Sol-gel process applications: A mini-review

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Sol-gel process is categorized as a well-known and reliable coating process. The useful characteristics of this method are composition selection, easy to coat complex mechanical parts, geometries, homogeneity of the coating layer and easiness of the process. To this end, the process has been implemented in many applications from powder industry to electronics. However, compared with coating techniques, this method suffers from slow process speed and inherent cracks in the body of solidified gel. This process is meant to provide a coating layer that acts as a protective barrier on the surface of the materials such as optic applications. However, there are many other uses such as sensing applications and powder making that might be unknown or not studied thoroughly. In this study, after a brief explanation of the process, some of the most important applications are reviewed.

1. INTRODUCTION

The process of sol-gel has been intensively investigated and used in recent years. The most important factors affecting its wide application are that the method is relatively easy rather than other coating processes and it provides a good enhancement for metallic biomaterial coating layers on the substrate [1-3]. In order to prepare the solution (sol) part, usually calcium and phosphorus, as CaP precursors, are used while followed by addition of two common solvents like distilled water and pure ethanol [4-6]. Mostly, ethanol is used to dissolve phosphorous precursors in shape of phosphorus pentoxide or triethyl phosphate while addition of a minute amount of water is the next step to increase the hydrolysis of the produced sol [7]. Similarly, for solving the calcium part which is mostly in shape of calcium nitrate, ethanol is the first option and the resulted solution is added in controlled drops to the hydrolyzed phosphorous solution [8]. Finally, with refluxing, the solution achieved in the previous step in different temperatures and the consequent solvent evaporation happens. This process repeats until a desirable viscosity of the solution achieved and in that state they call it sol-gel, as it is no longer a low viscosity solution. Chemical composition of the precursors are the significant affecting parameters on the temperature needed for apatite formation and the relevant chemical activities [9-15].

Figure 1 shows a schematic view of general sol-gel dip coating process. First, homogenous solution of CaP is prepared from precursors in an organic solvent. Afterwards, some reagents or water would be added to the solution and by some evaporation processes, the gel would be made out of the solution. In the next step, the prepared sol–gel slurry will stay through aging, drying and calcination processes to be prepared for use [16-18]. Again, it worth mentioning that due to the simplicity of the process, sol-gel process is very cheap and very capable with a high flexibility on either coating composition or sample geometry. The other advantageous factor of sol-gel is providing a very good adhesive coating layer means a strong substrate-coating bond [19]. The three steps of the mentioned dip coating process are dipping, withdrawing, and drying, as shown in Figure 8. The samples are immersed or dipped in the prepared solution and withdrawn in a constant speed. It is important to have a constant speed to maintain equal thickness spread throughout the whole surface of the substrate. Faustini, et al. [20], have proposed some models to explain the dip-coating process and the thickness distribution over sample surface in the process. In many other research reports, models and mechanisms of sol-gel coating and its properties are presented in detail [21-25].

2. STRATEGIES TO IMPROVE SOL-GEL METHOD

Since sol-gel, is an easy and cheap method with great coating properties on the substrate, its applications are being increased. Thus, one should somehow enhance the process to achieve the best results. Following are some proposed ideas in this context. The two crucial factors in sol-gel coating process are adhesion and delamination but the theoretical investigation of the process has not been provided. Besides, there is still a need to find the effect of addition of some new precursors to the base process and observe the changes in the process like corrosion resistivity, adhesion to the substrate layer, etc. In addition, sol formation parameters like PH, solvents, aging, temperature, molar ratios, kinetics of hydrolysis process, curing, crystal transition, crack formation during drying and heat treatment, etc. are sig-
significantly important to be studied to have a more thorough understanding of the process and control of the coating properties [21, 27-29].

Current sol-gel methods suffer from long preparation, aging and curing time, which cause limitations in the industrial use. Besides, there is always a possibility of phase separation during heat treatment, specifically in hybrid coating processes. As the problem stated, one should study and optimize new and old sol-gel routes, respectively. Sol-gel coating is done in different forms like dip coating, spraying and spinning. Recently, a new method of electrochemical deposition is proposed which utilizes a control over PH, colloid concentration and depositing voltage and time. Studies verified that this process is of a great ability to provide reliable coating layers. Furthermore, the coating layer done for complex geometries and with a controllable composition [21, 29-32]. To date, most of the sol-gel materials like TEOS and TMOS are proven somehow toxic and expensive to implement. One good solution to this problem could be using some environmental friendly materials such as silicates and titanates that are proven to have good coating properties made by sol-gel technique. Using some metal particles according to these new materials in the sol part of the solution will help to increase the toughness and thickness of the coating layers. Some of the good implemented metal particles for the coating layers are zing and magnesium particles which provide a very good corrosion protection for the coated substrates [21, 27, 29, 33].

3. SOL-GEL APPLICATIONS

As mentioned in the previous sections, the sol-gel process has many parameters to be controlled over the process. However, the process itself has a direct relation with its gel state, as there are many shapes could be derived from this state such as fibers, powders and thin films. On the other side, the composition of the solution and curing temperature and time are vital in achieving a high quality coating layer [21]. In the following sections, some of the current and potential applications of sol-gel coating are covered.

3.1. Thin films

Thin films are types of layers ranging in thickness from fraction of nanometers to fraction of micrometers. These films could be used as light barriers, reflectors, storage means, corrosion resistant layers, adhesion improvement layers, conduction enhancement, etc.

3.1.1. Optical coating

This process is used to modify the reflectance, absorption or transmitting quality of an optical object [34]. Many materials are used in different research reports to implement the coating from which TiO2 and SiO2 are mostly used to produce colored layers. The curing temperature of these processes are reported to be in the range of 180 to 500 [35,36]. On the other hand, in many research reports, there are applications of anti-reflection of these coating layers with the same materials inside the solution. Anti-reflective glasses and optics are used in solar applications and enhancing their energy absorption while increasing the substrate resistance against destructive waves [37-39]. Figure 2 represents a focused electron beam SEM image of the multilayered sol-gel optic coating. Table 1 represents char-

<table>
<thead>
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<td>Eraser rubbing</td>
<td>Taber abrasion</td>
<td>Pencil scratch</td>
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</table>
acteristics and properties of different sol-gel anti-reflective coating layers obtained by different groups.

3.1.2. Corrosion resistant coatings

The use of sol-gel protective coating could be performed on either metals or glasses [27, 34, 41, 44]. However, there are reports of coatings on plastics and polymeric materials [39, 46]. These coatings play the role of a barrier in order to diminish the effect of corrosive penetration to the substrate and hinder its degradation [44, 46]. Earlier, phosphate coatings were achieved on silicate glass panels in order to improve their chemical resistance against water with a thickness of 2m. This process provided cheaper glass panel with enhanced durability in harsh working environments and chemicals using small amount of protective materials [47, 48]. Materials used in solution composition are mostly SiO$_2$, ZrO$_2$, Al$_2$O$_3$, TiO$_2$ and CeO$_2$ for their good protection and stability. The materials used in metal coating with sol-gel are stainless steel, aluminum, copper and magnesium [27, 49, 50]. Table 2 provides a brief summary of different compositions of sol-gel on different substrates.

In other studies, researchers have worked on valve metals and their alloys, such as Ti [76]. They have improved the sol-gel coating layers through other methods, such as micro arc oxidation. The increasing application of these metals and specifically Ti and its alloys, lead to an increase in using sol-gel process in coating medical devices [77, 78].

Figure 2. FESEM micrographs of multilayer films: a) SnO$_2$-TiO$_2$-SiO$_2$, b) Ta$_2$O$_5$-TiO$_2$-SiO$_2$, c) ATO-TiO$_2$-SiO$_2$, d) ITO-TiO$_2$-SiO$_2$ [43].

Figure 3. Immersion test of AA7075-T6 uncoated, coated by hybrid silica GTS-D-R and by silica-Ce GTS-Ce-D-R in 0.1M NaCl at 25°C [41].
<table>
<thead>
<tr>
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<th>Substrate</th>
<th>Average thickness (mm)</th>
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<td>316 stainless steel</td>
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<td>[52]</td>
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<td>[54]</td>
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<td>Mild steel</td>
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<td>[55]</td>
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<tr>
<td>TEMOS-MAPTS</td>
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<td>SiO$_2$-Na$_2$O</td>
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<td>[65]</td>
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<td>[59]</td>
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<tr>
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<td>Al 2024-Ts</td>
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<td>[65, 66]</td>
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<td>[67]</td>
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<td>[69]</td>
</tr>
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<td>TEOS-GPTMS-PDMS</td>
<td>Al 2024-T3, Al 6061-T6</td>
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<tr>
<td>GPTMS, MAPTS</td>
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<td>SiO$_2$-MAPTS-MPTMS</td>
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<td>[74]</td>
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<td>TEOS-PHS</td>
<td>Mg AZ31B</td>
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<td>[75]</td>
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</table>
ferent metallic objects \cite{79, 80}. Figure 3 shows a comparison between different surfaces, coated and uncoated, in the duration of the corrosion experiment.

3.2. Composites

Composite sol-gel compounds are getting attention in cases that reinforced structure or matrix is needed. In the recent research reports, sol-gel composite layers such as SiC and alumina reinforced materials are of interest in applications such as turbine blades and ceramic tools \cite{81, 82}. Previously, these materials were fabricated by hot-pressing and composite layer assembly while the sol-gel process increases the easiness of the composite coating process. The sol part of the process has low viscosity and can easily penetrate to the complex geometry corners and create a reliable layer. Figure 4 represents a carbon nanotube (CNT) coated in alumina composite sol-gel process.

The only problem rising in making a dense sol-gel coating is that the shrinkage caused by drying out the samples produces tiny cracks and this problem gets worse in 3D applications. However, since the sol-gel process is a low temperature process, it could be done in room temperature. This characteristic enables us to produce coating layers consisting of organic molecules, fibers and powders \cite{83, 84}. Organic molecules applications in sol-gel composition could be in optics, catalysts and sensors \cite{83, 85, 86}. These applications are important and as an example, in optics, incorporation of organic molecules dispersed in transparent silicate gels lead to sustaining a higher laser pumping without any photo bleaching in the used dye, compared to the organic polymer matrices. There are many other applications could be considered for the composite coating layers such as adding hydrophobic components in the applications that are protecting a system or device from humidity or water vapor \cite{87}. These properties creates opportunities to mix limitless organic-inorganic mixes in composite sol-gel coating layers. Figure 5 shows a coated layer of a sensing NO\textsubscript{2} device.

On the other hand, there could be many metal-ceramic compositions, which are used to achieve different goals, each. Metals such as Ti, Pd, Cu, Sn, Pt, etc. has been introduced in either their elemental shape, their oxides or their salts. Besides these metals, the mixture of them has been implemented in many applications such as optics, sensors

Figure 4. a) Optical image of dried gel and, b) SEM image of carbon nanotube/alumina composite \cite{82}.

Figure 5. SEM images of a) surface and, b) cross section of Nb,O\textsubscript{5}-SE layer on YSZ \cite{88}.

Figure 6. SEM images of a) uncoated carbon fibers (CF), b) SiO\textsubscript{2} coated CF; c) SiC/SiO\textsubscript{2} coated CF; and, d) cross-section of coated CF \cite{90}.
Figure 7. SEM images of a) coarse, b) medium, c) fine 45S5 bioactive glass powders and d) a higher magnification showing nonporous surfaces of melt-derived powders [94].

Figure 8. SEM images of a) coarse, b) medium, c) fine 58S bioactive glass powders and d) a higher magnification showing the porous nature of the sol-gel–derived powder [94].
3.3. Powders

Another application of sol-gel process could be preparing powders, grains and spheres that might be expensive or difficult to prepare while using some other hi-tech processes. Ceramic powders are used in catalysts, pigments, abrasive applications and fillers in electric or magnetic devices and mechanisms [91, 92]. Many other capabilities are available for sol-gel derived powders such as hollow spheres and grains. This process produces powders with a controlled size and shape and higher structure homogeneity while the ratio of oxidization is lower, thanks to low temperature procedure. However, the disadvantages of producing powders with sol-gel could be slow processing, cost and low amount of product in each set of process [93]. Figure 7 and Figure 8 represent a comparison of particle shape and size produced under melting and sol-gel processes.

Another application of this method is to obtain high density and controlled shape of selectively oriented sphere materials in low temperatures. This process could be useful for high-temperature semiconductor powder fabrication with the highest quality. The two different procedures implemented to achieve this goal are aerosol and emulsion techniques [95, 96]. The advantage of these processes is that the inhomogeneity of the created structure is dependent on the droplet size and the droplet size could be easily controlled with a nebulizer or a suitable surfactant [97]. However, there rises a problem that the fabricated geometries are only limited to sphere shape and could not bring any edged geometry due to natural shape of a droplet. Yet with this disadvantage, the need for semiconductors and electronic materials from purity, reproduction ability and homogeneity are completely met [98, 99].

The other application of sol-gel-derived powders is to fabricate abrasive particles. In order to overcome the spherical shape and make them in a sharp geometry, the semi-solid gel would be crushed. In addition, during the curing and drying process, the inherent cracks of the materials structure eases the formation of a sharp geometry [18, 100, 101]. Figure 9 shows an SEM image of some abrasive particles made with this method.

4. CONCLUSION

Through an extensive research on sol-gel process and its applications, it is obvious that the process is a low-temperature nature, slow procedure and a moderate cost. However, the sol-gel process offers many advantages that overweight the disadvantages of this method. These characteristics could be explained as low viscosity that helps to cover and reach to the corners and difficult to reach areas in a complex geometry. The other property of this useful process is that the composition of the deposition layer is fully under control. This means that the applications could be limitless since many organic and inorganic materials and their mixes could be used as the desired deposition layer. Besides coating purposes, this process helps us produce composite layers, fibers, spheres, grains, etc. that might not be easy or cheap to be produced via high-tech processes such as plasma spattering. On the other side, there could be limits to this process as unwanted cracks in the solidified section and slow process speed. In a comparison, as this method improves the quality of parts and devices in a wide range of optics, sensing and powder making, it continues to be a reliable and yet to discover technique.

Notes

The authors declare no competing financial interest.

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