Chapter 7
Recent Progress on Novel Ag–TiO_2 Nanocomposites for Antibacterial Applications

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7.1 Introduction

Bacterial disinfection is one of the basic needs for a healthy society, as many diseases are originated from microbes (Deshmukh et al. 2018). Therefore, the scientific community is working to produce new and efficient antimicrobial materials to effectively protect the human body without affecting human lives. Various nanomaterials have been investigated for antibacterial applications, including polymers, metals, and metal oxide photocatalysts and their nanocomposites (Prakash et al. 2018), and this field is growing in search of very effective antimicrobial materials with superior antimicrobial properties under various circumstances (Hoseinnejad et al. 2018; Mukherjee and De 2018).

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Photocatalyst-based nanomaterials have emerged as novel multifunctional materials for multidisciplinary research and applications (Prakash et al. 2018; Singh et al. 2017a, b; Jai et al. 2016). In the field of antibacterial research particularly, photocatalysts such as titanium dioxide (TiO_2)-based nanomaterials have been designed and engineered to enhance their photocatalytic antibacterial functionality (Jai et al. 2016; Prakash et al. 2018). The engineering and tuning of their physicochemical properties enhance their optical properties, including enhanced rate of separation of charge carriers, charge transportation that eventually enhances photocatalytic antibacterial efficiencies (Prakash et al. 2018).

TiO_2 is a material well known for its photocatalytic activity. Since the discovery of its photocatalytic activity in 1972 by Fujishima and Honda (1972), TiO_2 has been used extensively as a photocatalyst material in a variety of fields and applications. It was found that under UV light irradiation, holes (h^+) and electrons (e^-) generated in the valence band (VB) and conduction band (CB), respectively, undergo surface reaction with atmospheric oxygen (O_2) or water (H_2O) molecules, leading to the formation of reactive oxygen species (ROS) (Prakash et al. 2018). The ROS thus generated on the surface of TiO_2 participate in photocatalytic degradation of various organic compounds (Singh et al. 2017a, b). Similarly, TiO_2 exhibits antibacterial activity, resulting in deactivation of bacteria (Jai et al. 2016; Prakash et al. 2018), which was first investigated by Matsunga et al. (1985) in the 1980s. Thereafter, TiO_2 has been extensively used as an antibacterial agent with potent killing ability for several kind of microorganisms under the influence of UV irradiation (Matsunaga et al. 1985, 1988; Prakash et al. 2018; Jai et al. 2016; Maness et al. 1999). In spite of its great potential to be used as an antibacterial or photocatalytic material, TiO_2 has the drawback of fast recombination of UV-generated e^- and h^+ pairs, inhibiting its functionality (Prakash et al. 2018). Also, TiO_2 is a wide bandgap material, which inhibits its potential application in extended visible light of the solar spectrum. However, TiO_2 is the most widely used antibacterial material for reasons of its higher chemical stability, lower production cost, and better availability. It has been of great interest among researchers to improve the antibacterial functionality of TiO_2 materials during the past few decades, and this is still a growing research area with the development of new materials and methodologies (Prakash et al. 2018; Deshmukh et al. 2018).

The antibacterial activity of TiO_2 has been found to be improved by assembling with functional nanomaterials, which also facilitates the charge separation and extends their utilization in visible light for maximizing its practical applications in a wide range. Among various functional nanomaterials, silver nanoparticles (Ag NPs) are widely known as an antibacterial material and have been extensively used in the biomedical field for killing bacteria (Jalali et al. 2016; Yang et al. 2016; Kędziora et al. 2018; Aziz et al. 2014, 2015, 2016, 2019). As compared to TiO_2, Ag shows antibacterial activity without any light activation. In addition, a nanocomposite of TiO_2-based nanomaterials with Ag NPs not only enhances the antibacterial activity under UV irradiation but also extends up to visible light-induced antibacterial activity through formation of a Schottky junction at the interface and surface plasmon resonance (SPR) properties, respectively (Prakash et al. 2018). These nanocomposites

have been studied in a broad range of antibacterial activities for reasons of the better electron transfer properties (charge separation) and visible light-activated antibacterial activities (Jai et al. 2016). For example, Quiñones-Jurado et al. (2014) reported that Ag NP-assisted visible light activity enhanced the antibacterial effect of TiO_2 because of the SPR properties, whereas TiO_2 itself did not show any activity under visible light. The nanocomposites of Ag and TiO_2 have shown complementary enhanced antibacterial effects for both the Ag and TiO_2 nanomaterials. For example, Yaşa et al. (2012) studied the antibacterial effect of Ag NPs and Ag-embedded TiO_2 nanocomposites. It was found that the nanocomposite exhibited greater antibacterial effect with an inhibition zone of 12–13 nm as compared to the inhibition zone of 8–9 nm of Ag NPs. Similarly, Mai et al. (2010) developed Ag–TiO_2 nanocomposites-based antibacterial coating and found that the positive antibacterial activity of TiO_2 showed an enhanced antibacterial effect of Ag as a result of galvanic effect (Cao et al. 2011). Several other factors affect the antibacterial effect of these nanocomposite materials, such as the shape, size, and concentration of the components in the composite. For example, Zhang and Chen (2009) studied the effect of size of Ag NPs in Ag–TiO_2 nanocomposites on their antibacterial activity. Ag NPs of various sizes were produced in Ag–TiO_2 nanocomposites, and Ag NPs of less than 3 nm showed complete inhibition in bacterial growth of *Escherichia coli*, attributed to the small size of the Ag NPs and the unique structure of the TiO_2 NPs. Deshmukh et al. (2018) studied the effect of concentration of Ag NPs anchored on TiO_2 nanocrystals for antibacterial activity under visible and UV light irradiation against *Staphylococcus aureus* and *E. coli* bacterial strains, reporting excellent antibacterial effect along with the dynamics of their antibacterial action. Similarly, Li et al. (2017a) demonstrated higher antibacterial effect with inhibition rate of more than 99% against these bacterial cells using Ag NPs-loaded TiO_2 cotton. Jalali et al. (2016) investigated antibacterial functionality of Ag NPs, Ag–TiO_2 NPs, and also NPs immobilized in a silane sol-gel matrix. The Ag–TiO_2 NPs exhibited better antibacterial response, as compared to Ag NPs only, against Gram-negative rather than Gram-positive bacteria. The Ag–TiO_2 NPs showed excellent antibacterial performance even when embedded in a silane matrix for a longer period, attributed to the slower release of Ag^+ from this nanocomposite.

These results show that the antibacterial materials based on the Ag–TiO_2 system could be very efficient for antibacterial activities because of the enhanced optoelectronic properties in the nanocomposite form. In this chapter, we review the latest advances in this field with emphasis on the mechanisms of their antibacterial action and details of various factors influencing their antibacterial activities.

7.2 TiO_2 and Its Antibacterial Activity

As we discussed in the previous section, TiO_2 is widely known for its photocatalytic activities along with antibacterial applications under the excitation of UV light because of its wide bandgap. Under the influence of UV light irradiation, e^- and h^+

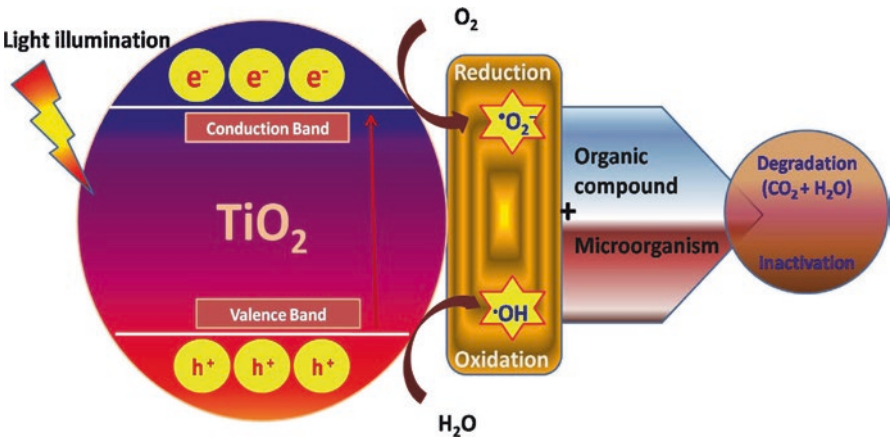

Fig. 7.1 Schematic showing photocatalytic action of TiO_2 nanomaterials under UV irradiation. As a result of illumination, reactive oxygen species (ROS) ($\bullet O_2-$,$\bullet OH$, H_2O_2) are generated and react with organic molecules and microorganisms on the surface of TiO_2 nanoparticles (NPs). (With permission from Prakash et al. 2018)

are generated in CB and VB, respectively, which react with water and oxygen molecules, leading to the formation of ROS (Fig. 7.1) (Prakash et al. 2018). These ROS, produced as a result of photocatalytic reactions, exhibit strong oxidizing behavior towards organic molecules, showing strong photodegradation activities (Prakash et al. 2018).

Similarly, when these ROS interact with bacteria or any other living organisms, the cell membranes of the bacteria or living organisms are damaged, causing the death of the cell (Prakash et al. 2018). Several ROS such as ·OH and $\cdot O_2$ are produced on the surface of TiO_2. However, ·OH is produced in the majority that effectively takes part in the photocatalytic activity of photodegradation and antibacterial effect (Joost et al. 2015). When interacting with the bacterial surface, TiO_2 causes photooxidation of the cellular components such as oxidation of plasma membrane phospholipids (Maness et al. 1999; Kiwi and Nadtochenko 2004; Joost et al. 2015). The antibacterial mechanisms of TiO_2 nanomaterials have been extensively investigated, suggesting that during antibacterial action first ROS damage the cell membrane, leading to leaking of the cellular components and oxidation, followed by complete inactivation of the cell as shown in the schematic of Fig. 7.2 (Liou and Chang 2012).

Maness et al. (1999) showed inactivation of *E. coli* bacterial cells under UV irradiation of TiO_2 as a result of lipid peroxidation of phospholipid within the cell membrane through ROS attack, leading to damaging of the cell respiratory system; eventually the cells died. Similarly, damage of DNA caused by the formation of H_2O_2 ROS under UV irradiation of TiO_2 material has been reported to be responsible for cell death (Hirakawa et al. 2004). Similarly, Sunada et al. (2003) proposed the photokilling antibacterial action mechanism of TiO_2 for *E. coli* bacteria with similar conditions and explained the process of the photokilling mechanism based

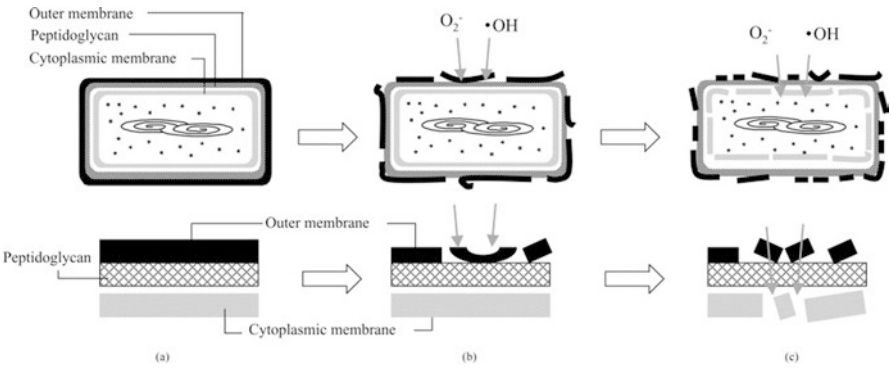

Fig. 7.2 (**a**–**c**) Schematic photokilling action mechanism in *Escherichia coli* on TiO_2 film. For clarity, the part of cell membrane affected by photoirradiation has been magnified. (With permission from Sunada et al. 2003)

on the structural differences of the cell walls in the bacteria. However, it was found that the excellent antibacterial activities of TiO_2-based nanomaterial were reported mainly under the influence of UV light irradiation, and no more, or poor, antibacterial effects were observed with irradiation of longer wavelength (Prakash et al. 2018; Joost et al. 2015) because of the wide bandgap of TiO_2 (bandgap is 3.03 and 3.20 eV for rutile and anatase phases, respectively) (Prakash et al. 2018). Various methods have been used to improve the antibacterial activity of TiO_2 under UV light irradiation and extend its antibacterial capability into the visible light region for maximum applicability. Recently, Guo et al. (2017) demonstrated that annealing of TiO_2 in the presence of metals introduced some defects that were attributed to the antibacterial activity, and also showed visible light absorbance without production of any ROS. On the other hand, Liu et al. proposed that the formation of a surface hetero-junction of different facets on polycrystalline TiO_2 promoted better charge separation and exhibited excellent antibacterial activities through ROS generation on the surface, leading to the inactivation of microbes (Liu et al. 2017). The formation of nanocomposites with Ag NPs is one of the best strategies for improving the antibacterial activity of TiO_2 because Ag NPs also show antibacterial effect as well as extending the applicability of TiO_2 into visible light (as discussed in the next sections).

7.3 Ag NPs and Their Antibacterial Activity

Metallic NPs are interesting nanomaterials to the scientific community as their properties at nanoscale can be tuned by engineering their shape and size, with potential utilization in several industries including biotechnology. These NPs have also been used in antibacterial and other medical applications (Patil and Kim 2017; Prakash et al. 2018). Recent developments in the biomedical field show that NPs are

being used in many medical treatments to provide a better platform for fighting several diseases (Prakash et al. 2018). Particularly, Ag NPs have been widely used for their excellent antibacterial action towards various bacteria and other microorganisms because of their large surface-to-volume ratio and their unique physiochemical properties and toxic nature (Prakash et al. 2018; Aziz et al. 2016; Prasad 2014). Extensive research has been carried out on the antibacterial action of Ag NPs but the exact mechanism of this antibacterial action is not very clear, with different researchers holding different views. In some cases, the mechanism of antibacterial action depends on the kind of bacteria, their size, or the concentration of the Ag NPs. It has been reported that smaller Ag NPs can make sufficient contact on the bacterial cell wall, resulting in better antibacterial action. However, all bacteria are not the same and differ in their chemical composition and structure, thus showing a different response when contacting Ag NPs. For example, the antibacterial action mechanism of Ag NPs towards Gram-positive and Gram-negative bacteria is different because of their different cell wall structure and composition. Gram-positive bacteria have a thick cell wall as compared to Gram-negative bacteria, with many layers of peptidoglycan polymer (Prakash et al. 2018). This structural difference in the cell membrane of these bacteria affects the permeability of Ag NPs or Ag ions for further antibacterial action. The mechanism also depends on the type of interaction when Ag NPs come into contact with the bacterial cell wall. For instance, Ag^+ interacts more efficiently with Gram-negative bacteria, changing the cell membrane by leaking into the cell wall and thus affecting the respiratory activities of the cell. Particularly, Ag NPs interact with phosphorus and sulfur in the bacterial cell membrane and other intercellular components, such as DNA bases and proteins, affecting the various bacterial activities and leading to its death (Joshi et al. 2018; Prasad and Swamy 2013). The various mechanisms of antibacterial action of Ag NPs and Ag^+ are shown in the schematic of Fig. 7.3 (Patil and Kim 2017). In a recent article, Verma et al. (2018) reported the antibacterial activities at molecular level with a detailed mechanism of the in vitro cytotoxicity effect of green synthesized Ag NPs against various cells. They demonstrated that the cytotoxicity effect was attributed to the variable interaction of the cell components with Ag NPs, followed by oxidative stress leading to cell death (Aziz et al. 2019). Similarly, Prema et al. (2017) reported that reductive decomposition of various cell components caused by the interaction of Ag NPs led to death of the cells.

The unique and fascinating electrical, optical, physical, and chemical properties of these NPs has led to their utilization in a wide range of applications such as catalysis, sensing, environmental, and biomedical uses, including antibacterial actions (Prasad et al. 2017, 2018). For example, noble metal NPs such as Ag and Au NPs are interesting nanomaterials that gained the attention of researchers of all fields, as already mentioned, because of their unique physiochemical and optoelectronic properties. These unique properties result from their SPR properties, which arise from the collective oscillation of free electrons on their surface (Fig. 7.4) (Singh et al. 2017a). The optical properties of these NPs can be refined by tuning their SPR properties by engineering their shape, size, and surrounding environment. Effects of these factors on SPR properties of noble metal NPs are reported in many

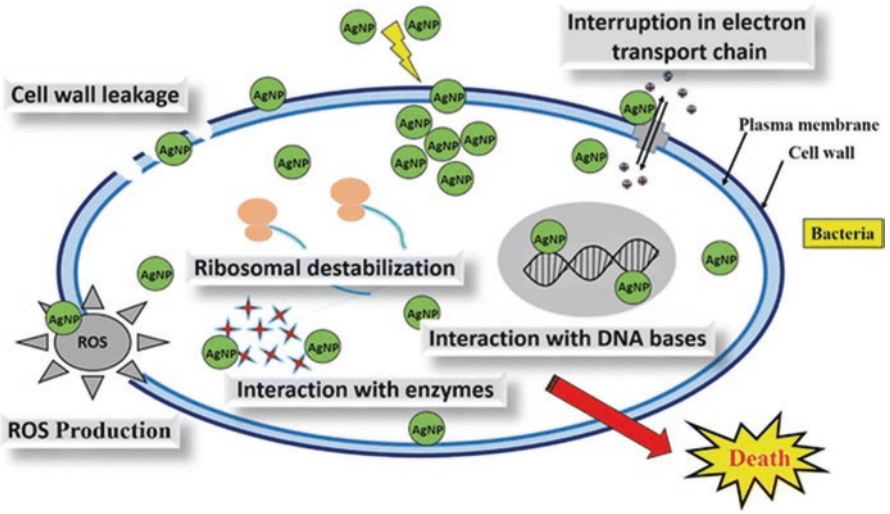

Fig. 7.3 Mechanisms of antibacterial activity for Ag NPs are diagrammatically represented. (With permission from Patil and Kim 2017)

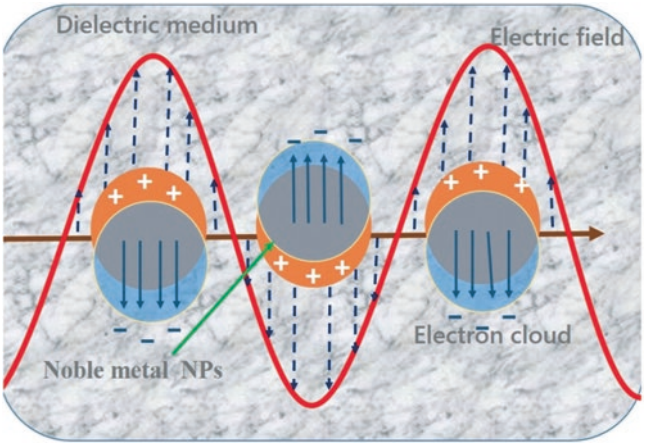

Fig. 7.4 Schematic representation of collective oscillations of surface electrons in response to incoming electromagnetic irradiation for noble metal NPs. (From Singh et al. 2017a)

recent reviews (Prasad et al. 2016; Singh et al. 2017a; Prakash et al. 2018). As discussed in the preceding section, TiO_2 is one of the most used antibacterial materials but has limited antibacterial application because of its wide bandgap. These noble metal NPs have been used extensively to enhance the visible light absorption properties of TiO_2 nanomaterials through SPR absorption.

Another advantage is that these plasmonic NPs form a Schottky barrier at the interfaces with TiO_2, acting as electron-trapping centers that inhibit the recombination

of e^- and h^+ pairs, facilitating the oxidation and reduction reaction at the surface and producing ROS (Prakash et al. 2018). Therefore, the nanocomposite of Ag NPs with TiO_2 not only extends the application of TiO_2 into visible light but also enhances antibacterial activity from the synergic antibacterial activities of both (Prakash et al. 2018; Jai et al. 2016). The enhanced antibacterial activities of Ag–TiO_2 nanocomposites and the mechanism of their antibacterial action are discussed in the next section, with special emphasis on the engineering of their optical properties and antibacterial applications.

7.4 Ag–TiO_2 Nanocomposites: Mechanism and Antibacterial Applications

As already mentioned, TiO_2 is used widely for photocatalyst as well as antibacterial material, and extensive research has been carried out in different conditions (Li et al. 2017b). Also, its wide bandgap means TiO_2 is UV light activated and its photocatalytic antibacterial activities occur only under UV irradiation. The major drawback in this case is the fast recombination of photo-generated e^- and h^+ pairs, causing less efficient photocatalytic activity (Jai et al. 2016; Prakash et al. 2018). Therefore, visible light activation of TiO_2 is essential for proper utilization of its photocatalytic and hence antibacterial activities because sufficient visible light is present in the solar spectrum compared to UV light. Thus, not only are issues of fast recombination of charge carriers overcome but also additional improved physiochemical properties for multifunctional applications are available. Making nanocomposites with noble metals is one of the best strategies to extend the photocatalytic activity of TiO_2 to visible light (Fig. 7.5) (Wilke et al. 2018; Prakash et al. 2018).

The major advantage of combining noble metals with TiO_2 is the formation of the Schottky barrier at the interfaces with TiO_2, acting as an electron-trapping center that inhibits the recombination of e^- and h^+ pairs, facilitating the oxidation and reduction reaction at the surface and producing ROS under UV light irradiation. This combination also provides visible light-activated composite materials with enhanced optical properties that exhibit antibacterial activity not only under UV-visible light irradiation but also in dark conditions, that is, without light activation, from SPR absorption (Au/Ag) or antibacterial activity (Ag) (Fig. 7.5) (Wilke et al. 2018; Prakash et al. 2018).

In particular, composites of TiO_2 with Ag are most suitable for enhanced antibacterial activities of TiO_2-based nanomaterials. Ag not only enhances the optical properties of TiO_2 to improve its photocatalytic activities from its SPR properties but also synergistically enhances its antibacterial activities as an antibacterial agent. As Ag is also known as a good antibacterial material that works without any light activation, therefore its composites with TiO_2 (which antibacterial property is limited to UV activation) extend its implementation in the biomedical field broadly with or without use of light activation. In complementarity, in Ag–TiO_2 nanocomposites, TiO_2 serves as the base matrix for Ag NPs for better dispersion on the surface, which

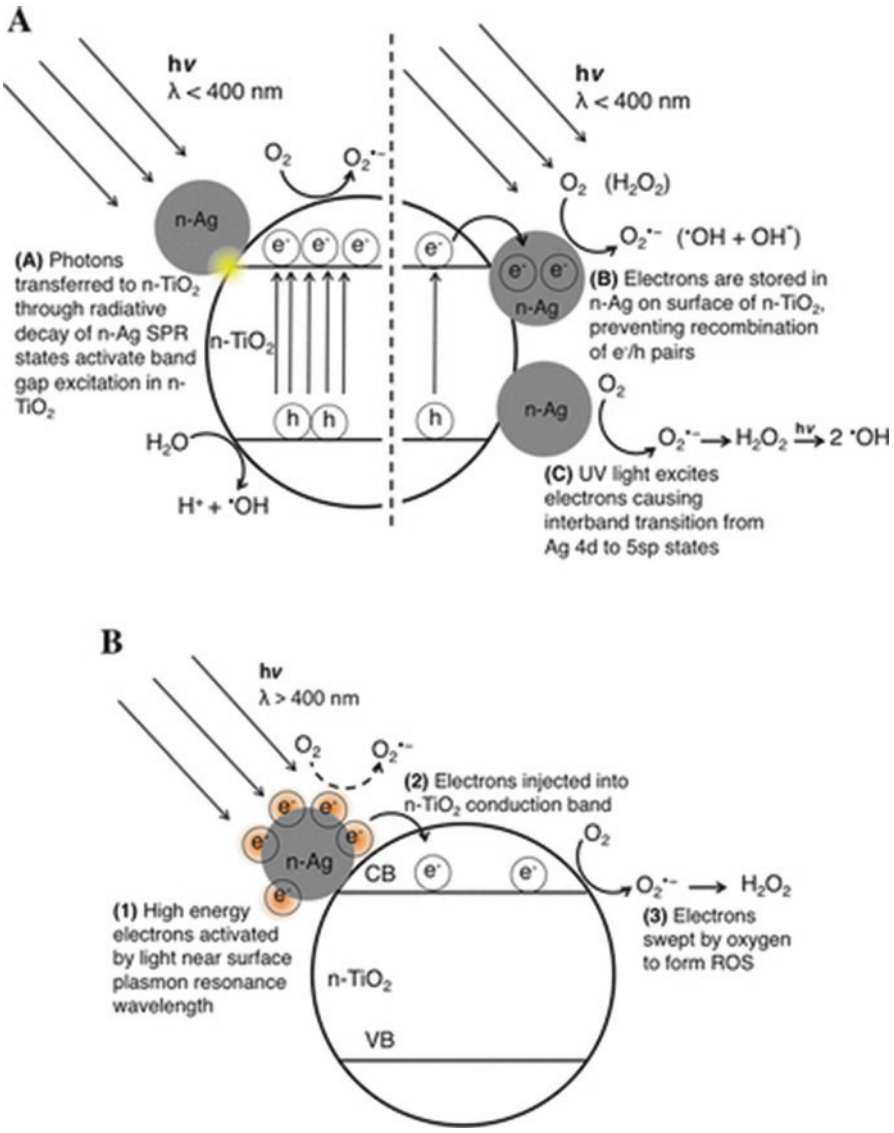

Fig. 7.5 Mechanism for photoactivity of n-Ag/n-TiO_2 and ROS production under ultraviolet radiation (**a**) and under visible light (**b**). (With permission from Wilke et al. 2018)

can be useful for optimizing the better SPR properties of Ag NPs (Prakash et al. 2018; Jai et al. 2016). In addition, it provides higher contact surface area for Ag NPs for uniform distribution on the surface. Several other factors such as structural modifications, the size and shape of Ag and TiO_2 nanomaterials, and their concentrations that provide efficient antibacterial materials with better antibacterial applications. For example, TiO_2 in a meso-porous structure is significant in antibacterial

applications when used as nanocomposites with Ag NPs. The enhanced antibacterial response from these Ag–TiO_2 nanocomposites results from the high surface area in the meso-porous TiO_2 structure and slow release of Ag ions from the nanocomposites as compared to Ag NPs alone (Prakash et al. 2016; Akhavan 2009; Akhavan and Ghaderi 2009). Similarly, several studies have been based on different structures, shape, size, and concentration of Ag and TiO_2 nanostructures with enhanced antibacterial activities (Dror-Ehre et al. 2009; Pal et al. 2007; Machida et al. 2005). This section reviews the antibacterial applications of Ag–TiO_2-based nanocomposites in different conditions with emphasis on various factors that effectively enhance their antibacterial activities. The mechanisms of their antibacterial action under different conditions are also discussed.

Extensive research has been conducted on the antibacterial effect of Ag–TiO_2 nanocomposites under UV light irradiation. Matsunaga et al. (1985) studied for the first time the sterilization of bacteria using metal–TiO_2 nanocomposites activated with UV light that provided significant results with enhanced antibacterial effect as compared to UV-activated TiO_2 only. This experiment also provided better understanding of modifying TiO_2 through nanocomposite formation with various noble metal nanostructures (Ag/Au) to improve its antibacterial activity under UV irradiation, which encouraged researchers to work extensively in this direction (Keleher et al. 2002; Machida et al. 2005). Later, the nanocomposites of TiO_2 with these metal NPs were explored to study photocatalysis and antibacterial effects, not only in UV but also extended to work under visible light and dark conditions very effectively because of the synergic effect of light absorption and antibacterial effect of individual components, as discussed in Fig. 7.5 (Prakash et al. 2018; Wilke et al. 2018).

As discussed earlier and in the mechanism shown in Fig. 7.5, in case of Ag–TiO_2 nanocomposites under UV irradiation, the antibacterial effect is enhanced by the Schottky effect that promotes the charge separation along with antibacterial action of the Ag NPs. As a result, a number of e^- are present on the surface of TiO_2 that produce ROS or released Ag ions (especially in aqueous solutions) which accelerate the antibacterial action, providing higher antibacterial efficiency as compared to only Ag NPs or TiO_2 nanostructures (Keleher et al. 2002; Zhang et al. 2003). For example, Zhang et al. (2003) demonstrated that a nanocomposite formed by depositing Ag NPs on the surface of TiO_2 nanostructures showed better antibacterial activities under UV light as compared to TiO_2 only against *Micrococcus lylae*; charge separation followed by UV-generated ROS was mainly responsible for antibacterial activity as studied with transmission electron micrographs. Bahadur et al. (2016) presented similar observations against several bacterial cells that showed significant enhancement in antibacterial activities with increase in Ag concentration. It was suggested that Ag ions were released and attached to the cell membrane, affecting various functions of the cells and destroying the respiratory system, eventually inactivating the cell. However, the interaction also led to the formation of ROS, accelerating the killing of bacteria and thus enhancing the antibacterial effect (Fig. 7.6).

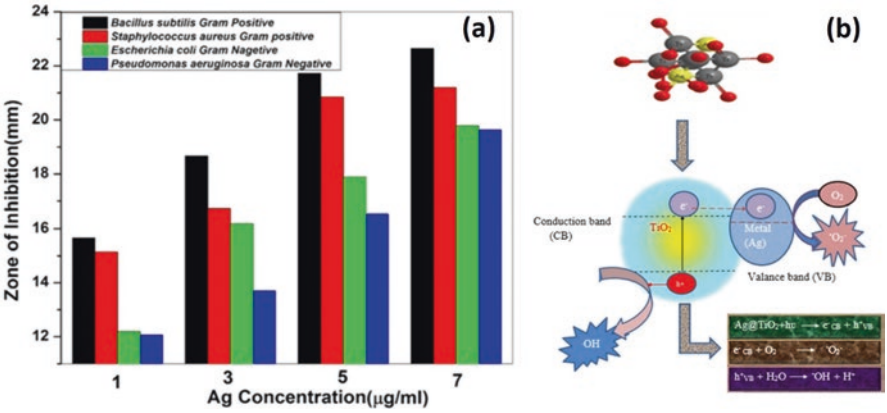

Fig. 7.6 (**a**) Bar graph for zone of inhibition versus Ag concentration. (**b**) Schematic diagram illustrating the mechanism of photo-excited electron and hole transfer among TiO_2 NPs and Ag NPs. (With permission from Bahadur et al. 2016)

In contrast, Page et al. (2007) did not observe any Ag ion release when antibacterial experiments were carried out in the dark using an Ag–TiO_2 nanocomposite coating. The activity was explained on the basis of charge separation and ROS formation leading to the death of the cells. It was found that antibacterial behavior was different for Gram-positive and Gram-negative bacteria because of the difference in cell wall structures. Similarly, Ubonchonlakate et al. (2012) showed that under UV irradiation, Ag–TiO_2 nanocomposite films exhibited better (100% antibacterial efficiency) effect as compared to TiO_2 whereas TiO_2 in pure and porous structures showed only 57% and 93% efficiency, respectively. Interestingly, it was found that 100% killing disinfection could be achieved in less UV irradiation time as compared to TiO_2 irradiation time as Ag attributed to the higher charge separation. Several studies on Ag–TiO_2-based nanocomposites for their antibacterial application have been reported under UV irradiation that indicated enhanced efficiency from the presence of Ag NPs. However, several other factors generally affect antibacterial activities such as preparation methods, kind of bacteria, structural composition, thickness of the nanocomposites in case of thin films, different phases of the TiO_2, and experimental parameters such as temperature, darkness, or electromagnetic irradiation (Machida et al. 2005; Page et al. 2007; Kubacka et al. 2008). It has been found that in any case, however, the Ag–TiO_2 nanocomposites exhibit better antibacterial response as compared to only Ag or TiO_2 nanomaterials (Akhavan 2009; Deshmukh et al. 2018; Jai et al. 2016; Jalali et al. 2016; Kubacka et al. 2008; Prakash et al. 2018; Chiang et al. 2014). For example, varying Ag composition in an Ag/Au–TiO_2 nanocomposite where alloy Ag/Au NPs were formed on the TiO_2 surface showed better antibacterial killing effect under the influence of UV irradiation as compared to visible light (Chiang et al. 2014). Page et al. (2007) studied the antibacterial effect of TiO_2 and Ag–TiO_2 coating on glass slides and found this very effective under the influence of UV irradiation (Fig. 7.7). These coatings were very effective against Gram-positive bacteria as compared to Gram-negative bacteria

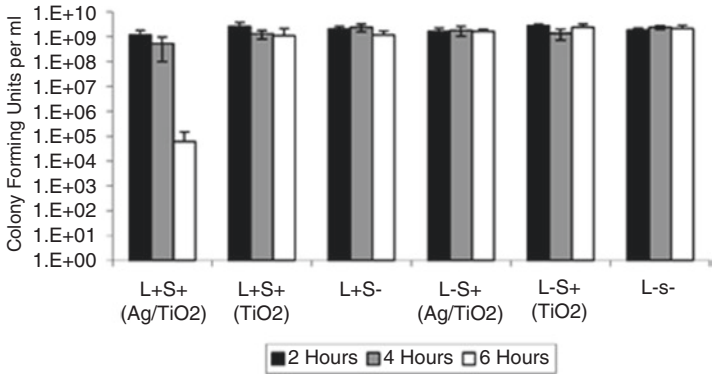

Fig. 7.7 Bacterial kills for the two-coat Ag–TiO_2 sol–gel-prepared coating against *Staphylococcus aureus* after 2, 4, and 6 h illumination with 365 nm radiation. The viable counts are expressed as colony-forming units ml^{-1}. L+S+ refers to the exposure of an active coating (identity in brackets) to UV light; L+S− refers to the exposure of an uncoated slide to UV light; L−S+ refers to an active coating (identity in brackets) kept in the dark; and L−S− refers to an uncoated slide kept in the dark. (With permission from Page et al. 2007)

where the charge separation mechanism and structural composition of the cell wall had major effects on the observed differences in antibacterial activities.

The preparation methods also showed differences in antibacterial efficiency under UV irradiation. For example, a comparable antibacterial study was performed by synthesizing an Ag–TiO_2 nanocomposite using impregnation and photodeposition methods against *E. coli* bacteria. Although nanocomposite Ag–TiO_2 materials prepared by both techniques exhibited good antibacterial effect, nanocomposites prepared by the photo-deposition method showed superior antibacterial effects (Kubacka et al. 2008). Interestingly, these Ag–TiO_2 nanocomposite materials are also very effective in dark conditions against various microbes (Binyu et al. 2011; Li et al. 2011). In dark conditions, the noble metal NPs deposited on TiO_2 surfaces can absorb the electrons from the bacteria by their Plasmon, and these electron transfers from the bacteria to interrupt their respiratory system leading to cell death (Li et al. 2011; Prakash et al. 2018). Binyu et al. (2011) studied the antibacterial effect of Ag–TiO_2 nanocomposites in darkness and compared the antibacterial results under the effect of UV light. In both experimental conditions, these Ag–TiO_2 nanocomposites showed excellent antibacterial response against *E. coli*.

So far, we have discussed the antibacterial effect of Ag–TiO_2 nanocomposites under UV light irradiation and found that the limitation of UV light activity of TiO_2 nanomaterials decreases the antibacterial activity efficiency. However, the presence of Ag NPs and formation of the Schottky barrier at the interface leads to suppression of recombination of charge carriers, providing more electrons and holes to take part in oxidation and reduction reactions, generating ROS and further inactivation of microbes. In addition, we have studied the antibacterial effect in dark conditions. Interestingly, in visible light, antibacterial activity is found to be enhanced as compared to that of UV light irradiation because of the localized surface plasmon

resonance (LSPR) properties of Ag NPs (Nigussie et al. 2018; Prakash et al. 2018). The presence of Ag NPs in Ag–TiO_2 nanocomposites increases absorption of visible light, which excites the electrons in LSPR. These excited electrons are transferred to the CB of TiO_2 for further formation of ROS through oxidation/reduction reactions that take part in either photocatalytic or antibacterial activities (Fig. 7.5) (Wilke et al. 2018).

Wilke et al. (2018) recently demonstrated that because of the photoactive nature of both Ag and TiO_2 under visible light irradiation, they showed better interaction for producing ROS that exerted toxic stress on bacterial cells, leading to damage of cell membrane and death. They also studied the similar behavior of Ag–TiO_2 nanocomposites in dark conditions (Wilke et al. 2016). Jiang et al. (2017) reported that these materials caused a slight lesion in the cell membrane leading to inhibiting cell growth. Similarly, from the formation of enhanced ROS under visible light, Ali et al. (2018) showed enhanced photocatalytic degradation as well as photocatalytic antibacterial activity against various microbes. Mai et al. (2010) studied the antibacterial behavior of an Ag–TiO_2 nanocomposite prepared by the sol–gel method in different conditions such as dark, heating, and visible light irradiation. There was not much effect of annealing on antibacterial activity, whereas in the dark as well as under visible light, these nanocomposites show better antibacterial response because of the Ag^+ release and plasmonic effect, respectively. A similar mechanism was proposed for Ag–TiO_2 film deposited on Ag NPs over the TiO_2 substrate by Akhavan et al. Akhavan (2009) demonstrated excellent antibacterial activities under visible, solar, as well as dark conditions. Several studies using systematic studies have proposed a similar mechanism for Ag-TiO_2 based nanocomposites (Bahadur et al. 2016; Zhao et al. 2011; Roguska et al. 2012).

Ag–TiO_2-based nanocomposites have also been used for studying toxicity effects on human cells (Korshed et al. 2017) and inhibition of biofouling on limestone (Becerra et al. 2018). Korshed et al. (2017) reported antibacterial action and toxicity effect of a novel Ag–TiO_2 nanocomposite prepared from picosecond laser against several microbes (*E. coli*, *Pseudomonas aeruginosa*, and *Staphylococcus aureus*) and human cells (A549, HePG2, HEK293, hCAECs, and HDFc), respectively, under visible light treatment. The visible light activation caused an enhancement in the level of ROS as compared to TiO_2 that had a major role in lipid peroxidation, depletion of cell membranes, and leaking of compounds, followed by death of the microbes. Similarly, decreased cell proliferation was recorded in human cells when treated with these Ag–TiO_2 nanocomposites. On the other hand, Cao et al. (2017) demonstrated that Ag–TiO_2 nanocomposites produced by the strong electrostatic adsorption (SEA) technique resulted in fine and well-distributed Ag NPs on the TiO_2 surface and exhibited excellent antibacterial response. They concluded that fine dispersion and small size of Ag NPs had a major effect on enhanced antibacterial action (Fig. 7.8).

Smaller Ag NPs are effective for releasing Ag^+ and can penetrate the cell membrane, followed by entering the cell and damaging cell functions. It was shown that SEA-based Ag NPs were releasing Ag^+ in a controlled manner, providing long-term antibacterial functionality. As shown in Fig. 7.8, the SEA-generated Ag NPs distributed

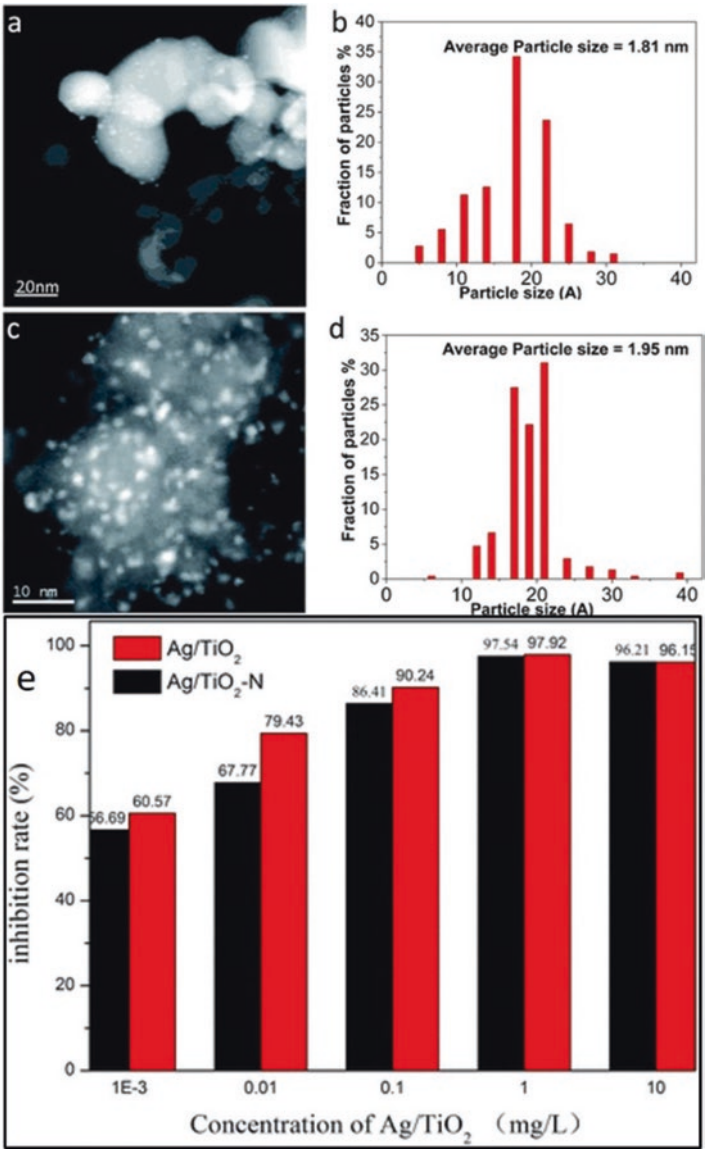

Fig. 7.8 Scanning transmission electron microscopy (STEM) image of Ag/TiO_2–N (**a**), Ag/TiO_2 (**c**), and particle size distribution (**b**, **d**). (**e**) Antibacterial rate of different concentrations of Ag/TiO_2. (From Cao et al. 2017)

over TiO_2 exhibited antibacterial activities through Ag^+ release and ROS formation. leading to inactivation of bacterial cells.

Cai et al. (2018) recently proposed a memory catalyst (MC) material based on Ag–TiO_2 nanocomposites that showed unique catalytic performance during the dark

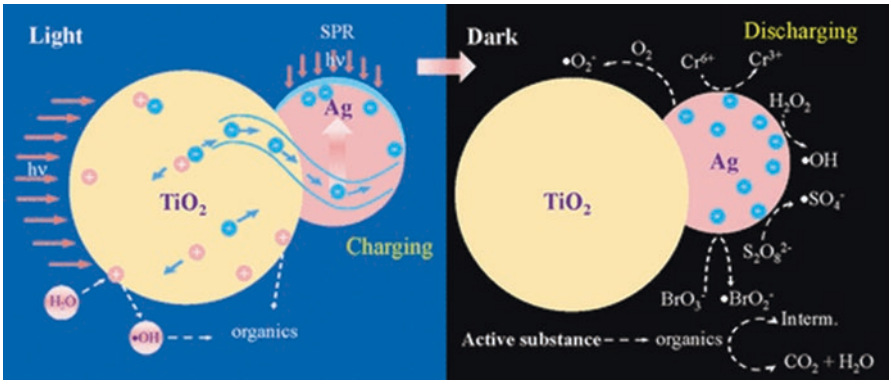

Fig. 7.9 Memory catalyst (MC) reaction mechanism. (With permission from Cai et al. 2018)

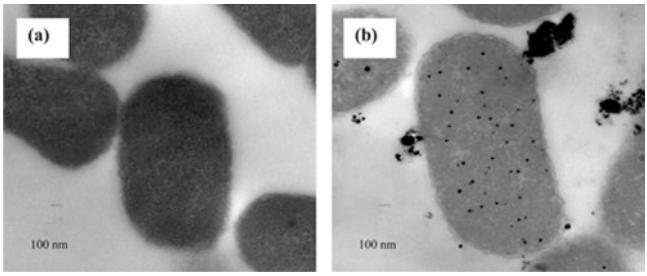

Fig. 7.10 TEM images of *E. coli* cells before (**a**) and after (**b**) treatment with 10% Ag/(C, S)–TiO_2 nanoparticles. (With permission from Hamal et al. 2010)

as a result of electron-storing ability through the electron-trapping effect of TiO_2 nanomaterials. It was suggested that these material could be the best plasmonic photocatalytic materials for antibacterial applications even without any influence of light irradiation (Fig. 7.9).

In other studies, it has been shown that Ag–TiO_2 nanocomposites show better antibacterial performance when forming multi-element composites by incorporating or doping other functional elements. For example, Hamal et al. (2010) demonstrated that Ag–TiO_2 nanocomposites when doped with functional elements such as C or S exhibited better multifunctional photocatalytic activities. They studied photocatalytic degradation as well as photocatalytic antibacterial activities of doped Ag–TiO_2 nanocomposites and found enhanced antibacterial activity against *E. coli* under visible light as well as dark conditions, attributed to the enhanced Ag^+ ion release caused by doping (Fig. 7.10).

Similarly, Jiang et al. (2016) suggested that a composite of Ag–TiO_2 with graphene oxide would be excellent for its antibacterial action attributed to the better release of Ag^+ (Fig. 7.11).

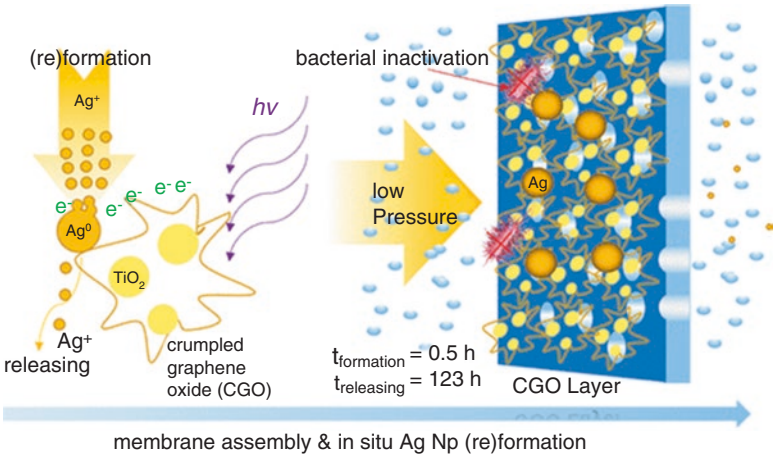

Fig. 7.11 Ag NP–TiO_2 on graphene oxide for antibacterial applications. (From Jiang et al. 2016)

Similarly, when these Ag–TiO_2 nanocomposites are embedded in some soft matrix such as polymer, they are more attractive from long-term stability and technological aspects. For example, Noori Hashemabad et al. (2017) reported that when TiO_2 nanoparticles were incorporated in polyethylene films, the antibacterial property was enhanced and the composites could be used as for food packaging to avoid such contaminations. Much study has been conducted using TiO_2 and polymer nanocomposites for enhanced antibacterial activity in different technological applications (Varnagiris et al. 2017; Kong et al. 2010; Santhosh and Natarajan 2015; Kubacka et al. 2009b). Embedding in a polymer matrix provided not only protection to the nanomaterials but also provided better stability from the open environment, specially for Ag NPs, which can be easily oxidized (Singh et al. 2013; Prakash et al. 2018). The nanocomposites of Ag–TiO_2 with polymer showed even better antibacterial activity as compared to Ag–TiO_2 nanoparticles only (Kubacka et al. 2009a; Tallósy et al. 2014; Wang et al. 2016). Tallósy et al. (2014) investigated the antibacterial response of TiO_2, Ag–TiO_2, and Ag–ZnO nanoparticles embedded in polymer films. They observed that in similar experimental conditions, Ag–TiO_2/polymer nanocomposite films showed better antibacterial activities as compared to either TiO_2/polymer or Ag-ZnO/polymer films in the dark as well as visible light irradiation (Fig. 7.12).

Similarly, Wang et al. (2016) demonstrated that Ag-poly(dopamine)–TiO_2 nanotube composites exhibited very stable and long-term antibacterial activity against microbes as a result of slow Ag^+ release from the polymer layer. Similarly, polyurethane acrylate-Ag/TiO_2 nanorod-based nanocomposites exhibited strong antibacterial photodegradation of *E. coli* when irradiated with UV light through ROS generation (Li et al. 2017a). In another report, the plasmonic effect of Ag–TiO_2 NPs embedded in polymer films decreased the amount of plasmonic photocatalyst and thus exhibited great enhancement in the antibacterial killing efficiency of the composites (Kubacka et al. 2009a; Wu et al. 2010)**.** These polymer-based plasmonic

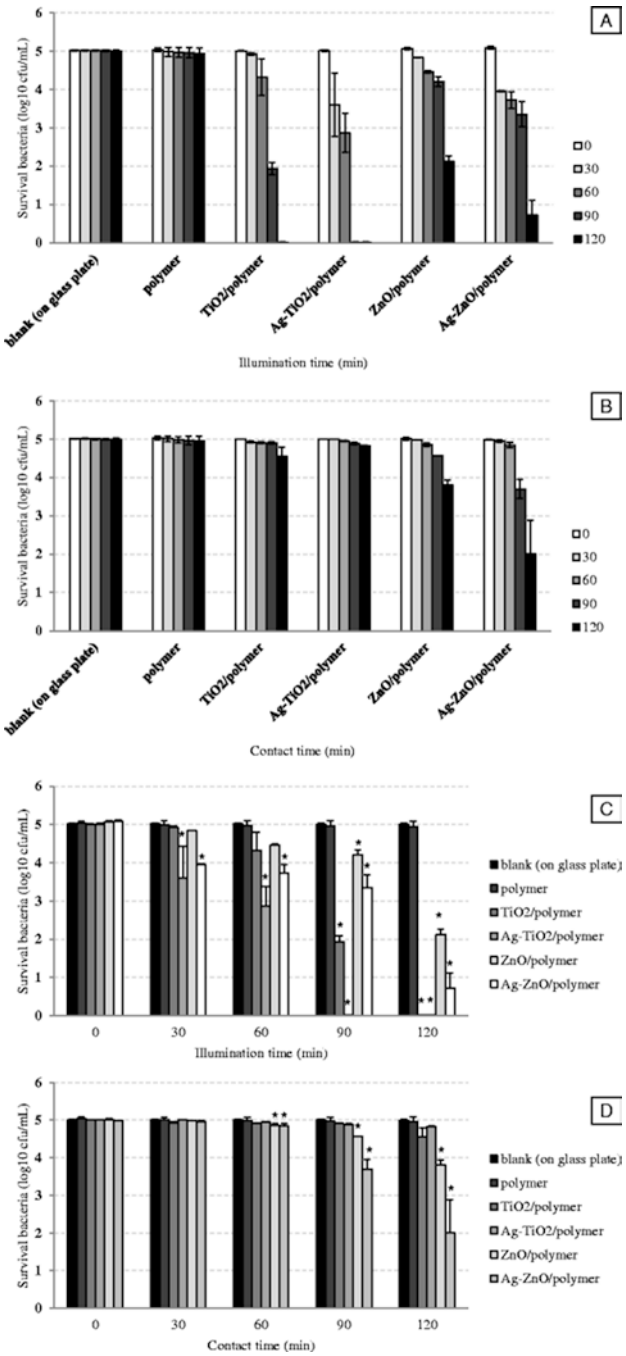

Fig. 7.12 Antibacterial effect of Ag–ZnO/polymer and Ag–TiO_2/polymer nanohybrid films against methicillin-resistant *Staphylococcus aureus* (MRSA) under LED light illumination (**a**) and in the dark (**b**), and with statistical analysis [under LED light illumination (**c**) and in the dark (**d**)]. (With permission from Tallósy et al. 2014)

photocatalysts have been efficiently used in packaging and biomedical applications (Kubacka et al. 2009a, b).

Similarly, Ag–TiO_2-polyethylene-based nanocomposites were used to inactivate pathogens by examining disinfection against various microbes such as *Staphylococcus aureus*, *Escherichia coli*, *Candida albicans*, and *Aspergillus niger* (Barani et al. 2018). Cross-linked polymer-based hydrogel nanocomposites embedded in Ag NP–TiO_2 nanosheets exhibited excellent antibacterial activity with strong photocatalytic degradation of dye molecules (Sarkar et al. 2017). Polyvinylidene fluoride (PVDF)-Ag–TiO_2-based nanocomposite membranes used as bifunctional materials exhibit excellent photocatalytic and antibacterial properties. The excellent bifunctionality was attributed to the introduced hydrophilicity of the Ag–TiO_2 nanocomposite materials (Chen et al. 2017). PVDF membranes produced by blending Ag–TiO_2–APTES nanocomposites were also shown to be effective bifunctional and self-cleaning materials for antibacterial as well as photodegradation applications (Peng et al. 2018).

7.5 Outlook and Summary

Ag–TiO_2 nanocomposite nanomaterials are important functional materials that are being used for several applications, including bacterial disinfection. These nanocomposites, in particular, are very useful in antibacterial activities by means of the synergic effect of Ag NPs and TiO_2. These nanomaterials have gained much attention from researchers because their synthesis process is easy and their physicochemical properties are excellent as well as tunable. Another important aspect about these nanocomposite materials is their antibacterial application in various conditions such as in dark and under UV and visible/solar light irradiation, attributed to the presence of Ag and TiO_2, respectively. In this chapter, recent progress on novel Ag–TiO_2 nanomaterials in the field of antibacterial applications is discussed with emphasis on the advances of mechanisms of antibacterial action in recent years as reported in the literature.

The chapter is divided in four sections. In Sect. 7.1, a general introduction on bacterial infection, need of antibacterial materials, and importance of Ag-TiO_2 nanomaterials are discussed. Section 7.2 describes the basics and antibacterial mechanism of TiO_2 materials; Sect. 7.3 discusses in brief the Ag NPs and their role in antibacterial applications. Section 7.4 provides a detailed overview of recent developments in antibacterial applications of Ag-TiO_2 nanocomposites with emphasis on antibacterial mechanisms. We hope this chapter will provide useful information about progress in the antibacterial research field.

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