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Multifunctional bioinspired sol-gel coatings for architectural glasses

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ABSTRACT

Although several multinational companies have recently released products incorporating bioinspired functional coatings, their practical integration in building envelopes is still an open issue. High production costs associated to the existing vacuum deposition technologies, as well as the difficulties in extending the number of functions achievable by a single coating, represent to date the main limitations to their diffusion on a large scale. This review summarizes the key topics in the field of functional coatings for architectural glasses, focusing in particular on the potential applications of sol-gel based antireflective and self-cleaning coatings, that have received a tremendous attention in the last years. It provides an overview of the recent research efforts aimed to improve their properties and to extend their range of applicability. The bioinspired principles, upon which such coatings are based, are also described and are related to the chemical and morphological properties of such surfaces.

1. Introduction. The modern architecture of transparency: issues of glazed surfaces

Since the advent of the industrial revolution, the role of buildings' external envelope has greatly changed. Massive envelopes, especially used in Mediterranean areas for bearing loads and for protecting against the surrounding environment, have been progressively substituted by light envelopes, built with modern materials, such as steel and glass. Starting from continental areas – northern Europe and North America – the use of light building envelopes has progressively spread over every climatic area, leaving a relevant number of issues unsolved. Thermal transmittance, visual transmittance and solar factor are only a few parameters that should be carefully examined during the design phase. Furthermore, the energetic issues, stated by the 2002/91/CE EU Directive [1], require new findings for large-scale sustainable solutions aiming to deposit thin films on architectural glasses. With reference to buildings designed for temperate and hot climates, while the thermal transmittance should be as low as to prevent thermal losses during winter and unwanted heat gains during summer, visual transmittance should be high enough to assure indoor visual comfort, at the same time [2]. Besides, solar factor of transparent external surfaces should dynamically change, as a function of the needing of solar direct gains [37].

With regards to thermal transmittance, it is evident that *U*-values of transparent envelopes are sensibly higher than those used in opaque façades. This is not only the effect of the presence of materials – such as glass – showing a high thermal conductance, but also to the thinness of transparent enclosures, indispensible for static requirements. The adoption of double and triple glasses, or modern double-skin façades, could reduce the heat transmission, aiming to minimize direct conduction through solid materials. Besides, even in these conditions, the total *U*-value of transparent envelopes could be higher than standard limits of late building regulations. The reduction of total envelope transmittance could be achieved only trying to minimize radiation losses, reducing thermal emissivity of transparent panels.

Even though it was considered a "magical material" by F. L. Wright, who wrote: "In the openings of my buildings, the glass plays the effect the jewel plays in the category of materials" [3], all of these requirements could not be contemporarily satisfied by glass sic and simpliciter.

As a matter of fact, as modern opaque façades require the adoption of multi-layer technologies, modern transparent envelopes, too, need multi-layer structures to satisfy specific requirements.

Glass coatings have been studied and currently employed since the second half of the XXth century [4]. Coatings can modify the

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surface properties of glass, aiming to optimize visual transmittance (antireflective coatings), thermal transmittance (low-E coatings), solar factor (solar control filters) and glass maintenance (self-cleaning coatings).

Nowadays, the impact of glass coatings in building industry is really relevant; in 2000 almost the 70% of the glass globally produced had various kinds of coatings (antireflective, low-E, solar control or, simply, decorative coating). This data should be, too, interfaced with the amount of world glass production, consisting in almost 10^9 m^2/y [37].

The use of highly performing glass in building envelopes can have a great influence on the control of comfort parameters in indoor spaces. It can act as an active filter in order to optimize the interactions between outdoor conditions (temperature, illumination) and indoor conditions in a sustainable viewpoint. The building envelope is often referred to as the "third skin" [6], i.e. it is expected to play an active role, just like a membrane between the external mutating environment and the built environment, in opposition to the traditional idea of massive walls. Without losing its peculiarities (transparency, lightness, thinness, re-cyclability) its properties can be tailored effectively using the recent discoveries in the fields of nanotechnology and biomimetics.

2. Innovative glass coatings: biomimetics and nanostructured materials

Biomimetics represents the effort of abstracting good design from the observation of nature. Programmed assembly and self-assembly are frequent in nature at any scale. The ancient Great Wall of China, the Pyramids of Egypt, the schools of fish, herds of wild animals on land, protein folding and oil droplets on water are all such examples. Programmed assembly describes predetermined planned structures. On the other hand, self-assembly is the effect of the spontaneous association of numerous individual entities into a coherent organization and well-defined structures to maximize the benefit of the individual without external instruction. The Great Wall was program-assembled over 2200 years ago, with a defined plan, and it is an ordered structure. Approximately 3 billion bricks have been used to build it: a number that reminds the DNA bases in the human genome [7].

For instance, an effective antireflective natural surface is the moth-eye. Its corneal lenses are covered with a very regular pattern of conical nanoscale protrusions, having a period of about 200 nm, minor than the wavelength of visible light (Fig. 1). Light reflection is reduced almost to zero, thus optimizing the small amount of light available by night. This fact can be explained in terms of a surface layer on which the refractive index varies gradually from the value of air to that of the bulk material. If there is a gradual change of index, net reflectance can be regarded as the result of an infinite series of reflections at each incremental change in index. Each reflection has a different phase. If a transition takes place over an optical distance of (λ)/2, all phases are present, there is a destructive interference and reflectance falls to zero. That means, in order to obtain a suitable antireflection effect in the visible range that the dimension of the single structure itself must be in the range of a quarter of a micrometer.

Antireflective coatings on glasses have attracted a great interest as it is among the few solids which transmit light in the visible region of the spectrum (300–800 nm) because of its amorphous structure [63].

Another relevant source of bioinspiration is represented by those natural surfaces that show a tremendous hydrophobic and self-cleaning effect. Examples include the wings of butterflies and the leaves of several plants. The best-known example of a hydrophobic self-cleaning surface is the leaf of the lotus plant (*Nelumbo nucifera*) [9,10]. Electron microscopy of the surface of lotus leaves shows protruding nubs about 20–40 μm apart, each covered with a smaller scale rough surface of nanoscale epicuticular wax crystalloids [11] (Fig. 2).

Other plants, like rice and taro, have a micro and nano-structured, showing CA $> 150°$ and sliding angles <10 degrees [11]. It has been demonstrated in literature that the hydrophobic behavior of such surfaces is due to both the surface roughness and its surface chemistry [12].

Droplets quickly roll off on the surface that remains dry. Even dirt particles find it more "convenient" to rest on the hilltops than to adhere. A rolling drop is then able to wash away the dirt particles, generating the so-called "self-cleaning effect".

2.1. Antireflective coatings

The earliest discovery of a single layer antireflective coating was made by Lord Rayleigh in the second half of the XIXth century: he casually noticed a tarnishing on glasses which increased their transmittance instead of reducing it, as expected. But the first ever antireflective coating was presumably made by Fraunhofer in 1817 [13]. As a result of an etching process he noticed that the reflection was strongly reduced [14].

The theory explaining the optical behavior of single and multiple homogeneous coatings is well understood [15,16].

Single layer antireflection coatings can be explained in terms of the creation of a double interface by means of a thin film generating two reflected waves. If these waves are out of phase, they partially or totally cancel. If the coating is a quarter wavelength thickness and the coating has a refractive index minor than the glass index of air, then the two reflections are 180° out of phase.

Two optical conditions must be satisfied, in order to have a complete destructive interference:

The phase condition. For the destructive interference of the reflected beams, the length of the optical path in the layer has to be

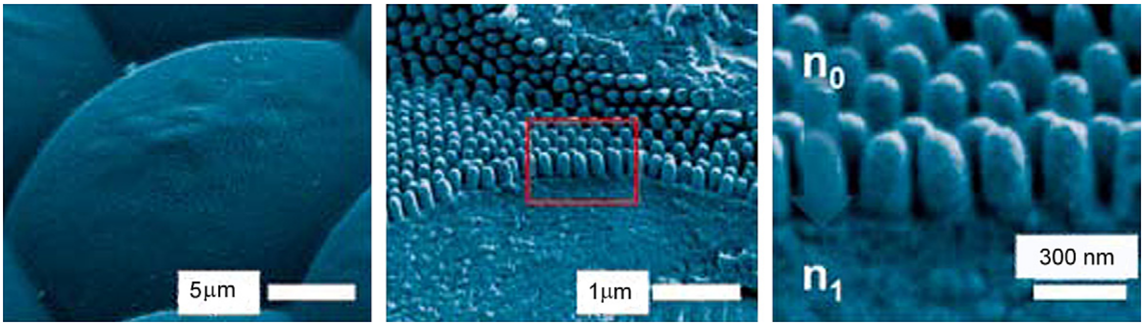

Fig. 1. Progressive ESEM magnification of the moth-eye surface morphology (Focus on Materials, Max Planck Institute for Metals Research Stuttgart, p. 1).

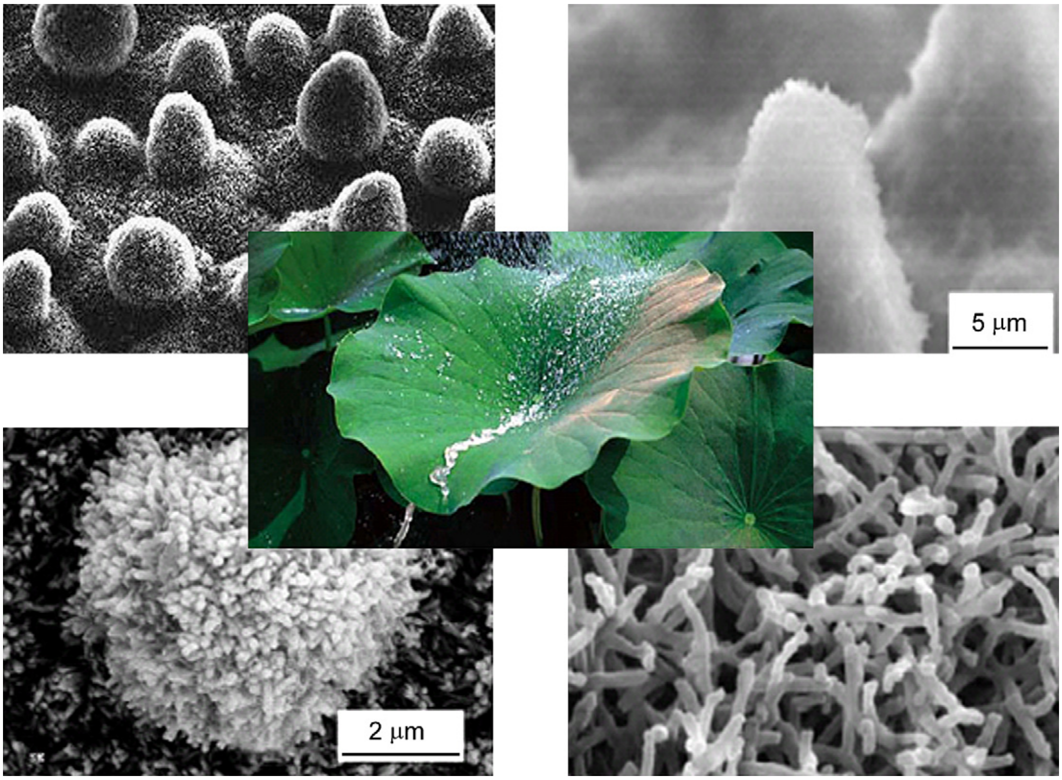

Fig. 2. Magnification of the lotus-leaf surface morphology.

equal to one half of the light wavelength. This quarter-wave condition gives the ideal thickness of the coating:

$$\lambda_0 = 4n_c h_c \quad (1)$$

where λ_0 is the wavelength at which destructive interference occurs, n_c is the refractive indexes of the coating, h_c is the thickness of the coating.

The amplitude condition. For complete destructive interference, the amplitudes of light reflected from the coating–air and substrate–coating interfaces have to be equal. This condition is satisfied when:

$$n_c = (n_c n_s)^{1/2} \quad (2)$$

where n_e and n_s are the refractive indexes of the environment and that of the substrate, respectively. If air is the environment ($n_e = 1$) then: $n_c = n_s^{1/2}$

The main approaches to fabricate artificial antireflective surfaces are schematically reported in Table 1. These methods differ in their technical realization, but they are based on the same optical principle – the interference effect of light. Whatever method is applied there is a defined transition region between ambient medium and substrate and this region is characterized by its effective refractive index and its physical thickness.

Table 1
Comparison between the main fabrication approaches available for AR coatings.

	λ/4 single layer	multi-layer (interference)	Gradient layers
Material	Porous, Glassy	Dense, alternating refractive index	Dense, glassy, nanostructured
Band width	Medium	Low	High
Angle dependence	Medium	High	Low
Residual Reflection	Coloured	Coloured	Coloured
Mechanical Stability	Low-good	Very good	Good

Antireflective (AR) optical coatings can be employed for a variety of applications in all aspects of use: for optical and electro-optical systems in telecommunications, glass lenses, eyeglasses, medicine, military products, but also lasers, mirrors, solar cells, IR diodes, multipurpose broad and narrow band-pass filters, architectural and automotive glasses and any kind of display [17], solar energy conversion systems, i.e. photovoltaic cells and solar thermal systems. As a matter of fact, glass transparency is strictly linked to the cell efficiency. Single layer antireflective coatings can lead to an increase of light transmittance consisting in about 8–9 percent points, with a consequent increase in terms of cell efficiencies [18].

With reference to their use in building engineering and construction industry, antireflective glasses are suggested for shop windows, control towers, museum glasses, advertisement panes, control panes in machinery, solar mirrors. Such films are strongly indicated for the creation of films on glasses employed in solar energy applications.

E-beam evaporation has long been the preferred deposition method for large-scale applications. However, magnetron sputtering techniques provide good uniformity for smaller area coatings [19]. The use of ion assisted and laser ablation deposition techniques in preparation of optical coatings have been the subject of research and development [20]. Both E-beam evaporation and magnetronic sputtering require vacuum and the size is also limited by the dimensions of the chambers. The cost of the equipments is quite elevated [21,22]. The high temperatures reached during this process and the high value of pressure are the main limits of these methods from an environmental point of view. The use of metal oxides such as silver have environmental implications concerning the entire life-cycle of the treated glass.

2.2. Self-cleaning coatings

“Manhattanizing” of cities and new, complicated designs of buildings cause a series of problems for designers and owners of buildings, concerning the maintenance costs of glasses [23]. The technology of self-cleaning coatings has developed rapidly in recent years. As a commercial product, their potential is huge. Given the wide range of possible applications, from window glass and cement to textiles, self-cleaning coatings may become an important labor-saving and sustainable device. Some of this potential is already being realized: self-cleaning paints are currently available in Europe [23] and within the past few years self-cleaning windows have been released by multinational glazing companies [24]. Self-cleaning glasses can avoid employing innovative robot systems for façade cleaning in tall buildings, especially in difficult-o-access areas.

Two approaches are possible in self-cleaning: hydrophobic and hydrophilic surfaces. Both of them clean themselves through the action of water, the former by rolling droplets and the latter by sheeting water that carries away dirt. Hydrophilic coatings, however, have an additional property: they can chemically break down adsorbed dirt when exposed to UV radiations.

2.2.1. Superhydrophilic surfaces

Titanium dioxide is a nontoxic and very stable oxide material. Luo et al. described superhydrophilic titania films that can be used as photo-induced catalysts for the decomposition reaction of organics in air to release oxygen ions under UV light radiation [25]. It is known that among three crystalline polymorphs, anatase, rutile and brookite, anatase shows the highest photocatalytic performance under exposure to the ultraviolet ray, consequently generating hydroxyl radicals and superoxide ions on its surface [26]. These radicals and ions with very strong oxidizing and reducing power decompose the organic ingredients on the surface of the material into water and carbon dioxide. Moreover, the surface structure of the titanium dioxide changes by irradiation with the ultraviolet ray and as a result, OH groups are generated, which make the material superhydrophilic [27]. More in detail, organic pollutants and oxides (NO, NO_2 and SO_2) at low concentration levels can be treated by TiO2 under UV irradiation [28].

In 2001 Pilkington Glass announced the development of the first self-cleaning windows, Pilkington Activ™, and in the following months several other major glass companies released similar products, including PPG’s Sunclean™. As a result, glazing is perhaps the largest commercialization of self-cleaning coatings to date. All of these windows are coated with a thin transparent layer of TiO_2, a coating which acts to clean the window in sunlight through two distinct properties: photocatalysis causes the coating to chemically break down organic dirt adsorbed onto the window, while hydrophilicity causes water to form ‘sheets’ rather than droplets – contact angles are reduced to very low values in sunlight (the coating becomes ‘superhydrophilic’), and dirt is washed away. Also Saint-Gobain adopted the same principle in the Bioclean™ self-cleaning glass.

TiO_2 films, deposited on window glasses, perform the so-called self-cleaning function using UV light and rain. The preparation of prototype TiO_2 coatings on float glasses is a simple process. Li et al. have provided a typical preparation of the TiO_2 coatings on float glasses [25]. The stable sols were put into a sprayer to be changed into a fog that is sprayed at a pressure of 1.3–2.0 atm onto the float glass moving at a velocity of 1.0–2.5 m/min. The coated glasses are dried first at 105 °C, and then at 300 °C for 10 min. The obtained product is the so-called self-cleaning glass. There are several techniques to coat the photocatalytic thin film on glass, e.g. sputtering, CVD, spin coating, dip coating, and spray coating. For a large architectural flat glass, spray coating is the most suitable among the wet coating techniques [25]. Self-cleaning glazings have been applied in a large number of buildings by architects. An important example is the famous architecture of China National Grand Theatre. Pilkington self-cleaning glasses were used in the Beach House, designed by Malcolm Carver or the Dragon’s Lair in London [29,61].

2.2.2. Superhydrophobic surfaces

An alternative approach to achieve self-cleaning properties on glass is superhydrophobicity [8]. The self-cleaning action stems from their high water contact angles; on these surfaces water forms almost spherical droplets that readily roll away carrying dust and dirt with them. Dirty water falling onto the hydrophobic coating is removed before it can evaporate. As droplets tend to roll only on surfaces with very high static contact angles, authors tend to quote only the static contact angle. But hysteresis, that is the difference between advancing and receding angles, is also fundamental. It should ideally be as close as possible to zero if drops are to roll easily, at low inclination angles of the surface. The requirements for a self-cleaning hydrophobic surface are a very high static water contact angle, qs the condition often quoted is $qs > 160°$, and a very low roll-off angle ($<10°$), i.e. the minimum inclination angle necessary for a droplet to roll off the surface.

The interesting aspect consists of the fact that increased roughness will result in an increase in terms of surface area and, thus, leads to an increased nominal surface energy. It has been demonstrated that the contact angle will increase with increased roughness of a hydrophobic surface, whereas the contact angle will decrease with increased roughness of a hydrophilic surface. This relationship, referred to as Wenzel’s law:

$$\cos\theta = r\cdot\cos\theta \tag{3}$$

Wenzel’s law can only be used if the water droplet is completely in contact with the rough surface. Actually, the contact between water and a hydrophobic rough surface cannot be “complete” and some air bubbles will be trapped at the interface. A more accurate interpretation of the so-called Cassie–Baxter state is given by:

$$\cos\theta_{\text{rough}} = r(1 + \cos\theta_{\text{true}}) - 1 \tag{4}$$

where r is the fraction of the solid surface in contact with water, θ_{rough} is the nominal contact angle of a rough surface, and θ_{true} is the contact angle with no trapped air bubbles. Two interfaces are then attributed to the contact between a droplet and a rough surface: the one between the droplet and the solid surface, and that between the droplet and the trapped air bubbles, influencing the value of the contact angle.

Several techniques are known for the micron-scale patterning of hydrophobic surfaces. Actually, most of the preparations involve strict conditions such as harsh chemical treatments, expensive materials (e.g., fluoroalkylsilanes [30,31] nanotubes [32]) and complex processing procedures including plasma etching [33], chemical vapour deposition, electrodeposition [34], calcinations [35] and the use of templates [36]. Many of the reported superhydrophobic polymeric films are often composed of un-crosslinked, thermoplastic polymers, and they are vulnerable to environmental attacks (e.g., solvent, heat).

A large part of them suffer from several drawbacks which have so far prevented widespread application. Above all, batch processing a hydrophobic material is a costly and time-consuming technique, and the coatings produced are usually hazy – precluding applications on large glass panes for architectural uses.

3. Limitations of existing coating technologies

The glass envelope of buildings has a key role in the design of smart and dynamic interfaces between the confined spaces and the outdoor conditions. The main limits in the available technologies are represented by the elevated costs and the limited durability of treated glasses when exposed to the external environment. Coatings are also considered as monofunctional treatments, with inevitable drawbacks (reduction of transmittance, high costs).

3.1. Durability of coatings – heterogeneity of materials

Typical optical coatings consist in a deposition of metal oxides on glass with CVD (chemical vapour deposition) [20] and PVD (physical vapour deposition) processes. The heterogeneity between the deposit and the glass substrate is the principal cause of the lack of durability of these coatings. Some researches have pointed out that low-E coatings – with magnetronic deposition – show a degradation of the deposit layer, during transport phase or under exposition in an environment with high moisture concentrations [37,38]. Techniques for increasing coatings durability are still under testing (see Fig. 3). One of the aspects is the adoption of pre-treatments of glass support, in order to enhance the superficial roughness and mechanical durability of substrate [38]. The heterogeneity of materials used in glass coatings, the limits of durability and the environmental implications of both the process and the recycling of coated glasses are other non-negligible issues. Life-cycle assessments have been published by Citherlet et al., about the impact of windows, including glazes and frames of different materials (PVC, aluminium, wood) [39].

3.2. Functions of coatings

Many of the coatings in commerce do not have multifunctional properties. In order to obtain, contemporarily, double or triple functions of the glass (e.g. low-E, antireflection and self-cleaning) it is necessary to add several different coatings to the glass substrate.

3.3. Reduction of visual transmittance of coated glasses

Some solar control or low-E coatings have lower visual transmittance than non-coated glasses, due to the deposition of noble metals (gold or copper) or of transition metals (such as iron, chromium and nickel). This could affect considerably visual comfort conditions under daylighting [40]. It has also been observed that some persons and plants react adversely to the fact that the sun's full spectrum of colours is filtered by low-E glazings, because may have an influence on melatonin balance. As a result of this, some designers tend to use low-E glasses only on the north, east and west facades, but preferring clear glasses on the south side [41].

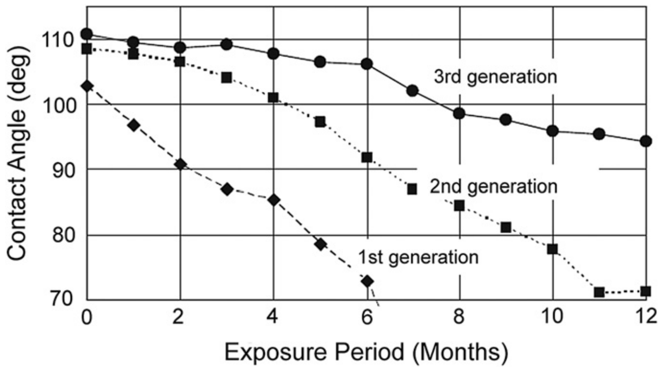

Fig. 3. Decrease of contact angles in sol-gel coatings after one year of outdoor exposure [25].

3.4. Instability at high temperature fields

It is a characteristic of some low-E coatings. Generally, low-E coatings are produced by two different processes: soft and hard coating process [42]. In both cases the low-E effect is due to the deposition of tin oxide films on treated glass surface. In detail, for the commonly used low-E coatings, the deposition consists of a sandwich layer formed by a thermal reflective silver layer, included in transparent dielectric layers. The difference between the refractive index of silver and dielectric layers, generates an interference of visible light that reduces visible reflectance and, therefore, increases visible transmittance [43]. At high temperatures the silver included in the low-E layer could have the characteristic of diffusing and agglomerating into islands, with a consequential decrease of visual transmittance. However, since 1990s some heatable and bendable coatings are available, and they are especially used in automotive field [43].

3.5. Cost of vacuum processes

One important drawback of the vacuum process is the high initial investment cost. It is evident that the vacuum process is suitable for the mass production of a high quality coating, especially for large area applications [22].

4. The sol-gel method

The sol-gel method has proved to be quite versatile as a result of intensive and extensive fundamental researches for three decades [44]. Materials processed by this method can be metallic, inorganic, organic and hybrid, ranging from highly advanced materials to common materials, from optics to architecture.

The relevance of the sol-gel method basically consists of (1) improvement of processing and properties of conventional materials and (2) creation of novel materials. A brief description of the method will be given. This technique also permits the self-assembly of nanostructured surfaces with a cheap "bottom-up" approach.

Fig. 4 shows the steps of the sol-gel processing of materials and examples of the microstructures of final products. A typical sol-gel method for fabricating materials starts with a solution consisting of metal compounds, such as metal alkoxides and acetylacetonates as source of oxides, water as hydrolysis agent, alcohol as solvent and acidic or basic catalysts. Metal compounds undergo hydrolysis and polycondensation at room temperature, giving rise to sol, in which polymers or fine particles are dispersed. Further reactions connect the particles, solidifying the sol into a wet gel, which still contains water and solvents. Usually, various shapes are formed during the sol to gel transformation. Vaporization of water and solvents produces a dry gel, one of the final products. Heating of gels to several hundred degrees or higher temperatures produces dense oxide materials as final products [5]. The main features are exposed in Fig. 4.

These explanations indicate that the sol-gel method is characterized by low processing temperature. Materials of various shapes and microstructures can be prepared. Bulk bodies can be made by casting the gelling sol into a mould. Fibers can be drawn from the viscous sol, whether a sol of appropriate composition is used. Coating films can be made by dip coating or spin coating of the sol. Unsupported films can be made by synthesizing the film at the interface between alkoxide solution and water. It is unquestionable the fact that nowadays the sol-gel technology expands rapidly and many new products are appearing on the market

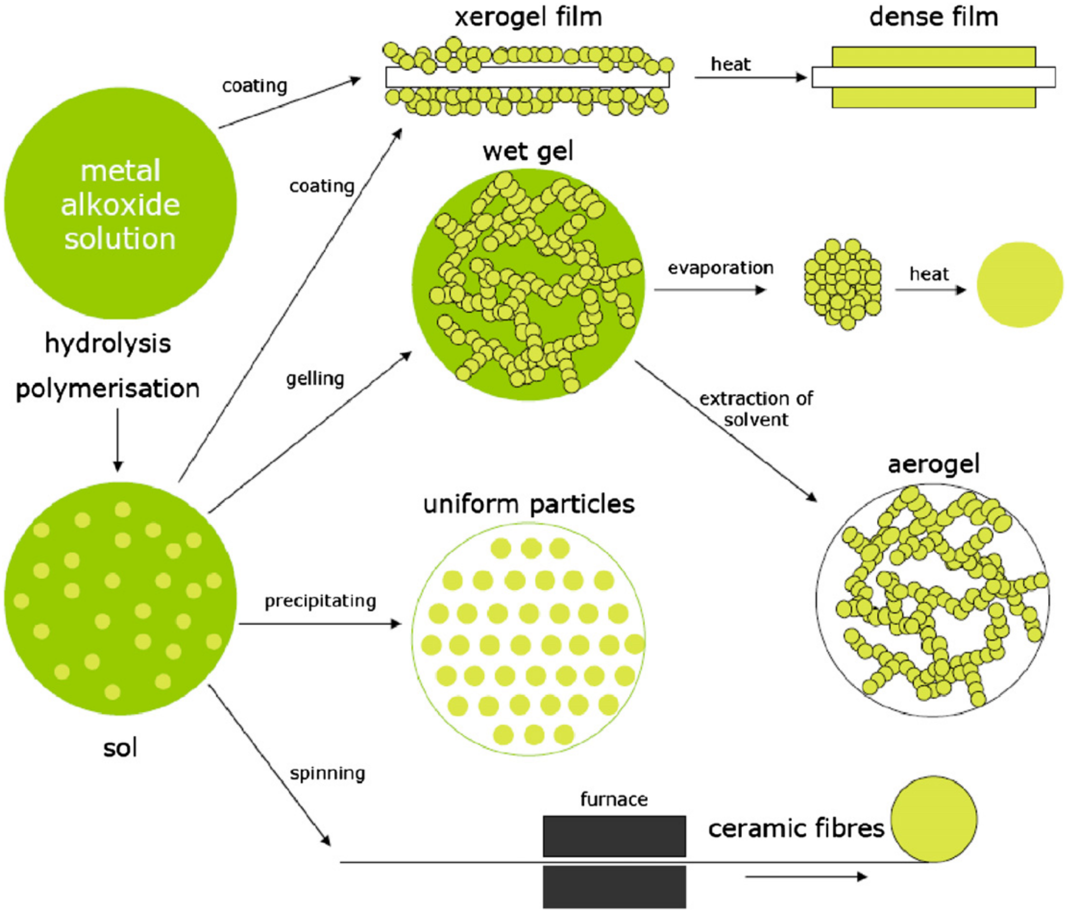

Fig. 4. Sol-gel technology and products.

[45,25]. This tendency has been influenced especially by the availability of novel hybrid and nanocomposite materials, the so-called Ormocer [46] systems, developed at the Fraunhofer Institute. In the Table 2 a comparison between different deposition methods on glasses is made, also considering operative and environmental implications.

5. Applications of sol-gel coatings on architectural glasses

As the awareness of the threat of global warming is becoming more and more well estabilished, increased efforts are being made to design energy-efficient buildings. Large energy savings can be achieved by the use of spectrally selective windows in buildings. Using glass that reflects a high percentage of incident radiation in the near infrared range, while permitting high levels of transmission in the visible, allows large reductions in air-conditioning costs by reducing the amount of solar energy entering buildings. In 2002 Soutar and Nee [47] reported the results of a project obtained by depositing multi-layer sol-gel coatings with the aim to selectively reflect radiation in the near infrared region of the spectrum allowing, at the same time, high light transmission, as it can be observed in Fig. 5.

Table 2
Comparison between different deposition methods on glass.

Characteristics	Vacuum based technology			Sol-gel process		
	E-beam evaporation	Sputtering	Chemical vapour Deposition	Dip-coating	Spin coating	Spray coating
Materials capability	Simple composition	Nearly unlimited	Low	Limited by precursors	Limited by precursors	Limited by precursors
Nature of process	Vacuum	Vacuum/Plasma	Vacuum/Plasma	Solution-based	Solution-based	Solution-based
Process controllability	Good	Good	Good	Good	Good	Fair
Substrate temperature	Low to high	Low to high	High	Low	Low	Low
Substrate size	Small to medium	Small to large	Large	Medium to large	Small to medium	Large
Coating coverage	One side	One side	One side	Two side	One side	One side
Thickness uniformity	Variable	Fair to good	Good	Fair to good	Fair to good	Fair to good
Deposition rate	Moderate	Long	Long	Long	Long	Moderate
Size limitation	Vac. Chamber	Vac. Chamber	Vac. Chamber	None	Up to medium size	Unlimited
Shape complexity	Limited	Moderate	Moderate	Limited	Flat only	Unlimited
Scale-up capability	Good	Fair	Good	Excellent	Fair	High
Cost of equipment	High	High	High	Low to moderate	Low to moderate	Moderate
Materials heterogeneity	High	High	High	Low	Low	Low
Environmental compatibility	Low	Low	Low	High	High	High

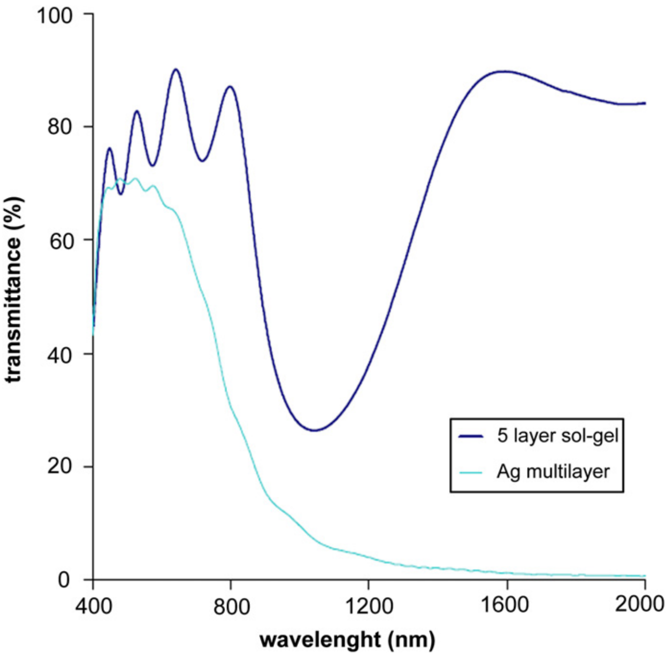

Fig. 5. Comparison between silver based low-E coatings and five layer solgel spectrally selective coatings [47].

It has been demonstrated in fact that an optimized sol-gel antireflective single layer coating can reduce light reflectance to less than 1% [64]. Hammarberg et al. [14] showed in fact that the transmittance of a low-E grazing can be largely increased if its antireflection treated by depositing a thin film of silicon dioxide on both sides of the sample. It was also proved possible to construct a TGU (triple glazing unit) window with AR-treated low-E and float glass panes having the same light transmittance as a standard float glass DGU (Double-glazing unit) window. The AR-treated TGU window thereby greatly decreases the *U*-value without affecting the visibility (Figs. 6–9).

The increase observed in the efficiency of silicon solar cells due to the reflection loss was observed by Chen et al. on AR-coated cells. Their efficiency increased from 12.1% to 17.4% [21] as a consequence of the presence of the sol-gel coating. Pettit et al. [18] observed how the cell efficiency can be easily increased reducing the reflectance of light on the glasses protecting cells or water pipes.

Lien et al. deposited a tri-layer sol-gel coating on solar cell achieving a 39% improvement in the efficiency of the monoscristalline Si solar cell [48].

The important role of glass in the photovoltaic industry has been well highlighted by Deubener et al. [49] in 2009. They described encapsulated glass-to-glass photovoltaic modules and identified solar photocatalytic glass surfaces as elements of a green architecture combining renewable power generating and destruction of air pollutants of urban environments. They also reported a current gain of 2.65% after measurements under standard test conditions with antireflective glass [49].

The most widespread class of sol-gel precursors, the alkoxides, are characterized by high compatibility with a large variety of glass materials. Tetraethyl orthosilicate (TEOS) or methyltriethoxysilane (MTEOS), for instance, provide the formation of a glass-like material, which helps to prevent several recycling problems concerning to the end of the life-cycle of the treated glass. Sakka described a fabrication method for inorganic coating materials based on metal alkoxides [50], which exhibited high durability against weathering and high resistance to long-time, outdoor contamination.

Akamatsu reported the fabrication of transparent silica-titania films characterized by a concave–convex surface by means of the use of a mixture of polymerized tetraethoxysilane silane (TEOS) containing tetraisopropoxytitanate and polymerized methyltriethoxysilane (MTES) for the automotive industry [25].

As it will be better explained in the following discussion of the state of art, to impart an hydrophobic behavior to glass surfaces, fluoroalkilsilanes are generally the most used functionalizing agents. This type of water-repellent glass has already been produced for windshields since 2003.

Kamitani et al. described sol-gel hydrophobic coatings for windshields, produced since 1997 by NSG (Nippon Sheet Glass). Hydrophobicity is provided by a fluoroalkyl group arranged in order on film surface [61]. To obtain higher environmental stability and abrasion resistance, a silica under-layer is applied on the glass surface and the total thickness of the film is less than 50 nm. In both cases a capping layer consisting in hydrorepellent fluorinated surface groups is necessary.

Hikita et al. [51] used colloidal silica particles and fluoroalkylsilane as the starting materials and prepared a sol-gel film with superliquid-repellency by hydrolysis and condensation of alkoxysilane compounds. Instead of blending low surface energy materials in the sols, Shang et al. [52] described a procedure to make transparent superhydrophobic surface by

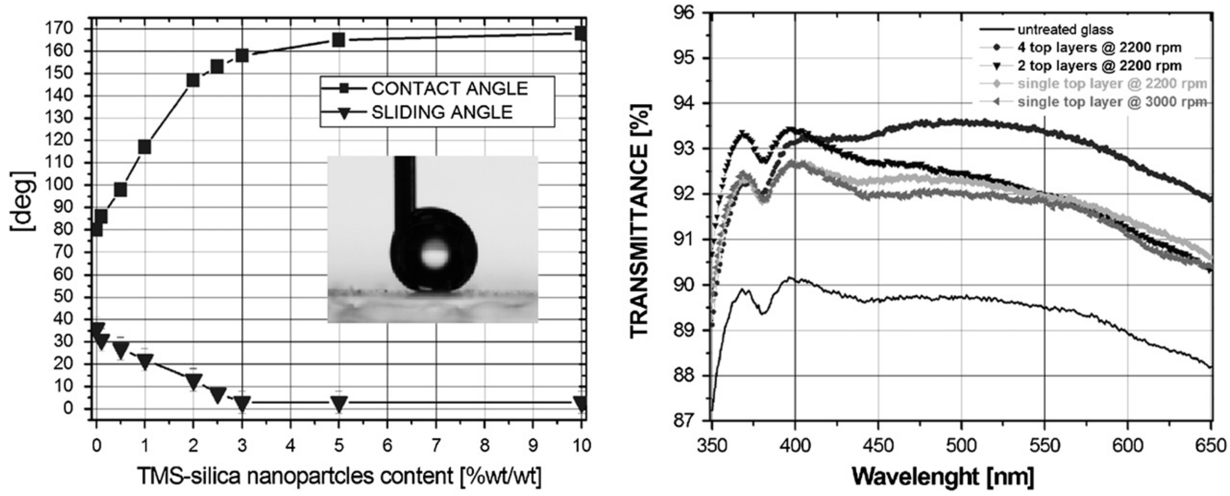

Fig. 6. (a) Contact angles and (b) transmission spectra of nanostructured coatings made at the National Nanotechnology Laboratory, CNR Lecce [58].

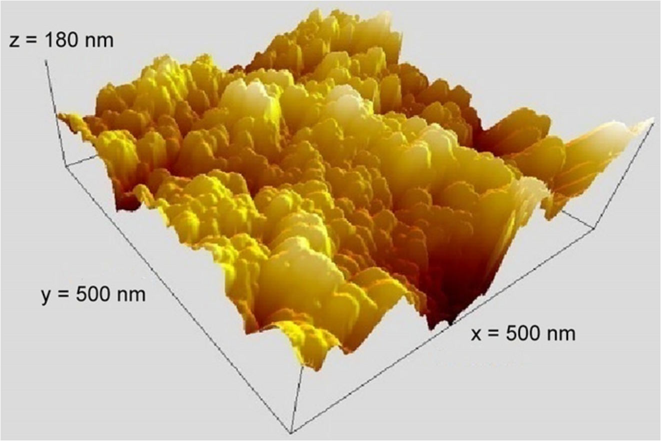

Fig. 7. Atomic Force Microscope measurements of superhydrophobic and antireflective coatings [58].

modifying silicabased gel films with a fluorinated silane. On a similar note, Wu et al. [53] made a microstructured ZnO-based surface via a wet chemical process and obtained the superhydrophobicity after coating the surface with long-chain alkanoic acids.

An exhaustive review on superhydrophobic surfaces has been written by Zhang et al. [54] in 2005. In particular they reported several approaches to achieve self-cleaning coatings having at the same antireflection (AR) properties too. These coatings were prepared by depositing SiO_2-particles containing coatings onto glass substrates that were previously modified through polyelectrolytes by electrostatic attraction. By depositing another layer of TiO_2 nanoparticles through electrostatic attraction, and removing the polymer by calcination at 500 °C it was possible to combine both the AR and self-cleaning properties of the coatings and tune them by varying the concentration of colloidal TiO_2 solution used in the preparation.

An other interesting multifunctional coating has been described by Okada et al.; they developed a multifunctional glazing which combined low-emissivity (low-e) properties and visible light-responsive photocatalytic activity, depositing a two-layer coating of F-doped SnO_2(SnO_2:F) – inner layer – and titanium dioxide (TiO_2) – outer layer [55]. Heat insulating properties and antifogging and antibacterial activity due to the titanium dioxide are then available. The SnO_2:F film with a thickness of approximately 400 nm was prepared by an atmospheric pressure chemical vapour deposition. The deposition of TiO_2 films was carried out using a d.c. magnetron sputtering system whose base pressure was less than $1 = 10^{-4}$ Pa.

The possibility to deposit single layer sol-gel coatings, for instance, is useful to combine precise properties with coatings having other specifications [56]. To maintain the high transparency of glass in the range of the visible spectrum and to protect the silver from corrosion, Brauer [57] described the necessity of additional antireflective and protective layers of high refractive materials.

Having the target to address all the previous mentioned issues, at the National Nanotechnology Laboratory of Lecce we have been recently focused on the development of long-term durable transparent superhydrophobic surfaces (Fig. 6a) via simple coating methods that can simultaneously construct a solid surface having both appropriate roughness (Fig. 7) and low surface energy without any additional hydrophobic capping layer [58]. By employing trimethylsiloxane (TMS)-surface-functionalized silica nanoparticles partially embedded into an organosilica gel matrix, solid surfaces were fabricated, having both appropriate roughness and low surface energy without any additional hydrophobic capping layer (Fig. 8). Tuning the relative content of hydrophobic nanoparticles and silica gel binder, we made it possible to optimize both the water repellence and the thermo-mechanical stability of the coated surfaces. The nanoporous nature of the upper layer also gave rise to a consistent antireflection effect (Fig. 6b). An acidic catalyzed solution which employs TEOS as a precursor, ethanol as a solvent and water is the ideal binder between a glass substrate and an upper acidic solution prepared using MTEOS as a precursor, ethanol, water and Hydrophobic silica nanoparticles having 20 nm diameter. This solution is better basified before immersing the nanoparticles.

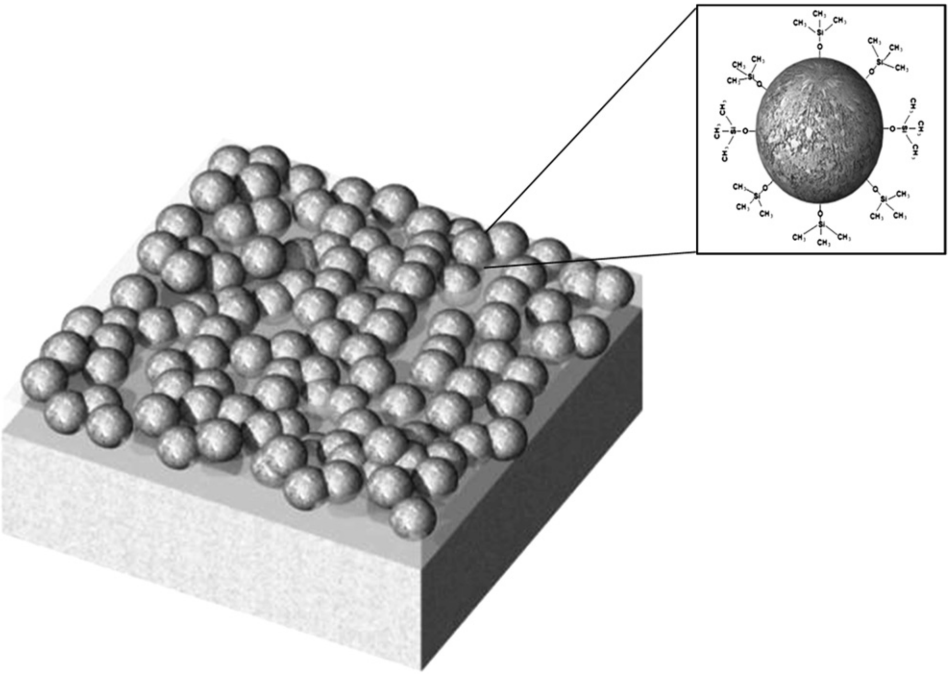

Fig. 8. Preparation of TMS-silica nanoparticles-based ultra-hydrophobic coating [58].

Fig. 9. Superhydrophobicity of transparent coatings on glass [58].

The solution can be applied by spin coating or dip coating on the glass, but it could also be spray-coated on large panes for architectural uses. After the coating is made, a heating is necessary to make the organic solvent evaporate and to leave the hydrophobic particles on the surface, partially embedded in the condensed upper layer. It can be considered an interesting design of a self-assembled multifunctional coating for glass substrates. The results obtained are exposed in the figures below.

6. Conclusions and future perspectives

The considerations exposed so far consent to assess that sol-gel coatings are capable of achieving several design objectives from different points of view (multifunctionality, low costs, versatility, durability). The contemporary satisfaction of these requirements allows to define architectural glasses as principal application of these innovative coatings. Protection glasses of PV modules, external surfaces of vertical or inclined facades, shop windows, transparent surfaces of museums or archaeological paths are only a few of possible new uses of these innovative coatings. In the following paragraphs all these new uses are briefly exposed.

6.1. Protection glasses of PV and solar modules

Even though it is unquestionable that the efficiency of photovoltaic and solar thermal systems can be increased by using antireflective coatings on protective glasses, it could be observed that further environmental considerations could lead designers to adopt a superhydrophobic and antireflective coating instead of a solely antireflective one. In contexts like countryside or even deserts, pollutants or just sand could settle on the external surface of treated glasses, thus reducing the initial efficiency of the system. In these cases, it can be preferable to adopt a superhydrophobic glass, in order to reduce the maintenance costs of cleaning and the consequent use of water and chemical products. The developed coating could be a cost-effective protection of this kind of glasses, able also to minimize durability lacks of traditional coatings.

6.2. External glass of PV façades and of tall buildings envelopes

Many of modern photovoltaic façades are made of solar cells embedded in double-glazing units. A self-cleaning coating on glasses used in this kind of facades can reduce significantly the maintenance costs (due to cleaning and to the use of detergents). On photovoltaic integrated facades [59] it would be important to use a self-cleaning coating on the single modules, in order to reduce the short-term effect of pollution and dirt on protective glasses and to maximize the production of energy, obtaining both a reduction in terms of costs and in terms of solar energy conversion.

6.3. Transparent roofs

Decreasing roof tilt angle, the negative effect of visual transmittance losses due to pollution increases rapidly. Cleaning intervals for uncoated glasses may be between 3 and 12 months depending on location, climate and local conditions [62]. On uncovered glass roofs this effect is due to the reduction of the washing away effect of rain. superhydrophobic- antireflective coatings could offer benefits also in these conditions. Benefits can increase in particular uses of glass roofs, such as greenhouse coverings. The self-cleaning effect could reduce surface pollution, while antireflection can stabilize total solar transmittance at high levels, in order to increase direct solar gains.

6.4. Antiglare glasses

In several cases [6] buildings having glassy skin located near highways can blind motorists. This is another case in which a superhydrophobic and antireflective sol-gel coating could be a cost-effective choice. A fair antireflective effect could reduce glare with a non-excessive increase in transmittance and, at the same time, the self-cleaning properties of such surfaces could significantly reduce the maintenance costs, having a high impact in glass architecture.

6.5. Shop windows

A good vision through the window, the exclusion of reflections and avoiding of colour alteration should be the principal peculiarities of a shop window. For this purpose, an antireflective glass could be the best choice. The developed sol-gel coating, combining a good adhesion to the glass substrate and high durability levels (due to the reduction of dust and pollution impact of façade's plan) could be a candidate for substituting traditional antireflective coatings.

6.6. Museums and archaeological paths

The increase of light transmittance through glasses can be employed in museums, where reflection makes it often difficult to observe the works exposed. In such cases antireflective glasses could be suitable. The sol-gel coating, deposited on an extra-clear glass could increase the general colour rendering index, leaving unaltered the perception of colours through glass. For the same reason, in archaeological paths it could be convenient to employ antireflective coatings, in order to assure the comfort to users.

6.7. *Windows for Alzheimer nursing homes*

Even in Alzheimer nursing homes antireflective glasses could be effectively used: as a matter of fact, people who suffer from such a disease can have psychological shocks at gazing their own image reflected by a mirror or a highly reflecting window glass pane.

6.8. *Reflector and projector glasses*

An antireflective and superhydrophobic coating on the glasses used in reflectors can increase the light transmittance of glasses and the energetic efficiency of the whole device. If the coating has both antireflective and self-cleaning effect, it could be possible to reduce the long-term effect of dirt settling on the external surface and to increase the light transmittance, reducing the luminous efficiency of the reflector.

6.9. *Structural effect of sol-gel coatings*

Several studies, like that of Sànchez-Gonzàlez et al. [60], have demonstrated the beneficial effect of sol-gel coatings on the increase of fracture strength of brittle materials, like glass.

6.10. *Multifunctional coatings*

A precise design of coatings having more than one property could be the key to solve many of the open issues of architectural glass technology. Several intrinsical limits of glass used in building envelopes could be overcome by depositing multifunctional coatings that enable designers to keep unchanged the light transmittance – for instance – even when enhancing the thermal properties of glazings by adopting a low-E coating. On the other hand, an antireflective and self-cleaning coating can be used effectively on photovoltaic cells or integrated photovoltaic facades.

In several cases, sol-gel antireflective coatings could be useful to limit the reduction of transparency in low-E coatings. No solar control, in fact, is required on the northerly exposure.

Some multifunctional products are already on market. Pilkington Activ™ Neutral is a neutral coloured glass that combines dual-action, self-cleaning properties with solar control performance for a cooler internal environment.

The sol-gel method could reduce costs and impacts of multi-functional coatings.

6.11. *Process temperatures and environmental implications*

A non-secondary advantage related to the use of sol-gel coatings in architecture is the relatively low range of temperatures required for the deposition and adhesion on glasses (extra-clear glasses, lime glasses and even tempered glasses). The thermal post-treatment of the solutions previously described, can be in the order of 150–200 °C. The environmental impact and the costs of processes could be significantly reduced with respect to all of the analogous treatments available in the state of art.

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