

Silver Nanoparticles Supported on TiO₂ and Their Antibacterial Properties: Effect of Surface Confinement and Nonexistence of Plasmon Resonance

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Abstract

Ag/TiO₂ nanocomposites are usually regarded as an effective synergy for high antimicrobial performance under ultraviolet-visible light conditions. This study confirmed that the surface plasmon resonance of Ag NPs plays an important role in relation to the NPs size and consequently with the antibacterial effect of the nanocomposite. We observed that under visible light the reactivity of TiO₂ cannot be amplified when it is supporting Ag NPs that have an inactive photocatalytically surface. The results confirmed that the antimicrobial effectiveness of nanocomposite based on Ag NPs supported-TiO₂ is closely associated to the contact surface area and to the electronic performance of the noble metal.

Keywords

Ag-TiO₂, Antibacterial, Silver Nanoparticles, Surface Confinement

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1. Introduction

The use of metallic silver of nanometric dimension (Ag NPs) has demonstrated excellent capability against many pathogen species, it is even considered better antibacterial than other silver compounds or silver ions embedded in a ceramic host [1]-[5]. The major publications on Ag NPs generalize that the antibacterial property increases with the reduction of particle size [6]-[9], other studies suggest that the Ag NPs particle shape affects the reactivity, for example; Yang P. *et al.* reported that larger particles and particles with asymmetric shapes, give rise to more complex surface plasmon responses due to their higher degree of polarizability [10]. Recently, new interpretations about of the Ag NPs reactivity are emerging, Xiu *et al.* consider that the Ag NPs size do not cause by themselves toxicity to bacteria at less that occurs release of silver ions [11].

Numerous studies about of nanoscaled metal oxides like TiO₂, ZnO and CuO have demonstrated promising results for antibacterial activity. Additionally, materials produced by combinations of Ag NPs and those agents above mentioned exhibit much stronger antibacterial abilities [12] [13].

Anatase TiO₂ is a common agent used for the elimination of microbiological and toxic contaminants, for air, water and for self-cleaning surface applications [14]. In principle, TiO₂ has proven strong catalytic activity via UV-light photons absorption, where electronic delocalization in the TiO₂ generates electron/hole pairs, which, when exposed to water molecules, produce hydroxyl radicals (•OH) and superoxide anions (•O₂). These radicals have the ability to oxidize organic and microbial matter [15].

Nowadays nanocomposites of Ag NPs supported on TiO₂ are promoted as some of the most powerful antibacterial agents; the reason is that by linking these two components the photocatalytic process could take place even under visible light [16]-[21]. However, it is still required to learn the nanocomposites performance beyond the photocatalytic contribution, since in the practice the use of antibacterial is limited to applications where they are not exposed to light radiation. Also, it is interesting to study how, by the use of a TiO₂ substrate, is it possible to enhance the contact of Ag NPs with the bacteria and understand if an Ag NPs smaller size increases the bactericidal effect of Ag/TiO₂ nanocomposite.

In this work, the Ag NPs were synthesized via reduction reaction using a TiO₂ aqueous suspension. The dimension and content of Ag NPs deposited on TiO₂ NPs attained on the different pH conditions were evaluated and correlated with the activity of Ag/TiO₂ nanocomposites against several representative bacteria; *Escherichia coli* and *Salmonella sp* and *Staphylococcus aureus*, which are some of the bacteria species that could easily cause skin diseases, intestinal infections and other illnesses.

2. Experimental

2.1. Materials

TiO₂ ≥ 99.5% 25 nm (Evonik Degussa) was used as substrate material to prepare Ag/TiO₂ nanocomposite. Silver nitrate 99.4% (Fermont) and Sodium hydroxide 99% (Caledon Laboratories LTD) were used to synthesize metallic silver NPs. Luria Bertani media (1.0% Tryptone 0.5% yeast extract and 1.0% NaCl) was used to Broth media. Microorganisms Control strains *Escherichia coli* ATCC 25922 (American Type Culture Collection, Rockville, Md.), *Staphylococcus aureus* ATCC 25923, and *Salmonella sp*.

2.2. Synthesis

Preparation of metallic silver on TiO₂ surface was based on chemical reduction route of AgNO₃. Aqueous suspension of TiO₂ NPs was prepared by adding 5 g of TiO₂ to 250 ml of deionized water and followed by sonication for 10 min. The slurry was heated at 80°C with vigorous mixing. The required amount of AgNO₃ solution was added to TiO₂ suspension, maintaining heating and stirring. Silver concentration was of 0.5, 1.5, 5.0, 25, 35 and 45% w/w versus TiO₂. The samples were named 0.5Ag/TiO₂, 1.5Ag/TiO₂, 5Ag/TiO₂, 25Ag/TiO₂, 35Ag/TiO₂ and 45Ag/TiO₂. The pH of the suspension was adjusted to 4, 9 and 12 by the required addition of a 0.5 M NaOH solution. The slurry at 80°C was mixed for two hours, after that, the solution was centrifuged and rinsed with water, the solid was dried in an oven at 80°C for 12 hours.

2.3. Characterization

The deposited amount of Ag on TiO₂ was measured by atomic absorption spectroscopy. Morphology, size and

dispersion of Ag NPs supported on TiO₂ nanoparticles were characterized by a TEM (Transmission Electron Microscope) TECNAI-F30 at 300 kV. The interaction between TiO₂ and Silver NPs was characterized by Raman Spectroscopy, using a Horiba JobinYvo N, model M.F.O with laser 532 nm and 100 mW. Ultraviolet visible (UV-vis) spectroscopy showed the excitation energy to induce photocatalysis reactions, spectra were recorded in the range of 200 to 800 nm, using a spectrometer UV-Vis Thermoscientific model Genesys 10 UV, the sample consisted of 0.005 g of nanocomposite in 2 mL of deionized water.

2.4. Antibacterial Test

The Minimum Bactericidal Concentration (MBC) for each Ag/TiO₂ sample was determined in duplicate. Tubes containing 3 ml of Luria Bertani media were prepared and Ag/TiO₂ nanocomposites were added at different concentrations (0.5, 1.0, 1.5, 2.0, 3.0, 5.0, 7.0, 8.0, 9.0 and 11.0 mg/mL). A reference sample supplemented with only TiO₂ and at the same concentrations was also evaluated. The solutions were sterilized at 121 °C and 15 lb/in² for 15 minutes, and then suspensions of bacterial strains containing between 10⁷ to 10⁶ CFU/mL were suspended in the liquid media. Upon overnight growth at 37 °C and 150 rpm, the MBC for each strain was determined by subculturing 100 μL from each tube followed by massive striation onto agent-free Luria Bertani agar. MBC endpoints were read as the lowest concentrations of agent with no growth after overnight incubation at 35 °C. Samples were properly covered to ensure absence of visible light.

3. Results

Figure 1 shows the yield of the reduction reaction of Ag⁽⁺⁾ to Ag⁽⁰⁾ during the synthesis of Ag/TiO₂ nanocomposite was affected by pH conditions. Literature indicates that the zero charge point of TiO₂ Degussa occurs at pH = 6.85 [22]. The studied pH values conveyed a different charge condition on TiO₂ surface. The Ag NPs content supported on TiO₂ at 4, 9 and 12 pH was analyzed by atomic absorption spectroscopy and the results shown that alkaline condition played an important role during the Ag NPs deposition on TiO₂ (**Figure 1**). Such behavior was more evident at high silver precursor concentrations, which can be observed from the samples 5Ag/TiO₂ to 45Ag/TiO₂ (**Figure 1**). For instance, Ag NPs content supported on TiO₂ for 5Ag/TiO₂ samples, at 4, 9 and 12 pH was of 1%, 3% and 4% w/w, respectively. Thus, it was proven, that in absence of the precipitate agent (pH 4) and without UV-light the TiO₂ surface could induce to a partial reduction of the AgNO₃ amount through oxygen vacancies (O⁻). In alkaline conditions the TiO₂ tended to be a better electro-attractive surface for nucleation Ag NPs, this was originated by deprotonation of the hydroxyl groups on the TiO₂ surface. It was observed that the Ag NPs obtained by reduction-deposition depended on the density of O⁻ sites in the TiO₂, which was optimized under the most alkaline condition (pH 12).

Figure 2 shows the Raman vibrational spectra for pure TiO₂ and those of 5Ag/TiO₂ nanocomposite samples

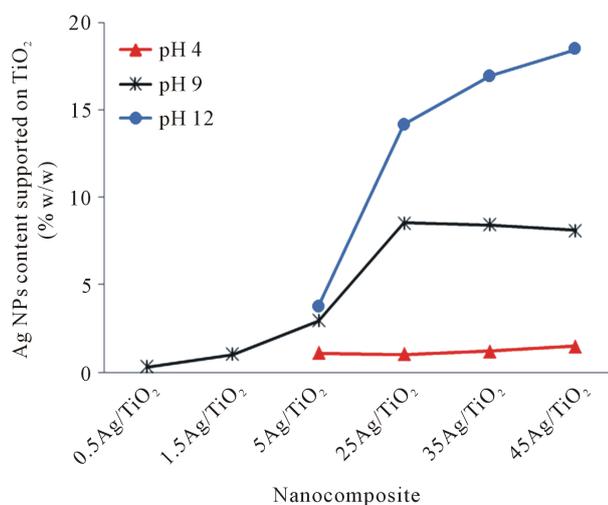


Figure 1. Comparison of Ag concentration supported to TiO₂ by the reduction reaction at different pH.

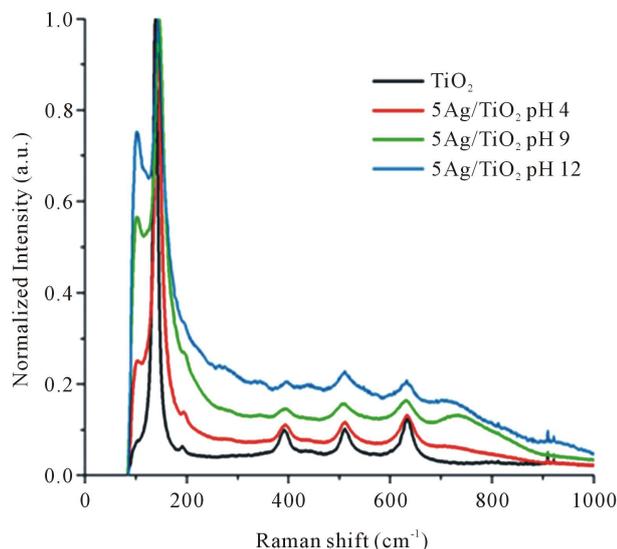


Figure 2. Raman spectra of neat TiO₂ and 5Ag/TiO₂ nanocomposites synthesized at different pH condition: 4, 9 and 12.

synthesized at different pH conditions. The Raman spectrum of TiO₂ substrate presented an intense signal at 144 cm⁻¹ which corresponds to the E_g mode and other low intense modes at 197, 399, 519 and 639 cm⁻¹ [23]. The Ag NPs deposition on TiO₂ particles was confirmed by the detection of others Raman peaks at 102, 259 and 735 cm⁻¹. Additionally, these peaks seem to increase for the 5Ag/TiO₂ synthesis when pH was raised from 4 to 12. This scenario suggests the formation of Ag NPs on TiO₂ surface which is enhanced by basic values of pH, where both silver ions reduction and Ag NPs deposition mechanisms are apparently favored.

Comparatively we observed of the **Figure 3** exist a relation between Ag NPs amount and the intensity of peak at 102, 144, 259 and 519 cm⁻¹. To higher Ag NPs concentrations was consistent a higher intensity at 102 and 259 cm⁻¹ peaks. On the other hand was observed that the peaks at 144 and 519 cm⁻¹ belongs to TiO₂, tended to overlap or even to disappear as result of the deposited Ag NPs amount increasing on surface TiO₂. Additionally was observed a shift and broadening of TiO₂ peaks at 399 cm⁻¹ (B_{1g}) and 639 cm⁻¹ (E_g). Researchers have referred to that Raman peaks become broader when decreases the size of nanoparticle. This effect has been attributed to a volume contraction and radial pressure increasing, which consequently changes the force constant and vibrational amplitude of the nearest neighbor bond [24]. Referring to this phenomenon of Raman vibrational restriction, we demonstrate that also could take place alterations in the TiO₂ interatomic distances with a surface pressure increasing to a more proportion Ag NPs deposited on TiO₂ surface.

Figure 4 shows the UV-vis absorption spectrum for 5Ag/TiO₂ samples obtained by silver deposition-reduction reaction at fixed pH values of 4, 9 and 12, respectively. UV-Vis Spectrometry was employed to characterize the photocatalytic property and predict antimicrobial activity under light conditions of Ag/TiO₂.

The optical properties and excitation frequency of the Ag/TiO₂ samples suspended in deionized water were obtained via diffuse reflectance analysis. The interaction of photon energies with the Ag/TiO₂ nanocomposites mainly occurred under UV wavelength. This means that the antimicrobial activity can be enhanced under UV condition by the reactivity of TiO₂ substrate. The position of absorption peaks for TiO₂ defines the excitation frequency of the semiconductor band gap, where only a slight wavelength change was observed from 283.5 nm to a maximum value of 334 nm, the narrowing of the energy band-gap confirmed the interface formation between Ag NPs and TiO₂. Surprisingly, the UV-Vis spectra revealed that the Ag NPs did not enhanced the catalytic response of TiO₂ at visible light and also the Plasmon resonance of Ag NPs was no showed. Based on this interpretation, the Ag/TiO₂ antimicrobial cannot generate reactive species by means of surface plasmon under visible light. Therefore, it is assumed that the polarizability at the surface of Ag NPs could be restricted. The peak for the Ag/TiO₂ samples obtained at different pH conditions suffered a modification on the full width of the Uv-vis spectrum which depends on the extent of the size or aggregation of Ag/TiO₂ particles, this shift towards longer wavelengths can be due to larger particles aggregates.

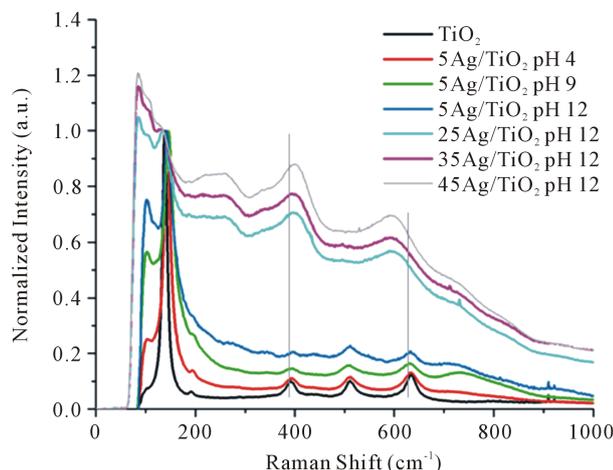


Figure 3. Raman spectra of neat TiO₂ and Ag/TiO₂ Nanocomposites with different loading amount of Ag NPs.

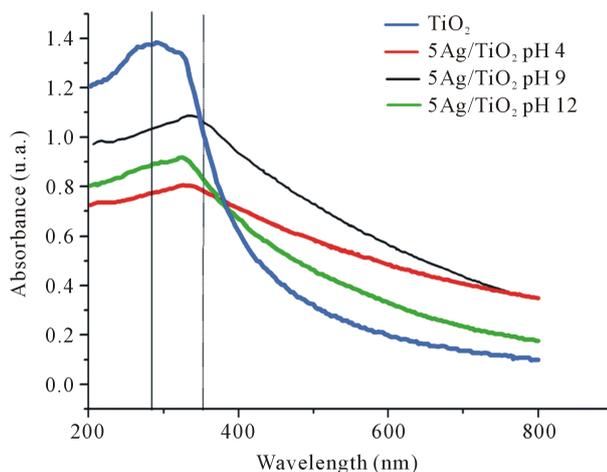


Figure 4. UV-vis spectra of neat TiO₂ and 5Ag/TiO₂ nanocomposites synthesized at different pH: 4, 9 and 12.

According to TEM micrographs it is evident that the Ag deposits on TiO₂ have nodular or spherical shape (**Figure 5**). These nanocomposites are composed by Ag NPs with narrow size distribution. In reference to the reaction yield, it can be observed a slight growth of Ag NPs size, which resulted of increasing the pH conditions and AgNO₃ concentrations. A moderated deposition of Ag atom clusters on TiO₂ was observed at pH 4 while the growth of Ag NPs was promoted at higher pH values and at a silver ion amount in excess. The particle size was predominantly smaller than 5 nm. The reduced size of the clusters may be related to the effect of confined electrons, which hinders the interaction of surface Plasmon resonance at visible light, such as was noted by UV-vis spectroscopy. This phenomenon can be associated with electronic barrier sets for Ag NPs with very small sizes, e.g. diameters < 20 nm, such as was explained by Tsivadze A, *et al.*, 2013 [25]. Moreover, we expect this condition could help on the control of the Ag ion releasing. TEM images showed that TiO₂ substrate attracts higher concentration of Ag NPs at the reduction reaction under the most basic condition, such as happened in the 45Ag/TiO₂ compound synthesized at pH 12. The Ag NPs distribution was improved at high silver concentration, which is one of the principal challenges to achieve efficiency to kill bacteria by the contact of Ag NPs.

The bactericide activity of Ag/TiO₂ nanocomposites was evaluated in absence of light, through detection of lowest concentration of Ag/TiO₂ nanocomposites where no growth is visually observed for Gram-negative bacteria *E. coli* and *Salmonella sp.*, and Gram-positive bacteria *S. aureus*. A summary of positive results is given in **Table 1**. Only the Ag/TiO₂ nanocomposites exhibited biocide effect at Ag NPs contents greater than 8.5% w.t.,

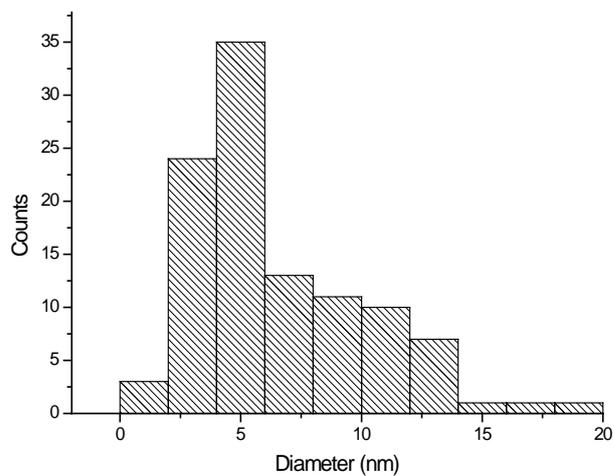
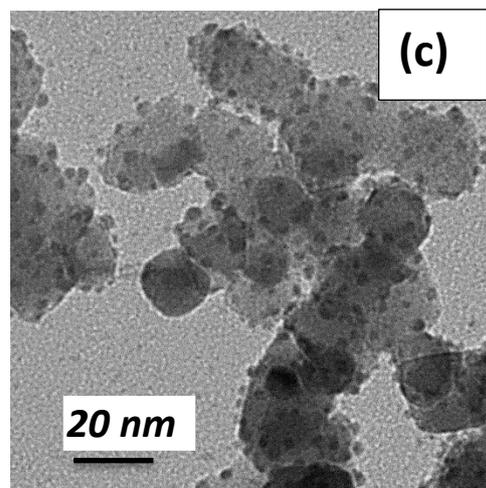
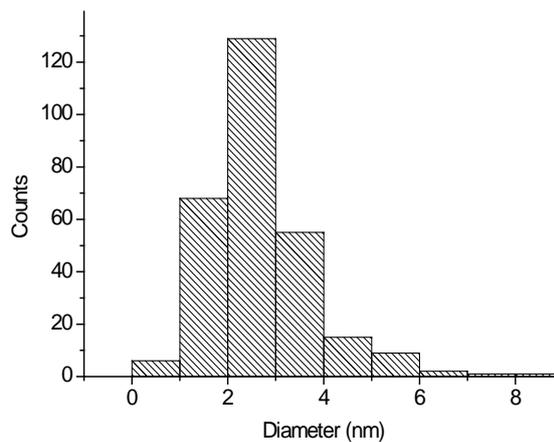
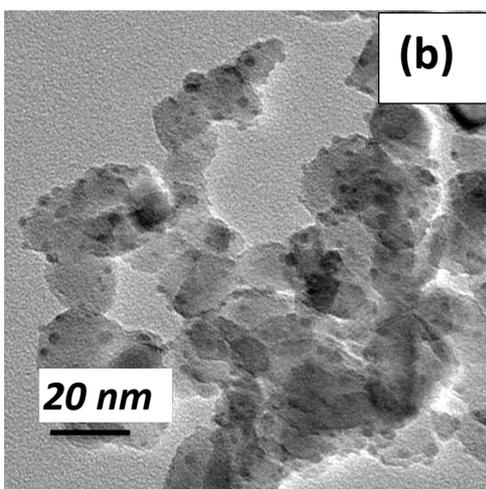
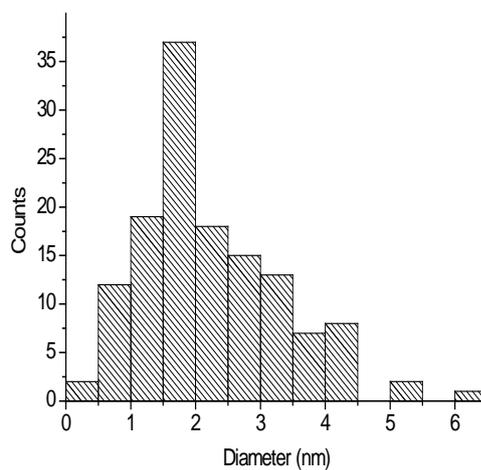
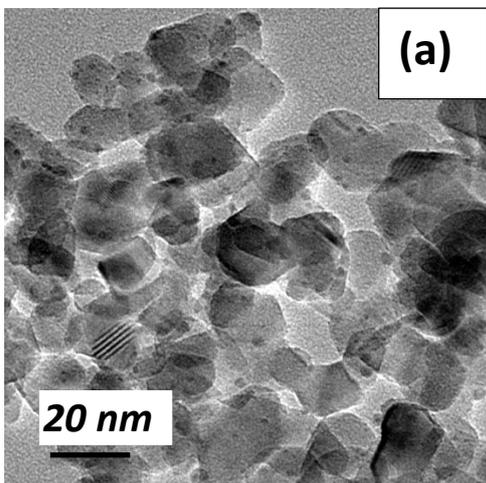


Figure 5. TEM micrographs showing AgNPs deposited on TiO₂ at different pH conditions: (a) 5Ag/TiO₂ pH 4, (b) 25Ag/TiO₂ pH 9 and (c) 45Ag/TiO₂ pH 12.

Table 1. Minimum bactericidal concentrations for Ag/TiO₂ nanocomposite against *S. aureus*, *E. coli* and *Salmonella*.

Nanocomposite	MBC (mg/mL)		
	<i>S. aureus</i>	<i>E. coli</i>	<i>Salmonella sp.</i>
25Ag/TiO ₂ pH 9	10	9	7
25Ag/TiO ₂ pH 12	10	7	7
35Ag/TiO ₂ pH 12	10	5	7
45Ag/TiO ₂ pH 12	10	4	7

which corresponded to the subsequent nanocomposite from of the 25Ag/TiO₂ composition synthesized at pH 9 (Figure 1), the other formulations with less Ag contents did not achieve the MBC on the tested amount of additive. In order to estimate the influence of pure TiO₂ on the bacteria growth inhibition, control tests were parallelly performed at these same concentrations of that tested for the nanocomposite; however antibacterial activity was not observed and is considered to be negligible mainly due to the test being performed under dark conditions. Thus hydroxyl groups or oxygen vacancies (O⁻) on TiO₂ surface have not enough antibacterial power.

E. coli bacteria was the most sensitive strain (Table 1), which showed to be highly affected in direct relation to the Ag NPs contents in the nanocomposite, it are related to the fact that they are gram negative and mainly could be susceptible to ionic interactions with Ag NPs. The second strain sensitive was *Salmonella sp.* which is also gram negative, but the MBC using the different formulation of nanocomposites was constant at 7 mg/mL; this means that the increase of Ag NPs loaded on TiO₂ at contents above 8.5% w.t. did not change the antibacterial effectiveness. *S. aureus* also presented a constant MBC with different formulations, when using a constant dose at 10 mg/mL.

4. Discussion

Ag NPs supported on TiO₂ can certainly increase the antibacterial performance more effectively than TiO₂ by itself. We obtained an adequate attachment of a high Ag NPs number on the TiO₂ surface, with a homogeneous dispersion and high available superficial area in strong alkaline suspension of TiO₂.

It was verified by UV-vis spectroscopy that TiO₂ photoactivity is enhanced by the adhesion of Ag NPs, however, the originated electronic overlap seems to be too weak to efficiently act under visible light. The explanation of the absence of reactivity in visible light was that; the Ag atoms not caused defects in the TiO₂ structural network and additionally by the deficiency of surface Plasmon resonance of Ag NPs.

The nonexistence of surface Plasmon resonance of Ag NPs and the vibrational restriction of TiO₂ bonding near to Ag NPs were unexpected. In fact, it actually reduced its catalytic activity due to electronic confinement barriers. In spite of the above mentioned, the antibacterial performance of silver nanocomposite was different of the bulk metallic silver properties, because even though the Ag NPs under this size (<5 nm) do not present the best catalytic property (plasmon resonance), the surface-to-volume ratio of Ag NPs ensured high surface area for the bacteria destruction by contact.

The limited antibacterial activity of Ag/TiO₂, under visible light or dark conditions could be overcome by reaching a minimum Ag NPs content of 8.5% w.t. This indicates that the Ag/TiO₂ toxicity was efficiently controlled by the activity of Ag NPs over any other possible oxidizing species released by TiO₂.

The effect of bacterial death was more easily achieved for *E. Coli* and *Salmonella sp.* (gram negative) presumably due to the electrostatic factor. For *S. aureus* (gram positive) the bacterial decline was more limited, which we could suppose that the gram-positive strain caused different permeability and structural resistance due to the content of peptidoglycan in cell wall [26]. These results indicate that, although the Ag NPs reactivity become size dependent, when it is ensured an extensive contact of Ag NPs with the bacteria population in consequently is achieved the bacteria targeted death and decline. An antibacterial activity increase at higher concentrations of Ag NPs against *E. Coli* was observed. Therefore, we could assume that the Ag NPs with electronic confinement barriers can destroy the bacteria membrane by the penetration of Ag NPs due to reduced particle size, similar as reported Wen, *et al.*, 2010 where Ag NPs produced pits or gaps in bacterial membrane of *E. coli* [27]. Thus, the interpretation of Xiu *et al.* [11] about of that the Ag NPs size do not cause by themselves toxicity

to bacteria at less that occurs release of silver ions is considered incorrect, because it was demonstrated that even on confined surface Ag NPs if can exist destruction of the bacteria.

It is possible to obtain a satisfactory antibacterial effect at a Ag NPs reduced concentration which could be preferred to efficiently act on common applications for packaging, medical or hygienic industries, and as opposed to require exposition of electromagnetic radiation to activate Ag/TiO₂.

5. Conclusions

Synthesis of Ag NPs on TiO₂ was possible in acid or basic reaction conditions. More number of oxygen vacancies on TiO₂ surface increased the nucleation of metallic Ag NPs. The limited antibacterial activity of Ag/TiO₂ nanocomposite under visible light or dark conditions could be overcome by reaching a minimum Ag NPs content.

The results confirmed that the antimicrobial effectiveness of Ag-supported TiO₂ is achieved principally due to a favored exposure and amount Ag NPs, without a photocatalytic effect of TiO₂ and a surface plasmon resonance effect of Ag NPs that can be considered.

An extended Ag NPs surface reduced the catalytic activity due to electronic confinement barriers. However, higher surface-to-volume ratio of Ag NPs ensured more surface area to act by direct contact against bacteria, changed the permeability of the cellular membrane.

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