REVIEW OF THE SYNTHESIS, CHARACTERIZATION AND APPLICATION OF ZIRCONIA MIXED METAL OXIDE NANOPARTICLES

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Abstract

There has been different synthetic route used for the synthesis of zirconia mixed metal oxide nanoparticles. The different synthetic methods coupled with other factors like concentration, PH, type of precursor used etc help to synthesize zirconia mixed metal oxide nanoparticles having different physicochemical properties. This paper discusses the different synthetic routes of sol-gel, hydrothermal and coprecipitation method for the formation of zirconia in combination with other metal oxide to form zirconia mixed metal oxide nanoparticles, the physicochemical properties of the synthesized zirconia mixed metal oxide nanoparticle, their characterization and application.

Keywords: Zirconia; Sol-Gel; Co-Precipitation; Hydrothermal; Mixed Metal Oxide.


1. Introduction

Mixed metal oxide nanoparticles which are also referred to as heterometal mixed oxide nanoparticles are obtained by the combination of two or more metal oxides to give synthesized products with improved properties. The different metals having different oxidation states can combine in different ratios to give mixed metal oxide nanoparticles. The synthesized mixed metal oxide nanoparticles vary in physical, chemical, and morphological properties and are being used in various fields as they have various applications (1).

Since the discovery of nanomaterials, which is the science that deals with particles with diameter size less or equal to 100 nm and the small size of the nanoparticles responsible for some of its unique properties (2). It has open up a great deal of research studies that have cut across different fields; chemistry, physics, medicine etc. Nanoparticles exhibition of high surface energy, large
surface area to volume ratio and their relatively small size relative to the bulk material \(^3\) has enable it to show unique catalytic \(^4\), thermal \(^5\), optical \(^6\), electrical properties \(^7\) and biological application \(^8\) that are being utilized across various fields.

Zirconia nanoparticles have been used for various syntheses because of its high strength, high fracture toughness and hardness. Pure zirconia can exist in three forms depending on the temperature- monoclinic, tetragonal and cubic. The monoclinic form exhibit thermodynamic stability at room temperature but at temperature above 1170 °C it transforms to the tetragonal form and cubic form at 2370 °C. Different synthetic method have been used to synthesize zirconia nanoparticles which include- hydrothermal process \(^9\), biological synthesis \(^10\), co-precipitation \(^11\), solid state reaction \(^12\), microwave synthesis \(^13\) and sol-gel method \(^14\). However, most of these nanoparticles are poorly crystalline or exhibit broad particle size distribution due to agglomeration \(^15, 16\). To Address the problem of agglomeration that is seen in the synthesis of single metal oxide nanoparticles \(^15, 16\) and to stabilize the high temperature polymorphs (tetragonal and cubic) to enhance their application in various fields, zirconia has been combined with other different metal oxides to form zirconia mixed metal oxide nanoparticles \(^17, 18\).

In this review, we discussed the different synthetic route that have been used for the preparation of zirconia mixed metal oxide nanoparticles which include sol-gel, hydrothermal, co-precipitation, chemical polymerization, stir casting technique, thermal casting and biological synthesis. In addition, the different characterization techniques that have been utilized and the various applications of the synthesized zirconia mixed metal oxide nanoparticles will be reviewed. Lastly, some future considerations and advances in this research path will be highlighted.

**Synthesis of Zirconia Mixed Metal Oxide Nanoparticles**

There are different synthetic routes that have been used to synthesize metal oxide and mixed metal oxide nanoparticles. Each of these synthetic routes has been grouped under different technical approach. The different technical approach could be in accordance with the form of growth media: vapor phase growth, liquid phase growth, solid phase formation and hybrid growth, form of the products: nanoparticles by means of colloidal processing, nanorods and nanowires by template-based electroplating, thin films by molecular beam epitaxy and nanostructured bulk materials and also in accordance with the fabrication and processing technique among which is the physical or top down and chemical or bottom up approaches.

The top-down approach involves reducing a bulk material to nanoscale dimension through physical methods while the bottom up approach is the formation of a structure from putting together the unit building blocks \(^19\). In the next part of this review, we briefly discuss some representative chemical methods that have been developed to synthesize zirconia in combination with other metal oxide to form zirconia mixed metal oxide nanoparticles.

**Sol-Gel Method**

Sol-gel method involves the hydrolysis of metal-organic compound precursor to produce oxo-hydroxide compound followed by condensation and polymerization to form a network of the metal hydroxide and a porous gel respectively with subsequent drying and heating of the gel leading to the formation of nanoparticles \(^20\). This method has been used to synthesize various zirconia mixed metal oxide nanoparticles, as seen in;
The synthesis and characterization of alumina-zirconia powders obtained by sol-gel method: Effect of solvent and water addition rate. After the experiment, it was reported that different solvent results in different textural properties and different water addition rate results in different structural properties of the synthesized material (21). In 2017, the sol-gel synthesis and characterization of zirconia containing hydrophobic silica nanoparticles was investigated by Tayseir, M, et al. From the characterization techniques, it was revealed that the structural and textural properties were different for pure silica and silica zirconia depending on the zirconium percentage. The characteristic result showed the influence of the zirconia content on the texture, structure and morphology of the synthesized silica (22). Bashir et al. synthesize ZrO2-ZnO nanoparticles using sol-gel synthetic route and reported that ZrO2-ZnO nanoparticles of smaller sizes were obtained only after doping zirconia with zinc oxide (18). Rossignol et al. prepared ZrO2-CeO2 materials by using sol-gel and co precipitation methods. It was reported that both the structure and the texture of the solids obtained depend on the synthetic route and the precursor used (23). The catalytic activity of CeO2-ZrO2 mixed oxide catalysts prepared via sol-gel technique using urea as hydrolysis catalyst and tested for CO oxidation was studied. It was reported that highly uniform nanosize solid solution particles of ceria-zirconia were attained under the conditions of the study. Stabilization of the surface area of the catalysts was achieved by the addition of zirconium. The CO oxidation activity of the mixed oxides was found to be dependent on Ce/Zr ratio which relates to the degree of reducibility. The catalytic activity of CO oxidation decreases with a decrease in Ce/Zr ratio (24). In another study, Abd El Hakam et al. carried out the structural, photo-catalytic and antibacterial activity of ZnO and ZrO2 doped ZnO nanoparticles and reported that undoped ZnO is photo-catalytically more active than ZrO2 doped ZnO with ZrO2 doped ZnO showing improved antimicrobial activity (25). Other syntheses by sol-gel method include; ZrO2-CrO2 (26), ZrO2-TiO2 (27) and ZrO2-GO (28).

Coprecipitation

Coprecipitation method involves precipitating the oxo-hydroxide form from a solution of a salt precursor (example chlorides and nitrates metal salts) in a solvent (e.g. H2O or NaOH) by using a precipitating medium. There is a nucleation process that is followed by growth phase when the critical concentration of the specie in the solution has been reached. Coprecipitation has been used to synthesize ZrO2 mixed metal oxide nanoparticles as follows;

Arsent’ev et al. synthesize ZrO2-CeO2 nanoparticles using coprecipitation method (29) and Rossignol et al prepared ZrO2-CeO2 materials by using sol-gel and coprecipitation methods. It was reported that both the structure and the texture of the solids obtained depend on the synthetic route and the precursor used (23). Kumar et al investigated the preparation, characterization and antibacterial application of MgO-ZrO2 mixed oxide nanoparticles. After the experiment, the antibacterial study was reported to show that the mixed nanoparticles can be used to treat infectious diseases caused by E.coli (30) while M Liu et al. carried out the investigation of (CeO2) x (Sc2O3) (0.11-x) (ZrO2)0.89 (x=0.01-0.1) electrolyte materials for intermediate temperature solid oxide fuel cell (31) and Maridurai et al. reported the synthesis and characterization of yttrium stabilized zirconia nanoparticles (32). Glushkova et al investigated the nanostructure evolution in partially stabilized Zirconia- based solid solutions prepared by coprecipitation and to assess the efficiency of freeze drying in preventing agglomeration of the powders (33).
Hydrothermal Method

Hydrothermal method is one of the examples of solvothermal synthetic route which is employed to prepare a variety of nanomaterials by dispersing the starting material in a suitable solvent and subjecting it to moderately high temperature and pressure conditions which lead to the formation of nanoparticles. When water is used as the solvent of the reaction, the method is called hydrothermal synthesis. Chemical parameters such as the type, composition and concentration of the reactants, ratio of solvent or reducing agent and thermodynamic parameters such as the temperature, pressure and reaction time play a unique part in the formation of the nanoparticle. Machmudah et al prepared ceria-zirconia mixed oxide by hydrothermal synthesis and reported that the size of the particles formed depends on the temperature\(^{(34)}\). J. R. Kim et al investigated Ceria-Zirconia mixed oxide prepared by continuous hydrothermal synthesis in supercritical water as catalyst. It was reported that the supercritical synthesis could lead to Ceria-Zirconia mixed oxides with higher thermal stability and better oxygen storage capacity as a result of its sparsely-agglomerated morphology with potential application as a catalyst \(^{(35)}\). Pitecescu et. al reported the formation of stable cubic phase because of the solubilization-reprecipitation process with the crystallinity of the synthesized nanoparticles increasing with time and temperature of the hydrothermal treatment \(^{(36)}\). X. Wang et al investigated the photocatalytic activity in visible light region ZrO\(_2\)-CeO\(_2\) synthesized by the calcinations of the precursor prepared through a one-step hydrothermal method. From the findings, it was reported that ZrO\(_2\)/CeO\(_2\) nanocomposite showed enhanced photocatalytic activity when compared to the monocomponent of ZrO\(_2\) and CeO\(_2\) \(^{(37)}\).

In addition to the above, there are other synthetic routes that have been used to synthesize zirconia in combination with other compounds or elements for various other applications. Patoliya et al. investigated the preparation and characterization of zirconium dioxide reinforced aluminium metal matrix composites by stir casting technique and reported that the mechanical properties like hardness, tensile strength and impact strength were improved with the increase in weight fraction of zirconium dioxide particles in the aluminium matrix \(^{(38)}\). A. Sultan et al. investigated the synthesis, characterization and electrical properties of poly pyrrole/zirconia nanocomposites using chemical polymerization method and its application as ethane gas sensor \(^{(39)}\). H. Tu et al. studied the synthesis and characterization of Scandia-Ceria stabilized Zirconia powders prepared by polymeric precursor method for integration into anode-supported solid oxide fuel cells \(^{(40)}\) while Mudila et al. worked on the electrochemical performance of zirconia/graphene oxide nanocomposites cathode designed for high power density super capacitor and reported that the nanocomposites show comparable level of charge-discharge behavior with long-term cycleability, suggesting that fabricated ZrO\(_2\)/GO nanocomposites electrodes are promising candidate for the high performance energy storage devices \(^{(41)}\). David et al. investigated the synthesis and characterization of Co\(_3\)O\(_4\)-ZnO-ZrO\(_2\) ternary nanoparticles and reported that as the concentration of the precursors increases, the size of the nanoparticles also increases to an extent due to agglomeration of the small metal oxide nanoparticle \(^{(42)}\). Tsai et al investigated the reactive oxygen species scavenging properties of ZrO\(_2\)-CeO\(_2\) solid solutions nanoparticles and reported that the ceria-zirconia nanoparticles are highly crystalline in nature and can be well dispersed in sodium citrate buffer at pH 7.4 and that the reactive oxygen species scavenging activity of CeO\(_2\) nanoparticles was promoted fourfold by incorporating zirconium into its crystal structure. The scavenging activity of these nanoparticles correlates with the amount of oxygen vacancies in the lattice \(^{(43)}\).
Characterization of ZrO$_2$ Mixed Metal Oxide Nanoparticles

Different techniques were used to characterize the size, crystal structure and the morphology of the synthesized zirconia mixed metal oxide nanoparticles such as: transmission electron microscopy (TEM), X-ray diffraction (XRD) and scanning electron microscopy (SEM). ZrO$_2$-CeO$_2$ nanoparticles has been synthesized and characterized by different researchers using different synthetic methods. Hou, et al. synthesizes zirconia-ceria by chemical precipitation to obtain irregular spheroids uniformly coated by cubic fluorite of CeO$_2$ nanoparticles from the result obtained from the SEM analysis. The size of the mixed composites increased by about 5nm than that of pure ZrO$_2$ nanoparticles from the result of the TEM analysis. Thereby, confirming that the CeO$_2$ shell was formed on the ZrO$_2$ surface with the PH value playing a significant role in coating tetragonal phase ZrO$_2$ nanoparticles. Rossignol, et al. synthesized ZrO$_2$-CeO$_2$ using sol-gel and coprecipitation method and obtained cubic and orthorhombic structure for the sol-gel and coprecipitation synthetic method respectively. Several ZrO$_2$-CeO$_2$ systems with different structures may be prepared using different precursor. The structure and the texture of the nanoparticles depend on the synthetic method and the precursor used.

The micrograph of samples obtained from ZrO$_2$ and ZrO$_2$-CeO$_2$ in Figure 1 (a and b) shows circular particles with nanometric size. During decomposition, metalorganic precursor tends to transform into micrometric structures. Nanometric particles with regular round morphology were observed. Micro-elemental analysis carried out by EDX demonstrated that the all sample consists in oxide synthetized.

<table>
<thead>
<tr>
<th>Method</th>
<th>Morphology (SEM)</th>
<th>Size (TEM)</th>
<th>Crystal Structure (XRD)</th>
<th>Reference</th>
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<tbody>
<tr>
<td>Coprecipitation</td>
<td>Rough appearance</td>
<td>5-8 nm</td>
<td>Monoclinic, Tetragonal</td>
<td>Glushkova, et al., 2006 (33).</td>
</tr>
</tbody>
</table>
Machmudah, et al. synthesized CeO$_2$-ZrO$_2$ nanoparticle using hydrothermal method. Sphere shaped with smooth surface morphology and the diameter size of the nanoparticles at different temperature was obtained using particle size analyzer. Increasing temperature in hydrothermal process gave positive influence on the structural characteristics and will enhance the nucleation rate and linear growth rates of particle production (34). Arsent’ev, et al., reported 10-12 nm size diameters for ZrO$_2$-CeO$_2$ synthesized by chemical precipitation with the phase depending on the percentage composition of each of the precursor present in the reaction (29).

**Application**
The application of ZrO$_2$ mixed metal oxide nanoparticles was studied. ZrO$_2$-CeO$_2$ nanoparticles can be used as resistive sensors for the detection of the media with reduced $pO_2$ as the composite has a response time and sensitivity due to the high diffusion coefficient on oxygen which is intrinsic for CeO$_2$ based materials (29). Other applications include as an antibacterial agent (25), as a dielectric substance (26), used in dental treatment (30), fuel cell (31) and as electrochemical agent (41).

<table>
<thead>
<tr>
<th>Zro$_2$-MIXED METAL OXIDE NANOPARTICLES</th>
<th>SYNTHETIC METHOD</th>
<th>APPLICATION</th>
<th>INFEERENCE</th>
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</thead>
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<tr>
<td>Zro$_2$/Zno</td>
<td>Sol-Gel</td>
<td>Optical Uses</td>
<td>Bashir Et Al 2013 (18)</td>
</tr>
<tr>
<td>Al$_2$O$_3$/Zro$_2$</td>
<td>Sol-Gel</td>
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<td>Angel Et Al 2012 (21)</td>
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<tr>
<td>Zro$_2$/Ceo$_2$</td>
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</tr>
<tr>
<td>Ceo$_2$/Zro$_2$</td>
<td>Sol-Gel</td>
<td>Catalytic Uses</td>
<td>Thammachart Et Al 2001 (24)</td>
</tr>
<tr>
<td>Zro$_2$/Ceo$_2$</td>
<td>Co Precipitation</td>
<td>Thermal Application</td>
<td>Arsent’ev Et Al 2014 (29)</td>
</tr>
<tr>
<td>Mgo/Zro$_2$</td>
<td>Co Precipitation</td>
<td>Antibacterial Uses</td>
<td>Kumar Et Al 2017 (30)</td>
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<tr>
<td>Ceo$_2$/Sc$_2$O$_3$/Zro$_2$</td>
<td>Co Precipitation</td>
<td>Fuel Cells</td>
<td>M. Liu Et Al 2010 (31)</td>
</tr>
<tr>
<td>Zro$_2$/Graphene Oxide</td>
<td>Wet Chemical Method</td>
<td>Electrochemical Agent</td>
<td>Mudila Et Al 2016 (41)</td>
</tr>
</tbody>
</table>
2. Conclusion

The literatures mentioned in this review have shown how zirconia mixed metal oxide nanoparticles has been synthesized through different synthetic method. The sizes, shapes and the desired applications of the synthesized nanomaterial have been regulated and controlled by a number of factors such as: synthetic method, precursor, temperature and the type of solvent used. Different characterization techniques were used to analyze the formed nanomaterial and TEM was used in most of the literatures to determine the particle size. Although, Zirconia has been synthesized in combination with other metal oxides (25, 29–30, 41) for various applications there have been few reports on the antibacterial activity of zirconia mixed metal oxide nanoparticles therefore, more work needs to be done to investigate the combination of zirconia with other metal oxide to obtain improved antibacterial activity as zirconia nanoparticles has been reported to have some shortcoming (46) despite having antibacterial property.

Conflicts of Interest: The authors declare that there are no conflicts of interest regarding the publication of this paper.

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