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Recent advances in solar driven nanomaterials for water treatment

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ATC2: Nanomaterials for wastewater treatment, Zagreb, Croatia, Sep 16-18, 2020



Water Pollution

Development of industry & Growth of population



Waste & Wastewaters



Serious threat to the natural water resources



Inorganic pollutants

Organic pollutants

micropollutants

priority substances

contaminants of emerging concern



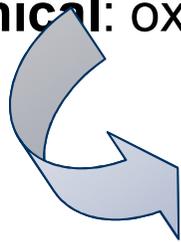
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(Waste)water Treatment Methods

- **Physical and physico-chemical:** adsorption, sedimentation, filtration, coagulation/flocculation...
- **Biological:** aerobic and anaerobic degradation

Mostly insufficiently effective for the removal of micropollutants

- **Chemical:** oxidation, reduction



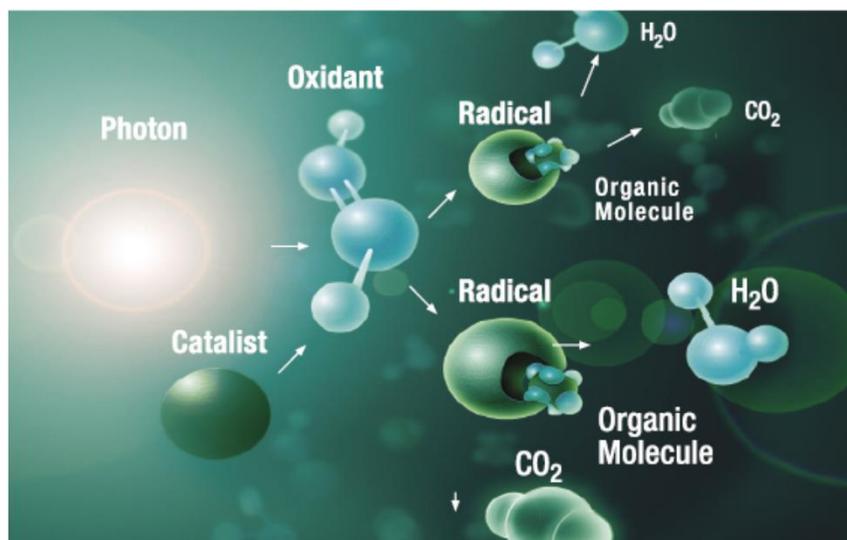
Advanced Oxidation Processes



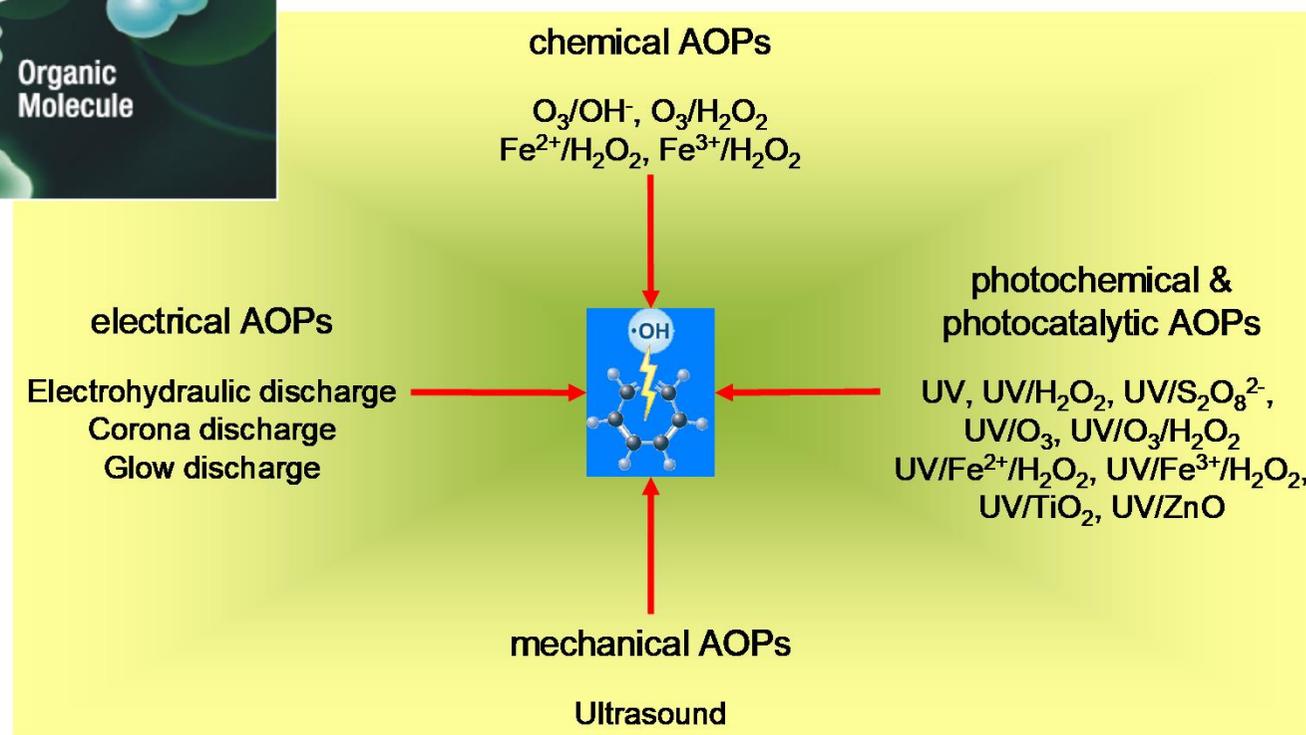
degradation/mineralization
of organics

biodegradability
improvement

lowering toxicity

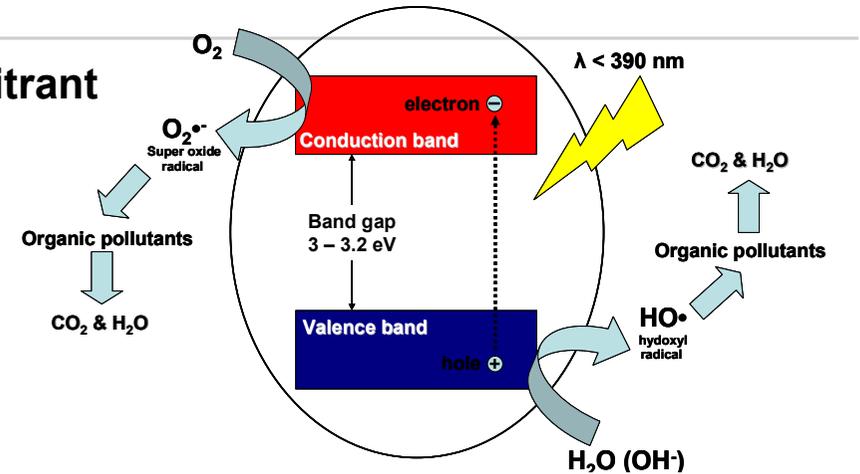


➤ based on generation highly reactive and non-selective species (**HO·**, HO₂·, O₂·⁻...)



TiO₂ photocatalysis

- pertain to group of photo-AOPs
- efficient for the degradation of various recalcitrant organic pollutants
- Functional properties TiO₂ (nano)particles:
 - chemical and thermal stability
 - attractive mechanical properties
 - photocatalytic activity (<390 nm)
 - low toxicity
 - low price



Limitations:

- tendency of nanoparticles to agglomerate during the treatment
- necessity for the separation of nanoparticles after the treatment
- limited activity under solar irradiation



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TiO₂ photocatalysis - *Photocatalyst immobilization*

- **Objective**
 - to avoid in-treatment agglomeration and post-treatment separation
- **Strengths**
 - easier catalysts separation and recovery for consecutive use
- **Weaknesses/challenges**
 - reduction of catalyst active sites, mass transfer limitations
- **Most common adhesives**
 - silica (various formulations), acrylic emulsion, chitosan
- **Most common supports**
 - reactor walls, glass or stainless-steel plates, carbon fibers, alumina sheets
- **Most common forms**
 - thin films or foams
- **Most common techniques**
 - dip coating, spin coating, simple spraying, electrodeposition

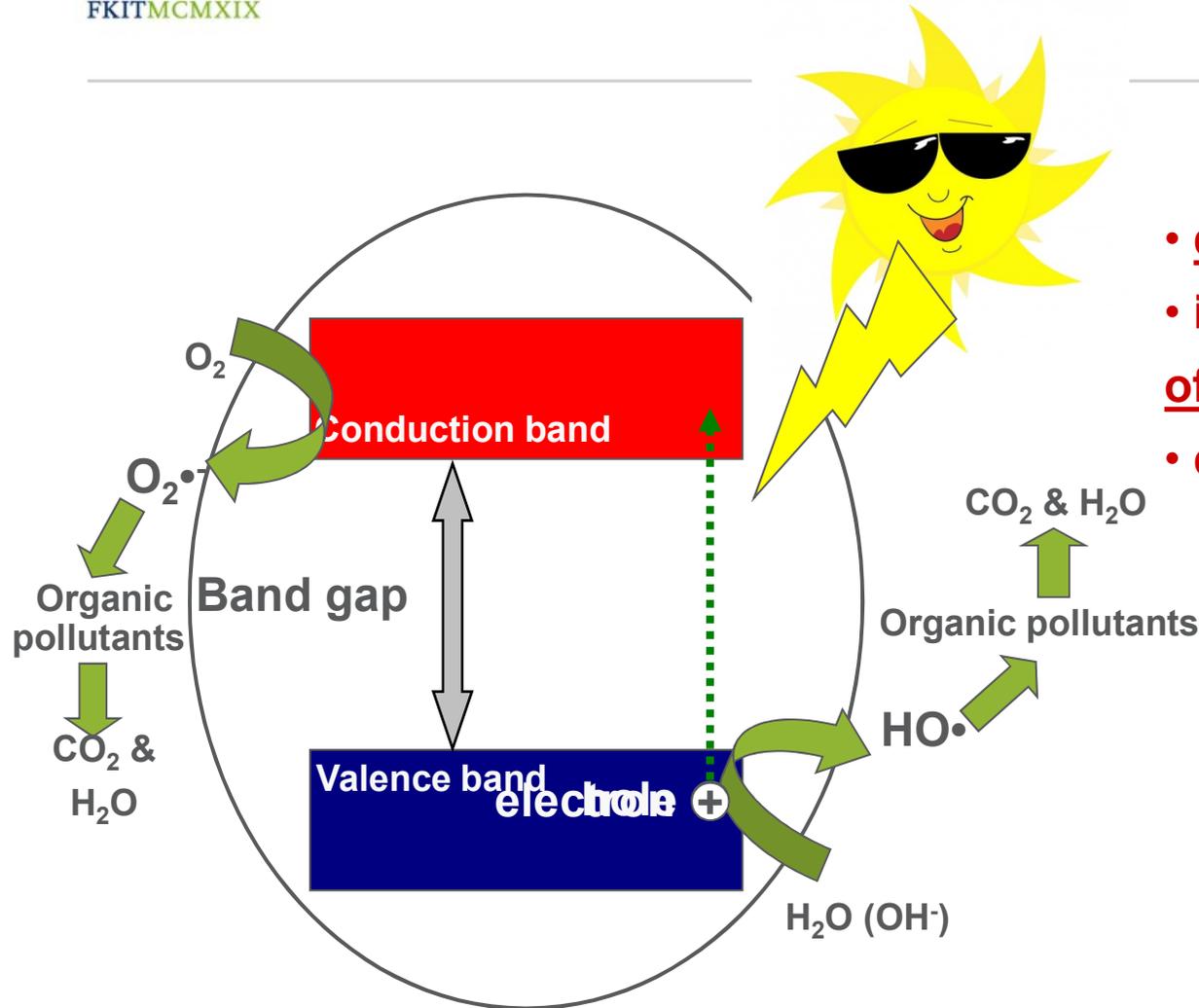


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TiO₂ photocatalysis

Improvement of activity under solar irradiation



Strategies

- doping with non-metals
- incorporation or deposition of noble metals (ions)
- composites with:
 - transition metals
 - carbon based materials
 - dye sensitizers
 - conductive polymers
 - semiconducting materials



TiO₂ photocatalysis

Improvement of activity under solar irradiation

• with non-metals

■ Synthesis / Methods:

- incorporation of non-metal into TiO₂ either in the bulk or as a surface dopant
- **sol-gel** (most simple) + more complex: sputtering, ion implantation, atomic layer or pulsed laser deposition

■ Most common elements:

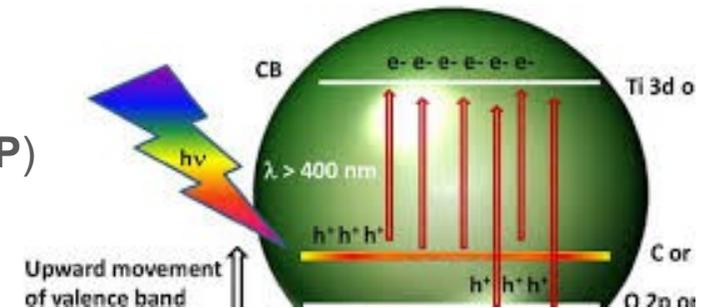
- **X**: Nitrogen (**N**), Sulphur (**S**), Carbon (**C**), Phosphorous (**P**)

■ Most common Ti-precursors:

- titanium tetrachloride, titanium isopropoxide, tetrabutyl titanate

■ Benefits:

- possibility for co-doping (N-F-TiO₂), narrowing of band gap (**X**), surface acidity (F - Fluorine), stability, non-toxic nature...



TiO₂ photocatalysis

Improvement of activity under solar irradiation

- **with noble metals**

Synthesis / Methods:

- deposition of noble metals onto TiO₂ surface
- ion-exchange, photodeposition, precipitation-deposition, atomic layer deposition

Most common elements:

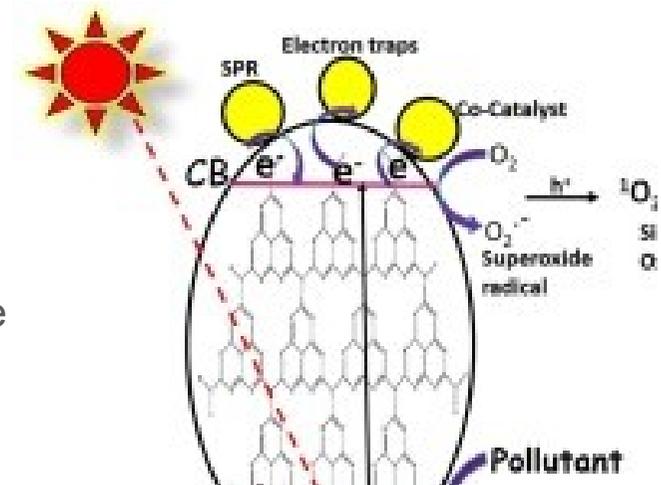
- X: Silver (Ag), Platinum (Pt), Palladium (Pd), Gold (Au)

Most common Ti-precursors:

- TiO₂ P25, as-prepared TiO₂ (using titanium isopropoxide or tetrabutyl titanate), titanium nanotubes

Benefits:

- enhancing of charge separation, acting as electron trap, delaying recombination, stability, non-toxic nature...



TiO₂ photocatalysis

Improvement of activity under solar irradiation

- **with transition metals**

■ Synthesis / Methods:

- incorporation of transition metals (ions) as impurities into TiO₂- lattice
- sol-gel & derivatives

■ Most common elements:

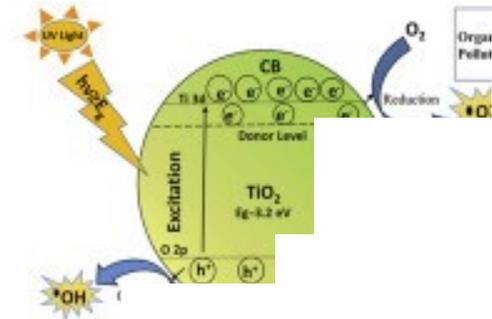
- X: Iron (Fe), Cobalt (Co), Chromium (Cr), Vanadium (V)

■ Most common Ti-precursors:

- as-prepared TiO₂ (using titanium isopropoxide or tetrabutyl titanate), TiO₂ P25

■ Benefits:

- formation of new energy levels between VB and CB of TiO₂, formation of Ti-O-X bond, lowering of band gap, more economical than usage of noble metals



TiO₂ photocatalysis

– *Improvement of activity under solar irradiation*

- ***with carbon based materials***

■ Synthesis / Methods:

- coupling with pre-sintetized carbon based materials
- In-situ hydrothermal/solvothermal, layer deposition, precipitation-deposition

■ Most common semiconductors:

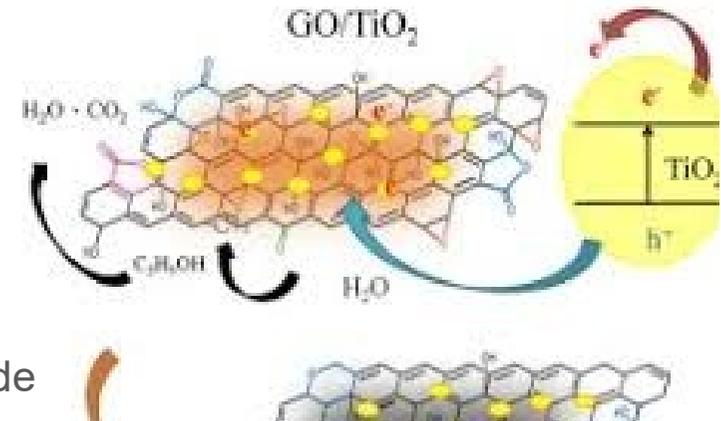
- Graphene (G), graphene oxide (GO) / reduced graphene oxide (rGO), carbon nanotubes (CN)

■ Most common Ti-precursors:

- TiO₂ P25, as-prepared TiO₂ (using titanium isopropoxide or tetrabutyl titanate)

■ Benefits:

- increase of surface area, suppression of electron and holes recombination





TiO₂ photocatalysis

– Improvement of activity under solar irradiation

- ***with semiconducting materials***

■ **Synthesis / Methods:**

- coupling of two semiconducting materials
- hydrothermal/solvothermal, sol-gel, layer deposition, precipitation-deposition

■ **Most common semiconductors:**

- zinc oxide (**ZnO**), cadmium sulfide (**CdS**), thin sulfide (**SnS₂**),

■ **Most common Ti-precursors:**

- TiO₂ P25, as-prepared TiO₂ (using titanium isopropoxide or tetrabutyl titanate)

■ **Benefits:**

- lowering of band gap, compensating the disadvantages of the individual components, inducing a synergistic effect such as an efficient charge separation and improvement of photostability

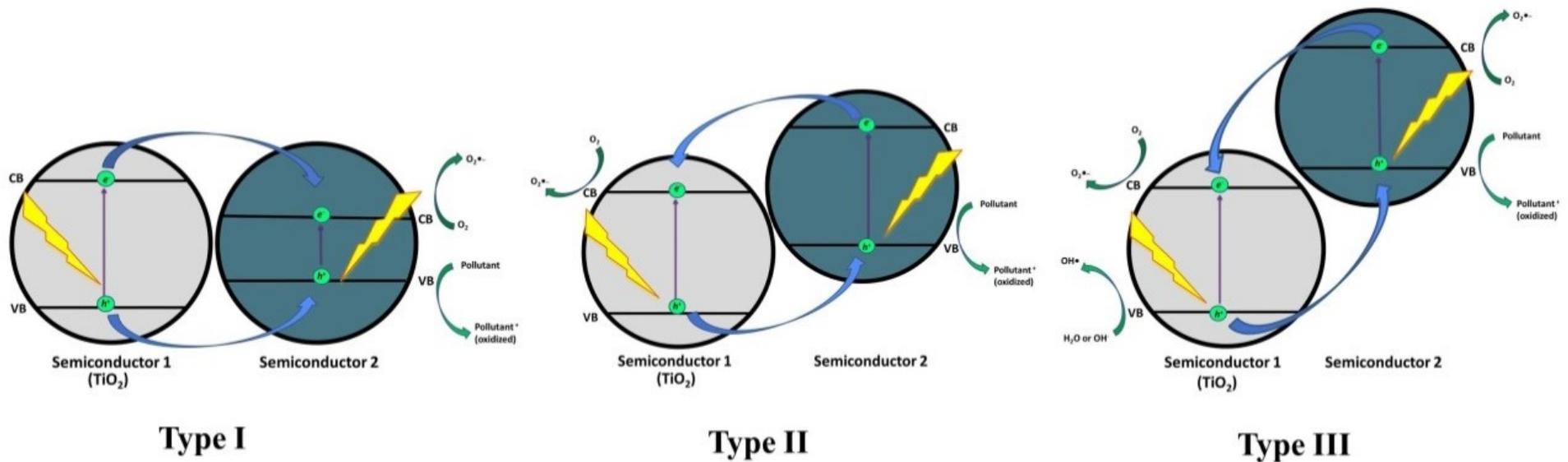


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Semiconducting material nanocomposites

➤ mostly involve TiO_2 and one or more semiconducting materials forming HETEROJUNCTION



main types of heterojunction architectures for TiO_2 /semiconductor composites



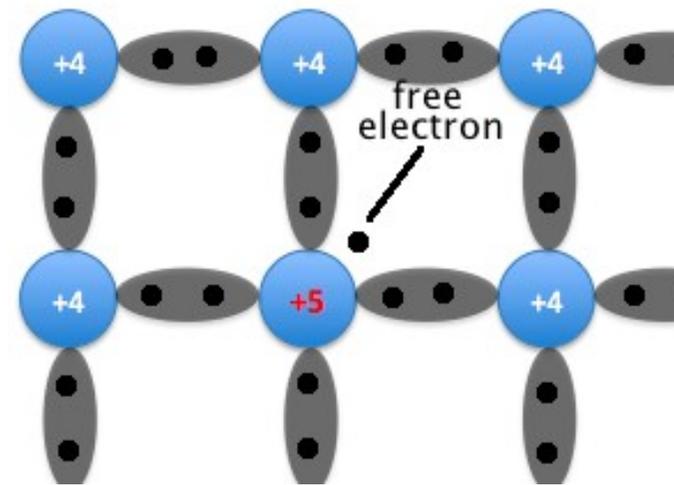
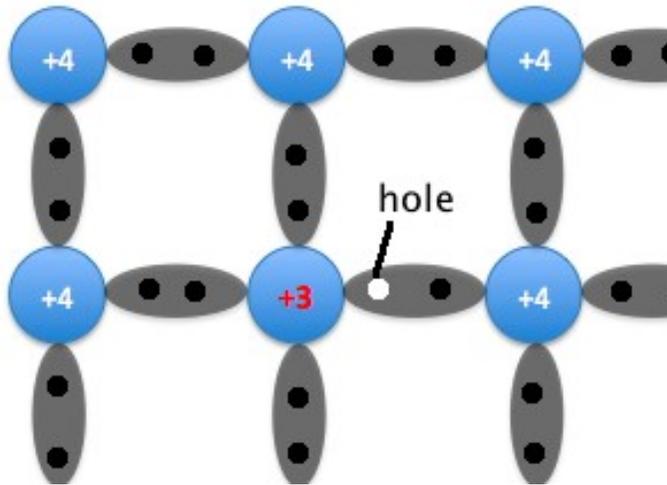
Semiconducting materials - types -

p-type

n-type

Replacement of atom in semiconductor lattice M^{3+} ($3 e^-$), e^-/h^+ balance is changed; impurity creates excess h^+ \rightarrow **acceptor**

Replacement of atom in semiconductor lattice M^{5+} ($5 e^-$), lattice hold 4, excess e^- in the lattice; impurity \rightarrow **donor**



p stands for „positive” - acceptor donates h^+ (**positive charge**)

n stands for „negative” - donor donates e^- (**negative charge**)

h^+ are majority charge carriers, while e^- minority carriers

$e^- > h^+$, e^- majority charge carriers, while h^+ minority carriers

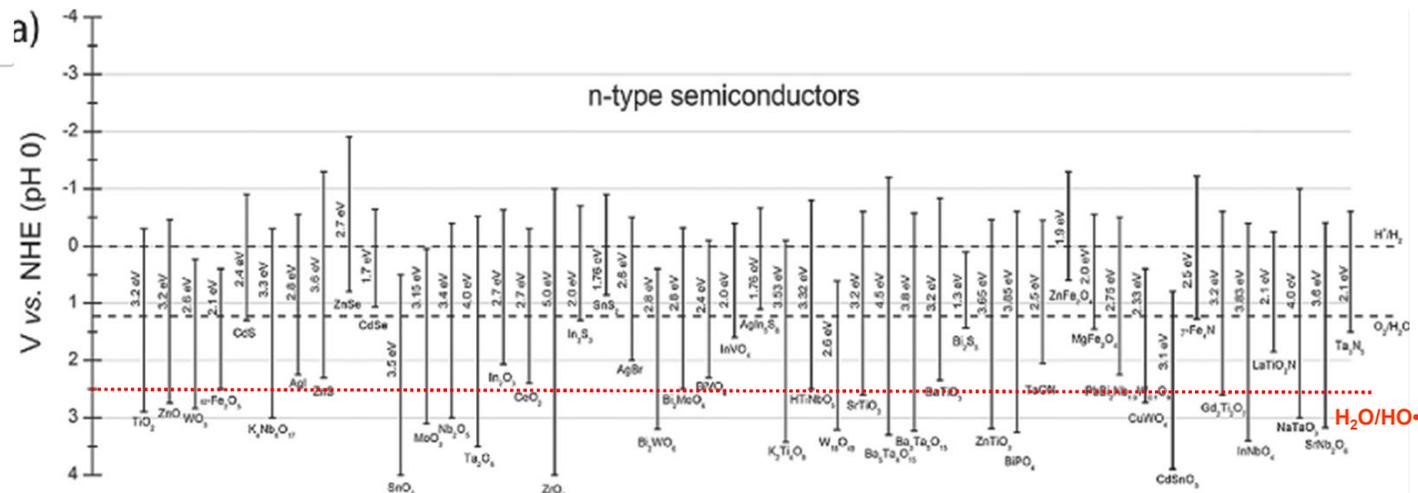




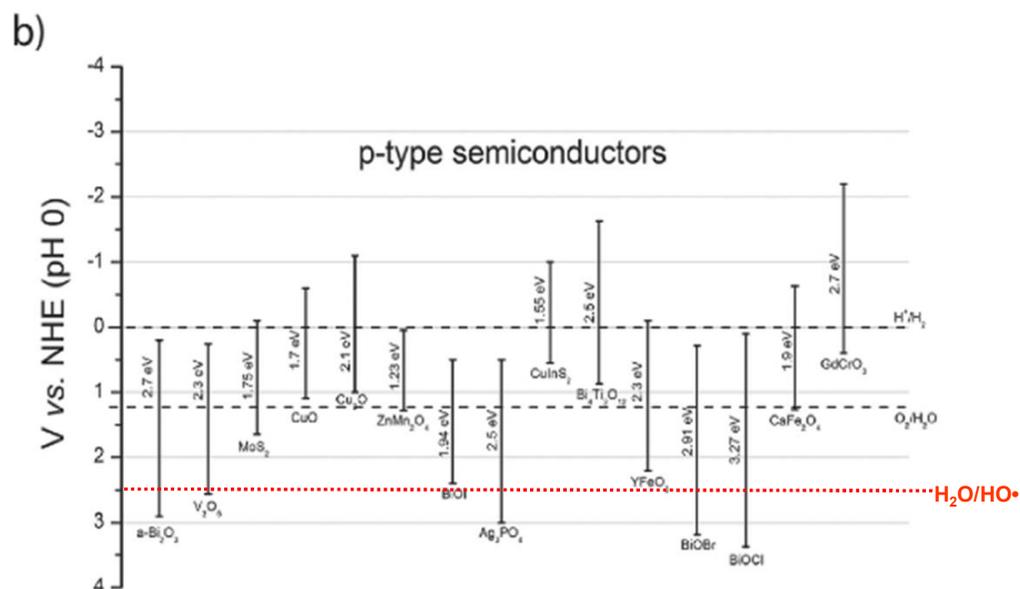
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Semiconducting materials - candidate's groups-



- Metal Oxides
- Metal Sulfides
- Silver- Based Semiconductors
- Carbon Nitride

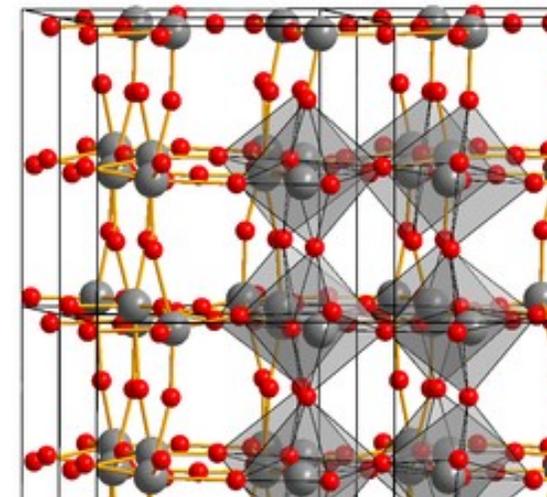


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TiO₂-based nanocomposites - examples -

Metal Oxides - Tungsten oxide (**WO₃**)

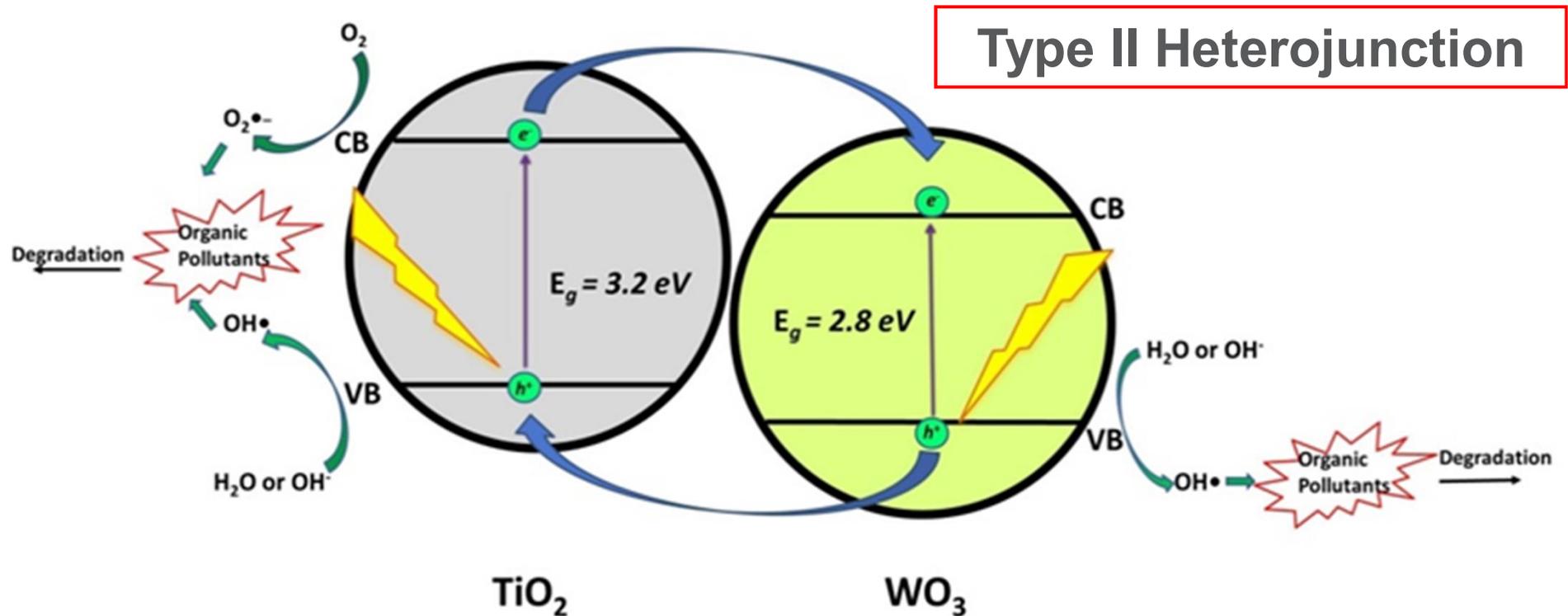
- occurs naturally in the form of hydrates - minerals:
 - tungstite ($\text{WO}_3 \cdot \text{H}_2\text{O}$)
 - meymacite ($\text{WO}_3 \cdot 2\text{H}_2\text{O}$)
 - hydrotungstite (H_2WO_4)
- n-type** visible light active photocatalyst with band gap of 2.4–2.8 eV
- good oxidative properties, nontoxicity, low cost, and stability in acidic solutions



TiO₂-based nanocomposites - examples -

Metal Oxides - Tungsten oxide (WO₃)

- WO₃ directly matches the band positions of TiO₂ to form a heterojunction



TiO₂-based nanocomposites *- examples -*

Metal Oxides - Iron oxide ($\alpha\text{-Fe}_2\text{O}_3$)

- there are sixteen known iron oxides and oxyhydroxides; the best known is rust
- Oxide of Fe^{III} - Fe₂O₃
 - $\alpha\text{-Fe}_2\text{O}_3$: alpha phase, **hematite**
 - $\beta\text{-Fe}_2\text{O}_3$: beta phase
 - $\gamma\text{-Fe}_2\text{O}_3$: gamma phase, maghemite
 - $\varepsilon\text{-Fe}_2\text{O}_3$: epsilon phase



- **hematite** is **n-type** visible light active photocatalyst with band gap of 2.0–2.2 eV

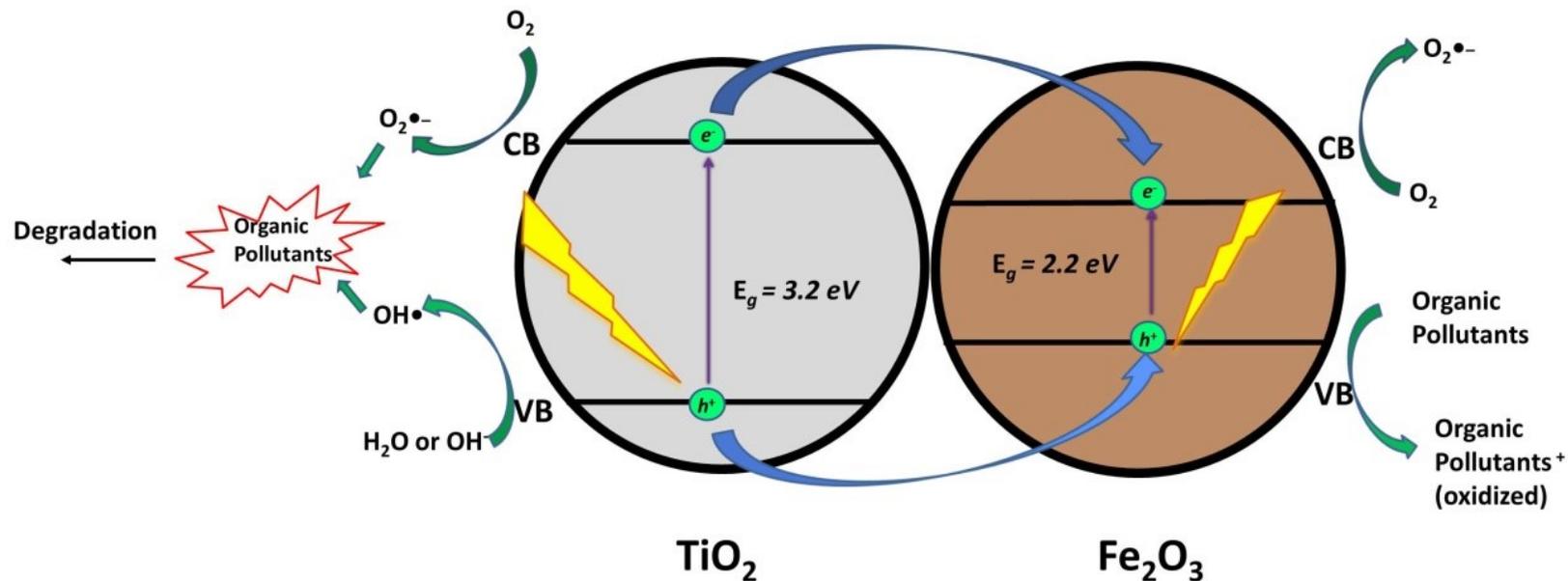
- promising candidate due to its abundance, nontoxicity, low cost, stability in aqueous solutions (pH > 3)

TiO₂-based nanocomposites - examples -

Metal Oxides - Iron oxide ($\alpha\text{-Fe}_2\text{O}_3$)

- $\alpha\text{-Fe}_2\text{O}_3$ directly matches the band positions of TiO₂ to form a heterojunction

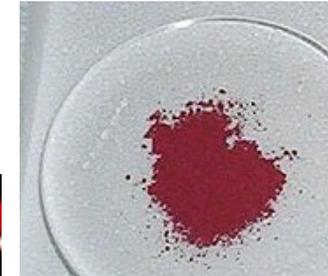
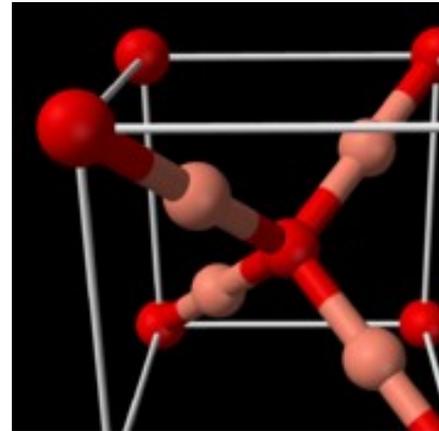
Type I Heterojunction



TiO₂-based nanocomposites *- examples -*

Metal Oxides – copper (I) oxide (**Cu₂O**)

- one of the principal oxides of copper, red-colored solid
- **Cu₂O** crystallizes in a cubic structure
- **Cu₂O** is **p-type** a visible light active photocatalyst with band gap of 2.0–2.2 eV



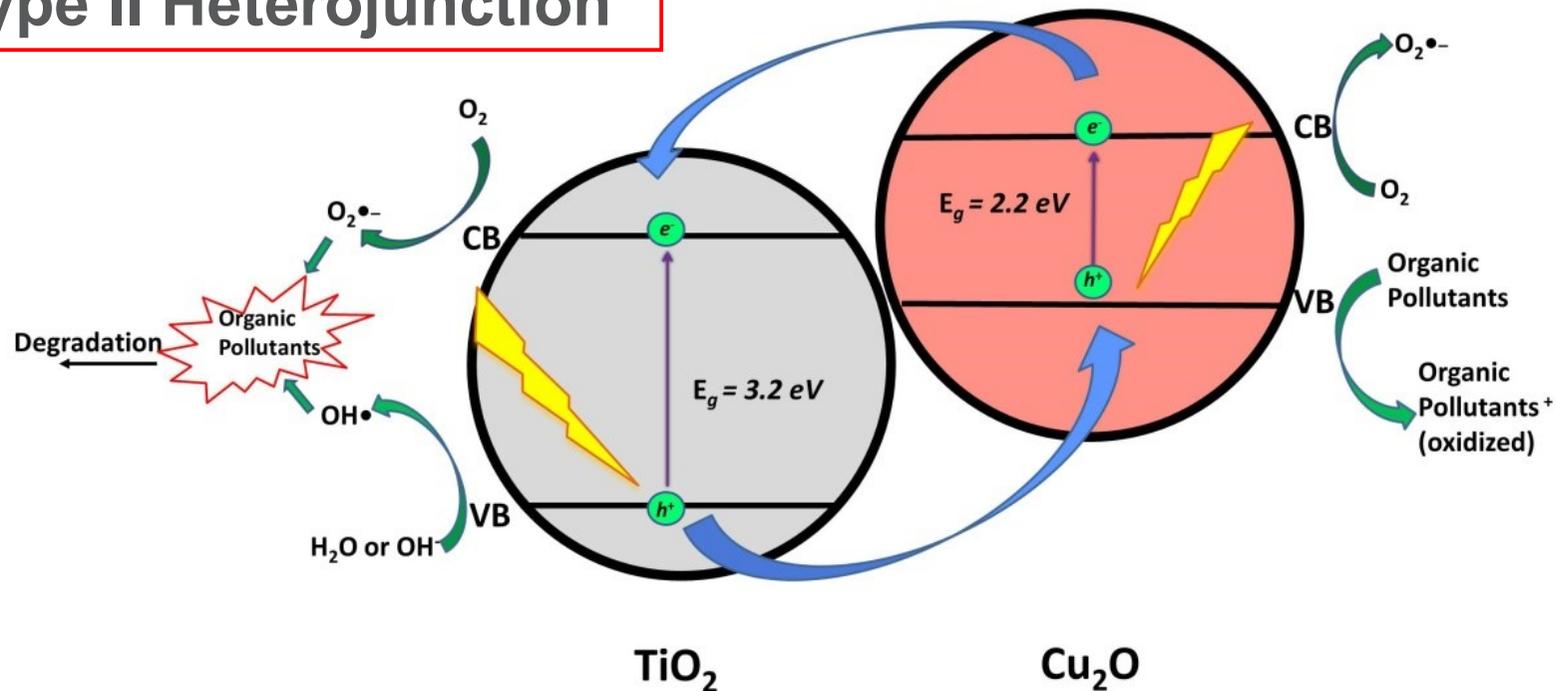
- promising candidate due to its abundance (exists as cuprite in nature), low toxicity, relatively low cost of copper

TiO₂-based nanocomposites - examples -

Metal Oxides – copper (I) oxide (Cu₂O)

- Cu₂O directly matches the band positions of TiO₂ to form a heterojunction

Type II Heterojunction

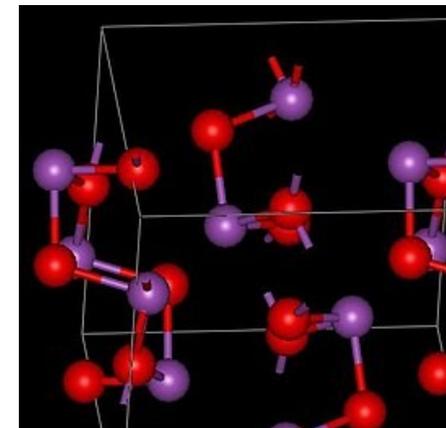




TiO₂-based nanocomposites *- examples -*

Metal Oxides – bismuth (III) oxide (**Bi₂O₃**)

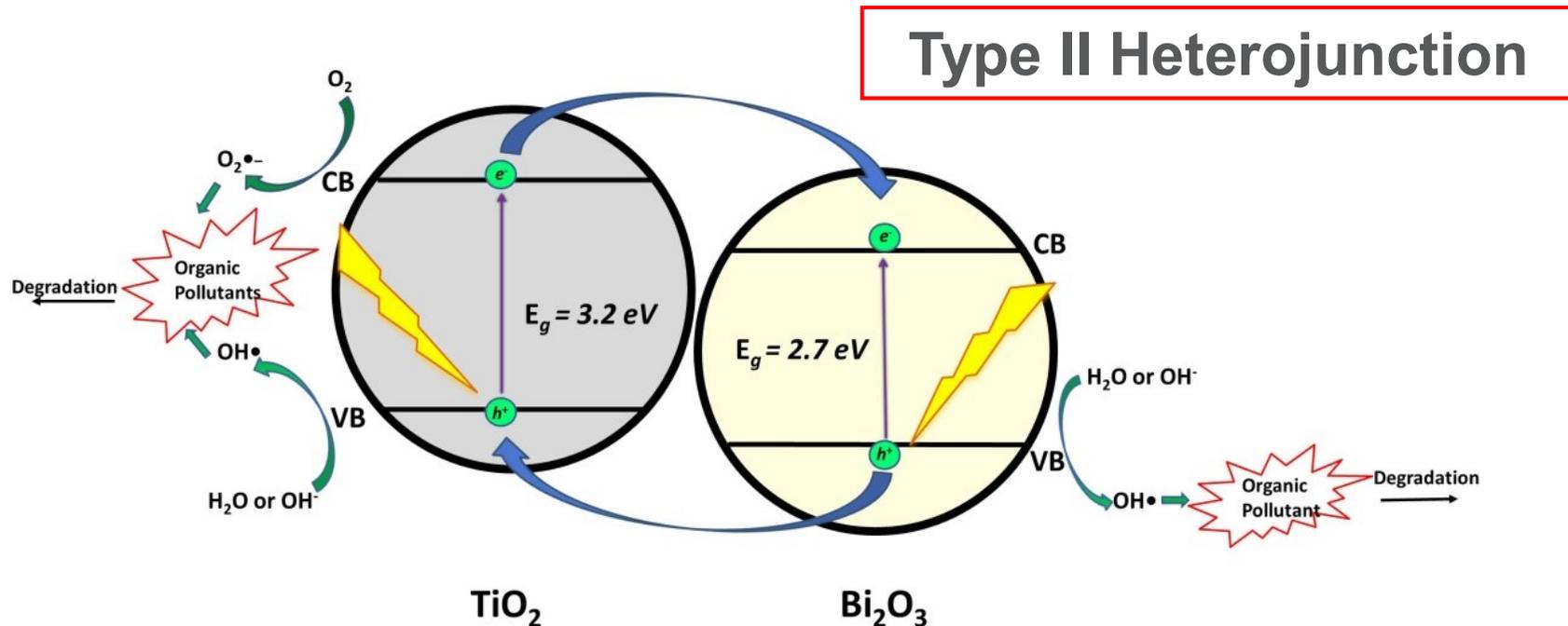
- the most industrially important compound of bismuth
- five crystallographic polymorphs, dependent on temperature: α -, β -, γ -, δ - and ϵ -phase
- the room temperature phase is **α -Bi₂O₃**
- **α -Bi₂O₃** is **p-type** a visible light active photocatalyst with band gap of 2.7 eV
- promising candidate due to its abundance (i.e. of Bi), relatively low toxicity



TiO₂-based nanocomposites - examples -

Metal Oxides – bismuth (III) oxide (Bi₂O₃)

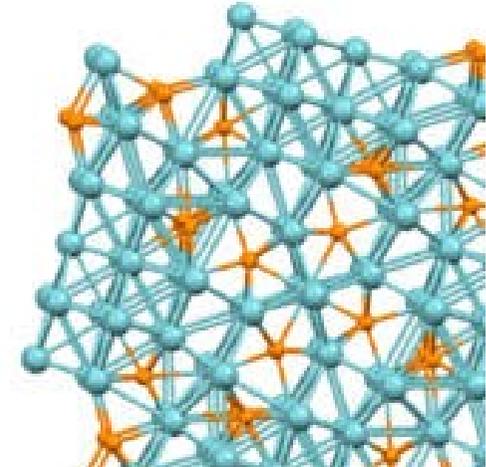
- α -Bi₂O₃ directly matches the band positions of TiO₂ to form a heterojunction



TiO₂-based nanocomposites *- examples -*

Metal Sulfides

- Commonly known as **chalcogenides**; sulfides, selenides and transition metals (Cd, Cu, Mo, Sn)
- less stable in a broad range of pH values, susceptible to photocorrosion
- **CuS** is **p-type** visible light photocatalyst ($E_g = 2.0$ eV)
- **CdS** is **n-type** visible light photocatalyst ($E_g = 2.1\text{--}2.4$ eV)
 - adverse effects due to its instability; leaching of toxic Cd²⁺
- **MoS₂** is **p-type** visible light photocatalyst
 - two-dimensional (2D), layered, indirect (1.1 eV) and direct (1.9 eV) band gap (monolayered), low-cost, high thermal stability
- **SnS₂** is **n-type** visible light photocatalyst ($E_g = 2.2$ eV)
 - unique structure (flower-like), innocuous comparing to **CdS**

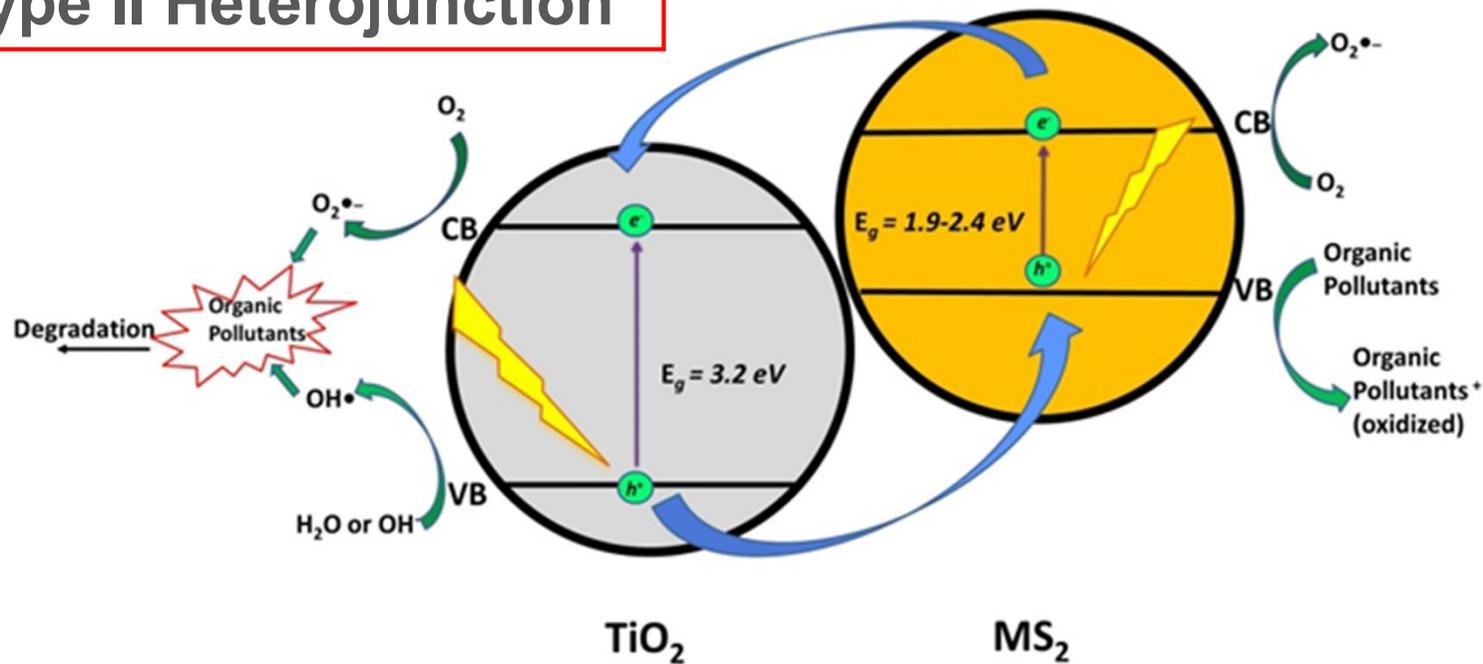


TiO₂-based nanocomposites - examples -

Metal Sulfides

- **MS₍₂₎** directly matches the band positions of **TiO₂** to form a heterojunction
 - **MS**; M = Cd or Cu, or **MS₂**; M = Mo and Sn

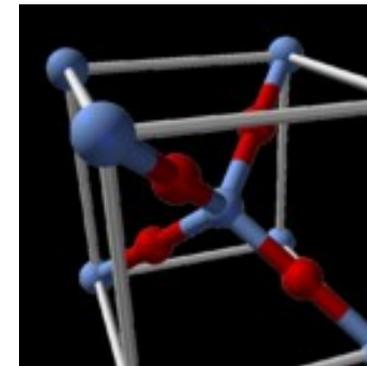
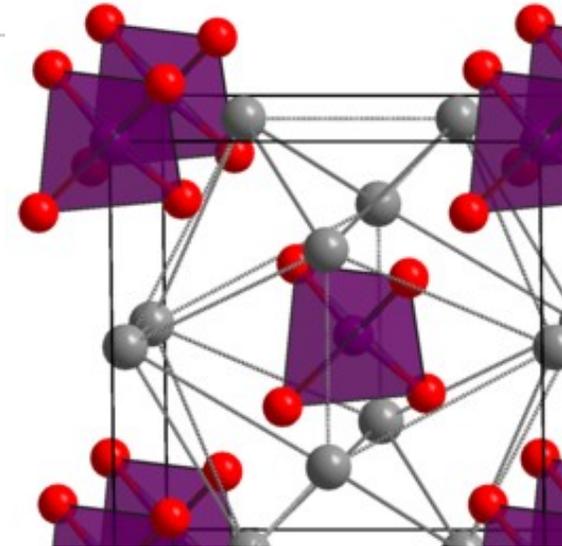
Type II Heterojunction



TiO₂-based nanocomposites *- examples -*

Silver-based

- **Silver phosphate (Ag₃PO₄)** is a promising **p-type** semiconductor with narrow band gap ($E_g \geq 2.4$ eV); exhibits a quantum efficiency of up to 90% and absorb wavelengths shorter than ~ 530 nm
 - still suffers from limitations; such as photocorrosion, small but not negligible solubility in water ($K_{sp} = 1.6 \times 10^{-16}$), and particle agglomeration upon synthesis
- **Silver oxide (Ag₂O)** is **p-type** a visible light active photocatalyst with band gap of 1.2 eV

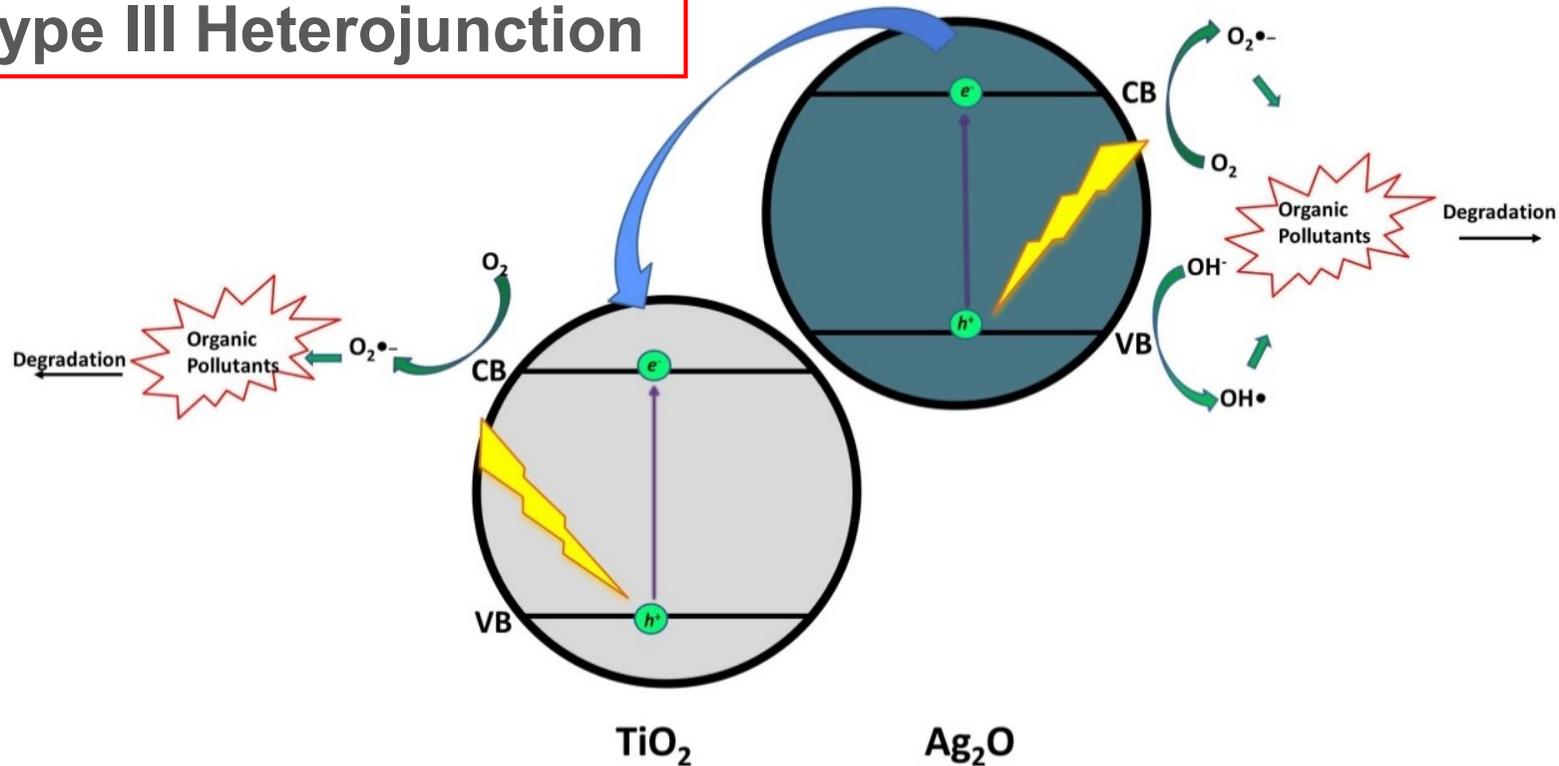


TiO₂-based nanocomposites *- examples -*

Silver-based

- Ag₂O** directly matches the band positions of **TiO₂** to form a heterojunction

Type III Heterojunction

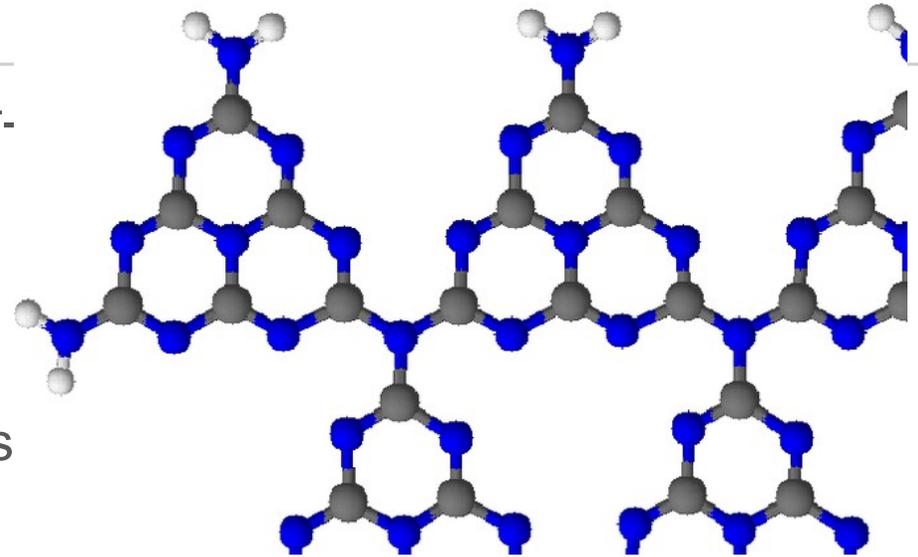




TiO₂-based nanocomposites *- examples -*

Carbon nitride

- **Carbon nitride** (**g-C₃N₄**), a two-dimensional, metal-free polymeric π -conjugated semiconductor material
- attracted attention of scientific community since pioneering work in 2009
- the most investigated photocatalysts inside carbon-based nanomaterials



- synthesized through the direct pyrolysis of nitrogen-rich precursors (melamine, cyanamide, dicyandiamide, and urea)
- properties: high stability, visible light response with the bandgap of 2.7 eV and non-toxicity
- drawbacks: low specific surface area and high rate of electron-hole recombination

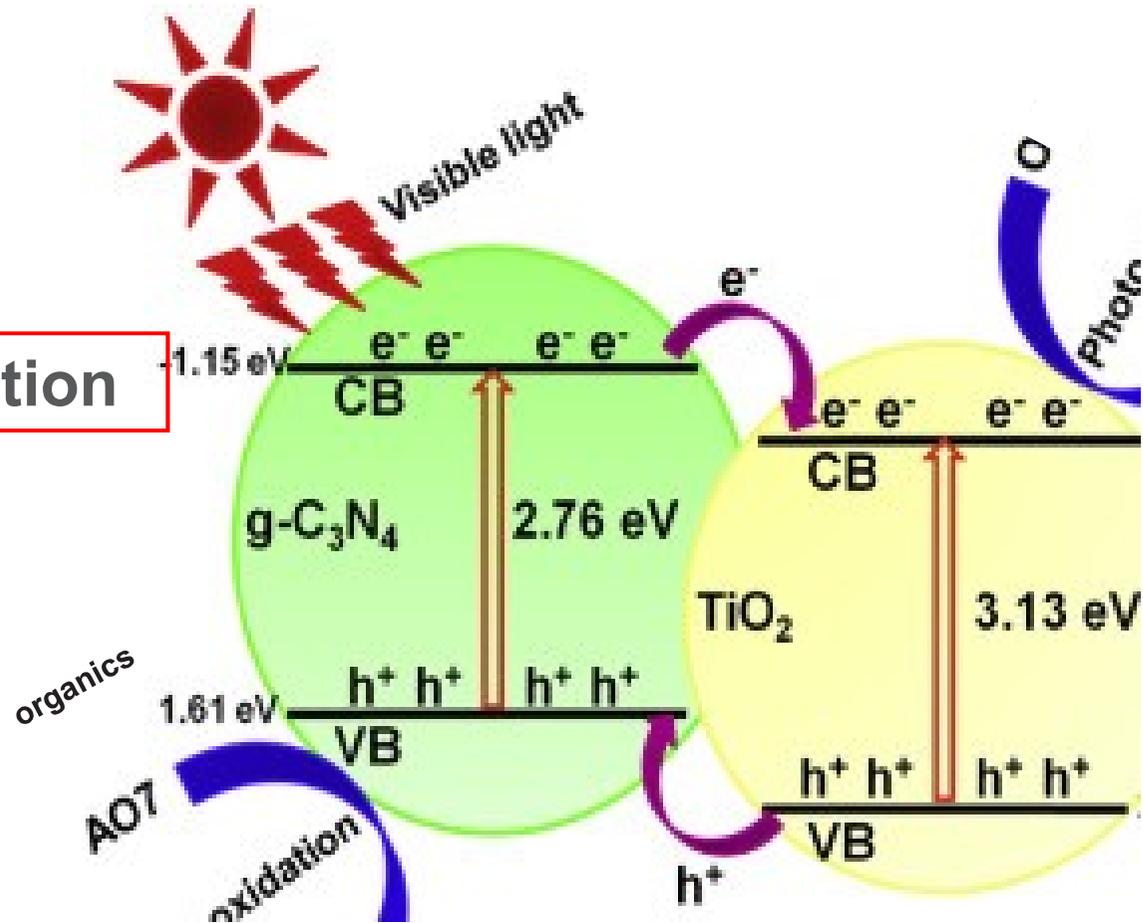


TiO₂-based nanocomposites - examples -

Metal Oxides

- Carbon nitride (g-C₃N₄) directly matches the band positions of TiO₂ to form a heterojunction

Type II Heterojunction





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QUESTIONS



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