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REVIEW ARTICLE

Recent progress on Ag/TiO_2 photocatalysts: photocatalytic and bactericidal behaviors

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Abstract

For many decades, titanium dioxide (TiO_2) semiconductor has been extensively applied in several environmental applications due to its higher photocatalytic performances toward different organic pollutants, pharmaceutical compounds, and bacteria. However, its shortfall response to visible light, and the expeditious recombination rate of the photogenerated electron–hole pairs, hampers its utilization. Doping TiO_2 semiconductor with silver nanoparticles is a sound strategy to (1) extend its photocatalytic activity to visible light, (2) prevent the electron/holes pairs recombination due to the formation of the Schottky barrier at the interfaces with TiO_2 that act as an electron-trapping center, and (3) enhance its bactericide performances. This review focuses on the recent progress on silver-doped titanium dioxide (Ag/TiO_2)-based photocatalysts. It addresses a wide range of Ag/TiO_2 synthesis techniques, their physicochemical properties and discusses thoroughly the important role of silver (Ag) nanoparticles in enhancing the removal capacity and antibacterial performances of the Ag/TiO_2 photocatalysts.

Keywords Silver-doped TiO_2 · Nanocomposites · Photocatalytic degradation · Antibacterial activity · Visible light

Introduction

For many decades, titanium dioxide (TiO_2) has shown great and considerable potential in removing organic contaminants and bacteria from sewage, owing to its interesting properties in terms of photoactivity, stability, availability, and low-cost (Yu et al. 2001; Lachheb et al. 2002; Abdellah et al. 2018; Canbaz et al. 2019; Lu et al. 2019). The photodegradation of different pollutants, as well as the microorganism inactivation, held as follows, the absorption of a photon by the TiO_2 semiconductor ($h\upsilon \geq Eg$) provokes electron excitation from the valence band to the conduction one, creating, therefore, positively charged holes (h^+). The electron–hole pairs migrate separately to the surface of TiO_2 and participate in a series of oxidation/reduction reactions with adsorbed species such as water and oxygen to generate highly reactive oxygen species (ROS). These reactive oxidizing species react with the impurities adsorbed on the surface leading to their decomposition to harmful compounds (Pelaez et al. 2012; Nasr et al. 2018). Nevertheless, due to their short lifetime, the photogenerated electrons and holes can recombine quickly in bulk or on the surface of TiO_2, causing a reduction in its photocatalytic performances (Koe et al. 2019). Furthermore, due to its broad bandgap (3.2 eV), TiO_2 is only activated under UV radiations, which only accounts for 5% of the solar spectrum compared to visible light (45%) (Etacheri et al. 2015; Duan et al. 2019). Therefore, felt it necessary to shift the TiO_2 absorption spectrum toward the visible region to fully harness the advantage of sunlight as an inexpensive and renewable energy source, several approaches have been proposed, including:

1. Doping with metal ions using transition metal or non–metal ions: the optoelectronic features of TiO_2 photocatalyst can be modified by doping either metal or non-metal ions into its lattice. Transition metals with an unfilled d-electron structure have the authority to transfer electrons from the 3d level of the dopant to the band conduction of TiO_2 to accommodate more electrons

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and trap photogenerated electrons or holes, reducing their recombination and shifting the optical response of TiO_2 toward higher wavelengths (Yadav and Jaiswar 2016; Endo et al. 2018; Halin et al. 2018; Zhang et al. 2019). Generally, metal doping can be occurred through interstitial doping involving their location on the TiO_2 surface or through substitutional doping by replacing Ti^{4+} ions with cations resulting in oxygen vacancy. Other than metals that act as cationic dopants, doping TiO_2 with anionic dopants using p-block elements such as carbon, nitrogen, sulfur, etc. improves its response in visible light and prevents the recombination phenomenon through the modification of its electronic band structure (Nagpure et al. 2017; Endo et al. 2018; Halin et al. 2018; Zener et al. 2018; Wysocka et al. 2019). In this case, doping is performed by replacing O^{2-} ions with anions. Among different non-metal dopants, nitrogen stills the most used due to its small ionization energy and its atomic size comparable with that of oxygen (Rtimi 2017; Milošević et al. 2018).

2. Coupling with semiconductors such as ZnO, WO_3, SnO_2, CdS, and Fe_3O_4: coupling TiO_2 with another semiconductor material with lower gap energy forming a heterojunction is an advantageous option. The semiconductor of low-gap energy plays the role of sensitizer by being excited first and then inducing the excitation of TiO_2 by the passage of photoelectrons from its conduction band to that of titanium dioxide (Bera et al. 2019; Zhang et al. 2020).
3. Modifying with graphene and its derivatives: graphene with its unique structure, high electron mobility, and attractive features prevents the charges recombination through the modification of the valence and conduction band levels (Guo and Zhen 2016; Tang et al. 2018; Chakhtouna et al. 2021).
4. And sensitizing with dyes: the first works carried out to achieve this objective were based on the adsorption of photosensitive dyes such as erythrosin B and ruthenium polypyridine on TiO_2 lattice (Kamat and Fox 1983; Islam et al. 2001). However, the major problem confronting these systems is generally the chemical and thermal instability of the used photosensitive dyes (Al-Attafi et al. 2018; Li et al. 2019).

In this respect, doping TiO_2 with noble metals seems a virtuous idea in achieving visible light active photocatalyst, and solving the recombination of the electron–hole pair, already mentioned above (Zhao et al. 2016; Endo et al. 2018; Pathak et al. 2019). To the best of our knowledge, the first publication concerning doping TiO_2 with noble metals was reported in 1978 by Tauster et al. (1978). Since then, many reports have been published on the modification of TiO_2 by noble metal nanoparticles such as Au, Ag, Pt, Pd, and many others (Harikishore et al. 2014; Endo et al. 2018; Matsunami et al. 2019; Yaqoob et al. 2020). Incorporating of those noble metals into the TiO_2 surface enhances its photocatalytic activity by acting as an electron trap due to the formation of a Schottky barrier between TiO_2–metal junctions, promoting interfacial charge transfer delaying recombination of the electron–hole pairs. Silver nanoparticles as an antibacterial agent have aroused great interest compared to other noble metals (Mahmoudi et al. 2015; Zhang et al. 2016a). Its high disinfection capacity is advantageous for applications in the wastewater treatment field, often loaded with bacteria. Following an extensive literature review, more than 512 papers containing "silver-doped titanium dioxide," "Ag/TiO_2 photocatalyst," or "Ag/TiO_2 nanocomposites" are published. Most of these papers are published at the beginning of the twenty-first century, and the number increased rapidly until now. These data are not surprising owing to the higher photocatalytic and bacterial performances of Ag/TiO_2 and Ag/TiO_2-based photocatalysts. Therefore, believing that a comprehensive review of Ag/TiO_2 photocatalysis is requisite to highlight the advantages of coupling TiO_2 semiconductor and silver nanoparticles and understand the mechanisms involved during the organic compounds and bacteria photodegradation. This review presents the recent progress in developing the Ag/TiO_2 photocatalysts from synthesis methods and characterization to photocatalytic application, under UV and visible light illuminations.

Ag/TiO_2 photocatalyst

Ag/TiO_2 synthesis methods and characterization

Photocatalytic performances of Ag/TiO_2 nanoparticles are strongly contingent on the synthesis condition and methodology. Several methods have been applied for Ag/TiO_2 photocatalysts synthesis with different morphologies, including impregnation, sol-gel, co-precipitation, hydrothermal, photo deposition process, etc. (Naik et al. 2013; Harikishore et al. 2014; Sarteep et al. 2016; Wenderich and Mul 2016; Zhang et al. 2016b; Zheng et al. 2019; Abbad et al. 2020). Each synthesis method has its own advantages and shortcomings in terms of performances and preparation. Still all of them have the end goal of creating Ag/TiO_2 nanoparticles with higher purity, homogeneity, and performances. The difference in the photo activity of silver-doped TiO_2 prepared with different methods can be discussed in terms of the oxidation state of silver on the TiO_2 surface, the particle size that should be in nanometer scale, silver concentration loading in the final photocatalyst and thermal treatment during the photocatalyst preparation (Zhang et al. 2008; Chen et al. 2013; Ryu et al. 2015). This section assesses different techniques and methods commonly used for the preparation of Ag/TiO_2 nanoparticles.

Sol–gel method

The sol–gel technique is the most widespread and promising technique that has been applied for producing silver-doped TiO_2 nanoparticles at room temperature and under atmospheric pressure (Akpan 2010). This method is simple as long as it does not require complicated synthesis conditions or instruments. This eco-friendly and inexpensive technique allows controlling the purity and homogeneity of the final product, the growth and size of the particles, and the flexibility of adding high concentrations of doping agent. The sol–gel process involves consecutive steps, namely:

1. Hydrolysis to convert the alkoxides into metal hydroxides
2. Condensation to form gels
3. Drying process to obtain silver-doped TiO_2 nanoparticles

Titanium precursor, which is usually titanium tetraisopropoxide (TIP), tetrabutyl orthotitanate (TBOT), or titanium tetrachloride ($TiCl_4$) is mixed a silver precursor; the most commonly used is silver nitrate, followed by hydrolysis performed at low temperature (does not exceed 100 °C). During the synthesis, the pH must be controlled to ensure uniformity of properties. Subsequent calcination at high temperature for further crystallization is often needed since the sol–gel technique frequently produces amorphous or low crystalline silver-doped TiO_2 photocatalysts (Sharma et al. 2018). The silver-doped titanium dioxide nanoparticles can be formed as follows (ethanol was used as solvent):

$$Ti(OH)_4 + C_2H_5O\text{–}Ag \rightarrow Ti(OH)_3\text{–}Ag + C_2H_5OH \quad (1)$$

$$4Ti(OH)_3\text{–}Ag + O_2 \rightarrow 4TiO_2\text{–}AgNP + 6H_2O \quad (2)$$

Optimizing the preparation conditions is pivotal for obtaining photocatalysts with notably higher activity. The photocatalytic behaviors of Ag/TiO_2 nanoparticles toward different pollutants depend on several parameters such as the type of metal precursors, total metal loading, solvents, reducing agents, and other parameters such as pH, temperature, water/precursor molar ration, etc. (Harikishore et al. 2014; Razak et al. 2018; Abbad et al. 2020). For example, Gupta et al. (2013) have studied the effect of silver precursor concentrations on the photocatalytic properties of Ag-doped TiO_2 nanoparticles against two kinds of bacteria. The photocatalyst was prepared via sol–gel technique starting from titanium (IV) tetrabutoxide, silver nitrate, water, and toluene in an acidic environment, followed by calcination at 450 °C. It was revealed, the photocatalyst size decreases as the amount of silver precursor increase from 3 to 7% (Fig. 1). Generally, when the particle size of the photocatalyst decreased, the surface area increases, allowing for more active sites and consequently higher photocatalytic performances. In addition, according to XRD results, it was observed that silver doping enhances the stability of the anatase phase, detected only in the XRD patterns of Ag-doped TiO_2 photocatalyst, unlike that of pure TiO_2, which revealed the presence of both anatase and rutile phases.

Mogal et al. (2014) have also investigated the influence of silver concentration on the final properties of the silver-doped titanium dioxide photocatalysts. The Ag/TiO_2 photocatalysts with a silver amount varying from 0.75 to 3.5 at% were synthesized via a single–step sol–gel route by dissolving silver and titanium precursors with methanol and ammonia. The resulting gel was dried and calcined at different temperatures ranging from 400 to 600 °C. The XRD results indicate that the silver content augmentation promotes the TiO_2 phase transformation from anatase to rutile and alters also the crystalline size of the final product. The crystallite sizes increased with increasing the silver dopant concentration (Fig. 2). Moreover, results indicate that 0.75 at % of doped silver amount content may be optimum, which can control the crystallite growth and agglomeration due to the grain–boundary pinning caused by dopant ions. The UV–Vis results show that the addition of 0.75 at % of silver ions generated the displacement of the absorbance toward longer wavelengths while increasing silver dopant concentration beyond 0.75 at % causes the absorbance to shift to shorter wavelengths. Similar results were observed as to the specific surface area. The 0.75 at % doped photocatalyst had the highest specific surface area and any further increase had a negative effect on the desired properties.

Prosperous synthesis of silver-doped TiO_2 powders via sol–gel using titanium tetra *n*-butoxide and silver nitrate as titanium and silver precursors, respectively was reported by Harikishore et al. (2014). XRD spectra of Ag/TiO_2 nanoparticles annealed at 500 °C confirmed the existence of anatase phase without any impurity phases of Ag or $AgNO_3$, confirming the complete doping of Ag in TiO_2. Furthermore, it was observed that the crystallize size and crystallinity of Ag/TiO_2 photocatalyst increased with annealing temperature, confirming the results previously by Mogal et al. 5 mol% of silver reduces undeniably the bandgap of the photocatalyst from 3.2 to 2.9 eV and extends its absorbance spectrum to longer wavelengths (Fig. 3).

Hydro/solvothermal methods

The hydrothermal method is one of the most exploited methods for producing silver-doped titanium dioxide semiconductors, especially when varied nano-morphologies are desired (Mogal et al. 2013; Zhang et al. 2016b; Hariharan et al. 2020). As the name suggests, the hydrothermal technique is a process for growing crystals from an aqueous solution under elevated temperatures and high-pressure environments. The higher temperature and pressure encourage the interaction of different precursors during synthesis and

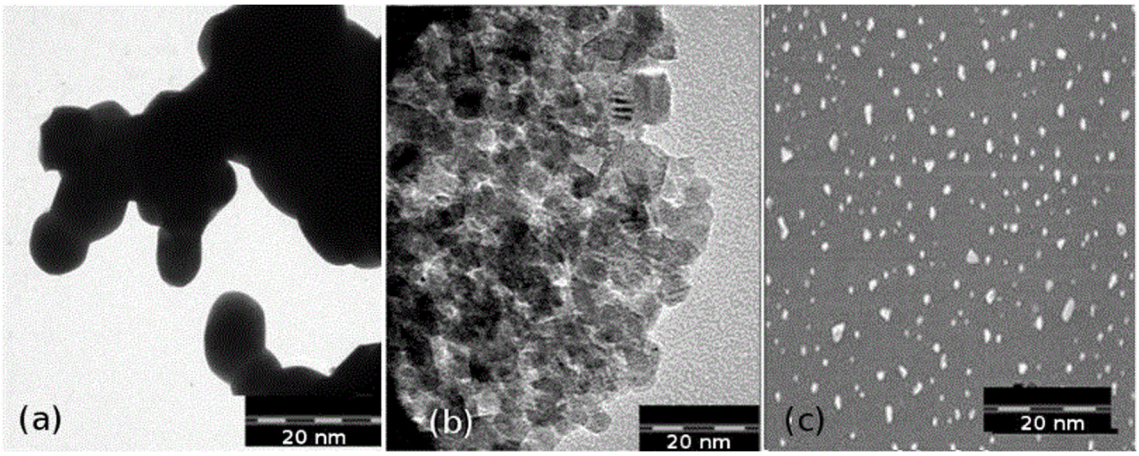

Fig. 1 TEM images of (**a**) TiO_2 and (**b**) 3% and (**c**) 7% Ag-doped TiO_2 nanoparticles annealed at 450 °C (Gupta et al. 2013)

produce high-quality crystals of Ag/TiO_2. The key steps in the hydrothermal synthesis of silver-doped TiO_2 nanoparticles are similar to the sol–gel method except that the hydrothermal method involves reactions in a sealed reactor known as autoclave under pressurized conditions. The advantages of the hydrothermal process lie in the fact that it is a simple, time-effective, environmentally friendly, and versatile method for the synthesis of Ag/TiO_2 nanoparticles with narrow size distribution and dispersion (Liu et al. 2009). Furthermore, the size of the doped photocatalyst can be easily controlled by varying processing conditions like pH, pressure, and temperature (Parangi and Mishra 2019). Hariharan and his collaborators (2020) have developed titanium dioxide nanoparticles doped with varying amounts of silver nanoparticles through of a green hydrothermal method for picric acid degradation and lung cancer cell lines destruction under visible light irradiation. Typically, different concentrations of silver nitrate were added to titanium (IV) isopropoxide, Aloe Vera gel as a reducing, agent and water. The mixture undergoes a hydrothermal treatment followed by calcination at 500 °C. Structural studies from XRD data showed that all the $Ag@TiO_2$ photocatalysts crystallized in the anatase phase (Fig. 4). After doping with 0.01 M of silver nanoparticles, the response of TiO_2 photocatalyst to visible light was increased and showed a shift toward increased wavelength, resulting in a reduction of its bandgap energy and therefore higher photocatalytic performances within 50 min.

Avciata et al. (2016) have also doped TiO_2 photocatalysts with silver by a hydrothermal method at 180 °C in 120 min using different reduction agents, namely sodium borohydride, PEG–600, Hydrazine, and ascorbic acid. The authors investigated the effect of reducting agents on the Ag/TiO_2 photocatalyst structure, physicochemical properties, and photocatalytic performances. It was found that all the Ag/TiO_2 photocatalysts, whatever the nature of the reducing agent, crystallized in the anatase phase and contain elemental silver. Moreover, it was observed that the crystallite sizes of all prepared nanoparticles ranged between 10 and 13 nm, indicating that the reducing agent has no effect either on the crystalline structure or on the crystallite sizes unlike the specific surface area that was dependent on the reduction agent. It can be seen that S_{BET} increased with using the PEG–600 as reduction agent. BET consequences are seen that a linear relationship between surface area and particle size. Silver-doped TiO_2 join to form together with the surfactant caused the formation of anatase in the formation of smaller particle size and higher surface area. These results showed that the best structure powder was obtained from PEG–600 used as surfactant and reducing agents. According to SEM micrographs, it was found that the nature of reducing agent also affects the morphology of the

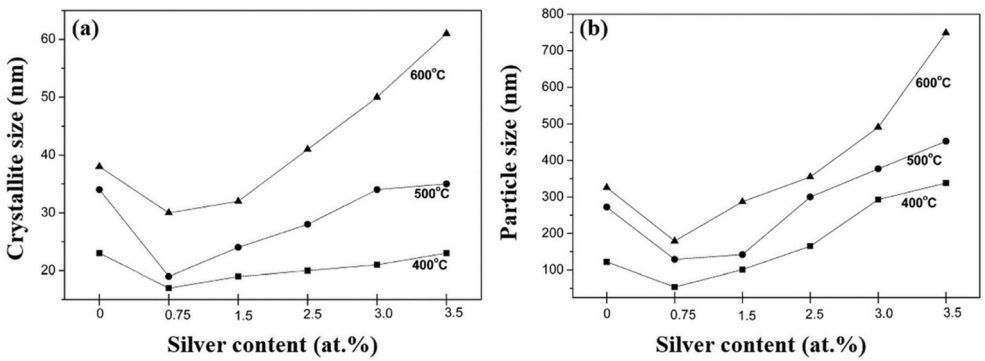

Fig. 2 Crystallite size (**a**) and average particle size (**b**) of silver-doped TiO_2 with different silver content, calcined at different temperatures (Mogal et al. 2013)

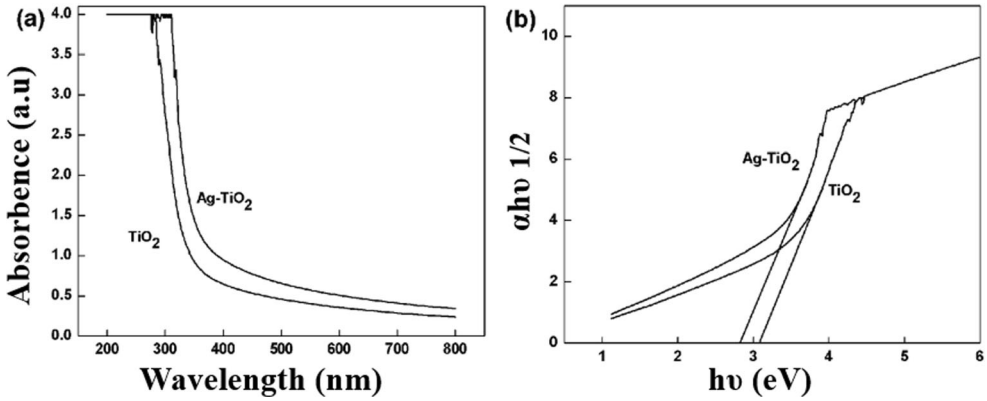

Fig. 3 **a** UV–Vis absorption spectra; **b** plot of $\alpha^{1/2}$ versus hυ for indirect transition of TiO_2 and Ag/TiO_2 samples (Harikishore et al. 2014)

doped photocatalysts. Those prepared by Hydrazine and Ascorbic acid have a striped structure, while others present a spherical structure (Fig. 5).

The solvothermal technique is almost identical to the hydrothermal method, the only difference between them lies in the solvent used. The hydrothermal technique refers to the use of water as a reaction system, while the solvothermal method involves the use of organic solvent, which plays an interesting role in the control of the structure, morphology, crystallinity, and shape distribution of the silver-doped TiO_2 photocatalyst (Li et al. 2015).

Chemical reduction technique

Chemical reduction of silver nanoparticles on the TiO_2 surface is one of the simplest techniques used for the preparation of Ag/TiO_2 nanoparticles with controlled particle sizes, shapes, and well-dispersion (Suriati et al. 2014). The principle of this method involves the adsorption of silver precursors on the TiO_2 nanoparticles surface, in the presence of reducing agents, namely sodium citrate, sodium borohydride, and other organic reagents, followed by chemical reduction (Zhou et al. 2015). By way of example, Ag-deposited TiO_2 particles were successfully formed by a chemical reduction method using a

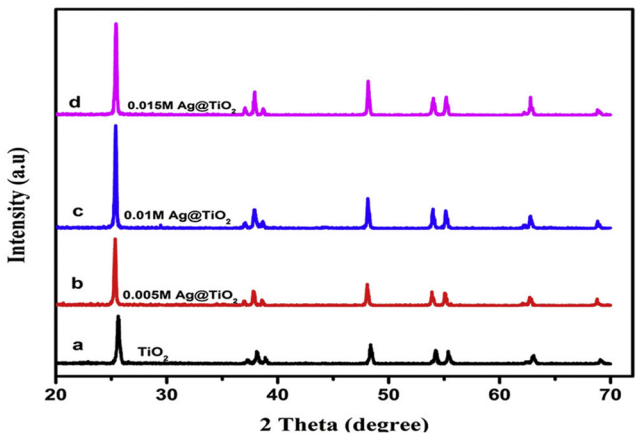

Fig. 4 XRD patterns of pure TiO_2 and Ag-doped TiO_2 photocatalysts (Hariharan et al. 2020)

semi-batch reactor for *Escherichia coli* bacteria destruction (Do et al. 2006). Indeed, a required content of silver nitrate and sodium dodecyl sulfate as a reducing agent was added to a suspension of TiO_2 already prepared. After mixing, Ag-deposited TiO_2 suspensions were prepared by feeding in hydrazine hydrate aqueous solution using a micro feed pump. The obtained Ag-deposited TiO_2 nanoparticles have undergone a calcination at 500 °C. TEM photographs confirmed the deposition of a small amount of silver nanoparticles with a size of 5 nm on the TiO_2 surface as shown in Fig. 6. Structural studies from XRD data showed that the Ag-deposited TiO_2 nanoparticles, with different molar concentrations of $TiO_2/AgNO_3$ crystallized according to a tetragonal anatase structure. Figure 7 illustrated the results of UV–Visible spectra of pure TiO_2, Ag nanoparticles, as well as the different Ag-deposited TiO_2 nanoparticles. All Ag-deposited TiO_2 samples showed a redshift in the absorption edge and strong absorption in the visible light range (> 400 nm).

Photo-deposition process

A photo-deposition process is an attractive approach for producing silver-doped TiO_2 photocatalysts. Its principle is simple. The illumination of a mixture of TiO_2 semiconductor and silver precursor in an aqueous solution for a certain period is sufficient to reduce silver ion (Ag^+) to silver metal (Ag^0) and ensure their deposition on the TiO_2 surface (Wenderich and Mul 2016). In these types of reactions, alcohol is necessary to prevent positive charges from growing during photo-deposition process. In addition, the intensity of the light is also an interesting parameter that must be controlled in such techniques. It has been proven that the average particle size is strongly dependent on the light intensity; indeed, its increase leads to a decrease in the average particle size of the silver-doped TiO_2 photocatalyst. In addition, the concentration of silver precursor can influence the particle size of the photocatalyst; a lower concentration leads to smaller particles. According to literature, Clark and Vondjidis (1965) were the

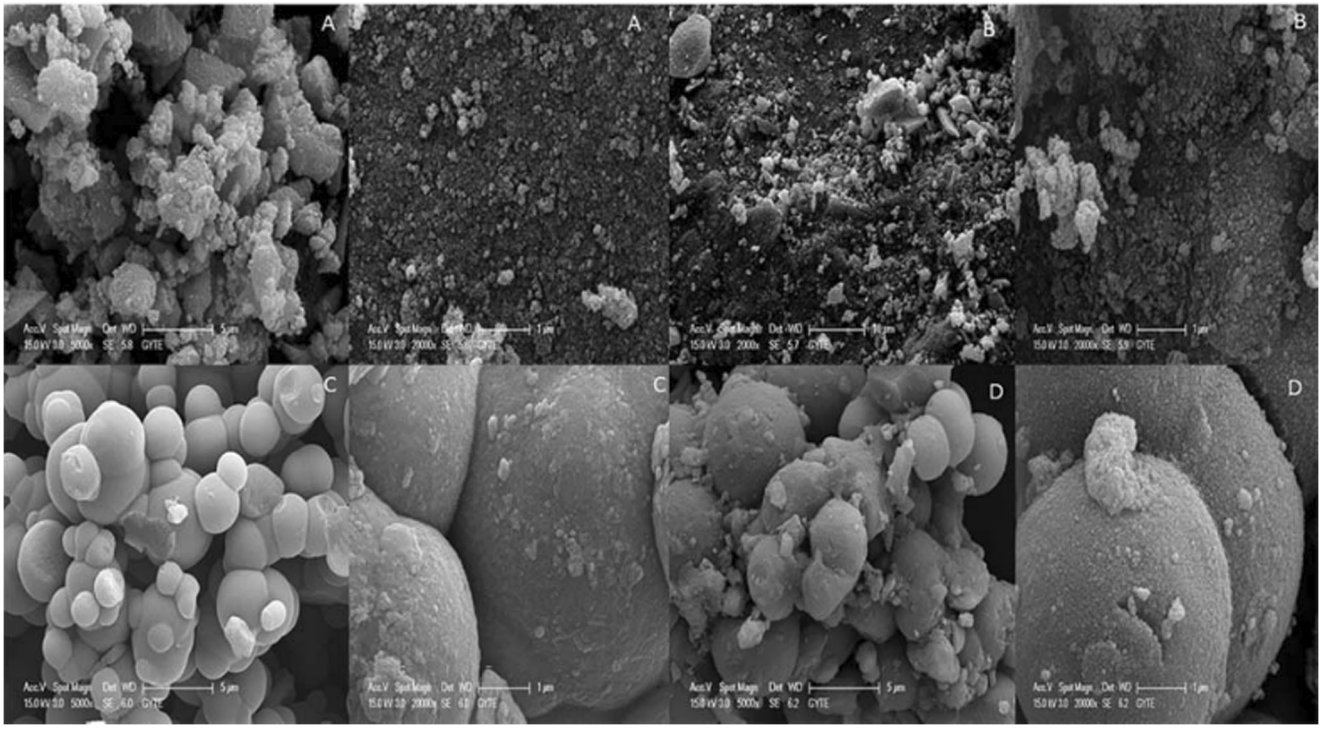

Fig. 5 SEM images of the Ag-doped TiO_2 (**A**), Ascorbic acid (**B**), Hydrazine (**C**), and PEG–600 (**D**) Sodium borohydride (Avciata et al. 2016)

first to prepare silver-doped titanium dioxide using photo-deposition technique using UV-irradiation. With this technique, it was possible to obtain well-dispersed nanoparticles of silver on titanium dioxide surface. Since then, great interest and more attention have been granting to the photo-deposition process.

Shokri et al. (2013) have successfully synthesized Ag-doped TiO2 nanomaterials through photo-deposition technique for chloramphenicol antibiotic removal from aqueous suspension. The Ag/TiO_2 photocatalyst was prepared by a typical photo-deposition method, where different silver nitrate concentrations are doped onto TiO2–P25 (Degussa) in acidic conditions (pH = 3) and irradiated with UV light for 3h (30 W, λmax = 254 nm) followed by calcination at 300 °C. From the XRD results, it was observed that the Ag/TiO_2 nanoparticles crystallized on both anatase and rutile phases; anatase is the

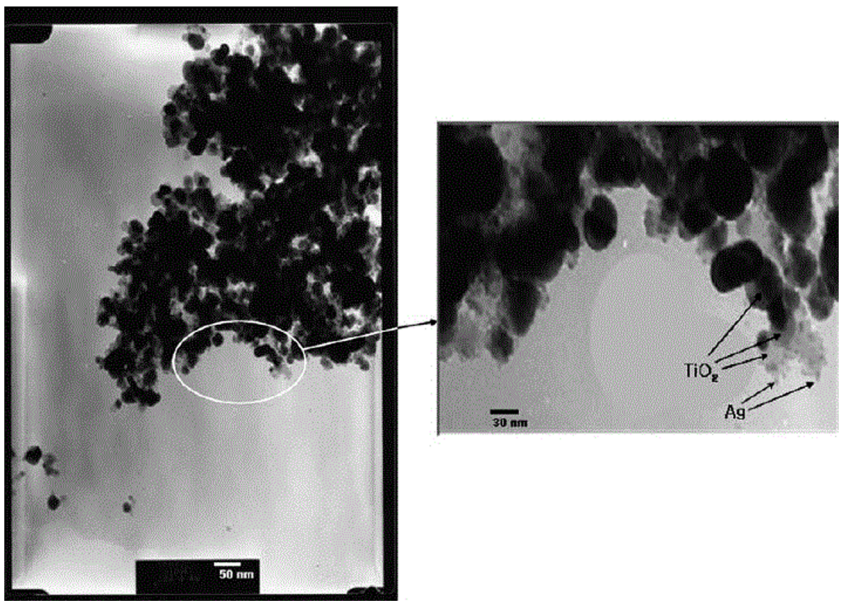

Fig. 6 TEM photographs of Ag-deposited TiO_2 nanoparticles (Do et al. 2006)

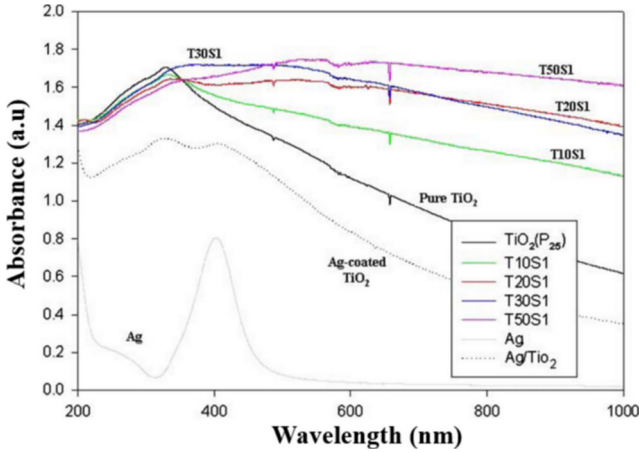

Fig. 7 UV–Vis absorption spectra of Ag, pure TiO_2, and Ag-deposited TiO_2 powders (Do et al. 2006)

dominant phase with a percent of 80% against 20% of rutile (Fig. 8). SEM micrographs proved that the spherical shape of the TiO_2 nanoparticles did not change after the loading of Ag nanoparticles. These results were confirmed by TEM images, as shown in Fig. 9. The shape and size of the titania crystallites were unchanged as a result of surface modification by Ag nanoparticles. The Ag nanoparticles (black dots indicated) were located on the surface of the individual TiO_2 nanoparticles, making them more accessible to light irradiations, triggering elements of the photocatalytic activity.

The authors have also evaluated the effect of the doping content of Ag on the CAP degradation rate. They showed that the TiO_2 loaded with silver exhibited a significant increase in photocatalytic performances compared to the pure TiO_2. Moreover, the photocatalytic performances enhance with increasing the silver dopant concentration until reached a value which is considered as the optimum amount of silver for doping to obtain higher photocatalytic performances. Beyond this value, the silver nanoparticles act as recombination centers, leading to a decrease in the photocatalytic activity of the photocatalyst. Similar results were found by Behnajady et al. (2008) during the preparation of Ag/TiO_2 nanoparticles, with

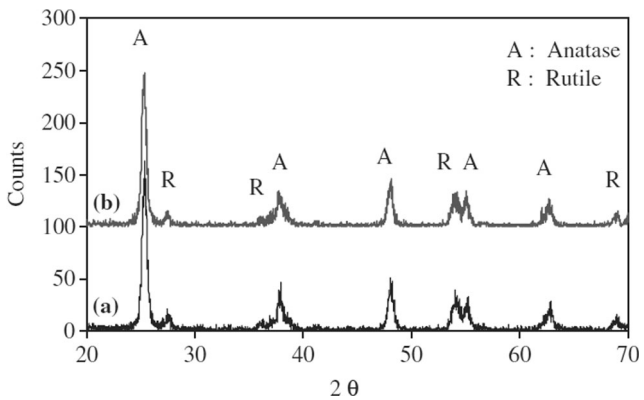

Fig. 8 X-ray diffraction patterns of un–doped (**a**) and Ag-doped (**b**) TiO_2 (Shokri et al. 2013)

different silver concentrations ranging between 0.5 and 2.5%. Photocatalytic tests showed that 0.5% is the optimum value for achieving huge photocatalytic activity and reducing the recombination of the photogenerated electron /hole pairs at the TiO_2 surface.

Impregnation

The impregnation method is one of the simplest techniques to produce Ag/TiO_2 photocatalyst. It consists of mixing under stirring a solution of $AgNO_3$ with a suspension of TiO_2 in water or other organic solvents for a well–defined period (Mogal et al. 2013). The solvent is removed by drying followed by calcination at high temperatures. In this respect, Ag-doped titanium dioxide photocatalysts with different silver content were successfully prepared by liquid impregnation technique for Sparfloxacin photodegradation (Kulkarni et al. 2018). Regarding the synthesis method, the desired amount of silver precursor was added to TiO_2 nanoparticles dispersed in deionized water and stirred magnetically for 3 h, the slurry was then kept overnight for liquid impregnation, dried and calcined 450 °C in a muffle furnace. The principle is almost the same for all existing works in the literature, what changes is the synthesis conditions such as the contact time, the percentage of silver or TiO_2 used, the addition of some additives to bring other properties and finally the calcination temperature to achieve the desired phases. XRD analysis showed that the prepared Ag-doped TiO_2 nanoparticles crystallized in the anatase. It was also revealed that increasing the silver doping on anatase TiO_2 decreases the crystallite size. SEM and TEM micrographs confirmed the non-uniform distribution of agglomerates of cylindrical $Ag–TiO_2$ nanoparticles (Fig. 10), leading to higher surface area and consequently greater photocatalytic efficiency of prepared Ag/TiO_2 nanoparticles. In addition, it was found that the 2% Ag/TiO_2 nanoparticles have better potential toward the mineralization of SPF in acidic medium (pH 4), over 90% photocatalytic degradation of SPF achieved in only 100 min.

Co–precipitation method

In this method, the salt solutions of titanium dioxide and silver are mixed together under the effect of a supersaturation induced by a change in experimental parameters like temperature, pH or ionic strength, in a common solvent, where both precursors are soluble in it (Norris et al. 2008). The particles are precipitated in the form of metal hydroxides which, after calcination, form oxides. The growth of the germs is limited either by controlling the concentration of the precursor, the pH, or the temperature. Surfactants or stabilizers can also be used to modify morphology. Hussain et al. (2016) have prepared with success a silver-doped TiO_2 photocatalyst via a co-precipitation method using ethanol as a solvent for

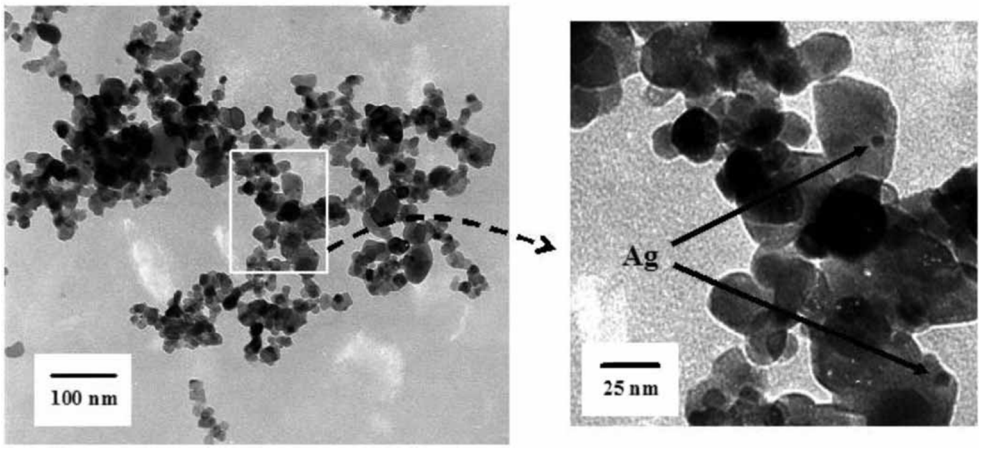

Fig. 9 TEM micrograph of 0.96 wt% Ag/TiO_2 nanoparticles prepared by photo-deposition method (Shokri et al. 2013)

environmental and sensing applications. In a typical procedure, silver nitrate in the presence of potassium hydroxide was added to TiO2–P25 suspension and stirred for 24 h at ambient temperature. The resulting product was centrifuged, washed and dried. With this technique, it was possible to prepare silver doped TiO_2 photocatalyst with a structure similar to that of un-doped TiO_2. In fact, the addition of silver nanoparticles had no change in the anatase–phase structure of the TiO_2. Something else, the silver nanoparticles with FCC crystal structure, uniform spherical shape, and no agglomerates were homogeneously dispersed over the external TiO_2 surface (Fig. 11). Moreover, the resulting photocatalyst shows a low bandgap and higher absorption of light (~ 3 times) compared to pure TiO_2, due to the presence of silver nanoparticles acting as electron scavengers, reducing the electron–hole pair recombination. The obtained Ag/TiO_2 nanocomposite was found to be multifunctional. It can be used either as an efficient photocatalyst for the removal of both model organic dyes and dyes collected from the textile industry under UV irradiation or as a sensitive electrode for electrochemical detection and degradation of H_2O_2.

What are the advantages of Ag/TiO_2 photocatalyst?

After presenting the different synthesis methods used for producing silver-doped TiO_2 nanoparticles, this part aims to highlight the advantages of doping TiO_2 semiconductor with silver nanoparticles and to understand how these nanoparticles improve the photo-conversion yield and allow the extension of TiO_2 light absorption to the visible light. However, before launching this, it was found necessary to start by reminding first the mechanism of pure TiO_2 semiconductor photoactivity. The fundamental mechanisms of TiO_2 photocatalysis have been repeatedly discussed in many studies (Ni et al. 2007; Pelaez et al. 2012; Diaz-Uribe et al. 2018; MiarAlipour et al. 2018; Nadimi et al. 2018; Nasr et al. 2018). As described in the introduction part, heterogeneous photocatalysis is based on the principle of generating an electron–hole pair during the absorption of a semiconductor, customarily TiO_2, photon energy equals or exceeds its bandgap ($h\nu \geq E_g$). The electron–hole pairs generated take part in a series of oxidation/reduction reactions with species adsorbed on the TiO_2 surface, as shown in Fig. 12, to generate

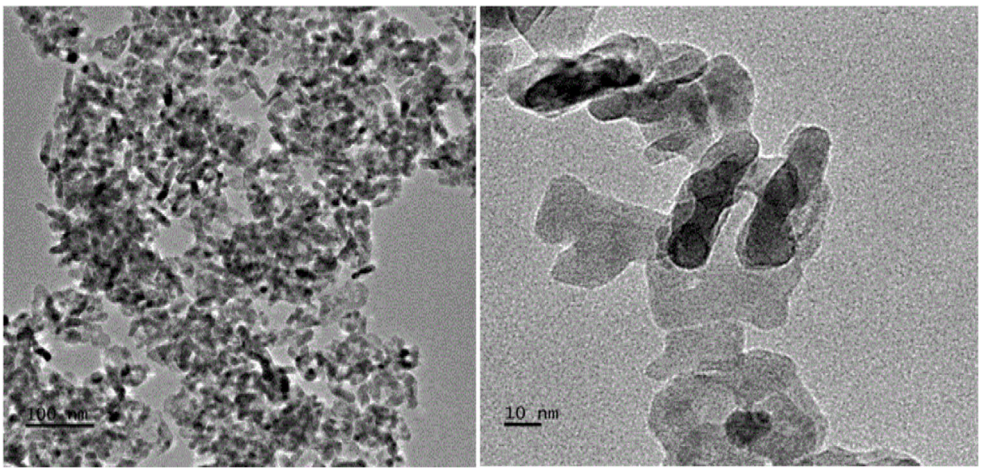

Fig. 10 TEM micrographs of 2% Ag/TiO_2 nanoparticles (Kulkarni et al. 2018)

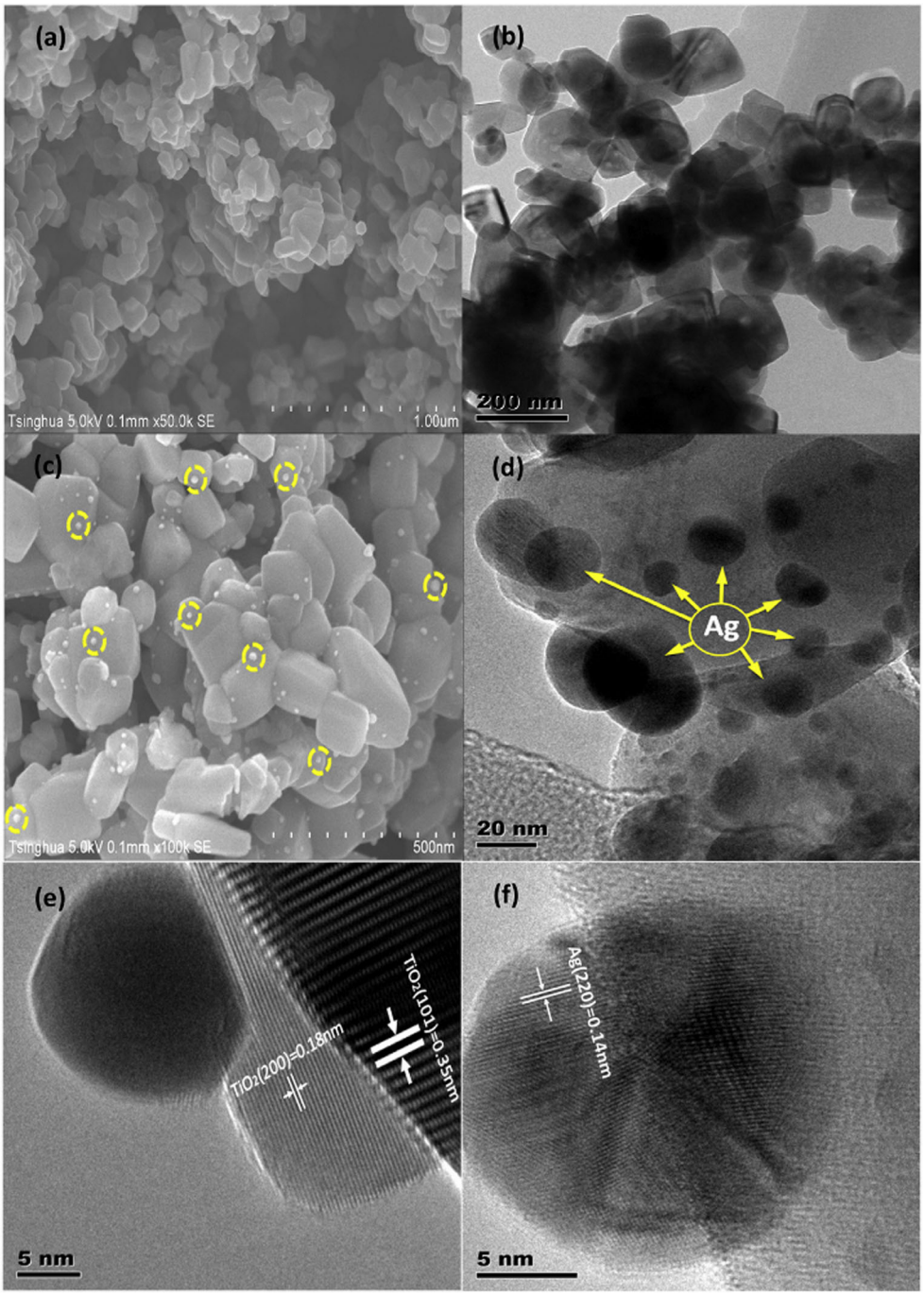

Fig. 11. **a**, **b** FESEM and TEM images of pure anatase TiO_2, **c**, **d** Ag/TiO_2 (**d**) TEM, **e**, **f** HRTEM images of Ag/TiO_2 nanocomposite and Ag NPs, respectively (Hussain et al. 2016)

highly reactive oxygen species (ROS). These species react with the adsorbed organic compounds or microorganisms present on the TiO_2 surface leading to their decomposition to harmful compounds such as H_2O and CO_2. However, the shorter lived of electrons and holes often reduce their availability for participation in redox reactions. Moreover, the recombination phenomenon is manifested by the release of energy in the form of unproductive heat or light accompanied by a decrease in the process efficiency. The challenge faced is how to increase the lifetime of electrons and holes in TiO_2 photocatalyst before recombination takes place?

Doping TiO_2 with silver nanoparticles is one of the successful approaches proposed to retard the electron–hole pairs recombination and to shift the light absorption range of TiO_2 photocatalyst toward visible light (Harikishore et al. 2014; Noreen et al. 2019). Several studies reported that the presence of silver nanoparticles enhances TiO_2 photocatalytic activities by two distinct features:

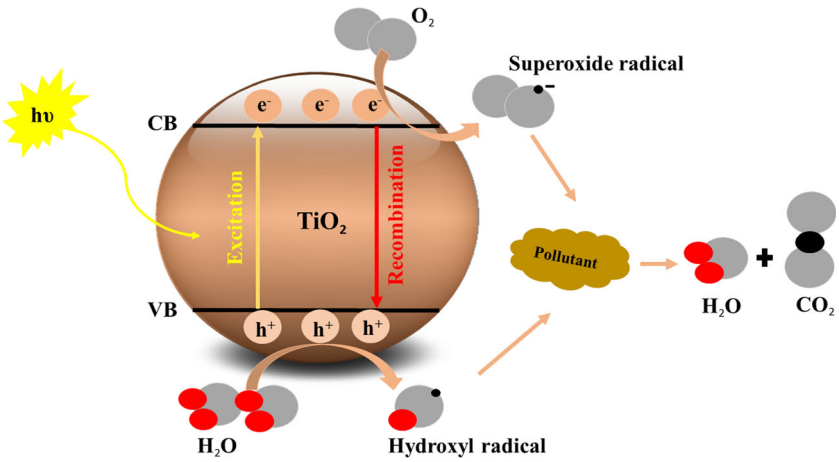

Fig. 12 TiO_2 semiconductor photocatalysis principle

1. Acting as an electron trap and capture electrons transferred from the conduction band of TiO_2 semiconductor and transfer these electrons to oxygen, which in its turn converts them into superoxide radicals. Photogenerated holes in the valence band remaining on the TiO_2 react with water molecules and help in the formation of hydroxyl radicals. These free radicals are effectively used for pollutants photocatalytic oxidation and bacteria inhibition (Fig. 13) (Din et al. 2017).
2. Creating surface plasmon resonance (SPR) effect which extends the light absorption to the visible light region and improves TiO_2 photocatalytic efficiency simultaneously (Khana et al. 2015; Furube and Hashimoto 2017). Besides, due to their excellent antibacterial properties with or without the use of light activation, silver nanoparticles enhance synergistically the TiO_2 antipathogenic activities and extend its implementation in the biomedical field broadly (Prakash et al. 2019).

Ag/TiO_2 ternary nanocomposites

Despite all merits previously presented, photocatalytic water treatment, assisted by nanosized nanoparticles, shows some drawbacks that limit its practical applications. In fact, the difficulty of separation and recovery of Ag/TiO_2 nanoparticles from aqueous solutions during the photocatalytic process, in addition to the difficulty to apply on continuous flow systems pushed many researchers to immobilize silver-doped TiO_2 nanoparticles on different materials such as carbonaceous nanomaterials (Chen et al. 2014; Lee et al. 2015; Noreen et al. 2019), magnetic materials (Tedsree et al. 2017; Mehrvar 2018; Scott et al. 2019), polymers, and biopolymers materials (Singh et al. 2014; Rtimi et al. 2015; Santhosh and Natarajan 2015; Jbeli et al. 2018; Li et al. 2018b; Haghighat et al. 2019). This section aims to present the different supports used to overcome the problems related to the recovery of the Ag/TiO_2 nanoparticles after the photocatalysis process.

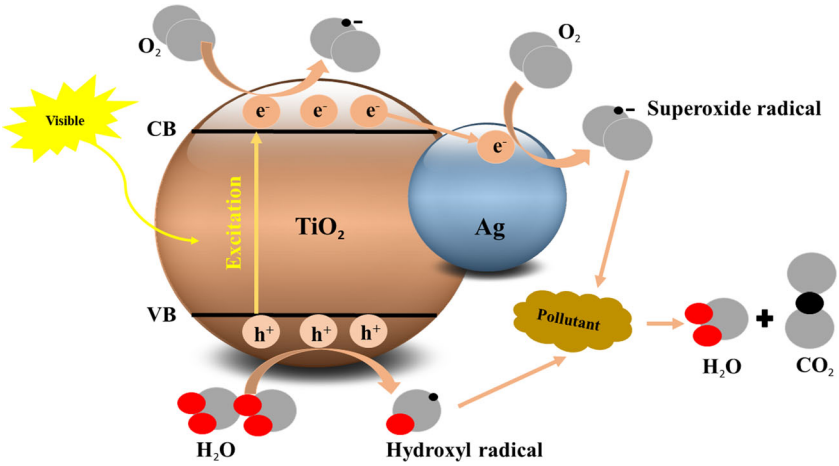

Fig. 13 Photocatalytic activity of Ag/TiO_2 photocatalyst

Carbonaceous nanomaterials

Recently, carbonaceous nanomaterials have attracted great interest to immobilize Ag/TiO_2 nanoparticles, due to their extraordinary and tunable properties including physical, chemical, thermal, mechanical, and electronic properties (Srikanth et al. 2017). Chen et al. (2014) have prepared a ternary composite based on silver, titanium dioxide, and graphitic carbon via an easily accessible route for methyl orange and phenol photodegradation, as illustrated in Fig. 14. The TiO_2 nanoparticles were first synthesized via a hydrothermal method. Silver nanoparticles were then deposed on the TiO_2 surface via a photo-deposition process, in the presence of polyethylene glycol (PEG) as a reducing agent and tracked by g–C_3N_4 coating on Ag/TiO_2 microspheres. Graphitic carbon nitride was chosen thanks to its narrow energy bandgap and visible light absorption (Zang et al. 2015; Zhou et al. 2019a). TEM images of the resulting microspheres (Fig. 15) shown that the silver nanoparticles, with a size of 5 nm were successfully photodeposited as an interlayer between the TiO_2 as an inlayer and g–C_3N_4 as an out layer, acting as an electron–conduction bridge. UV–Vis results showed an enhancement of visible-light absorption of g–C_3N_4/Ag/TiO_2 compared to pristine TiO_2, leading to higher photocatalytic activity under visible-light irradiation. This improvement is generally related to the surface plasmon resonance (SPR) of silver nanoparticles and the synergetic combination of g–C_3N_4, Ag and TiO_2 microspheres.

Zhao and his coauthors (Tio et al. 2016) have successfully prepared an Ag/TiO_2/graphene composite through a combination of sol–gel and solvothermal methods with improved visible light methylene blue photodegradation. The prepared nanocomposite possessed the benefits of TiO_2, silver, and graphene oxide. Reduced graphene oxide (rGO), with its unique properties, enhances the adsorptive capacity of TiO_2 while silver nanoparticles act as an electron trapper to prevent electron–hole recombination. XRD analysis demonstrates the crystallographic structure of the ternary nanocomposite Ag/TiO_2/rGO revealing the presence of the peak assigned to anatase TiO_2 phase, reduced graphene oxide (rGO) and silver nanoparticles, which confirm the successful preparation of the ternary nanocomposite Ag/TiO_2/rGO. Moreover, SEM micrographs and TEM images (Fig. 16) confirmed the good dispersion of both silver and TiO_2 nanoparticles into the reduced graphene oxide (rGO) sheets. The authors have also investigated the photocatalytic activity of the Ag/TiO_2/rGO ternary nanocomposite by the photodecomposition of methylene blue (MB) dye, under visible light irradiation. The nanocomposite exhibited excellent photocatalytic activity toward methylene blue dye under visible light compared to TiO_2 (Degussa–P25), Ag-doped TiO_2, and TiO_2/rGO, due to the localized surface plasmon resonance effect, resulting from the electron transfer from silver to graphene.

Similar results were obtained by Zhang et al. (2017) using Ag–TiO_2/rGO nanocomposite for Rhodamine B removal and CO_2 reduction under visible light. The resulting nanocomposite was found to be able to remove 99.5% Rh B dye after 40 min and reduce CO_2 to methanol and ethanol under visible light irradiation due to its fine particle size, high homogenous distribution, and larger specific surface area, while the TiO_2 nanoparticles were found incapable of photocatalysis. These results confirmed the role of both silver and rGO in extending the TiO_2 photo-response to the visible light region and reducing the recombination phenomena of photogenerated electron hole pairs. The authors have also proposed the mechanism that can be involved during the photodegradation of Rh B dye (Fig. 17). The photogenerated electron from the conduction band of TiO_2 photocatalyst can be easily trapped by graphene and transferred to silver nanoparticles, retarding concurrently the separation of electron–hole pairs and at the same time, reacting with other surface molecules to form highly strong oxidizing superoxide ions and hydroxyl radicals, which are

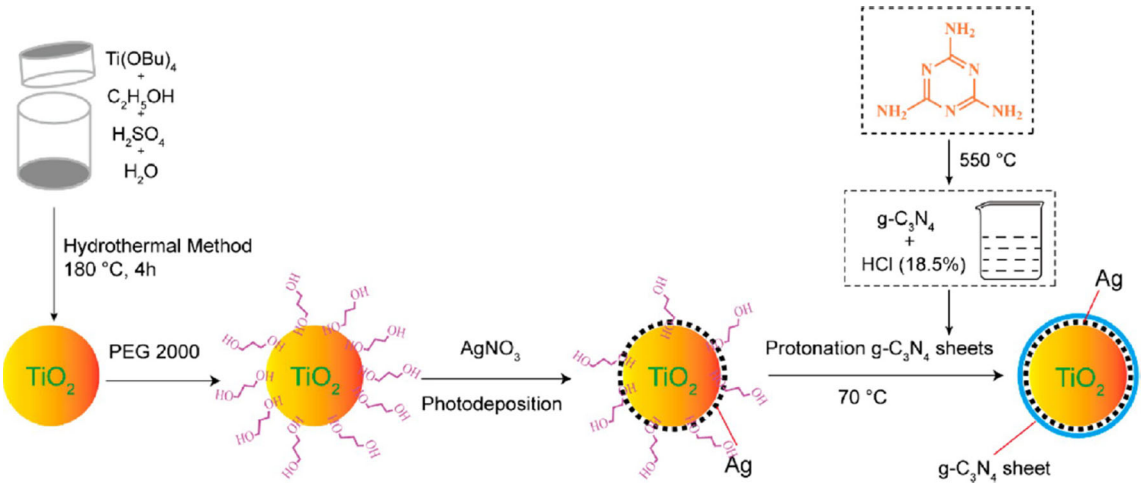

Fig. 14 Ag/TiO_2–g–C_3N_4 microspheres preparation (Chen et al. 2014)

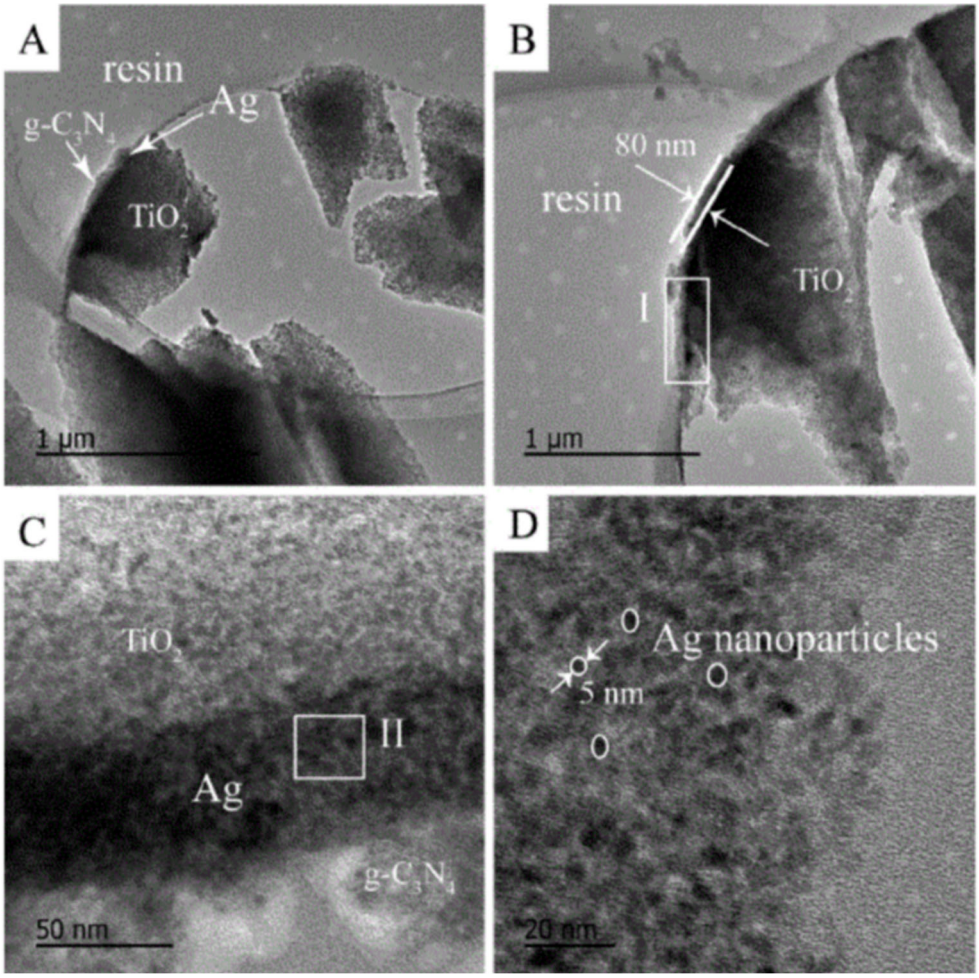

Fig. 15 TEM images of the g–C_3N_4 /Ag/TiO_2 microspheres photocatalyst (Chen et al. 2014)

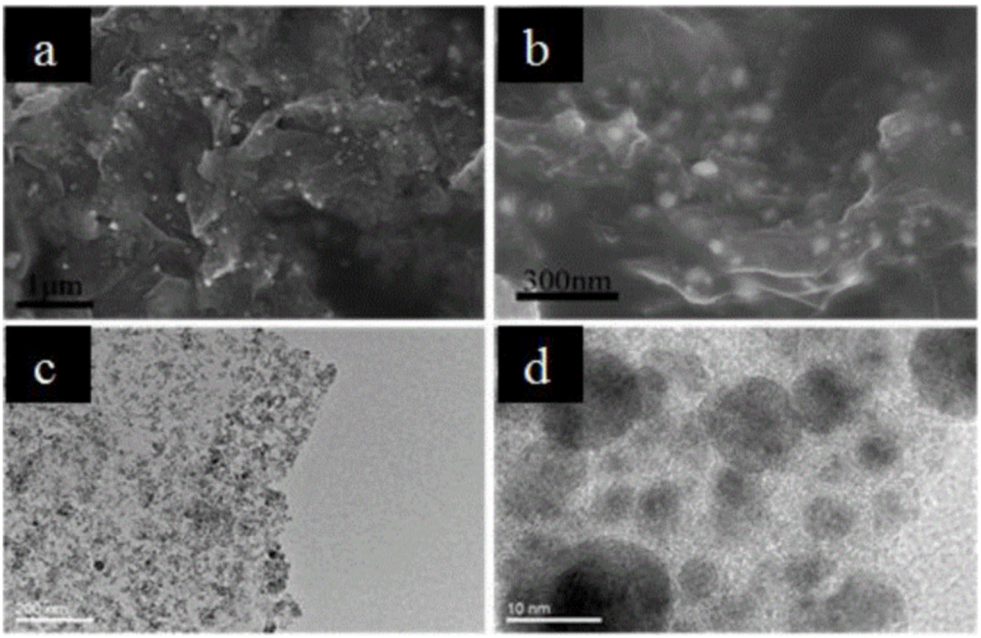

Fig. 16 **a**, **b** SEM microphotographs and **c**, **d** TEM images of Ag/TiO_2/rGO (Tio et al. 2016)

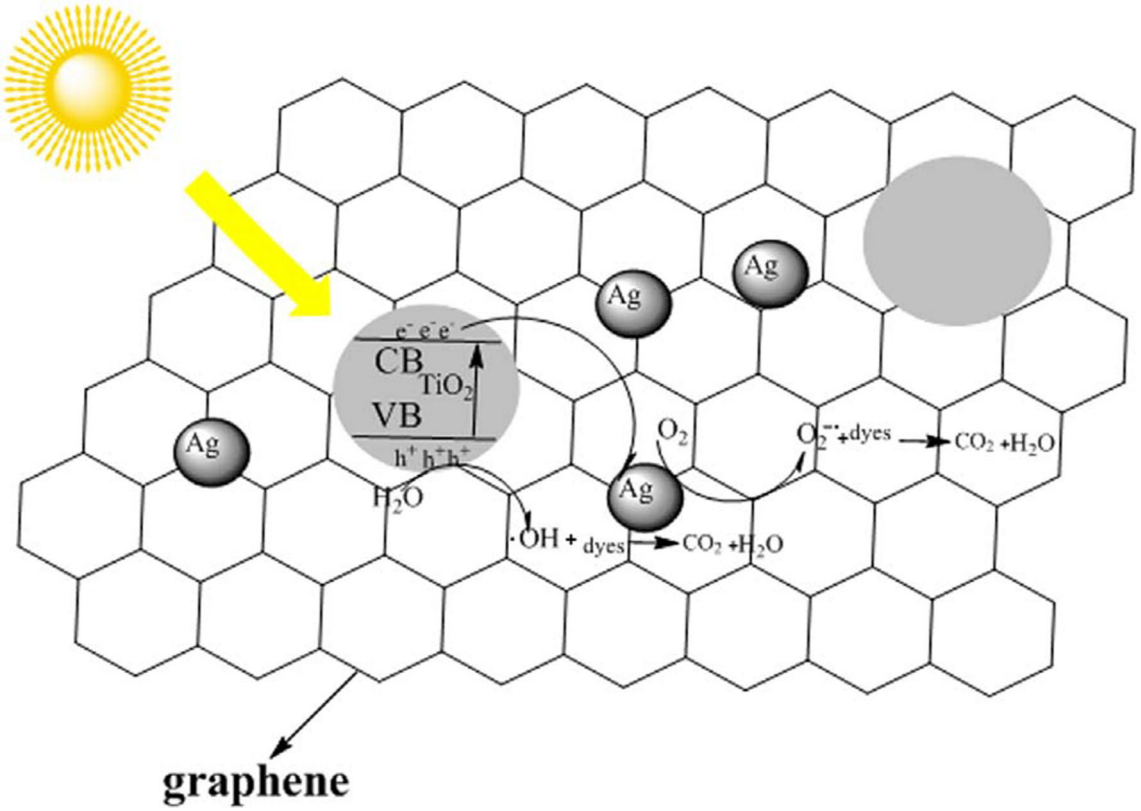

Fig. 17 The possible photocatalytic mechanism for dye degradation (Zhang et al. 2017)

responsible for the exceeding dye degradation under visible light irradiation.

Magnetic materials

Considering the difficulty of separating silver-doped TiO_2 nanoparticles from aqueous solutions after treatment, especially in a continuous flow, an effective strategy has been proposed. It consists to combine Ag/TiO_2 photocatalyst with magnetic materials such as transition metals or their oxides to facilitate the recovery and recycling of the nanosized photocatalyst by applying an external magnetic field. The obtained photocatalyst merges distinct multiple functions in one nanostructure: (1) the high photocatalytic efficiency of the TiO_2 nanocrystals, (2) the ability of Ag nanoparticles to extend the photocatalytic activity of the system to the visible region, and (3) the magnetic properties of magnetic materials to facilitate the recovery of the photocatalyst after treatment.

Ferric sulfate or chloride, manganese chloride, cobalt chloride, nickel chloride, ferrous sulfate, or chloride are the most magnetic species used to synthesize silver-doped TiO_2 photocatalysts, due to their multi-functionality for adsorption, reduction, and complexation (Zhan et al. 2014; Chang and Wu 2019). Tedsree et al. (2017) have prepared magnetically recoverable nanocomposites based on silver-doped titanium dioxide and iron oxide via three step methods, namely coprecipitation, sol–gel, and chemical decomposition as follow: magnetite Fe_3O_4 nanoparticles synthesized by co-precipitation of Fe^{2+} and Fe^{3+} ions in basic solution, are coated with TiO_2 nanoparticles and lastly decorated with silver nanoparticles in colloidal suspension via chemical decomposition. The prepared magnetic nanocomposites show uniform homogeneity, strong magnetic properties, narrower bandgap, and better photocatalytic activity to degrade methylene blue under visible light irradiation with doable recycle process, due to the bi-effect of silver nanoparticles on the improvement of charges separation and the inhibition of the recombination of photogenerated electron–hole pairs owning to its strong electron catch capability. Newly Ag and Fe co-doped TiO_2–MWCNT photocatalyst, with high surface area, and superparamagnetic performances was prepared by Neto and his co-authors (Bellato et al. 2017) for the removal of phenol from aqueous media. The advantages of this composite lie in the fact of combining the high photocatalytic efficiency of TiO_2 photocatalyst, the benefits of silver nanoparticles previously cited, the magnetic properties of iron, and the electronic and adsorption properties of multi-walled carbon nanotubes. The preparation method consists firstly in the deposition of silver nanoparticles on the commercial TiO_2 surface via a photodeposition technique, in which silver ions are converted to silver nanoparticles under UV irradiation, co-doped with iron oxide and coated on multi-walled carbon nanotubes as

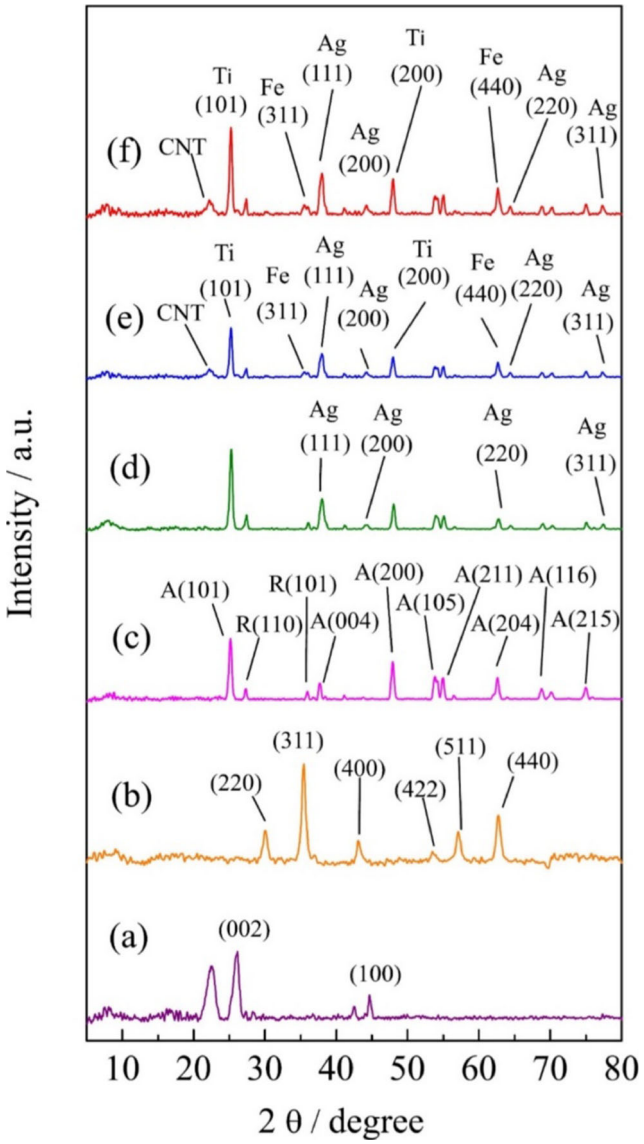

Fig. 18 X–ray diffraction patterns of **a** MWCNT, **b** iron oxide, **c** TiO_2, **d** Ag–TiO_2, **e**, **f** Fe–Ag/TiO_2–MWCNT before and after photocatalysis process (Bellato et al. 2017)

support. The obtained composite has greater specific surface area due to the introduction of MWCNT in the photocatalysts that avoids the particle agglomerations, which was approved with SEM images. The TiO_2/Ag/iron nanoparticles were homogenously dispersed along the carbon nanotubes surface. XRD analysis demonstrates the crystallographic structure of the composite and reveals that the Fe/Ag co-doped TiO_2 and MWCNT amalgamation is probably a physical process. The diffractogram of the resulting photocatalyst was not amended compared to pristine compounds (Fig. 18). Raman spectrum of the synthesized photocatalyst indicated the strong interaction between the TiO_2–Ag, iron oxide nanoparticles, and multi-walled carbon nanotubes. Furthermore, light absorption spectra in the Ag–Fe co-doped TiO_2–MWCNT photocatalyst shifted to longer wavelengths in the visible range, due to the creation of a new molecular orbital arising from the electronic interactions betwixt the molecular orbitals of both titanium and iron oxides. Moreover, the material after reuse presents similar morphology and structure to that of the original material, confirming the high chemical stability of the elaborated composite.

The authors have also evaluated the efficiency of the prepared composite on the photodegradation of phenol in an aqueous solution. The Fe–Ag/TiO_2–MWCNT photocatalyst participates in fully phenol degradation with an initial concentration of 50 mg L^{-1} and partially total organic carbon removal after 180 min, due to the synergetic effect of each component of the composite. The photoactivation steps of the composite photocatalyst and phenol photodegradation are summarized in Fig. 19. Indeed, the electron promoted to the conduction band can be trapped by silver nanoparticles and transferred to the multi-walled carbon nanotubes, increasing the charge separation, preventing the recombination phenomena and participating in the regeneration of superoxide ion radicals ($O_2^{\bullet-}$). Likewise, the iron oxide present in the photocatalyst is able to act as photoinduced holes and electrons chasers, improving the photocatalytic activity even after ten consecutive cycles. Thus, the interplay between the composite components increases the transport of electrons, prevents the recombination of charges, and allows the use of visible radiation in the phenol photodegradation.

Polymers and biopolymers

Polymers were applied as an effective support to immobilize silver-doped TiO_2 nanoparticles owing to their low-cost, chemical inertness, mechanical strength, low density, and high durability (Singh et al. 2013; Zhao et al. 2018; Berber 2020; Mabroum et al. 2021). Generally, loading polymer with silver-doped TiO_2 nanoparticles is done in most cases by solution casting technique. The TiO_2 nanoparticles doped with silver are prepared according to the technique previously mentioned in "Ag/TiO_2 synthesis methods and characterization" section followed by their dispersion on the polymeric matrix via a casting method. In this context, Ag/TiO_2 nanoparticles were successfully coated onto the external surface of polyacrylonitrile (PAN) fibers via an easily dip-coating technique (Liu et al. 2016). SEM images demonstrate that the PAN fibers before coating shows a smooth surface with some grooves, while after dip coating process, their surface becomes coarse and bumpy, which illustrates the existence of Ag/TiO_2 NPs on the surface of PAN fiber (Fig. 20). The prepared composite showed dazzling photoresponse under visible light region, excellent reusability after 5 cycles and more or less acceptable photocatalytic activity toward methylene blue (MB) dye.

Ansari et al. (2014) have evaluated the photocatalytic efficiency of Ag–TiO_2-doped Polyaniline film toward methylene blue dye under visible light. The preparation method consists

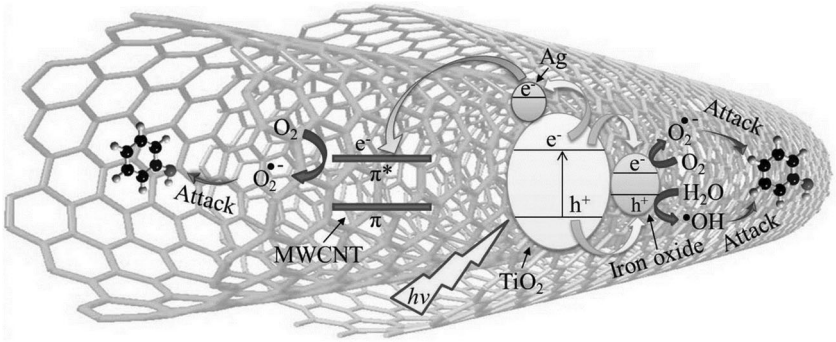

Fig. 19 Proposal of the photocatalytic activation mechanism and phenol degradation (Bellato et al. 2017)

of mixing Ag–TiO_2 nanoparticles with the emeraldine base of polyaniline under magnetic stirring for total dissolution. XRD analysis indicated the co-occurrence of TiO_2 (tetragonal) and silver (FCC) in the Ag/TiO_2@Pani composite, with an average size of 16 and 6 nm, respectively, as two different and distinct materials without interdiffusion (Fig. 21). Furthermore, owing to its higher photoelectric characteristics (good conductivity, and lower charge transfer resistance), the Ag/TiO_2@Pani nanocomposite showed excellent visible light photocatalytic activity toward methylene blue dye with good reusability without any loss in its morphology, structure, and visible light activity, which is advantageous for such application. The authors proposed a mechanism for explaining what actually happened (Fig. 22). In fact, under visible light irradiation, the polyaniline absorbs light to induce a π–π* transition, injecting excited–state electrons into the conduction band of TiO_2 photocatalyst, which reacts with adsorbed molecules to produce strong oxidizing radicals. Furthermore, the equilibrated Fermi level electrons of silver are shot up rapidly into the TiO_2 conduction band via a surface plasmon resonance (SPR) mechanism, leading to more oxidative radicals, enhancing, therefore, the photocatalytic activity of the Ag/TiO_2@Pani photocatalyst.

Biodegradable polymers seem to be a good option for immobilizing Ag/TiO_2 nanoparticles, their unique structure, renewability, biodegradability, abundance, and low-cost make them a source of material with attractive performances (Jawaid et al. 2016; Olivera et al. 2016). An eco-friendly composite based on silver, titanium dioxide, and cellulose scaffold, with different molar ratios of silver were prepared via the combination of both sol–gel and dip-coating processes at room temperature for *Escherichia coli* (*E. coli*) inhibition (Li et al. 2018b). Silver-doped TiO_2, with diameters varying from 30 and 50 nm, were uniformly immobilized over the cellulose surface without agglomerations (Fig. 23). At low ratio of silver, it was found that the nanoparticles exhibited the form of the nanowire (1D), and as the ratio of silver increased, the particles crystallizing in a 3D network, leading to higher antibacterial performances against *E. coli*, where more than 99% were curbed. Chitosan, the second most abundant natural polymer, is another support that is extensively used for the immobilization of Ag/TiO_2 nanoparticles. In this regard, Li et al. (2018a) have successfully prepared silver-doped titania–chitosan (STC) composites for *E. coli*, *Staphylococcus aureus*, and *Pseudomonas aeruginosa* inhibition using an inverse emulsion cross-linking reaction. SEM micrographs demonstrate that the composite shows spherical micron particles, differing greatly from chitosan, which presents an irregular sheet-like structure and dimensional inhomogeneity. X-ray photoelectron spectroscopy confirmed the co-existence of both metallic silver (Ag^0) and silver ion (Ag^+) on the Ag-doped TiO_2–chitosan composite surface due to the oxidation of a little amount of silver nanoparticles on the composite surface as a consequence of the storage process. The presence of the TiO_2 on the composite surface was confirmed by the appearance of the peaks associated with the splitting of Ti $2p_{3/2}$ and Ti $2p_{1/2}$. The composite UV/Vis absorption spectra showed a red shift in the absorption edge and strong

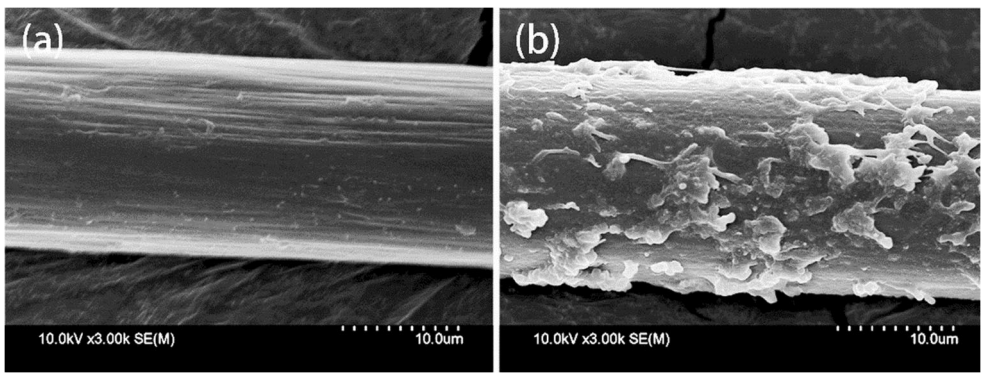

Fig. 20 SEM microphotographs: **a** PAN fiber, **b** Ag/TiO2-coated fiber (Liu et al. 2016)

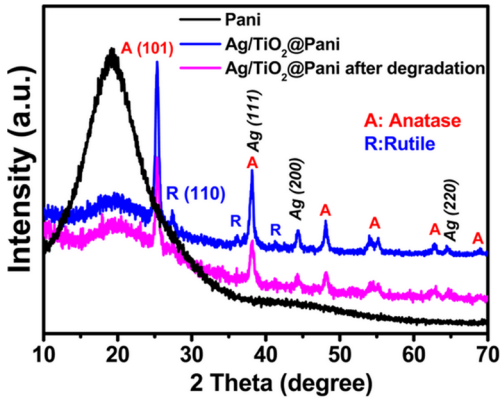

Fig. 21 XRD patterns of Pani and Ag/TiO_2@Pani nanocomposite film before and after MB degradation (Ansari et al. 2014)

absorption in the visible light range, confirming the role of silver nanoparticles on expanding the photo response of TiO_2 to the visible range. Furthermore, the composite exhibited the best antibacterial activity against both bacteria. The antibacterial mechanism of the silver-doped titania–chitosan composite under visible light conditions will be detailed in the last part of this review.

Ag/TiO_2 photocatalyst for environmental applications

Photocatalytic efficiency of Ag/TiO_2 photocatalyst

Owing to its promising photocatalytic activity, Ag/TiO_2 photocatalyst has shown an important role in the removal of a large range of pollutants in aqueous solutions under UV and visible light. That includes anionic and cationic dyes, organic and pharmaceutical compounds, metal ions, and bacteria. As discussed above, the enhancement of the photocatalytic performances of Ag/TiO_2 photocatalyst is attributed to a combination of the increase in the lifetime of the photogenerated electron–hole pairs and narrowing of the bandgap and red shift in light absorption. This section aims to present some

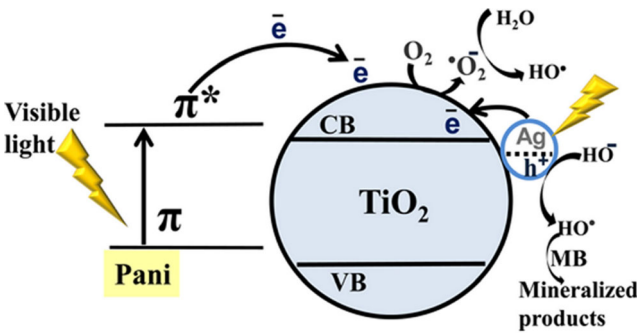

Fig. 22 Proposed mechanism for the degradation of MB by the Ag/TiO_2@Pani nanocomposite film (Ansari et al. 2014)

applications of binary and ternary Ag-doped for the removal of environmental contaminants from sewage.

Organic dyes

Removal of dyes from industrial water is the most frequently reported result describing the photocatalytic effectiveness of silver-doped TiO_2 photocatalysts. Organic dyes as a major source of water pollution, are non-biodegradables, toxic, and carcinogenic to both aquatic and human beings (Zhou et al. 2019b). Recently, Çifçi (2016) has evaluated the photocatalytic degradation of methylene blue (MB) and methyl orange (MO) under both UVA and visible light, using Ag-doped TiO_2 photocatalysts. The authors have prepared a series of photocatalyst with different silver ratios ranging between 0.5 and 2% using a sol–gel method to study the influence of silver amount on the Ag-doped TiO_2 photocatalytic performances. It was observed that 1% Ag-doped TiO_2 photocatalyst exhibited higher photocatalytic activity toward both dyes. Photocatalysts with quantities less than 1% do not show any photocatalytic activity enhancement compared to the pure TiO_2, while those with a higher quantity beyond 1% have relatively low activity, due to the shielding effect of silver nanoparticles on the surface, preventing the light penetration. Furthermore, the authors have examined the effect of environmental parameters on the photocatalyst activity, and it was found that pH is the most important parameter that affects the MB decolorization in Ag–TiO_2/UVA process, while initial MO concentration was the most parameter that affects its photodegradation, high MO concentration causes the reduction of light penetration into solution and consequently lower the photocatalytic degradation. Furthermore, the strong objective of this work was to determine the final product resulting from MB and MO photodegradation and evaluate their toxicity.

According to ESI–MS analysis, it was observed that both methylene blue (MB) and methyl orange (MO) were degraded to single ring structure products, namely aminoquinone, benzoquinone, and phenylsulfinate ions, which are subsequently converted at the end of the process to inorganic ions such as carbon dioxide, nitrate, sulfate, water, and chlorine. Likewise, Gupta et al. (2006) have followed the photodegradation of a binary dye mixture, namely crystal violet (CV), and methyl red (MR) as cationic and anionic dyes, respectively under UV irradiation, using silver ion-doped TiO_2 prepared via a liquid impregnation method. The photocatalyst obtained does not present any adsorption properties toward both dyes. However, irradiation of the Ag^+-doped TiO_2 photocatalyst with a UV fluorescent lamp (16 W) eliminates more than 99% of the mixture on only 90 min of irradiation. This is due to the silver ions that act as electrons scavengers. The Ag^+ reduces the recombination of charges and favors oxidation by producing more reactive oxygen

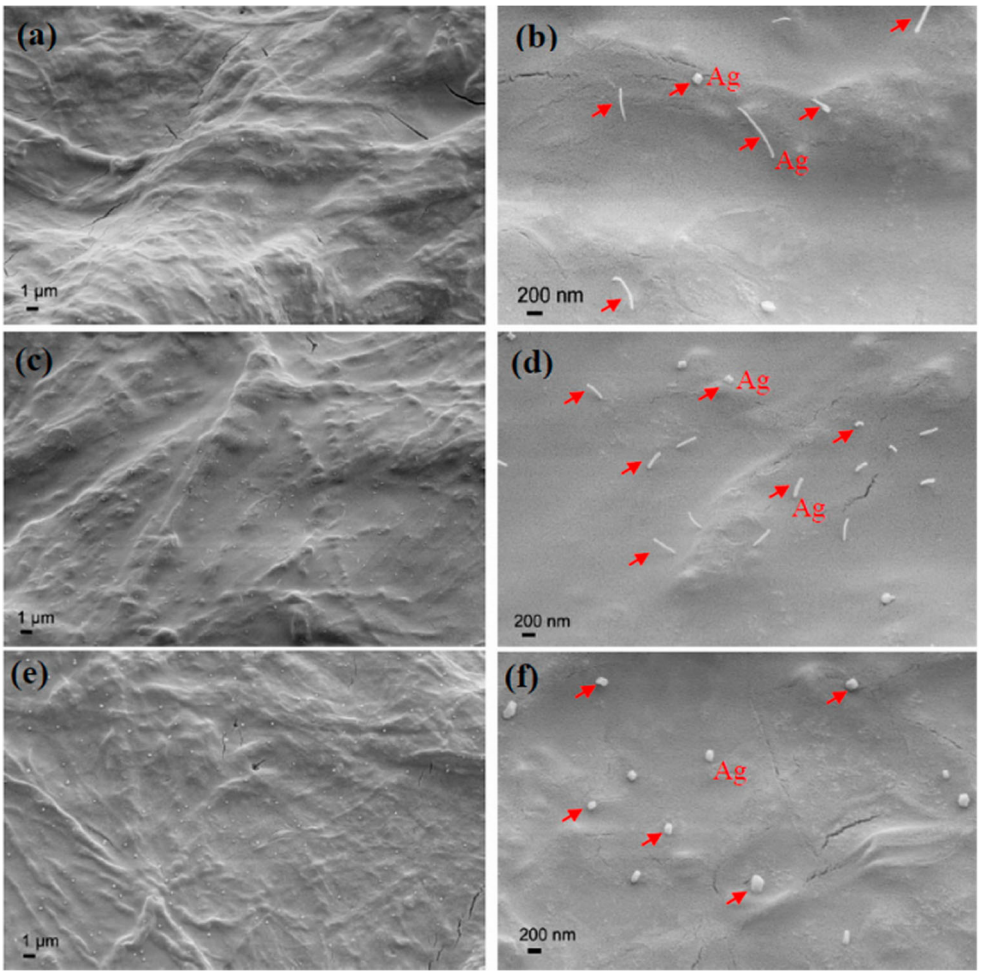

Fig. 23 SEM images of Ag/TiO_2/cellulose composite films at lower and higher magnification: **a**, **b** 0.2 mol%, **c**, **d** 1.0 mol%, **e**, **f** 5.0 mol% ratio of Ag to TiO_2 (Li et al. 2018b)

species. The authors have also studied the effect of pH and different interfering substances on both dyes photodegradation. It was observed that pH does not have any effect on CV degradation, unlike the MR dye. A remarkable decrease in the percentage of degradation is observed beyond this pH value. This decrease may be attributed to the repulsion phenomena between the dye molecules and the Ag^+-doped TiO_2 particles charged negatively at pH exceeding 6.6 (pH_{pzc}=6.6). The effect of different interfering substances on photocatalytic activity of Ag^+-doped TiO_2 photocatalyst toward both dyes showed that the photodegradation of CV was influenced only by cation ions as it is a cationic dye, whereas the degradation of MR was inhibited by Cl^-, Ca^{2+}, and Fe^{2+} ions while other ions did not influence it. This can be attributed either to the filter effect resulting from the UV light adsorption by salts or to the competitive trapping of the oxidizing species. A magnetically separable and recyclable Ag-supported magnetic TiO_2 photocatalyst was applied for the degradation of methyl orange (MO) in aqueous solutions under visible light irradiation and different experimental conditions (Jin et al. 2018). XRD results confirmed the presence of the three expected constituents and the absence of impurities. The average diameter of the resulting magnetic photocatalyst was 60–100 nm. According to XRF spectroscopy, the TiO_2, Fe_3O_4, and Ag contents of the nanocomposite were 47.5%, 50.1%, and 2.4%, respectively. Moreover, photocatalytic tests showed that the synthesized $Ag/TiO_2/Fe_3O_4$ composite achieved a faster and more efficient MO removal under visible light than pristine TiO_2 or silver-doped TiO_2 at the same experimental conditions, due to its narrow bandgap that participates to increase its potential in applications involving visible light.

Pharmaceutical compounds

Silver-doped TiO_2 photocatalysts were also used for the removal of pharmaceutical compounds from wastewater, in view of their complex structures and harmful effects on both human health and the environment (Sophia et al. 2016). Pazoki and his co-authors (2016) investigated the photocatalytic efficiency of Ag/TiO_2 photocatalyst produced using a photodeposition method for the removal of dexamethasone (DXM) in aqueous matrices under both UV and visible light. XRD analysis confirmed the co-existence of both anatase and

rutile phases with a ratio of 80% and 20%, respectively after the deposition of silver on TiO_2 nanoparticles, which can play an interesting role in photocatalytic performances. For optimizing the efficiency of Ag-doped TiO_2 photocatalyst under both UV and visible light irradiations, the authors have evaluated the effect of several parameters, namely the initial photocatalyst dose, initial pollutant concentration, temperature, pH, and hydrogen peroxide addition on the photocatalytic performances of the prepared photocatalyst. Indeed, it was showed that the increase of the photocatalyst amount leads to an enhancement of its photocatalytic efficiency toward dexamethasone, while, increased photocatalyst concentration beyond an optimal concentration produced adverse effects. This can be explained by the fact that a higher concentration of the photocatalyst could block visible light to excite the photocatalyst, which produces a small amount of $O_2^{\bullet-}$ and $OH^{\bullet}$ radicals that are responsible for the dexamethasone photodegradation. Similar results were found concerning temperature, the efficiency of photocatalytic degradation increased as the temperature increases until an optimal value, and beyond this value, the efficiency decreases. Indeed, rising temperature until 35 °C, leads to an enhancement in the photocatalyst capacity owing to the oxidation rate increase at the interface between the photocatalyst and the solution. Whereas beyond this reaction temperature, the adsorptive capacities associated with the organics and dissolved oxygen may be reduced leading to a reduction in the DXM degradation rate. As well, it was observed that at acidic pH, the Ag/TiO_2 photocatalyst present higher photocatalytic activity, which is absolutely normal, since the Ag/TiO_2 is charged positively and DXM is charged negatively, unlike alkaline pH, where both molecules are positively charged, resulting to a decrease on photocatalytic degradation efficiency. Moreover, an increase in DXM concentration allows to a decrease in the reaction rate under both UV and visible light. In addition, it was found that the photodegradation of DXM was sensible to the variation of H_2O_2 dosage, an increase in hydrogen peroxide dosage from 10 to 20 mg/L led to an increase in the photodegradation efficiency, while a further increase above 15 mg/L produced adverse effects. The photodegradation mechanism of the pharmaceutical wastes is similar to that of dyes. According to the authors, the DXM photodegradation is initiated by the attack of methylene groups by $OH^{\bullet}$ radicals generated by the photocatalyst, leading to the formation of ketone group due to the mineralization of carbon atoms. Radicals attacks also attacked the ring double bonds, causing the release of water molecules and CO_2 (Rasolevandi et al. 2019).

Phenol compounds

Phenol compounds are considered as one of the most organic pollutants discharged into the environment causing unpleasant taste and odor of drinking water (Oblak et al. 2018). Owing to its properties and structure, silver-doped TiO_2 photocatalyst has shown higher photocatalytic efficiency toward phenolic compounds. In this context, a visible light active Ag/TiO_2 nanoparticle photocatalyst was prepared and tested for phenolic degradation (Wahyuni et al. 2017). The resulting photocatalyst showed better photocatalytic activity toward phenolic molecules degradation under visible light illumination than the undoped TiO_2. The authors evaluated the effect of Ag particles size, Ag loading, and reaction time. It was observed that the TiO_2 containing small nano-sized Ag particles showed better photocatalytic degradation than those containing larger Ag particles. Indeed, lower particle size enhances the active surface area of nanoparticles, which results in higher photocatalytic efficiency. Moreover, Ag loading and reaction time affected the phenol photodegradation. Photocatalyst with Ag concentration equal to 1500 mg/L present the best photocatalytic performance. Shet and his co-authors (Shet and K 2016) have successfully synthesized silver-doped titanium dioxide nanoparticles for the degradation of phenol under visible light. In order to check whether the degradation of phenol was caused by photocatalysis, the authors followed the phenol removal as a function of time under different experimental conditions (dark or light, with or without the photocatalyst …etc.). It was observed that 13% of phenol was decomposed by light due to the photolysis phenomena, 20% under dark in the presence of the photocatalyst, which may attribute to the phenol adsorption on the photocatalyst surface and 93% in the presence of the photocatalyst and under solar light irradiation, confirming the photocatalytic activity of the prepared photocatalyst. The phenol photodegradation was influenced by different operational parameters including, initial phenol concentration and photocatalyst amount, pH, and many others. For example, the photocatalysis activity of the photocatalyst was much higher in the acidic medium than neutral or alkaline ones due to the charge state change as a function of pH. Above the value of pH_{pzc}, both TiO_2 and phenol surfaces are negatively charged, making the adsorption of phenol molecules difficult, and consequently weakened photocatalytic performances. The phenol degradation was also improved by increasing the photocatalyst amount until reaching an optimal concentration and then decreased. This can be explained by the fact that with increasing the amount of the photocatalyst, the number of active sites in the solution increases, promoting adsorption of phenol on the external photocatalyst surface, while exceeding the concentration considered optimal, the photocatalyst blocks the light penetration to its surface, reducing consequently its photocatalytic capacity. The phenol degradation rate was also decreased by increasing the initial concentration of phenol. This curtailment may be attributed to the oxidizing radical amount generated, which probably is not sufficient to attack all the phenol molecules present in the

aqueous medium. In addition, in order to avoid prevent the problems accompanying the nanoparticles recovery in continuous flow systems, both batch reactor and fluidized bed reactor with immobilized Ag-doped TiO_2 nanoparticles were used for photocatalysis of phenol for large-scale applications, and it was found that fluidized bed reactor operating in batch mode with recycling was more suitable for the photodegradation of the phenolic compound compared to that carried out in a batch reactor, opening new possibilities for future research avenues.

Real wastewater

Treating real wastewater containing a mixture of organic compounds, suspended solids, nitrogen and phosphorous compounds, heavy metals, and microorganisms (Schaider et al. 2014; Mankiewicz-Boczek et al. 2017) by photocatalysis process in general and Ag/TiO_2 as photocatalyst, in particular, is one of the important subjects. Silver-doped TiO_2 photocatalysts are also shown their higher photocatalytic efficiency toward simulated and real wastewater (Badawy et al. 2014; Chaker et al. 2016; Tio et al. 2017; Mehrvar 2018; Gomes et al. 2019). Chaker et al. (2016) have synthesized Ag-doped mesoporous TiO_2 photocatalyst using a simple chemical method developed for the disinfection of real wastewater from a sewage treatment plant in the North of France, spiked with various toxic compounds, namely toluene, carbamazepine, methylene chloride, cholesterol, caffeine … etc. At optimal conditions, Ag doped mesoporous TiO_2 was able to totally pollutants mineralization after 3 and 4 h under UV and visible light irradiations, respectively. Similarly, Rodríguez–Méndez et al. (Tio et al. 2017) have prepared Ag/TiO_2 nanoparticles with different concentrations of silver via a sol–gel method for disinfection of real wastewater from an activated sludge biological treatment and containing pathogenic bacteria, known by their strong resistance. It was found that the increase of silver amount in the photocatalyst has no effect in the disinfection tests; small amount of silver shows similar results to those obtained by adding a higher silver concentration. The $1\%Ag/TiO_2$ photocatalyst at 0.2 g/L presents higher performances toward the fecal and total coliform microorganisms such as *Escherichia coli*, *Yersinia enterocolitica*, *Yersinia pestis*, and *Yersinia pseudotuberculosis* after 3 h of solar photocatalysis disinfection process. Nevertheless, its photocatalytic performances were very low against persistent microorganisms including *Kiebsiella pneumoniae ATCC 700603*, *Shigella flexneri ATCC 12022*, *Salmonella typhimurium ATCC 14028*, and *Pseudomonas aeruginosa.* Such microorganisms present strong resistance to the hydroxyl radicals attacks due to the excretion of lactose. Badawy and his collaborators (2014) have investigated the effect of Ag/TiO_2 photocatalyst with different ratios of Ag for the treatment of simulated hospital wastewater under sunlight. This wastewater is a mixture of five pharmaceuticals compounds, namely chloramphenicol, diclofenac, salicylic acid, sulfamethoxazole, and paracetamol. Compared to pristine TiO_2, the Ag/TiO_2 photocatalyst presents high photocatalytic capacity in degrading the pollutants in question, due to the better charge separation caused by silver nanoparticles. Moreover, it was found that the 0.1% Ag/TiO_2 presents higher photocatalytic performances than photocatalysts with higher concentrations of silver, confirming the results previously found by other works, concerning the effect of silver concentration on the photocatalytic performances of the photocatalyst. In addition, the authors have studied the effect of key parameters such as pH, the concentration of photocatalyst and calcination temperatures on the pharmaceutical compound degradation. It was observed that the reaction rate increased with increasing photocatalyst concentration, while an excess causes a dwindle in the reaction rate due to the screening effect phenomenon, already discussed. As well, best efficiency was obtained when the initial pH of simulated hospital wastewater was around 5 and given the fact that each of the studied pharmaceutical compounds has its own pKa value, the photocatalyst has an affinity toward some compounds more than others, for example, the photodegradation rate of diclofenac with high electron density was better and faster than that of sulfamethoxazole with the lower one. In fact, the higher the electron density, the higher the photocatalytic activity. Similar results were found by Mehrvar (2018) using an $Ag/TiO_2/Fe_2O_3$ photocatalyst for the degradation of confectionery wastewater. Additionally, to its interesting physicochemical properties that lead to higher photocatalytic activity under both UV and visible light, the photocatalyst exhibited also super-magnetic properties that facilitate its recuperation after the process by applying only an external magnetic field. Despite the examples presented above, it seems that the use of Ag-doped TiO_2 for the disinfection of real wastewater has not been sufficiently explored, since it contains a wide range of organic and inorganic compounds, heavy metals, and bacteria. Optimizing the degradation processes of real wastewater is difficult because of the complexity of this matrix requiring more reactive oxygen species and a lot of time.

Bactericidal potential of Ag/TiO_2 photocatalyst

For many decades, silver nanoparticles have been the subject of several studies because of their unique and interesting biological, physico-chemical, and optical properties (Durdu 2019). They have been exploited for many applications, including health care, consumer, medical, food, and industrial purposes (Calderón-jiménez et al. 2017). However, it was observed that the cytotoxicity of silver nanoparticles toward microorganisms, viruses, and cancer cells can be enhanced when it was incorporated into an Ag/TiO_2 nanocomposite,

due to the synergic effect of TiO_2 and silver nanoparticles (Wang et al. 2012). The exact anti-(bacterial/viral and cancer) mechanisms of Ag/TiO_2 photocatalysts are still not known, but a lot of works have attributed its strong cytotoxicity to the dual synergistic effects of silver ions and reactive oxygen species (ROS), especially hydroxyl free radicals, generated during the photocatalytic process (Ma et al. 2011; Kiwi et al. 2014). This section aims to present the recent progress on Ag/TiO_2 and Ag/TiO_2 based photocatalysts as well as the possible mechanisms involved in the removal of different microorganisms (Gram+ and Gram–), viruses and cancer cells.

Antibacterial activity

The Ag/TiO_2 photocatalysts are efficient to act as biocides to kill bacteria belonging to both Gram-positive (Gram+) and Gram-negative (Gram–) groups such as *Escherichia coli* (Liu et al. 2012), *Staphylococcus aureus* (Zawadzka et al. 2016), *Klebsiella pneumonia* (Ryu et al. 2015), *Staphylococcus epidermidis* (Ramesh et al. 2012), *Pseudomonas aeruginosa* (Gupta et al. 2013), *Bacillus subtilis* (Khan et al. 2013), *Penicillium expansum* (Yaithongkum et al. 2011), and many others. Size, shape, and silver concentration are the major factors influencing the antibacterial activity of silver-doped TiO_2 nanocomposites and determining their interaction behavior with cells (Yu et al. 2011; Bahadur et al. 2016; Muflikhun et al. 2019). Ag/TiO_2 photocatalysts, with smaller particle sizes (with diameters below 10 nm) exhibit effective higher bactericidal activity against bacterial species than those with bigger sizes (Frommelt et al. 2019; Dung et al. 2020). The smaller the size, the larger the surface area to come in contact with cells and consequently higher antibacterial activity. It is also stated that the silver amount of the final photocatalyst affects its antimicrobial activity (Dong et al. 2018). Generally, the degradation efficiency decreased when silver content is higher than the optimum concentration. In this context, a series of multifunctional silver-doped titanium dioxide (Ag/TiO_2) nanocomposites with various silver contents (0.5 to 3%) were synthesized by sol–gel method for use in antibacterial and antiviral applications (Moongraksathum et al. 2019). The prepared particles displayed rhomboidal shapes with major and minor axes in the ranges of 12–32 nm and 3–8 nm, respectively. TEM images demonstrate that the silver nanoparticles with a diameter ranging from 1 to 3 nm were uniformly deposited on the surfaces of the TiO_2 particles (Fig. 24A). Moreover, the antibacterial activity of the prepared photocatalyst was tested against *E. coli*. Modified TiO_2 with 1 wt% of silver exhibited the highest antibacterial effectiveness compared to pure TiO_2 (Fig. 25B), more than 99.99% of *E. coli* bacteria was inhibited after 60 min of UVA irradiations, due to the higher production rate of reactive species generated by the photocatalyst, which accumulate near the cell membranes of bacteria, resulting in the leakage of the intracellular components causing their death.

Li et al. (2018a), as mentioned in "Polymers and biopolymers" section have successfully prepared silver-doped titania–

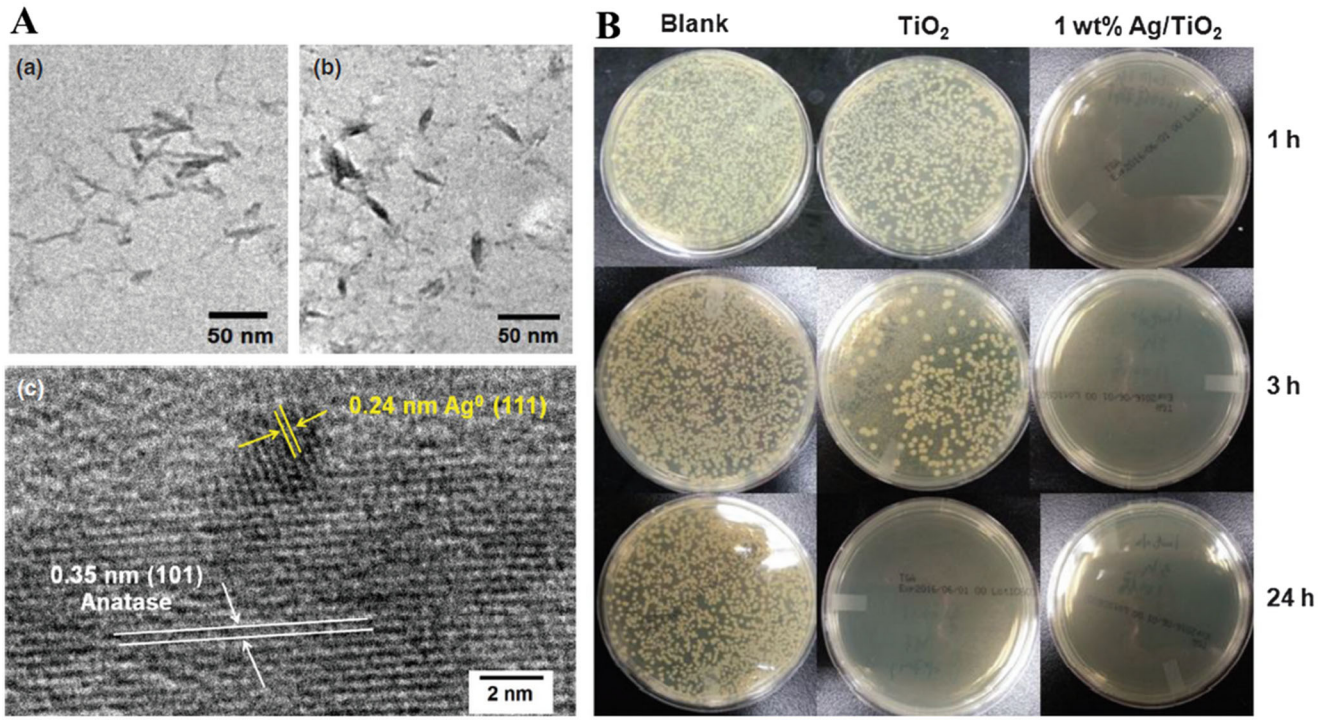

Fig. 24 **A** TEM images of (a) TiO_2 and (b) 1%Ag/TiO_2; (c) HRTEM image of 1%Ag/TiO_2, **B** Antibacterial effectiveness against *E. coli* after 1, 3, and 24 h of UVA irradiation (Moongraksathum et al. 2019)

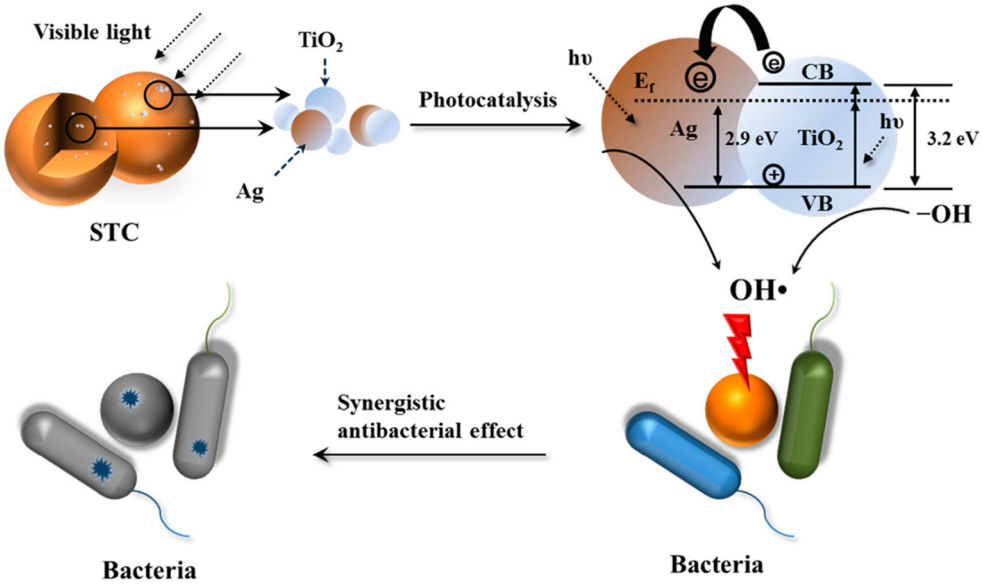

Fig. 25 Antibacterial mechanisms of Ag–TiO_2 photocatalyst under visible light irradiations (Li et al. 2018a)

chitosan (STC) composites for *E. coli*, *S. aureus*, and *P. aeruginosa* bacteria inhibition using an inverse emulsion cross-linking reaction. Preliminary tests showed that the photocatalyst with fine particle size presents the best antibacterial activity against the three bacteria compared to those with huge particle diameter indicating that the antibacterial activity of the photocatalyst is strongly dependent on its particle size. In addition, it was found that the antibacterial activity of the photocatalyst changes related to the species of bacteria. The photocatalyst has the best antibacterial activity against *E. coli* followed by *S. aureus* and finally *P. aeruginosa*, which proves that the photocatalyst behaviors to bacteria change according to the morphology, the shape, and the type of bacteria (Gram+ or Gram–). Indeed, the peptidoglycan cell wall of Gram-negative bacteria is thin compared to that of Gram-positive bacteria, permitting the easy penetration of oxidizing radicals to the cytoplasmic membrane, causing the total death of the bacteria. The mechanism of the inhibition process was proposed to occur through three pathways, (1) the irradiation of the photocatalyst, (2) the generation of active hydroxyl groups, and (3) the attack of the bacterial cell wall by silver ions and hydroxyl radicals leading to cell damage and death (Fig. 25). Similar results were found by Habib et al. (2019) using Ag-doped TiO_2 nanoparticles immobilized on polyamide nanofiltration (NF) membrane against *E. coli* and *B. subtilis* bacteria. The prepared photocatalyst presents higher antibacterial activity toward both bacteria, while it was found that its antibacterial capacity against *E. coli* was greater than *B. subtilis*, due to the different cell wall structure and thickness of peptidoglycan layer in both types of bacteria. The basic structure of bacteria consists of the cell walls, cell membranes, nucleoids, and cytoplasm. Moreover, the cell wall of Gram-positive bacteria is composed of many layers of peptidoglycan as compared to Gram-negative bacteria, which is characterized by a thin peptidoglycan layer charged negatively more susceptible to positively charged Ag/TiO_2 nanoparticles. Moongraksathum and Chen (2017) have studied the antibacterial activity of Ag/CeO_2–TiO_2 coatings against *E. coli* and *S. aureus* bacteria. Compared to pure TiO_2, the Ag/CeO_2–TiO_2 photocatalyst proved effective against both *E. coli* and *S. aureus* under UVA radiation on merely 30 min, not only to the silver nanoparticles released in the aqueous medium known by their high antibacterial activity but also to cerium oxide photocatalyst that participates to the formation of more ROS that accumulates nearby the bacteria external walls involving lipid peroxidation reactions and consequently causing their death (Farias et al. 2018). Similarly, tremendous improvement in bacteria was observed by modifying Ag(3%)-TiO_2 nanotubes with only 3% of FeOx magnetic oxide as a result of the synergistic effect between Ag and Fe that accelerates the bacterial reduction of *E. coli* within 60 min (Mangayayam et al. 2017). To conclude, the antibacterial mechanisms of Ag/TiO_2 photocatalysts are generally considered as a multi-factor, multi-way, and multi target process, where ROS and silver ions (Ag^+) played an interesting role. Other than ROS and silver ions synergy, Rtimi et al. (2013) suggested that the inactivation of *E. coli* bacteria can be also occurred through the interfacial charge transfer between Ag and Ag_2O. Silver in the Ag-TiON composite in contact with air has the tendency to form AgOH, which can easily decompose to Ag_2O. A photo-induced charge transfer from Ag_2O to TiO_2 is implied for the mechanism of interfacial charge transfer between Ag_2O and TiO_2 formed after oxidation.

Antiviral and antifungal activities

Ag/TiO_2 photocatalysts play also an important role as antiviral agents against viruses such as coronavirus, PEDV, TGEV (Kim et al. 2006), HSV–1 (Hajkova et al. 2007), H1N1, and enterovirus type 71 (Moongraksathum et al. 2019). This virucidal efficacy can be attributed to the dual benefits of silver ions released and reactive oxygen species generated on the TiO_2 surface. In this context, Moongraksathum and his co-authors (Moongraksathum et al. 2019) have investigated the antiviral activity of Ag/TiO_2 photocatalyst against influenza A (H1N1) virus and enterovirus type 71, which are involved in the outbreaks of nosocomial transmission by direct or indirect contact with contaminated surfaces or objects. The photocatalyst demonstrated efficient inhibitory activities against the two viruses, influenza A (H1N1) virus and enterovirus type 71, almost 100% of pathogens were killed. The authors suggested that this viricidal efficacy is results from the synergic effect of ROS produced on the TiO_2 surface and silver ions available after their release into an aqueous environment, as already explained in the bacteria case. In fact, silver nanoparticles are capable of adsorbing to cells, and exert their antiviral activity either through their interaction with the viral genome (DNA or RNA) or via inhibiting their viral replication (Zhang et al. 2016a; Calderón-jiménez et al. 2017; Elshamy et al. 2019). Kim et al. (2006) have studied the antiviral performances of Ag/TiO_2, prepared via a sol gel method against coronavirus and found that the obtained photocatalyst presents good antiviral activity toward the virus cell into question. Basically, silver-doped TiO_2 photocatalyst in contact with the virus inhibits the virus multiplication and cell respiration. Basically, silver-doped TiO_2 photocatalyst in contact with the virus inhibits its multiplication and prevents the respiration of the cells, leading therefore to their death. However, due to lack of data, the exact mechanism of antiviral activity of silver-doped TiO_2 nanoparticles still obscure, which requires more efforts in this field.

Anticancer potential

Silver-doped TiO_2 photocatalysts were also played important role in the medical field generally and cancer therapy particularly as an anticancer agent. Ag/TiO_2 nanoparticles were found to be able to kill a wide range of cancer cells, owing to the synergetic effect of both silver nanoparticles and reactive oxygen species (ROS) generated on TiO_2 surface, which plays a veritable role in such applications. Ahamed et al. (2017) have evaluated the anticancer potential of Ag-doped TiO_2 nanoparticles prepared via a sol–gel method and loaded with different amount of silver (0.5–5%), against three types of cancer, namely human lung (A549), human liver cancer (HepG2), and breast cancer (MCF–7). Both the dimethylthiazol diphenyltetrazolium bromide (MTT) and the neutral red uptake (NRU) assays showed that pure TiO_2 did not any impact on the selected human cancers unlike the doped photocatalyst which shows interesting results. The cell viability decreased as the silver concentration in the photocatalyst increased, confirming that silver nanoparticles were unable to wield cytotoxicity on the three types of cancer cells, and the kill cancer cells can be caused by the high quantity of ROS generated by Ag/TiO_2 photocatalyst. The benign nature of the prepared photocatalyst toward two non-cancerous normal cells was also evaluated, and it was observed that the Ag-doped photocatalyst presents no effects on the normal cells, confirming its ability to select the desired cancerous cells and spare normal ones.

The cytotoxicity of Ag/TiO_2 photocatalyst against MCF–7 cell-lines were also studied by Nageswara et al. (2019). Ag/TiO_2 photocatalyst showed concentration-dependent cytotoxic profile in MCF–7 cell lines. It was observed that the percentage of viable cells decreases as the concentration of Ag/TiO_2 nanoparticles increases. This can be explained by the fact that when augmenting the concentration, adsorption of NPs on cell membranes gets easier, leading to enhanced penetration, and facilitating the binding to the DNA bases causing cellular death. The microscopic analysis carried to observe morphological changes showed that the cell proliferation was significantly reduced. Cell shrinkage and cell detachment were also observed (Fig. 26). Lipid peroxidation test showed that the reactive oxygen species (ROS) generated by Ag/TiO_2 photocatalyst are responsible for its cytotoxicity. It was shown also that lipid peroxidation increased substantially with increasing Ag/TiO_2 concentration, due to the generation of ROS in the structure and function of the cell membrane. Similarly, Hariharan et al. (2020) have investigated the anticancer activity of TiO_2 photocatalyst doped with differing silver amounts against lung cancer cell lines (A549). The higher the silver concentration, the lower the cell viability, confirming the results found previously by Nageswara et al. (2019). ROS are the only answerable species on cancer cell death. Bonan and his co-authors (Ferreti et al. 2019) have also investigated the anticancer performances of Ag/TiO_2 nanofibers against oral cancer cells. The Ag/TiO_2 nanofibers cytotoxicity was found dependent on the photocatalyst concentration. Low concentration induces lower anticancer activity, while high photocatalyst concentration shows highly satisfactory results (full prevention of the reproduction and migration of murine AT–84 cells). The authors suggested that the high performance of Ag/TiO_2 nanofibers is presumably the result of the nanoscale size associated with enhanced surface area, super-hydrophilic property, superior surface reactivity, and important ROS generation.

Possible reactors for the scale-up of Ag/TiO_2 photocatalyst

The conception and the design of suitable photocatalytic reactors for environmental scale-up applications remain one of the challenges confronting the majority of photocatalyst materials in various application areas, especially that of wastewater

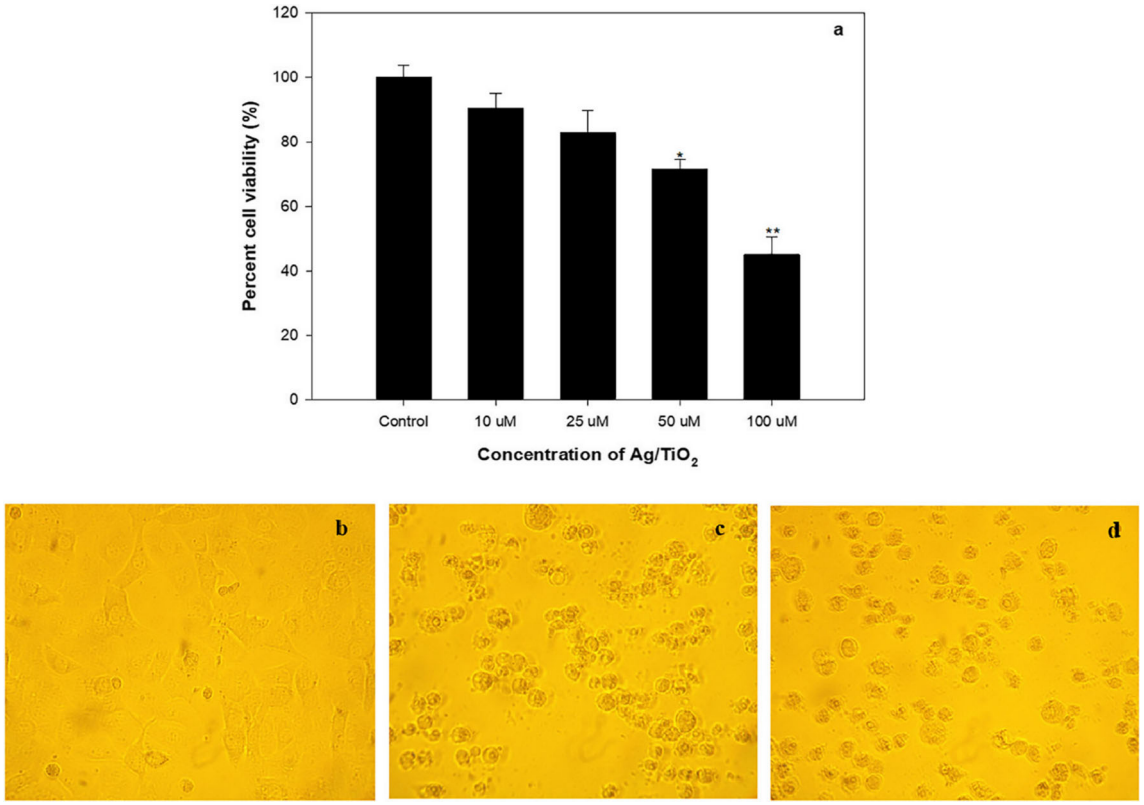

Fig. 26 Cytotoxicity assessment using MTT assay. **a** MCF7 cells exposed to varying concentrations of synthesized Ag/TiO_2 for 24 h. The morphological analysis using phase contrast microscopy **b** untreated control, **c** Ag/TiO_2 50 mM, and **d** Ag/TiO_2 100 mM (Nageswara et al. 2019)

purification. Suspended photocatalysts are usually lost their photocatalytic performances when immobilized into different supports, as a result of the smaller contact area with the pollutants, which make the photocatalysis process more complicated (Belver et al. 2018). Nevertheless, the cost requirements of the post-treatment recovery for small photocatalyst nanoparticles have prompted various researchers to develop new photoreactors with high resolution and interesting properties. In fact, various types and geometries of photoreactors have been used in photocatalytic wastewater treatment including the plate reactor, annular flow reactor, packed-bed reactor, cascade reactor, fixed-bed reactor, etc. (Mazierski et al. 2016; Sacco et al. 2020). The selection of the photocatalytic reactor depends strongly on the experimental conditions, the type of the photon source (artificial or solar radiations), the mode of operation, and the type of the photocatalyst as well (Abdel-Maksoud et al. 2016; Rincón and La Motta 2019). Bibliographic research on large-scale applications of Ag/TiO_2 photocatalysts demonstrates that the number of the investigated, designed, and patented silver-doped TiO_2 photoreactors for wastewater remediation at large-scale applications is still limited (Montalvo-Romero et al. 2018).

Conclusion

This review provides a detailed overview of the current progress on silver-doped TiO_2 photocatalysts through the presentation of different synthetic processes, their physicochemical characteristics, and their ability in degrading a wide range of pollutants from sewage. In fact, notwithstanding that TiO_2 is one of the effective photocatalyst most recommended for the degradation of persistent contaminants, including organic dyes, pharmaceutical compounds, bacteria, and viruses. The quick recombination of the photogenerated charges and the inefficient exploitation of visible light remain the major problems limiting its large-scale applications. Modifying the TiO_2 lattice with noble metals such as silver was found more advantageous to enhance the TiO_2 photocatalytic performances and shift its photo-response to the visible light region. Silver is inexpensive, non-toxic, resistant to corrosion, and practical if scale-up applications are envisaged. In addition, it plays an important role in reducing the recombination of TiO_2 charges. In fact, thanks to their efficiency in trapping the excited electrons at the surface of the

photocatalyst, silver nanoparticles act as an electron acceptor material facilitating electron–hole separation due to the formation of the Schottky barrier, resulting in charge carrier recombination suppression, generating more powerful oxidizing radicals, and leading therefore to higher photocatalytic performances. Thus, research studies carried out in this area demonstrate that the Ag/TiO_2 and Ag/TiO_2-based composites present important textural, chemical, and physical properties compared to the pure TiO_2, which make them more effective for organic pollutants removal and even for real wastewater disinfection. Furthermore, thanks to the synergistic effect of reactive oxygen species and silver ions, the Ag/TiO_2 photocatalysts showed higher antibacterial, antiviral, and anticancer properties against bacteria, viruses, and cancer cells. In addition, it was demonstrated that the synthesis methods and the operational parameters such as pH, temperature, initial concentration of pollutant/bacteria, silver amount, etc. have a significant influence on both photocatalytic degradation and bacteria inhibition, which requires more thoroughness and precision to design new promising reactors with high resolution for industrial applications. Moreover, more efforts should be addressed for a clear understanding of the exact mechanisms involved during the inhibition of bacteria, viruses, and cancer cells with a view that these results are not limited to the ink on the paper, especially with the appearance of new diseases and pandemics as in the case of SARS–CoV–2 (COVID–19). If the silver-doped TiO_2 photocatalysts have shown higher antiviral activity against several viruses as already mentioned, why we did not think about using them against the Coronavirus (COVID–19)? For example, spread thin layers of Ag/TiO_2 nanoparticles on the hospital's surfaces or even on gloves and respiratory masks?

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Declarations

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Consent for publication
Not applicable.

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