

Review Article

Sol–Gel Synthesis of Nanostructured Mesoporous Silica Powder and Thin Films

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Received 2 September 2022; Revised 15 May 2023; Accepted 16 May 2023; Published 8 February 2024

Academic Editor: Baskaran Rangasamy

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Mesoporous materials are special nanoporous materials containing well-defined mesochannels with a pore diameter between 2 and 50 nm. The high surface area, ordered structure, tunable pore size, and easiness of functionalization have made mesoporous silica powder and thin films interesting materials for a wide range of applications including drug delivery, absorption, separation, catalysis, energy conversion, and storage. The sol–gel process has emerged as a promising technique for the synthesis of nanostructured mesoporous silica materials as it provides the advantages of low-temperature processing and easy control of the synthesis parameters. Although it offers several advantages over other synthesis techniques, it also has the drawbacks of high sensitivity to processing conditions. Hence, this review paper aims to give critical insights into the sol–gel process, the chemistry of sol–gel silica, the formation mechanism of mesoporosity, and the effects of the reaction parameters. A good understanding of these phenomena is essential to better control and optimize the properties of the final material for specific needs and applications. Additionally, this review paper discusses the different methods applied to the synthesis of nanostructured ordered mesoporous thin film silica, including the Electrochemically Assisted Self-Assembly method of synthesis. The EASA method is a novel and promising technique for the synthesis of well-ordered and vertically aligned pore channels of mesoporous thin films as it is required for mass transport applications. Moreover, the effects of sol composition, pH, applied potential, and deposition time on the final thickness of the thin film are elaborated on in detail. Furthermore, this comprehensive review highlights the potential and opportunities for future research and development in the area to further advance and use its full potential advantages.

1. Introduction

Mesoporous silica materials have received much attention due to their high surface area, ordered structure, tunable pore size, and easiness of functionalization. Because of these properties, these materials have a diverse range of applications such as drug delivery, absorption, separation, catalysis, and energy conversion and storage [1–3]. According to the International Union of Pure and Applied Chemistry (IUPAC), materials with pores in the size 2–50 nm range are called mesoporous materials [4]. Their preparation dates back to 1992 when a group of researchers at the Mobil Research and Development Corporation first synthesized mesoporous materials from different silica precursors using a liquid crystal templating approach, where surfactant molecules served as a structure-directing agent (SDA) to create the porosity after its removal [2]. They assigned it Mobil Crystalline Materials (MCM). The

MCM-41 silica has a hexagonal arrangement of uniform channels with pores size of about ca. 3 nm [2]. Later in 1998, a group of researchers at Santa Barbara, University of California synthesized another type of hexagonally arranged mesoporous material, namely Santa Barbara Amorphous no 15 (SBA-15) using nonionic triblock copolymer surfactants as SDA in the acidic reaction medium [5]. SBA-15 possesses a larger pore size (ca. 6 nm) and a thicker pore wall than MCM-41 [6]. They have cylindrical pore channels with different mesoporosity. The former one the cylindrical nanopores are connected through lateral channels and the latter one has regularly connected silica nanopores. The morphology and textural properties of the pores in these materials can be easily tuned by modifying the synthesis parameters, including the choice of surfactant or SDAs. SDAs such as quaternary ammonium halides, alkylamine, poly(ethylene oxide), and block copolymers have been reported so far for the preparation of mesoporous materials

with various structural and textural properties [6]. These different SDAs can form a lyotropic liquid crystal of phases in different orientations such as cubic, hexagonal, and lamellar, which in turn changes the pore structure of the final synthesized material. Mesoporous materials are usually classified into silicon-based and nonsilica-based mesoporous materials. Nonsilica-based mesoporous materials such as titania, zirconia, niobium oxide, and manganese oxide of transition metal oxides have been reported to be prepared based on the sol-gel method. Because of the transition state properties, these transition metal oxides mesoporous materials could be used for catalyst application [7]. However, these kinds of mesoporous materials are susceptible to hydrolysis and redox reactions. Also, the calcination of these materials may cause phase transitions and breakdown of the structural integrity which makes it difficult to remove the templates and create porosity in the final material [7, 8]. Hence, these factors make the nonsilicon-based mesoporous metal oxide materials less attractive to many researchers, and therefore, this review paper focuses on the preparation of silicon-based ordered mesoporous materials.

There are various techniques reported to prepare ordered mesoporous silica materials such as the sol-gel method, microwave-assisted technique, and chemical etching method [7, 9]. The microwave-assisted techniques have the advantage of rapid synthesis techniques but at the expense of disruption of some pore structures. The chemical etching technique requires selective chemical etchant and sometimes the etchant disturbs the pore structure. In addition, the mesoporous materials prepared via the chemical etching technique have been reported to have a higher cell cytotoxicity effect for biomedical applications compared to the other preparation techniques [10]. Therefore, for a specific application of mesoporous materials, a particular method of synthesis should be used. Among those techniques, the sol-gel process is the versatile method extensively used to prepare nanostructured mesoporous materials as it provides the advantages of low-temperature processing and easy control of synthesis parameters. It also allows incorporation of functional groups into the final material providing additional prosperity and functionality making the final material suitable for a specific application. This review article briefly discusses the sol-gel process and the sol-gel chemistry of silica as well as the origins and mechanisms of formations of mesoporous silica materials in two morphologies powder and thin film forms. Hence, this review paper briefly points out that a good understanding of the chemistry of sol-gel silica, and the effects of the reaction parameters are required to tune the structure of mesoporous silica for various applications. To the best of my knowledge, there is no such type of published review paper briefly narrating the advantages and limitations of current methods to prepare mesoporous silica in different morphologies including the recent electrochemically assisted self-assembly (EASA) method.

As the name implies, the overall sol-gel process usually involves two stages: precursor initially arranged to form inorganic networks of oligomeric intermediates, a sol, and intermediates further linked to form a 3D crosslinked network, a gel. The sol-gel preparation process, also called the modified Stober

method is based on the soft templating approach, whereby, a supramolecular self-assembled arrangement of a SDA like surfactants is used to create the appropriate pore in the final material [1, 11, 12]. Stöber et al. [13] were the first group of researchers to synthesize monodispersed silica particles from tetra-alkyl silicate precursors in a mixture of alcohol, water, and ammonia as a catalyst. Later on, modification of the method was done by Grün et al. [14] where they introduced a cationic surfactant as a SDA in the reaction mixture and obtained mesoporous silica particles [12]. Zhao et al. [5, 15] used different surfactants such as alkyl polyethylene oxide of $C_{16}EO_{10}$, $C_{18}EO_{10}$, and triblock poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) copolymer surfactants to prepare SBA-11(cubic), SBA-12(3-d hexagonal), and SBA-15(hexagonal) mesoporous materials. Careful manipulation of the sol-gel processing parameters such as temperature, reaction time, precursor concentration, pH, type, and concentration of surfactant can be made to prepare the different structures of mesoporous materials [16, 17]. Also, the ratio of polyethylene oxide to polypropylene oxide (EO/PEO) in the copolymer can affect the structure of the silica mesophase formation, a lower ratio of this moiety favors the formation of a lamellar structure while a higher ratio of EO/PEO promotes the formation of cubic mesostructure silica. Furthermore, the particle size and morphology of mesoporous silica can be tuned by varying the reaction parameters, through the use of cosolvents, cosurfactants, or by adding various inorganic salts [18]. The optimum temperature to prepare good quality ordered silica gel is reported to be between 35°C and 80°C [15].

Besides, the preparation of mesoporous silica powder, an ordered mesoporous silica thin-film synthesis method is also discussed in the article. Recently, nanostructured ordered porous thin-film materials comprising of high surface area and large pore volume have become promising materials for a wide area of applications such as energy, health, sensors, and separation [19, 20]. Ordered and vertically aligned mesopore channels to the film surface are more sensitive than their nonordered homologues because of a faster diffusion process through the regular mesostructured, which makes them an ideal material for the abovementioned areas of applications. Ordered porosity here means the pore channels are uniform and regularly arranged, whereas in disordered porosity, the pore channels are distorted. Because of the abovementioned reasons for interest in mesoporous silica thin-film materials [19], simple, fast, and economical preparation of monodispersed, well-ordered, cracks, and aggregates free, straight-oriented channels of mesoporous thin-film materials has been an interesting area of research. There are three main (among others) methods of preparation of nanostructured mesoporous silica thin-film materials starting from a sol-gel solution such as the evaporation induced self-assembly (EISA) method [21], EASA [19, 22] method, and the Stober solution growth method [23]. Each of the methods has its advantages as well as limitations as elaborated briefly in Section 4. Among these, the EASA method is reported to be the simple, fast, and economically feasible method to synthesize monodispersed well-ordered cracks and aggregate free-ordered porous thin-film materials.

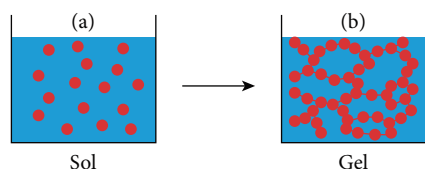


FIGURE 1: Diagram of sol (a)-to-gel (b) transition.

Despite the simplicity and easiness of the EASA method, it has not been well explored and further advance is needed to make use of its full potential advantages. Hence, this review paper paves the way for future research and development in the area.

2. The Sol–Gel Process

The sol–gel method is one of the well-developed synthesis techniques to prepare nanostructured materials. It is a widely employed method in the field of nanotechnology for the bottom-up preparation of nanostructured metal oxides as well as mixed oxide composites. This method has the advantages of relatively low-temperature processing and the possibility for easy control of processing parameters to prepare desirable materials, such as ceramics and glasses in the form of powders, thin films, fibers, xerogels, or aerogels [24]. The method consists of two general reaction steps, such as hydrolysis and condensation. The first stage is hydrolysis, where the precursor solution and solvent undergo a hydrolysis reaction. The second stage is the condensation reaction which takes place between the hydrolyzed species leading to the formation of bonds between two metals bridged by an oxygen atom.

The sol and gel formation involves the arrangement of inorganic networks through the formation of a colloidal suspension (sol) and the gelation of this suspension to form an inorganic network in a continuous liquid phase (gel) [25]. A sol (Figure 1(a)) is a stable dispersion of colloidal particles or polymers in a solvent. The short-range interaction forces, such as electrostatic repulsion force dominate over the van der Waals attractive force, which is responsible for the stability of the solid particles in the colloidal phase (sol) while the gravitational force on the particles is negligible. A gel (Figure 1(b)) is a 3D continuous network, which encloses a liquid phase, in a colloidal dimension. Thus, at the gelation stage, bigger continuous network formation occurs via a polycondensation reaction. Besides, liquid entrapping within the solid network takes place leading to an expansion of the solid phase, and an increase in the viscosity of the system, as illustrated in Figure 1 [26].

Beyond gelation, further chemical reactions and structural rearrangements take place in the wet gel leading to a phenomenon that increases the stiffness of the gels called aging. Aging is due to the presence of reacting species in the wet gel which undergoes a condensation reaction resulting in a more cross-linked network formation that strengthens the network and stiffens the gel [27].

2.1. The Sol–Gel Chemistry of Silica. Silicon dioxide also called silica is a crystalline or amorphous solid formed from either a regular or an irregular arrangement of SiO_2 repeating units. It has been widely prepared by the sol–gel

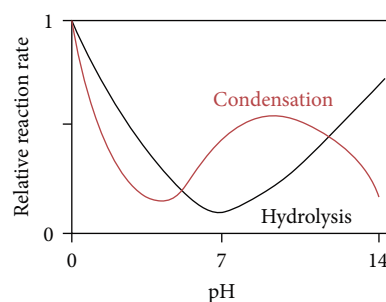
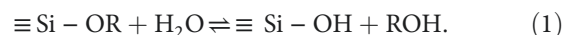


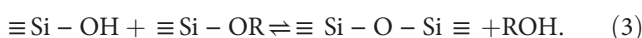
FIGURE 2: pH dependence of silica alkoxide rate of hydrolysis and condensation reaction, reproduced from [25] with permission from John Wiley & Sons, Inc.

processing method, in which a precursor solution, solvent, and acid or base catalyst are mixed to obtain the final material via a polycondensation reaction. The most common precursors used for the synthesis of nanostructured silica materials using the sol–gel process are silicon alkoxides such as tetramethoxysilane, abbreviated “TMOS,” and tetraethoxysilane, abbreviated “TEOS” [27]. The sol–gel process of silica is based on two reaction steps. The first step is a hydrolysis reaction (Equation (1)) that takes place between the silica precursor solution and a solvent. It involves the replacement of the alkoxide groups ($-\text{OR}$) with hydroxyl groups ($-\text{OH}$) and releases the corresponding alcohol (ROH) molecules. The second process is a condensation reaction that occurs between two silanol groups ($\text{Si}-\text{OH}$) (Equation (2)) or between a silanol group ($\text{Si}-\text{OH}$) and an alkoxide Equation (3)) to produce siloxane bonds ($\text{Si}-\text{O}-\text{Si}$), and water and alcohol as by-products, respectively [28].

Hydrolysis:



Condensation:



The sol–gel method of silica preparation is generally carried out under basic or acidic pH as in neutral conditions the reaction is very slow. The reaction rate and mechanism of hydrolysis and condensation of the sol–gel silica system are dependent on the pH of the reaction condition, as illustrated in Figure 2. This can be elaborated by the point of zero charges (PZC). The PZC is a pH at which the net charge of the particle surface is zero, for silica lies between pH 1.5 and 4 [11]; hence, decreasing the pH of the solution below PZC leads to positively charged siliceous species and increasing the pH of the solution above the PZC creates a negatively charged siliceous species. This has consequences on the rate and mechanism of the hydrolysis and condensation reaction steps and, in turn, controls the rate of gelation and the ultimate network structure.

Thus, under an acidic medium hydrolysis is fast, and condensation is relatively slow which leads to slow nucleation.

TABLE 1: Structure of different structure-directing agents.

SDA	Cationic surfactant	Nonionic triblock copolymers
Trade name	Cetrimonium bromide (CTAB)	Pluronic
Chemical structure	$\text{H}_3\text{C}(\text{H}_2\text{C})_{15}\text{N}^+(\text{CH}_3)_3 \text{Br}^-$	$\text{H} \left[\text{O} \text{---} \text{CH}_2 \text{---} \text{CH}_2 \right]_x \left[\text{O} \text{---} \text{CH}_2 \text{---} \text{C}(\text{CH}_3) \text{---} \text{CH}_2 \right]_y \left[\text{O} \text{---} \text{CH}_2 \text{---} \text{CH}_2 \right]_z \text{OH}$

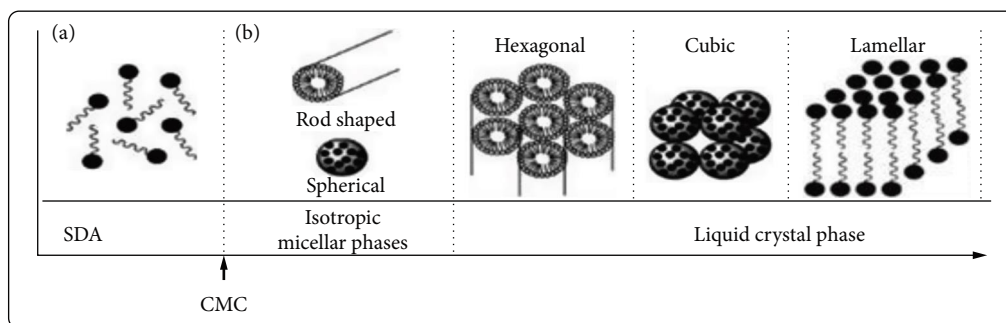


FIGURE 3: Organization of surfactants (a) into (b) micelles and different structures of (c) lyotropic liquid crystal phases [1].

This fact leads to fewer siloxane bond formation and a high concentration of silanol groups, hence ultimately leading to the formation of a linear inorganic network. Under the basic reaction conditions, hydrolysis is slow, and condensation is fast which leads to fast nucleation, leading to highly branched polymeric species [1, 25].

After the gelation process, further polymerization reactions and physical rearrangements continue in the silica gels. The process is called aging. During aging, the continuous condensation reaction creates a new bridging bond, such reaction stiffens and strengthens the network. Aging is due to the following processes:

- (i) The presence of condensable or even precursor monomers in the wet gel eventually condenses to the existing network resulting in gradual changes in the structure of gels.
- (ii) The flexibility of the original gel network allows neighboring Si—OH or Si—OR groups to approach each other to undergo a condensation reaction causing the expulsion of liquid and consequently contraction of the network [29].

Depending on the requirements of the final materials, the wet gel may undergo further processing techniques such as coating, spinning, evaporation, and careful extraction of solvent to obtain, film, fiber, xerogel, and aerogel products, respectively.

3. Mechanism of Formation of Nanostructured Mesoporous Silica Materials

The sol–gel preparation of mesoporous silica materials can be carried out in the presence of SDAs, such as surfactants, which tend to associate with micellar structures in an aqueous medium over which the inorganic species condenses

around to form an inorganic network. The removal of the template from the system creates a pore in the final silica material. The template can be eliminated by either calcination or solvent extraction. It is possible to obtain mesoporous materials with different structural and textural characteristics by varying the type and chemical structure of the templating agents.

There are different types of SDAs such as cationic, anionic, or nonionic surfactants, and nonionic triblock copolymers. An example of such SDAs and their chemical structure is shown in Table 1.

Surfactants are amphiphilic compounds composed of both a hydrophilic head and a hydrophobic tail (Figure 3(a)). In aqueous media, at a certain concentration called critical micellization concentration (CMC), surfactants self-organize into a structure called micelles. This micelle initially has spherical symmetry and at a higher concentration of micelles or through cooperative interaction with the inorganic precursor, it can change to a lyotropic liquid crystal of different phases, such as cubic, hexagonal, and lamellar (Figure 3) [1]. Hence, consequently, the inorganic precursor can condense around the different structures of lyotropic liquid crystal phases, like a skin around the body of the template, to produce porous silica with different textures and characteristics after the removal of the template.

The interaction between the organic part (surfactants) and the inorganic species (silica precursor) to drive the liquid crystal mesophase formation depends on the charge on the surfactant, S^+ or S^- , on the inorganic species, I^+ or I^- , and on the presence of mediating ion, i.e., M^+ , M^- , or M . All mutual interaction enabling Coulombic attractions, i.e., S^+I^- , S^-I^+ , $S^+M^-I^+$, or $S^-M^+I^-$, hydrogen bonding, i.e., S^0I^0 or S^0 (MI) are possible. When the sol–gel synthesis is made under basic reaction conditions (pH above PZC of silica), where silica has a negatively charged surface, a cationic surfactant can be

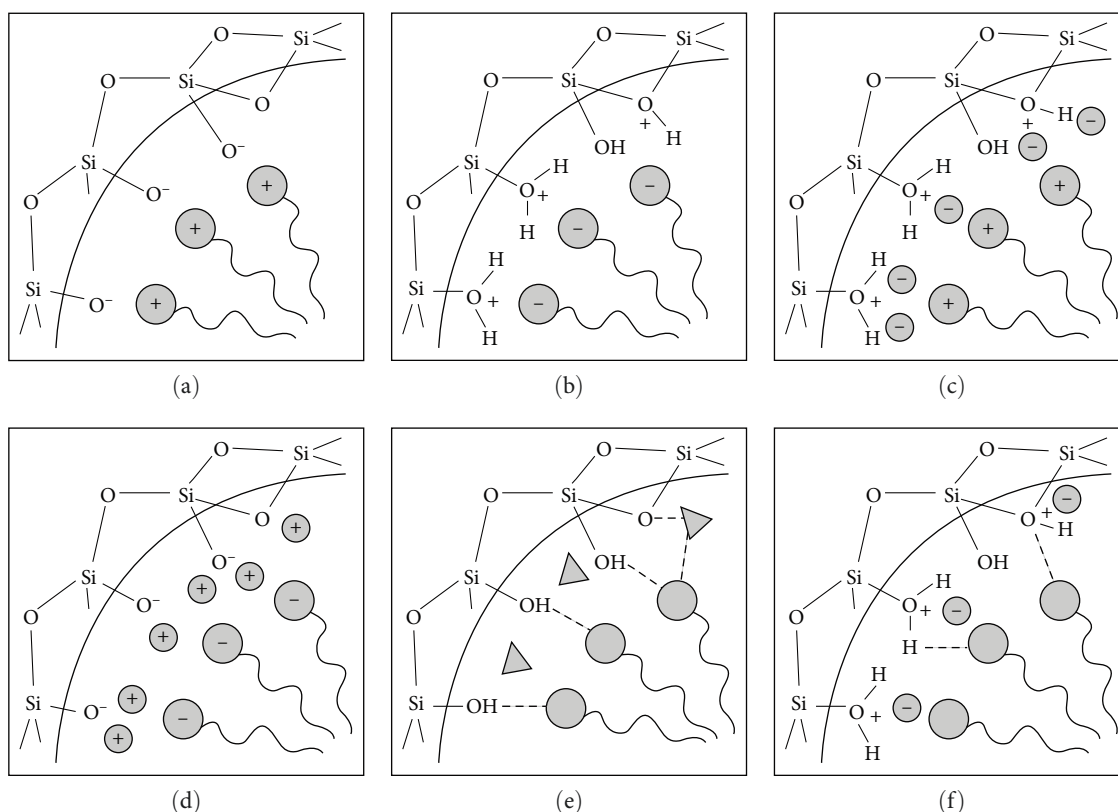


FIGURE 4: The possible interaction mechanisms between the inorganic species, the head group of the surfactants, and the mediating ion, under (a) acidic reaction condition, S^+I^- synthesis pathway, (b) basic reaction condition, S^-I^+ synthesis pathway, (c) in the presence of M^- mediating ion, $S^+M^-I^+$ synthesis pathway, (d) M^+ mediating ion, $S^-M^+I^-$ synthesis pathway, and at pH equal to PZC of silica reaction conditions, (e) S^0I^0 synthesis pathway, or (f) $S^0(MI)^0$ where a mediating ion (M) is used, reproduced from [30] with permission from John Wiley & Sons, Inc.

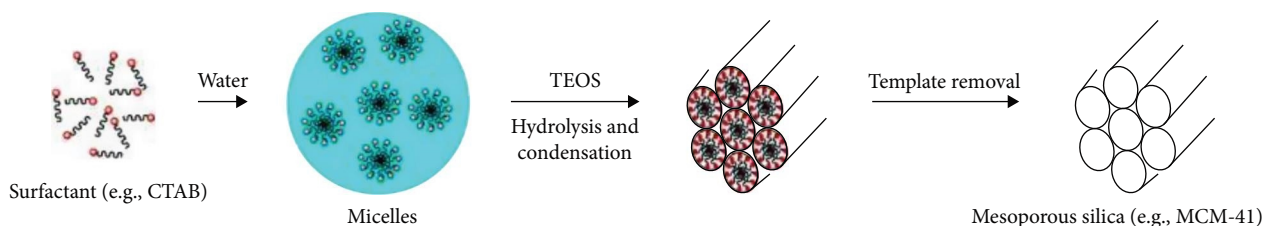


FIGURE 5: The schematic diagram for the formation of mesoporous silica [12].

used as a SDA, and the synthesis pathway is referred to as S^+I^- (Figure 4(a)) [30, 31].

Under an acidic reaction medium, where silica has a positively charged surface, an anionic surfactant can be used as a SDA, the synthesis pathway is referred to as S^-I^+ (Figure 4(b)). Otherwise, a mediator ion (M^+ or M^-) can be used to create a possible interaction between the surfactant (S) and inorganic species (I) (Figures 4(c) and 4(d)). In all these pathways, electrostatic interaction is the dominant force of interaction. Moreover, at pH around the PZC of silica, where the surface charge of silica is zero, nonionic surfactants or triblock copolymers, can be used as a SDA via a dominant hydrogen bonding interaction between surfactant (S) and the inorganic specie (I), the synthesis pathway is referred to as S^0I^0 (Figure 4(e)) or $S^0(MI)^0$ (Figure 4(f)) when a mediator ion M is used [30].

In short, the process of mesoporous silica preparation based on the sol-gel technique involves the hydrolysis of precursor solution in the presence of the template around which the hydrolyzed silanol group condenses to form siloxane linkage ($Si-O-Si$) of an inorganic network. Removal of the template from the system via either calcination or solvent extraction produces a porous silica material. The short schematic diagram of this process is depicted in Figure 5.

3.1. The Sol-Gel Synthesis of SBA-15. Santa Barbara Amorphous type material or SBA-15 silica has a 2D hexagonal structure of pores. It was first developed by researchers at the University of California at Santa Barbara. It exhibits a well-defined pore structure with monodispersed pore sizes combined with a high surface area which attracts a wide

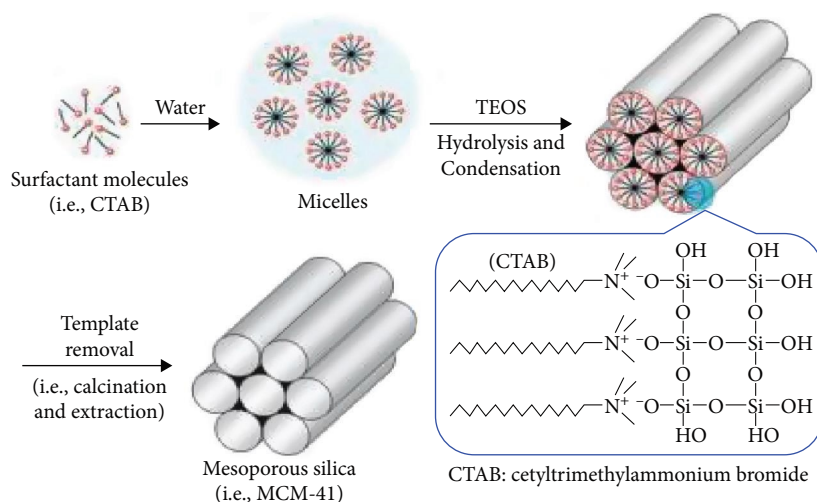


FIGURE 8: A representative scheme of the formation mechanism of MCM-41, reproduced from the Royal Society of Chemistry [37].

MCM-41 silica is done under basic reaction conditions, using alkoxide silica as a precursor solution and cationic surfactants, such as cetyltrimethylammonium bromide (CTAB) as a SDA. CTAB is a cationic surfactant that can interact with the negatively charged siliceous species through the electrostatic attraction of the S^+I^- mechanism, which cooperatively assembles into a liquid crystal of hexagonal arrays over which the inorganic species condenses to form a hexagonal structure of cylindrical mesoporous silica after removal of the template through calcination or solvent extraction [34]. This method offers the possibility to control the particle size and morphology of mesoporous silica by changing the concentration of reagents, reaction temperature, as well as type, and concentration of the SDA, etc. Nevertheless, pure mesoporous silica MCM-41 has poor hydrothermal stability due to its thin pore wall structure. That means relatively low-temperature thermal treatment under the steaming condition may destroy the ordering of pure silica MCM-41 within a short time [26], which limits its applications in hot aqueous conditions. However, the hydrothermal stability of the mesoporous silica MCM-41 structure can be improved by the following strategies:

- (1) Addition of various salts to the synthesis gel.
- (2) Hydrothermal treatments and increasing the crystallization time by which the level of silica condensation within the mesoporous framework increases leading to an improvement of the thickness of the pore walls of the silica framework [35].

A good example of the addition of salt to improve the hydrothermal stability of the silica framework is the grafting of Al onto pure silica MCM-41. The deposition of Al onto the surface of silica reduces the silanol groups to form Si—O—Al bonds on the surface or near-surface region, which protects the siloxane (Si—O—Si) bonds from steam-induced hydrolysis [35]. Hence, the addition of Al in the pure silica framework improves the overall integrity of the MCM-41 structure.

A typical room temperature sol-gel synthesis of MCM-41 involves the addition of a precursor solution into the

dissolved cetyltrimethylammonium bromide (CTAB) in a basic medium followed by stirring the solution for 3 hr at room temperature. Eventually, a white precipitate forms and is subject to washing with distilled water or alcohol and filtering to collect the precipitate. Followed by overnight drying at room temperature and removal of the template from the system can be done by calcination of the sample at 823 K for 15 hr [36]. A scheme of the formation mechanism of MCM-41 is depicted in Figure 8.

4. Sol-Gel Preparation of Nanostructured Mesoporous Silica Thin Films

Sol-gel process is the cheapest method to prepare a silicon dioxide thin film. It is based on the application of the sol solution on the surface of a substrate by different techniques such as dip, spray, spin, flow, and roll-coating. After solvent removal, the mesoporous thin film will be produced [38, 39].

Recently, nanostructured ordered porous thin-film materials comprising of high surface area and large pore volume have become promising materials for a wide area of applications such as energy, health, nanolithography, sensors, and separation [19, 20]. Because of the abovementioned reasons for interest in mesoporous silica thin-film materials [19], simple, fast, and economical preparation of monodispersed, well-ordered, cracks, and aggregates free, straight-oriented channels of mesoporous thin-film materials has been an interesting area of research. There are three main (among others) methods of preparation of nanostructured mesoporous silica thin-film materials starting from a sol-gel solution such as the EISA method [21], the Stober solution growth method [38], and the EASA method [22]. Each method has advantages and limitations that are elaborated further below. Beyond mesoporous silica, nonporous thin films of silica have also several applications in energy, electronics, photonics technology, etc. Several techniques have been developed to prepare thin films, including chemical vapor deposition, sputter deposition, epitaxial, and thermal oxidation. These techniques require a vacuum and high temperature for the

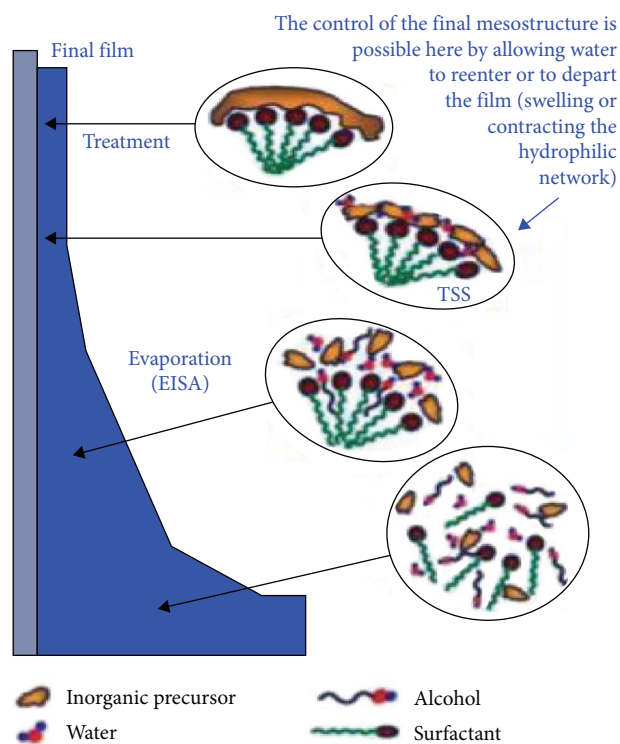


FIGURE 9: Mesostructured thin film formation via dip-coating, reproduced from [21] John Wiley & Sons, Inc.

deposition of the layer of thin films over the substrate surface, making them relatively expensive.

4.1. The Evaporation Induced Self-Assembly (EISA) Method.

The most widely used method is the “evaporation induced self-assembly” (EISA) process, as depicted in Figure 9. The method was first reported by Yang et al. [39] and Lu et al. [40] and further developed by Grosso et al. [21]. The formation of the mesoporous thin-film material via the EISA method is based on a dilute sol solution, involving the mixing of the sol-gel precursor solution, solvent, and catalyst together with a SDA (e.g., cationic, anionic, or nonionic surfactants and block copolymers). The solution is then cast onto a substrate (via dip, spin, or spray coating), followed by evaporation of the solvent, and removal of the template produces the final mesoporous thin-film material [21, 41, 42]. Initially, the concentration of the surfactant in the solution is diluted and heat treatment to evaporate the solvent increases the concentration of the surfactant in the solution. This increase in the concentration of the surfactant drives the self-assembly of the organic-inorganic hybrid into a liquid crystal (LC) phase. Subsequently, the concentration of the surfactant increases beyond the CMC at which a micelle is formed. An organized LC mesophase is formed between the organic and inorganic entities in which the inorganic network is not fully condensed. Here, the solvent molecules in the film equilibrate with the relative humidity (RH) of the environment, and adjustment of RH can be made to tune the structure of the final material. Finally, the inorganic species condenses to form a stabilized mesostructured network, and the porosity is generated via the removal of the template [3]. Generally, it has four main processing steps illustrated in Figure 9 [21].

Step 1: The initial sol solution contains the silica precursor, the SDAs, and the solvent. It has a slow rate of condensation.

Step 2: Solvents removed by evaporation and CMC of surfactant molecules are reached to form a micelle

Step 3: The evaporation is complete; and at this stage, tuning of the final film can be made by adjusting the RH.

Step 4: Condensation of the inorganic species and stabilization of the mesostructured silica network

There are critical processing parameters that determine the structure of the final thin film, such as the surfactant/precursor ratio, the chemical nature of the inorganic precursor solution, and the RH at which the evaporation takes place [21]. These parameters sum up into two categories: (i) the chemical parameters, related to the nature and quantity of surfactant and inorganic precursor and (ii) the processing parameters related to the evaporation process which is the diffusion of alcohol, water, and catalysts to or from the film [43, 44]. The knowledge of the chemistry and the isoelectric point of the inorganic species in solution is important to tune the electrostatic interaction between the organic-inorganic species. For instance, near the isoelectric point of the inorganic species neutral surfactants are required to favor the mesostructure formation. Above the isoelectric point, the inorganic species carry a net negative charge, and therefore cationic surfactants favor the mesostructuring and vice versa [21, 43]. The processing parameters play a role once the sol solution is deposited onto the substrate. For instance, a diluted sol solution favors the fast evaporation of volatile species leading to the formation of uniform mesostructures, whereas a more viscous sol solution may retard the evaporation of volatile species leading to the formation of intermediate multiphase mesostructures [3, 45].

The EISA technique is a simple, fast, and efficient method for the preparation of crack-free uniform and controllable thickness films [3, 21]. Nevertheless, it has drawbacks in the alignment of the mesopore channels. The final thin films are horizontally aligned to the surface of the substrate which is a limitation in mass transport applications [46, 47]. Besides, it requires a flat surface of the substrate for the proper coating of the thin film [14, 48]. Deposition onto nonplanar surfaces is not suitable via simple sol-gel coating techniques. Another alternative method to prepare silica thin film from direct sol-gel solution is the Stober solution growth method and electro-assisted deposition techniques.

4.2. Nonporous and Porous Silica Film Preparation via Stober Solution Growth Method.

The Stober solution growth method is the best alternative method to prepare thin-film materials. It involves immersing the substrate into the sol-gel reaction mixture containing precursor solution and solvent under base (ammonia) catalyzed conditions. For the efficient growth of the thin film over the substrate, an attractive interaction force needs to be created between the hydrolyzed sol solution and the substrate. Initially, in the reaction mixture, primary particles are

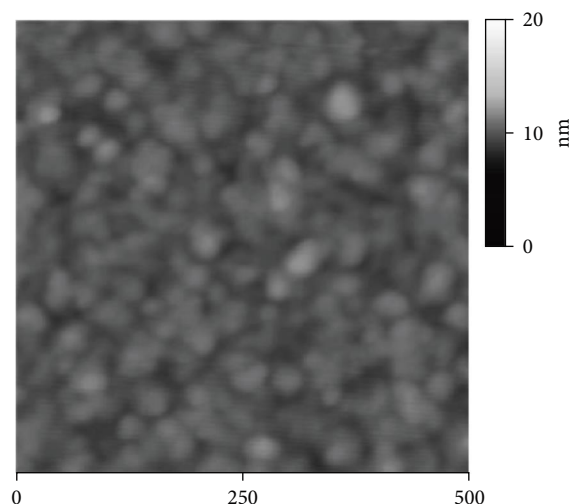


FIGURE 10: AFM image of silica thin film over silicon substrate [49].

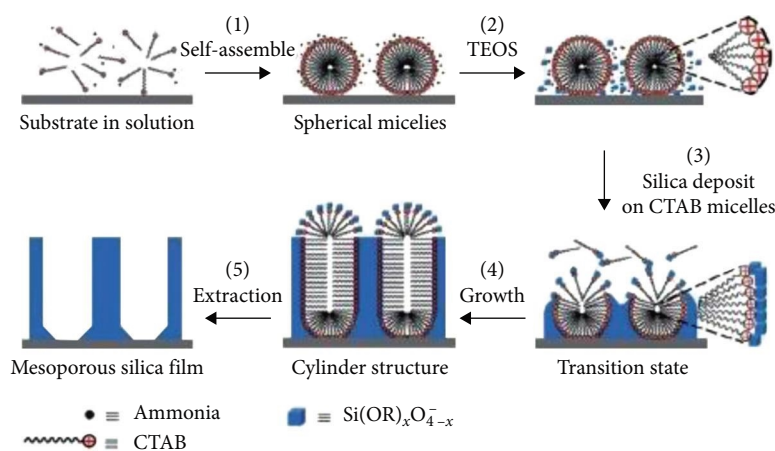


FIGURE 11: Illustration of ordered mesoporous silica film formation via the Stober-solution growth method, reproduced from [23] John Wiley & Sons, Inc.

formed and combined to form an aggregate until a size where electric double layer interaction prevents further agglomeration [38]. After this stage of surface reaction, limited growth occurs over the surface of the substrate and the initially formed irregular-shaped particles become more monodisperse by condensation of hydrolyzed species and small oligomers [38, 49]. The grown layer thickness is relatively difficult to control from direct solution growth. However, it can be controlled by introducing a known number of particles with a known radius into the reaction mixture which serves as a nucleation site that grows and subsequently condenses to form a layer of monodisperse silica over the substrate surface. An example of an AFM image of a silicon dioxide thin film grown on a silicon substrate is depicted in Figure 10. Silica deposited on bare Si (hydrophilic surface) substrate for 960 min showing smooth and uniform crack-free film.

The second method to prepare mesochannel thin films is the Stober solution growth method. This method is based on immersing the substrate into the solution containing surfactant, inorganic precursor solution, and solvent, under basic

media (i.e. ammonia), also called the Stober solution [23]. The basic pH promotes the condensation of silanols into siloxane bridges (Si—O—Si). Using this method, it is possible to prepare perpendicularly oriented mesoporous thin films on various substrates such as indium tin oxide (ITO), silicon nitride, and silicon substrates [50].

This method is based on five main process steps, illustrated in Figure 11.

- Step 1: Surfactant adsorption onto the substrate (through hydrogen bonding, π - π , van der Waal, and electrostatic interaction) surface and micelle formation over the substrate surface.
- Step 2: Precursor solution addition together with solvent and ammonia, at this stage, the precursor solution hydrolyzes to associate around the micelle surface through electrostatic interaction.
- Step 3: The surfactant-precursor association undergoes a structural transition from spherical to a cylindrical structure via an interaction (through

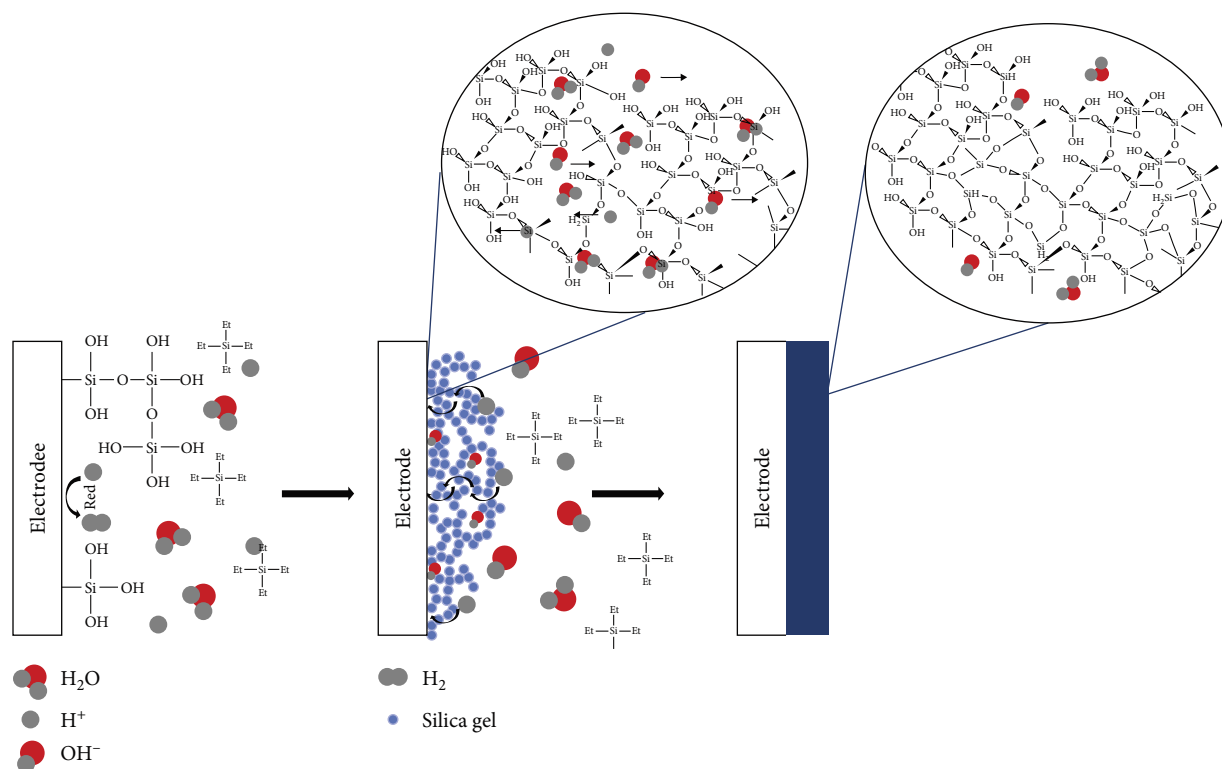


FIGURE 12: Schematic diagram of silica film growth via electro-assisted mechanism [51]. The conventional sol-gel coating process has limitations on the preparation of crack-free thicker ($>1\ \mu\text{m}$) silica thin films. But electrochemically assisted technique offers to prepare thicker and uniform films due to the generation of hydroxide ions which creates an additional driving force for catalytic condensation reaction leading to the concomitant formation of thicker (ca. $10\ \mu\text{m}$) silica thin film over the substrate surface [48, 53].

ammonia-mediated hydrogen bond formation between the adjacent micelles and the inorganic species interaction) that lowers the curvature energy of the micelles [23].

- Step 4: Condensation of newly hydrolyzed precursors around the SDA and growth of the films.
- Step 5: Removal of a template to get the final mesoporous silica thin film [23].

It is an effective method to prepare crack-free, ordered mesoporous channels perpendicularly oriented to the plane of the substrate surface with possible control of the film thickness via tuning the reaction parameters, including ethanol to water ratio, surfactant to precursor ratio, film growth time, ammonia concentration, and the reaction temperature [23, 48, 51]. However, it relatively has a limited choice of substrates, (needs an active surface for successful attractive interaction with the SDAs) as well as the need for a flat surface for the successful growth of the thin film on the substrate.

4.3. Nonporous and Porous Silica Film Preparation via an Electrochemical-Assisted Method. The electrochemical-assisted sol-gel deposition of thin films is a recent technique, which offers deposition of a wide range of materials, such as silica, titania, and zirconia, as well as nanocomposites on conductive substrates [52]. This method is based on the generation of hydroxide ions via applied cathodic potential near the electrode

and solution interface which catalyzes the condensation of the hydrolyzed sol solution leading to the concomitant formation of an inorganic network over the surface of the substrate, as depicted in Figure 11 [52]. The preparation of silica thin film using this method involves immersing the electrode of an electrochemical cell in a solution containing a mixture of the precursor solution (silicon alkoxide), solvent, an acid, and supporting electrolyte. With the application of sufficient cathodic potential hydroxide ions are generated close to the surface of the electrodes via the reduction of protons or water according to the following reactions [52, 53]:



This production of hydroxide ions increases the pH of the solution near the substrate solution interface, while the bulk solution remains acidic. This site-selective increase in pH has the advantage that preventing the formation of silica particles in the bulk solution. This increase in pH due to hydroxide ion generation triggers the polycondensation of the hydrolyzed alkoxy silane solution leading to the concomitant formation of silica thin films over the substrate surface [52]. The film thickness can be monitored by the electrochemical parameters (time of deposition, applied potential) and a crack-free uniform silica thin film can be produced

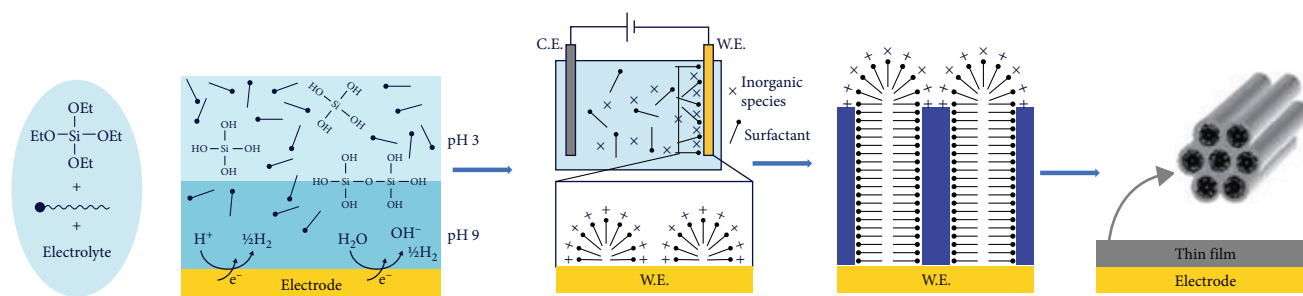


FIGURE 13: Schematic representation of electrochemically assisted self-assembly synthesis of mesoporous silica thin film [20].

with a thickness of up to ca. $10\ \mu\text{m}$ [53]. An example of a schematic diagram of silica thin film formation is shown in Figure 12.

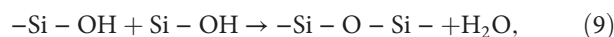
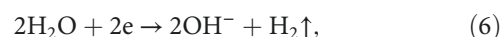
EASA is a recent method of mesoporous thin film preparation that allows the synthesis of ordered, and vertically oriented thin films normal to the plane of the substrate surface as first realized by Walcarius et al. [19] and Goux et al. [22]. It has the advantage that providing growing thin films in conducting surfaces (including nonflat or complex hidden surfaces) which is difficult to obtain using the common sol-gel coating (dip, spin, spray) techniques [51, 54]. The principle is based on the application of a cathodic potential to an electrochemical cell immersed in a hydrolyzed sol solution in the presence of a template. The applied potential generates hydroxide ions near the substrate/electrode interface increasing the pH of the solution, consequently triggering the polycondensation reaction and concomitant formation of film onto the electrode surface. Finally, porosity in the mesostructure thin film is created by the removal of the template from the system, as illustrated in Figure 12 [19, 20, 41, 51]. It is different from the common electrochemical deposition process because the film growth is not an electrochemical step but is driven by the hydroxide catalyst generated by the applied cathodic potential [55]. The basics of pore formation in the inorganic network are based on the introduction of SDAs (i.e., surfactants) in the solution.

A popular example of mesoporous silica thin film which can be prepared by EASA is MCM-41. Due to its well-defined and tunable pore size, and easiness of functionalization, this material has received much research attention for potential applications in electrochemistry. The well-known SDA used in the preparation of mesoporous silica MCM-41 is cetyltrimethylammonium bromide (CTAB) surfactant, as reported by Walcarius et al. [19]. It is a quaternary ammonium cationic surfactant. At first, the CTAB surfactant self-assembles into spherical micelles onto the substrate surface, and this process is observed to be supported by the application of cathodic potential [51, 55]. Next, the hydrolyzed silica precursor (silanol) interacts with the spherical micelle of the surfactant which cooperatively undergoes a lyotropic liquid crystal of mesophase of cylindrical symmetry, around which the inorganic species condenses leading to concomitant growth of mesoporous silica thin film [3]. The removal of the surfactant molecules from the system leads to the formation of a pore in the inorganic network. This process is depicted in a schematic diagram in Figure 13.

Generally, the EASA process is based on the following four basic steps:

- Step 1: Mix precursor solution, solvent, and surfactants with an electrolyte (to facilitate the conductivity of the solution).
- Step 2: Immersing the electrochemical cell into the solution, at this stage, the surfactant molecules assemble into a micelle over the surface of the electrode and associate with the inorganic species via cooperative interaction (through hydrogen bonding, electrostatic, van der Waals interaction).
- Step 3: The application of cathodic potential induces the liberation of hydroxide ions, which increases the pH of the solution and catalyzes the polycondensation reaction to form the inorganic network around the surfactants.
- Step 4: Removal of the template produces the final mesoporous silica thin film [34, 37].

A typical mesoporous silica thin film preparation using the EASA method involves immersing the electrode of the electrochemical cell into a mixture of a solution containing precursor solution, template (e.g., surfactants), solvent, and supporting electrolyte [55]. The electrodes can be of conducting planar or nonflat surfaces with sizes ranging from micro- to macro-meter areas [20]. In an aerated aqueous media using alkoxy silane as a precursor, the process can be written by the following four basic reactions [30, 33]:



where $-\text{SiOH}$ and $\text{surf}-\text{OH}$ refer to the silanol groups in the hydrolyzed silane molecule and the hydroxide group on the electrode surface, respectively. There is evidence that the cathodically applied potential helps not only to increase the pH of the solution but also helps the cooperative assembly of surfactants onto the electrode surface [20]. Such assembly is claimed to prepare mesoporous silica channels

grown perpendicular to the plane of the electrode surface with uniform thickness on various electrode surfaces (gold, carbon glass, platinum, copper indium titanium oxide, stainless steel, etc.) [56–58].

The thickness of the film can be tuned by varying the deposition parameters such as deposition potential and time, precursor concentration, and pH of the solution [42, 56, 57].

4.3.1. Effect of Sol pH. An optimum pH of the initial sol is vital to hydrolyze a sufficient amount of the precursor for polycondensation and the concomitant growth of the films. Cheng et al. [56] demonstrated the formation of a silica thin film on an indium titanium oxide (ITO) substrate using TEOS as a silica precursor at different pH ranges. They found that the optimum pH for uniform and ordered mesoporous silica formation is 3. At pH below 2, condensation of silica occurs in the bulk solution leading to the formation of silica particles, which limits the formation of uniform films on the substrate. At pH near 4.0, the hydrolysis of TEOS is very slow to produce a sufficient amount of hydrolyzed silanol for the polycondensation reaction. Thus, no mesoporous thin films can be formed at a pH near 4.0 [56].

4.3.2. Effect of the Sol Composition. The sol composition, particularly the surfactant/precursor molar, is an important factor to be optimized for the formation of structured and highly ordered mesoporous silica films. Goux et al. [22] demonstrated the concentration dependence of precursor and surfactant solution for the formation of aggregate free-oriented mesoporous silica thin films using TEOS precursor solution and CTAB surfactant on ITO substrate. They found that the thickness of the mesoporous silica formation is highly dependent on the concentration of the precursor solution. They observed that increasing the alkoxide precursor solution in the range of 50–125 mM while keeping the surfactant/precursor ratio to 0.32, results in a linear increase of film thickness without the formation of aggregates [22]. However, increasing both concentrations of the surfactant as well as the precursor solution while keeping the ratio at 0.32 results in a heterogeneous thicker silica film but also the formation of aggregates. Nonetheless, this phenomenon is also dependent on deposition time and applied potential. Thus, at a higher concentration of the precursor solution and longer deposition time, it is possible to prepare thicker silica films but with the possible consequence of aggregate formations [22].

4.3.3. Effect of Applied Potential and Deposition Time. The application of an appropriate cathodic potential is required to generate the hydroxide ion at the electrode/solution interface that catalyzes the polycondensation of the hydrolyzed precursor solution. The source of hydroxide formation is either from a reduction of water or oxygen and in some cases from the supporting electrolytes. The application of the potential is also believed to help the self-assembly of surfactants over the surface of the substrate in a way that helps the growth of mesoporous thin films in a vertical direction [55]. Oriented mesoporous silica thin film can be formed at early times of electrodeposition applying an appropriate cathodic

potential. Walcarius et al. [19] demonstrated the effect of deposition time on the formation of mesoporous silica thin films using TEOS solution for silica precursor and CTAB surfactant on the various substrates (copper, gold, platinum, glassy carbon, and ITO). Increasing the deposition time results in the formation of thicker silica films but with an important consequence of the aggregate formation and hence the production of a heterogeneous thin film. This formation of silica aggregate at a prolonged deposition is due to the diffusion of OH⁻ ion formed at the solution interface to the bulk solution, a region far from the electrode surface where no active self-assembled surfactant is found. This results in polycondensation of the hydrolyzed silica in the bulk solution leading to the formation of aggregates made of silica spheres with a thickness larger than the mesoporous silica thin film thickness [19]. This unwanted aggregate of silica is not strongly attached to the mesoporous silica thin film and can be removed using Scotch tape [28]. Thus, according to Walcarius et al. [19] and Giordano et al. [55], only a few seconds (<30 s) of deposition times are optimal to obtain homogeneous, aggregate-free, mesoporous silica thin films of up to a thickness of ca.150 nm on various conducting supports (gold, copper, platinum, glassy carbon, and ITO). Although, the application of more negative potential results in thicker film production, the optimum potential required to deposit the film depends on the nature of the electrode materials [20, 58].

Typically, sol to surfactant solution ratio (using a cationic surfactant template and alkoxide precursor) is 0.32, and a 15 s deposition time at a pH of 3.0 (near the PZC of silica) and room temperature with a potential of ca.–1.3 V are reported as the optimal condition to obtain homogeneous ordered mesoporous silica thin films with appropriate removal of the template via solvent extraction [22, 56, 59].

5. Applications of Mesoporous Silica Materials

Mesoporous silica materials have attracted great scientific interest for various applications due to their unique characteristics. Structural properties including uniform and tunable pore size (within the range of 2–6 nm), uniform and tunable morphology, high surface area (700–1,000 m²/g), large pore volume (>0.9 cm³/g), biocompatibility as well as the possibility of surface functionalization [60]. Because of the abovementioned unique characteristics, these materials are suitable for applications commonly in adsorption and release purposes in drug delivery, environmental remediations, catalyst supports, energy conversion and storage, and electrochemical sensors. Increasing the effective surface area of a poorly water-soluble drug in contact with the dissolution medium has been known to enhance drug dissolution. This can be achieved by loading drugs onto ordered mesoporous silica materials, allowing for homogeneous and reproducible drug loading and release via stimulation of an external triggering force like pH, temperature, redox potential, photoirradiation, etc. [61]. Silica materials are generally nontoxic, biodegradable, and biocompatible to be used as carrier materials for controlled drug loading and release. However, it is reported that unreacted silanol groups found on the surface of the silica may interact with the surface of phospholipids of red blood cell membranes leading to

hemolysis [62]. Surface modification can be made on the silica nanoparticles so that the system reaches the correct target tissue mainly to treat a cancerous cell. With a tunable pore size, mesoporous silica can be loaded with anticancer agents, and their size and shape can be controlled to maximize cellular internalization. Curcumin-loaded mesoporous silica is reported by Kotcherlakota et al. [63] as an effective drug delivery system for cancer treatment. Curcumin-loaded amine-functionalized KIT-6, MSU-2, and MCM-41 mesoporous silica materials showed higher cellular uptake and inhibition of the cancer cell compared to pristine curcumin. For instance, mesoporous silica MCM-41 and SBA-15 are industrially produced by, W.R.Grace, Nanocompositix and Glantreo companies for commercial application as targeted drug delivery agents to encapsulate active pharmaceutical ingredients, as well as for catalyst support.

Mesoporous silica nanoparticles are also reported to be suitable candidates for environmental remediation applications such as heavy metal ions and phosphate removals from water and soil as well as in carbon dioxide and volatile organic compound capture from polluted air. Nasreen et al. [64] applied mesoporous silica as an adsorbent for the removal of different heavy metals such as chromium, lead, mercury, and arsenic in aqueous media and found an adsorption potential between 71% and 99%. This indicates the potential of mesoporous silica materials for environmental remediation. Functionalization can be made to the mesoporous silica for selective adsorption of a certain component from a sample matrix. Due to excellent chemical stability, ease of their functionalization of the pore surface, and the possibility of incorporation of catalysts, porous silica materials have received great attention as catalyst supports. Due to the nature of narrow size distribution in MCM-41-type mesoporous silica, shape-selective catalysis is observed in the epoxidation of bulky alkene substrates using grafted mesostructures [65]. Grafting can be made onto the surface silanol group. The main benefit of using mesoporous silica as catalyst support is the possibility of mechanical separation of the products usually done via centrifugation. It will not damage the catalyst or the mesoporous framework so the catalytic material can be regenerated and recycled easily. Furthermore, mesoporous silica has become the best alternative to graphite as anode material for lithium-ion batteries, due to its high capacity, low discharge potential, abundance, high lithium-ion storage, and environmental friendliness [66, 67]. Because of the large volume changes encountered during the lithiation/DE lithiation process, this type of anode material is not practical yet. However, to overcome these challenges, researchers are designing a composite material in which the porous silica can be coated with a conductive layer. For example, anode material made from carbon-coated porous silica results in better stability and electrochemical conductivity [68].

Beyond the above areas of application, mesoporous silica thin film materials are widely studied for sensing applications to develop electrochemical sensors. The EISA method of mesoporous film production has drawbacks in that the final film has mesopore channels oriented parallel to the film surface, preventing the effective transport of molecules

across the film [19]. Contrary to EISA, EASA is an efficient method to prepare uniform thin films characterized by ordered and vertically aligned mesopore channels to the film surface. These are more sensitive than their nonordered homologues because of a faster diffusion process through the regular mesostructured, which makes them an ideal material to fabricate an electrochemical sensor device [69].

6. Conclusions and Outlook

In this paper, the sol-gel preparation of nanostructured mesoporous silica materials in powder and thin film morphology was elaborated. Sol-gel process is one of the most common bottom-up processing methods of nanostructured materials. It can produce materials with tailored properties for a specific need and applications. It is the most popular, simple, and economical method to produce nanostructured mesoporous metal oxides in different morphologies. Although it has numerous advantages, the sol-gel methods also have some limitations and challenges that need to be addressed. One of the drawbacks is the toxicity and cost of some of the precursors used in the sol-gel process. Another challenge is the high sensitivity to processing conditions, even small variations can significantly affect the final product. To overcome these challenges and further advance sol-gel-based technology, researchers are continuously exploring new methods and approaches. One such approach is the use of alternative precursors, such as natural products, to reduce the cost and environmental impact of the sol-gel process. In addition to this, a good understanding of the chemistry of sol-gel reactions, and the effects of the reaction parameters are required to better control and optimize the properties of the final material for specific needs and applications. This will lead to the advancement of more efficient and reliable sol-gel processes. Among porous materials, the sol-gel preparation of nanostructured metal oxide mesoporous materials is recently an active area of research. Due to high surface area, ordered structure, tunable pore size, and easiness of functionalization, nanostructured mesoporous materials have a diverse range of applications such as drug delivery, absorption, separation, catalysis, and energy conversion and storage. MCM-41 and SBA-15 are among the best-studied mesoporous silica materials which can be synthesized by using cationic surfactants and nonionic copolymers as SDAs, respectively. There are three main (among others) methods of preparation of nanostructured mesoporous silica thin-film materials starting from a sol-gel solution such as the EISA method, the Stober solution growth method, and the EASA method. The final thin film prepared using the above methods has common drawbacks in that the film has mesopore channels oriented parallel to the film surface, preventing the effective transport of molecules across the film, which limits it for mass transport applications. The other well-developed methods to prepare thin film materials include chemical vapor deposition, sputter deposition, epitaxial, and thermal oxidation. These techniques require a vacuum and high temperature for the deposition of the layer of thin films over the substrate surface which makes them relatively expensive processes. Among these, the EASA method is reported to be the simple, fast, and economically feasible

method to synthesize monodispersed well-ordered cracks, and aggregate free-ordered and vertically aligned porous thin-film materials as required for mass transport applications.

Despite the simplicity and easiness of the EASA method, it has not been well explored and it has opened up new possibilities for research and development to further advance and make use of its full potential advantages. Hence, this review paper paves the way for future research and development in the area.

Conflicts of Interest

The author declares that there is no conflicts of interest.

Acknowledgments

The author would like to acknowledge the European Commission for the sponsorship via the Erasmus scholarship program.

References

- [1] Z. A. Alothman, "A review: fundamental aspects of silica mesoporous materials," *Materials*, vol. 5, no. 5, pp. 2874–2902, 2012.
- [2] J. S. Beck, J. C. Vartuli, W. J. Roth et al., "A new family of mesoporous molecular sieves prepared with liquid crystal templates," *Journal of the American Chemical Society*, vol. 114, no. 27, pp. 10834–10843, 1992.
- [3] L. Mahoney and R. T. Koodali, "Versatility of evaporation-induced self-assembly (EISA) method for preparation of mesoporous TiO₂ for energy and environmental applications," *Materials*, vol. 7, pp. 2697–2746, 2014.
- [4] IUPAC, "Manual of symbols and terminology, appendix 2, part 1, colloid and surfaces chemistry," *Pure and Applied Chemistry*, vol. 31, no. 4, pp. 578–638, 1972.
- [5] D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, and G. D. Stucky, "Nonionic triblock and star diblock copolymer and oligomeric surfactant syntheses of highly ordered, hydrothermally stable, mesoporous silica structures," *Journal of the American Chemical Society*, vol. 120, pp. 6024–6036, 1995.
- [6] H.-P. Lin, C.-Y. Tang, and C.-Y. Lin, "Detailed structural characterizations of SBA-15 and MCM-41 mesoporous silicas on a high-resolution transmission electron microscope," *Journal of the Chinese Chemical Society*, vol. 49, no. 6, pp. 981–988, 2002.
- [7] S. Kumar, M. M. Malik, and R. Purohit, "Synthesis methods of mesoporous silica materials," *Materials Today: Proceedings*, vol. 4, no. 2, pp. 350–357, 2017.
- [8] F. Schüth, "Non-siliceous mesostructured and mesoporous materials," *Chemistry of Materials*, vol. 13, no. 10, pp. 3184–3195, 2001.
- [9] L. Jia-heng, Z. Jun, C. Yong-xi, and G. Li-ping, "Different synthesis methods for ordered mesoporous silicas and their characteristics comparison," *Journal of Wuhan University of Technology-Mater. Sci. Ed.*, vol. 18, pp. 1–4, 2003.
- [10] M. M. Ashour, M. Mabrouk, I. E. Soliman, H. H. Beherei, and K. M. Tohamy, "Mesoporous silica nanoparticles prepared by different methods for biomedical applications: comparative study," *IET Nanobiotechnology*, vol. 15, no. 3, pp. 291–300, 2021.
- [11] J. W. Yoo, D. S. Yun, and H. J. Kim, "Influence of reaction parameters on size and shape of silica nanoparticles," *Journal of Nanoscience and Nanotechnology*, vol. 6, no. 11, pp. 3343–3346, 2006.
- [12] A. Mehmood, H. Ghafar, S. Yaqoob, U. F. Gohar, and B. Ahmad, "Mesoporous silica nanoparticles: a review," *Journal of Developing Drugs*, vol. 6, pp. 174–188, 2017.
- [13] W. Stöber, A. Fink, and E. Bohn, "Controlled growth of monodisperse silica spheres in the micron size range," *Journal of Colloid and Interface Science*, vol. 26, no. 1, pp. 62–69, 1968.
- [14] M. Grün, I. Lauer, and K. K. Unger, "The synthesis of micrometer- and submicrometer-size spheres of ordered mesoporous oxide MCM-41," *Advanced Materials*, vol. 9, no. 3, pp. 254–257, 1997.
- [15] D. Zhao, J. Feng, Q. Huo et al., "Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores," *Science*, vol. 279, no. 5350, pp. 548–552, 1998.
- [16] T. Yamada, H. Zhou, K. Asai, and I. Honma, "Pore size-controlled mesoporous silicate powder prepared by triblock copolymer templates," *Materials Letters*, vol. 56, no. 1–2, pp. 93–96, 2002.
- [17] F. Trindade and M. J. Politi, "2-sol-gel chemistry—deals with sol-gel processes," in *Nano Design for Smart Gels*, pp. 15–34, Elsevier, 2019.
- [18] V. Chaudhary and S. Sharma, "An overview of ordered mesoporous material SBA-15: synthesis, functionalization and application in oxidation reactions," *Journal of Porous Materials*, vol. 24, no. 3, pp. 741–749, 2017.
- [19] A. Walcarius, E. Sibottier, M. Etienne, and J. Ghanbaja, "Electrochemically assisted self-assembly of mesoporous silica thin films," *Nature Materials*, vol. 6, no. 8, pp. 602–608, 2007.
- [20] G. Herzog, E. Sibottier, M. Etienne, and A. Walcarius, "Electrochemically assisted self-assembly of ordered and functionalized mesoporous silica films: impact of the electrode geometry and size on film formation and properties," *Faraday Discussions*, vol. 164, pp. 259–273, 2013.
- [21] D. Grosso, F. Cagnol, G. J. de A. A. Soler-Illia et al., "Fundamentals of mesostructured through evaporation-induced self-assembly," *Advanced Functional Materials*, vol. 14, no. 4, pp. 309–322, 2004.
- [22] A. Goux, M. Etienne, E. Aubert, C. Lecomte, J. Ghanbaja, and A. Walcarius, "Oriented mesoporous silica films obtained by electro-assisted self-assembly (EASA)," *Chemistry of Materials*, vol. 21, no. 4, pp. 731–741, 2009.
- [23] Z. Teng, G. Zheng, Y. Dou et al., "Highly ordered mesoporous silica films with perpendicular mesochannels by a simple Stöber-solution growth approach," *Angewandte Chemie International Edition*, vol. 51, no. 9, pp. 2173–2177, 2012.
- [24] A. E. Danks, S. R. Hall, and Z. Schnepf, "The evolution of 'sol-gel' chemistry as a technique for materials synthesis," *Materials Horizons*, vol. 3, no. 2, pp. 91–112, 2016.
- [25] U. Schubert, "Chemistry and fundamentals of the sol-gel process," in *The Sol-Gel Handbook*, pp. 3–27, Wiley, 2015.
- [26] P. Innocenzi, *The Sol to Gel Transition*, pp. 1–61, Springer International Publishing, 2016.
- [27] C. J. Brinker, *Sol-Gel Science, The physics, and Chemistry of Sol-Gel Processing*, Academic Press, Inc., 1990.
- [28] I. A. Rahman and V. Padavettan, "Synthesis of silica nanoparticles by sol-gel: size-dependent properties, surface modification, and applications in silica-polymer nanocomposites—a review," *Journal of Nanomaterials*, vol. 2012, Article ID 132424, 15 pages, 2012.
- [29] J. D. Wright, *Sol-Gel Materials Chemistry and Applications*, Taylor and Francis Group, 2001.
- [30] F. Hoffmann, M. Cornelius, J. Morell, and M. Fröba, "Silica-based mesoporous organic-inorganic hybrid materials," *Angewandte Chemie International Edition*, vol. 45, no. 20, pp. 3216–3251, 2006.

- [31] Y. Wan, Y. Shi, and D. Zhan, "Designed synthesis of mesoporous solids via nonionic-surfactant-templating approach," *Chemical Communications*, no. 9, pp. 897–926, 2007.
- [32] J. R. Bruckner, J. Bauhof, J. Gebhardt, A.-K. Beurer, Y. Traa, and F. Giesselmann, "Mechanisms and intermediates in the true liquid crystal templating synthesis of mesoporous silica materials," *The Journal of Physical Chemistry B*, vol. 125, no. 12, pp. 3197–3207, 2021.
- [33] H.-P. Lin and C.-Y. Mou, "Structural and morphological control of cationic surfactant-templated mesoporous silica," *Accounts of Chemical Research*, vol. 35, no. 11, pp. 927–935, 2002.
- [34] J. Y. Ying, C. P. Mehnert, and M. S. Wong, "Synthesis and application of supramolecular templated mesoporous materials," *Angewandte Chemie International Edition*, vol. 38, pp. 56–77, 1999.
- [35] J. T. Tompkins and R. Mokaya, "Steam stable mesoporous silica MCM-41 stabilized by trace amounts of Al," *ACS Applied Materials & Interfaces*, vol. 6, no. 3, pp. 1902–1908, 2014.
- [36] H. I. Meléndez-Ortiz, L. A. García-Cerda, Y. Olivares-Maldonado, G. Castruita, J. A. Mercado-Silva, and Y. A. Perera-Mercado, "Preparation of spherical MCM-41 molecular sieve at room temperature: Influence of the synthesis conditions in the structural properties," *Ceramics International*, vol. 38, pp. 6353–6358, 2012.
- [37] P. Yang, S. Gai, and J. Lin, "Functionalized mesoporous silica materials for controlled drug delivery," *Chemical Society Reviews*, vol. 41, no. 9, pp. 3679–3698, 2012.
- [38] D. L. J. Vossen, M. J. A. de Dood, T. van Dillen et al., "Novel method for solution growth of thin silica films from tetraethoxysilane," *Advanced Materials*, vol. 12, no. 19, pp. 1434–1437, 2000.
- [39] H. Yang, N. Coombs, I. Sokolov, and G. A. Ozin, "Free-standing and oriented mesoporous silica films grown at the air–water interface," *Nature*, vol. 381, no. 6583, pp. 589–592, 1996.
- [40] Y. Lu, H. Fan, A. Stump, T. L. Ward, T. Rieker, and C. J. Brinker, "Aerosol-assisted self-assembly of mesostructured spherical nanoparticles," *Nature*, vol. 398, pp. 223–226, 1999.
- [41] L. Liu and A. Walcarius, "Kinetics of the electrochemically-assisted deposition of sol–gel films," *Physical Chemistry Chemical Physics*, vol. 19, no. 23, pp. 14972–14983, 2017.
- [42] Y. Guillemin, J. Ghanbaja, E. Aubert, M. Etienne, and A. Walcarius, "Electro-assisted self-assembly of cetyltrimethylammonium-templated silica films in aqueous media: critical effect of counteranions on the morphology and mesostructure type," *Chemistry of Materials*, vol. 26, no. 5, pp. 1848–1858, 2014.
- [43] M. A. Carreon and V. V. Gulians, "Mesostructuring of metal oxides through EISA: fundamentals and applications," in *Ordered Porous Solids*, pp. 413–440, Elsevier, 2009.
- [44] V. R. Koganti and S. E. Rankin, "Synthesis of surfactant-templated silica films with orthogonally aligned hexagonal mesophase," *The Journal of Physical Chemistry B*, vol. 109, no. 8, pp. 3279–3283, 2005.
- [45] C. J. Brinker, Y. Lu, A. Sellinger, and H. Fan, "Evaporation-induced self-assembly: nanostructures made easy," *Advanced Materials*, vol. 11, no. 7, pp. 578–584.
- [46] K.-C. Kao, C.-H. Lin, T.-Y. Chen, Y.-H. Liu, and C.-Y. Mou, "A general method for growing large-area mesoporous silica thin films on flat substrates with perpendicular nanochannels," *Journal of the American Chemical Society*, vol. 137, no. 11, pp. 3779–3782, 2015.
- [47] R. Shacham, D. Avnir, and D. Mandler, "Electrodeposition of methylated sol–gel films on conducting surfaces," *Advanced Materials*, vol. 11, pp. 384–388, 1999.
- [48] G. Giordano, C. Durante, A. Gennaro, and M. Guglielmi, "Multilayer deposition of silica sol–gel films by electrochemical assisted techniques," *The Journal of Physical Chemistry C*, vol. 120, no. 50, pp. 28820–28824, 2016.
- [49] H. Okudera and A. Hozumi, "The formation and growth mechanisms of silica thin film and spherical particles through the Stöber process," *Thin Solid Films*, vol. 434, no. 1–2, pp. 62–68, 2003.
- [50] M.-A. Pizzoccaro-Zilamy, C. Huiskes, E. G. Keim et al., "New generation of mesoporous silica membranes prepared by a Stöber-solution pore-growth approach," *ACS Applied Materials & Interfaces*, vol. 11, no. 20, pp. 18528–18539, 2019.
- [51] L. Liu and D. Mandler, "Electrochemical deposition of sol–gel films," in *Handbook of Sol–Gel Science and Technology*, L. Klein, M. Aparicio, and A. Jitianu, Eds., pp. 531–568, Springer, Cham, 2016.
- [52] G. Giordano, C. Durante, A. Gennaro, and M. Guglielmi, "Electrochemical 3D-growth of amorphous silica gel," *Journal of Electroanalytical Chemistry*, vol. 784, pp. 153–158, 2017.
- [53] L.-K. Wu, J.-M. Hu, and J.-Q. Zhang, "One step sol–gel electrochemistry for the fabrication of superhydrophobic surfaces," *Journal of Material Chemistry A*, vol. 1, no. 46, pp. 14471–14475, 2013.
- [54] A. Walcarius, "Mesoporous materials and electrochemistry," *Chemical Society Reviews*, vol. 42, no. 9, pp. 4098–4140, 2013.
- [55] G. Giordano, C. Durante, A. Gennaro, and M. Guglielmi, "Electrochemical deposition of silica sol–gel films on stainless steel: preliminary analysis of key variables," *Journal of Sol–Gel Science and Technology*, vol. 76, no. 2, pp. 233–240, 2015.
- [56] J. Cheng, S. J. Rathi, P. Stradins, G. L. Frey, R. T. Collins, and S. K. R. Williams, "Free standing silica thin films with highly ordered perpendicular nanopores," *RSC Advances*, vol. 4, no. 15, pp. 7627–7633, 2014.
- [57] S. Pevzner, O. Regev, and R. Yerushalmi-Rozen, "Thin films of mesoporous silica: preparation and characterization," *Current Opinion in Colloid & Interface Science*, vol. 4, no. 6, pp. 420–427, 1999.
- [58] P. N. Deepa, M. Kanungo, G. Claycomb, P. M. A. Sherwood, and M. M. Collinson, "Electrochemically deposited sol–gel-derived silicate films as a viable alternative in thin-film design," *Analytical Chemistry*, vol. 75, no. 20, pp. 5399–5405, 2003.
- [59] A. Walcarius, "Mesoporous materials-based electrochemical sensors," *Electroanalysis*, vol. 27, no. 6, pp. 1303–1340, 2015.
- [60] C. Chircov, A. Spoială, C. Păun et al., "Mesoporous silica platforms with potential applications in release and adsorption of active agents," *Molecules*, vol. 25, no. 17, Article ID 3814, 2020.
- [61] M. Vallet-regi, M. Colilla, I. Izquierdo-barba, and M. Manzano, "Mesoporous silica nanoparticles for drug delivery: current insights," *Molecules*, vol. 23, no. 1, Article ID 47, 2018.
- [62] C. Bharti, N. Gulati, U. Nagaich, and A. K. Pal, "Mesoporous silica nanoparticles in target drug delivery system: a review," *International Journal of Pharmaceutical Investigation*, vol. 5, no. 3, pp. 124–133, 2015.
- [63] R. Kotcherlakota, A. K. Barui, S. Prashar et al., "Curcumin loaded mesoporous silica: an effective drug delivery system for cancer treatment," *Biomaterials Science*, vol. 4, no. 3, pp. 448–459, 2016.
- [64] S. Nsreen, U. Rafique, S. Ehrman, and M. A. Ashraf, "Synthesis and characterization of mesoporous silica nanoparticles for

- environmental remedation of metals, PAHs and phenols,” *Ekoloji*, vol. 27, no. 106, pp. 1625–1637, 2018.
- [65] T. Maschmeyer, F. Rey, G. Sankar, and J. M. Thomas, “Heterogeneous catalysts obtained by grafting metallocene complexes onto mesoporous silica,” *Nature*, vol. 378, no. 6553, pp. 159–162, 1995.
- [66] M. Ashuri, Q. He, and L. L. Shaw, “Silicon oxides for Li-ion battery anode applications: toward long-term cycling stability,” *Journal of Power Sources*, vol. 559, Article ID 232660, 2023.
- [67] M. Khan, X. Ding, H. Zhao et al., “SiO₂-based lithium-ion battery anode materials: a brief review,” *Journal of Electronic Materials*, vol. 51, pp. 3379–3390, 2022.
- [68] M.-R. Buga, A. A. Spinu-Zaulet, C. G. Ungureanu et al., “Carbon-coated SiO₂ composites as promising anode material for Li-ion batteries,” *Molecules*, vol. 26, no. 15, Article ID 4531, 2021.
- [69] C. Robertson, R. Beanland, S. A. Boden et al., “Ordered mesoporous silica films with pores oriented perpendicular to a titanium nitride substrate,” *Physical Chemistry Chemical Physics*, vol. 17, pp. 4763–4770, 2015.