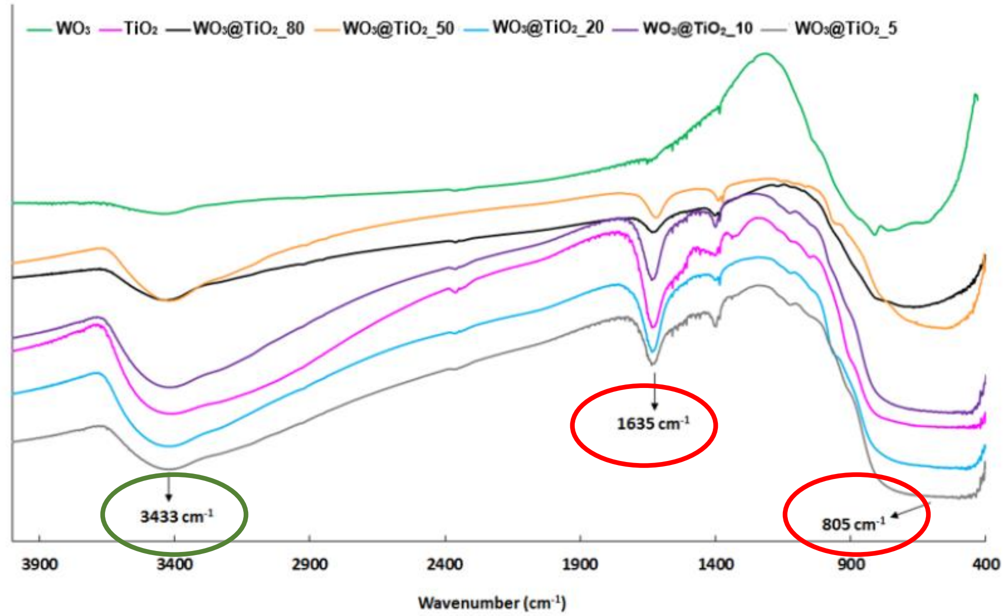


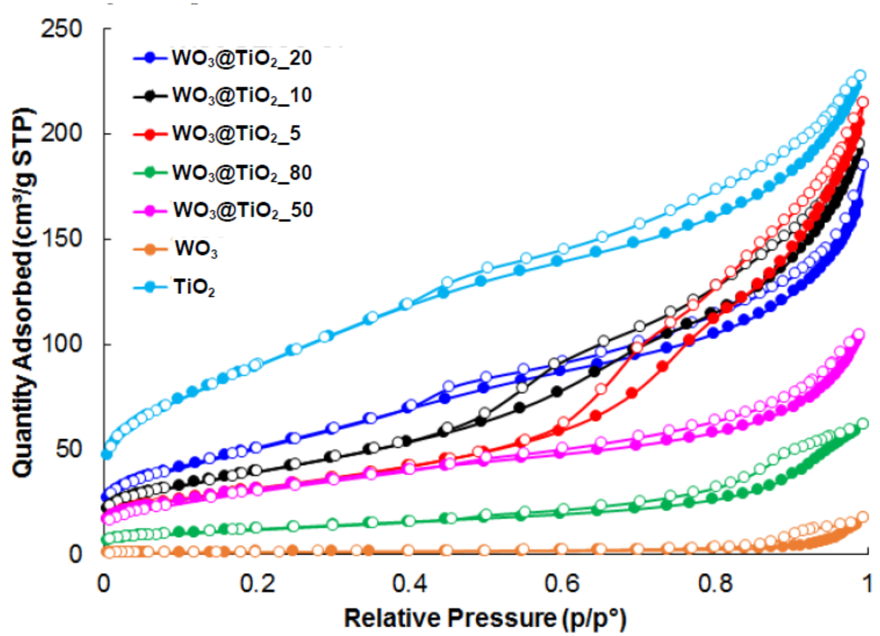
Sample	Ti (mass %)	W (mass %)	TiO2 (mass %)	WO3 (mass %)
WO3@TiO2_20	68.63	31.38	74.30	25.70
WO3@TiO2_20*	96.50	3.50	97.33	2.67











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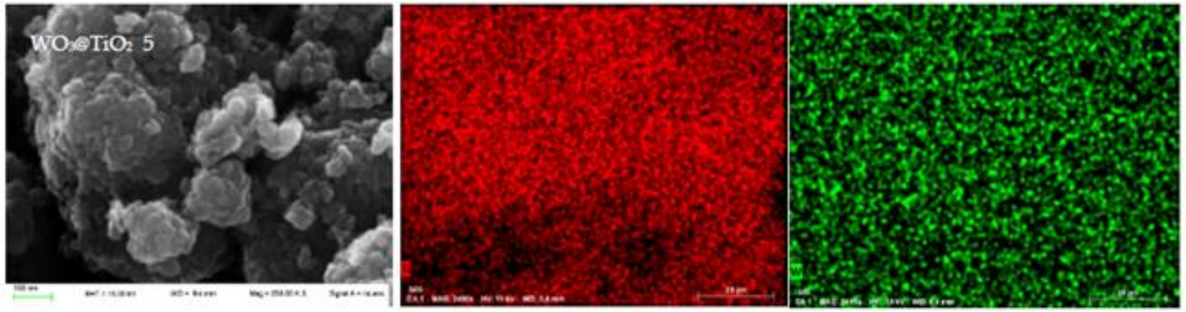
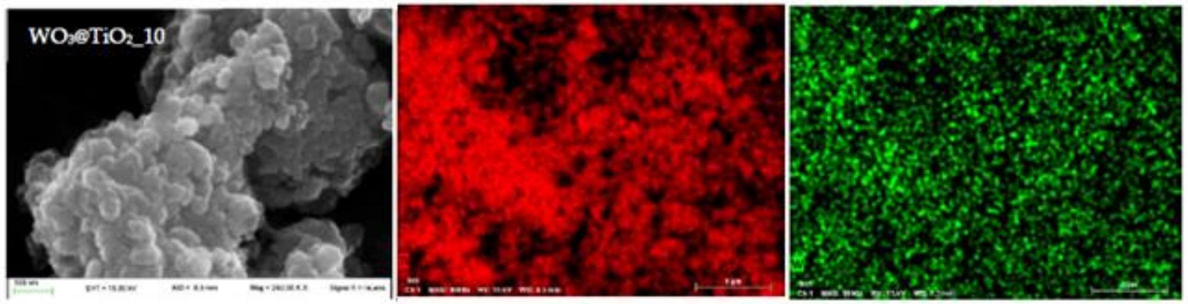
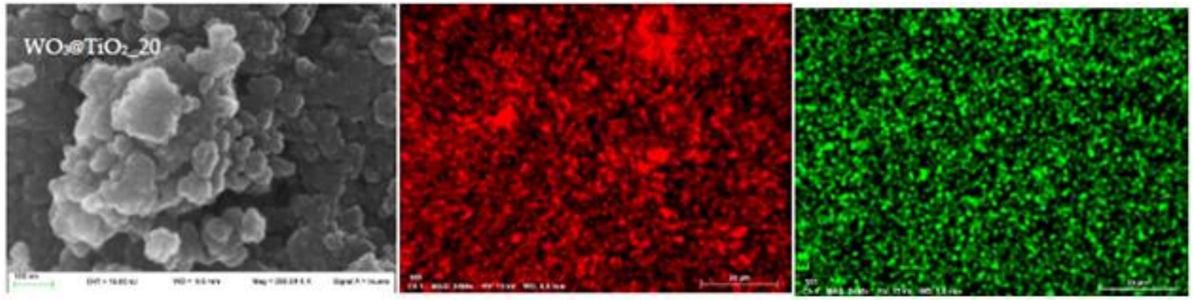
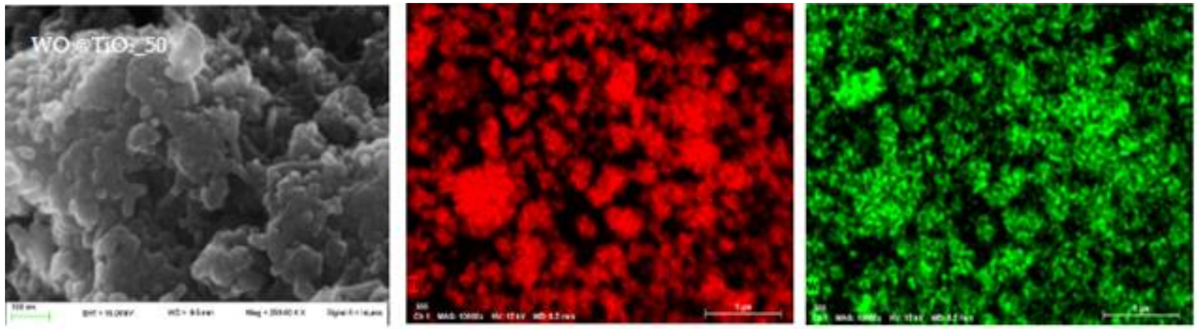
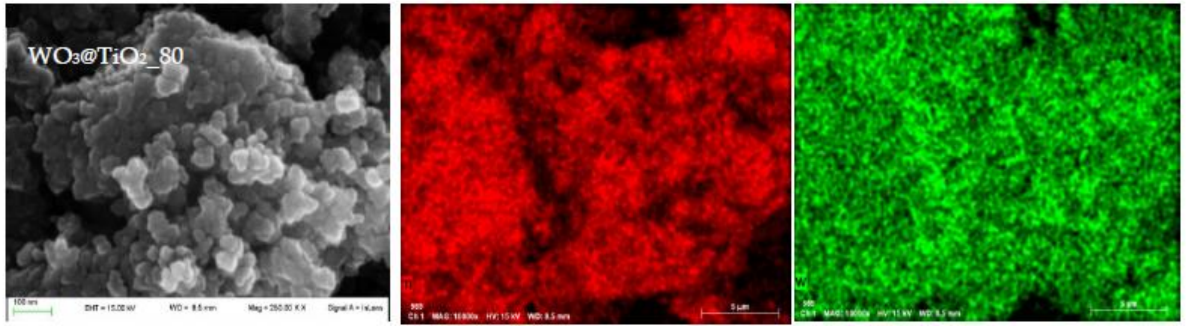




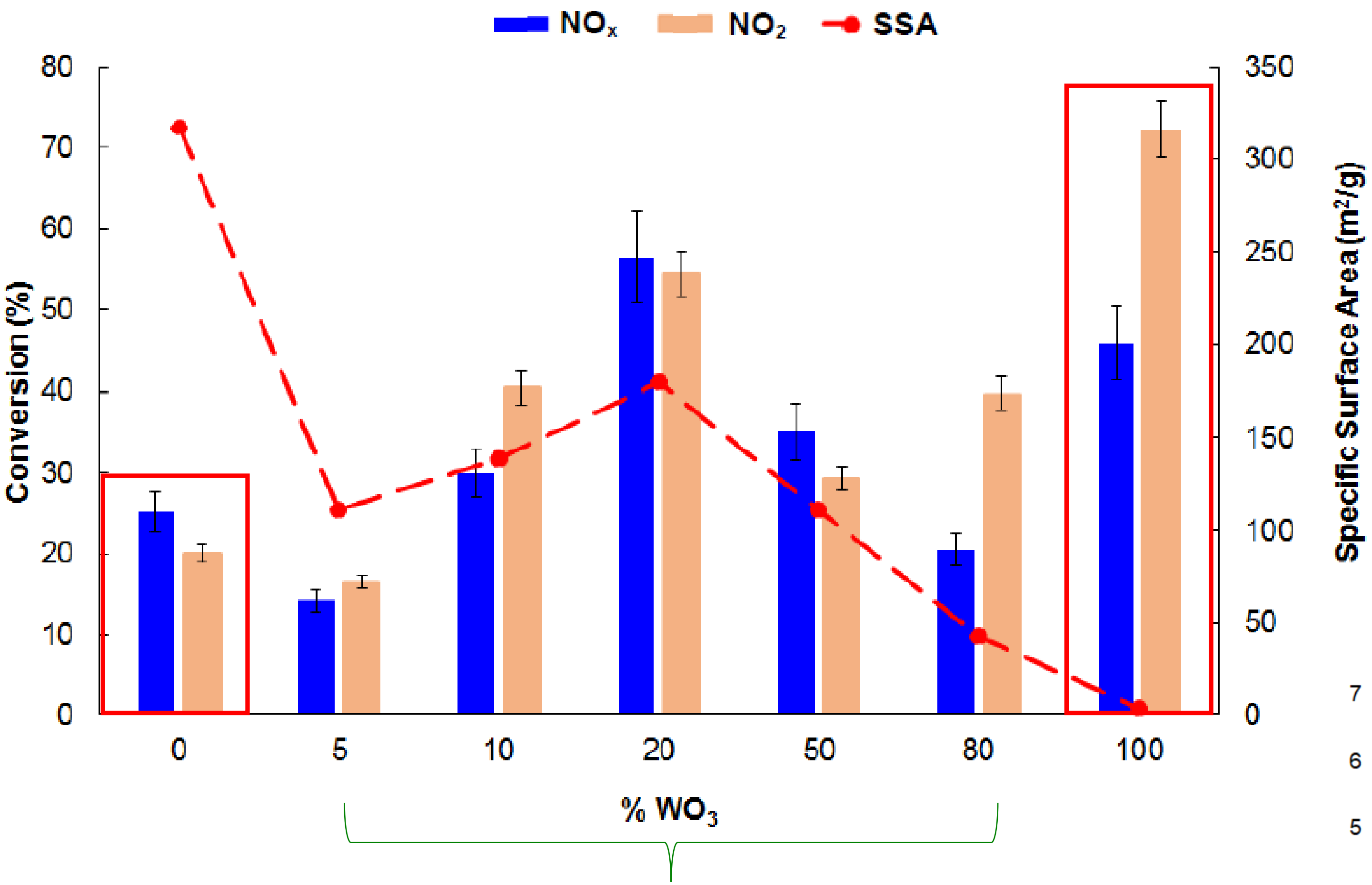






- ✓ Globular-like morphology
- ✓ Particles size 60-5 nm
- ✓ the particles are aggregated by sharing corners or edges that probably involve the formation of Ti-O-W bonds

NO_x degradation



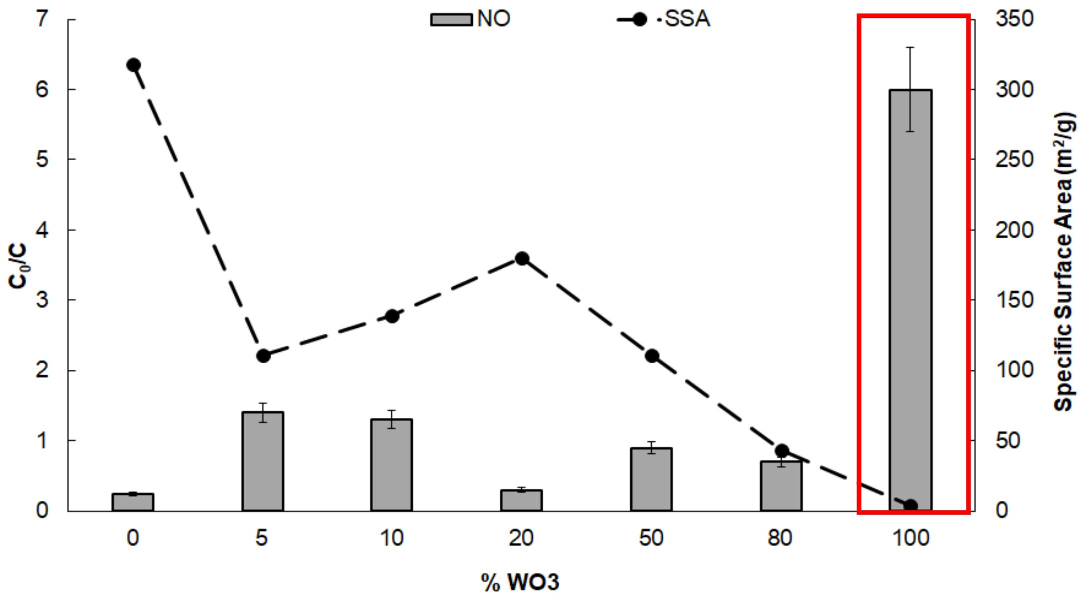
NOx initial concentration: 500 ppb

$$NO_2 + 1/2N_2 \rightarrow 2NO$$

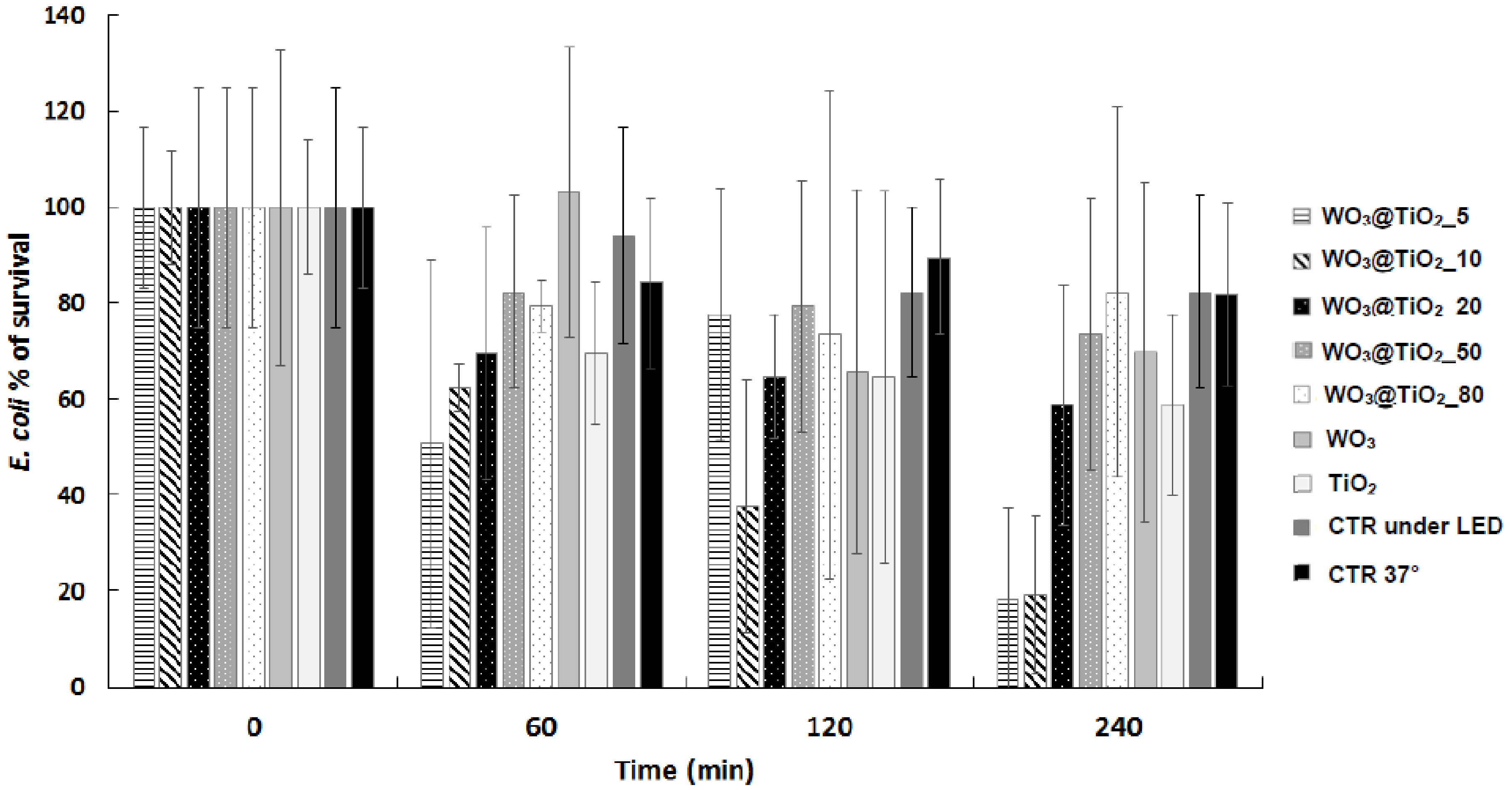
Res Chem Intermed 43, 2017, 7159–7169

This makes pristine WO_3 not efficient in the NO_x abatement, because, in air NO is immediately reoxidized to NO_2.

The effect related to the different surface area values cannot be ignored.



Bacteria inactivation



None of the tested samples displays antibacterial activity under visible light irradiation, in agreement with what was reported in the literature for the $WO_{3/}TiO_2$ catalyst.

ACS Omega 5. 2020, 31673–31683

Based on the morphology of nanoparticles, we speculate that the nanoparticle aggregation of TiO_2/WO_3 hinders a suitable surficial interaction with the bacteria and the catalyst cytotoxicity .

Conclusions

- ✓ It was demonstrated that the photoactivity of TiO_2/WO_3 heterostructures are strongly related to their composition
- ✓ For $WO_3@TiO_2$ materials characterized by low tungsten trioxide content (<20%), TiO_2 and WO_3 are present as separate phases, each playing their own photocatalytic role, whereas coupled photocatalysts are not formed
- ✓ The composite with a WO_3 load of 20% was the most efficient photocatalyst, extending the electrons and holes recombination time and promoting the transfer rate of electrons at the interface
- ✓ The high activity of the material can be explained with its high surface area value and with the presence of WO_3 centers on the surface of TiO_2 acting as electrons/holes separators
- ✓ If the WO_3 load is higher than 20%, a fast e^-/h^+ recombination can occur and the ability of tungsten trioxide to reduce NO_2 to NO prevails over the composites' capability to photo-oxidize NO_2 to NO_3^-
- ✓ The photodegradation activity of the heterostructures can be attributed to the oxidizing effect of holesit was demonstrated that high-temperature calcination leads to a partial sublimation of the WO_3 component that causes a decrease in heterostructure activity
- ✓ As for the lack of the bacteria degradation, we tentatively suggest that the aggregation of nanoparticles hinders an efficient surface contact between bacteria and catalyst.