An Overview of Nano-Particles Effect on Mechanical Properties of Composites

Olatunde I. Sekunowo, Stephen I. Durowaye, Ganiyu I. Lawal

Abstract—Composites depending on the nature of their constituents and mode of production are regarded as one of the advanced materials that drive today’s technology. This paper attempts a short review of the subject matter with a general aim of pushing to the next level the frontier of knowledge as it impacts the technology of nano-particles manufacturing. The objectives entail an effort to; aggregate recent research efforts in this field, analyse research findings and observations, streamline research efforts and support industry in taking decision on areas of fund deployment. It is envisaged that this work will serve as a quick hand-on compendium material for researchers in this field and a guide to relevant government departments wishing to fund a research whose outcomes have the potential of improving the nation’s GDP.

Keywords—Advanced materials, Composites, Mechanical properties, Nano-particles.

I. INTRODUCTION

Nano-particles are particles with at least one dimension smaller than 1 micron and potentially as small as atomic and molecular length scales (~0.2 nm). Nano-particles can have amorphous or crystalline form and their surfaces can act as carriers for liquid droplets or gases. To some degrees, nano-particulate matter can be considered a distinct state of matter in addition to the solid, liquid, gaseous, and plasma states, due to its distinct properties (large surface area and quantum size effects). Examples of materials in crystalline nano-particles form are fullerenes and carbon nanotubes, while traditional crystalline solid forms are graphite and diamond [1]. Nanomaterials are materials that have structural components smaller than 1 micrometer in at least one dimension. While the atomic and molecular building blocks of approximately 0.2 nm of matter are considered nanomaterials, examples such as bulk crystals with lattice spacing of nanometers but macroscopic dimensions overall, are commonly excluded [1]. Many authors limit the size of nanomaterials to 50 nm [2] or 100 nm [3], the choice of this upper limit being justified by the fact that some physical properties of nano-particles approach those of bulk when their size reach these values. However, this size threshold varies with material type and cannot be the basis for such a classification. A legitimate definition extends this upper size limit to 1 micron, the sub-micron range being classified as nano [1].

Significant development and application of composites began in the second half of the 20th century, thereby increasing diversity in the areas of their usage. This stemmed mainly from the increasing need for materials with better mechanical characteristics such as strength, stiffness, good oxidation resistance and low weight. These functional characteristics are highly indispensable in the manufacture of parts for the automotive, aerospace and recreation industries. Engineering composites generally remain a key player in this regard [4]. Specifically, through the development brought about by nanotechnology, composites whose reinforcements are nanoscale appear to be the material of the 21st century. The birth of nanotechnology dawned in 1959 when Richard Feynman presented his famous article “There’s Plenty of Room at the Bottom” and since then, nanotechnology has grown dramatically. The American Ceramic Society in 2004 defined Nanotechnology as: “The creation, processing, characterization, and utilization of materials, devices, and systems with dimensions in the order of 0.1-100nm. These materials are known to exhibit novel and significantly enhanced physical, chemical, biological, mechanical properties, functions and varied phenomena.

II. WHY NANO-PARTICLES?

Advanced analysis of the physical and chemical characteristics of nano-particles will continue to be essential in revealing the relationship between their size, composition, crystallinity, morphology, electromagnetic response properties, reactivity, aggregation, and kinetics. It is important to note that fundamental properties of nano-particles are still being discovered, such as magnetism in nano-particles made of materials that are non-magnetic in bulk form. Advances in nanotechnology are driven by rapid commercialization of products containing nanostructures and nano-particles with remarkable properties. This is reflected in the enormous number of publications on nanotechnology [1]. Particles have been proven to be the most common and cheapest reinforcement with potential for conferring unique mechanical characteristics on composites. Particle reinforcement is also reputed to produce discontinuous reinforced composites exhibiting isotropic properties desirable in engineering materials coupled with better thermal stability. For instance, the useful temperature range of particle reinforced aluminium based composite is 20-150°C which is significantly higher than other forms of reinforcements. Another attraction is that conventional fabrication methods may be used to produce a
wide range of product forms, making them relatively inexpensive compared to composites that are reinforced with continuous fiber or filaments. Particle shape and size also play an important role to influence the composite responses under different stress conditions. Generally, nano-particles interactions have profound implications on the macroscopic behaviour of materials as each structural level contributes to the materials’ resulting mechanical characteristics. Thus, it has become increasingly important to understand and manipulate composite materials at the nanoscale level to develop new functional materials for both engineering and biomedical applications.

III. CLASSIFICATION OF NANO-PARTICLES

Nano-particles are generally classified based on their dimensionality, morphology, composition, uniformity, and agglomeration. The large number of publications on nanomaterials can be explained by the fact that nanoscience and nanotechnology encompass a wide range of fields, including chemistry, physics, materials engineering, biology, medicine, and electronics. Morphological characteristics to be taken into account are: flatness, sphericity, and aspect ratio. A general classification exists between high-and low-aspect ratio particles. High aspect ratio nano-particles include nanotubes and nanowires, with various shapes, such as helices, zigzags, belts, or perhaps nanowires with diameter that varies with length. Small-aspect ratio morphologies include spherical, oval, cubic, prism, helical, or pillar. Collections of many particles exist as powders, suspension, or colloids [1].

Nano-particles can be composed of a single constituent material or be a composite of several materials. The nanoparticles found in nature are often agglomerations of materials with various compositions, while pure single-composition materials can be easily synthesized today by a variety of methods. Based on their chemistry and electro-magnetic properties, nano-particles can exist as dispersed aerosols, as suspensions/colloids, or in an agglomerate state. For example, magnetic nano-particles tend to cluster, forming an agglomerate state, unless their surfaces are coated with a non-magnetic material. In an agglomerate state, nano-particles may behave as larger particles, depending on the size of the agglomerate. Hence, it is evident that nano-particles agglomeration, size and surface reactivity, along with shape and size, must be taken into account [1].

IV. NANO-PARTICLES DISPERSION

Two of the major problems related to nano-particles dispersion with a conventional beads mill are re-agglomeration and damage to the crystalline structure of the particles. The Ultra Apex Mill was developed to solve these problems by enabling the use of ultra-small beads with a diameter of less than 0.1mm. The core of this breakthrough development is centrifugation technology which allows the use of beads as small as 0.015mm. When dispersing agglomerated nano-particles, the impulse of the small beads is very low which means there is little influence on the particles. The surface energy of the nano-particles remains low so the properties are not likely to change. As a result, stable nano-particles dispersions can be achieved without re-cohesion. The Ultra Apex Mill is superior to conventional beads mills that are limited to much larger bead sizes. Its technology has pioneered practical applications for nano-particles in various fields: composition materials for liquid crystal display screens, ink-jet printing, ceramic condensers and cosmetics [5]. The Ultra Apex Mill has realized a breakthrough in conventional dispersing limits. Particle size limitation in the nano-fields has become much smaller by using 0.015-0.03mm diameter beads. Re-agglomeration is prevented and new products can be developed from common materials. The basic concept is that the impulse power of the small beads is very low which allows the crystal shape of the material to be maintained during milling. This allows the Ultra Apex Mill to create new products with special properties that are not attainable with conventional machines. This breakthrough technology has been paid much attention in the nano technology field [5].

V. SELF PROPAGATING HIGH TEMPERATURE SYNTHESIS

Self-propagating High-temperature Synthesis is a form of reaction synthesis that relies on the heat evolved from a localized chemical reaction to propagate the overall combustion reaction to the rest of the green compact. This exothermic propagation reaction can be used to produce many different product phases. Primarily, Self-propagating High-temperature Synthesis methods are used to produce ceramic or intermetallic products because of the significant heat developed. The materials produced can then be utilised as final parts or further processed into composites or sintered using standard techniques. The primary advantage of Self-propagating High-temperature Synthesis is in the potential synthesis of high-strength engineered ceramics at much lower cost than standard ceramic processing methods [6]. It is achieved by mixing reactant powders and subsequently igniting a reaction between them to form a desired product phase. This process takes far less equipment and time than standard ceramic powder production methods such as: calcination, roasting, sol gel and atomization [7]. These production methods take much longer or require higher-temperature processing than Self-propagating High-temperature Synthesis [8].

Another cost-saving aspect is the minimal amount of equipment required, consisting of only: a punch and die, a bench top press, reactant powders, mixing equipment and an ignition source. The ceramic particles that result from Self-propagating High-temperature Synthesis can be utilized in several applications, an example of which is as a reinforcement in metal matrix composites (MMCs). Since decrease in the particle size of the reinforcement phase results in increasing composite strength, it is desirable to have control over the particle size during SHS. The ceramic addition process is typically difficult due to the ceramic particles not wetting readily in the molten phase and this limitation is addressed by SHS through higher temperatures during
addition. Nanoparticles of TiC and Al₂O₃ produced by SHS were integrated into an aluminium metal matrix to form aluminium metal matrix composites. The TiC particles produced via SHS form spheres of relatively uniform diameters [9]. A positive correlation between the size of the products and the combustion reaction was suggested by Moore [10]. Specifically, it was assumed that a reduction in particle size could potentially be achieved by reducing the combustion temperature accomplished by one or more of the followings: changing reactant, adding diluents, changing green density, and pre-cooling the reactants [11].

VI. CARBON NANOTUBES (CNTS)

Carbon Nanotubes are one of the most important materials of future and have reached a stage of attracting the interests of many companies world-wide for their large scale production. They possess remarkable electrical, mechanical, optical, thermal and chemical properties, which make them a perfect fit for many engineering applications. The various methods of production of carbon nano-tubes include arc discharge, laser ablation, flame synthesis, high pressure carbon monoxide, electrolysis, pyrolysis and chemical vapour deposition (CVD). CVD is a potential method for economic large scale production of carbon nanotubes due to its relative simplicity of operation, process control, energy efficiency, raw materials used, capability to scale up as large unit operation, high yield and purity [12].

Carbon nanotubes have been under scientific investigation for more than fifteen years because of their unique properties that predestine them for many potential applications. The field of nanotechnology and nanoscience push their investigation forward to produce CNTs with suitable parameters for future applications. It is evident that new approaches of their synthesis need to be developed and optimized. Rarely used ways of arc discharge deposition which involves arc discharge in liquid solutions in contrary to standard used deposition in a gas atmosphere and the methods for uniform vertically aligned CNTs synthesis using lithographic techniques for catalyst deposition as well as a method utilizing a nano-porous anodized aluminium oxide as a pattern for selective CNTs growth have been reported [13]. The possible applications of CNTs include conductive films, solar cells, fuel cells, super capacitors, transistors, memories, displays, separation membranes and filters, purification systems, sensors, clothes, etc.

CNTs can be constructed in two basic forms, single-walled nanotubes (SWNTs). The other one is multi-walled nanotubes (MWNTs). Single-walled nanotubes consist of a single tube of graphene as shown in Fig. 1 whereas multi-walled nanotubes are composed of several concentric tubes of graphene fitted one inside the other. The diameter of CNTs varies from a few nanometres in the case of SWNTs to several tens of nanometers in the case of MWNTs and the lengths of the CNTs are usually in the micrometre range [14]. The fact that a SWNT and a MWNT of the same length do not have the same weight has been neglected until now. Therefore, it is very important to establish the relationships between the weight and the density of CNTs and their geometrical characteristics (inner diameter, outer diameter, and number of walls) [15].

![Fig. 1 Wrapping of graphene sheet to form SWNT](image1)

![Fig. 2 Currently used methods for CNTs synthesis](image2)

CNTs in sizeable quantities could be produced using various methods that are summarised in Fig. 2. High temperature preparation techniques such as arc discharge or laser ablation were first used to produce CNTs but nowadays these methods have been replaced by low temperature chemical vapour deposition techniques, since the orientation, alignment, nanotube length, diameter, purity and density of CNTs can be precisely controlled in the latter [16]. The most utilised methods and some of other non-standard techniques like liquid pyrolysis and bottom-up organic approach have been reported. Most of these methods require supporting gases and vacuum, but the growth at atmospheric pressure has been already reported [17]. However, gas-phase methods are volumetric and hence they are suitable for applications such as composite materials that require large quantities of nanotubes and industrial-scale synthesis methods to make them economically feasible. On the other hand, the disadvantages of gas-phase synthesis methods are low catalyst yields, where only a small percentage of catalysts form nanotubes, short catalyst lifetimes, and low catalyst number density [18]. Arc discharge belongs to the methods that use higher temperatures above 1700°C for CNTs synthesis which usually cause the growth of CNTs with fewer structural defects in comparison with other techniques. The arc discharge synthesis of MWNTs is very simple in the case when all growth conditions are ensured. The most utilized methods use DC arc discharge between two graphite usually water-cooled electrodes with diameters between 6 and 12 mm in a chamber filled with helium at sub-atmospheric pressure. Nevertheless, some other works with the use of hydrogen or methane atmosphere have also been reported [13].

Thermal [19] or plasma enhanced catalytic chemical vapour deposition is now the standard method for the CNTs production. Moreover, there are trends to use other CVD
They found that surface free energy plays a key role in studied CNTs growth via catalytic pyrolysis of acetylene. Nebol’sin and Vorob’ev via pyrolysis of ferrocene–ethanol aerosol right before CNTs technique was in situ formation of metal catalyst nanoparticles composed of both liquid hydrocarbon and catalyst precursor. Byeon et al. developed a new aerosol assisted chemical vapour deposition process is a catalytic CVD-based method involving pyrolysis of mixed liquid aerosols composed of both liquid hydrocarbon and catalyst precursor. Byeon et al. developed a new aerosol assisted chemical vapour deposition process to synthesize vertically aligned CNTs arrays with outstanding height of 4.38 mm with very low metal contents in a short time of 20 mins without supporting materials and water-assistance. An essential part of this technique was in situ formation of metal catalyst nanoparticles via pyrolysis of ferrocene–ethanol aerosol right before CNTs synthesis. In another work, Nebol’sin and Vorob’ev studied CNTs growth via catalytic pyrolysis of acetylene. They found that surface free energy plays a key role in determining the catalytic activity of the liquid droplet on the CNT tip and is responsible for the constant nanotube diameter.

An interesting paper describing the usage of a less common liquid carbon source, namely various pinene components isolated from turpentine for MWNTs production by spray pyrolysis was recently published by Lara-Romero et al. A green natural carbon source for CNTs fabrication through neem oil extracted from the seeds of the neem (Azadirachta indica). This was tested in the work of Kumar et al. Similarly, coconut oil can also be used as a natural renewable precursor for MWNTs synthesis. Ionescu et al. presented a safe and easy way to scale up the CNTs growth which is applicable in industrial production, by the use of spray pyrolysis CVD in the absence of hydrogen at low carrier gas flow rates and at relatively low synthesis temperature (typically 750°C). They concluded that this approach promises great potential in building various nano-devices with different electron conducting requirements.

Nowadays, solid state pyrolysis for CNTs synthesis is less frequently used compared to previously discussed methods. Kucukaylan and colleagues synthesized MWNTs through pyrolysis of the sulphuric acid carbonized by-product of sucrose. They observed the presence of sulphur in catalyst particles trapped inside nanotubes, but no sulphur was present in the side-walls of the CNTs. Clauss et al. thermally decomposed two nitrogen-rich iron salts, ferric-ferro cyanide and iron melonate in a microwave oven, which was used to heat a molybdenum wire after being coated with the precursor and protected from ambient atmosphere. While the ferric-ferro cyanide precursor did not give any nanotube containing products, the iron melonate precursor furnished tubular carbon nanostructures in a reproducible manner. This result may be due to the graphite-like nature of the melonate anions presented in iron melonate.

Flame pyrolysis technique is presented very uniquely by the research group of Liu et al. as a new method for mass CNTs production using simple equipment and experimental conditions. The authors called it V-type pyrolysis flame. They captured successfully CNTs with less impurities and high yield using carbon monoxide as the carbon source. Acetylene/air premixed gas provided heat by combustion. Pentacarbonyl was used as the catalyst and hydrogen/helium premixed gas acted as diluted and protection gas. The diameter of obtained CNTs was approximately between 10 nm and 20 nm, and its length was dozens of microns. Moreover they studied the effect of sampling time, hydrogen and helium to the CNTs growth process.

More recently, Jasti and Bertozzi described in their frontier article the potential advantages, recent advances, and challenges that lie ahead for the bottom-up organic synthesis of homogeneous CNTs with well-defined structures. The current synthetic methods used for CNTs fabrication produce mixtures of structures with varying physical properties. Jasti and Bertozzi demonstrated the CNTs synthesis with control of chirality, which relies on utilizing hoop-shaped carbon macro-
cycles, i.e. small fragments of CNTs that retain information regarding chirality and diameter, as templates for CNTs synthesis as shown in Fig. 3. Their strategy lies in two basic areas: the synthesis of aromatic macro-cyclic templates and the development of polymerization reactions to extend these templates into longer CNTs. This approach is particularly attractive because it can be used for synthesis of both zigzag and armchair CNTs of different diameters, as well as of chiral CNTs with various helical pitches [13].

VIII. SPECIFIC EMPIRICAL RESULTS

7075 aluminum matrix composite reinforced with SiC nano-particles of size 50nm was fabricated via powder metallurgy and a spectacular increase in wear and creep resistance compared to the composite reinforced with 13μm SiC particles was noticed [49]. The effect of 25μm, 5μm, and 70nm SiC particles on dimensional stability in an aluminum alloy was also compared. The temperature sensitivity of aluminum decreases in the presence of both micro and nano-sized silicon carbide, though the effect of nano-sized silicon carbide on dimensional stability is much higher than that of micro-sized ones [50]. Further, the volume percentage of nano-particles needed to achieve this improvement was considerably smaller than micro-particles volume percentage. For example, the tensile strength of an aluminum alloy reinforced with 1% volume of Si₃N₄ of size 10nm has been found to be comparable to that of the same alloy reinforced with 15% volume of SiC particle in the micro-size range of 3.5μm with the yield strength of the nano-metric composite being significantly higher than that of the micro-metric [51]. This underscores the imperative for the development of a critical particle size regime that serves to guide manufacturers and such information is presented in (Table I) [52]. This becomes necessary in view of the need for a functional knowledge of mechanism responsible for properties improvement in materials having discontinuous structures. These days the use of nano-tubes as a reinforcement is also gaining prominence. Actually, nano-tubes usage as reinforcement is highly desirable in certain applications. SiC, TiC, WC, TaC, TiB₂, AlN, and Al₂O₃ are some of the most common types of nano-particles that have been utilized. On the overall, the characteristics of nano-particles reinforced composites can be summarised as: drastic change in fracture mode which usually manifests in the change from intergranular fracture of monolithic metal to transgranular fracture of nano-composites, moderate to significant improvement in strength, significant improvement in resistance to creep, thermal shock and wear, significant enhancement in thermal stability.

IX. THE CHALLENGES

Whatever CNTs preparation method is applied, the CNTs are always produced with a number of impurities whose type and amount depend on the technique used. Most of the discussed techniques produce powders which contain only a small fraction of CNTs and also other carbonaceous particles such as nanocrystalline graphite, amorphous carbon, fullerenes and different metals such as Fe, Co, Mo or Ni that were introduced as catalysts during the synthesis. These impurities interfere with most of the desired properties of CNTs and cause a serious impediment in detailed characterisation and applications. Therefore, one of the most fundamental challenges in CNTs science is the development of efficient and simple purification methods [53]. Most common purification methods are based on acid treatment of synthesized CNTs [54].

Due consideration is not accorded the influence of particles on micromechanics of deformation in terms of location of particles, grain size, and dislocation density. Several solutions to this problem have been attempted through the formulation of systems that incorporate analysis of discontinuous bodies to include the particle effect. The modified shear lag theory [55] of Nardone and Prewo, the Eshelby-based particle-compounded model and the effective medium approximation model by Stroud are the most popular approaches [56]. These materials take into account one or more of the following strengthening factors:

A. Orowan Effect

This posits that the stress that must be applied to force a dislocation to by-pass an obstacle such as a particle is equivalent to the resistance of closely spaced hard particles to bypass a dislocation. The Orowan effect is not significant if the particles are coarse in the micro-size range and the inter-particle spacing is large [55]. However, under a highly dispersed nano-sized particle in a metal matrix, Orowan strengthening becomes more favourable. Similarly, creep resistance and thermal stability are consistently enhanced, even for very small volume fraction (<1%). The Orowan strengthening mechanism has been validated by a transmission electron microscope revealing strong dislocation bowing and tangling around the particles themselves, further confirming what is stated above [55].

B. Thermal Mismatch

Matrix and reinforcement have different coefficients of thermal expansion. Hence, during cooling, plastic deformation occurs at the interface resulting in defects such as dislocations.
Thus, due to the increment of interfacial area occasioned by particle size, the density of dislocation is also increased [56].

C. Load Bearing

The strong bond due to the cohesion between particle and matrix contributes to the load carrying capacity of the material [55]. The sum of the bond of cohesion between particles increases as the particle size reduces. When all these factors are taken into account, the increase in mechanical properties with the decrease in size can be geometric. The above not withstanding, there is still an uncertainty in theoretical modelling and experimental characterization of nano-scale reinforced materials. The main challenges dovetail around two issues which are: appropriate processing method that guarantees homogeneous of second phase to disperse within the matrix, and achievement of a strong interfacial bonding.

X. EMERGING TRENDS IN NANO-PARTICLES COMPOSITES PRODUCTION

For processing nanotube composites, many approaches involve several steps that may include high energy sonication, chemical polymerisation of the corresponding monomer in the presence of CNTs, electrochemical synthesis of polymers on CNTs electrode, solution–evaporation processing, surfactant-assisted processing through formation of a colloidal intermediate, functionalisation of nanotubes with the polymer matrix, and high shear mixing [57]. A commonly used solution–evaporation method for preparing nanotube–polymer composites involves mixing nanotubes dispersions with a solution of the polymer and then evaporating the solvent in a controlled way. The low viscosity of the polymer solution allows the nanotubes to move freely through the matrix. The solution mixing approach is limited to polymers that dissolve readily in common solvents. An alternative is to use thermoplastic polymers (i.e., polymers that soften and melt when heated), and then apply melt processing techniques. Thus, shear mixing can be used to produce a homogeneous dispersion of nanotubes and extrusion to produce nanotube alignment or to fabricate objects in the required form by injection moulding.

Another alternative method for preparing nanotube–polymer composites is to use the monomer rather than the polymer as a starting material, and then carry out in situ polymerisation. The problem of insolubility of carbon nanotubes due to strong Vander Waals attractions and chemical inertness hinders their uniform dispersion and incorporation in any matrix. An homogeneously dispersed filler in the polymer matrix reduces the possibility of nanotube entanglement, which can lead to significant changes in composite behaviour. The nanotube aggregation within a polymer system would certainly have a negative impact on its stiffening ability [58]. As yet, the nature of these entanglements and their influence on the composite properties is a little-understood area. To overcome nanotube aggregation, functionalisation of nanotubes is done with groups that facilitate their incorporation into a material through covalent bonding.

XI. CONCLUSION

From the foregoing, it is established that nano-composite materials offer improved performance when compared to monolithic alloys and micro-composites. The possible applications of these materials are numerous and involve several market fields. Although, particles size reduction to nano-meter scale poses new technological challenges such as particle agglomeration and de-bonding from matrix. The role of atomic-scale forces of Van der Waals attraction and electrostatic repulsion must also be taken into account to fully understand the mechanics of particles interaction. Improvements in mechanical property have resulted in major interest in nanocomposite in various automotive and general industrial applications. These include potential for utilization as mirror housing on various vehicles types, door handles, engine covers and intake manifolds and timing belt covers. More general applications currently being considered include usage as impellers and blades for vacuum cleaners, power tool housings, mower hood and covers for portable electronic equipment such as mobile phones, pagers. Advances innanotechnology are driven by rapid commercialization of products containing nanostructures and nanoparticles with remarkable properties.

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<tr>
<th>TABLE I</th>
<th>CRITICAL PARTICLE SIZE FOR PROPERTIES IMPROVEMENT</th>
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<tbody>
<tr>
<td>Properties</td>
<td>Critical size [nm]</td>
</tr>
<tr>
<td>Hardness and Plasticity modification</td>
<td>&lt; 100</td>
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<tr>
<td>Strengthening and Toughening</td>
<td>&lt; 100</td>
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<tr>
<td>Inducing Electromagnetic phenomena e.g. super paramagnetism</td>
<td>&lt; 100</td>
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<tr>
<td>Softening of hard magnetic materials</td>
<td>&lt; 20</td>
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<tr>
<td>Change of Refractive index</td>
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<tr>
<td>Catalytic activity</td>
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