

## Nanocomposite materials for photocatalytic degradation of pollutants

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### Abstract

Photo-oxidation processes assisted by nanosized semiconductors are receiving increasing attention due to their potential application in environmental field. The ability to strongly exploit the original potential of photoactive nanomaterials and access their properties relies on the ability to integrate them in photo-reactors and to effectively deposit them on large surfaces, thus bridging the gap between the nanoscopic and mesoscopic scale and avoiding nanoparticle release in the environment. In order to integrate nanoparticles in functional structures and, finally, devices, their incorporation in suitable host matrices is crucial to achieve processable nanocomposite materials. Here, a comprehensive overview on the preparation of photocatalytic nanocomposite materials and their application for pollutants degradation will be provided. In particular, we will focus on modern synthetic approaches to synthesize UV and visible light active nanocatalysts, on their post-synthesis surface functionalization and incorporation in suitable host matrices toward nanocomposite preparation. Finally, some examples from recent literature on their application in environmental remediation (degradation of water or pollutants) and bactericidal and self-cleaning coatings will be reported.

### 1. Introduction

During the last decades semiconductor-assisted photocatalytic oxidation processes have received paramount relevance due to their potential application in photocatalysis, environmental remediation, self-cleaning and bactericidal coatings, new generation solar cells, hydrogen production, sensing.[1-

7] In this perspective, TiO<sub>2</sub> represents the most widely used photocatalyst due to its chemical stability, commercial availability and excellent catalytic properties.[8] In particular, nanosized TiO<sub>2</sub> demonstrated improved performances with respect to its bulk counterpart, thanks to its extremely high surface-to-volume ratio which can greatly increase the density of active sites available for adsorption and catalysis. In addition, the size-dependent band gap of nanosized semiconductors allows tuning the electron-hole red-ox potentials to achieve selective photochemical reactions. In addition, the reduced dimensions of the nanocatalysts allow the photo-generated charges to readily reach the catalyst surface, thus reducing the probability of undesired bulk recombination. Nevertheless, the use of nanocatalyst dispersed powders presents relevant technological drawbacks related to the catalyst recovery and recycle, which indeed are crucial due to the risk of release of nanopowders in the environment.[1, 9] In order to overcome such technological limitations, many attempts have been made to immobilize catalysts onto substrates, such as glass beads, glass fibers, silica, stainless steel, textiles or incorporation in polymers [10-15]. However, such coatings often result in the aggregation of the nanocatalysts, thus limiting their activity efficiency due to dramatic reduction of the active surface area.[16] Another severe drawback is due to the poor mechanical stability of such coatings which results in possible detachment in substrate or catalyst handling, during the photocatalytic reaction. Therefore, the design and implementation of novel TiO<sub>2</sub>-based catalysts deposited onto suitable substrates is a challenging task in order to obtain materials exploitable for environmental applications. A way to reduce the aggregation of the catalysts and increase the mechanical stability of the coatings is their integration in polymer/inorganic hybrids, to achieve a functional nanocomposite.[13, 14, 17-21] Nanocomposite is a multiphase solid material where one of the phases has at least one dimension lower than 100 nm. Although such a definition could in principle include porous media, colloids, gels and copolymers, it is more usually taken to mean the solid combination of a bulk matrix and nano-dimensional phase(s) differing in chemical composition and in physical chemical properties. The catalytic, optical, mechanical, electrical, thermal, electrochemical properties of the nanocomposite will differ markedly from that of the component materials.[22, 23] Inorganic-organic hybrid materials play a major role in the development of future oriented advanced functional materials. Indeed, they have recently attracted the attention of the scientific community for their interesting functionalities, arising from synergic combination of unique size- and shape dependent properties of inorganic nanofillers (i.e. catalytic, optical, electrical or magnetic) and those outstanding of host polymers (i.e., mechanical flexibility, low weight, and prompt processability).[24-28] Such multifunctional materials can be successfully used in high-added-value applications for fabricating components of catalysts, protective coatings, varnishes, packages, sensors, lenses, electronics, mechanics, dental fillings, molds, inks, and

adhesives.[29-32] Interestingly, nanocomposite materials offer the opportunity to incorporate in the same host matrix multiple functions deriving from distinct nanocatalysts such as semiconductor nanoparticles (NPs) (i.e. TiO<sub>2</sub> or ZnO), metals, (i.e. plasmonic NPs), magnetic oxides, or carbon nanotubes and graphene. Such a peculiarity allows a suitably tuning of the photocatalytic properties of the final nanocomposite, to extend the range of wavelength useful for photocatalysis to the visible region, to make them re-coverable by using magnetic field or to increase their efficiency by enhancing the lifetime of the electron-hole pair (e<sup>-</sup>/h<sup>+</sup>).[33-35] However, one of the main challenge is to incorporate photocatalytic nanomaterials in properly designed host polymers, for instance hybrid inorganic-organic and fluorinated polymers, since photocatalysts can degrade any organic material, and thus also the possible organic matrix in which the NPs are embedded.

This review intends to provide a comprehensive overview on photocatalytic nanocomposite materials, their preparation routes and applications for pollutants degradation. Particular attention will be focused on modern synthetic approaches to synthesize UV and visible light active nanocatalysts and on their post-synthesis surface functionalization and incorporation in suitable host matrices toward nanocomposite preparation. Finally, some examples from recent literature on their application in environmental remediation (degradation of water or air pollutants), bactericidal and self-cleaning coatings and cultural heritage protection will be reported.

## **2. Preparation of photocatalytic nanocomposite materials**

The preparation of photocatalytic nanocomposite materials can be ideally divided in three steps: (i) synthesis of an effective photocatalysts; (ii) its surface functionalization to promote (iii) incorporation in the most suitable host matrix according to the final application.

In this section, we will review recent progress of modern material science in synthesizing nanosized UV and visible light active catalysts, the advances achieved in their functionalization to tune their surface chemistry as a function of the selected host matrix and we will report on the fabrication of photocatalytic nanocomposite materials.

### ***2.1 Synthesis of photoactive nanocrystals and nanoparticles***

The photocatalytic process generally exploits semiconductors that are able to generate electron-hole pairs upon band-gap photo-excitation. Photogenerated e<sup>-</sup>/h<sup>+</sup> species are able to produce reactive oxidizing species (ROS) which can lead to the photocatalytic transformation of a pollutant.[36-38] Unfortunately, only e<sup>-</sup>/h<sup>+</sup> pairs generated in wide band gap semiconductors (E<sub>g</sub> > 3 eV) possess the redox potential needed to promote pollutants degradation, therefore only 4% of solar light results

effective in generating electron–hole pairs.[35] In addition, two crucial processes are known to define the overall catalytic efficiency, namely the competition between the recombination and the trapping of the charge carriers, followed by the competition between the recombination of the trapped carriers and the interfacial charge transfer. Accordingly, improved charge separation and inhibition of charge carrier recombination are essential in enhancing the overall quantum efficiency for interfacial charge transfer.[39-43]

TiO<sub>2</sub>, especially at the nanosized scale, is the most widely exploited semiconductor photocatalyst for a variety of inherent features, including chemical stability, commercial availability and excellent catalytic properties. [1, 2, 44] Persistent efforts are devoted to overcome its limited sunlight absorption, to improve the e<sup>-</sup>/h<sup>+</sup> pair lifetime and to face the concerns related to a safe recover of the nanosized photocatalysts, especially when the pollutant degradation is intended to take place in water or wastewater. Such issues represent the main guiding principles that drive researchers to develop innovative synthetic strategies towards TiO<sub>2</sub> nanocrystals (NCs) with improved photocatalytic performances. The modification strategies of TiO<sub>2</sub> NCs can be summarized as follow: i) morphological modifications, such as promote an increase in surface area and porosity,[45, 46] and/or ii) chemical modifications, in order to bring additional components in the TiO<sub>2</sub> NC structure, thus resulting in heterostructures that merge the properties of their specific components [47], and, concomitantly, provide additional original properties, arising from the actual combination of components.[48] The second approach includes modification of the semiconductor particles with red-ox couples or noble metals and/or doping or coupling with narrower band gap semiconductors.[35, 49] Current advance in material science allows flexibly designing and preparing such a class of compounds for photocatalytic applications. In particular, chemical synthetic routes benefit from the possibility of an *a priori* design of the original components to be specifically combined into new catalytically active nanocomposites. Recently advances in the fabrication of nanoparticles (NPs) and NCs have been achieved, thanks to the comprehensive understanding of the NC and NP shape control mechanisms, investigating morphology and multifunctionality issued in their design and careful controlling of the synthetic processes (monodispersity, surfacechemistry control).[50, 51] Such developments can enable the production of a wide range of conventional and innovative photocatalytic nanostructures.

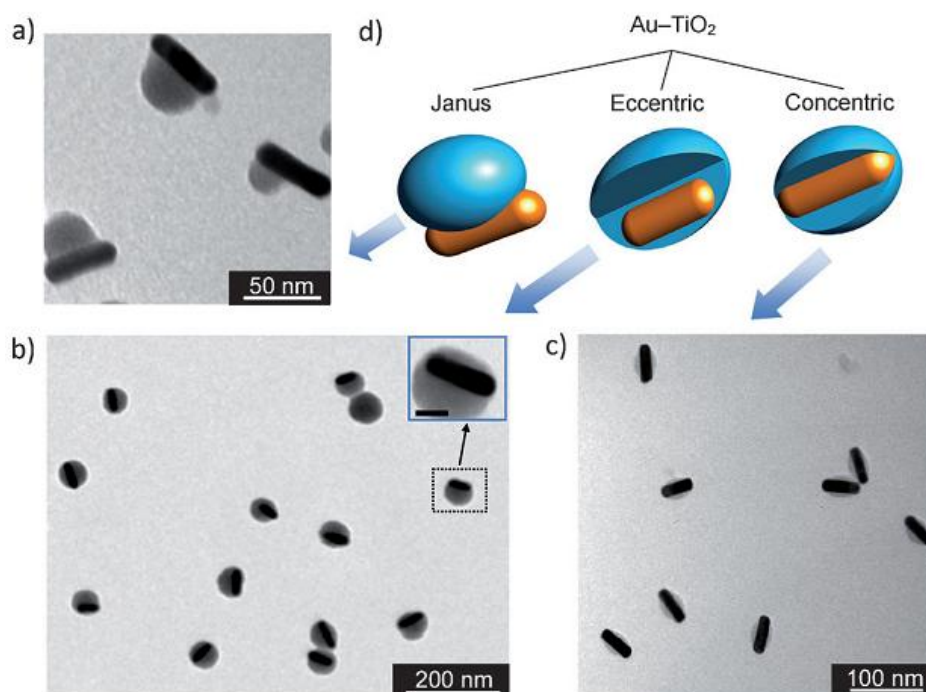
The following subsections will provide an overview of the cutting-edge synthetic strategies recently proposed in literature, in order to obtain TiO<sub>2</sub>-based nanomaterial suitably designed for photocatalytic degradation of pollutants. Our attentions will be focused on noble metal based multifunctional heterostructures, organic-inorganic hybrid heterostructures, semiconductor/metal oxide NPs and NCs, doped metal oxide NPs with tailored crystallographic facets.

### *2.1.1 Noble metal based multifunctional heterostructures*

The combination of plasmonic metal NPs, especially Au and Ag NPs, with semiconductors is an outstanding strategy to improve the photocatalytic efficiency of semiconductors due to the unique optical and electric properties of plasmonic metals.[52-57] Indeed, in the presence of an oscillating electromagnetic field, the conduction band free electrons of the metal NPs undergo collective oscillations in resonance with the frequency of light. This process is resonant at a particular frequency of the light and it is known as the plasmon resonance. The position of the plasmon band is dependent on several factors including chemical environment, aggregation state, and shape of the NPs.[58, 59] Indeed spherical particles show only one plasmon absorption centred at 520 nm for Au NPs and at 420 nm for Ag NPs. On the contrary, in anisotropic NPs electrons can oscillate with a different amplitude along the different side of the NPs resulting in a splitting of the plasmon band. On the contrary, cylindrical shaped NPs, namely nanorods (NRs), exhibit two plasmon resonances, one due to the transverse oscillation of the electrons, positioned at the same wavelength of spherical particles, and the other one due to the longitudinal plasmon resonance at longer wavelengths.[60, 61] The longitudinal localized plasmonic resonance increases with larger aspect ratios, allowing tuning across the whole visible-NIR.[62] Such a peculiarity is very appealing for achieving visible light active heterostructures. Different strategies to couple plasmonic NCs with semiconductors have been set up to optimize their efficiency in corresponding applications. One of the simplest approaches is the adsorption of metal precursors on the surface of a metal oxide semiconductor followed by chemical reduction in solution medium. Alternatively pre-synthesized Au NPs can be adsorbed on the surface of the support by simply mixing an Au NP colloidal solution with the semiconductor dispersion.[55] One of the commonly observed disadvantages of this method is the aggregation of NPs during the adsorption stage that reduces the efficiency of the final application. The anchoring of Au NPs onto a chemically modified surface of semiconductors, by using linker molecules, was found, by few research groups, to reduce Au NPs aggregation or coalescence.[52, 63]

As reported by Kochuveedu et al., Au NPs with controlled size and shapes were firstly prepared by conventional methods and then linked to the surface of APTMS modified SiO<sub>2</sub>/TiO<sub>2</sub> NPs. This method avoids aggregation of metal NPs and allows an effective control on the ratio of metal NPs to TiO<sub>2</sub>. [55, 64] Recently, Han and co-workers, reported anisotropic growth of titania shell on various gold nanostructures, and they observed higher catalytic activity with Janus type hybrid particles compared to core-shell type particles with complete titania shell (Figure 1). In order to obtain, anisotropic structures, firstly, cetyltrimethylammonium bromide (CTAB) coated Au NRs

were prepared by using a seed-mediated growth method and then, a ligand exchange process was applied to coat Au NRs with hydroxypropyl cellulose. At last, titanium precursor was slowly hydrolysed in ammonium environment to obtain geometry-controlled Au–TiO<sub>2</sub> nanostructures (Figure 1).[65]



**Fig. 1.** a–c) TEM images of TiO<sub>2</sub>-coated short gold NRs with a) Janus, b) eccentric, and c) concentric geometries, which were prepared by adding TDAA (3 mL) in one portion, TDAA (3 mL) in three portions, and TDAA (9 mL) in three portions, respectively. The inset in (b) shows a thinner TiO<sub>2</sub> shell on one side and a thicker one on the opposite side (scale bar=25 nm). d) Schematic representations of the TiO<sub>2</sub>-coated short gold NRs with various geometries. Reprinted with permission from ref. [65]

Besides the direct hydrolysis of semiconductor precursors on metal NPs, some other templates were used to prepare sandwich-type nanostructures. For example, Zhang et al. prepared a sandwich-like structure composed of SiO<sub>2</sub>/Au/TiO<sub>2</sub> by sol–gel process.[66] In this method, SiO<sub>2</sub> particles of 400 nm diameter were first synthesized and functionalized with APTES and then the Au NPs were attached, followed by coating of amorphous TiO<sub>2</sub> shell on SiO<sub>2</sub>/Au hybrid particles. Besides, polystyrene nanospheres were also used as template to prepare Au NC-embedded hollow mesoporous oxide microspheres.[67] Au NRs were firstly prepared, followed by the adsorption onto polystyrene nanospheres. In the next step, the polystyrene nanospheres carrying Au NRs were incorporated into mesostructured TiO<sub>2</sub> or ZrO<sub>2</sub> microspheres through an aerosol-assisted self-assembly process. Hollow mesoporous microspheres containing metal NCs were obtained by removing polystyrene nanospheres and surfactant through calcination that leads to the

crystallization of metal oxides. The template approach introduced in this work could be easily extended to different metal NCs. Xiao's work predominantly focused on the application of a self-assembly approach to synthesize Au NPs/ TiO<sub>2</sub> nanotube arrays (TNTAs) binary hybrid nanostructures. Briefly, previously synthesised dodecanethiol-capped Au NPs can be tethered to the interior and exterior surfaces of TNTAs by applying 3-mercaptopropionic acid (MPA) as an interconnecting bifunctional ligand. The ensemble of results showed that the Au NPs/TNTA nanocomposite exhibits significantly enhanced performance in photocatalytic degradation of methyl orange compared to its counterparts of blank TNTA, P25 particulate film, flat anodic TiO<sub>2</sub> layer (FTL), and Au NPs/FTL.[68]

Hydrothermal and solvothermal processes are two common wet chemical methods that fall in category of thermal methods. In the hydrothermal process, metal oxide or metal oxide precursor are mixed with metal precursor and base in water. The thermal treatment of the mixture is carried out in an autoclave at a temperature higher than that of the boiling water. During this process metal precursors adsorbed on the surface of semiconductors are reduced. The same protocol is applied for the solvothermal process except that the aqueous medium is replaced with appropriate solvents. These methods often suffer from the problem of aggregation of metal NPs. Thermal evaporation is one of the physical methods to deposit metal NPs on semiconductor surface, where highly pure metal is evaporated at very high temperatures and the metal vapours are allowed to deposit on the surface of a semiconductor.[52]

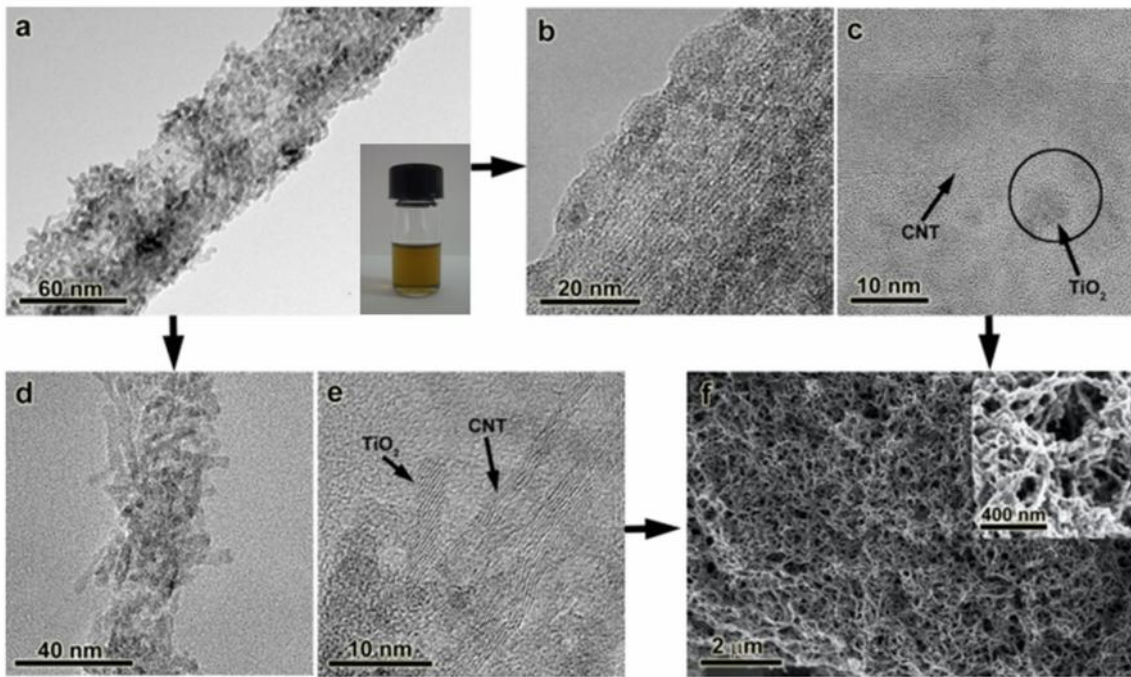
In the photodeposition method, electrons and holes are produced first upon irradiation of TiO<sub>2</sub> or ZnO with light. These electrons are then used for the reduction of metal precursor to metal, which is simultaneously deposited on the surface of the semiconductor. The presence of a hole scavenger such as alcohol is important to avoid the accumulation of positive charge during the photodeposition. Usually the TiO<sub>2</sub> or ZnO nanostructures are dispersed in a metal precursor for the required time to allow the complete adsorption of metal ions on the surface of the support. The product is then exposed to light with appropriate intensity, resulting in the deposition of metal NPs on the semiconductor. The important parameter in this method is the intensity of the light, since the average particle size decreases as the intensity of light increases. [39, 40, 69-71]

Interestingly, Tang et al. set up a nanohybrid plasmonic photocatalyst, comprising Ag-AgX (X = Cl, Br, I) NPs anchored on titanate nanotubes, which was fabricated via a silver ion incorporation process followed by hydrogen halide injection and light-irradiation. The Ag-AgX-titanate nanotubes (Ag-AgX-TNT) hybrid with a high surface area could synergistically adsorb and degrade methylene blue (MB) under visible light.[72]

### *2.1.2 Carbon-based hybrid heterostructures*

In recent years, carbonaceous nanomaterials have provided new challenges in the field of photoactive hybrid nanocomposites as co-catalyst to enhance the photocatalytic efficiency of TiO<sub>2</sub>. Carbon nanotube (CNT) TiO<sub>2</sub> based hybrids, provide a typical example of photoactive heterostructures which showed promising properties for the photocatalytic degradation of organic pollutants in water.[73] In this framework, a challenging goal is to merge the control over size, shape crystalline phase and surface energy of the exposed crystallographic facet of TiO<sub>2</sub> NCs with the requirement to generate a close contact between TiO<sub>2</sub> surface and CNTs. We recently reported the shape-controlled synthesis of TiO<sub>2</sub>-CNT based heterostructures by an “hot-injection” colloidal approach. Such heterostructures rely on anatase TiO<sub>2</sub> NRs or, alternatively, nanospheres that nucleate directly at the surface of single walled carbon nanotubes (SWCNTs) functionalized with oleic acid molecules, showed in Figure 2.[33] The photocatalytic activity of these new materials, immobilized onto a quartz substrate, was tested in a standard oxidative reaction, involving the discolouration of the azo-dye methyl red (MR) under UV and visible light, demonstrating an enhancement of the reaction rate up to 3 times with respect to a commercially available standard TiO<sub>2</sub> powder (TiO<sub>2</sub> P25). CNTs combined with TiO<sub>2</sub> can improve the photocatalytic activity by: (i) providing a high density of active sites for adsorption and catalysis, (ii) delaying electron–hole recombination and (iii) inducing visible light catalysis by the modification of the band-gap and/or sensitization.[74] However, several papers claim that such an improvement is strictly related to the occurrence of a close interface between the SWCNT and TiO<sub>2</sub> NCs as demonstrated by HRTEM and Raman Spectroscopy, in accordance with related works reported in literature.[75, 76]





**Fig. 2.** Transmission (A–E) and scanning (F) electron microscopy images of a typical SWCNTs/TiO<sub>2</sub> sample. High resolution-TEM images of SWCNTs coated with TiO<sub>2</sub> dots (B, C) and SWCNTs coated with TiO<sub>2</sub> NRs (A,D,E).The inset in (F) shows a high magnification SEM image of SWCNTs/TiO<sub>2</sub> NRs. Reprinted with the permission from ref. [33] Copyright (2015 ) Elsevier

Besides CNTs, graphene has emerged over the past years as one of the most exciting materials in the field of photocatalysis. This interest is motivated by the intention to exploit graphene as an ideal electron sink or electron transfer bridge. In combination with photoactive semiconductors as TiO<sub>2</sub> or ZnO it can cover simultaneously all the three aforementioned goals to improve the photocatalytic activity of suitable semiconductors.[73] Recently, Dai and co-workers designed a nanocomposite able to combine the advantages of graphene oxide (GO) with the photocatalytic efficiency of TiO<sub>2</sub> NCs with dominant (001) facet. GO is expected to enhance photocatalytic properties because of its high surface area, its ability to provide and high number of delocalized electrons and its high transmittance in the visible spectral range that can promote the light irradiation of TiO<sub>2</sub>. On the other hand, fluorine ions on the TiO<sub>2</sub> nanosheet surface stabilize the (001) facet of TiO<sub>2</sub> thus providing the advantage of displaying a dominant high reactive crystallographic surface. The synthetic approach was demonstrated simple and scalable: F-TiO<sub>2</sub> nanosheets were prepared by an hydrothermal route and have been combined with GO nanosheet by ultrasonication. Authors exploited GO just like a surfactant, so that with the help of ultrasonication, F-TiO<sub>2</sub> nanosheet are intercalated into stacked GO layer, leading to the exfoliation of GO. The nanocomposite was found more efficient with respect to both the bare F-TiO<sub>2</sub> and P25. Such a behaviour was explained considering the high electron and hole separation promoted by the presence of GO in a specific

amount as demonstrated by photocurrent measurements.[77] Carbon quantum dots (C-Dots) have been recently included in the framework of carbonaceous material exploited to enhance the photocatalytic activity of semiconductor photocatalysts. A recent work reported the one-step synthesis of C-Dot/TiO<sub>2</sub> nanocomposite by a smart solvothermal approach. The conventional preparative protocols, for TiO<sub>2</sub>/carbon materials based nanocomposites, imply the nucleation of TiO<sub>2</sub> in presence of pre-formed carbon nanomaterial or the simple mix of carbon nanomaterial and pre-synthesized TiO<sub>2</sub> NCs. In contrast, the solvothermal approach allowed the TiO<sub>2</sub> precursor (tetrabutyl titanate) and C-Dot precursor (citric acid) reaction in the same chemical environment, thus directly giving rise to a final nanocomposite. SEM, XRD, XPS and HRTEM have demonstrated that the photocatalyst relies on microspheres formed by anatase nitrogen doped TiO<sub>2</sub> NPs carrying a surface richly decorated by 5nm sized C-Dots. Further, thanks to the abundance of C-Dot on the surface of TiO<sub>2</sub>, the nanocomposite showed the same behaviour of the pristine C-Dot in fluorescence spectroscopy analysis.[78]

### 2.1.3 Semiconductor/metal oxide heterostructures

In this section, we will report on the combination of TiO<sub>2</sub> NCs with one or more materials, generally a semiconductor, able to provide additional properties to TiO<sub>2</sub>. The general idea of a photocatalytic active heterostructures relies on combining TiO<sub>2</sub> with a second narrower band gap semiconductor able to generate the e<sup>-</sup>/h<sup>+</sup> pair upon irradiation with visible light, so that the electrons can migrate towards TiO<sub>2</sub> conduction band, while holes are trapped in the second material. As a consequence, the presence of a second semiconductor can extend the efficacy of TiO<sub>2</sub> into the visible region, while defects that can be induced by the formation of the composite, can act as charge carrier traps thus reducing the electron and hole recombination events. Notably, heterostructures should be rationally designed in order to produce a favourable band offset and band position. Such a class of photocatalysts can be produced by means of various methods as chemical synthesis, solution or gas phase deposition and template fabrication.[79] An emerging class of materials whereby TiO<sub>2</sub> can be successfully combined are the ternary calcogenide as AgInS<sub>2</sub> due to their excellent catalytic performance, and wide optical response in visible range. A heterojunction of TiO<sub>2</sub>/AgInS<sub>2</sub> was successfully obtained by a one pot hydrothermal method that employed commercial TiO<sub>2</sub> P25 as titanium source. The reported protocol resulted in AgInS<sub>2</sub> particles of irregular shape linked to TiO<sub>2</sub> P25, leaving unchanged its structural and morphological features of TiO<sub>2</sub>. The heterostructure showed an enhanced absorption under visible light with a band gap of 2.75 eV in good agreement with density of state calculations. According to surface photovoltage

spectra the heterostructure is expected to be efficient in separating the photogenerated electron and hole pairs.[80]

An original approach for the generation of a semiconductor/semiconductor heterojunction takes advantage from the use of polyelectrolytes for their ability to assemble NCs. Logar and coworkers have described a polyelectrolyte-assisted fabrication route for semiconductor/semiconductor and metal/semiconductor composite 3D photocatalysts. These hybrid nanocomposites rely on titanate nanobelts (TiNBs) assembled with nanosphere of Cu or alternatively CuO. As preparation approach, the authors have integrated the LbL film-assembly, with the weak polyelectrolyte assisted NP loading, onto the surface of TiNBs. Polyelectrolytes have played a twofold role: i) they act as nanoreactors, accommodating the formation and the uniform distribution of Cu and CuO NPs on the surface of TiNBs, and ii) control the formation and the morphological features of the final 3D heterostructure network. The proposed approach indeed resulted in 3D structured photocatalysts with an enhanced heterojunction area that is expected to enable efficient harvesting of solar light and ensures a high interconnection between the TiNBs and Cu or CuO.[81]

Considerable attention is devoted to  $\text{WO}_3$  as co-catalyst for the formation of heterostructures with  $\text{TiO}_2$ . Such a choice is driven not just by the band offset, but also by the narrower band gap of  $\text{WO}_3$  ( $\sim 2.8$  eV). Patrocínio et al prepared a  $\text{TiO}_2/\text{WO}_3$  heterostructure by a sol gel approach that uses pre-synthesized positively charged  $\text{TiO}_2$  particles, combined with a  $\text{WO}_3$  negatively charged sol. The difference in term of electrical charge allows assembling the two components on FTO by means of Layer-by-Layer technique up to 30 bilayer. The thermal treatment at  $450^\circ\text{C}$  induced the formation of orthorhombic  $\text{WO}_3$  and anatase  $\text{TiO}_2$  heterojunction with high photocatalytic efficiency under UV light irradiation.[82]

#### *2.1.4 Doped metal oxide nanoparticles*

The problem of extending the spectral sensitivity of photocatalysts to visible light is one of the main challenges in the design of nanomaterials for photocatalysis oriented applications. The earliest attempts relied on the modification of a photocatalyst by doping with metal cations. However, metal doping resulted in the formation of non-active extrinsic absorption or creation of additional centres of charge recombination. On the contrary, since 2001, non-metal doping has been considered as an interesting strategy to promote the development of visible light active photocatalyst.[49] Among the others, the report by Asahi on the nitrogen doped  $\text{TiO}_2$  launched intense investigation in the field of doped nanosized photocatalysts.[83]

The main strategies for the synthesis of N-doped photocatalyst include, but are not limited to, sputtering of  $\text{TiO}_2$  in  $\text{N}_2$  atmosphere, hydrolysis of inorganic  $\text{TiO}_2$  precursors in presence of

aqueous ammonia or ammonium salt, co-precipitation, impregnation, sol-gel methods with N containing reagents or calcination under N containing atmosphere generally provided by ammonia or urea.[84] Zhang and co-workers recently provided an outstanding example of doped TiO<sub>2</sub>. Their hydrothermal approach was able to comply several requirements that are critical for maximizing the photocatalytic activity of TiO<sub>2</sub>. Indeed the authors designed a photocatalyst consisting in anatase TiO<sub>2</sub> nanowires (Ws) doped with N and F, with dominant [001] crystal facet (F-N-TiO<sub>2</sub> Ws). The F-N-TiO<sub>2</sub> Ws were in anatase phase, moreover the high anisotropy could promote the charge transport along the longitudinal dimension, thus slowing down the e<sup>-</sup>/h<sup>+</sup> recombination rate, the dominant {001} surface maximizes the photoefficiency and finally the F and N co-doping is expected to allow the photoactivation in the visible spectral range. [85]

Kalysry and co-workers systematically investigated the role played by calcining atmosphere (air, N<sub>2</sub> and O<sub>2</sub>) in structural, morphological and inherent photocatalyst ability of TiO<sub>2</sub> and Si-doped TiO<sub>2</sub> synthesized by both solvothermal and sol gel techniques. The obtained results demonstrate that calcination in N<sub>2</sub> atmosphere is able to promote a N-doping of TiO<sub>2</sub>. [86]

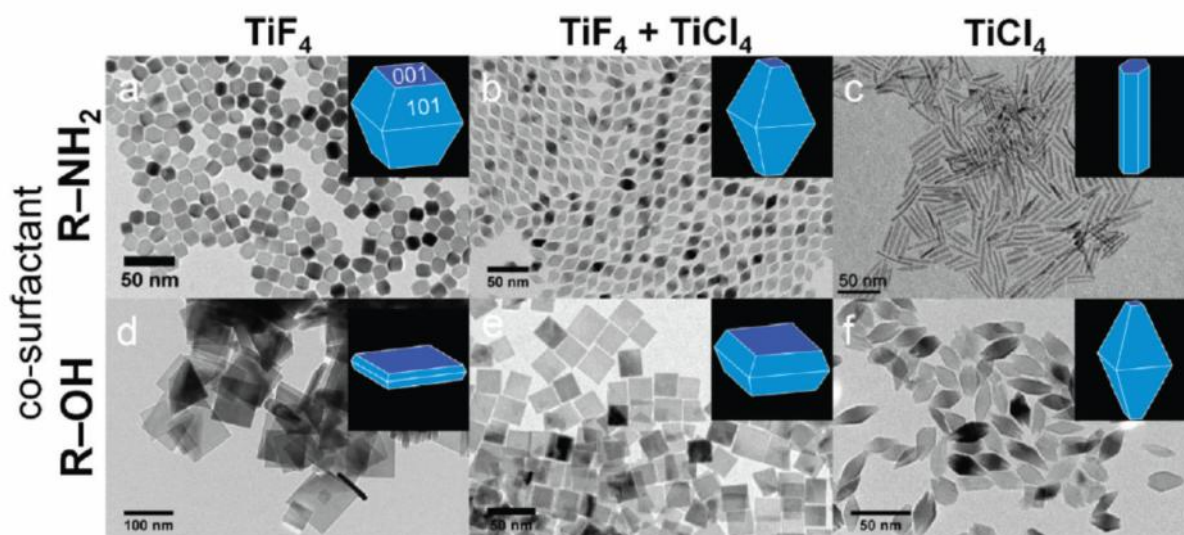
### *2.1.5 TiO<sub>2</sub> nanocrystals with tailored crystallographic facets.*

In recent years, a fervent research activity has been devoted to the synthesis of TiO<sub>2</sub> NCs with tailored facets. The investigation in this field has been driven from several motivations: the development of TiO<sub>2</sub> NCs with dominant specific facets allows to control the design of TiO<sub>2</sub>-based heterostructures,[33, 70, 87] provides a platform for producing preferential reactions and promotes the spatial separation of photoexcited charge carriers with huge consequences on the efficiency of photocatalysis related applications.[88-90]

It is well known that the {101} and {001} facets of anatase act as photocatalytic reduction and oxidation reaction locations respectively. As a consequence the production of superoxide radicals through reduction of O<sub>2</sub> molecules is expected to be more efficient in TiO<sub>2</sub> NCs with dominant {101} facet[91]. Concomitantly an increase in the concentration of trapped holes with the increase of {001} surface area was observed, as assessed by a systematic EPR investigation on TiO<sub>2</sub> NCs with a different percentage of {001} facets.[92, 93]

Several preparation approaches, including gas oxidation route, topotactic transformation, crystallization transformation and wet chemistry routes were explored to control crystal facets of TiO<sub>2</sub>, however the most exploited methods are probably those based on the wet chemistry approach as solvothermal, hydrothermal, and non-hydrolytic routes, due to the versatile ability in controlling the nucleation and growth. The facet control, along with the shape control, achieved in the synthesis process relies on the inherent different surface energy possessed by the different crystallographic

facets, as facets with higher energy exhibit a growth rate higher than those with lower surface energy. As a consequence, higher energy crystallographic facets take up a very small fraction of the surface of the final crystals or even vanish. Thus, tailoring crystallographic facets implies a careful control of the surface energy of the growing TiO<sub>2</sub> crystals. In wet chemistry routes, this goal can be achieved by exploiting suitable compounds (organic or inorganic) that selectively adsorb on a specific surface, thus minimizing its surface energy and maximizing its growth.[94] The typical morphology controlling agent for TiO<sub>2</sub> crystal with dominant {001} facet is HF, that was exploited by Yang and co-workers who have reported for the first time the synthesis of TiO<sub>2</sub> single crystal with 47% of high energy {001} surface with the typical shape of truncated bipyramid.[95]. HF was also exploited to obtain TiO<sub>2</sub> NCs with high percentage of {001} facet. Sofianou and co-workers prepared nanoplates of anatase TiO<sub>2</sub> by a solvothermal method, employing titanium tetraisopropoxide as TiO<sub>2</sub> precursor and HF as facet controlling agent. The same work investigated the effect of post-synthesis treatment on the percentage of the exposed {001} facet. In particular, the {001} percentage was calculated to be 68% after a simply washing procedures, while it decreased down to 46.3% upon calcination. The authors explained such a change considering that anatase crystal tends to reach its equilibrium state, with the expansion of energetically favoured {101} facet and the shrinkage of the relative higher energy {001} crystal facet.[96] The refinement of the synthetic approaches in this field led Gordon and co-workers to develop of versatile and processable TiO<sub>2</sub> NCs with tailored facets. Their work allowed not only to obtain organic capped TiO<sub>2</sub> NCs with dominant {001} facet, but also to engineer the percentage of {001} and {101} facets by playing on the co-surfactant. The synthesis is carried out by means of a hot injection approach, in presence of a mixture the typical surfactants as oleic acid, 1-octadecene, 1-octadecanol or oleyl-amine. The TiO<sub>2</sub> precursor is a titanium (IV) halide as TiCl<sub>4</sub>, TiF<sub>4</sub> or an equimolar mixture of both. In particular TiF<sub>4</sub> works also as F<sup>-</sup> source, the main shape directing agent in maximizing the amount of {001} surface. As a result, in the presence of TiF<sub>4</sub>, when 1-octadecanol was employed in the surfactant mixture to replace oleyl-amine a much higher percentage of {001} facet was obtained (Figure 3).[97]



**Fig. 3** TEM images of TiO<sub>2</sub> NCs synthesized using the precursor TiF<sub>4</sub> (a,d), a mixed precursor of TiF<sub>4</sub> and TiCl<sub>4</sub> (b,e), and TiCl<sub>4</sub> (c,f). Those depicted in a–c and d–f are synthesized in the presence of oleyl-amine and 1-octadecanol, respectively. Reprinted with the permission from ref. [97] Copyright (2015 ) ACS

## 2.2 Surface modification

The ability to strongly exploit the original potential of photoactive nanomaterials and access their properties relies on the ability to integrate them in photo-reactors and to effectively deposit them on large surfaces, thus bridging the gap between the nanoscopic and mesoscopic scale. In order to integrate NPs in structures and devices and achieve processable nanocomposites, their integration in suitable host matrices is crucial.[98] In particular, the host matrix should (i) prevent NPs to leach into water and air phase, thus strongly limiting the potential threat associated to dispersion of NPs into the environment, (ii) allow the recovery and reuse of photoactive NPs and (iii) enable their use as re-usable micro-particles, or in pollutant degradation reactors, or even onto large surfaces, as a coatings or paints. However, in order to promote the incorporation of NPs in host matrixes, nanocatalysts should be suitably functionalized by engineering their surfaces. The NP functionalization procedure should comply several fundamental requirements, in order to effectively exploit and enhance NP properties in the host matrix. Generally the main goals are: (i) increasing stability of the NP dispersion in the host matrix, with the advantage to make available the peculiar nano-object properties, (ii) preventing NP agglomeration, (iii) achieving a high compatibility and effective binding in the host matrix and finally (iv) increasing the stability of the whole composite, thus preventing the particles from leaching. For this purpose, several anchor groups or functional moieties can be introduced to the surface of the NPs. Moreover, reactive groups like vinyl, acryl, methacryl or epoxide at the surface of NPs can react with corresponding

groups of the host matrix, thus generating covalent interactions and cross-linking between NPs and the matrix. Introduction of functional groups to particle surfaces can be achieved by conventional functionalization methods such as silanization, ligand exchange or NP surface coating. As counterpart corresponding functional silanes and siloxanes, organically cross-linking components are in course of investigation as precursors for incorporation into the polymer matrix.

Silanization of TiO<sub>2</sub> NPs is a widely used procedure implemented to improve the dispersion of NPs in the typical formulations used for conservation of monuments and cultural heritage building. The presence of a silica shell on NPs improves their dispersion and, at the same time, preserves the photocatalytic properties of NPs while enhances the mechanical properties of the treated surfaces. Several studies indeed have investigated the SiO<sub>2</sub> modified TiO<sub>2</sub> NPs in the field of protection of building materials.[99-102] For example, in a recent paper the surface of TiO<sub>2</sub> P25 was modified by mixing titania NPs with TES40, namely a mixture of monomeric and oligomeric ethoxysilanes in presence of n-octylamine by sonication. The obtained product was used as consolidant material for a very fragile dolostone. As a result, a crack-free, homogeneous and coarse coating on the stone surface was achieved. The authors ascribed such features to the surfactant n-octylamine, which reduces the capillary pressure while the gel is drying. At the same time, a TiO<sub>2</sub>-SiO<sub>2</sub> gel, can efficiently penetrates into the pores of the stone, behaving as a consolidant, because it has the potential to improve its mechanical resistance, thus converting an extremely friable stone into a building material with self-cleaning properties arising from the presence of TiO<sub>2</sub>. [101] Silica modified TiO<sub>2</sub> NPs were also investigated with the purpose to integrate TiO<sub>2</sub> NPs in polycarbonate film. The resulting nanocomposite should improve the mechanical stability, the wettability, and the photocatalytic activity. The coated surfaces have displayed considerable photocatalytic activity and superhydrophobicity after exposure to UV-A light. TiO<sub>2</sub>/SiO<sub>2</sub> sol-gel was prepared by adding commercial TiO<sub>2</sub> NPs (Sachtleben Hombikat UV100) to a mixture of TEOS, ethanol, water and hydrochloric acid. After a dilution with ethanol, the resulting sol was dip coated onto the polycarbonate surface into open air and finally dried in air at 80°C for 24 h.[103] To obtain high-quality NCs with tunable sizes and shapes, most synthetic colloidal routes employ coordinating agents i.e. organic molecules with long a hydrocarbon apolar chain and a polar head group coordinating NC surface. These molecules, such as carboxylic acid (mainly oleic acid) and amines (mainly oleylamine and hexadecylamine), stabilize NCs in nonpolar, hydrophobic solvents, but often create an insulating barrier around each NC and block the access of molecular species to the NC surface, which is detrimental for incorporation in new matrices. As a consequence, an effective incorporation of NCs in a new polymeric matrix can require a modification of the nano-object surface chemistry in order to improve their chemical affinity towards a new chemical environment

(i.e from an apolar medium to a polar medium) without affecting their size, shape and crystallographic structure. Such a modification can occur by a ligand exchange procedure, which in principle replaces the original hydrophobic ligand with specifically designed species. For instance, replacing the pristine capping ligand with double bond terminated carboxylic acid TiO<sub>2</sub> NRs and Fe<sub>2</sub>O<sub>3</sub> NCs were covalently anchored onto active silicon substrates by an UV-driven approach, which exploits the homolytic rupture of the double bond under UV irradiation.[104] Recently, NC surface modification with inorganic salt was successfully developed in order to switch their dispersability from apolar solvents to polar solvents. Talapin and co-workers exploited metal free inorganic ligand as S<sup>-</sup>, HS<sup>-</sup>, Se<sup>-</sup>, HSe<sup>-</sup>, mixed chalcogenide as TeSe<sub>3</sub><sup>2-</sup> and OH<sup>-</sup>, K<sub>2</sub>S<sup>-</sup> NH<sub>2</sub><sup>-</sup> to transfer NCs from organic solvents as hexane or toluene to very polar solvent as formamide. The protocol comprises the mixing of the pristine solution of organic capped NCs with the inorganic ligand in formamide which is immiscible with toluene or hexane. The mixture promotes the complete NC transfer in the polar phase where the nano-objects are stabilized by electrostatic repulsion among anions adsorbed on their surface. Remarkably, the colloidal stability of the dispersion is mainly regulated by the solvent dielectric constant.[105] An analogous approach comprises the use of NOBF<sub>4</sub>, that allows, as a further step, the possibility to reversibly switch NC surface from hydrophobic to hydrophilic, preserving all NC features. Two protocols were developed: the first relays on the simple mixing of the pristine NC solution with NOBF<sub>4</sub> dispersed in CH<sub>2</sub>Cl<sub>2</sub>, and collecting them by centrifugation, so that the precipitate results dispersible in several hydrophilic media including DMF, DMSO, or acetonitrile; the second one relays on a typical ligand exchange procedure which involves the preparation of a two phase mixture of NCs dispersed in toluene and NOBF<sub>4</sub> dispersed in acetonitrile. A constant stirring promotes NC transfer from the upper apolar phase to the lower acetonitrile phase. The protocol was tested on several NCs. The removal of organic ligand was confirmed by DLS and TEM which have proven the aggregate free nature of the system and the reduction of interplanar distance due to the absence of the original capping agent.[106]

However, according to the physical-chemical properties of the host matrix, the pristine capping ligand could also be exploited for incorporation in polymers. As an example, as synthesized oleic acid capped TiO<sub>2</sub> NRs were successfully embedded in PMMA copolymer leading to an optically clear nanocomposite[107] and CTAB plasmonic NPs have been embedded in poly(sodium styrenesulfonate) (PSS) polyelectrolyte, exploiting electrostatic interactions between the positively charged native CTAB layer and the negatively charged PSS.[108]



### ***2.3 Incorporation in host matrices***

The incorporation of photocatalytic inorganic NPs in polymers allows the preparation of nanocomposite materials that have gained extraordinary relevance in the last years for environmental purposes. Photocatalytic nanocomposites combine the flexibility, processability, good film forming property and lightweight of polymers, with the size and shape dependent photoactivity of the nano-sized inorganic counterpart.[109] Merging such functionalities in nanocomposites makes them an outstanding class of structural materials for fabricating photocatalytic membranes, paints and self-cleaning coatings for removing pollutants from water and air, and for self-sterilizing surfaces for reducing bacterial infections.

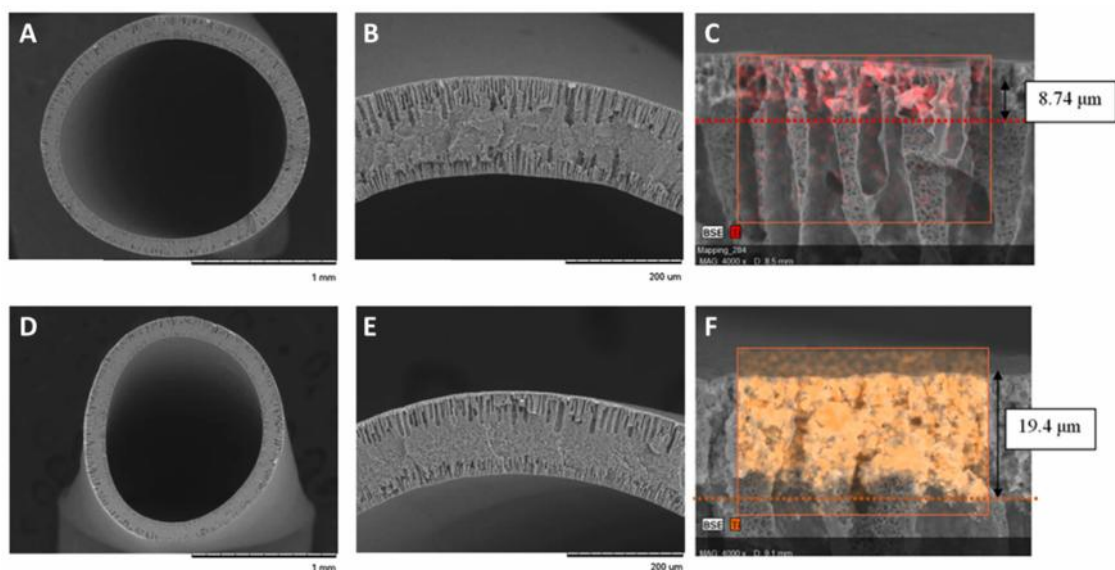
Polymeric resins, as acrylic polymers and copolymers, vinyl polymers, organosilicone compounds and fluorinated polymers, are the most suited to manufacture photocatalytic and antimicrobial components and nanostructured TiO<sub>2</sub> is an optimal photoactive nanofiller for such polymers.[100, 110, 111]

The design of photocatalytically active polymer based nanocomposites has however to take into account the development of approaches to remediate to the photocatalytic mineralization process of the organic matrix,[111-113], finding a compromise between maintaining a reasonable degree of photocatalytic activity and a reasonable stability of the organic matrix. [20, 114] For these reason perfluorinated polymers and hybrid inorganic-organic sol-gel materials such as organo-silane are the most promising host matrices for the preparation of photocatalytic nanocomposites.[29, 115]

Perfluorinated polymers were selected as organic matrix for embedding photoactive NPs, because the strength of the C-F bond is able to protect the organic matrix for mineralization processes induced by photocatalysts. Commercial TiO<sub>2</sub> P25 NPs-halloysite nanotubes (HNTs) were embedded in polyvinylidene fluoride (PVDF) for the construction of a novel flat sheet membrane that were installed as a photocatalytic separator, in a photocatalytic membrane reactor (PMR) for the degradation and removal of hydrocarbons from bilge water.[116] HNTs were used as support of the TiO<sub>2</sub> P25 NPs that were chemically immobilized to the surface -OH groups of HNTs via N- (aminoethyl)aminopropyltrimethoxysilane for preventing their agglomeration and allowing their uniform dispersion in the PVDF matrix. The PVDF/TiO<sub>2</sub>-HNT nanocomposite membranes were fabricated via the wet phase-inversion technique, by dispersing TiO<sub>2</sub>-HNTs (1 wt%) in dimethylacetamide solvent (81 wt%) and then in PVDF (18 wt%). The uniform distribution and the high efficiency of the TiO<sub>2</sub>-HNTs photocatalyst in the PVDF matrix confers to the PMR a hydrocarbon degradation and removal of ca. 99.9%.

A nanocomposite based on PVDF and TiO<sub>2</sub> NPs has been used to fabricate the outer layer of a novel photocatalytic dual layer hollow fiber membrane, where the inner layer was neat PVDF

(Figure 4).[117] Such a membrane has been used to remove nonylphenol in water, which is one of refractory degradation intermediates of nonylphenol ethoxylates surfactant and among the most toxic and prevalent endocrine disrupting compounds found in the environment. The TiO<sub>2</sub> NPs (7.5 wt%) were dispersed in PVDF (15wt%) by using dimethylacetamide (77.5wt%) as a common solvent and then, the mixture was extruded using a triple orifice spinneret to form the dual layer hollow fiber membrane. The co-spinning process provides a uniform dispersion of TiO<sub>2</sub> NP photocatalyst inside the membrane outer thin layer that encompasses most of the membrane activities, enhances the contact of the photocatalyst with UV light and hence it improves the membrane photocatalytic performance.[118]



**Fig. 4:** Overall and (B) partial cross section SEM images and (C) EDX chemical mapping of Ti species in dual layer hollow membrane with different TiO<sub>2</sub>/PVDF ratio 0.5 ; (D-F) SEM images and Ti species EDX chemical mapping of dual layer hollow membrane with TiO<sub>2</sub>/PVDF ratio 1. Reprinted with permission from ref. [117]

Tri-dimensional hydrophilic polyvinyl acetate (PVAc)-based fibrous membranes loaded by photocatalytic TiO<sub>2</sub> NPs, 60–230 nm in size, were fabricated by an air jet spinning (AJS).[119] Such an innovative strategy relies on the production of nanofibers by stretching the nanocomposite solution with a high-speed compressed air jet. The nanocomposite was prepared by dispersing the TiO<sub>2</sub> NPs in PVAc by using dichloro-methane as a common solvent, and hydrogen bonding interactions between PVAc and the surface Ti–OH groups of TiO<sub>2</sub> NPs led to a huge number of active sites for loading the fiber matrix by TiO<sub>2</sub> NPs. The fabricated AJS PVAc-based composite fibrous membranes have average fiber diameters of 505–901 nm, an apparent porosity of about

79–93% and interconnected pores of 1.58–5.12  $\mu\text{m}$  in mean size, which result in effective methylene blue degradation and good organic matrix stability.

Photocatalytic nanostructured  $\text{TiO}_2$  showed interesting antimicrobial properties providing inactivation and inhibition of viable cells, such as bacteria and fungi.[120] Thus, in the last few years, great interest has raised for the manufacturing of indoor paint formulations based on antimicrobial  $\text{TiO}_2$  NPs having great potential in the disinfection of public places such as hospitals, in which infections are due to Gram-positive and Gram-negative bacteria proliferation and attachment on surfaces.[121]

Zuccheri et al. incorporated at low concentration commercial  $\text{TiO}_2$  P25 NPs in a water based aliphatic urethane acrylic polyurethane copolymer resin containing isocyanate catalyst. Such a formulation was used for manufacturing a paint that shows an efficient and wide spectrum bactericidal effect against diverse pathogens as *S. aureus*, *P. aeruginosa* and *E. coli* when activated by common indoor fluorescent light, which is a source harmless for human cells.  $\text{TiO}_2$  NPs uniformly dispersed through all the surface of the sample with no detectable agglomeration and their embedding had no detrimental effect on the resin UV stability. The nanocomposite paint presented good adhesion and hardness, without surface holes, significant roughness, irregularities and cracks and showed high inhibition percentages of viable cells after 24 h exposure. Namely, the inhibition percentages are 23.2 for *E. coli*, 4.6 for *P. aeruginosa* and 1.7 for *S. aureus* and hence it is suited for preventing bacterial colonization.[122]

$\text{Fe}_3\text{O}_4@ \text{TiO}_2$  core-shell NPs were incorporated in an epoxy resin for manufacturing functionally graded nanocomposites for antibacterial purposes. Graded nanocomposites were fabricated starting from homogeneous NP suspensions in an epoxy pre-polymer using a magnetophoretic process, leading to an enrichment of  $\text{TiO}_2$  NPs at the surface of the nanocomposite. Namely, the formulations of  $\text{Fe}_3\text{O}_4@ \text{TiO}_2$  core-shell NPs embedded in the liquid epoxy were cured for 2 h at  $60^\circ\text{C}$ , under an external magnetic field gradient, generated by two permanent magnets in repulsion configuration. The composite surfaces show effective antibacterial performance with inactivation in less than few hours and up to 8 cycles of stable repetitive bacterial inactivation that was ascribed to the suitable amount of NPs and their anisotropic distribution in the sub-surface layers facing the bacteria.[123]

Y. Cai et al. prepared a novel nanocomposite material made of photocatalytic  $\text{TiO}_2$  NPs P25 (20 wt%) embedded in a resin formulation based on two monomers, namely 2, 2-bis [4-(2-hydroxy-3-methacryloxypropoxy) phenyl-propane and 2-hydroxyethyl methacrylate (55/45 wt%/wt%), photoinitiated by camphorquinone, 2-(dimethylamino) ethyl methacrylate, ethyl-4-(dimethylamino) benzoate and diphenyliodoniumhexafluorophosphate as dental adhesive resin with antibacterial and

bioactive properties. After the UV-light induced polymerization, such a material retains a UV antibacterial effect for at least 30 minutes against five bacterial strains, including *E. Coli*, *S. epidermidis*, *S. pyogenes*, *S. mutans* and *E. faecalis*. The prolonged post-UV antibacterial effect could help reduce the chance of contamination by pathogenic microbes and it is therefore promising for applications in biomaterials or implant coatings.[124]

The in/outdoor air quality can be improved by applying TiO<sub>2</sub> based nanocomposite paints at the surface of components such as glass windows, pavements, walls and concretes.[125, 126]

Nanocomposites made of a water based commercial acrylic paint incorporating commercial TiO<sub>2</sub> NPs, namely P25 and PC500, respectively were used for outdoor nitrogen oxide (NO) photo abatement. The paint formulations were based on photocatalytic TiO<sub>2</sub> NPs (9 wt.%), water (30 wt.%), extenders (9 wt.% of CaCO<sub>3</sub> and silicates), polymer extender slurry (8 wt.%), binder slurry (20 wt.%) and additive slurry (6 wt.%). The paint acts as a 3D support of the photocatalyst and it allows a larger amount of TiO<sub>2</sub> NPs to absorb light and to contact with pollutants, when compared with a 2D photocatalytic surface.[127]

TiO<sub>2</sub> NPs, surface modified with acetyl acetone and para-benzene sulfonic acid, were dispersed in aqueous pickering stabilized methyl methacrylate/n-butyl acrylate (50/50 wt% MMA/BA) copolymer latexes. The nanocomposite pickering stabilized latexes were prepared by miniemulsion polymerization mixing the TiO<sub>2</sub> NP aqueous solution in the oil phase of the monomers MMA and BA, the co-stabilizer (octadecyl acrylate) and the 2,20-Azobis(2-methylpropionitrile) initiator. Such an approach aims to avoid the accumulation of the TiO<sub>2</sub> NPs at the substrate–film interface, which reduces the performance of the nanocomposite films at the air–film interface. The hybrid latexes were used to coat concrete specimens and the films showed excellent self-cleaning activity to degrade Rhodamine B under UV-light exposure.[128]

Functional materials based on photocatalytic inorganic NPs embedded in hybrid organic-inorganic matrices, achieved by soft chemistry routes such as sol-gel processes or via polymerization of functional organosilanes, were recently applied for manufacturing smart membranes, separator devices and functional coatings for environmental purposes. Such materials are characterized by a high dispersion of NPs, high surface roughness, increased surface hydrophobicity and a decreased risk of photodegradation of the organic component of the matrix.

When applied as coatings for stones, the organic part of the matrix reduces the surface energy of the stone, thus giving to its surface hydrophobic character, while the embedded NPs increase further the surface roughness of the coating, enhancing its hydrophobicity and conveying to it photocatalytic activity.[129]

Photocatalytic mesoporous titania-silica nanocomposites were synthesized by mixing TiO<sub>2</sub> P25 NPs (2% wt/v) in ethoxysilane oligomers in the presence of a nonionic surfactant (n-octylamine), as self-cleaning protective coating for a limestone. TiO<sub>2</sub> P25 NPs were dispersed in an ethyl silicate that contains hydrolyzable ethoxy groups providing approximately 41% of silica upon complete hydrolysis, in the presence of n-octylamine. Such a surfactant prevents aggregation of the NPs in the starting sol, acts as catalyst of the sol gel transition, increases the pore size of the final material and reduces the capillary pressure, thus preventing coating cracking. Sol-gel transition occurs spontaneously, producing an effective nanocomposite coating on the limestone and the surfactant is removed by ambient air drying. The resulting nanocomposite material creates an effective adhesive, crack-free and hydrophobic coating with improved mechanical resistance ensuring conservation of the limestone. The coating conveys to the limestone surface self-cleaning properties, because it is able to almost completely bleach methylene blue stain (88%) after 6 h of UV-light exposure with a total color difference values ( $E^*$ ) of 7.[102]

A novel UV-light curable nanocomposite material formed of a methacrylic-siloxane resin loaded with 1 wt.% of oleic acid and 3-(trimethoxysilyl)propylmethacrylate silane (OLEA/MEMO)-coated TiO<sub>2</sub> NCs was manufactured as potential self-curing and hydrophobic coating material for protection of monuments and artworks, optical elements and dental components. OLEA-coated TiO<sub>2</sub> NCs, pre-synthesized by a colloidal chemistry route, were surface modified by a treatment with the methacrylic based silane coupling agent MEMO. The resulting OLEA/MEMO-capped TiO<sub>2</sub> NCs were dispersed in MEMO, that is a monomer precursor of the organic formulation, used as “common solvent” for transferring the NCs in pre-polymer components of the formulation. In designing the formulation, the capability of the TiO<sub>2</sub> NCs to degrade the polymer matrix was taken into account. In particular, a low NC loading and a high content (85% by weight) of the siloxane monomer was used, while, correspondingly, the amount of methacrylic monomers was kept low.[29] The embedded NCs significantly increase curing reactivity of the neat organic formulation both in air and inert atmosphere, thanks to the photoactivity of the nanocrystalline TiO<sub>2</sub> which behaves as free radical donor photocatalyst in the curing reaction, finally turning out more effective than the commonly used commercial photoinitiator. The NCs were found to accelerate cure rate and increase cross-linking density, promoting multiple covalent bonds between the resin pre-polymers and the NC ligand molecules, and moreover, they limit inhibition effect of oxygen on photopolymerization. The NCs distribute uniformly in the photocurable matrix, and increase glass transition temperature and water contact angle of the nanocomposite with respect to the neat resin.

A transparent and hydrophobic semi-crystalline SiO<sub>2</sub>-TiO<sub>2</sub> hybrid material was formulated as coating for monument conservation. The SiO<sub>2</sub>-TiO<sub>2</sub> coating was prepared from a mixture of

tetraethoxysilane and titanium-tetra-isopropoxide incorporating the organosilane hydroxyl-terminated polydimethylsiloxane. The organosilane was added to the SiO<sub>2</sub>-TiO<sub>2</sub> based material as it provides hydrophobic properties and enhances the toughness and flexibility of the silica network, thus preventing the gel from cracking during drying. The complete hydrolysis of tetraethoxysilane was achieved by oxalic acid, which also controls the gel drying. The coating obtained on marble is transparent, homogeneous and crack-free with a crystallite size of 5 nm and presents hydrophobic properties. The coating is able to remove both methylene blue stains and biofilm on treated samples and does not modify the color and the water vapor permeability of the marble surface.[130]

### **3. Applications**

#### ***3.1 Environmental remediation: water and air pollutants degradation***

Air and water pollution is notoriously a serious problem facing all anthropic activities throughout the world, due to urbanization, heavy industrialization and the changing lifestyles of people. The nanomaterials may play major roles in environmental remediation due to their high surface area (surface-to-volume ratio) and their associated high reactivity.[131] In literature, plethora of reports on the efforts to obtain valid alternative materials to TiO<sub>2</sub> that, until a few years ago, was used as almost the one photocatalyst for environmental remediation carried out by using both artificial and natural UV-vis irradiation.[132] One of the most engaging applications of photocatalysts is the degradation of organic pollutants in water and air streams. In particular, NPs in various shapes/morphologies, as adsorbents, catalysts and their composites with polymers are used for the detection and removal of gases (SO<sub>2</sub>, CO, NO<sub>x</sub>, etc.), contaminated chemicals (heavy metals, nitrate, arsenic etc.), organic pollutants (aliphatic and aromatic hydrocarbons) and biological substances (viruses, bacteria, parasites and antibiotics).[131] These materials were used for diverse purposes, such as treatment of natural waters, soils, sediments, industrial and domestic waste water, mine tailings and polluted atmosphere.

##### ***3.1.1 Water treatment***

Chemical pollution from heavy metals, solvents, dyes, pesticides, etc. is one the major threats to water quality. Chemicals enter the aquatic medium in several ways, either dumped directly, such as industrial effluents, or from wastewater treatment plants (WWTP).[133] Indeed, urban wastewater treatment plants (WWTP) are among the main sources of antibiotics release into the aquatic environment worldwide, and therefore these are considered as hotspots of antibiotics and promote the genetic selection and generation of antibiotic resistant bacteria in water.[7] Currently available

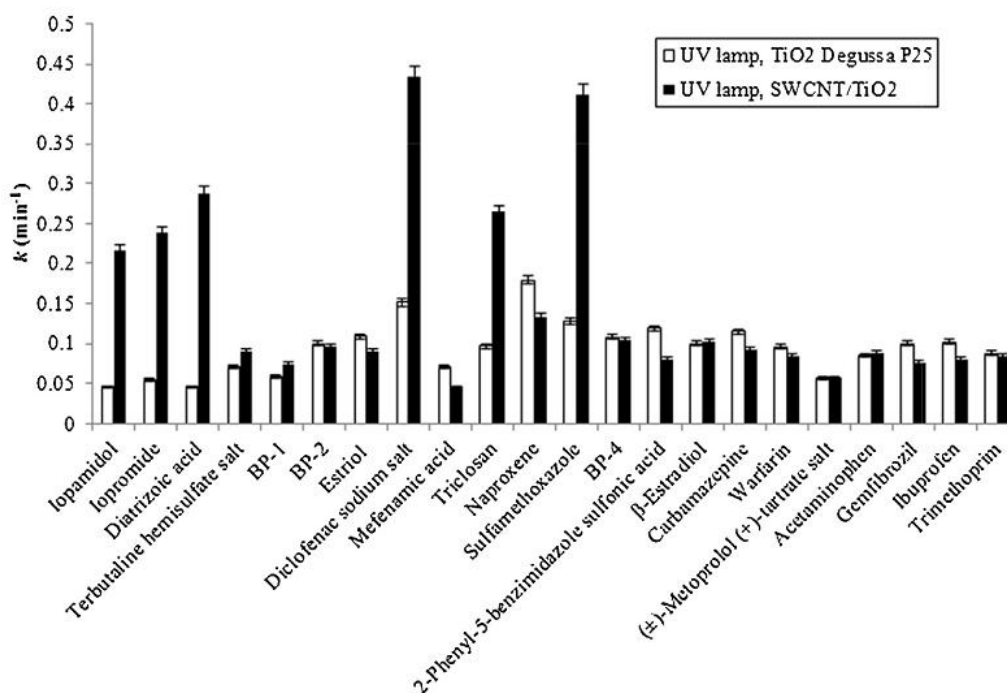
water treatment technologies such as adsorption or coagulation merely concentrate the present pollutants by transferring them to other phases, but still remain there not being completely “eliminated” or “destroyed”.[134] Other conventional water treatment methods such as sedimentation, filtration, chemical and membrane technologies involve high operating costs and could generate toxic secondary pollutants into the ecosystem. Chlorination was the most commonly and widely used disinfection process, which produced by-products that are mutagenic and carcinogenic to human health.[134] For these reasons, in recent years, most of the research activities in the field of “Advanced Oxidation Processes (AOPs)” have been oriented toward the development of innovative and effective technologies applicable for the removal of emerging organic pollutants in water and wastewater. The advantages of the AOPs include fast reaction rates and non-selective oxidation allowing the treatment of multiple contaminants at the same time. They also have the potential to reduce the toxicity of the contaminants.[135] Nevertheless, a common drawback of AOPs is the high demand of electrical energy for devices such as ozonisers, UV lamps, ultrasounds, which result in rather high treatment costs. Solar-based photocatalytic AOPs seem to be very promising due to their capability of working even with visible light, leading to a reduction of the operating costs of large-scale aqueous-phase applications.[34] The photocatalytic degradation of organic pollutants in water is mainly based on reactions, taking place at the surface of semiconductor particle and involving photogenerated  $e^-/h^+$  pairs and adsorbed molecules.[36] Both  $e^-$  and  $h^+$  promote the formation of highly reactive species,  $\cdot OH$  radical, by reacting with  $H_2O$ , OH groups adsorbed on the catalyst surface or  $O_2$  dissolved in water, or, as an alternative can directly attack the organic matter according to the experimental conditions.[39]

Several semiconductors were tested as catalyst in UV assisted photocatalytic AOPs ( $TiO_2$ ,  $ZnO$ ,  $Fe_2O_3$ ,  $CdS$ ,  $GaP$  and  $ZnS$ )[134, 136] being  $TiO_2$  and its derivatives the most promising in terms of degradation performances and chemical stability.  $TiO_2$  P25 from Degussa (now Evonik) is one of the most commonly used commercially available catalyst.

So far, most extensive studies were carried out by using catalysts suspended in the target molecule aqueous solution.[137] Although the large scale application of catalyst slurries was prevented by technological strains and high cost related to the catalyst recovery, the immobilization of catalysts onto substrates is known to cause a drop in performance due to the reduction of the overall active surface area. Several efforts have been then made to overcome these drawbacks, and particularly to immobilize the nanosized catalysts onto substrates with high surface area, such as glass beads, glass fibers, silica, stainless steel, textiles, honeycombs, activated carbon, etc. For instance, coating alumina and silica 2D tissue fibers with a  $TiO_2$  based nanocomposite prepared by sol-gel approach

allowed to achieve photocatalytic performances in methyl red degradation comparable with those of TiO<sub>2</sub> P25 in suspension at the concentration of 0.1 g/L.[17]

Another promising approach is the exploitation of micrometric supports which can be dispersed in the contaminated water and recovered by decantation or filtration. As an example, TiO<sub>2</sub> NRs grown on the surface of SWCNT were successfully employed for the degradation of a mixture of 22 organic pollutants in real secondary wastewater effluent under UV and simulated solar light. Murgolo et al. demonstrated that the photocatalytic efficiency of nano-sized TiO<sub>2</sub> supported on SWCNTs is higher than conventional TiO<sub>2</sub> P25 for degradation of iopamidol, iopromide, diatrizoic acid, diclofenac, triclosan and sulfamethoxazole. For the remaining organics, the degradation rates are comparable (Figure 5). This photocatalyst presents a quite high specific efficiency and can be easily removed from the aqueous solution by a mild centrifugation or a filtration step and, consequently, resulting reusable for subsequent batch of photocatalytic treatment.[34]



**Fig. 5.** First order kinetic constants ( $k$ ) during UV photocatalytic treatments for the investigated organic pollutants employing both nano-sized TiO<sub>2</sub> supported on SWCNTs and conventional suspended TiO<sub>2</sub> Degussa P25 catalysts in ultrapure water. Initial catalyst concentration 100 mg/L. Reprinted with permission from ref.[34]

Several nanocomposites based on ZnO nanostructures (NPs, NRs, nanowires, hollow sphere, nanoflower), modified with plasmonic NPs (namely Au or Ag) were reported in literature for the degradation of organic dyes in water under UV-vis light.[52]



Nanocomposite based on TiO<sub>2</sub> nanostructures modified with Au or Ag NPs were found effective in removing dyes and organic pollutants (pharmaceuticals, endocrine disruptors, personal care products).[35, 39]

Another promising application of photocatalytic nanocomposite in water treatments is the combination of separation and catalytic processes using a membrane photocatalytic reactor (MPR), in which photocatalytic TiO<sub>2</sub>/PVDF nanocomposites are used to manufacture ultrafiltration membranes able to separate decomposed material and to perform photocatalytic degradation of pollutants. [115, 117, 138, 139]

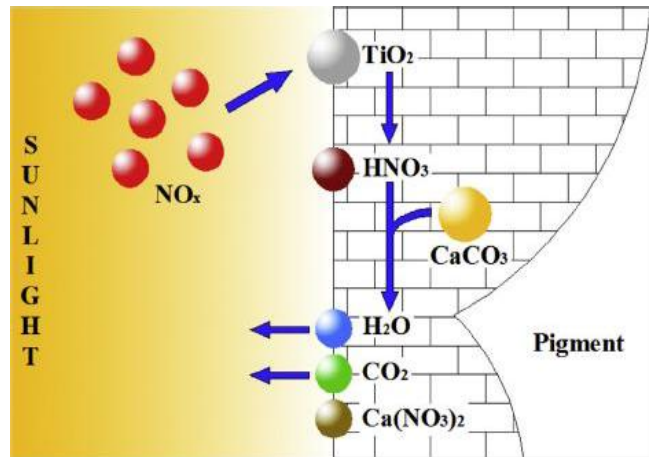
In particular PVDF/modified halloysite nanotube clay (M-HNTs) membrane demonstrated more than 99% of hydrocarbon removal. The PMR showed reasonable permeation flux and anti-fouling properties and the TiO<sub>2</sub> leaching from the nanocomposite during membrane permeation was found about 1.0 ppb. [115, 116, 140] PVDF/TiO<sub>2</sub> dual layer membrane achieved a 85% removal of nonylphenol after 4 h of UVA irradiation in submerged membrane photoreactor with a kinetic rate of 0.0092 min<sup>-1</sup>. [118]

### 3.1.2 Air treatment

Air pollution is a major environmental issue effecting people across the world. According to the World Health Organization (WHO), more than 2 million people worldwide die every year from air pollution. NO<sub>x</sub> and VOCs (volatile organic compounds) emission from cars, buildings and industries are the main source of pollution in urban areas. For this reason, the European Commission developed several directives that tried to regulate emissions and ambient concentrations of air pollutants (2008/50/EC, 2011/81/EC).[141][142] Photocatalytic oxidations of NO<sub>x</sub> and VOCs assisted by semiconductors could be a promising approach to face air pollution.[143] Recent studies suggested that TiO<sub>2</sub> photocatalysis of atmospheric gases plays a role in the chemical balance of the atmosphere, especially as it relates to atmospheric trace species including nitrogen oxides, nitric acid, sulfur dioxide, ozone, hydrogen peroxide and VOCs.

*NO<sub>x</sub> removal.* NO<sub>x</sub> are considered the primary pollutants of the atmosphere, since they are responsible for health and environmental problems like photochemical smog, acid rain, tropospheric ozone, human diseases, ozone layer depletion and even global warming caused by N<sub>2</sub>O.[144, 145]

The possibility to exploit TiO<sub>2</sub> based photocatalysis in NO<sub>x</sub> degradation processes was widely studied demonstrating that UV irradiated TiO<sub>2</sub> oxidizes NO and NO<sub>2</sub> into nitrate (Figure 6) .[146]



**Fig. 6.** Schematic illustration of the mechanism of the neutralization process of pollutants by  $\text{TiO}_2$  based cementitious materials. Reprinted with permission from ref.[44]

Several functional materials were proposed, based on  $\text{TiO}_2$  NPs were either deposited at the surface of the material (such as glass, pavement) or embedded in paints or concrete.[2, 126, 147, 148] Numerous photocatalytic cementitious materials were patented in the world, although several efforts are still needed to understand the effectiveness of titania mixtures and their influence on overall photocatalytic performance. In Japan, a paving stone called NOxer<sup>TM</sup> was developed, which makes use of the catalytic properties of  $\text{TiO}_2$  to remove  $\text{NO}_x$ , mainly from vehicle emissions.[44] Another photocatalytically-active concrete was TioCem<sup>®</sup>(cement with TX Active<sup>®</sup> inside), manufactured by Heidelberg Cement Technology Center, GmbH, containing  $\text{TiO}_2$  which is able to promote catalytic degradation of  $\text{NO}_x$  and other air pollutants. [149] In Europe, some demonstration projects performed by Italcementi Group also confirmed the ability of  $\text{TiO}_2$  cement (TX Aria) to destroy automotive gas emissions. These projects involved repaving Borgo Palazzo Street in Bergamo (Italy), Modigliani Street in Segrate (Italy), and Jean Bleuzen Street in Vanves, near Paris (France).[44] Another interesting application relied on  $\text{TiO}_2$  containing paints to be used on cementitious materials. PICADA group (Photocatalytic Innovative Coverings Application for Depollution Assessment) studied the photocatalytic effects of two different photocatalytic paints. The first paint was a commercially available mineral paint (1mm thick) for aesthetic surfaces and contains about 3% wt of  $\text{TiO}_2$ . The second paint was a water-based translucent paint obtained from Millennium Chemicals Co. produced using siloxanes as binders and containing 10%<sub>v/v</sub> of  $\text{TiO}_2$ . The experimental results showed that the degradation rates for the mineral and translucent paints were  $0.21\text{g/m}^2/\text{s}$  and  $0.06\text{g/m}^2/\text{s}$ , respectively in a  $30\text{m}^3$  chamber.[150] CristalACTiV<sup>TM</sup> is another commercial acrylic paint incorporating commercial  $\text{TiO}_2$  NPs, namely P25 and PC500, with promising performances. The PC500 photocatalyst exhibits smaller  $\text{TiO}_2$  NPs compared with P25, which in principle should favors the photoactivity of PC500. Indeed, the paint formulations

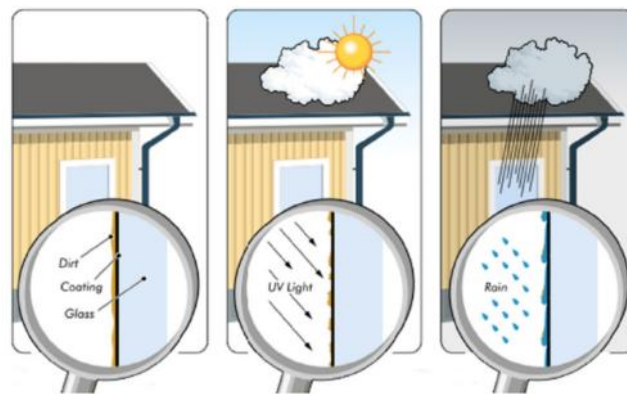
incorporating CristalACTiV™ PC500 and P25 photocatalysts present a NO conversion of ca. 70% and 50%, respectively and a selectivity of ca.45% and 35%, respectively under laboratory conditions, determined according to the standard ISO 22197-1:2007(E). In outdoor tests, the paints based on PC500 and P25 NPs show a NO conversion of 95% and more than 80%, respectively.[127] Photocatalytic paints demonstrated effective in degrading NO<sub>x</sub> also in indoor applications.[151] Maggos et al. measured a significant NO and NO<sub>2</sub> photocatalytic degradation by two types of photocatalytic paints: a mineral silicate paint and a water-based styrene acrylic paint (between 74 and 91% for NO and between 71 and 27% for NO<sub>2</sub>, 6 h of illumination, static mode).[152] In a real-scale study, Maggos et al. measured near to 20% removal of NO<sub>x</sub> by a photocatalytic paint in a car park.[153] In this case, the experimental set-up consisted of a flow type reactor adapted from the ISO 22197-1 standard.[154] NO<sub>2</sub> in the gas phase, and nitrate ions adsorbed on the photocatalytic surface were detected as final products. Various parameters influencing the NO degradation efficiency were studied: the coating composition, the substrate nature, the initial concentration of NO, the polluted air flow rate and the humidity.[153] As an example Gandolfo et al. reported a 30% NO conversion using a photocatalytic paint loaded with 7% of TiO<sub>2</sub> NPs [126]

*VOCs removal.* In addition to ubiquitous presence of inorganic trace gases in the atmosphere, there are also numerous VOCs present at atmospheric trace pollutants. The presence of VOCs has great environmental concerns due to its role in the production of tropospheric ozone and secondary organic aerosol. Many VOCs are known to be toxic and considered to be carcinogenic. The common VOCs are halogenated hydrocarbons, ketones, alcohols and aromatic compounds widely used in many industries, and are often found in the emission flow. Adsorption and subsequent reactions of VOCs on TiO<sub>2</sub> surfaces act as a potential removal pathway. Early studies exploring photoreactions of VOCs on TiO<sub>2</sub> were mainly motivated by the potential application of TiO<sub>2</sub> in air purification. Studies from this prospective showed that Ultraviolet (UV) related technologies are very effective compared with other oxidation processes on removing the air contaminants. Indeed, this process convert organic compounds into benign and odourless constituents, such as water vapour (H<sub>2</sub>O) and carbon dioxide (CO<sub>2</sub>).[155] Strini et al. investigated BTEX (benzene, toluene, ethylbenzene and o-xylene) removal from air using TiO<sub>2</sub> nanopowder embedded in white Portland cement. Removal efficiencies between 5% and 54% were noticed with the highest photocatalytic activity for o-xylene, followed by ethylbenzene > toluene > benzene. In particular, in this study the effects of variation of pollutant concentration, irradiation level and TiO<sub>2</sub> percentage in the cementitious materials were studied. The cementitious photocatalytic material showed a significant

photocatalytic activity with linear dependence versus pollutant air concentration and irradiance. On the other hand, the variation of  $\text{TiO}_2$  content in the cementitious mixture showed a non-linear relationship, thus pointing out a relative loss of efficiency at higher concentrations.[156] Salthammer et al. used modified  $\text{TiO}_2$ -catalysts for the manufacture of building products like wall paints with the purpose of photocatalytic removal of air pollutants under indoor conditions. In this case, the effective rate coefficient at the active surface is a function of the molecular gas kinetic properties, the diffusive motion, and the air exchange rate. Moreover, wall paints are equipped with organic binders like acrylic blends, vinyl acetate, styrene, and unsaturated fatty acids, which are also sensitive to photoreactions.[157] Mejía et al. observed that the photoactive systems  $\text{TiO}_2$ /textile fibers are promising supports for  $\text{TiO}_2$  due to their low cost, high surface area, flexibility and relative stability. Studies on  $\text{TiO}_2$  coated fabrics for pollutant degradation showed a potential for large scale application. Results indicate that  $\text{TiO}_2$ /nylon prepared by sol-gel at 24 h showed photocatalytic activity leading to the higher degradation of gaseous methanol.[158]

### 3.2 Self-cleaning surfaces

Self-cleaning materials have gained considerable attention for both their unique properties and practical applications, from indoor applications in fabrics, furnishing materials, window glasses, to exterior construction materials, roof tiles, car mirrors and solar panels.[159, 160] The self-cleaning activity is mainly related to wettability of the surface, which is characterized as either hydrophilic or hydrophobic.[160, 161] Hydrophobic surfaces possess water repellent and low adhesive properties: water drops roll over the surface thereby removing the contaminants. Whereas in hydrophilic surfaces, the water drops spreads over the surfaces forming a film, which remove away the dirt and other impurities (Figure 6).[6, 159, 162]

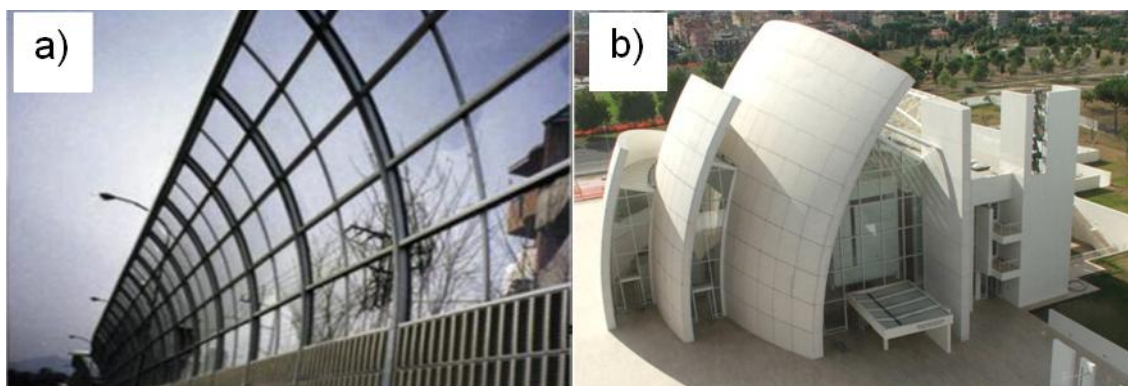


**Fig. 6.** Sketch depicting mechanism of the interplay between  $\text{TiO}_2$  photocatalytic activity and surface wettability Reprinted with permission from ref. [161]

A great amount of work has been devoted in recent years to design the photocatalytic hydrophilic surfaces to decompose the dirt and other impurities under sunlight/indoor light. The superhydrophilic and oleophilic character of  $\text{TiO}_2$  was first reported by Wang et al., which observed that when a polycrystalline film of anatase  $\text{TiO}_2$  is irradiated with UV light, the contact angle turns from  $72^\circ$  to  $0^\circ$ . The mechanism behind such a reversible wettability is still controversial. Several hypothesis were proposed including: generation of light-induced surface vacancies, photoinduced reconstruction of surface hydroxyl groups and photoinduced removal of the carbonaceous layer present on  $\text{TiO}_2$  surfaces exposed to air.[162] [163] In contrast to superhydrophilic photocatalytic materials, there are very limited examples of superhydrophobic photocatalytic surfaces.[162] Nevertheless, these surfaces show several advantages as self-cleaning materials over superhydrophilic surfaces, including reduction in bacterial adhesion, superior cleaning action due to “lotus effect” and anti-misting character. In recent years, various strategies have been used to produce these materials, such as functionalization of  $\text{TiO}_2$  surfaces with PTFE, PDMS, fluorinated alkyl moieties and modification of surface morphology. [159, 162] In this case, the presence of the hydrophobic coatings prevents complete hydrophilic conversion of  $\text{TiO}_2$  upon irradiation while the  $\text{TiO}_2$  surfaces display photocatalytic and hydrophobic properties simultaneously.[159] The combination of photocatalytic activity and wettability is very advantageous in view of designing effective and multifunctional self-cleaning coatings. Indeed, the degradation of a contaminant on a surface can be achieved by the photocatalytic reaction induced by  $\text{TiO}_2$ , while the high wettability can promote the definitive removing of broken down deposits. These two properties merged in one surface, can give rise to an extraordinary number of applications in environmental field including antibacterial antifogging coatings and remarkably can provide a solution to the increasing environmental pollution of buildings and monuments. Self-cleaning surfaces and self-cleaning coatings have opened a scenario of growing interest from both fundamental and technological perspective. Among the first products based on solar photocatalysis with  $\text{TiO}_2$  to be marketed were self-cleaning coatings for window glass and photovoltaic or solar panels with improved transmittance of natural sunlight. Activ<sup>TM</sup> glass developed by Pilkington group represents the first example of self-cleaning glass, a hydrophilic coating consisting of a 15 nm thick nanocrystalline  $\text{TiO}_2$  film deposited on a glass surface (Figure 7).[44, 162]

An analogous system is provided by pane glass Neat Glass, produced by Cardinal Glass Industries. The self-cleaning technology of Neat Glass relies on a  $\text{TiO}_2$  layer, able to remove organic contaminants by photocatalysis, combined with a thin layer of silicon dioxide, making the glass surface very hydrophilic and smooth.[161] In particular, self-cleaning cover glasses for tunnel lights

are one of the typical commercial application using this effect. In Japan, the decrease in light intensity of sodium lamps (emitting UV–Vis light) due to organic thin film formation from vehicle exhaust compounds is a serious problem in most tunnels. When the lamp is coated with  $\text{TiO}_2$ , it can decompose the contaminant, remaining clean and transparent for long-term use.[164] In addition to glass surfaces, the best use of  $\text{TiO}_2$  self-cleaning properties is related to construction and coating materials for walls in buildings, since these materials are exposed to sunlight and natural rainfall. Since the late 1990s,  $\text{TiO}_2$ -based materials like tiles, aluminum siding, plastic films, fabrics for tents and cements have been already marketed, especially in Japan. Hydrotech<sup>TM</sup> was successfully applied in building materials, coatings and paints made by TOTO Ltd., for indoor and outdoor applications. The photocatalytic products were manufactured by spraying a liquid suspension of  $\text{TiO}_2$  on the surface.[162, 164] Whereas, in Europe the first real project on the self-cleaning activity of  $\text{TiO}_2$  in cementitious materials was for designing the mix for “Dives in Misericordia” Church in Rome, Italy, by Italcementi S.p.A. (Figure 7).[165] This company developed different types of cement with a  $\text{TiO}_2$  surface, TX Aria<sup>TM</sup>, TX Active<sup>TM</sup>, and TX Millennium<sup>TM</sup>, claiming that covering 15% of urban surfaces of the city of Milan with concrete containing TX Active® would reduce the pollution up to 50%.[44]



**Fig. 7.** Application of different uses of self-cleaning exterior building materials. a) the self-cleaning sound-proof wall. Reprinted with permission from ref. [164]; b) “Dives in Misericordia” Church in Rome, Italy, by Italcementi S.p.A. Reprinted with permission from ref. [165]

Furthermore, nanoformulations were applied over ancient traditional materials, as stones and bricks, realising smart surfaces able to implement enhanced functionalities, enabling their own conservation, similar to those of freshly-built surfaces. Indeed, in recent years new products with self-cleaning and protective properties offer an important contribution to the cultural heritage of several countries. However, the concerns related to the urban environment and the air quality can cause or accelerate the deterioration of several architectural elements, altering both their aesthetical

aspect and their physical–chemical properties. Stone is one of the most widely used building materials, but it is quite vulnerable to environmental pollution. Deterioration process of stone is related to: i) the increasing of polluting gases and fine particulates that cause the disaggregation of materials; ii) the crystallization of soluble and insoluble salts inside the porous network the surface provokes the recession of stones and iii) the acid rains that give rise to the so-called ‘‘black crusts’’.[128] In this self-cleaning applications, TiO<sub>2</sub> based nanocomposite is deposited on the substrate as a thin film of thickness ranging from a few tens of nanometers to a few micrometers.[102] The application of protective coatings should cope with some fundamental requirements that make this challenge even more difficult. The coating should be i) hydrophobic, in order to prevent the infiltration of water, ii) compatible with the substrate and reversible, iii) resistant to weathering and sun UV radiation; iv) it must not damage the esthetic aspect of the monument v) the solvent should be aqueous and at neutral pH.[166] Further the method for application of the coating must be simple, such as a spraying procedure, and additional steps as calcinations must be avoided, because the coating requires an in situ application, on the external surface of a stone building.[102]

Another new strategy is the integration of polymer properties with nanomaterials properties by set-up of multifunctional coatings able to provide surface protection and self-cleaning properties to building materials. The Si-based resin (Alpha SI30 is a polysiloxane) exploited as protective and water repellent agent for lapideous materials.[167] In combination with TiO<sub>2</sub> NPs, 20-30 nm in size, give rise to an effective hybrid nanocomposite that significantly improves the properties of the bare polymer as protective agent for three different stone surface: Angera, Botticino and Carrara. Indeed, it was demonstrated that in presence of TiO<sub>2</sub>, the contact angle increases for the hybrid nanocomposite compared to the bare polymer obtaining a superhydrophobic coating in the case of Carrara marble. Such a superhydrophobic character was preserved after UV exposure. Hydrophobicity is a critical requirement, because it avoids water infiltration, which entails salt crystallization and the consequent stone fragmentation as demonstrated also by outdoor experiments.[167]

However, in these cases the dispersion of TiO<sub>2</sub> NPs in an organic medium in order to obtain self-cleaning coatings or paint formulations is a difficult issue, since a uniform distribution of TiO<sub>2</sub> NPs in the polymer is fundamental, along with their positioning at the surface of the hybrid material. In these systems, the stability of the dispersion was provided by the occurrence of solid particles, adsorbed on the oil/water interface. Hydrophobically modified TiO<sub>2</sub> NPs were exploited as the sole stabilizer to produce hybrid latexes made of Methyl methacrylate (MMA) and n-butyl acrylate (BA). Such a system forms coherent films with perfect honey-comb structures at room temperature.

The hybrid latexes were exploited to coat concrete specimens and their self-cleaning properties were investigated by following the Rhodamine B decolouration under UV exposure. The photocatalytic activity resulted to be affected by the concentration of TiO<sub>2</sub> employed during the synthesis and by the diffusion of the Rhodamine.[19] Further, hybrid nanocomposite with self-cleaning activity for application in the environmental protection of monument can also be developed by integrating TiO<sub>2</sub> and/or SiO<sub>2</sub> with hydrophobic polymer as polymeric resins, acrylic and vinyl polymers, organosilicone compounds and fluorinated film. Ritmi et al. reported an innovative uniform transparent PE-TiO<sub>2</sub> film able to improve the performance of self-cleaning surfaces where the TiO<sub>2</sub> layers do not disrupt the PE-network. Polyethylene (PE) used as the substrate to sputter TiO<sub>2</sub> presents thermal resistance up to 110 C-120 C for short periods. The reported results showed the reduction in the contact angle of PE-TiO<sub>2</sub> as a function of the irradiation time due to the increase in the hydrophilic nature of the PE-TiO<sub>2</sub> film under light. In particular, the PE-TiO<sub>2</sub> photo-switching from a hydrophobic to a hydrophilic surface was observed within 60 min under light while the reverse process was complete within 24 h in the dark.[168]

Kapridaki et al. developed a transparent-hydrophobic hybrid semi-crystalline SiO<sub>2</sub>-TiO<sub>2</sub> coating incorporated in an organosilane, the hydroxyl-terminated polydimethylsiloxane (PDMS). If the TiO<sub>2</sub> exhibits self-cleaning properties while the PDMS introduces hydrophobic properties, the presence of semi crystalline SiO<sub>2</sub> can improve the mechanical resistance of the surface. The hybrid nanocomposite TiO<sub>2</sub>-SiO<sub>2</sub>-PDMS revealed particularly effective in deterioration of biofilm on a marble surface under UV light. [169] Furthermore, in recent years, several groups reported fabrication of superhydrophilic wool and cotton fibers using TiO<sub>2</sub>/SiO<sub>2</sub> composites, which displayed photocatalytic self-cleaning activity against bacterial adhesion and for removal of food, coffee and wine strains[3, 162]

Most research efforts, as reviewed here, are devoted to imitate the excellent strategies perfected by nature over billions of years. Nevertheless, the self-cleaning surfaces artificially designed and fabricated are yet to match their naturally occurring counterparts, while the preparation synthetic techniques have indeed evolved into more environmentally compatible and cost-effective processes. These photocatalytic self-cleaning materials can be used in many applications including antibacterial, antifogging, antireflective coatings and can provide a solution to the growing problem of environmental pollution.

### ***3.3 Bactericidal coating***

Nanocomposite materials can be also used for inactivation of pathogens in solution as well as at the solid-air interface. Polyester, textiles and polymer films can be functionalized by photoactive NPs



in order to generate a suitable coating able to inactivate microorganisms. It is generally accepted that when microorganisms, as *Escherichia Coli*, undergo  $\text{TiO}_2$  photocatalytic attack the cell wall damage, followed by cytoplasmic membrane damage lead microorganism inactivation.[170] In particular, ATR-FTIR spectroscopy was employed to investigate lipopolysaccharides, phosphatidylethanolcholine and peptidoglycan peroxidation of *E. coli* cell in presence of porous film containing Degussa P25  $\text{TiO}_2$  NPS. As a result, while the polysaccharide bands, acyl bands,  $>\text{CH}_2$  bands,  $\text{CH}_3$  bands, amide bands and of oligosaccharide bands of *E. coli* and lipopolysaccharide bilayer were observed to disappear, the formation of peroxidation products (aldehydes, ketones and carboxylic acids) occurred. Further, during the photocatalysis process, photogenerated holes trapped on the  $\text{TiO}_2$  surface are scavenged by *E. coli* and lipopolysaccharides. In particular, it is suggested that scavenging of holes by organic matter results in the formation of organic radicals ( $\text{R}\bullet$ ) and this process is considered as initial stage in the radical chain oxidation processes in the cell membrane.[171] Several models, describing the photocatalytic disinfection, highlight that microorganism are required to be in contact with the photocatalyst surface in order to trigger the disinfection reaction.[172] In this regard, Bonnefond and co-workers examined polymeric films loaded with  $\text{TiO}_2$  NPs observing differences in terms of bacteria adhesion according the film composition.  $\text{TiO}_2$  (10% or 20% in weight) NPs were exploited as the sole stabilizer to produce hybrid latexes made of Methyl methacrylate (MMA) and n-butyl acrylate (BA). Such system forms coherent films with perfect honey-comb structures at room temperature.[19] The evaluation of the *E. coli* inactivation on prepared polymers under simulated solar light demonstrated complete bacterial inactivation within 240 min for the film containing 10 wbm% of  $\text{TiO}_2$  (air-film interface), whereas the one containing 20 wbm% of  $\text{TiO}_2$  required longer cycles. According authors photogenerated  $\text{e}^-$  and  $\text{h}^+$  in the 20%  $\text{TiO}_2$  sample require a longer diffusion length to reach the surface and initiate the photocatalytic bacteria inactivation.[18] Analogous results were obtained in antibacterial  $\text{TiO}_2/\text{In}_2\text{O}_3$  films sputtered on polyester. In particular the  $\text{TiO}_2$  was immobilized on polyester by direct current magnetron sputtering while the  $\text{In}_2\text{O}_3$  was subsequently deposited by direct current pulsed magnetron sputtering. Experimental results showed a significant improvement in *E. coli* inactivation time under visible light (Actinic lamp) irradiation in presence of  $\text{In}_2\text{O}_3$ .[173]

The field of preservation of monuments and architectures surfaces can take the advantage of suitable coating integrated with photoactive NPs. Within this framework, NPs of  $\text{TiO}_2$  can be used as bactericide agents against the biological activity induced both in building facades as well as in the interior. Kapridaki et al. exploited for a similar application a multifunctional transparent-hydrophobic hybrid semi-crystalline  $\text{SiO}_2\text{-TiO}_2$  coating incorporated in an organosilane, the

hydroxyl-terminated polydimethylsiloxane (PDMS). The hybrid nanocomposite  $\text{TiO}_2\text{-SiO}_2\text{-PDMS}$  revealed particularly effective in deterioration of biofilm composed of *Klebsiella Pneumonia*, *Pasteurella pneumotropica*, *Sphingomonas*, *Burkholderia Cepacia* (*Pseudomonas*) on a marble surface under UV light (Figure 8).[130]



**Fig. 8.** Self-Cleaning of biologically decayed marble treated with  $\text{SiO}_2\text{-TiO}_2$  coating incorporated PDMS Reprinted with the permission from ref.[130] Copyright 2015

#### 4. Conclusion

Current material science approaches allow to flexibly design and prepare photoactive nanomaterials with precise control on their shape and size even characterized by different crystalline domain thus merging different functionality (photoactivity, magnetic, plasmonic or bactericidal properties) in one material, finally providing nanocatalysts with unprecedented or enhanced performances. At the same time, suitable polymers, such as fluorinated polymers or organosilane hybrids, provide a proper host environment for the formation processable photoactive nanocomposite materials to be easily integrated in photoreactor for water or air remediation, painted on wall or integrated in the cementitious materials or pavements to achieve self-cleaning properties and face air pollution in urban area or can be coated on different surfaces to obtain bactericidal properties or to provide protection and conservation of cultural heritage.

Here we have intended to provide an overview of the recent advances in the fields of the synthetic approaches to UV and visible light active nanocatalysts, on the post-synthesis surface functionalization for their integration in original functional nanocomposite for photocatalytic applications. Finally, some examples of such photoactive nanocomposite applications for environmental remediation (degradation of water or air pollutants) and bactericidal and self-cleaning coatings have been reported.

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