Removal of Water Emerging Contaminants Using Nanostructured Titania Photocatalysts in Advanced Oxidation and Reduction Reactions

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Abstract

Advanced nanostructures of titanium dioxide are intensively investigated in nanotechnological applications for environmental protection. The latest developments in the field pay special attention to innovative and highly performing titania nanomaterials with original functionalities and tailored properties (visible light activated photocatalysts-VLA), the elucidation of the corresponding mechanisms (interaction of light with matter at the nanoscale and resulting photoinduced electron transfer reactions) as well as the design and fabrication of devices (photocatalytic reactors) for efficient removal of emerging contaminants from water (Fig.1).

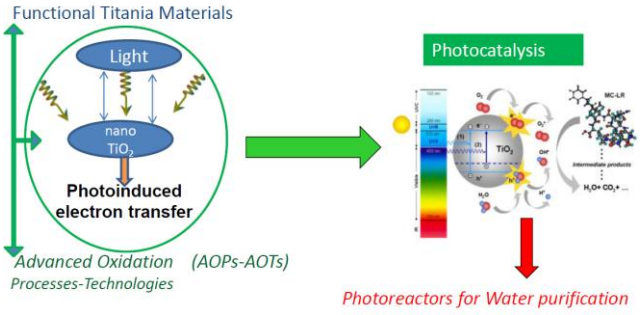

Figure 1. Holistic approach combining nanostructured titania materials, advanced oxidation processes and photocatalytic reactors for water purification.

Keywords: Titania photocatalysis; emerging water contaminants; advanced oxidation and reduction reactions.

1. Introduction

Water reservoirs are seriously affected by hazardous pollutants of emerging concern including industrial and pharmaceutical compounds, toxins, hormones (endocrine disruptors), and pathogenic microorganisms (Fig. 2). There is a need for coordinated research aiming at pollutants detection, assessment, and abatement (Likodimos *et al.*, 2010). In this direction, besides the development of novel analytical techniques targeting to identify/determine traces of new extremely harmful contaminants (Han *et al.*, 2013), the implementation of innovative approaches for their elimination is one of the higher scientific/technological challenges/priorities for the protection of the environment (Moustakas *et al.*, 2013). TiO_2 photocatalysis is a powerful advanced oxidation process/technology (AOP-AOT) able to oxidize virtually all organic contaminants via reactive oxygen species (ROS), while at the same time producing no harmful end products.

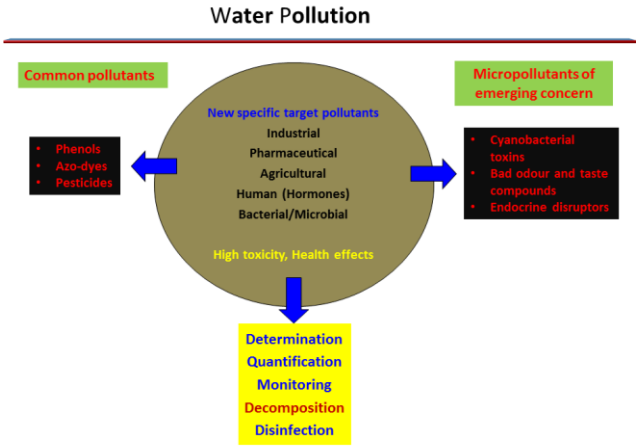

Figure 2. Emerging water contaminants efficiently decomposed using TiO2 photocatalytic treatment.

Commercial TiO_2 (Aeroxide®P25-Evonik) is one of the best performing photocatalysts under UV light. It is believed that the coexistence of both anatase and rutile structural modifications is at the origin of this particular behavior however, the underlying mechanism needs further investigation. One important issue concerns the need to develop novel materials disposing higher photocatalytic activity than that of the P25 benchmark photocatalyst. In a positive scenario, it is necessary to optimize the preparation conditions and proceed to a detailed characterization of the materials, in order to

establish the relationship between their physicochemical properties and their photocatalytic performance.

2. Results and Discussion

Recently, a series of highly performing nanocrystalline TiO_2 photocatalysts were prepared by the sol-gel method (Likodimos *et al.*, 2016). The evolution of their structure and microstructure as a function of the temperature was investigated. Calcination at 1023 K resulted in the formation of an anatase/rutile mixed phase TiO_2 nano-material with optimal photocatalytic performance, exceeding that of P25 over a wide range of organic water pollutants including phenol, 2,4-dichlorophenoxyacetic acid and imazalil, in the pH range between 3 and 7. This highly efficient photocatalyst comprised anatase nanocrystals essentially "free" from lattice deformation and microstrains, as well as larger, yet strained, rutile nanocrystals compared to those of P25, for which an additional electron trapping lattice site was identified. Electron transfer from the rutile to the anatase lattice trap states was confirmed under visible light, Fig. 3.

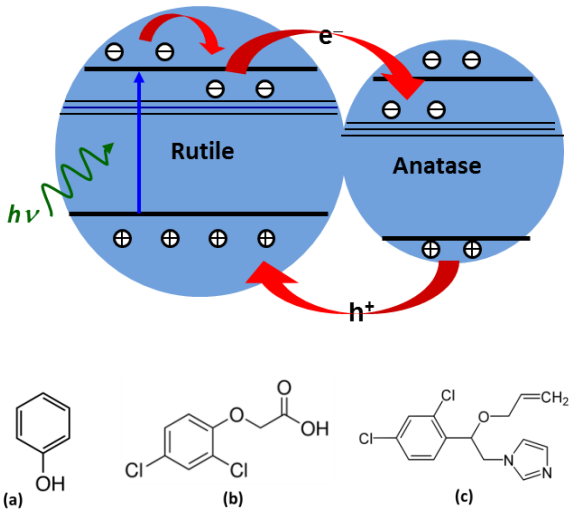

Figure 3. Photoinduced charge transfer mechanism between rutile and anatase nanocrystals justifying the optimal photocatalytic performance of mixed-phase TiO_2 nanomaterials for the decomposition of organic water pollutants: phenol (a); 2,4-dichlorophenoxyacetic acid (b); and imazalil (c).

The favorable combination of high crystal quality anatase nanocrystals with strong interfacial coupling permits efficient rutile-to-anatase electron transfer. This favorable situation is expected to reduce electron-hole recombination and boost the photocatalytic activity of the sol-gel mixed phase material in comparison with the P25 photocatalyst. It has been thus demonstrated that improvement of the anatase nanoparticle crystal quality even at the expense of surface area and interfacial coupling to rutile nanoparticles are key to the design and engineering of mixed phase titania for solar light photocatalytic applications.

Table 1. Optical properties of TiO_2 polymorphs.

TiO_2	Anatase	Rutile	Brookite
Energy gap (eV)	3.2	3.0	3.1
Wavelength (nm)	387	413	400

Titanium dioxide is a wide-gap semiconductor and its optical properties strongly depend on its structural modification (anatase, rutile, brookite). The material energy gap is between 3.0 and 3.2 eV (Table 1), thus limiting the photocatalytic activity in the UV range, which represents only 4-5% of the solar irradiation reaching the earth. One of the most significant scientific advances to date has been the development of visible light activated (VLA) TiO_2 photocatalytic materials (Pastrana-Martinez *et al.*, 2013). Different strategies to modify TiO_2 for the utilization of visible light in photocatalytic water treatment have been developed, including non-metal and/or metal doping, dye sensitization, coupling semiconductors, etc (Pelaez *et al.*, 2012). Many efforts have also been focused on the investigation of the photocatalytic mechanisms (Banerjee S. *et al.*, 2014) and the determination of the active species (Fig.4).

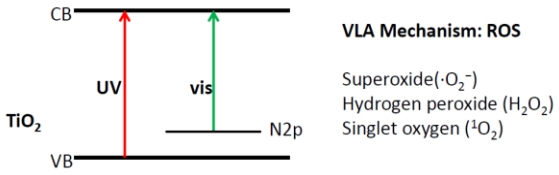

Figure 4. Possible photocatalysis mechanisms on visible light activated (VLA) titania materials.

Thus, the degradation of Microsystin-LR (MC-LR) cyanotoxin (very harmful hepatotoxin, Fig.5) was studied using titania doped with nitrogen and fluorine (NF-TiO_2) irradiated with visible light (Pelaez *et al.*, 2016). Using selected radical scavengers the role of different reactive oxygen species (ROS) was elucidated.

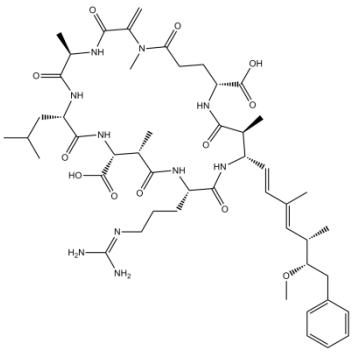

Figure 5. Molecular structure of Microsystin-LR cyanotoxin (heptapeptide) decomposed using visible light in the presence of NF-TiO_2 photocatalyst.

It has been proved that under visible light, the formation and reactivity of ROS depend on solution pH and that the hydroxyl radicals (•OH) are not crucial in VLA NF-

TiO_2 photocatalysis. In addition it was conformed that the VLA mechanism involves reduction of molecular oxygen by photo-generated electrons. The photocatalytic performance of titania and related applications are influenced by the morphology and the possibility to immobilize the photocatalyst in the form of a thin film on a functional substrate, thus avoiding costly post filtration/separation steps usually encountered with slurries.

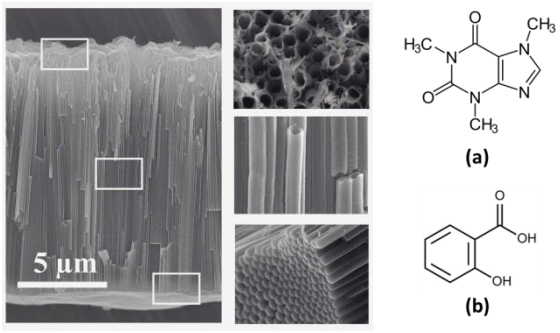

Figure 6. Self-organized TiO_2 nanotubes (left) developed following anodization of a Ti foil in ethylene glycol containing NH_4F. Fine tune of the anodization conditions permits the optimization of the photocatalytic properties against caffeine (a) and salicylic acid (b) photodegradation, via efficient control of tubes morphology, length, diameter, and wall thickness.

In this direction, self-organized, well aligned and vertically oriented arrays of TiO_2 nanotubes (TNTs) were developed on flexible titanium foils by anodic oxidation in corrosive media (Fig. 6). Their photocatalytic properties were evaluated with degradation of two important emerging pollutants frequently present in wastewaters, caffeine (psycho-stimulant) and salicylic acid (anti-inflammatory-analgesic) (Arfanis *et al.*, 2017). It was confirmed that the materials morphology strongly affects their efficiency, which is taken into account in the design of photocatalytic reactors combining catalyst immobilization with increased mechanical stability. The anodization of metallic titanium is not the only method to immobilize the photocatalysts. Despite metals, titania deposition can be performed under controlled conditions on numerous different substrates such as glasses and ceramics (including composite ultrafiltration and nanofiltration membranes). Thus recently, a photocatalytic membrane reactor for efficient water purification was fabricated and optimized (Falaras *et al.*, 2012). The reactor is based on innovative nanostructured titania photocatalysts combined with ceramic membranes (Fig. 7) and focuses on the photodegradation of contaminants during the filtration process, permitting efficient and low cost water quality improvement under normal solar light conditions, with high efficiency and low cost (Athanasekou *et al.*, 2015).

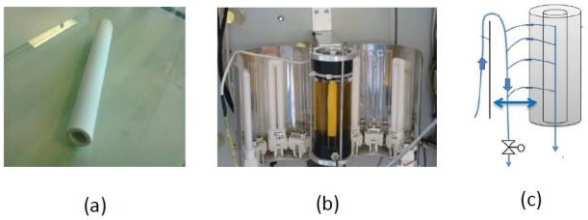

Figure 7. (a) γ-alumina ultrafiltration tubular membrane used as substrate to deposit the photocatalysts (conventional or VLA). Nominal Pore size 5nm, length of 15cm, ID and OD of 7 and 10mm with the ultrafiltration layer (1.5µm in thickness) located on the internal side; (b) The membrane incorporated in the reactor core; (c) Three-channel water flux. Illumination and pollutant decomposition is possible on both external and internal surfaces.

The device is able to decompose a great variety of hazardous pollutants of emerging concern including industrial and pharmaceutical compounds, toxins, hormones and pathogenic microorganisms (Papageorgiou *et al.*, 2012). Energy autonomy is possible by using optical fibers that replaced the expensive UV lamps. The up scaled device is able to exploit the solar radiation and manage large water treatment capacity by using a number of multichannel membranes. Following a fluid mechanic approach, the pressure along the membranes was determined, and a computational code was developed that calculates the requested pressure drop in relation to water volumetric flow and system geometry. The obtained results are consistent with final upscale goal aiming at implementing future demonstration of such technology for the treatment of 50 cubic meters of contaminated water per day (Athanasiou *et al.*, 2016).Moreover, the hybrid photocatalysis-filtration technology can be further adapted to develop an autonomous solution for water treatment/saving/ recycling in remote areas. The proposed device will be able to make possible its power supply via a “solar PVs-batteries-smart grid inverters” system and its irradiation via LED lighting & solar light. In fact, solar/LEDs irradiation system and optic fibbers will be accommodated inside the membrane monolith channels and inside the immersion-quartz sleeves. The unit will have the ability to eliminate a mixture of organic matter, suspended solids, bacteria and common chemicals occurring in grey water from hotel usage. These include: surfactants, detergents, bleaches, dyes, fragrances, flavorings, preservatives, pesticides, pharmaceuticals, personal care products, small quantities of fats and oils, organic solvents like acetone, alcohol, petroleum products, bacteria (e.g. Fecal coliform, E. coli, Streptococcus and Staphylococcus) and pathogenic organisms (viruses and protozoa).In addition to AOPs-AOTS, TiO_2 photocatalysis can be also considered as an advanced reduction process-technology (ARP-ART), presenting significant applications in light-driven photocatalytic reduction reactions.

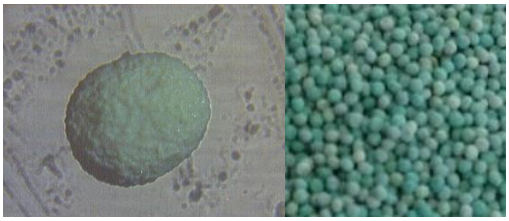

Figure 8. Copper decorated titania–alginate beads (0.5 mm in diameter) used as efficient photocatalysts in Cr(VI) reduction.

Indeed, titania–alginate polymer hybrids decorated with copper (Cu) and copper oxide (Cu_2O) nanoparticles (TiO_2/SA/Cu/Cu_2O) were developed (Athanasekou *et al.*, 2017). The novel hybrid titania materials (beads, Fig. 8) successfully promoted the photocatalytic reduction of Cr (VI) into Cr (III) under irradiation with UV/Vis light, overcoming the disadvantage of pure TiO_2 that requires acidic aqueous solutions for the photocatalytic decomposition of hexavalent chromium (carcinogen).The concept of advanced reduction processes-technologies (ARPs-ARTs) can be expanded to green procedures mimicking natural photosynthesis. In fact, innovative VLA inorganic / organic core – shell TiO_2 photocatalysts (m-TiO_2) synthesized using a modified sol-gel procedure (Fig. 9), besides their well-established activity for pollutants photocatalytic decomposition, were recently tested for their efficiency and selectivity towards CO_2 conversion environment (Moustakas *et al.*, 2013).

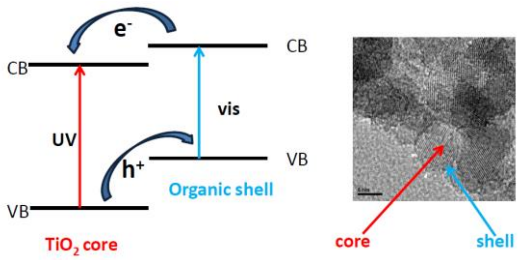

Figure 9. TEM image of VLA core-shell titania photocatalyst (right); corresponding charge transfer mechanism under light excitation (left).

The first results have confirmed that the core-shell titania materials are exceptionally efficient in the photocatalytic conversion of CO_2 to CH_4 under high-purity conditions.

3. Conclusions

Advanced titania photocatalysts with new morphologies and visible light activation have been prepared. The corresponding mechanisms were elucidated. The novel photocatalysts are highly efficient in visible light induced photocatalytic degradation of liquid (and air pollutants). Titania photocatalysts combined with modified ultra/nano filtration membranes were used in the construction of a photocatalytic laboratory-scale reactor. The reactor modeling and design up-scale was completed. TiO_2 NTs were successfully used in photocalytic degradation of caffeine and salicylic acid. Photocatalytic reduction of Cr(VI) to Cr(III) (the latter being at least 100 times less toxic than the former) was achieved using Cu/Cu_2O nanoparticles decorating TiO_2-alginate beads. VLA core-shell titania (m-TiO_2) shows significant activity in the photocatalytic CO_2 reduction mainly towards methane formation. We continue to work on all three stages (materials, physicochemical processes, reactors) in order to improve efficiencies and reduce cost of photocatalytic conversion applications. The above results significantly contribute to the development of a novel and efficient water cleaning technology exploiting solar energy and nano-engineered titania photocatalysts in combination with nanofiltration membranes for the destruction of extremely hazardous toxins and pollutants. Such innovations open new perspectives in the field, establishing TiO_2 photocatalysis as a very promising Advanced Oxidation and Reduction Process/Technology (AOP-ARP/AOT-ART).The investigation of these photoinduced redox reactions opens new roads and high perspectives in the field of nanotechnology driven solar energy research. New dynamic applications are considered, including photofuel cells using pollutants as sacrificial agents, photoelectrochemical solar cells for self-driven water splitting (hydrogen production) and gas phase photocatalytic reactors for CO_2 conversion to useful chemicals (e.g. hydrocarbons).

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