

# Nanomaterials Based Superhydrophobic and Antimicrobial Coatings

Malobi Seth and Sunirmal Jana\*

Specialty Glass Technology Division, CSIR-Central Glass and Ceramic Research Institute, India

**\*Correspondence to:**

Dr. Sunirmal Jana  
Specialty Glass Technology Division  
CSIR-Central Glass and Ceramic Research  
Institute, 196 Raja S.C. Mullick Road  
Jadavpur, Kolkata 700 032, West Bengal, India  
**Tel:** +91 33 2473 3496  
**Fax:** +91 33 2473 0957  
**E-mail:** [sjana@cgcri.res.in](mailto:sjana@cgcri.res.in)

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## Abstract

Now-a-days, it is obvious that nanomaterials can play significant role in every sphere of our modern lives. On this aspect, use of nanomaterials in developing advanced functional materials or towards enhancement in surface related physical properties including superhydrophobic or superhydrophilic properties is very important both in fundamental and applied research. In this regard, most of the researchers agreed that there is a close relationship between superhydrophobicity of material surface with its antimicrobial activity. This review briefly highlights the use of some inorganic/organic based nanomaterials such as Ag, Cu, ZnO, TiO<sub>2</sub> as inorganic materials and graphene, chitosan nanoparticles as organic materials in making superhydrophobic antimicrobial coatings. Based on reported literature, possible mechanisms of antimicrobial activity of the nanomaterials derived superhydrophobic coatings have been discussed. It is worthy to note that the coatings with the advancement in self-cleaning and anti-biofouling as well as superhydrophobic and antimicrobial properties are highly potential for enormous applications in biomedical fields including medical textiles, personal protective equipment (PPE), surgical appliances, biodevices, and so on. In this review, the challenges and future prospect of the nanomaterials based superhydrophobic coatings have also been discussed briefly. This mini review may encourage researchers towards development of superhydrophobic and antimicrobial coatings on various substrates like plastics, glasses, and cotton fabrics for making PPE to protect the dedicated medical / healthcare personnel from the currently pandemic COVID-19 disease caused by severe acute respiratory syndrome coronavirus 2.

## Keywords

Nanomaterials, Superhydrophobic coatings, Antimicrobial coatings

## Introduction

Inspired by a special surface property of insect wings or lotus leaf, the superhydrophobic materials have attracted tremendous attention to materials researchers towards development of such materials for a wide range of applications including healthcare and biomedical kits / devices [1]. Superhydrophobic surfaces are capable to exhibit static water contact angle (SCA)  $\geq 150^\circ$  and water sliding angle (WSA)  $\leq 10^\circ$ . The surface of these materials typically consists of hierarchical surface texture with micro-nano scale surface roughness and a layer of low surface energy material [2]. The presence of low surface energy material prevents adhesion/penetration of water molecule into the surface by the formation of air pockets between the hierarchical rough surface structure. Now-a-days, various nanomaterials have been used to generate desired hierarchical surface roughness. Among these, metal and metal oxide-based nanomaterials such as Ag [3], Cu

[4], ZnO [5], TiO<sub>2</sub> [6] and biopolymers including graphene, chitosan nanoparticles [7, 8] need special mention because of their wide utilization in biomedical fields. These nanomaterials are non-toxic, biocompatible and biodegradable and can easily be synthesized adopting facile solution technique. In addition, they possess antimicrobial properties [3-8]. It is well known that the nanomaterials due to their large surface to volume ratio offer large numbers of active sites towards antimicrobial reactions. When these nanomaterials are used for fabrication of a superhydrophobic coating, the developed nano coating exerts antimicrobial properties by the release of metal ions or reactive oxygen species that usually kill microorganisms (like bacteria, fungi, and viruses) in an effective way. It is to be noted that the microbial growth requires moisture. The superhydrophobic surface repels water molecules and so, it is difficult for microorganisms to grow on such surfaces [6]. In accordance to these possible mechanisms of antimicrobial activity, there are extensive studies already have done on the reduction of bacterial and fungal adhesion onto superhydrophobic surfaces in comparison to hydrophobic or hydrophilic surfaces [1]. Besides these nanomaterials, graphene is another nanomaterial of significant importance because of its antimicrobial property and superior mechanical strength [9]. Reduced graphene oxide-based nanomaterials have been used for fabrication of antimicrobial and superhydrophobic coatings with excellent mechanical strength and corrosion resistance property [10-13]. It is worthy to note that superhydrophobic and antimicrobial surfaces have found applications in medical textiles [14], military clothing [2], and anti-biofouling coatings on surgical appliances and biodevices [15].

This review briefly highlights the use of some inorganic/organic based nanomaterials such as Ag, Cu, ZnO, TiO<sub>2</sub> as inorganic nanomaterials and graphene, chitosan nanoparticles as organic nanomaterials for fabrication of superhydrophobic antimicrobial coatings. Moreover, possible mechanisms of antimicrobial activity of the nanomaterials based superhydrophobic coatings as well as the challenges and future prospect of these coatings have also been discussed. This review may encourage researchers towards development of superhydrophobic and antimicrobial coatings on plastics/glasses/cotton fabrics for making personal protective equipment to protect the dedicated medical /healthcare personnel from the currently pandemic COVID-19 disease caused by severe acute respiratory syndrome coronavirus 2.

## Fabrication of Superhydrophobic and Antimicrobial Coatings

There are two key factors that are responsible to create superhydrophobic property of a coating deposited onto a substrate (Figure 1) like glass, cotton fabrics, etc. [2]. These are – (a) creation of hierarchical rough surface with micro-nano dual scale roughness and (b) deposition of a low surface energy material to be chosen from long chain fatty acids, thiols, fluorinated silanes, amines, etc. [2]. It is seen that the hierarchical roughness can be created onto a substrate surface by incorporation of Ag, Cu, ZnO, TiO<sub>2</sub>, graphene, chitosan nanoparticles by solution process [3], sol-gel method [2, 5,

15], chemical reduction [4], spray coating technique [6, 8], electroplating method [16], template method [17], and so on. In the later stage, the hierarchical rough surface is to be modified by using a low energy material adopting various techniques including layer by layer deposition [3], solution process [2, 4, 6, 15], chemisorption [18], and self-assembly [14]. The existence of trapped air in the rough surface that created due to the presence of micro and nanostructures impede water droplets to come in contact with the substrate surface and it is one of the key factors for obtaining antimicrobial activity of a nanomaterial based superhydrophobic surface.

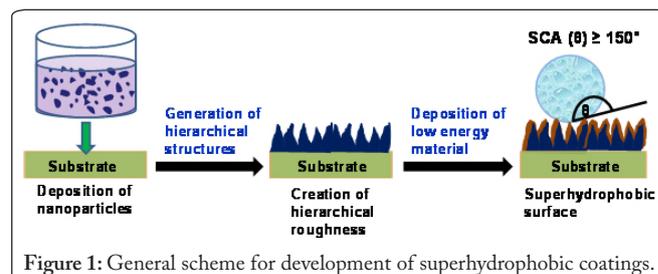


Figure 1: General scheme for development of superhydrophobic coatings.

## Nanomaterials as Antimicrobial Agents

Both semiconductor and dielectric metal oxide-based nanomaterials have been used to fabricate superhydrophobic and antimicrobial coatings on various substrates like glass, cotton fabrics, plastics. ZnO is a biocompatible metal oxide that is widely used in biomedical field for its low cost and ease of synthesis, self-sterilisation, low cytotoxicity, photocatalytic, and antimicrobial properties. Also, ZnO nanoparticles have been reported to have great activity towards bactericidal [5], fungicidal [19], and virucidal [20] properties. These are also used for the fabrication of antimicrobial superhydrophobic cotton fabrics [5], Ti surfaces for biomedical implants [16] and other functionalised surfaces [21]. TiO<sub>2</sub> is also known for its antimicrobial properties because it is an excellent photocatalyst and largely used on superhydrophobic and antibacterial coatings [17]. On the other hand, nano Ag, Cu and their composite nanomaterials have been reported owing to their antimicrobial properties on superhydrophobic coatings [3, 4, 22]. Silica is a dielectric material. However, nano SiO<sub>2</sub> is most extensively studied for fabrication of superhydrophobic surfaces. Recent report shows that functionalised SiO<sub>2</sub>-based superhydrophobic coatings have significant bactericidal activities [15, 18]. Not only inorganic material-based nanomaterials but also organic materials like chitosan nanoparticles are known for their biocompatibility, biodegradability and widespread antibacterial and antifungal activities towards the fabrication of superhydrophobic and antimicrobial coatings on cotton fabrics [8]. Ag nanoparticles have been found to be quite an efficient nanomaterial for killing a variety of virus including Influenza A [23], HIV-1, Herpes simplex virus (HSV-1), Hepatitis A (HAV-10), and Coxsackievirus B4 (CoxB4) [24]. Moreover, Zn, Ag and Cu ions [20], ZnO [25], TiO<sub>2</sub> [26], graphene oxide [27], chitosan nanoparticles [28], etc. have been reported to have significant virucidal activities.

## Antimicrobial Activity of Superhydrophobic and Antimicrobial Coatings

Recently, many studies suggested that there is a close relationship between surface roughness, trapped air in superhydrophobic interfaces and microbial adhesion with overall antimicrobial activity. It is noteworthy that superhydrophobic coatings can create a plenty of air pockets into the rough surfaces which significantly reduce the available anchoring sites of microbial cells (water-phase carrying microbes) to prevent their adhesion onto the surfaces [18]. Additionally, in these cases where the hierarchical roughness is generated by vertically grown spikes or spinules of metal or metal oxide hierarchically structured nanomaterials, the microbe especially bacterial cell wall stretches itself to find appropriate surface for interaction to such a large extent that ultimately gets ruptured causing cell death [29]. The size of nanoparticles present onto the surfaces also has a significant effect on the surface wettability and consequently, on bacterial adhesion [6]. Hence, the surface morphology has to be optimized in such a way that the superhydrophobicity and antimicrobial activity can be maximized. It is also agreed by most of the researchers that the presence of antimicrobial ions on the superhydrophobic surfaces can further enhance the antimicrobial ability. On this aspect, metal ions like  $Zn^{2+}$ ,  $Ag^+$ , and  $Cu^{2+}$  can penetrate inside microbial cell wall and DNA molecules to lose their replicability or the ions inactivate the functions of the cells resulting cell death [20, 30]. Some reports also indicate that the presence of reactive oxygen species (such as superoxide radical, hydroxyl radical, and singlet oxygen) on the metal oxide surfaces specially for nano sized  $ZnO$  and  $TiO_2$  is also responsible for causing damage to the microbial cell wall, proteins, and nucleic acids [21, 31]. On the other hand, antiviral activity of nano  $Ag$  has also been reported due to direct binding of  $Ag$  nanoparticles to viral envelope glycoproteins and inhibiting the viral penetration into the host cell [24]. Thus, it can be concluded that the synergistic effect of the ability of metal and metal oxide nanomaterials to damage/kill microbes and the prevention of adhesion of microbes on superhydrophobic surfaces can lead to enhance antimicrobial activity of the materials surfaces.

Bacterial contamination of different surfaces has specific importance in medical and biological research field. The presence of various pathogenic bacteria, which transfer from polluted host surfaces to human body, is responsible for many contagious diseases. The replication speed and behaviour modifications of bacteria are the main factors that have tremendous effects on therapeutic processes in medical science. It is known that the replication of bacteria on different host surfaces involves three main steps - adhesion, colonization, and growth [1]. A little disruption in any of the replication steps can stop their biological effects and growth processes onto the surfaces. As the superhydrophobic surfaces can prevent the adhesion of bacteria without use of any antibiotics, these surfaces can be effective against antibiotic resistant bacteria and can widely be used in medical implants, surgical appliances, and biodevices.

## Challenges and Future Prospect

Although, significant efforts have already been given by the scientific community for the research of antimicrobial (antibacterial, antifungal, and antiviral) activities of various nanomaterials based coatings but further extensive studies are highly essential for practical use of these materials as per requirement based on clinical trials against a variety of microorganisms for applications in biomedical equipment, personal protective equipment (PPE- gloves, face mask, head cover, gown, leg covers, etc.) in medical hospitals [32]. For these practical applications, new and standardized protocols have to be specified by studying the stability of such coatings under cleaning practise by medical and healthcare professionals. Specially, while almost all bacteria can adapt themselves genetically against different antibiotics, the superhydrophobic surfaces are important options for overcoming their magical gene adaptation abilities to prevent antibiotic-resistant bacteria [1]. These antimicrobial coatings with the superhydrophobic surface also having self-cleaning, antibiofouling and blood repellence properties may be very promising for the PPE, biomedical electronic devices, and implants. In this respect, further in-depth research is most necessary for applications of the coated PPE for medical and healthcare professionals to fight against currently pandemic Covid-19 disease worldwide.

## Conflict of Interest

The authors declare no conflict of interest.

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