

RESEARCH ARTICLE

Ag@TiO₂ Core-Shell Nanoparticles as Antifungal Agents: Synthesis, Characterization and Antifungal Activity Screening

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ABSTRACT

One pot simultaneous reduction of AgNO₃ and hydrolysis of Ti (IV) isopropoxide form core-shell type Ag@TiO₂ nanoparticles. The following are their notable characteristics: electronic absorption, XRD, FTIR, TGA, DSC and HR-TEM techniques. XRD patterns reveal that anatase form of TiO₂ and the noble metal (Ag) are present in them. That there is below 50nm is understood through high resolution transmission electron microscopic measurements. Agar diffusion method examined the antifungal properties of Ag@TiO₂ core-shell nanoparticles against *Candida Albicans*, *Candida Glabrata*, *Aspergillus Niger* and *Aspergillus Flavus*. The Ag@TiO₂ core-shell nanoparticles show enhanced antifungal activity. These factors give the idea that TiO₂, if supported on the exterior of the Ag NPs without aggregation is confirmed to be an efficient novel antifungal agent.

Keywords: Core-shell nanoparticles, Characterization, Agar diffusion method, Antifungal activity, Antifungal agent.

1. INTRODUCTION

Fungal infections are caused by opportunistic fungi and that too in people who are suffering by immune weakness as they are either victims of HIV or when they are pregnant. Antifungal agents which are in use are limited. So the need for such antibiotics with innovative antimicrobial mechanisms is felt everywhere [1].

Nanotechnology is seen to be popular in objects of daily use of people of all walks of life. It has given way to new products infused with its qualities. Its salient feature is that nanoparticles can be trusted for more structural integrity and also more efficient chemical, optical, mechanical and magnetic qualities than materials used in bulk measures. This characteristic is possible because of the variations applied in terms of size, distribution and structure of particles. Though nanomaterials are derived from many other elements and metals, silver nanoparticles (Nano-Ag) have shown immensely that they are more efficient than other choices of this kind and because they possess superior

effectiveness against fungi bacteria and eukaryotic micro-organisms as they exhibit large surface to volume ratio. Its toxicity is less than that of other metals to mammalian cells. Another feature is that antimicrobial activity aggravates when the size of Ag nanoparticles decrease. But one drawback is that these particles when have a diameter smaller than 200nm would incline to aggregate instinctively and so their stability in material such as air, water etc. is not reliable for better productivity. This will cause a downgraded result. As a remedy to this, large variety of materials such as TiO₂, SiO₂, Al₂O₃ etc. and activated carbon fibres are put in to help. Ag nanoparticles or the ultra-fine Ag nanoparticles could be consistently produced escaping aggregation. Titania, being one of the oxide semiconductors has been established as the most appropriate one for environment application because it has high level merits such as chemical stability, non-toxicity, low cost and excellent degradation of organic pollutants. TiO₂ nanoparticles are easy to be attached to the cell membranes and to be accumulated. TiO₂ nanoparticles can be used for various purposes

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in paint, plastic, paper, rubber, food etc. They can also be used as UV blockers instead of the bulk forms, in sunscreens and plastics for their noted performance in the absorption of UV light and stability in photo degradation [2, 3, 4, 5].

Recently, core-shell composite structures have emerged as a type of new nanostructures, as they have been understood with low toxicity, chemical stability, long lasting action period and thermal resistance versus organic antimicrobial agents. These particles are helpful as they provide a new possibility as good agents for antimicrobial substances because of their unique structures with the shell to protect the particles and also to stabilize them against corrosion. These nanoparticles with antifungal characteristics are useful in construction materials because they can bring advantages like enhancing hygienic properties, preventing microbial growth and maintaining their mechanical properties [6, 7, 8].

This study mainly synthesizes Ag@TiO₂ core-shell NPs and characterises the shell by electronic absorption, XRD, FTIR, TGA, DSC and HR-TEM techniques. The antifungal activity of the prepared Ag@TiO₂ core-shell NPs was also examined against *C. Albicans*, *C. Glabrata*, *A. Niger* and *A. Flavus* by agar diffusion method.

2. MATERIALS AND METHODS

2.1. Reagents

The materials are procured from different sources: Titanium (IV) isopropoxide from Sigma Aldrich, AgNO₃ from Merck, other chemicals are of AnalaR grade, water is of Milli-Q type [9].

2.2. Synthesis of Ag@TiO₂ core-shell nanoparticles

There is a minor difference in the method of the preparation of the core-shell type Ag@TiO₂ which is described in the literature. In short, 20 mm each of Ti (IV) isopropoxide and acetylacetone in 30 ml of isopropanol are prepared as the mixture was sonicated for 15 minutes. Then 10 mm solutions of AgNO₃ in 5 ml of milli-Q water is prepared. After that 20 ml of DMF is added and then it was stirred thoroughly. After that 30 ml of the sonicated solution was added and stirred well for 10 minutes. And for 1 hour the

mixture was refluxed at ~60-70° C. The refluxing was continued for 1 hour after the solution became greenish black. The precipitation was obtained and this was sonicated further for 2 hours for it to disperse. When the toluene was added a precipitation was formed and washed several times with toluene and then it was redissolved in isopropanol. After the evaporation of the solvent at room temperature a greenish black powder of Ag@TiO₂ core-shell nanoparticles [10, 11].

2.3. Characterization

Perkin Elmer Lambda 35 spectrophotometer was used to record UV-Visible spectra. FTIR spectroscopic measurements were carried out using Perkin Elmer FTIR Spectrum RXI spectrometer. Recording of the X-ray diffraction (XRD) patterns was successfully done by using X'pert PRO PAN analytical diffractometer operating with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$) source. By using a JEOL JEM -3010 Electron microscope operating at 300keV, High Resolution Transmission Electron Microscopy (HRTEM) photographs were taken. The magnifying power used is in between 600–800 k times. AFM images were taken in a VECO/Digital instruments Nanoscope III atomic force microscope [12, 13, 14].

2.4. Antifungal activity

Using the agar diffusion method, the in vitro antifungal activity of Ag@TiO₂ core-shell NPs were tested against the fungal species *C. Albicans*, *C. Glabrata* and *A. Flavus*. In the beginning stage, the stock cultures revitalized by inoculating in broth media and grown at 27° C for 48 hours. The agar plates of the media (Czapek-Dox Agar: Composition (g/l) Sucrose-30.0; Sodium nitrate-2.0, K₂HPO₄-1.0, MgSO₄·7H₂O-0.5, KCl-0.5, FeSO₄-0.01, Agar-20) were formed and wells were made in the plate. Each inoculation is done in all the plates with 48 hrs old cultures (100 μ l 10⁴ CFU) and kept evenly on the plate. The wells were filled with various levels of concentrations of samples after 20 minutes. Inoculation is done in all the places at 27° C for 96 hours and the diameter of the inhibition zone were recorded [15, 16, 17, 18].

3. RESULTS AND DISCUSSION

3.1. UV-Visible spectral analysis

The absorption spectrum of Ag@TiO₂ is shown in figure 1. It has a broad band centred at 425 nm. However, it is reported that the plasmon absorption band of the small Ag particles prepared using borohydride reduction is around 380 nm. The red shift in the Ag@TiO₂ spectrum may be due to increase in the particle dimension and /or change in the dielectric constant of the surrounding matrix upon encapsulation [19, 20, 21, 22, 23].

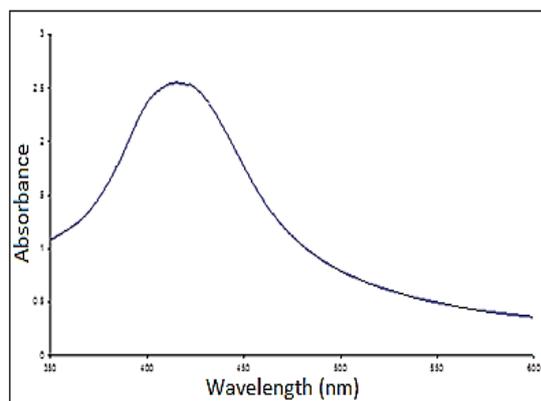


Figure 1. UV-Visible spectrum of Ag@TiO₂ core-shell NPs

3.2. XRD analysis

The identity, relative proportion and average grain size of the core-shell nanoparticle are determined with the help of standard X-ray powder diffraction. From figure 2 (a&b) we can see the X-ray diffraction pattern of pre and post annealed Ag@TiO₂ (at 650 °C in the air for 5hrs) respectively. Figure 2(a) details that the air dried Ag@TiO₂ core-shell nanoparticle is completely amorphous because the peak corresponding to TiO₂ and Ag is absent. Figure 2 (b) shows 4 characteristic peaks of Ag@TiO₂ core-shell nanoparticles. The peak at $2\theta = 25.42^\circ$ (101) corresponds to the anatase form of TiO₂. The peaks at 37.99, 45.12, 64.93° (2θ) were identified to originate from (111), (200) and (220) planes of Ag respectively. This shows the face centered cubic phase with cell parameter $a = 4.012 \text{ \AA}$. The average crystal grain size calculated using Scherrer equation is found to be 39 nm.

3.3. FTIR Spectrum

The FTIR spectrum of Ag@TiO₂ is displayed in figure 3. The air dried sample of Ag@TiO₂ shows no characteristic peaks due to DMF. The defective OH vibrations are obtained below 3500cm⁻¹. The peaks observed at 3362

and 1625cm⁻¹ are ascertained to the OH stretching and bending vibrations of water molecule respectively whereas the peak observed at 531 cm⁻¹ is due to the Ti-O stretching vibration. In the FTIR spectrum of Ag@TiO₂, the alkoxide C-O stretching and CH₂ bending vibrations are observed at 1114 and 1382cm⁻¹ respectively. From this we can say that, alcohol may be adsorbed on the surface. The CH₂ stretching vibrations generally appears below 3000cm⁻¹ region, but in this case it is not well resolved in the spectrum. Thus, the FTIR spectrum is comparable to earlier reports in the literature [23].

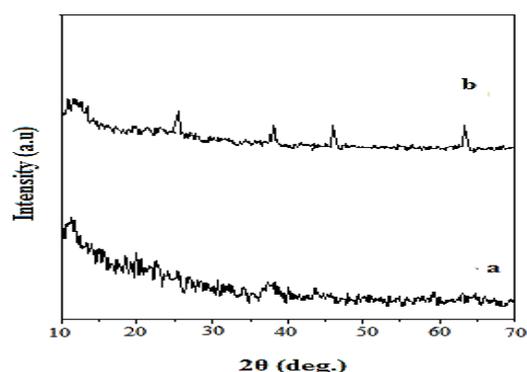


Figure 2. XRD pattern of a) air dried Ag@TiO₂ core-shell NPs and b) Ag@TiO₂ core-shell NPs annealed at 650 °C

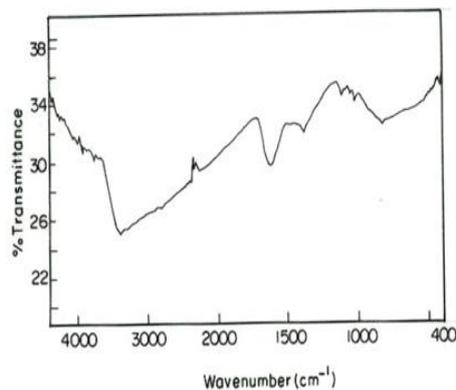


Figure 3. FT-IR spectrum of Ag@TiO₂ core-shell NPs

3.4. High Resolution Transmission Electron Microscopy (HR-TEM)

The HR-TEM images of Ag@TiO₂ are shown in figure A1(a-c). We can see most of the dark images of Ag core in the size regime. Figure A1(a) is an illustration of the formation spherical particles of silver core with a particle diameter 15-20nm and a range

of particle morphologies. Most of the particles appear in this image is spherical or oval in shape but faceted structures are also found. All the particles are seen to be associated with TiO₂ shell. The boundary between core (Ag) and shell (TiO₂) is quite clear (figure A1(b & c)). Figure A1(b & c) illustrate HR-TEM image of single Ag@TiO₂ particle. Through this it is made clear that each particle is covered by a thin capping of TiO₂ shell of thickness in the range 2-3 nm. The aggregation of fine particles of Ag is represented by dense regions and associated TiO₂ as shown in figure A1(a).

Through microscopy it is understood that free silver and oxide particles are not present. The existence of completely covering shells is proved by reactivity studies. Checking the shell's stability in acidic solution (HNO₃) confirms the capping of TiO₂ shell on the Ag core. The Ag cluster when stabilized by citric acid is readily and soon dissolved in acidic solution (pH = 2). But Ag@TiO₂ is almost stable in HNO₃ solution even if TiO₂ shell is thin. Both clusters take origin individually or in the form of a TiO₂/Ag sandwich structure if the formation of TiO₂ clusters in DMF is so independent. The dissolution of Ag clusters is very much witnessed. That the TiO₂ shell on the Ag core is uniform and provides the protection against acid induced corrosion [24, 25, 26] is affirmed by the stability test in acidic solution.

3.5. Energy Dispersive X-ray analysis (EDX)

The deposition of TiO₂ nanoparticles on the Ag surfaces are shown on EDX spectrum (figure 4). The presence of Ag, Ti and O are affirmed by the EDX outcome of the coated Ag core with TiO₂ shell. No other but Ti and O peaks are obtained from the TiO₂ shell. They mark the purity of the core-shell nanoparticles.

3.6. Atomic Force Microscopy (AFM)

Figure A2(a&b) shows the two-dimensional (2D) and three - dimensional (3D) AFM images of Ag@TiO₂ core-shell NPs. These are in different sizes. Nanosize particles are in plenty. The estimated value of average roughness (Ra) and root mean square roughness (Rq) are 2.474 and 5.190 nm respectively.

The Roughness skewness (Rsk) for Ag@TiO₂ core-shell NPs is found as - 4.704 nm. The indication of this negative value is that the valleys are greater over the scanned area. Roughness kurtosis (Rku) for Ag@TiO₂ core-shell NPs is 25.575 nm. The Rku values clarify that the surface of Ag@TiO₂ core-shell NPs is a spiky surface.

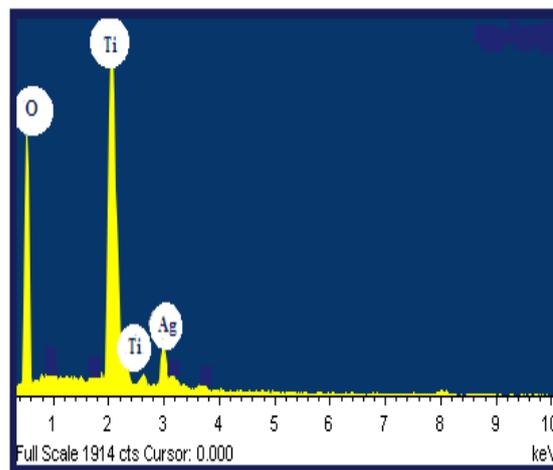


Figure 4.EDX spectrum of Ag@TiO₂ core-shell NPs

3.7. Antifungal activity of Ag@TiO₂ core-shell nanoparticles

The antifungal activity of Ag@TiO₂ core-shell nanoparticles against the fungal species, C.Albicans, C.Glabrata, A.Niger and A.Flavus is measured using the agar diffusion method. The results appear in figure 5.

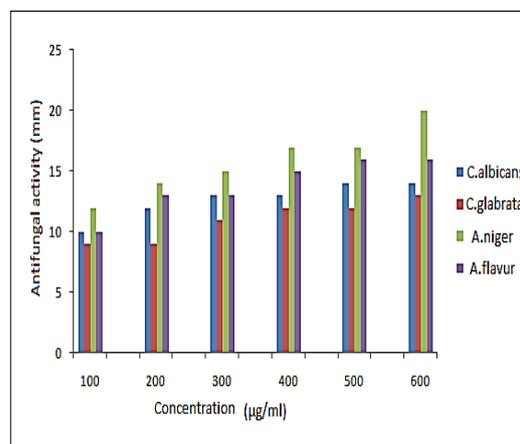


Figure 5. Antifungal activity of Ag@TiO₂ core-shell NPs

The data received shows the high antifungal activity of Ag@TiO₂ core-shell NPs against C.Albicans, C.Glabrata, A.Niger and

A.Flavus. When the concentration of core-shell NPs increases, the antifungal activity increases. The MIC observed in this study for Ag@TiO₂ core-shell NPs are 100 µg/ml. The inhibition zone of A.Niger is higher than that for C.Albicans, C.Glabrata and A.Flavus.

In addition to these the disruption of trans-membrane energy metabolism may be taken for the cause of the antifungal activity of silver nanoparticles. Apart from this the formation of insoluble compounds in the cell wall disrupts the electron transport chain. The inactivation of the cell wall sulphhydryl group may result in the formation of the insoluble compounds. On the contrary silver ions can create mutations in fungal DNA by displacing the hydrogen bonds. A great effect on the blocking of the growth of the microorganisms is from the reaction of the surface modified nanoparticles with the peptide glycol layer of the cells [27]. So it is understood that the Ag ions from Ag cores could be released through porous TiO₂ shells. It may be responsible for the core/shell structures to prevent corrosion and prolonging the release time of Ag ions and preserving the sustained antifungal behaviour [28, 29, 30].

4. CONCLUSION

The preparation of Ag@TiO₂ core-shell nanoparticles is accomplished well. The analysis of its structure using different methods and technique: UV-vis spectroscopy, XRD, FTIR, TGA, DSC and HR-TEM is done. The core-shell NPs show good antifungal activities because of the deposition on the TiO₂ on the surface of Ag NPs, which checks aggregation. The anti-fungal activity of Ag@TiO₂ core-shell NPs grows as the core-shell NPs in the medium concentrates. The concentration required differs in the case of different fungi, but the Ag@TiO₂ core-shell NPs are relatively safe and do not cause for any serious side-effects when compared to other anti-fungal drugs. Hence the absorption of these core-shell NPs with antifungal medicines may advance their activity.

REFERENCES

- [1] S.Silver, Bacterial Silver Resistance: Molecular Biology and Uses and Misuses of Silver Compounds, FEMS Microbiology Reviews, Vol. 27, 2003, pp. 341–353,
- [2] H.J.Klasen, A Historical Review of the Use of Silver in the Treatment of Burns. II. Renewed interest for silver, Burns, Vol. 26, No. 2, 2000, pp. 131–138, [http://dx.doi.org/10.1016/S0305-4179\(99\)00116-3](http://dx.doi.org/10.1016/S0305-4179(99)00116-3).
- [3] K.Govindaraju, ΔS.Khaleel Basha, V.Ganesh Kumar and G.Singaravelu, Silver, Gold and Bimetallic Nanoparticles Production Using Single-Cell Protein (Spirulina platensis) Geitler, Journal of Material Science, Vol. 43, No. 15, 2008, pp. 5115–5122, <http://dx.doi.org/10.1007/s10853-008-2745-4>.
- [4] G.J.Zhao and S.E.Stevens, Multiple Parameters for the Comprehensive Evaluation of the Susceptibility of Escherichia Coli to the Silver Ion, Biometals, Vol. 11, No. 1, 1998, pp. 27–32, <http://dx.doi.org/10.1023/A:1009253223055>.
- [5] C.Baker, A.Pradhan, L.Pakstis, D.J.Pochan and S.I.Shah, Synthesis and antibacterial properties of silver nanoparticles, Journal of Nanoscience and Nanotechnology, Vol. 5, No. 2, 2005, pp. 244–249, <https://doi.org/10.1166/jnn.2005.034>.
- [6] Shunsheng Cao, Juanrong Chen and Jie Hu, The fabrication and progress of core-shell composite materials, Australian Journal of Chemistry, Vol. 62, No. 12, 2010, pp. 1561-1576, <http://dx.doi.org/10.1071/CH08420>.
- [7] O.Akhavan, Lasting Antibacterial Activities of Ag–TiO₂/Ag/a-TiO₂ Nano Composite Thin Film Photocatalysts under Solar Light Irradiation, Journal of Colloid and Interface Science, Vol. 336, No. 1, 2009, pp. 117–124, <http://dx.doi.org/10.1016/j.jcis.2009.03.018>.
- [8] S.D.Oh, S.H.Lee, S.H.Choi, I.S.Lee, Y.M.Lee, J.H.Chun and H.J.Park, Synthesis of Ag and Ag–SiO₂ Nanoparticles by Irradiation and Their Antibacterial and Antifungal Efficiency Against Salmonella

- Enterica Serovar Typhimurium and Botrytis cinerea, Colloids and Surfaces A: Physicochemical and Engineering Aspects, Vol. 275, 2006, pp. 228–233, <http://dx.doi.org/10.1016/j.colsurfa.2005.11.039>.
- [9] Q.Y.Chang, L.Z.Yan, M.X.Chen, H.He and J.H.Qu, Bactericidal Mechanism of Ag/Al₂O₃ Against Escherichia Coli, Langmuir Vol. 23, No. 22, 2007, pp. 11197–11199, <http://dx.doi.org/10.1021/la701006r>.
- [10] Y.Inoue, M.Hoshino, H.Takahashi, T.Noguchi, T.Murata, Y.Kanzaki, H.Hamashima and M.Sasatsu, Bactericidal Activity of Ag–Zeolite Mediated by Reactive Oxygen Species Under Aerated Conditions, Journal of Inorganic Biochemistry, Vol. 92, No. 1, 2002, pp. 37–42, [http://dx.doi.org/10.1016/S0162-0134\(02\)00489-0](http://dx.doi.org/10.1016/S0162-0134(02)00489-0).
- [11] S.X.Chen, J.R.Liu and H.M.Zeng, Structure and Antibacterial Activity of Silver Supporting Activated Carbon Fibers, Journal of Materials Science, Vol. 40, No. 23, 2005, pp. 6223–6231, <http://dx.doi.org/10.1007/s10853-005-3149-3>.
- [12] Y.H.Kim, D.K.Lee, H.G.Cha, C.W.Kim and Y.S.Kang, Synthesis and Characterization of Antibacterial Ag–SiO₂ Nano Composite, Journal of Physical Chemistry C, Vol. 111, No. 9, 2007, pp. 3629–3635, <http://dx.doi.org/10.1021/jp068302w>.
- [13] M.Ksibi, S.Rossignol, J.M.Tatibouet and C.Trapalis, Synthesis and Solid Characterization of Nitrogen and Sulfur-Doped TiO₂ Photocatalysts Active under Near Visible Light, Materials Letters, Vol. 62, No. 26, 2008, pp. 4204–4206, <http://dx.doi.org/10.1016/j.matlet.2008.06.026>.
- [14] W.P.Wang, J.L.Zhang, F.Cheng, D.He and M.Anpo, Preparation and photocatalytic properties of Fe³⁺-doped Ag@TiO₂ core-shell nanoparticles, Journal of Colloid and Interface Science, Vol. 323, No.1, 2008, pp. 182–186, <http://dx.doi.org/10.1016/j.jcis.2008.03.043>.
- [15] Q.H.Zhang, W.G.Fan and L.Gao, Anatase TiO₂ nanoparticles immobilized on ZnO tetrapods as a highly efficient and easily recyclable photocatalyst, Applied Catalysis B: Environmental Vol. 76, No. 1, 2007, pp. 168–173, <http://dx.doi.org/10.1016/j.apcatb.2007.05.024>.
- [16] J.G. Yu, X.J. Zhao and Q.N. Zhao, Effect of surface structure on photocatalytic activity of TiO₂ thin films prepared by sol–gel method, Thin Solid Films Vol. 379, No. 1, 2000, pp. 7–14, [http://dx.doi.org/10.1016/S0040-6090\(00\)01542-X](http://dx.doi.org/10.1016/S0040-6090(00)01542-X).
- [17] R.Cai, K.Hashimoto, K.Itoh, Y.Kubota and A.Fujishima, Photo killing of Malignant Cells with Ultrafine TiO₂ Powders, Bulletin of the Chemical Society of Japan, Vol. 64, No. 4, 1991, pp. 1268-1273.
- [18] M.E. Ahmed, Y. Shu and S. Tsugio, Control of silica shell thickness and microporosity of titania–silica core–shell type nanoparticles to depress the photocatalytic activity of titania, Journal of Colloid and Interface science, Vol. 300, No. 1, 2006, pp. 123-130, <http://dx.doi.org/10.1016/j.jcis.2006.03.073>.
- [19] M.Bonini, A.Wiedenmann and P.Bagliioni, Synthesis and characterization of magnetic nanoparticles coated with a uniform silica shell, Materials Science and Engineering C, Vol. 26, No. 5, 2006, pp. 745-750, <http://dx.doi.org/10.1016/j.msec.2005.09.042>.
- [20] E.C.Antonio, P.Carlos, A.Eduardo, S.Julio and M.J.Antibacte. Journal of Materials Science, Vol. 41, 2006, pp. 5208.
- [21] Yue lin, Wang Qiqiang, Zhang Xiaoming, Wang Zhouping, Xia Wenshui, and Dong Yuming, Synthesis of Ag/TiO₂ Core/Shell Nanoparticles with Antibacterial Properties, Bulletin Korean Chemical Society, Vol. 32, No. 8, 2011, pp. 2607-2610, <http://dx.doi.org/10.5012/bkcs.2011.32.8.2607>.

- [22] J.Pulit, M.Banach, R.Szczygłowska and M.Bryk, Nanosilver Against Fungi. Silver Nanoparticles as an Effective Biocidal Factor, *Acta Biochimica Polonica*, Vol. 60, No. 4, 2013, pp. 795–798.
- [23] T.Renjis, A.Tom, S.Kumaran Nair, M.Navinder Singh, Aslam, C.L.Nagendra, Reji Philip, K.Vijaya Mohanan and T.Pradeep, Freely Dispersible Au@TiO₂, Au@ZrO₂; Ag@TiO₂ and Ag@ZrO₂ Core-Shell Nanoparticles: One-Step Synthesis, Characterization Spectroscopy and Optical Limiting Properties, *Langmuir*, Vol. 19, No. 8, 2003, pp. 3439-3445, <http://dx.doi.org/10.1021/la0266435>.
- [24] E.J.Threlfall, I.S.T.Fisher, L.Ward, H.Tschape and P.Gerner-Smidt, Harmonization of Antibiotic Susceptibility Testing for Salmonella: Results of a Study by 18 National Reference Laboratories within the European Union-Funded Enter-Net Group. *Microbial Drug Resistance*, Vol. 5, No. 3, 1999, pp. 195–199, <http://dx.doi.org/10.1089/mdr.1999.5.195>.
- [25] R.D.Walker, Antimicrobial Susceptibility Testing and Interpretation of Results, *Antimicrobial Therapy in Veterinary Medicine*, Iowa State University Press, Ames, 2000, pp. 12–26.
- [26] Tsutomu Hirakawa and P.V.Kamat, Charge Separation and Catalytic Activity of Ag@TiO₂ Core-Shell Composite Clusters Under UV-Irradiation, *Journal of the American Chemical Society*, Vol. 127, No. 11, 2005, pp. 3928-3934, <http://dx.doi.org/10.1021/ja042925a>.
- [27] Nadia G.Kandile, H.T.Zaky, M.I.Mohamed and Hemat M.Mohamed, Silver Nanoparticles Effect on Microbial and Antifungal Activity of New Heterocycles, *Bulletin of the Korean Chemical Society*, Vol. 31, No. 12, 2010, pp. 3530-3538, <http://dx.doi.org/10.5012/bkcs.2010.31.12.3530>.
- [28] Y.Lin, W.Qiqiang, Z.Zhouping, W.Wenshui and D.Yuming, Synthesis of Ag@TiO₂ Core-Shell Nanoparticles with Antibacterial Properties, *Bulletin of the Korean Chemical Society*, Vol. 32, No. 8, 2011, pp. 2607-2610, <http://dx.doi.org/10.5012/bkcs.2011.32.8.2607>.
- [29] K.Sampath and C.Jayabalakrishnan, Ruthenium(III) Thiosemicarbazone Complexes: Synthesis, Characterization, DNA Binding, Antibacterial, In vitro Anticancer and Antioxidant Studies, *DJ Journal of Engineering Chemistry and Fuel*, Vol. 1, No. 1, 2016, pp. 40-53, <http://dx.doi.org/10.18831/djchem.org/2016011004>
- [30] C.Wu, A Review of Nanowire Growth via Vapour Deposition, *DJ Journal of Engineering Chemistry and Fuel*, Vol. 1, No. 3, 2016, pp. 1-7, <http://dx.doi.org/10.18831/djchem.org/2016031001>

APPENDIX

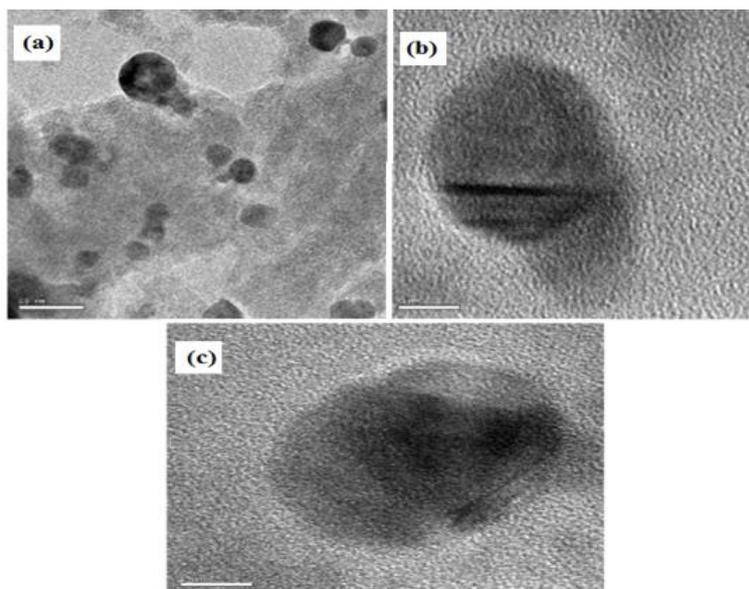


Figure A1(a, b & c).HR-TEM images of Ag@TiO₂ core-shell NPs

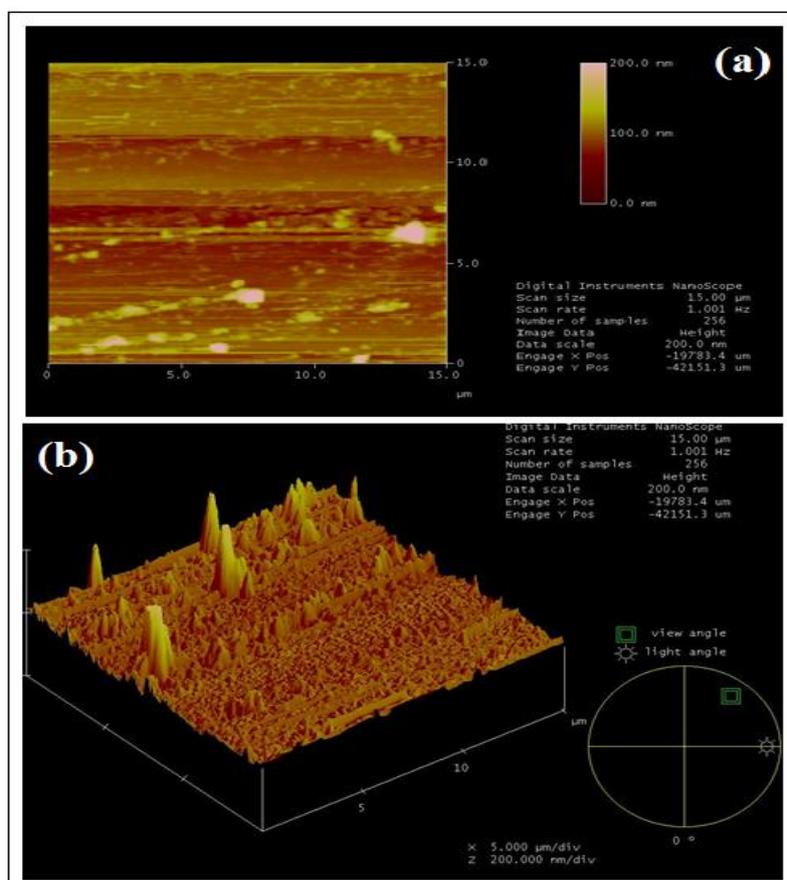


Figure A2(a & b).AFM image of Ag@TiO₂ core-shell NPs