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## 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 exploit the strong 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. Such a strategy can bridge 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 on their incorporation in suitable host matrices toward nanocomposite preparation. Finally, some examples from recent literature on their application in environmental remediation and as bactericidal and self-cleaning coatings will be reported.

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### 1. Introduction

During the last decades semiconductor-assisted photocatalytic oxidation processes have received considerable attention due to their potential application in photocatalysis, environmental remediation, self-cleaning and bactericidal coatings, new generation solar cells, hydrogen production and sensing [1–7]. In this perspective, TiO<sub>2</sub> represents the most widely used photocatalyst due to its high 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 redox potentials to achieve selective photochemical reactions. Also, the reduced dimensions of the nanocatalysts allow the photo-

generated charges to easily reach the catalyst surface thus reducing the probability of undesired bulk recombination. Nevertheless, the use of nanocatalyst dispersed powders presents significant 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 and fibers, silica and stainless steel substrate, textiles or to incorporate them 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]. A nanocomposite is defined as 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,

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gels and copolymers, more typically means 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]. Also, 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 the unique size- and shape dependent properties of inorganic nanofillers (i.e. catalytic, optical, electrical or magnetic) and the significant ones 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 types of nanocatalysts such as semiconductor nanoparticles (NPs) (i.e.  $\text{TiO}_2$  or  $\text{ZnO}$ ), metals, (i.e. plasmonic NPs), magnetic oxides, or carbon nanotubes and graphene. Such a peculiarity allows a useful tuning of the photocatalytic properties of the final nanocomposite, to extend the range of wavelength needed 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 ( $e^-/h^+$ ) [33–35]. However, one of the main challenges 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 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 main steps: (i) synthesis of an effective photocatalyst; (ii) its surface functionalization to promote (iii) its incorporation in the most suitable host matrix according to the final application.

In this section, we will review recent progress in modern material science on synthesis of 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 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 photoexcitation. Photogenerated  $e^-/h^+$  species are able to produce reactive oxidizing species (ROS) which can lead to the photocatalytic transformation of a pollutant [36–38]. Unfortunately, only

$e^-/h^+$  pairs generated in wide band gap semiconductors ( $E_g > 3 \text{ eV}$ ) 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 one between the recombination of the trapped carriers and the interfacial charge transfer. Accordingly, improved charge separation and inhibition of charge carrier recombination are essential for enhancing the overall quantum efficiency of interfacial charge transfer [39–43].

Continuous efforts are devoted to modify  $\text{TiO}_2$ -based catalysts in order to overcome  $\text{TiO}_2$  limited sunlight absorption (band gap value 3.2 eV for bulk anatase  $\text{TiO}_2$ ), to improve the  $e^-/h^+$  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 strategies towards the synthesis of  $\text{TiO}_2$  nanocrystals (NCs) with improved photocatalytic performances. The modification strategies of  $\text{TiO}_2$  NCs can be summarized as follows: (i) morphological modifications, aiming to increase in surface area and porosity [44,45], and/or (ii) chemical modifications, in order to introduce additional components in the  $\text{TiO}_2$  NC structure, thus resulting in heterostructures that combine the characteristics of their specific components [46] and, concomitantly, provide additional original properties [47]. 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 [35,48]. Current advance in material science allows to flexibly design and prepare 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 suitably combined into new catalytically active nanocomposites. Recently advances in the fabrication of nanoparticles (NPs) and NCs have been achieved, thanks to the careful control of the synthetic processes (monodispersity, surface chemistry), the investigation of morphology and multifunctionality issued in the NP and NC design and the comprehensive understanding of the NC and NP shape control mechanisms [49,50]. Such developments can enable the production of a wide range of conventional and innovative photocatalytic nanostructures.

The following subsections intend to provide an overview of the cutting-edge synthetic strategies recently proposed in literature, in order to obtain  $\text{TiO}_2$ -based nanomaterial suitably designed for photocatalytic degradation of pollutants. Our attention will be focused on noble metal based multifunctional heterostructures, organic-inorganic hybrid materials, semiconductor/metal oxide NPs and NCs, doped metal oxide NPs with tailored crystallographic facets.

#### 2.1.1. Noble metal based multifunctional nanosized 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 [51–56]. 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 radiation 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 [57,58]. Indeed spherical NPs 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 dimensions of

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