

# Zirconia, from optoelectronics to oral environment applicability

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Of all the advanced ceramic materials used in various fields in the contemporary ceramic era, zirconia surpasses by its top position and continues to surprise by the constant expansion of its application possibilities, starting from the wide use in optoelectronics, nanotechnology, to its role as biomaterial in modern medicine and up to the revolutionary perspectives of fight against pandemic situation. From the discovery of its excellent mechanical, biological and shape memory properties, to the stabilization of the tetragonal and cubic phases through alloying especially with rare earth ions and first of all the unique characteristic called transformation-toughening, new and new special features of zirconia are coming constantly into the spotlight of scientists. Thus, the present study is the first review in the scientific literature in terms of heterogeneity in coverage of the most important applications of zirconia, aiming to create a bridge from past to future issues, and a multidisciplinary topical debate in the scientific community.

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## 1. Introduction

Zirconia ( $ZrO_2$ , zirconium oxide or baddeleyite) is an inorganic metallic oxide material, a translucent solid mineral, sometimes transparent in its natural form, whose Arabic etymological origin „Zargun” comes from the two Persian words „Zar” (Gold) and „Gun” (Colour), meaning „golden in colour” [1].

Due to its excellent physical and chemical properties, zirconia is recognized worldwide as one of the emblematic materials of the modern ceramic era of the 21<sup>st</sup> century [2].

Together with uranium and cerium, zirconium dioxide was accidentally extracted by German chemist Martin Heinrich Klaproth [3], while analyzing a precious mineral from the class of silicates (Zircon), in 1789, and named by him for the first time as "Zirkonerde" (zircon earth, or zirconia). It was later isolated by the Swedish chemist Jöns Jakob Berzelius in 1824 [3].

The increasing interest regarding zirconia, in the last decades, is based on the widening expansion of its applicability in various technological fields such as optoelectronics, catalyst support, as an insulator in transistors for nanoelectronic devices, in solid oxide fuel cells [4], spintronics [5], biosensors, and biomedical field [6].

In terms of the introduction of zirconia in the biomedical field, the wide debate between scientists, industrialists and clinicians dates back more than three decades, arising from the need to introduce an alternative to titanium and titanium alloys as the “gold” standard for various human structure replacements. Although these materials have gained standard use because of their exceptional biocompatibility, encouraging mechanical

properties, and well documented favorable results [7], their disadvantages exist and are important to emphasize. We refer thus to the aesthetic (in certain clinical situations), immunological inconveniences [8], the cellular sensitization [9], and to the phenomenon of galvanism after contact with biological fluids and fluorides etc., reason for which the search for the “ideal” biocompatible material, with adequate toughness, strength, corrosion, wear and fracture resistance continued to be in the spotlight of scientists.

In this regard, zirconia, occupying a unique place amongst oxide ceramics due to its excellent properties, is a promising alternative for titanium. The scientific literature classifies zirconia as advanced biocompatible ceramics, differentiating it from the “traditional” ones by its high value-added content [10].

From the category of additives meant to increase the structural stability of zirconia, could be mentioned: magnesia ( $MgO$ ), calcium oxide ( $CaO$ ), alumina ( $Al_2O_3$ ), and the rare-earth oxides ( $Y_2O_3$ ,  $Gd_2O_3$ ,  $Yb_2O_3$ ) contributing to the stabilization of the material for applications under highly corrosive conditions [11].

At the same time, the addition of "stabilizing" oxides has the role of strengthening zirconia and allows to generate multiphase materials known as partially stabilized zirconia (PSZ) [12], such as the partial stabilized by 2÷5 mol%  $Y_2O_3$ , which thus becomes *yttria stabilized tetragonal polycrystal zirconia* (Y-TZP) [13]. On the other hand, complete stabilization by  $\leq 8$  mol%  $Y_2O_3$  is known as *fully stabilized zirconia* [14], [15].

It thus becomes clear that, at present,  $ZrO_2$  ceramics have become increasingly complex and high-performance materials, that can be divided into *functional ceramics* (with electrical or magnetic functions) and *structural or engineering ceramics* (mechanical function).

Microstructurally zirconia is a highly-resistant, polycrystalline ceramic material. The unique property of zirconia is its structural polymorphism, which is pressure- and thermal- dependent. Depending on the temperature, zirconia can have three crystallographic structures: monoclinic (M), cubic (C) and tetragonal (T) [16], as shown in Fig. 1. The monoclinic crystalline phase (M- $ZrO_2$ ) remains stable at room temperature up to  $1170^\circ C$ , and presents the lowest mechanical properties. Increasing this temperature, M- $ZrO_2$  transforms into tetragonal form (T) with great mechanical properties, and then into cubic (C) from  $2370^\circ C$  to the melting point,  $2680^\circ C$ , with moderate mechanical properties, followed by a fluorite form at  $2680^\circ C$  temperature, and over this value, the structure become liquid [16].

Volume changes during the phase transitions are recognized as stress-induced phase transformations. Thus, due to a force (stress) applied on the zirconia surface there

is a transition from T to M, which can produce cracks in the material, but in a first time this crystalline modification is followed by an expansion that seals the crack, a kind of *self-curing mechanism* that gives a unique quality to zirconia [17]. Finally, if the fatiguing forces and stresses in humid environments increase, the mechanism fails and results in a loss of strength of the crystalline structure over time [18], which can lead to catastrophic failures.

Additives or stabilizers, especially  $Y_2O_3$ , are used to limit  $T \rightarrow M$  phase transformations, to stabilize the crystal structure at room temperature, and thus to optimize the mechanical properties of zirconia, the phase transitions being considered to slow down directly proportional to the increase in the amount of additive [19].

Fig. 2 shows the evolution of publications related to zirconia, in the last two decades (Source WEB OF SCIENCE, WOS). The number of studies increased continuously, with a maximum in the last year, which shows that there is a growing interest on zirconia.

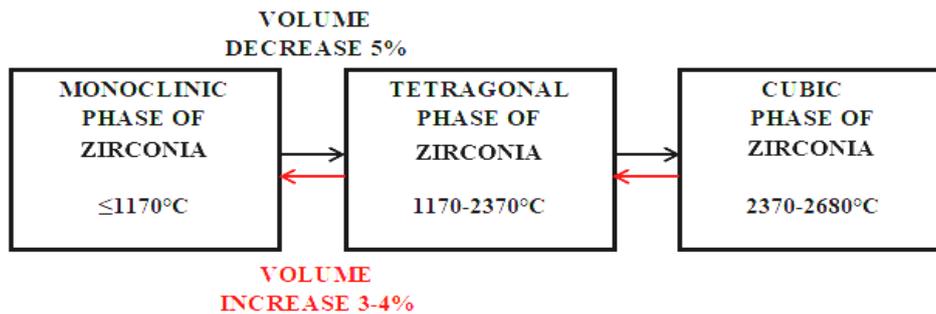


Fig. 1. Temperature-dependent polymorphic phases of zirconia (color online)

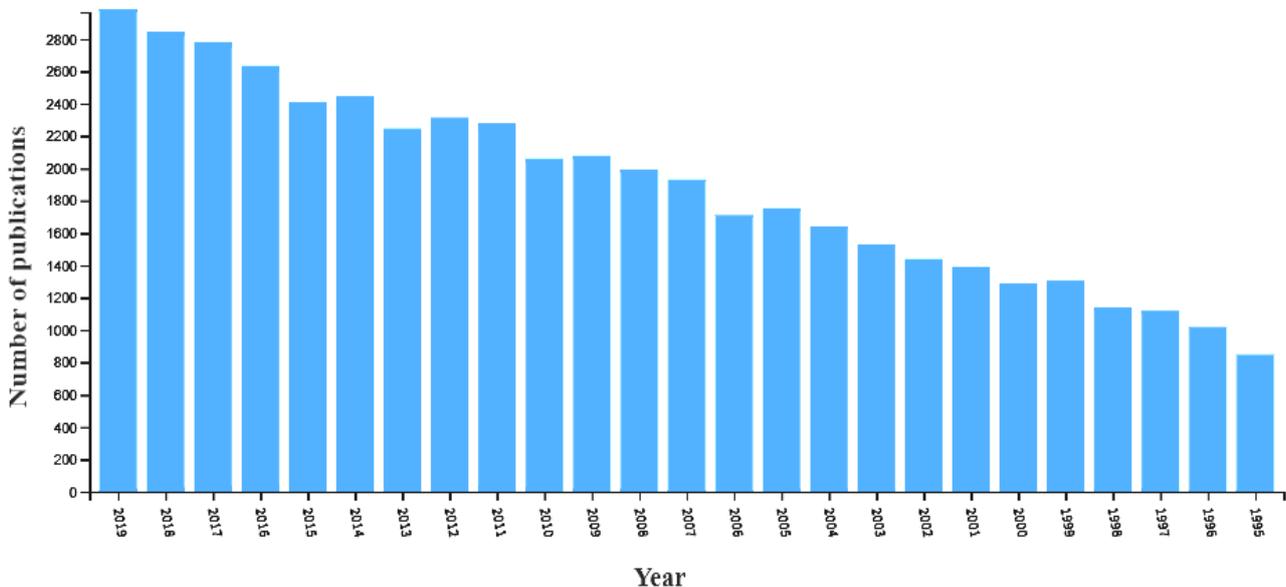


Fig. 2. Evolution in time of publications related to zirconia (Source WEB OF SCIENCE, WOS) (color online)

## 2. Properties of zirconia

### 2.1. Physical properties

One of zirconia's major physical modifications in terms of disadvantages is the low-temperature degradation, also known as *ageing phenomena*. It consists in the decay of the mechanical properties due to the progressive spontaneous transformation of the metastable tetragonal phase into a monoclinic one at temperatures above 200°C in the presence of water vapors. Under these conditions there is a significant reduction in the strength, toughness and density of the material [20]. For these reasons, the reduction in grain size of zirconia and/ or increase in the concentration of stabilizing oxides may reduce the transformation rate and implicitly the degradation of its crystalline structure [21]. Zirconia is also counted to have low thermal conductivity and an extremely high melting point (2700°C) and a boiling point almost double (4300°C).

### 2.2. Chemical properties

Zirconia is an amphoteric metal oxide, chemically unreactive, but which exhibits both anion- and cation-exchange capacities depending on the pH solution and the nature of the buffer [22]. Having both acidic and basic chemical properties, the applications of zirconia as a catalyst or catalyst support are more than promising [23].

Zirconia is chemically inert and has a non-polar surface [24], so it must be modified with functional groups (such as phosphate esters) in order to be used in various applications.

### 2.3. Mechanical properties

Zirconia possesses mechanical properties comparable to those of stainless steel, such as Young's modulus (210 GPa vs. 193 GPa) [25], the resistance to traction in the range 900–1200 MPa and compression up to 2000 MPa [1].

However, the mechanical properties of zirconia vary depending on the phase of the crystalline structure, the grain size, but also on the type and quantity of additives used to stabilize the respective phase. Thus, ZrO<sub>2</sub>-based ceramic materials stabilized with yttria display better properties comparing to zirconia-based ceramic materials which are stabilized by calcium oxide and magnesia, while the metastable tetragonal phase is the most desired and toughest form [14].

### Shape-memory effect (SME)

As shown in Fig. 1, ZrO<sub>2</sub> has three polymorphic phases: monoclinic (M), tetragonal (T) and cubic (C), among which, of interest being the T→M martensitic transformation accompanying SME [26].

As pointed out by Lai *et al.* [27], the shape memory effect is the ability to transform to a “remembered” predefined shape upon the application of heat.

But martensitic transformations could cause undesirable cracking in zirconia-based materials. This problem can be overcome either by adding ceria, magnesia or yttria as additives to zirconia, or by using ZrO<sub>2</sub> in small scale to reduce the mismatch stress at grain boundaries and increase the surface area to relax the stress during the martensitic transformation [26], [28].

The shape memory effect of zirconia-based materials was exploited in various applications, such as: bulk polycrystalline zirconia-based shape memory ceramics [28], artificial muscles [29], MEMS (micro-electro-mechanical systems), or energy damping [26].

### 2.4. Biological properties

The investigations demonstrated that zirconia is biologically inert, meaning biocompatible, since no adverse reactions with tissues are reported; moreover, zirconia shows no cytotoxic effects [30].

The biocompatibility of a material refers mainly to its compatibility with different tissues and/or living systems, and involves the absence of any inflammatory, irritative, allergic, immune, toxic, mutagenic, or carcinogenic reactions (*bioinertia*), and on the other hand, generating the most useful beneficial cellular or tissue response in a specific situation, and optimizing therapeutic performances (*bioactivity*) [31].

Thus, any material inserted in the human body must be initially tested for its biocompatibility.

Biocompatibility testing of zirconia, under different physical forms, on supporting connective tissue cells such as fibroblasts and fibrocytes began with *in vitro* tests performed by Bukat *et al.* three decades ago [32], followed by comparative studies with titanium by Ito *et al.* [33], and many others as well. The conclusion regarding the cytotoxicity of different zirconia powders on these cell lines is one questionable, there being evidence that only the wear products of zirconia could somehow present toxicity [34].

Regarding the cytotoxicity of zirconia on lymph and monocyte lines as well as on macrophages, initial studies conducted around 2000s by Catelas *et al.* [35], [36], and Sterner *et al.* [37] demonstrate the absence of induction of the inflammatory marker TNF  $\alpha$  as compare to Ti and alumina particles.

Finally, the results of multiple *in vivo* biocompatibility tests on soft tissue (muscle tissue) and hard tissue (bone tissue) of various physical and structural forms of zirconia [34] are convergent and confirm the undeniable advantage of zirconia on living tissues.

## 3. Areas of applicability of zirconia

The unusual combination of attractive features of zirconia (fracture toughness and strength, the biocompatibility, ionic conductivity, low thermal conductivity, refractive properties due to its high dielectric constant and resistance to thermal shock, etc.) make zirconia to be a valuable material for a wide range of

applications from optoelectronics, to bioengineering and oral environments. But these amazing properties, especially fracture toughness and strength, are compromised after prolonged exposure to water vapors at intermediate temperatures (the so-called *low-temperature degradation*, LTD), therefore addition of stabilizers or additives are necessary to overcome these problems [19]; [38].

### 3.1. (Opto)electronics

The excellent optical (wide bandgap, high refractive index, and high transparency in the visible and near infrared) and electrical (high dielectric constant) properties of zirconia [39] make it to be an attractive material for optoelectronic applications [40].

Recently, Boujnah's research team reported the impact of native point defects on the optical and electrical properties of cubic ZrO<sub>2</sub>, pointing out that the understanding the physical behavior of such point defects could be exploited in some solar energy applications [41].

Low-temperature ZrO<sub>2</sub> thin films obtained through polymeric route by Boratto *et al.* [40] showed high impedance and capacitance, demonstrating that zirconia obtained films are an interesting alternative for application in flexible electronic devices as insulating/dielectric layers.

Yttria tetragonally stabilized zirconia (Y-TZP) is widely used as solid state electrolyte, wear resistant components, and optical fiber connectors, like ferrules due to its high strength and toughness, high melting temperature, chemical stability, ionic, electrical and optical properties [19].

Another recent study reported the rapid and low-cost fabrication of a flexible and controllable Q-switched Zirconia-Yttria-Aluminium-Erbium-doped pulsed fiber laser with a pencil-core of graphene as saturable absorber, for applications in biomedical laser surgery, medical devices and treatment [42].

Ag-sensitized films of silica-zirconia doped by Yb<sup>3+</sup> ions and additional Na<sub>2</sub>O, obtained by sol-gel synthesis followed by a thermal annealing at 1000°C, presented a broadband and efficient energy transfer process between Ag dimers/multimers and Yb<sup>3+</sup> ions, resulting in a strong photoluminescence emission around 980 nm under UV light excitation [43]. These findings could be exploited in photovoltaic solar cells and light-emitting near-infrared devices applications.

The light-scattering effect of ZrO<sub>2</sub> microparticles and nanoparticles in a double-layered film was applied for the first time by Syrokostas *et al.*, to enhance light fluence on the perovskite layer in carbon-based mesoscopic perovskite solar cells [44].

Another interesting application of zirconia is gas sensors' development.

#### Gas sensors' applications

Gas sensors have huge implication in detection of noxious emissions, providing healthy and safe living and working environments [45].

Zirconia is a useful material to develop gas sensors. Y<sub>2</sub>O<sub>3</sub>-doped ZrO<sub>2</sub> was used as O<sup>2-</sup> ion-conductive ceramic electrolyte in potentiometric planar oxygen sensors [46].

Recently, Wang and co-workers developed yttria-stabilized zirconia solid electrolyte-type sensors coupled with CdTiO<sub>3</sub>, with high sensitivity in a wide detection range of C<sub>2</sub>H<sub>2</sub>, and good reproducibility [47].

Miura *et al.* reviewed recent progresses on design and configuration of zirconia-based gas sensors for monitoring and detection major hazardous gases in air carbon monoxide (CO), hydrocarbons, ammonia (NH<sub>3</sub>), nitrogen oxides (NO<sub>x</sub>), sulfur dioxide (SO<sub>2</sub>), hydrogen sulfide (H<sub>2</sub>S), and hydrogen (H<sub>2</sub>) [45].

Current trend is the using of zirconia nanoparticles (ZrO<sub>2</sub>NPs) for improving potentiometric oxygen sensors [46].

In addition, zirconia, at the nano-scale exhibits unusual and interesting properties, and other applications will be further discussed in the next section.

### 3.2. Nano-zirconia applications

Nanotechnology is the science dealing with preparation, manipulation and characterization of nano-sized objects. From bulk to micro- and to nano-scale, materials exhibit unusual and interesting properties. Nano-sized zirconia possesses unique electrical, thermal, catalytic, sensing, optical, mechanical, and biocompatible properties [48], and also antimicrobial, antioxidant and antiproliferative activities [6], and could induce mild or no cytotoxic effects [49].

During the past few decades, the application of zirconia nanoparticles (ZrO<sub>2</sub>NPs) in various fields (electronics, biomedical applications including biosensors, implants, cancer therapy, dentistry and pharmaceuticals) was one of the concerns in the spotlight of researchers [49].

The interesting properties of nano-zirconia were exploited in development sensors. Thus, in 2017 is mentioned the first report about fabrication of nanostructured zirconia - based immunosensor for detection of cardiac troponin I (cTnI) biomarker related to acute myocardial infarction [50]. This sensor presented a wide linear detection range (0.1–100 ng/mL) and impressive sensitivity [3.9 μA mL/(ng cm<sup>2</sup>)].

Moreover, ZrO<sub>2</sub>NPs was used to design sensors for humidity [51] or for the electrochemical determination of gallic acid in red and white wine [52].

A recent study [53] reports the photocatalytic activity of ZrO<sub>2</sub>NPs and Fe-doped ZrO<sub>2</sub>NPs that could be exploited in sundry wastewater treatment applications.

Nano-zirconia powders are used in dentistry to achieve a strong porous coating of solid surfaces in order to improve the mechanical properties and their biocompatibility [54].

The fields of application of ZrO<sub>2</sub> nanopowders are thus found in the biomedical field, as well as in tissue engineering scaffolds and dentistry, the lately including the incorporation of these powders in diatomite based-

ceramics [55], resulting in obtaining hybrid ceramics with better fatigue resistance, low material porosity and low fatigability. Efforts to optimize these mechanical properties were focused on stabilizing the tetragonal structure of zirconium (TPZ) with a number of additives, such as ceria and yttria; indeed, ceria-based nano-zirconia exhibited excellent strength for dental prostheses, and also they have more than double the fracture toughness and bending strength compared to yttria-based nano-zirconia ceramics [56].

Research team of Mitra [57] prepared novel composites based on zirconia-silica nanoparticles (synthesized from colloidal solution of silica and a zirconyl salt) embedded in a resin system (containing: bisphenol A glycidyl dimethacrylate, ethoxylated bisphenol A dimethacrylate, triethylene glycol dimethacrylate, 1,6-bis(2'-methacryloyloxyethoxycarbonylamino)-2,4,4-trimethylhexane, photoinitiators and stabilizers) with applications as dental restorative materials, which offer optimized physical properties such as high translucency, high polish and polish retention, and wear resistance. Recently, Yang *et al.* [24] developed interesting resin composites based on bisphenol A diglycidyl methacrylate and urethane dimethacrylate, containing nano-zirconia fillers with surface modified with 10-methacryloyloxydecyl dihydrogen phosphate and dipentaerythritol penta-acrylate phosphate. The presence of modified nano-ZrO<sub>2</sub> improved the mechanical properties (mechanical strength, high elastic modulus values, etc.) of the composite, thus these materials are promising in dental restoration applications.

The use of nano-zirconia to design novel advanced nanomaterials with theranostic applications to detect and treat coronaviruses is an open issue. The application of nanomaterials in treatment and detection of coronaviruses was highlighted by Nikaeen *et al.* in their recent study [58]. Zirconium quantum dots have already been used for optical detection of coronavirus [59].

It could be mentioned that metallic NPs, metal oxide NPs (such as ZrO<sub>2</sub>NPs) and quantum dots have shown intrinsic antiviral activity [60], so they could be used to design advanced healthcare materials to fight against COVID- 19.

Despite their interesting properties, the research studies related to zirconia nanoparticles are still in their infancy (Fig. 3).

Another interesting topic related to ZrO<sub>2</sub>NPs is “green” synthesis of ZrO<sub>2</sub>NPs. Various methods are used to prepare nano-zirconia, such as pyrolysis of zirconium oxychloride salt organic precursors, thermal decomposition, aqueous precipitation, solvothermal, hydrothermal and sol-gel methods, but all these procedures require energy, high costs and environmentally hazardous chemical precursors during synthesis processes [6]. Nowadays, “green” synthesis has been adopted as the best alternative to the classical methods because it offers numerous advantages such as: biocompatibility, antioxidant, antimicrobial and anti-cancer properties of “green” prepared ZrO<sub>2</sub>NPs. In addition, the “green”

methods are simple, low-cost and environmentally safety procedures.

*Pseudomonas aeruginosa* bacteria were used by Debnath *et al.* [61] for the first time for ZrO<sub>2</sub>NPs biosynthesis. The obtained biogenic ZrO<sub>2</sub>NPs by this novel microbial “green” technology proved to be efficient agents for removing tetracycline from the wastewater, and could be used in the near future, for purification of antibiotic contaminated water.

Not only bacteria could be used for ZrO<sub>2</sub>NPs biosynthesis, but also fungi and plants [6]. The plants are preferred, since plants are abundant in nature, and vegetal extracts contain many biological active molecules like proteins, polysaccharides, flavonoids, tannins, etc.

The plant extract based synthesis (named also *phytosynthesis*) of ZrO<sub>2</sub>NPs was firstly reported by Sathishkumar and co-workers [62] who fabricated “green” ZrO<sub>2</sub>NPs using *Curcuma longa* tuber extract.

By using leaf extract of *Eucalyptus globulus*, Balaji *et al.* obtained “green” ZrO<sub>2</sub>NPs with antioxidant and anticancer activity [6].

Majedi *et al.* [63] prepared ZrO<sub>2</sub>NPs from zirconium acetate and lemon juice as the precursors; these obtained ZrO<sub>2</sub>NPs have a potential application as an electrolyte material in oxide fuel cells.

Cinnamon (*Cinnamomum zeylanicum*), a common spice was used to “green” generate zirconia-reduced graphene oxide nanocomposite with excellent photocatalytic activity [64].

Figure 4 shows a suggestive representation of “green” synthesis of zirconia nanoparticles and the main applications of “green” ZrO<sub>2</sub>NPs.

### 3.3. Heterogeneous catalysts

Heterogeneous catalysts occupy a key position in the chemical industry which reveals their applicability in our daily life. Their major role in the synthesis of important pharmaceutical scaffolds is perfectly explicable, if we take into account the fact that more than 90% of the chemical manufacturing depends on the catalytic processes [65].

Due to their changeable phase composition, redox, acid/base properties and semiconductor behavior, zirconia-based oxides are used as a part of heterogeneous catalysts, in combination with copper and other metals. This multifunctional composite displays high activity and selectivity in various classes of reactions and, in particular, in processes linked to (bio)alcohols upgrading and methanol economy [66].

Another heterogeneous solid type catalyst with numerous applications in oil refinery and petrochemical industries, popular due to its high activity for light alkane isomerizations and cracking reactions, is represented by the complex SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> (sulfated zirconia) [67]. In this sense, it is worth mentioning the key function of SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> in producing liquid fuels in high octane gasoline [68], as well as the high catalytic activity for biodiesel *via* esterification [69], and for biolubricants synthesis [70].

Last but not least, one of the most important catalytic combinations of zirconia is that with ceria. The ceria-doped zirconia or zirconia-doped ceria materials display unique redox properties, increased oxygen storage capacity and better thermal stability in comparison with ceria or zirconia alone [71]. Among the most successful

applications of this heterogeneous catalyst is mentioned the simultaneously controlling the automotive exhaust emissions, such as CO, hydrocarbons, and NOx, a major source of air pollution [72].

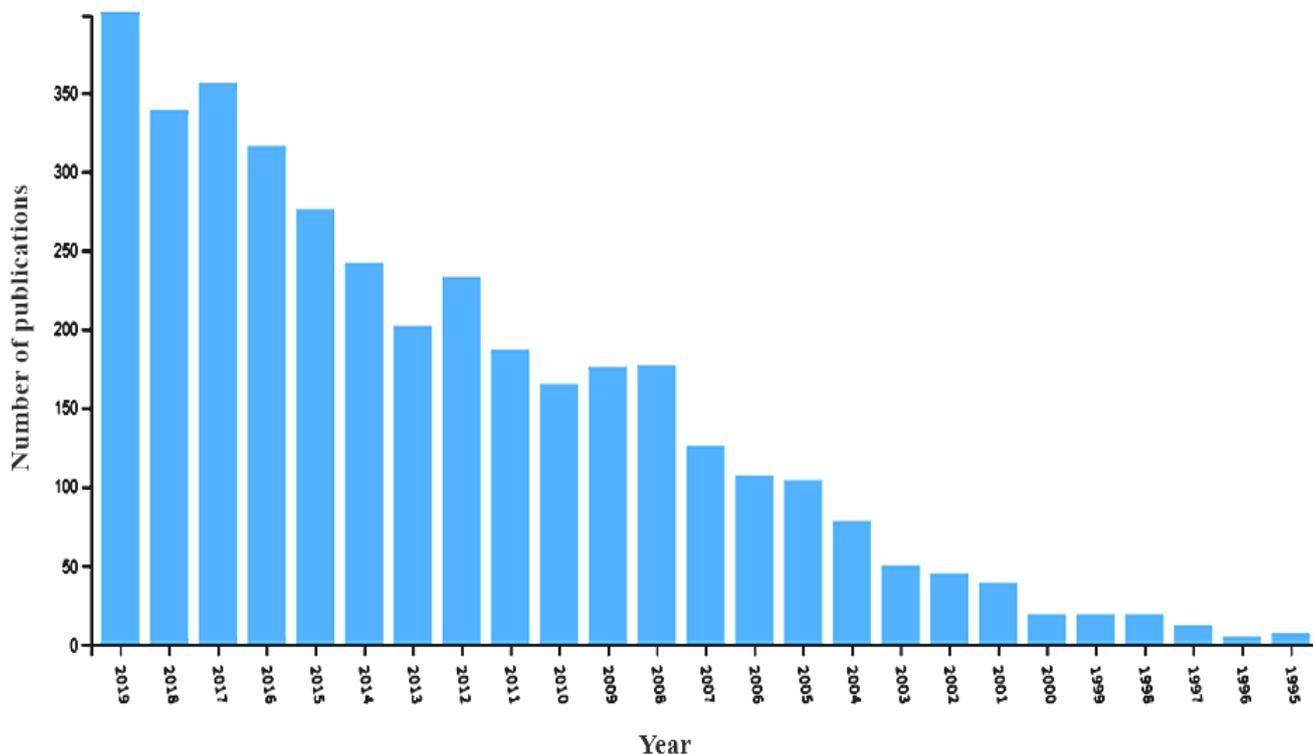


Fig. 3. Evolution in time of publications related to zirconia nanoparticles (Source WEB OF SCIENCE, WOS) (color online)

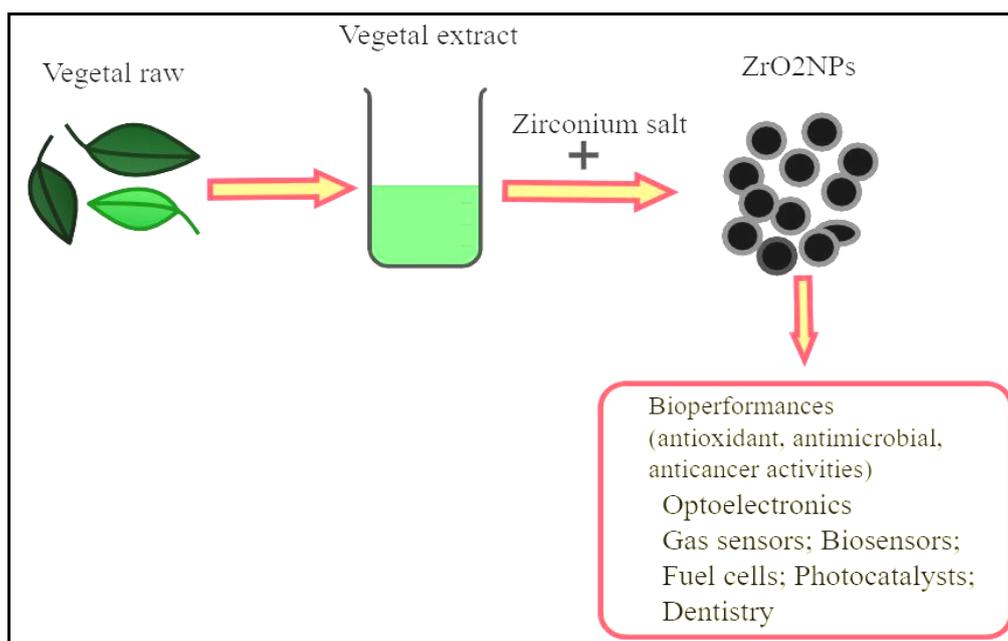


Fig. 4. „Green“ synthesis of zirconia nanoparticles - schematic representation (The figure was created with Chemix, <https://chemix.org/>) (color online)

### 3.4. The nuclear industry

Nowadays, the need for materials that can combat the severe radiation environments of the nuclear industry has become a vital challenge in the face of ever-increasing demands for nuclear energy. Therefore, it has been demonstrated that cubic zirconia acts as a promising matrix for the immobilization and transmutation of radioactive wastes [73]. Furthermore, recent studies have indicated strong evidence for the applicability of yttria-stabilized zirconia as an inert matrix fuel in nuclear reactors [74]. Regarding the fully stabilized zirconia, reports highlight a remarkable radiation tolerance against ion irradiation, making it clearly a candidate for applications in high radiation environments [75]. All this confirms the durability and reliability of this material and argues the current applications of zirconia-based materials in the nuclear industry, such as: advanced nuclear fuel incineration matrix for radioactive elements (such as Pu) [76], in treatment of reprocessing solutions, high-level waste treatment, recovery of fission products and high-temperature ion-exchange separations [22], etc.

### 3.5. Biomedical and Bioengineering applications

#### 3.5.1. Biosensors

Every day, we are exposed to many pathogens (i.e. infectious agents that cause diseases), and currently, the world is facing a global pandemic associated with the COVID-19 virus. It is imperative to develop performant techniques to rapidly detect pathogens, which is a critical step in order to quickly ensure effective treatment for infectious diseases and to control the disease spread.

In this respect, nucleic acid based biosensors (NABs) are rapid and reliable analytical tools which have applications in the clinical diagnostics market to detect a broad spectrum of metabolic and infectious diseases. The principle underlying the working of the biosensors based on deoxyribonucleic acid (DNA) is Chargaff's rule of base pairing (for DNA, A:::T, G□□□C) [77].

DNA – the “smart” biomolecule, which stores, transmits, and translates the genetic information for development and functioning of most living organisms, possess a unique architecture consisting of two polynucleotide strands coiled in a helical duplex structure based on the classical Watson–Crick base pairing interactions, allowing interactions with itself or with other biological molecules or with bio-inspired membranes [78], or with photosensitive molecules [79–81], and biogenic silver nanoparticles [82], giving rise to materials having amazing applications in various fields such as: opto-electronics, (bio)photonics, nanomedicine, etc.

For pathogen detection, electrochemical biosensors offer a great potential [83]. Thus, zirconia-based electrochemical DNA biosensor proved to be a rapid and sensitive tool for *M. tuberculosis* detection [84].

Biosensing platforms based on nanocomposites containing zirconia and reduced graphene oxide were developed for non-invasive oral cancer detection [85], and for the detection of oxidative stress biomarker 3-Nitro-L-tyrosine [86].

Zirconia was also applied to develop ferrule sticks used in microfluidic assembly for optically aligned flow cell coupled with a photonic crystal fiber optofluidic, as a part of a refractive index transduction platform for label-free biosensing [87].

Since increased urea level in blood and urine causes various kidney diseases, the rapid estimation of urea is very important. Thus, Srivastava *et al.* [88] reported for the first time, the development of a TiO<sub>2</sub>–ZrO<sub>2</sub> nanocomposite incorporated mediator free microfluidics sensor for urea detection. This research group observed that addition of zirconia to titania can prevent phase transformation from anatase to rutile, leading to enhanced catalytic, photocatalytic and electrochemical properties due to changes in electronic band structure.

#### 3.5.2. Artificial muscles

One of the key technologies to accelerate the development of *artificial-intelligence-embedded systems*, robotics, and automation, is represented by artificial muscles which are smart materials with **shape memory**. Potential intelligent materials for developing artificial muscles are shape-memory ceramics (SMCs) since they are chemically inert (and then, have oxidation resistance) and are highly refractory (and hence are more suitable for applications at elevated temperatures). SMCs can exhibit a shape-memory effect by virtue of a reversible thermoelastic martensitic transformation from a high-temperature tetragonal phase (referred to as austenite) into a low-temperature monoclinic phase (referred to as martensite) [29].

Signatures of the shape-memory effect were first reported in 1986 [89] for magnesia (Mg-TZP) and in 1988 [90] for ceria-stabilized (Ce-TZP) zirconia bulk ceramics.

Du *et al.* reported for the first time, the use of shape-memory ceramics (SMCs) based on zirconia (8CeO<sub>2</sub>–0.5Y<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub>) coiled nanofibers, in artificial muscle applications at extreme temperatures [29]. These SMC yarns/springs exhibited an output stress of 14.5–22.6 MPa, a tensile strength of ~100–200 MPa, and a work density of ~15–20 kJ/m<sup>3</sup>, values that are much higher than those of human muscles and some other smart polymers with shape memory effect.

#### 3.5.3. Orthopedic replacements

Worldwide a growing number of people (especially geriatric group) suffer at the level of skeletal system of degenerative bone disease etiology or due to accidents with deeply debilitating consequences. In the rehabilitation procedures, the use of metallic

replacements (such as Co-Cr alloys, Ti, Ta, and their alloys) for a prolonged period of time, can be a significant problem, because of inflammatory response and bone resorption [91].

The year 1969 marked with Helmer and Driskell, the first scientific study related to the exceptional biomedical properties of zirconia [92], but in fact the introduction of  $ZrO_2$  in biomedical field occurred 20 years later, by manufacturing the first ball heads for Total Hip Replacements (THR), which is actually the current main bio-medical application of this ceramic biomaterial [93].

The beginnings of zirconia as ball heads material started with testing of various solid solutions such as  $ZrO_2$ -MgO,  $ZrO_2$ -CaO,  $ZrO_2$ - $Y_2O_3$ , but which were replaced after years of research efforts with structures such as zirconia – yttria ceramics, characterized by fine grained microstructures and known as Tetragonal Zirconia Polycrystals (TZP) [1]. Since 1995, the ISO 13356 standard [94] described the minimum requirements of TZP ceramics as implants for surgery, and until near the year 2000, more than 300 000 TZP ball heads were reported that had been implanted and only two failed [1].

In the same period, during the 2000s, the weak wear resistance and the concerning amount of metal ions present in the serum and their potential toxic effects both locally and systemically of metal hip implants (such as Co-Cr

alloy) came to light, so that the replacements were almost completely stopped for a long time, explaining the growing success of TZP [95]. Today, due to its excellent physical properties, biocompatibility, and superior aesthetics, the area of applicability in the orthopedic field of Y-TZP has expanded, including the manufacture of hip and knee prostheses, temporary supports and tibial plates [12].

### 3.5.4. Dentistry

Since the end of the 1990s, the form of partially stabilized zirconia (PSZ) has generated enormous interest in the modern dental community, primarily due to favorable chromatics (white opaque color, similar to the color of natural teeth, the ability to transmit light), and last but not least due to its excellent physical (transformation toughening of PSZ), chemical, mechanical properties (high flexural strain and fracture toughness) [25], and biocompatibility. In the following sections were selected for a more detailed presentation, two of the specialties from dentistry, which currently have passed to the most currently use of zirconia crystals, the historical retrospective of the first clinical applications of zirconia in oral medicine being presented in Table 1.

Table 1. First scientific reports of the main zirconia applications in dentistry

Dental field	Type of restoration	Year	References
Endodontics	Root canal posts	1995	Meyenberg <i>et al.</i> <sup>96</sup>
Orthodontics	Orthodontic brackets	1990	Tsukuma <i>et al.</i> <sup>97</sup>
Prosthodontics	Inlays	2012	Monaco <i>et al.</i> <sup>98</sup>
	Onlays	2013	Ma <i>et al.</i> <sup>99</sup>
	Veneers	2012	Alghazzawi <i>et al.</i> <sup>100</sup>
	Single crowns	2007	Çehreli <i>et al.</i> <sup>101</sup>
	Fixed dental prostheses (FDS)	2001	Pospiech <i>et al.</i> <sup>102</sup>
	Implant-supported crowns (ISC)	2004	Kohal <i>et al.</i> <sup>103</sup>
	Removable telescopic crown-retained dentures	2007	Zafiroopoulos <i>et al.</i> <sup>104</sup>
Implantology	Removable complete dentures	2011	Bühler <i>et al.</i> <sup>105</sup>
	Coating of Ti-Implants	1975	Cranin <i>et al.</i> <sup>106</sup>
	Abutments	2000	Glauser <i>et al.</i> <sup>107</sup>
	Implants	2004	Kohal <i>et al.</i> <sup>103</sup>
	Implant drills	2005	Hartmann <i>et al.</i> <sup>108</sup>

#### 3.5.4.1. Prosthodontics

Currently in prosthodontics, zirconia is widely used as an oral biomaterial due to its good biocompatibility, low cytotoxicity, good chemical stability, high mechanical strength, superior fatigue resistance, high toughness, and a Young's modulus similar to that of stainless steel alloy that is why zirconia is named as "ceramic steel". In dentistry, zirconia is used as tetragonal  $ZrO_2$  polycrystal modified with yttria ( $Y_2O_3$ ), in order to improve the physical properties of zirconia and to stabilize its structure at elevated temperatures [30]. In order to avoid the

formation of ceramic cracks during martensitic transformations (tetragonal-to-monoclinic phase and *vice versa*) upon heating/cooling processes, different amounts of stabilizers must be added: yttria ( $Y_2O_3$ ), magnesia (MgO), alumina ( $Al_2O_3$ ), ceria ( $CeO_2$ ), and calcium oxide (CaO) [30].

Prosthetic rehabilitations in the dental field refer to those treatments aimed to treat different forms of edentulousness, in order to restore the functionality of the dento-maxillary apparatus (chewing, speech, swallowing), as well as for the optimal restoration of the facial aesthetic aspect. The growing interest in aesthetic restorations in recent decades, as a result of concerns about toxic and

allergic reactions to certain alloys, natural look demand, social pressure and the development of new manufacturing using computer-aided design/manufacturing (CAD/CAM) technologies, has led to introduction of metal-free restorations, such as all-ceramic systems [17].

Regarding the advanced digital methods used nowadays to three dimensional design of Y-TZP prosthodontic frameworks, by using CAD/CAM technology, with numerical control that performs a preset production of the zirconia fixed restorations, after an optical impression of the prepared teeth [109].

The technological process is based on the extraction by milling from a solid block (most commonly made from zirconia ceramic partially sintered with 2%÷3% mol yttria) of the desired restoration, this method being the most subtractive method used, considering the hardness of zirconia [110].

Thus, the spectrum of contemporary prosthetic restoration of monolithic (integral) zirconia is an extremely tender one, starting from the fabrication of the oxide masses of dental veneers, full and partial coverage crowns or fixed partial dentures (FPDs) (Figure 5), primary double crowns, as well as an opaque framework (skeleton opaque).



Fig.5. Monolithic zirconia (Ceramil Zolid FX Multilayer Amann Girrbach) FPD (color online)

An infrastructure of zirconia provides, by its high resistance, a reinforcement to ceramic plates (such as alumina or lithium disilicate), the latter having much higher proportions of glass phase than zirconia, so a higher translucency and aesthetic features closer to natural teeth, but a much lower mechanical strength [111].

This explains why zirconia-based fixed dental prostheses (well known as *dental bridges*) have a wider application than other ceramics, because they can be used in the posterior regions of the arch, respectively in the molar area, the resistance to masticatory pressures being superior [25], including the implant supported bridges.

Although some manufacturers claim the possibility of complete restoration of an arch on integral zirconia structure, the zirconia-based fixed dental prostheses with more than 5 dental units are reported to be doomed to complications (framework fracture, loss of retention, abutment tooth extraction, endodontic problems and gingival bleeding) [112-113].

### 3.5.4.2. Implantology

Professor Per-Ingvar Branemark (University of Göteborg) was the first who discovered the osseointegration concept (in 1908) when titanium blocks placed into the femur of a rabbit got ankylosed with the surrounding bone and could not be retrieved. Since then, numerous research studies have established titanium as a valuable biomaterial for oral reconstruction and rehabilitation [114], due to its mechanical properties and biocompatibility.

The year 1960 marked the introduction of oral implants by Brånemark, as a decisive treatment option for the replacement of missing teeth. The current titanium and titanium alloys are most widely used in implantology due to their excellent biocompatibility, favorable mechanical properties, and long term follow-up in clinical trials. Although titanium is a notorious material, in certain clinical conditions it may present certain inconveniences, such as the increasing occurrence of allergies, stock of titanium particles in regional lymph nodes and organs, particularly the lungs and bones [115], unaesthetic dyschromias of frontal implant-prosthetic restorations (the dark grayish color of the upper incisors, which is often visible through the peri-implant mucosa), oral galvanism that occurs in contact with saliva and fluoride, inflammatory and immune response and bone resorption [9]. Due to these disadvantages, along with an increasing requirement for metal - free reconstructions, innovative implant technologies that produce ceramic implants are being developed. Thus, zirconia ceramics were first introduced over 30 years ago in the field of oral implantology, but the initial use was limited to the coating of metal-based endosseous implants in order to improve osseointegration [34], along with various other forms of ceramic coatings, including bioactive ceramics (hydroxyapatite, bioactive glasses) and inert ceramics (aluminum oxide) [21].

Aesthetics aspects, the biocompatibility, osseointegration, and superior soft-tissue response of zirconia implants make them promising materials as an alternative to titanium implants [114].

The merit for introducing the first completely metal free implants (ceramic implants) in 1960 belongs to Sami Sandhaus - renowned professor of Romanian origin, a pioneer and legend of implantology [116]. He revolutionized the world of implantology by creating the CBS (Crystalline B one Screw) implant made of aluminum oxide monocrystal. Although these implants demonstrated a good rate of osteointegration, their biomechanical properties were discouraging, especially the fracture toughness and flexural strength were unsatisfactory, which is why they were withdrawn from the market in the early 1990s. During this time the first zirconia dental implant system (1987) had already been developed by the same clinician (The Sigma implant Incermed, Lausanne, Switzerland), followed by almost two decades of *in vitro* and *in vivo* experimental research on animals. The first implant-abutments made of densely sintered zirconia ceramics with improved properties were applied clinically

around 2000s [107], followed by a first clinical case report of a two-piece zirconia dental implant only in 2004 [103].

Currently, the one-component dental implant made of tetragonal polycrystal zirconia stabilized with 3 mol% yttria (Y-TZP) is the most utilized form due to its high flexural strength (reported to range from 900 to 1200 MPa), favorable wear, corrosion and fracture resistance [117], but also of the chromatic characteristics favorable from the aesthetic point of view (whitish-opaque colour), and the reduced microbial colonization. However, compared to titanium, the zirconia implant also has disadvantages that cannot be neglected, ranging from short-term clinical trials, to significant sensitivity, surface defects that make them brittle, the aging phenomena in the presence of wet environments [117-118], and perhaps not least to the uncertainties regarding their osseointegration [9], [21].

Although zirconia may be used as an implant material by itself, as discussed above, zirconia particles are also used integrally to fabricate bone cutters and implant drills [119], or partially, as a coating material of titanium implants or implant drills, in order to minimize the temperature effects on the surrounding bone tissue and the material advantage that they wear slowly, allowing them to be used repeatedly. Regarding the phenomenon of tissue overheating and degradation of disinfection agents on zirconia vs conventional steel drills, recent thermographic studies demonstrate the resistance of the first category to the corrosive action of disinfecting chemicals and the temperature produced during drilling [120], non-destructive examination method by thermography in infrared proving its unquestionable reliability in many other fields of dentistry [121-124].

Moreover, zirconia is biocompatible, nontoxic and also it is chemically inert, and remains stable even implanted in the human body [30], without any adverse reactions.

#### 4. Conclusions and perspectives

This review presented for the first time, a state-of-the-art of wide ranging applications of zirconia-based materials, from optoelectronics to prosthodontics.

However, finding new unusual applications of zirconia still remains a challenge.

In the actual pandemic context, another open topic could be the use of zirconia-based materials in designing new performant methods for rapid detection of Covid-19.

In the fight against viruses and other pathogens, the zirconia-based nanomaterials with strong antimicrobial activity represents an open issue and researchers' efforts could be targeted in this way.

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