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Synthesis of ortho phenylene diamine by oxidative polymerization technique

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ABSTRACT: phenylenediamines oxidation is associated with a photographic process. o-Phenylenediamine and especially substituted p-phenylenediamines have been used as developers in photography to reduce silver halides to silver metal and thus to convert the latent image to a negative and, subsequently, to a positive picture. The reduction of silver ions, and the consequent oxidation of phenylenediamines, took place under alkaline conditions.

KEYWORDS: Ortho phenylene diamine, redox-active, oxidative polymerization, Bond interactions

I.INTRODUCTION

Conducting and intrinsically colored polymers are extensively used in diverse applications. The design of their specific uses calls for the development of the appropriate processing techniques. Polyaniline, one of the most studied conducting polymers [1–6], is valued for its conductivity, redox activity, and responsivity to external stimuli. The conductivity of standard polyaniline is of the order of units $S\text{ cm}^{-1}$ [7] and it has a semiconducting character. Finally, the polymer character accounts for its mechanical properties [8] and endows polyaniline with materials features. Polyaniline finds uses in many fields [9,10]. In addition to conductivity, polyaniline ranks among electroactive polymers, i.e. polymers that exhibit a change in size or shape when stimulated by an electric field [11], a property exploited in actuators. On the other hand, they can be used for the electrical stimulation of biological objects or their monitoring [12]. High electrical polarizability makes polyaniline base applicable in electro rheological fluids [13,14]. Polyaniline is coloured and displays electrochromism, i.e. optical absorption maxima shift as polyaniline is oxidized or reduced [15]. Morphologies, displayed by polyaniline at nanoscale [16,17], such as nanotubes, thin films, or colloidal particles, are of importance in nanotechnologies. Polyaniline is a reactive polymer and its involvement in chemical reactions is used for its modification [18] or in sensors. The variability of electrical, optical, electrochemical, chemical properties of polyaniline thus makes this polymer attractive for many application fields [19]. Ortho-substituted anilines, such as o-methylaniline or o-methoxyaniline, are known to produce conducting polymers upon oxidation. It is reasonable to expect that ophenylenediamine, i.e. o-amino aniline, may produce a conducting polymer, too. Although the title of this section implies that we deal with polymers, the polymeric character of the oxidation products still has to be proved. Many papers claim the formation of poly(o-phenylenediamine) during the oxidation of o-phenylenediamine with ammonium peroxydisulfate [20], iron(III) chloride[21–23], iron(III) sulfate [24], hydrogen peroxide] or potassium dichromate [25].

Sensors and biosensors

Virtually all the sensors based on polyphenylenediamines are represented by the electrochemically polymerized films. They were designed as amperometric, potentiometric, or capacitive versions [26]. Electrochemically prepared polymer coating on the electrode produces a membrane, which can provide the selective transport of analytes to the electrode. The method of molecular imprinting, i.e. the preparation of the membrane in the presence of analytes, has often been employed.



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Supercapacitors

Super capacitors are energy-conversion devices which combine the benefits of batteries, based on an electrochemical redox processes, and capacitors, using the physical principles of energy storage.

Water treatment

The polymers of the polyaniline family, to which polyphenylenediamine belongs, are known to be efficient adsorbents of acids, dyes, and various heavy and noble-metal cations [27]. In combination with nanostructures these polymers display, and their catalytic properties, they are well predetermined for application in water purification. Poly(o-phenylenediamine) was used for the selective degradation of antibiotics in aqueous solutions or simulated waste waters. The polymer proved to be an efficient adsorbent of lead ions.

II. SIGNIFICANCE OF THE SYSTEM

Chemical oxidative polymerization has accorded various functional polymers. Typical are polyaniline, poly-toluidine, polypyrrole, polyaminopyridine, polythiophene, and polyphenylenediamine, showing high conductivity. Among them, polyphenylenediamine homopolymer has attracted attention recently because it has been reported to be a highly aromatic polymer containing 2,3-diami-nophenazine or quinoxaline repeat unit and exhibits unusually high thermo stability. The objectives of present investigation are to Synthesize ortho phenylene diamine by oxidative polymerization with Silver Nitrate, Potassium persulphate, Copper Sulphate and Ferric Chloride hexa hydrate nano particles and to Characterize the resultant with SEM & FTIR studies

III. METHODOLOGY

Preparation

A. Oxidative polymerization

Three phenylenediamine isomers exist and are used as bases or as salts, usually dihydrochlorides. In alkaline solutions the base form is present, while in acidic aqueous solution the protonated salt forms prevails, the proportions between both forms being pH-dependent. This is important for practical experiments because the oxidation of the protonated forms would differ from that of the bases, as is well documented for aniline. Phenylenediamines have two primary amino groups that can be used in the oxidative linkage of monomers. Various polymer structures resulting from this process can be proposed. The polyaniline-like chain with pendant amino groups is probably the most obvious. Especially at higher oxidant concentration, however, both amino groups may be involved in producing a phenazine-like ladder structure. The ladder could be visualized as two entwined polyaniline chains. The oxidation products, however, have different properties and also their structures are likely to be different. Others chain constitutions, including branched or crosslinked chains, can be proposed and are most probably met in practice.

B. SYNTHESIS OF ORTHO PHENYLENE DIAMINE WITH FOUR DIFFERENT DOPENTS

5.4g of ortho phenylene diamine and 13.5g of three different dopents like silver nitrate, potassium persulphate, Copper sulphate, Ferric chloride hexa hydrate were taken in a separate 250 ml beakers containing 20ml of double distilled water and 20ml of alcohol. Both the solutions stirred well and mixed with each other carefully. The solution was left undisturbed for a day for precipitation. The precipitate formed was filtered through funnel using standard filter paper and alcohol. The filtrate was kept in oven for drying. The dried nano powders of ortho phenylene diamine were doped with silver nitrate, potassium persulphate, Copper sulphate, Ferric chloride hexa hydrate were obtained and characterized with SEM and FTIR Techniques.

IV. EXPERIMENTAL RESULTS

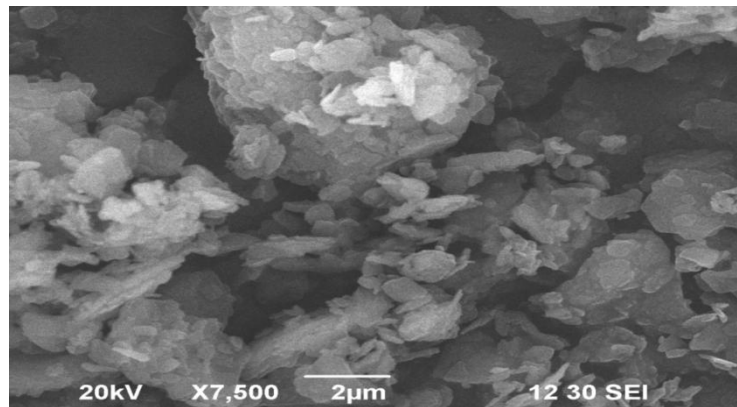


Figure 1. Sem image of ortho phenylene diamine doped with Silver Nitrate

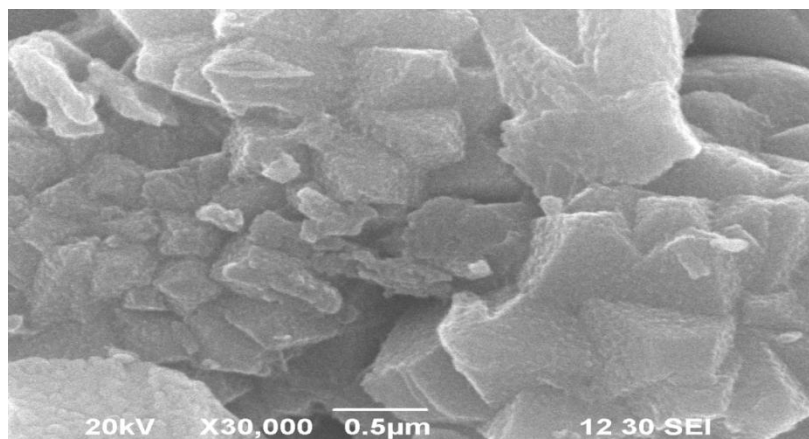


Figure. 2. Sem images of ortho phenylene diamine doped with Potassium persulphate

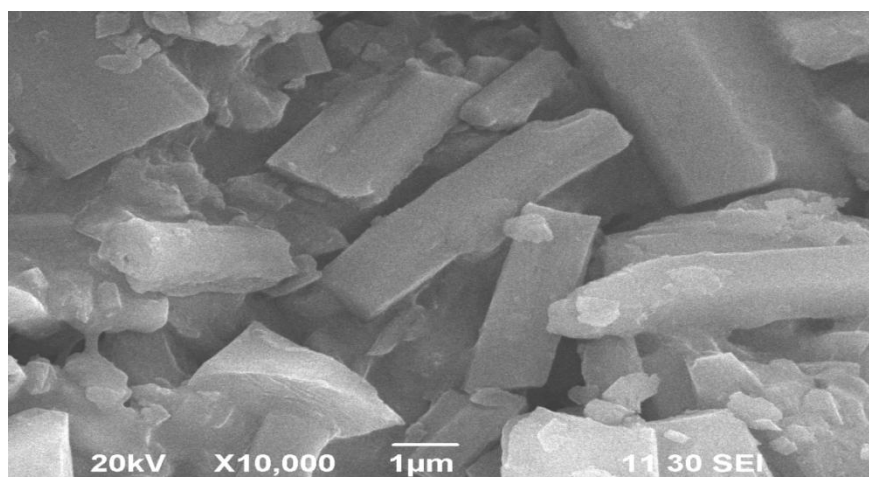


Figure 3. Sem images of ortho phenylene diamine doped with Copper Sulphate

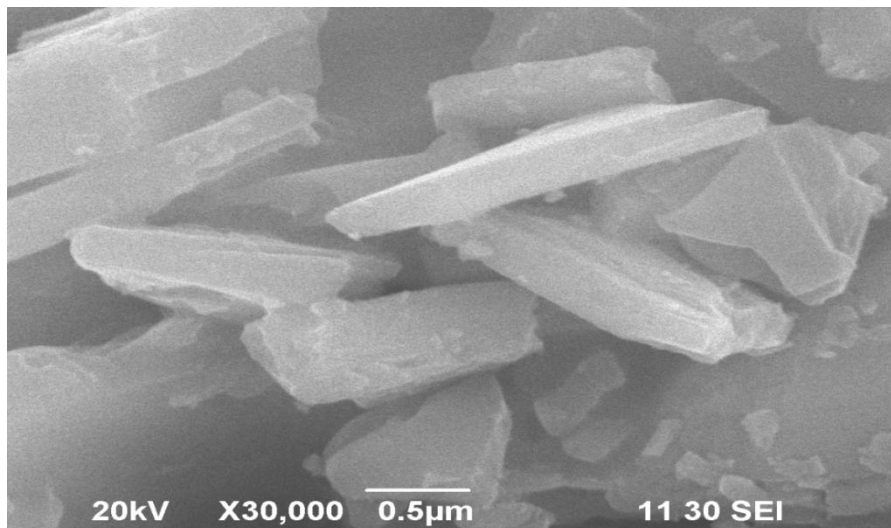


Figure4. Sem images of ortho phenylene diamine doped with Ferric hexa hydrate

FTIR:

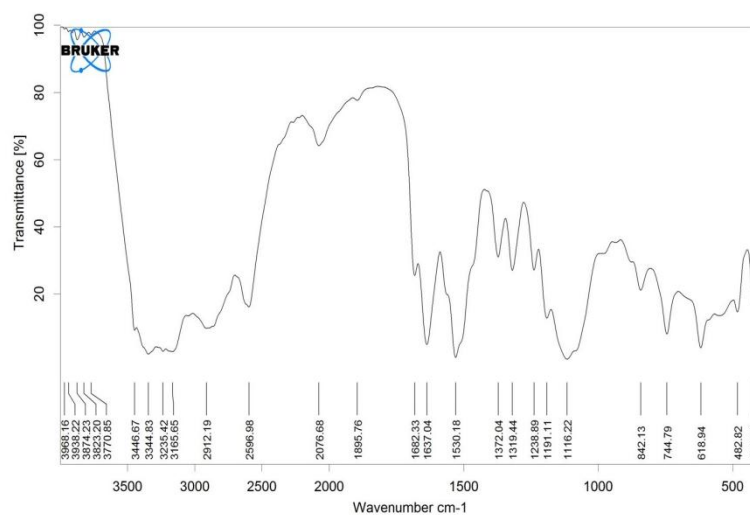


Figure 5. FTIR of Ortho phenylene diamine doped with Silver Nitrate

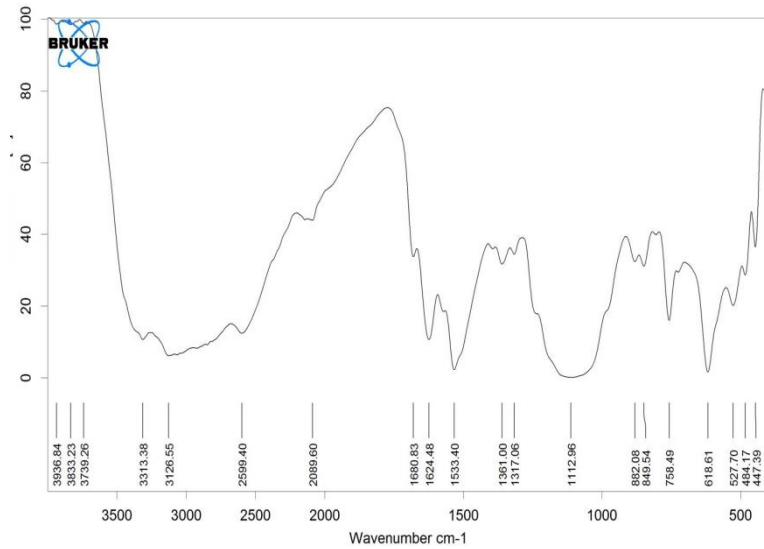


Figure.6 .FTIR of ortho phenylene diamine doped with Potassium persulphate

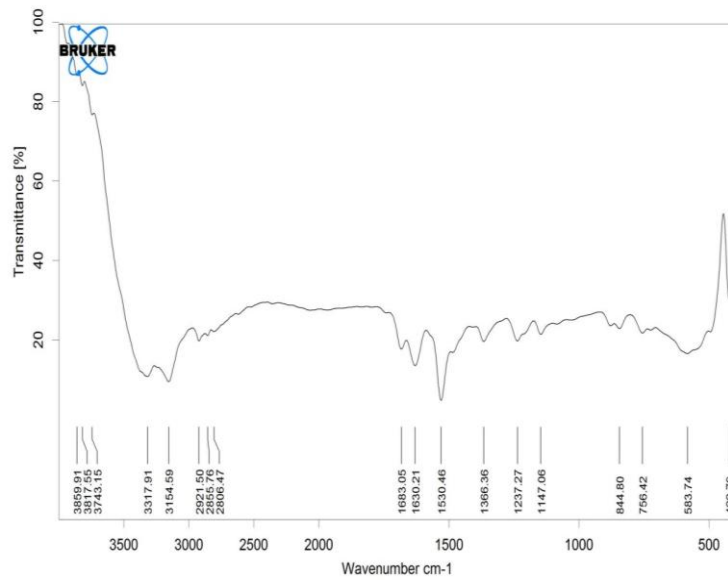


Figure.7. FTIR of ortho phenylene diamine doped with Copper Sulphate

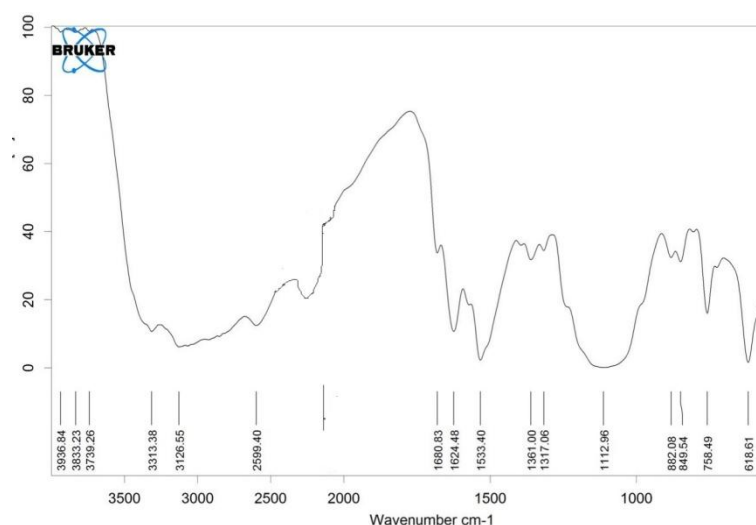


Figure 8. FTIR of ortho phenylene diamine doped with Ferric hexa hydrate

V.DISCUSSION

Scanning electron microscope image of figure 1 shows the size distribution of Ortho phenylenediamine doped with silver nitrate nano particles which has an irregular morphology. Based on the result that the particle consists of elemental Ag we can conclude that the sphere is Ag metal. The fact that the belt consists of C and N elements may suggest that these belts are oxidative products of oPD by AgNO₃. It is also noted that the fibers are not solid and are composed of many stone-like agglomerates and some short nanorods that linearly align along the fiber axis. Moreover, there are almost no discrete nanostones or short nanorods in the final products, indicating that they preferentially assemble into a longer structure. Figure 2 shows the sem images of Ortho phenylene diamine doped with potassium persulphate nano particles which was found to be globular like arrangement. The SEM image of OPDA/PPS result shows that the polymers are well ordered due to the incorporation of the surfactant in to the polymer. Figure 3 scanning electron microscope showed the size distribution of Ortho phenylene diamine doped with Copper sulphate nano particles in small size atomic arrangement morphology with the magnification of 2000 to 30000 nm. The SEM image reveals a well interconnected dense network structure of PDA nanospheres. Bond interactions (single bridge compounds) was increase and consequently the fiber shape was appear as shown in the figure. Figure 4 scanning electron microscope showed the size distribution of Ortho phenylene diamine doped with Ferric hexa hydrate nano particles in clear rod shaped morphology with the magnification of 2000 to 30000 nm. The crystalline grain size is mainly determined by both the formation energy of growth unit and the lattice energy, besides different synthesis conditions. The particles are arranged in random and bunches. Figure 5-8 shows the FTIR spectrum of Figure Ortho phenylenediamine doped with silver nitrate, Pot.persulphate, copper sulphate and Ferric hexa hydrate respectively. FT-IR characterizations were performed using a Perkin-Elmer 1650 FTIR spectrophotometer using the KBr technique. For fig. (5) a broad peak around 3344 cm⁻¹ for NH-stretching vibration and peaks corresponding to imine stretching mode appear at 1682 cm⁻¹. Similarly peak at 1530 cm⁻¹ is assigned to the N = Q = N, skeletal vibrations fig.(6,7&8) appears a peak at 3154 cm⁻¹ due to intramolecularly hydrogen bond (single bridge compounds) and peaks at 618,758



cm⁻¹ due to aromatic substitution. A broad band centered at 3313 cm⁻¹ due to the characteristic free N-H stretching vibration suggests the presence of secondary amino groups. Sharp band at 3317 cm⁻¹ is corresponding to the hydrogen-bonded N-H vibration. A very weak shoulder peak at about 2599 cm⁻¹ might be due to C-H stretching on aromatic phenazine and pyrimidine rings. The two sharp IR adsorptions in 1533-1680 cm⁻¹ are associated with aromatic ring stretching. Generally, the peak at 1630- 1683 cm⁻¹ is assigned to the following quinoid ring. The peak at 1530 cm⁻¹ is sharper but the peak at 1112 cm⁻¹ is broader. The fact that the peak at 1530 cm⁻¹ has almost the same area as the peak at 1474-1483 cm⁻¹ suggests the same quinoid and benzenoid unit contents in the copolymers. A weak peak at 1361 cm⁻¹ is attributable to the C-N stretching vibration in quinoid imine units.

VI. CONCLUSION

The chemical oxidation of phenylenediamines in acidic aqueous media yields the corresponding oligomers or polymers. Nano particles of ortho phenylene diamine doped with silver nitrate, potassium persulphate, copper sulphate and ferric hexa hydrate with various concentrations were synthesized. The synthesized samples were analysed by scanning electron microscope. Scanning electron microscope pattern revealed the arrangement of particles sized in the synthesized nano particles. Scanning Electron Microscope revealed the copper sulphate and ferric hexa hydrate doped ortho phenylene diamine showed the highly magnified rod shaped atomic arrangement. The synthesized doped ortho phenylene diamine nano particles showed regular, small, large size bunches and rod shaped arrangement. From the above conclusion atomic arrangement, the nano particle synthesized are fine and showed the good performance. o-Phenylenediamine dimer also reduced silver ions to metallic silver and is proposed, consequently, to polymerize. The oxidation of o-phenylenediamine with silver nitrate was suggested to yield o-benzoquinone. In contrast to polyaniline, polyphenylenediamines are rated as non-conductors and their conductivities are low. Similarly to polyaniline, these polymers display a salt-acid transition and they are redox-active. They act as reductants of noble-metal compounds to the corresponding metals or as precursors in the carbonization to nitrogen-rich carbons. Applications proposed in the literature are outlined; they include the corrosion protection of metals, catalysis, electrorheology, sensors, energy-conversion devices, electrochromism, noble-metal recovery, and water treatment

REFERENCES

- [1]. Gospodinova N, Terlemezyan L. Conducting polymers prepared by oxidative polymerization: Polyaniline. *Prog Polym Sci* 1998; 23:1443-1484.
- [2]. Feynman R. There's plenty of room at the bottom. *Science*; 1991; 254:1300-1301.
- [3]. Mazzola L. Commercializing nanotechnology. *Nature Biotechnology*; 2003; 21:1137-1143.
- [4]. Paull R, Wolfe J, Hebert P, Sinkula M. Investing in nanotechnology; *Nature Biotechnology*; 2005; 21:1134-1147.
- [5]. T. Gessner, K. Gottfried, R. Hoffmann et al., "Metal oxide gas sensor for high temp. application," *Microsystem Technologies*; 2000; 6:169-174.
- [6]. W. Ueda, M. Sadakane, and H. Ogihara, "Nano-structuring of complex metal oxides for catalytic oxidation," *Catalysis Today*; 2008;32: 2-8.
- [7]. J. H. Kim, E. K. Kim, C. H. Lee, M. S. Song, Y.-H. Kim, and J. Kim, "Electrical properties of metal-oxide semiconductor nano-particle device," *Physica E*; 2005; 1-4; 432-435.
- [8]. P.D.Pria, "Evolution and new application of the alumina ceramics in joint replacement," *European Journal of Orthopaedic Surgery and Traumatology*; 2007; 253-256.
- [9]. H. Farsi and F. Gopal, "Theoretical analysis of the performance of a model super capacitor consisting of metal oxide nanoparticles," *Journal of Solid State Electrochemistry*; 2007; 11:1085-1092.
- [10]. A. C. Dillon, A. H. Mahan, R. Deshpande, P. A. Parilla, "Metal oxide nano-particles for improved electrochromic and lithium-ion battery technologies; *Thin Solid Films*; 2008; 516:794-797.
- [11]. Friends of the Earth Report—Nanomaterials, Sunscreens and Cosmetics: Small Ingredients Big Risks; 2006; 7248-250.
- [12]. Greßler, S., Gazso, A. Nanotechnology in Cosmetics. *Nano Dossiers*; 2010; 3; 24-27.
- [13]. Whitesides GM. The 'right' size in Nanobiotechnology. *Nature Biotechnology*; 2003; 21:1161-1163.
- [14]. Taton TA. Nanostructures as tailored biological probes. *Trends Biotechnol*; 2002; 20:277-279.
- [15]. Parak WJ, Gerion D, Pellegrino T, Zanchet D, Micheel C, Williams CS, Boudreau R, Gros MA, Larabell CA, Alivisatos AP. Biological applications of colloidal nanocrystals. *Nanotechnology*; 2003; 14; 15-27.
- [16]. Yan H, Park SH, Finkelstein G, Reif JH, LaBean TH. DNA-templated self-assembly of protein arrays and highly conductive nanowires. *Science*; 2003; 301; 1882- 1884.
- [17]. Keren K, Berman RS, Buchstab E, Sivan U, Braun E. DNA-templated carbon nanotube field-effect transistor *Science*; 2003; 302:1380-1382.
- [18]. Raj, S. and Jose, S. Nanotechnology in Cosmetic: Opportunities and Challenges. *Journal of Pharmacy and Bioallied Sciences*; 2012; 4; 186-193.
- [19]. Iyer, S. New Non-Toxic Silver Nano Particles May Soon Target Cancer Tumors. *Article from Medical Daily Science/Tech*; 2014; 7; 132-138.
- [20]. Shoseyov, O. and Levy, I. Nano BioTechnology, BioInspired Devices and Materials of the Future; 2008; 5; 322-234.



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- [24]. European Commission Public Health: Are Silver Nanoparticles Safe? Implications for Health, the Environment and Microbial Resistance;2007;3;13-15.
- [25]. Kim, K.-J Antifungal Effect of Silver Nanoparticles on Dermatophytes. Journal of Microbiology and Biotechnology; 2008; 18;1482-1484.
- [26]. Noorbakhsh, F Antifungal, Effects of Silver Nanoparticle Alone and with Combination of Antifungal Drug on Dermatophyte Pathogen Trichophyton Rubrum; International Conference on Bioscience, Biochemistry and Bioinformatics; IPCBEE;2011; 5; 364-367.
- [27]. Scientists Warn against Harmful Effects of Silver Nanoparticles Used in Cosmetics and More; 2014; 4; 232-234.