

Active Coatings: Examples and Applications

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Abstract: Currently, electrochemical plating, conversion coatings, anodizing, deposition of thin films (organic, inorganic or hybrid), laser surface alloying, cladding and organic coatings are employed to improve surface properties such as hardness or corrosion resistance. For example, the development of new “smart” coating systems implies not only mechanical covering of the protected surface with a dense barrier coating but also provides active properties which can allow continued physical or chemical protection, even after partial mechanical damage of the coating, by self-healing effects. In other cases, the active properties imply biological effects, by releasing of chemicals from “drug delivery” systems, or photoelectric effects due to doping the surface with adequate elements. These “smart” properties can be achieved by inclusion of specific additives into the coating system and can stimulate the superficial reactions after some damage. The sol-gel coating process is one of the most promising methods to create protecting coatings producing sensitive inorganic surfaces in general. In this environmentally friendly process, inorganic or inorganic-organic hybrid polymers are obtained by controlled hydrolysis and condensation reactions of molecular precursors. This article compares examples of the recent patents of active coatings and some of their important industrial utilizations.

KEY WORDS: Surface treatments, active coatings, hybrid polymers. sol-gel processes.

1. INTRODUCTION

In recent years, design of active coatings such as “artificial cells” systems have produced materials that can facilitate the healing of damaged substrates. This may be exemplified by a sol-gel system with polymer nanocontainers used as reservoirs of active nanoparticles. After a punctual damage caused by a mechanical impact, the polymeric nanocontainers crack and release a corrosion inhibitor to fill the affected zone and induce a self healing effect over it.

Scientific research on “smart” coating systems is still in its initial stage. However, progress in this field is ultimately increasing the fabrication of a generation of adaptive materials that both monitor their structural integrity and mend themselves before any catastrophic failure can occur [1]. Thus, a quick search in the Patent's Worldwide database of the European Patent Office found 2074 results for the words “active coatings” in the title or abstract, however only 1612 patents are claims the properties of sol-gel chemical composition. Almost all of them were claimed in the XXI century, pointing to the current interest on coating systems with “smart” behaviour. Initially, works were concentrated on self-healing effect for corrosion protection, but actually other properties are being added into these active coatings systems, like biological activities or photoelectric effects, for example.

A challenge in materials science is to design active synthetic systems that can improve this behavior, by not only feeling the presence of a defect or of localized environmental changes, but also by re-establishing the integrity and continuity of the damaged area or increasing the photoelectric effect due to light irradiation alterations. Such “smart” coatings would significantly extend the lifetime and utility of a vast array of manufactured items. The coatings should undergo repair in a relatively autonomous manner, without an external intervention. Furthermore, the coatings should ideally be able to repair damage more than once, so as new cracks or fissures appears. These self-healing effects would make the coatings ideal for surgical implants, aerospace and automotive applications and allow the fabrication of structures with enhanced sustainability.

The increasing of the number of papers and patents that have appeared dealing with bulk and more sophisticated, micro- or nanostructured materials, focused on the synthetic approach or on

the specific application, in principal on hybrid organic-inorganic coatings with “smart” behaviour. Such interest arises from the several unique features of these materials, which is often related to the increasingly important role played by the interfacial forces and by the chemistry of surface molecular layers as the size of the dispersed phase decreases [2].

In general, the inventors claim the intellectual properties as the chemical composition as the production procedures of the coatings with some specific properties. The mechanical, adhesive, cohesive, electrical, optical, photochemical, catalytic and magnetic properties of these new hybrid materials are often a synergistic combination or utterly new ones with respect to those of the constituents. Thus, organic polymers with improved toughness [3], elasticity, low surface energy [4], enhanced hardness [5], hydrophilic or hydrophobic properties [6-8], durability against ultra violet light (UV) and heat resistance, availability of reactive functional groups or catalytically active host sites, can be produced by diffusion, inclusion or dispersion of an inorganic component, where the coordinative or covalent binding provide the required stabilization of incompatible phases with large interface area. Entirely new materials and applications can be attained with respect to the traditional ones, as in the case of the combination of typical molecular properties, from electrical, photochemical, magnetic, catalytic, biological activity with the adjustable mechanical ones of organic and inorganic polymers and networks [2].

Sol-gel processes are generally used to fabricate hybrid organic-inorganic materials including self-assembled films. A sol is a liquid solution containing a colloid suspension of a material of interest dissolved in an appropriate solvent. Condensation reactions between the dissolved precursor molecules result in structures forming within the sol. The size, growth rate and morphology of these structures depend on the kinetics of the reactions within the solvent, which in turn are determined by parameters such as solution concentration, amount of water present, the temperature and pH of the solvent, agitation of the solvent and other parameters. When time enough is given, condensation reactions will lead to the aggregation of growing particles or chains until eventually, a gel is formed. The gel can be visualized as a very large number of cross-linked precursor molecules forming a continuous, macroscopic-scale, solid phase, which encloses a continuous liquid phase consisting of the remaining solution. In the final steps of the sol-gel process, the enclosed solvent is removed (generally by drying) and the precursor molecules cross link (a process called aging) resulting in the desired solid [7-8].

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Sol-gel synthesis of materials offers several advantages over other synthetic routes. These advantages can include mild processing conditions (low temperature and pressure, mild pH, etc.), inexpensive raw materials and a high level of control over the resulting structure. Regarding the shape of the final product, there is essentially no limitation, because the liquid sol can be cast in any conceivable form before allowed to gel, including thin films, fibers and micro- or nanoscale particles [7-8].

Recent patents have addressed the state-of-the-art in fabricating such materials and indicated that there has been progress in creating useful systems. In this work are presented some examples of recent patents of active coatings with “smart” applications in biology, engineering and engineering fields.

2. COATINGS WITH BIOLOGICAL ACTIVITIES

Coatings with biological activities are being developed to increase the implant biocompatibility or to alter the hydrophobicity or hydrophilicity by addition of drug nanoreservoirs. In this case, drug delivery compounds are incorporated to a sol-gel system to be released during implant/tissue integration.

The inventors of the patent numbers WO07092043 [7] and US2007071789[8], claim the intellectual properties of a implantable medical devices employing a sol-gel coating composition that works as a bioactive material reservoir, and the application of sol-gel coatings composition for improved adhesion on organic and inorganic substrates.

These inventions provide methods of creating sol-gel compositions with enhanced bioactive material incorporation and methods to further control the rate of bioactive material release into the physiological environment from medical devices during clinical use. These methods provide for enhanced adhesion between inorganic/organic substrates and provide sol-gel compositions that can be used as sustained-release bioactive material reservoirs and/or as bioactive material coatings on implantable medical devices. Also, this invention allows enhanced adhesion of bioactive material by modifying the chemical environment during sol-gel processing. This modification alters the hydrophobicity or hydrophilicity of the forming material, which affects how bioactive material molecules interact with the forming material and its chemical environment during sol-gel processing.

Modification of the chemical environment during sol-gel processing can also affect the characteristics of the formed material after removal from the sol-gel environment in such a way to affect the release rate of bioactive materials into the physiological environment once implanted in a patient. Specifically, depending on the characteristics of a particular bioactive material, the chemical environment of the sol-gel process is adjusted to control how the bioactive materials will interact with the environment during the sol-gel process. As a non-limiting example, the addition of an organically modified silane to the sol-gel mixture can increase the hydrophobicity of the forming gel [7].

The sol-gel compositions of the invention patented by WO07092043 [7] can also enhance adhesion to a substrate by providing pores in the form of continuously interconnected channels that allow for strong interdigitation between inorganic substrates and organic coatings.

It includes a medical device comprising a structural element and a bioactive material reservoir, where this reservoir comprises a coating applied to the surface of the structural element. The coating formed by a sol-gel process was developed to improve characteristics of bioactive material added into the matrix composition. The rate of release of the bioactive material into the physiological environment after implantation is controlled by the tailoring of the sol-gel processing. The coating is applied on the surface of the structural element to enhance the adhesion between an inorganic and an organic surface.

Bioactive materials used in accordance with the cited invention [7] can, in one embodiment, be selected from the group consisting of an anti-restenotic agent, an anti-inflammatory agent, an HMG-CoA reductase inhibitor, an antimicrobial agent, an anti-neoplastic agent, an angiogenic agent, an anti-angiogenic agent, a thrombolytic agent, an anti-hypertensive agent, an anti-arrhythmic agent, a calcium channel blocker, a cholesterol-lowering agent, a psychoactive agent, an anti-depressive agent, an anti-seizure agent, a contraceptive, an analgesic, a bone growth factor, a bone remodeling factor, a neurotransmitter, a nucleic acid, an opiate antagonist and combinations thereof. Bioactive materials can also be selected from the group consisting of paclitaxel, rampamycin, everolimus, tacrolimus, sirolimus, des-aspartate angiotensin I, nitric oxide, apocynin, gamma-tocopheryl, pleiotrophin, estradiol, aspirin, atorvastatin, cerivastatin, fluvastatin, lovastatin, pravastatin, rosuvastatin, simvastatin.

The medical devices uses can include a vascular conduit, a stent, a plate, a screw, a spinal cage, a dental implant, a dental filling, a brace, an artificial joint, an embolic device, a ventricular assist device, an artificial heart, a heart valve, a venous filter, a staple, a clip, a suture, a prosthetic mesh, a pacemaker, a pacemaker lead, a defibrillator, a neuron-stimulator an implantable sensor, and an external sensor [7].

The patent US2006171990 [9], entitled “Drug delivery materials made by sol-gel technology”, also concerns a method to produce a drug delivery system by encapsulating a biologically or therapeutically active agent in a shell by a combination of the encapsulated agent with a sol. After deposition on implants' surface this solution is converted into a solid or semi-solid drug delivery material.

The European Patent Application EP 0680753A2 [10] describes a sol-gel derived silica material containing a biologically active substance such as a therapeutically active agent, where the release rate of the active agent is controlled by the addition of penetration enhancers such as polyethylene glycol or sorbitol, or the addition of other modifying agents which can enhance the release of the active agent by either aiding dissolution via swelling processes or by inhibiting diffusion in order to modify the permeability of the matrix. These modifying agents may be used for more precise adjustment of release rates of the active agents can include, for example, water-soluble substances such as sugars or salts of organic acids. Thus, this substance may accelerate the release rate of active agents from the matrix because of their solubility in body fluids and lead to their dissolution and increase the permeability of the sol-gel-produced matrix. Other modifying agents that increase the permeability of the matrix in the presence of body fluids may include polyanionic compounds such as salts of polystyrene, sulfonic acid, polyacrylic acids, carboxy-methyl celluloses, dextrane sulphate or cellulose sulphate, and the like. Each of these release-modifying agents accelerates the release of the active agent [10].

Thus, there is a need for biocompatible drug delivery materials which may be produced as coatings or bulk materials, especially for the production of implants or coated implants, which can reliably and reproducibly provide an adjustable controlled release of an active agent incorporated therein. The sol-gel process seems to be the most economic and biologically versatile solution to cover the implantable device. In particular, due to the possibility to use the same chemical composition of the nanocontainers for different drug compositions.

3. COATINGS FOR ENERGY APPLICATIONS

In this field of application there are patents developed to electric conductive glasses [11], sensors devices [12], hydrogen manipulations [13], radioactive proposes [14], with solar applications [15], etc.

The object of the invention presented by WO07094019 [11] is the preparation of a tungsten oxide (WO_3)-based colloidal paste that allows providing transparent films on conductive glasses in an easy and cost-effective manner. Particularly, this invention relates to a method for preparing a substrate coated with at least one thick layer of tungsten oxide, comprising at least one step of coating said substrate with a colloidal solution of tungsten oxide obtained with the sol-gel method, said colloidal solution being added with a thickener and a surfactant.

An example to other field of electrical applications was directed towards achieving coatings with high transparency in the visible region and good electrochemical properties. Elucidation of the structural and optical features of the films yielded information on the aspects relevant to their usage in transmissive electrochromic devices. In the patent US2007190361 [12], the films have been produced to exhibit properties for counter electrode in electrochromic smart windows in which they are able to retain their transparency under charge insertion, high enough for practical uses. The thin films have applications as passive counter electrodes in electrochromic devices, sensors and photocatalytic agent. The deposition of this film can be obtained by spin coating of CeTi_2O_6 solution produced by sol-gel process, which comprises both titanium and cerium precursors (cerium chloride heptahydrate and titanium propoxide), on to electrically conducting or insulating glass substrates and annealing in air. The Ce:Ti mole ratio in the deposition sol for the preparation of the film is identified in the range of 0.4:1 and 0.6:1 [12-16].

The patent WO07090072 [13] describes an apparatus and methods to provide electrochemical hydrogen manipulation. The electrochemical cell is provided utilizing an acid doped polybenzimidazole (PBI) membrane having proton conductivity. The PBI membrane can be produced by a sol-gel process.

Also, the invention is a method of operating an electrochemical cell, including at least the following steps: applying an electric potential between a first electrode and a second electrode of an electrochemical cell, wherein the first electrode has a higher electric potential with respect to zero than the second electrode, wherein the first and second electrodes have an acid doped PBI (with proton conductivity) membrane between them; and flowing a hydrogen gas across the first electrode and evolving hydrogen at the second electrode. Thus, each hydrogen molecule reacted at the first electrode produces two protons which pass through the membrane to the second electrode of the cell, where they are rejoined by two electrons to form a hydrogen molecule [13].

Under the sol-gel process, polymerization to produce PBI polymers can be carried out using polyphosphoric acid (PPA) as both the polycondensation agent and the polymerization solvent starting from tetraaminobiphenyl (TAB) and dicarboxylic acid. After polymerization, the PBI solution in PPA can be directly cast at approximately 200°C to 220°C without isolation or redissolution of the polymers. Upon casting, hydrolysis of the PPA to PA induces a sol-gel transition that produces membranes with higher ratios of PA to PBI repeating unit than currently believed possible with other PBI membrane production techniques. The main chemical composition discussed in the patent referenced above had approximately 32 moles of PA per PBI repeating unit [13].

One advantage of the electrochemical cells, systems and related methods provided under the invention is that they can generally be operated without having to humidify the gas from which hydrogen is removed. It is believed that electrochemical cells utilizing PBI membranes produced by traditional non-sol-gel processes, and other non-PBI fuel cells all require that the hydrogen source gas be humidified prior to hydrogen transfer. It is believed that utilization of sub-saturated hydrogen source gas will result in immediate and progressive performance degradation. The sol-gel PBI based systems under the invention do not exhibit such degradation.

Without wishing to be bound by theory, it is believed that the higher ratio of PA to PBI repeating unit enables this aspect of performance. Thus, in some embodiments, the apparatus and methods provided include the distinction that the hydrogen source gas is unhumidified. In this context, unhumidified means that the gas is less than saturated with water, and no step has been taken to increase the saturation level of the gas [13].

The method to treat radioactive residues presented by US2006264570 [14] patent is constituted by storing of aqueous solutions of radioactive substances. This invention relates to an improved sol-gel process as well as to the aerogel product obtainable thereby, which is characterized by a very high mechanical resistance and a high pore volume; moreover the invention also refers to a method for the transformation of nuclear material into a shape which can be easily and economically stored, such a method comprising the use of the above said improved sol-gel process: by translation, therefore, the present invention relates also to a method for treating and storing radioactive effluents comprising the use of the improved sol-gel process hereinafter disclosed.

The aerogels are among the possible products of a sol-gel process. The aerogels are now mainly used as study materials aimed to thermoacoustic insulation and catalysis, as well as to intermediate products to manufacture glasses or ceramic glasses; moreover they can be used as very low dielectric constant insulating layers in the manufacture of integrated circuits [14].

In this case, the sol-gel-process to prepare aerogels comprises the preparation of a solution of a compound having the formula $\text{X}_m\text{-M}(\text{OR})_n\text{-m}$, in which M is a cation belonging to Groups 3, 4 or 5, n is the cation valence, m is 0, 1 or 2, X is R1 or OR1, R and R1 are hydrocarbon radicals. The process is followed by the hydrolysis of the above compound to give a sol, gelation, drying, densifying and sintering [14].

To solar energy applications, the use of sol-gel coatings can be exemplified by the description patented by WO07089387 [15]. This invention may be used in applications such as one or more of solar collectors: parabolic-trough power plants, compound parabolic concentrating collectors, solar dish-engine systems, solar thermal power plants, and/or solar collectors, which rely on mirrors to reflect and direct solar radiation from the sun.

In resume, a sol-gel coating is applied on a glass surface to produce a first mirror surface. The sol-gel coating is heated to drive off the solution and forms a solid protective coating over the reflective surface. The sol-gel coating includes a silicon precursor and water, alcohol, acid or base, and/or a hydroalcoholic mixture; heat treating the sol-gel at from about 200°C to 1000°C for densifying and forming a glassy silica based protective coating over the reflective coating of the first surface mirror [15].

The patent WO07085911 [17] also claims an intellectual property about the chemical composition of a sol-gel coating to light irradiation proposes. It provides a method for synthesizing titanium (IV) oxide (titania) nanoparticles comprising synthesizing a titania inorganic crystalline matrix within a sol-gel reaction process under conditions that constrain the growth of the matrix such that a majority of the nanoparticles are of a narrow size distribution in the composition and do not exceed a maximum diameter of around 100 nm. In this sol-gel reaction, the process can occur under aqueous conditions, or within an organic polymer matrix under non-aqueous conditions. Aqueous dispersions and pastes comprising the substantially size-homogeneous composition of titanium (IV) oxide nanoparticles are also provided. The titanium (IV) oxide nanoparticles demonstrate improved photoactivity when exposed to UV irradiation, and can also include visible light absorbing centers such that activity is extended into the visible light range.

The sol-gel coatings can carry different kind of photoactive elements to increase the electronic reactions on glass surface and

due to this possibility can induce different physical reactions by light irradiation effects.

4. ABRASIVE APPLICATIONS

In case of abrasive applications, the objective is produce coatings with hard and ultra-hard particles, like mentioned by the patent WO07088461 [18]. Thus ultra-hard abrasive particles are provided with glass coats under sol-gel conditions and heat treatment. The glass coats may be porous or fully dense, types and compositions may be chosen and tailored to have thermal expansion, thermal shock, color and chemical properties to suit specific applications. The glass is bonded via chemical bonds to the hard or ultra-hard particle surface atoms and the glass composition and structure, and resultant properties of such glass, are chosen to match and be compatible with both the bulk hard or ultra-hard particle properties and eventual bond matrices into which a plurality of the coated particles are to be incorporated.

The patent number US2007089642 [19] is related to a durable hard coating production method. The sol-gel solution basically comprise nanosized silicon nitride particles and a binder. The invention further relates to shaped bodies composed of a substrate with a durable hard coating which has been produced from a slip according to the invention.

The nanosize solid particles are preferably metal oxide particles or systems which are converted into nanosize particles after hardening by high-temperature treatment. In particular, the nanosize solid particles are selected from among SiO₂, TiO₂, ZrO₂, Al₂O₃, AlOOH, Y₂O₃, CeO₂, SnO₂, iron oxides and Ta₂O₅ or among precursors of these solid particles which are converted by means of the sol-gel process into these solid particles, with SiO₂ particles and/or precursors of SiO₂ particles which are converted by means of the sol-gel process into nanosize SiO₂ particles being particularly preferred.

The nanocomposites which are preferred according to the invention and their production by the sol-gel process are known in the prior art, in particular from DE10326815A1 [20]. In this case, it is preferred that the nanosize solid particles are surface-modified with a surface-modifier having a molecular weight of less than 1500, in particular a surface modifier containing an anhydride group, acid amide group, amino group, SiOH group, hydrolyzed radicals of silanes and/or a β-dicarbonyl group.

In particular, the coatings of this invention [19] are produced from alcoholic SiO₂-forming sols in which high-purity silicon nitride powders are dispersed. Since silicon nitride tends to undergo hydrolysis in the presence of water, water-based formulations should not be used; instead alcoholic SiO₂-forming sols are preferred. Furthermore, the use of high-purity starting chemicals (silicon nitride powder, silanes, alcohols, etc.) is preferred since very high-purity layers which, in particular, meet the requirements of the solar industry are obtained in this way.

In the case of abrasive applications of sol-gel coatings, the objective is produce coatings with hard and ultra-hard particles which also contain chemical elements with high oxidation temperature. This factor can increase the life-time of the mechanical devices with this kind of cover.

5. CURRENT & FUTURE DEVELOPMENTS

This paper provides a review of some recent patents of synthesis, biological, mechanical and physical properties of sol-gel active coatings.

These active coatings show great promise for use devices in biological, energy, and structural applications, in which enhanced mechanical and physical properties are required. Substantial progress has been made in the development, processing and micro-structural aspects of nanoparticles and nanocrystalline materials over the recent years. Also, the sol-gel processing routes can be an easy way to synthesize nanoparticles, mainly because of the low temperature used. The versatility of the chemical composition combinations and the great range of applications are rendering the sol-gel processing popular in industrial devices.

The stability of nanocrystalline structure for the cited applications should also be one of the main challenges faced by the inventors, since no references to this aspect are commonly addressed in the related literature. Therefore, materials scientists have an important role to play in designing, developing and modeling of new nanomaterials and their functional structures with lasting superior properties for advanced engineering applications.

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