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Review

Sol-gel chemistry, templating and spin-coating deposition: A combined approach to control in a simple way the porosity of inorganic thin films/coatings

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ABSTRACT

Porous materials are powerful functional devices that can find applications in many fields, from nanotechnology to biomedicine, from catalysis to membrane separation. In general, porous materials can be processed in various forms, but a rising interest is growing around inorganic thin films and coatings, due to the increased number of applications based on their use. Among the different strategies proposed till now for preparing inorganic porous thin layers/coatings, a simple and versatile route consists in the combined use of sol-gel chemistry, templating, and spin-coating deposition. Therefore, in order to provide a helpful toolbox for users, an extended discussion around the physico-chemical principles behind each of these steps is here reported, also highlighting the advantages and disadvantages of each procedure, together with critical points.

1. Introduction

According to the IUPAC definition, porous materials are divided into three classes named respectively: micro- (with pore width less than 2 nm), meso- (between 2 and 50 nm) and macroporous (over 50 nm) materials [1,2]. Porous materials have been widely studied in the past and they are still attracting the attention of many researchers because their peculiar properties, namely high surface area, tunable pore sizes and surface chemical reactivity, make them suitable for many technological applications [3,4].

Since inorganic porous materials can be obtained in several forms and shapes (i.e., nanostructured particles, bulky monoliths/aerogels, nanowires, thin films/coatings), many studies are focused on the production of oxides, mainly silica [5–8], titania [9,10], anodic alumina and composites [11,12]), as well as other ceramics, such as natural and/or artificial modified clays, zeolites (leader products in the microporous range) [13], silicon wafers [14,15], metal carbides and nitrides [16–19].

In recent years, the synthesis of thin porous oxidic/ceramic films [20,21] has received a great attention, especially in the field of membrane science and technology. For instance, composite asymmetric membranes consisting of macroporous substrates and thin micro- and mesoporous films have been developed to fabricate devices which can be used for the separation of chemicals, but also for more sensitive applications, such as dosing of chemicals in drug-delivery systems, microfluidics and Lab-on-a-chip devices, sensors, catalytic substrates and many others [22–24]. Furthermore oxidic/ceramic coatings with a well organized porosity are of interest for developing devices which can be exploited in advanced environmental applications. As reported by Franzoso et al. [25], one of the main issues to be solved nowadays is to fulfill the always increasing demand of fresh water by human population. Since the continental rainfall cannot sustain the demand of water, remediation processes of contaminated water are becoming more and more important [26]. In this context, the possibility of using “smart” membranes (with a specific porosity/reactivity) to be exploited for the clarification and remediation of wastewater is attracting the

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attention of worldwide experts [27,28]. Another very interesting application of porous oxidic thin films is in dye-sensitized solar cells (DSSCs), which offer a very promising alternative for future energy supply [29]. This technology requires a photo-anode, which is typically made by a layer of mesoporous titania deposited onto a conductive glass substrate. Since the electron diffusion in such layer depends also on the porosity of the system, a better control of these parameters (in particular on the way of deposition) is very important for optimizing their photovoltaic performances [30]. These few case studies highlight how the production of thin films with controlled porosity is becoming a topic very attractive not only for a specific field of research, but rather in a multidisciplinary viewpoint.

The sol-gel polymerization process represents a key procedure for the bottom-up synthesis of such systems, but often this process is not enough versatile to form stable pores of appropriate size, therefore it is necessary to resort to templating agents [31,32]. In this respect, molecular and/or polymeric amphiphiles (i.e., surfactant and/or block copolymers) can be employed not only to take advantage of their self-assembly into micelles with well-defined size and geometry, but also to exploit the spontaneous organization of micelles in ordered arrangements which act as structure driving agents (in the soft-templating procedure, *vide infra*) [33,34].

Another important key-factor in the preparation of these advanced porous materials is also the deposition technique selected, which can influence both the porous architecture of the solidified film and the coating thickness [21]. Among the several deposition techniques, spin-coating on appropriate substrates gave valuable results [35,36]. The peculiarity of spin-coating deposition, in fact, is the fast spin rate, which induces the almost complete elimination of extra-solvents and the freezing of the templated nanostructure, leaving a well-ordered network of nanosized domains that reflects the arrangement of the driving agents [37,38].

Given the variety of porous oxidic materials existing and the number of methods useful for inducing controlled-porosity, a discussion around them is mandatory. Moreover, in the literature, several reviews are focused on sol-gel [5,32,39], templating [9,40,41] or deposition techniques [42–44], but only few of them [5,45] consider these three aspects together. The following paragraphs are therefore devoted to the description of a possible route to follow for obtaining well-ordered inorganic porous oxides, focusing on the sol-gel chemistry, soft-templating, and spin-coating deposition processes, as in our opinion their combination constitutes the simplest and most effective route to achieve the purpose. With the aim of helping users in the field of highly-porous organized films, advantages and disadvantages of each synthetic step are deeply discussed and the relative critical points highlighted. Additionally, soft- and hard-templating synthetic procedures are discussed and compared.

2. Sol-gel chemistry

2.1. Historical and economical (contemporary market) summary

The term “sol-gel” was firstly coined by Graham et al. in 1864 [46]. In particular, Graham and collaborators observed that the hydrolysis of TetraEthyl OrthoSilicate (TEOS) under acidic conditions produced SiO_2 in the form of a “glass-like material” [39]. From that point, and continuing in the following years, several advances have been made by many researchers worldwide. In particular, an extensive step forward was done by the Mobil Oil Company in 1992 with the development of a siliceous material with a periodic porous structure, known as M41S, synthesized with the help of a surfactant as template [47,48]. This class of highly-ordered porous materials (with pores typically oriented in a cylindrical array) found applications mainly in catalysis. The use of such mesoporous materials with homogeneously distributed pores and high surface areas as catalytic substrates in oil refinery opened to their industrial and technological development. In the same years also the academy increased fundamental and applied research on sol-gel chemistry. Under this point of view the work published by Hench and co-worker in 1990 [39] is a milestone and can be considered the first important systematic study on the sol-gel chemistry and mechanisms. For a wide and well-detailed discussion around sol-gel chemistry historical achievements, authors suggest to carefully read the information contained in Ref. [5].

In addition, as reported by Ciriminna et al. [5], in the last 30 years there was a remarkable growing interest around sol-gel chemistry and, starting from the late 1980s, the sol-gel method has been continuously and thoroughly investigated, becoming an important tool for the development of novel materials with applicability in several productive areas. Most of the interest around the sol-gel approach is due to its high potential impact on the market. Important advantages of sol-gel processes over conventional materials and technologies are the low synthesis temperatures and the high purity of final products, which are key aspects to reduce production costs of high-performance and functional materials.

The worldwide demand of the market concerning sol-gel products is estimated for $ 2.2 billion in 2017 (in 2011 it was estimated to be $ 1.4 billion), mostly for silica-based materials and liquid formulations (i.e., for nanocoatings) [5]. In fact, the foremost sol-gel applications are currently in the coatings industry. Relevant examples are anti-reflective glass for facades, museums display cases, showrooms, silicon solar cells, nonhazardous anti-corrosive sol-gel coatings to replace chromate conversion coatings, sol-gel optical coatings for TV screens and protective coatings in general. However new expanding applications have to be considered, for instance in the optical and opto-mechanical industry and in cosmetics. Besides those also biomedicine applications are expected to boost the market of sol-gel products. In fact nanocarriers for controlled drug delivery, made of siliceous regularly-mesoporous supports prepared via sol-gel techniques (and templated via soft templating), received special attention in recent years, since they are suitable tools for an efficient delivery of drugs or diagnostic agents to the target sites reducing at the same time the systemic drug toxicity and the adverse side effects to healthy tissues. Moreover, these carriers can be loaded with a relatively large variety of drug molecules (e.g., small molecules, peptides, nucleic acids) which are protected from cleavage by external agents [49].

Market data and forecasts confirm the rapidly growing interest in sol-gel processes and products, also witnessed by increasing efforts of companies in R&D and by the expansion of the number of providers of silica precursors. This trend clearly demonstrates that the sol-gel technique is a stimulating field of research able to attract large economical investments.

2.2. Sol-gel synthesis: reactivity in different chemical environments

The sol-gel process involves polycondensation reactions of monomers into a colloidal solution (*sol*) which evolves into an integrated network (*gel*) of either nanoparticles or bulky polymerized networks [5,8]. Typical precursors of such kind of reactions are metal alkoxides or chloride salts, but also other types of precursors can be used [50,51]. Considering silica, the most frequently used silicon-containing precursors are branched alkoxides of the $Si(OR)_4$ type, in which OR designates alkoxide groups.

Usually alkyl moieties (-R) are methyl (CH_3) or ethyl ($-C_2H_5$) groups, giving TetraMethyl OrthoSilicate (TMOS) or TEOS, respectively [52]. Beside them, also other alkoxide-derived precursors are