

Review on Recent Development in Nano-Catalysis

¹A.G. Thokal, ²Tejas Patil, ³Naved Nakadar, ⁴Vikram Kale

¹Assistant Professor, ^{2,3,4}Bachelor of Engineering

^{1,2,3,4}Department of Chemical Engineering,

^{1,2,3,4}Bharati Vidyapeeth College of Engineering, Navi Mumbai, Maharashtra, India.

Abstract: Recent developments and studies in nano-catalysis research are reviewed. They demonstrate the important role of nano-catalysts in the advances of catalytic sciences and technology. Special emphasis is given to the characterization and synthesis of nano-sized, supported metal and metal oxide structures. The whole process might have a great impact to resolve the energy crisis and the environmental crisis that were caused by traditional chemical engineering. Furthermore, we hope that this article will provide a reference point for the noble metal nanomaterial's development that leads to new opportunities in nano-catalysis.

Keywords-Nano-catalyst, Metal Nano-Particles, Polymer Stabilization, Nano Science, Nano Structures.

1. INTRODUCTION

Catalysis plays a pivotal role in energy production, chemical industry, and environmental remediation. More than 60% of chemical products and 90% of chemical processes in the world are either based or substantially dependent on catalysis. These proportions will steadily increase to satisfy our ever-growing demands for sustainable processes with superior atom-economic impacts and inferior environmental impacts. Catalysis is significant due to the unique capabilities of catalysts in accelerating chemical reactions by reducing the energy barrier (i.e., activation energy) of their transition states and in controlling reaction pathways toward selective synthesis of target products. Catalysts can be homogeneous or heterogeneous, depending on whether they exist in the same phase as the substrates or not. Because homogeneous catalysts are readily soluble and accessible to the substrates in reaction media, they possess high catalytic activity and selectivity under mild conditions. Moreover, their structures are well defined at the molecular level. These features render these molecular catalysts capable of rationally tuning their catalytic properties by modification of their ligands and metals and tuning the reaction pathways. However, homogeneous catalysts are employed in <20% of industrial processes due to the tedious and expensive separation of catalysts from the final products. Conversely, heterogeneous catalysts are extensively employed in industry due to their easy separation and recovery, as well as their high stability even exposed to harsh reaction conditions. However, heterogeneous catalysts are made up of combining two different homogeneous catalysts this will increase the selectivity, stability, separability and high efficiency of the catalysts. On the various parameters the nano-catalysis process is affected. The size, shape, composition and surface chemistry affect the efficiency of the nano-catalysts [5].

1.1 WHAT IS NANO-CATALYSTS?

Nano-catalysis is one of the most exciting subfields to have emerged from nanoscience. Its central aim is the control of chemical reactions by changing the size, dimensionality, chemical composition and morphology of the reaction center and by changing the kinetics using Nano patterning of the reaction center. Nano-catalysts are composed of small particles of a catalytically active material, typically with a diameter range of 1–100 nm, they have attracted intense interest during recent decades. They can be applied in different areas, such as catalysis, electrocatalysis, sensors, filters, nanoscale electronics, fuel cells, cosmetics, energy, environment, engines, water purification, and optoelectronics. The first scientific goal and challenge is associated with the synthesis of these particles with maximum control over size and shape to tailor their physical and chemical properties and to optimize their performance in a specific reaction. The second challenge is to understand how the composition and atomic-scale structures of NPs produce optimal catalytic reaction performance. Recent developments in nanotechnology and material science will aid research in the characterization, rational design, and engineering of new types of multifunctional nano-catalysts for the achievement of green and sustainable chemical processes. This research provides new opportunities to understand the nature of the active sites, the metal-support interaction mechanism, and the origin of the structure–reactivity relationship by careful design and synthesis of specific size and shape catalyst particles at the nanoscale [5].

2. NANO-CATALYSTS SIZE, SHAPE, COMPOSITION AND SURFACE CHEMISTRY:

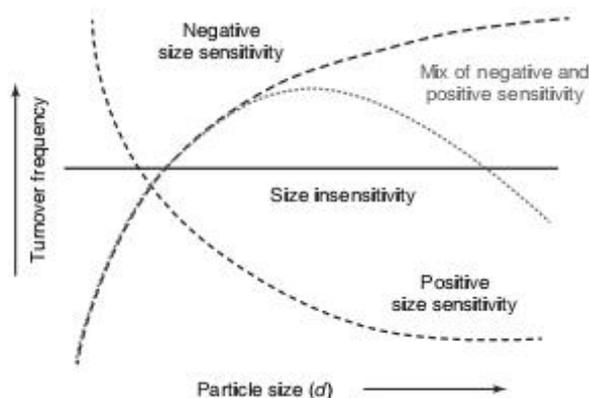
2.1 SIZE EFFECT

Nanocatalysts are characterized by their unique nanoscale properties, which originate from the highly reduced dimensions of their catalytically active domains. The effect of particle size in the context of nanocatalyst has been well understood. The lowly coordinated atoms that are located in defects in solid catalyst particles, such as terraces, edges, kinks, and vacancies, have been considered to be active sites. By reducing the domain size of catalyst particle as far as possible, the number of active sites can be maximized. The effect of particle size is frequently employed to describe the relationship between the reaction and the particle size of catalyst, especially in the size ranging from 1 to 10 nm. For both supported and unsupported particles, considerable efforts have been dedicated to the elucidation of the influence of metal particle size on catalytic reactivity. Gold nanoparticles (Au NPs) are a classic example of this topic. Although bulk gold has been considered to be catalytically inert, 2–5 nm particles that are dispersed on reducible oxides are highly active toward CO oxidation at low temperatures. This prominent size-dependent effect has been interpreted based on the variations in the geometric and/or electronic properties of active gold atoms at smaller particle sizes. an exponential increase in TOF in CO oxidation on Rh NPs as the size of NP decreased from 7 to 2 nm. Another prime

example for the effect of particle size is displayed in the Fischer–Tropsch (FT) reaction, which is catalyzed by supported cobalt. Studies by Iglesia and coworkers showed that the surface-specific activity (TOF) is independent of the size of cobalt particle in the size range of 9 to 200 nm. For smaller (<10 nm) Co particles, however, a decrease in FT reaction performance has been reported. It has been determined that Co particles that are smaller than 6 nm were less active in TOF per accessible site compared with large particles [5].

FIGURE 1: SIZE EFFECT [5]

2.2 MORPHOLOGY EFFECT



The concept of morphology-dependent nano-catalysis has been primarily explored for metal nanostructures. A well-known example involves iron crystals that are industrially applied for ammonia synthesis. The formation rate of ammonia on Fe crystal follows the order (111) \gg (1 0 0) > (11 0), which suggests that the production rate of ammonia can be highly promoted if the iron catalyst particle can expose more reactive (111) facets. The impact of morphology on the catalytic properties was also demonstrated for Pt NPs. Tetrahedral Pt particles with their (111) facets exposed were more active for the electron-transfer reaction between hexacyanoferrate and thiosulfate than cubic Pt particles with their (10 0) facets exposed, even when the diameters of both materials ranged from 4 to 5 nm. Enhanced chemical activity of surfaces for stepped Au (211) and Au (332) has been observed compared with smooth Au (111) surfaces. The roughness of the surface, that is, the presence of highly undercoordinated atoms, is important for the dissociation of O₂. Morphology-dependent nano-catalysts on metal oxide NPs have also been observed. A few recent examples convincingly demonstrate the morphology-dependent behaviors of oxide particles with definite shapes. Rod-shaped Co₃O₄ with a higher exposure of the reactive (110) planes, for which catalytically active Co³⁺ species are abundant, showed particularly high activity toward low-temperature CO Oxidation [5].

2.3 COMPOSITION EFFECT:

Pt is the most common and generally accepted as the best electrode catalyst used in polymer electrolyte membrane fuel cells. Over previous years, numerous efforts to develop alternative catalysts to Pt have primarily focused on Pt-based bimetallic alloys, in which Pt is partially replaced by less expensive metals, such as Fe, Ru, Co, and Ni. The oxygen reduction reaction (ORR) on Pt and Pt-based alloys has been extensively investigated by experimental and computational methods. The formation of a Pt-skin layer is accompanied by a lower Pt-depleted layer in many Pt-3d alloys. Several studies of O adsorption on Pt-skin surfaces have revealed that the binding strength on Pt-skin surfaces is weaker than the binding strength on a pure Pt(111) surface, which may facilitate the removal of adsorbed O and increase the ORR rate. Recently, Hyman et al. examined the Pt₃Ni(111) surface and determined that the first layer only consists of Pt and the second layer is strongly Pt depleted (48% of Pt compared with 75% of Pt in a bulk material). It has been proposed that a thermodynamic procedure or estimating the potential shift of surface alloys using periodic DFT. They suggested a positive potential shift for Pt-skin surfaces of Pt₃Fe, Pt₃Co, and Pt₃Ni, indicating that the skin structure is electrochemically more stable than pure Pt surfaces. This information indicates that the adsorption and electrochemical stability properties can be significantly modified with changes in the compositions of surface structures. Among other distinct benefits, such as a decrease in the cost of a catalytically active element, the use of alloys in NP catalysis can cause the following effects: (i) decreased poisoning effects, (ii) the opening of new reaction pathways, which cause distinct selectivity, (iii) the enhancement of catalytic activity due to synergistic effects and changes in the electronic properties of nanocatalysts, and (iv) an improved thermal stability of catalytically active elements [5].

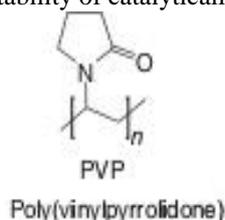


Figure 2: Major polymer families employed as metal NP support for catalysis

2.4 SURFACE VOLUME RATIO:

The effects may also influence the spacing of the energy levels of NPs. The chemical reactivity of a heterogeneous catalyst is proportional to the total specific surface area per unit volume; thus, the high surface areas of NPs provide the possibility of functioning as efficient catalysts [5].

3. SYNTHESIS OF NANO PARTICLES

MNPs exhibit unique physical and chemical properties when their dimensions are reduced to the nanoscale. MNPs, especially noble MNPs, have a characteristic high surface-to-volume ratio, and consequently, a large fraction of surface atoms that are exposed to reactant molecules, renders them a promising catalyst in chemical synthesis. Controlling the size, shape, and structure of MNPs is technologically important due to the strong correlation between these parameters and optical, electrical, and catalytic properties. Promising synthetic methods that provide suitable NPs that are responsible for target catalytic reactions are extremely important.

3.1 WET CHEMICAL REACTION:

These methods can be generally classified into gas-phase and liquid-phase-based methods. The preparation of MNPs can generally be prepared via “bottom-up” and “top-down” synthetic routes. In the gas-phase method, bulk material is evaporated to obtain a supersaturated gas phase, which subsequently produces nuclei and becomes MNPs. In the liquid-phase method, which is also known as the wet method, precursors react to form a supersaturated solution of zero-valent metal atoms, which nucleate and further grow to MNPs. Metal salts are usually reduced in the presence of suitable capping agents, such as thiols, amines, surfactants, or polymers, which stabilize the NPs from agglomeration. Stabilization of the metal particles is governed by two main factors: electrostatic repulsion among particles and steric hindrance from stabilizer molecules. With these methods, the core size and the surface properties of metal nanoclusters can be effectively controlled by adjusting the experimental parameters, such as the metal to-ligand ratio, chemical structure of the protecting ligands, the nature of the reducing agent, reaction temperature and time, and pH of the solution [5].

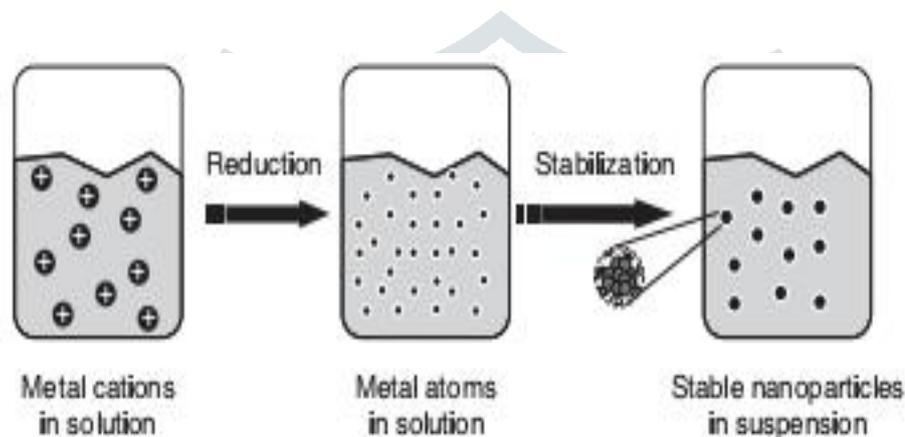


Figure 3: Formation of MNPs via reduction of metal salt precursors [5]

4. STABILIZATION OF METAL NANOPARTICLES (MNPs)

All preparation methods must use stabilizing agents, which adsorb at the particle surface. Three types of NP stabilization exist, that is, electrostatic stabilization, steric stabilization and electrostatic stabilization. In electrostatic stabilization, anions and cations from the initial materials remain in solution and associate with the NPs. The particles are surrounded by an electrical double layer, which produces a Coulombic repulsion that prevents agglomeration. In steric stabilization, aggregation is prevented by the adsorption of large molecule.

5. POLYMER-STABILIZED MNPs

Polyvinyl pyrrolidone (PVP) is the most common polymer for MNP stabilization. Part of the PVP adsorbs on the NP surface, whereas the remaining part freely dissolves in the suspension to create a second protective shell. This method provides stability to Ag and Au hydrosols, and simple variations of the PVP–metal ratio yield structures with very different shapes and sizes. The disadvantage of using PVP is the separation of catalytic particles from the product and the unused reactants at the end of reaction. To solve this problem, it has been employed that PVP-stabilized Pt, Pd, and Rh NPs that were immobilized in an ionic liquid (IL)–1-n-butyl-3-methylimidazolium hexafluorophosphate. These NPs were synthesized by reducing the corresponding metal halide in refluxing ethanol, which yields a narrow size distribution that depends on the metal–PVP ratio. They exhibited reasonable catalytic activity and stability in hydrogenation of olefins under mild conditions. The hydrogenation products were easily isolated from the IL phase by decantation. The catalyst was recycled several times without loss of activity. Preparation of Supported Metal Nanoparticles Supported NP catalysts are extensively recognized as an important class of industrial catalysts that are closely related with versatile key technologies in petrochemical industries, conversion of automobile exhausts, chemical sensors, and manufacturing of fine and specialty chemicals. There are numerous criteria for practical supported metal catalysts, including specific catalyst–support interactions, resistance to agglomeration, site isolation, excellent accessibility of substrate molecules, mechanical robustness, and low synthetic cost. The approaches for the preparation of supported MNPs can be generally divided [4].

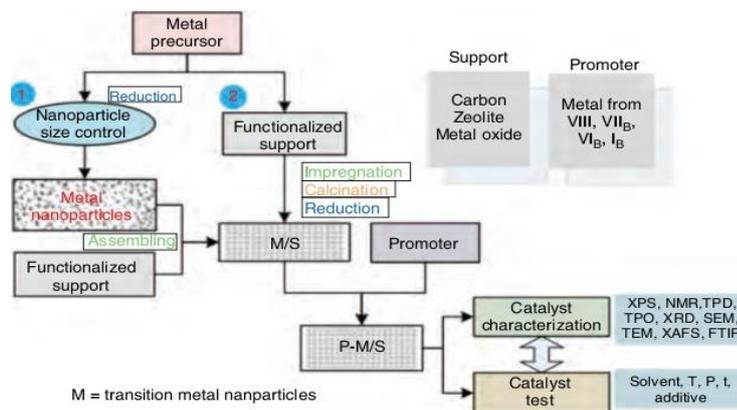


Figure 4: Fabrication of the support catalysis [4]

into chemical, physical, and physicochemical routes Deposition of Preformed Metal Nanoparticles onto Supports Metal nanoclusters are very promising building blocks in preparation of heterogeneous catalysts with a controllable structure, which can be synthesized in a solvent and deposited on a support without distinct aggregation. The deposition of preformed MNPs on the

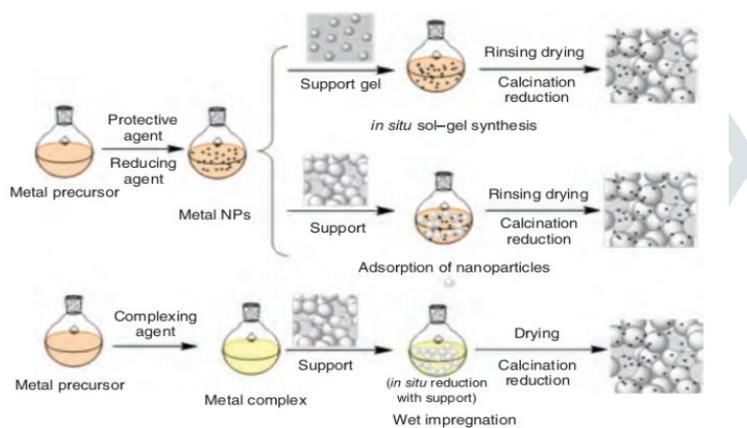


Figure 5: Catalyst preparation routes [5]

functional support is highly advantageous. The particle size of the NPs that are synthesized by the colloidal sols is less affected by the support than the case in which other methods such as impregnation are employed. Intensive research is currently devoted to this methodology for the findings of MNPs with well-defined size, shape, composition, and surface chemistry. Metal nanoclusters, which're dispersed across the surface of an oxide or other support, can be much more active and selective as catalysts than larger metal particles [5].

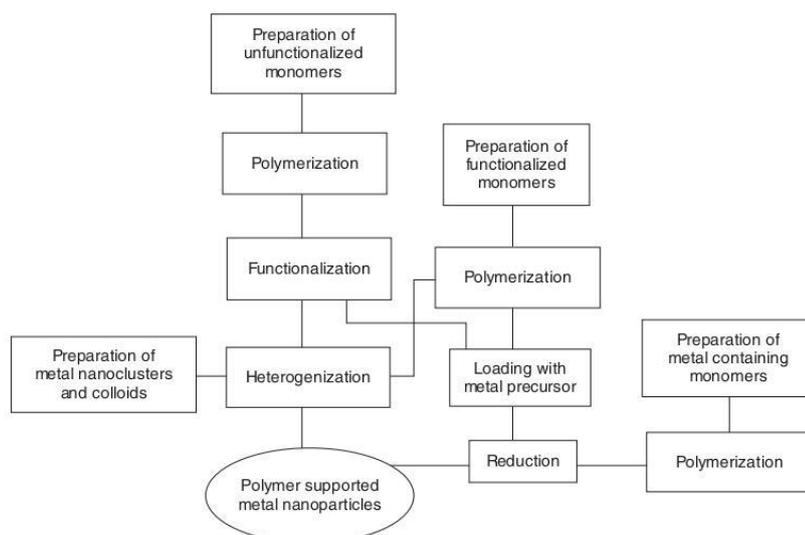


Figure 6: Routes for the preparation of metal nano-particles supported on functional polymer [5]

6. BIOSYNTHESIS OF TiO₂ NANOPARTICLES

Living systems are involved in the production of nanoparticles which are more stable as compared with chemically synthesized nanoparticles. Nanoparticles synthesized using microorganisms are found to have less aggregation behavior due to presence of more repulsive forces. Utility of nanoparticles is mainly dependent upon its size, shape as well as stability. Hence, researchers focus on the biogenic synthesis of nanoparticles which can fulfill the criteria. TiO₂ nanoparticles which naturally exists in three

different crystalline forms anatase, rutile and brookite can be produced using biological agent. Extensive research is carried on the biosynthesis of nanoparticles. Biosynthesis of nanoparticles is one of the growing areas in the field of nanotechnology. Various reports are available on the utilization of bacteria, fungi, algae, plant material and enzymes for the biosynthesis of nanoparticles. The mechanisms involved in the microbial synthesis of nanoparticles are bio absorption, extracellular complexation or precipitation of metals, bioaccumulation, reflux systems, and alteration of solubility and toxicity via reduction or oxidation and lack of specific metal transport systems Energy source, pH and overall oxidation reduction potential were found to be important factors in the synthesis of TiO₂ nanoparticles, while in the case of *Saccharomyces cerevisiae*, oxidase enzyme plays an important role hemolysin and also urease which are responsible to develop multidrug resistance ability in the pathogens [3].

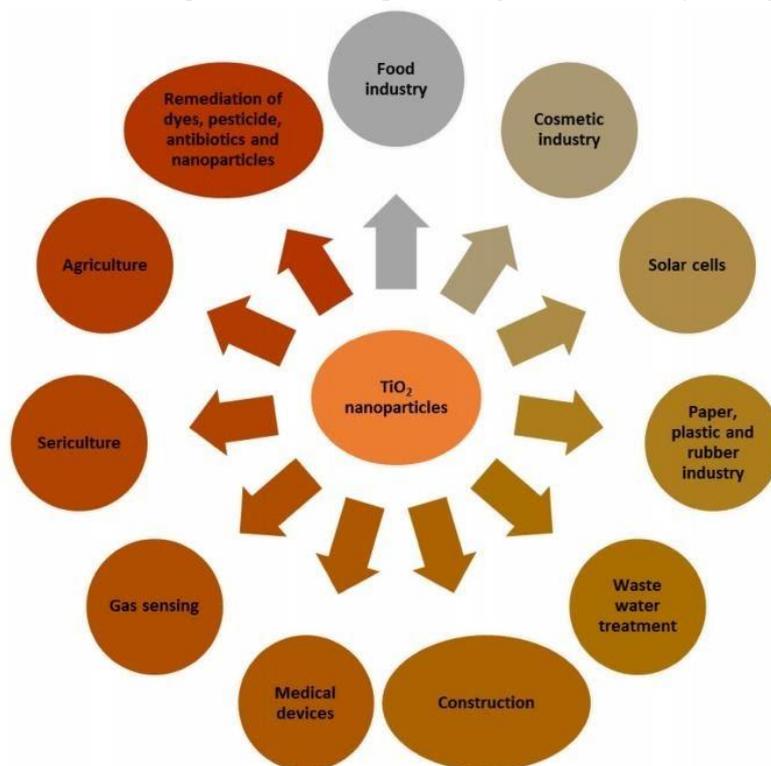


Figure 7 Applications of biosynthesized titanium dioxide Nanoparticles [3]

7. CONCLUSIONS

Recent advances in nanotechnology and design provides various preparation method for metal Nano particles and supported with size. MNP distribution to overcome the limitations of traditional synthetic methodologies. In industries applications of catalysts are rapidly increasing nowadays We must not forget that the preparation of MNPs and supported MNPs must be approached in a sustainable manner. With reducing the waste and toxicity of the components. And increasing manufacturing facility, production costs. Broad spectrum use of titanium dioxide nanoparticles has gained attention among researchers. Extensive research is ongoing on the chemical and biological synthesis of nanoparticles. TiO₂ can sustain in the environment for long period and its antimicrobial activity makes them strong disinfectant which will be 3 times stronger than chlorine, and 1.5 times stronger than ozone. Air purifiers containing TiO₂ avoid smoke, pollen, virus, bacteria and harmful gas and grab the free bacteria present in the air by altering percentage of 99.9% due to the highly oxidizing effect of photo catalyst (TiO₂). Protection of lamp houses, walls in tunneling and white tents from becoming sooty and dark, can be achieved due to the self-cleaning and high photo catalytic potential of TiO₂.

REFERENCES

- [1] Gai. P. L. Recent advances in nanocatalysis research, *Current Opinion in Solid State and Materials Science* 6 (2002) 401–406
- [2] M. H. Magnusson, K. Deppert, L. Samuelson. Size selected Gold Nano particles by Aerosol Technology, *Nanostructured Materials*, Vol. 12, pp. 45-48, 1999
- [3] Meghmala S. Waghmode, Aparna B. Gunjal, Javed A. Mulla, Neha N. Patil, Neelu N. Nawani. *Studies on the titanium dioxide nanoparticles: biosynthesis, applications and remediation*, Springer Nature Switzerland AG 2019
- [4] Jiaqing Wang and Hongwei Gu. *Novel Metal Nanomaterials and Their Catalytic Applications*, *Molecules* 2015
- [5] Jing Guan, Xindong Mu, Guoqiang Xu, Xicheng Wang and Xiufang Chen. *Nanocatalysis*, *ENCYCLOPEDIA OF PHYSICAL ORGANIC CHEMISTRY* 2017
- [6] A. N. Shanahan, J. A. Sullivan, An insight into the superior performance of a gold nanocatalyst on single wall carbon nanotubes to that on titanium dioxide and amorphous carbon for the green aerobic oxidation of aromatic alcohols, *New Carbon Materials*, 2017, 32(3): 242-251
- [7] Jha A, Prasad K, Kulkarni A (2009) Synthesis of TiO₂ nanoparticles using microorganisms. *Coll Surf B: Biointerfaces* 71:226–229
- [8] Beveridge TJ, Hughes MN, Lee H, Leung KT, Poole RK, Savvaidis I (1997) Metal–microbe interactions: contemporary approaches. *Adv MicrobPhysiol* 38:177–243
- [9] Durairaj B, Muthu S, Xavier T (2015) Antimicrobial activity of *Aspergillus niger* synthesized titanium dioxide nanoparticles. *Adv Appl Sci Res* 6:45–48