Silver nanoparticles synthesized on titanium dioxide fine particles

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ABSTRACT

Silver nanoparticles with a narrow size distribution (20 nm mean size) were synthesized over the surface of two different commercial TiO_2 particles using a simple aqueous reduction method. The reducing agent used was $NaBH_4$; different molar ratios TiO_2:Ag were also used. The nanocomposites thus prepared were characterized using TEM, STEM, SEM, EDS, XPS, XRD, DLS and UV-VIS absorption spectroscopy; the antibacterial activity was assessed using the standard microdilution method, determining the minimum inhibitory concentration (MIC) according to the National Committee for Clinical Laboratory Standards. From the microscopy studies (TEM and STEM) we observed that silver nanoparticles are homogeneously distributed over the surface of TiO_2 particles and TiO_2:Ag molar ratios play an important role. The size of silver nanoparticles was controlled in the range of 10 - 30 nm. It was found that the antibacterial activity of the nanocomposites increases considerably comparing with separated silver nanoparticles and TiO_2 particles.

Keywords: metal nanoparticles, silver and titanium oxide composites, and antibacterial activity.

1 INTRODUCTION

Titanium dioxide (TiO2) is one of the most popular semiconductor materials, it can be found commercially available and can be used in many catalytic applications [1-8]. TiO2 has a wide band gap (3 eV and 3.23 eV for anatase and rutile respectively) which makes this material transparent to visible light, it is, no photon absorption occurs at wavelengths beyond 380 nm and catalytic reactions using pure TiO2 must be carried out using ultraviolet photons. Titanium dioxide is a material that also presents antibacterial activity [9-12]; this antibacterial activity has been studied over E. coli and B. Megaterium using environmental light [13]. Few studies have investigated the application of TiO2 in life science [14]. It has been reported that catalytic and bactericide properties of TiO2 can be improved by growing particles of a noble metal (Ag, Au or Cu) over its surface [13]. In this work, silver nanoparticles were synthesized on the surface of TiO2 fine particles using a simple aqueous reduction method and the composites thus obtained (TiO2@Ag) were characterized using TEM, STEM, SEM, EDS, XRD, UV-VIS spectroscopy, DLS and XPS. An antibacterial activity test (NCCLS M7-A4, 1997) was conducted in order to confirm the improved bactericide properties of the composites obtained.

2 EXPERIMENTAL SECTION

2.1 Materials

TiO_2 particles (DuPont™ Ti-Pure® R-902 and Degussa P25), $AgNO_3$ (Sigma Aldrich, ACS Reagent), $NaBH_4$ (Sigma Aldrich, ACS Reagent) and NH_4OH (30 % w/w aqueous solution, Sigma Aldrich, ACS Reagent) were used as received without further purification.

2.2 Synthesis Method

For a typical procedure, 0.2000 g (2.5 mmol) of commercial TiO_2 particles were dispersed in 100 mL of deionized water by using ultrasonic by approximately five minutes, immediately 0.0169 g (0.1 mmol) or 0.0425 g (0.25 mmol) of $AgNO_3$ were added. The solution was magnetically stirred for about 30 minutes at pH = 7. After this, sodium borohydride, which was previously dissolved in 10 mL of deionized water, was added as reducing agent. The pH of the reaction media was adjusted to 10 by dropping NH_4OH, finally the solution was magnetically stirred for 30 minutes. After this time, the products obtained (TiO_2@Ag) were filtered, washed and dried for further characterization. Hereafter, DuPont™ particles will be named as TiO_2_1 and Degussa particles will be named as TiO_2_2. Three different samples were synthesized; the samples obtained using TiO_2_1 and molar ratios of 25:1 and 10:1 (TiO_2:Ag) will be named as TiO_2_1@Ag25 and TiO_2_1@Ag10 respectively. The sample prepared using TiO_2_2 and a molar ratio of 10:1 (TiO_2:Ag) will be named as TiO_2_2@Ag10.

2.3 Characterization

The produced composites were characterized by UV-VIS spectroscopy using a S2000-UV-VIS spectrometer from OceanOptics Inc. Dynamic Light Scattering analysis was performed in a Malvern Zetasizer Nano ZS. X-Ray Diffraction pattern were obtained on a GBC-Difftech MMA model, with Cu K_{α} irradiation at λ= 1.54 Å. Transmission Electron Microscopy (TEM) analysis was performed on a JEOL JEM-1230 at an accelerating voltage of 100 kV, the STEM images were obtained on a JEOL 2010F. Scanning Electron Microscopy (SEM) analysis was performed on a Phillips XL-30 SEM equipped with an EDS spectrometer EDAX DX-4 Model. XPS analysis of the powder samples was carried out using a Kratos AXIS ULTRA XPS system fitted with a monochromated Al K_{α} X-ray source and a hemispherical analyser with eight channeltrons. The source was operated at 10 mA and 15 kV. UV-VIS spectroscopy, SEM, EDS, XRD and XPS analysis were made using dried powders and TEM, STEM and DLS analysis were made using aqueous dispersions of the TiO_2@Ag composites.

2.4 Antibacterial test

The antimicrobial activity of the synthesized composites was tested using the standard microdilution method, which determines the minimum inhibitory concentration (MIC) leading to inhibition of bacterial growth (NCCLS M7-A4, 1997). Disposable microtitration plates were used for the tests. The composites in dispersion form were diluted 2-128 times with 100 μL of Mueller-Hinton broth inoculated with the tested bacteria at a concentration of 10^5 CFU/mL. The minimum inhibitory concentration (MIC) was read after 24 h of incubation at 37 °C as the MIC of the tested substance that inhibited the growth of the bacterial strain. The dispersions were used in the form in which they had been prepared. Therefore, control bactericidal tests of solutions were performed containing all the reaction components.

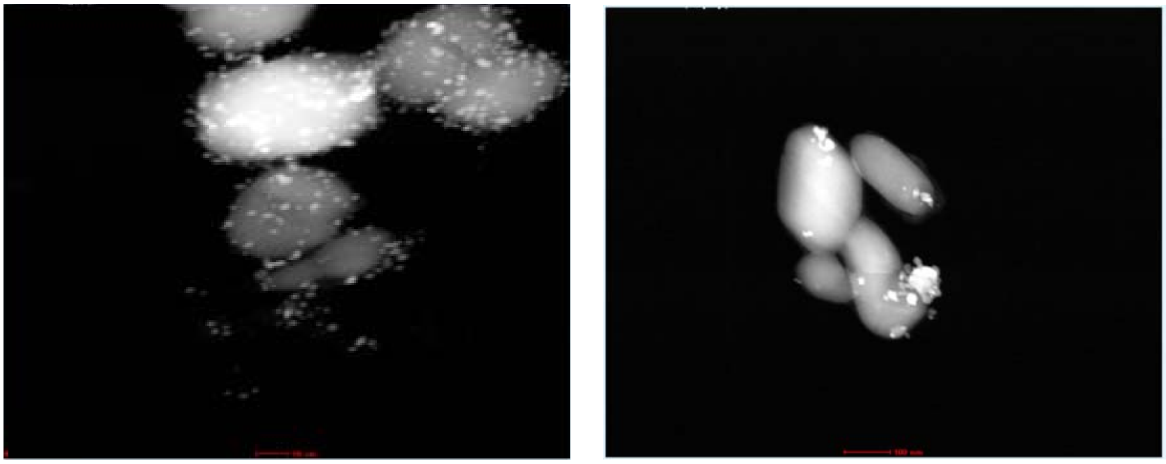
3 RESULTS AND DISCUSSION

3.1 Synthesis

Silver ions (Ag^+) can be deposited over the surface of TiO_2 particles by a cationic adsorption. TiO_2 is an anphoteric oxide with an isoelectronic point IEP = 6 [15]. When the pH value of a TiO_2 dispersion is lower than 6 the main surface specie is —OH_2^+, when the pH value of a TiO_2 dispersion is bigger than 6 the main surface specie is —O^-, in the latter case the surface of TiO_2 particles is negatively charged and silver ions can be deposited over its surface [13]. In this work, in order to ensure a complete adsorption of the silver ions, a mixture of TiO_2 particles and silver ions (added as silver nitrate) was magnetically stirred for about 30 minutes at pH = 7. After that, the reduction reaction proceeded on the surface of TiO_2 particles.

3.2 TEM and STEM

Using TEM we can confirm the size of the TiO_2_1 particles and, the most important information extracted is the irregular thin layer observed on the surface of TiO_2 particles, this could be a layer made of SiO_2 and Al_2O_3 (according with the results obtained in EDS analysis). TiO_2_2 particles have a spherical morphology and a particle size ranging from 15 nm to 70 nm. Using TiO_2_1 particles and increasing the amount of silver nitrate in reaction we can not produce more Ag nanoparticles as we expected, instead silver nanoparticles already formed on the surface of TiO_2_1 grow. The reason of this unexpected behavior could be the presence of the irregular SiO_2-Al_2O_3 thin layer on the surface of TiO_2_1 particles. SiO_2 and Al_2O_3 have no reactivity if they are not activated [16], so Ag nanoparticles are formed only on the spots where there is no SiO_2-Al_2O_3 thin layer; in a moment, these spots are replete and the remaining silver ions are deposited over the first silver nanoparticles formed and finally they grow. If we use TiO_2_2 instead of TiO_2_1 and if we maintain the concentration of Ag^+ as a constant, the amount of silver nanoparticles over the surface of TiO_2 particles increases considerably, the reason of this could be, again, the presence of the SiO_2-Al_2O_3 thin layer on the surface of TiO_2_1 and the fact that Degussa P25 is reported as the most reactive phase of TiO_2 [17].



a) b)

Figure 1. STEM images of the samples a) TiO_2_1@Ag25 and b) TiO_2_1@Ag10. These images show that silver nanoparticles are bigger in sample TiO_2_1@Ag10 than in sample TiO_2_1@Ag25.

3.3 Antibacterial results

Minimum inhibitory concentration values were obtained for the synthesized composites tested against *E. coli* (Gram negative bacteria, ATCC 25922) and *S. aureus* (Gram positive bacteria, ATCC 25923). The results are presented as average values on table 1 (the Kruskal-Wallis test was applied). Control sample containing all the initial reaction components showed no antibacterial activity.

Material	Minimum Inhibition Concentration[c] (μg/mL)	
	Bacteria	
	E. coli	*S. aureus*
TiO_2_1	-[a]	-[a]
TiO_2_2	-[a]	-[a]
TiO_2_1 @Ag25	130.2 (0.651)	250 (1.25)
TiO_2_2 @Ag10	358.5 (35.94)	333.3 (33.3)
TiO_2_2 @Ag10	190.1 (19.01)	208.3 (20.67)
Ag nanoparticles[b]	13.02	16.67

[a] No antibacterial activity was found with the concentrations tested in this work.
[b] 20 nm Ag nanoparticles were synthesized under the same conditions as the composites but without the presence of TiO_2 particles.
Values on parentheses represent the calculated content of silver in the composites.

Table 2. Minimum Inhibition Concentrations of TiO_2 particles, Ag nanoparticles and TiO_2@Ag composites.

TiO_2_1@Ag25 sample has higher antibacterial activity than the other composites and present higher antibacterial activity than TiO_2 particles. If we compare the MIC of TiO_2_1@Ag25 with that of silver nanoparticles we can see that the MIC of the latter is lower but the silver content in TiO_2_1@Ag25 sample is much lower (almost 20 times) than the MIC of silver nanoparticles, then, we can say that there is a real synergetic antibacterial activity in these composites. The fact that TiO_2_1 and TiO_2_2 particles showed no antibacterial activity is due to the test conditions, the test was performed on dark. It is reported [8, 14] that bactericide activity of TiO_2 is directly related to ultraviolet light absorption and formation of free radicals, so in dark conditions TiO_2 particles present no bactericide activity which is consistent with our results. By the other hand, all the TiO_2@Ag composites show antibacterial activity even though no light is present. The antibacterial mechanism of these composites is under investigation by our group.

4 CONCLUSIONS

Silver nanoparticles were synthesized over the surface of two different commercial TiO_2 particles. The composites thus obtained were characterized, using XRD, XPS and UV-VIS analysis it was demonstrated that the nature of the nanoparticles prepared is elemental silver; these silver nanoparticles are well distributed over the surface of TiO_2 particles and their average size is about 20 nm. The antibacterial activity of TiO_2 nanoparticles was improved and is dependent on the sort of TiO_2 particles. In this work, the best results were achieved using TiO_2 Dupont™ particles, a TiO_2:Ag molar ratio of 1:25.

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