Chapter 2
Synthesis Approaches for Nanodielectric Materials

Vinod Kashyap, Sukhvant Singh, Sumit, and Lipeeka Rout

Abstract It is highly critical to acquire desirable performance and durability of materials for various engineering applications. To overcome these issues, in recent years, studies on nanodielectric material are found to be one of the most dynamic fields of research among scientists. A multi-component nanostructure that can lead to the change of several dielectric properties is termed as nanodielectric. These materials provide extensively high-dielectric properties due to which they can act as a suitable material for energy storage device applications, in particular for capacitors. Nanodielectric materials were associated with high-dielectric and insulating properties. Such properties of nanodielectric material have commonly been observed in nanocomposites and ceramics materials. More recently, nanoparticles were being incorporated in various metal oxide and polymer support to achieve the enhanced dielectric property of the materials. Fundamentally, the basic principle of nanodielectric materials lies on a large internal area of the surface. Owing to their wide range of properties, it is highly necessary to make the nanodielectric material using the proper synthetic procedure. The most important factor to achieve the dielectric property of the material is to synthesize the nanocomposite or to incorporate the nanoparticle with uniform size distribution. A well-dispersed nanoparticle can enhance the dielectric property of the material. Since many variables can affect the dielectric property such as particle size, dispersion, and aspect ratio, synthesis of these materials is of

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high priority and highly important. Keeping the above in mind, the current chapter will give a thorough study of various synthetic methods which can be utilized for the synthesis of suitable nanodielectric material. In the current chapter, the authors have explained various available methods for the synthesis of nanodielectric material.

Keywords Nanodielectric materials · Sol–gel · Hydrothermal method · Electrospinning · Spray pyrolysis

2.1 Introduction

Presently, it is imperative to increase the use of energy and renewable sources due to the rising energy demand and the depletion of fossil resources [1]. The development of renewable energy generation is one of the major scientific interest in order to achieve the productivity of energy consumption [1]. The development of nanomaterials fills two primary needs: the establishment of their functioning and their applications in the practical field [2]. Since the introduction of DC electricity and the electric bulb by Thomas Edison in the late nineteenth century, electric power has become an effective source of energy for the human world [2].

For their prospective applications, dielectric materials with high dielectric constant and low dielectric loss have drawn a lot of attention [3, 4]. Nanodielectric materials were found to have superior dielectric properties and possess immense interest owing to their potential applications as capacitor materials [5, 6]. These capacitor materials can be further utilized for electronic devices, gate dielectrics, electroactive materials, management of grid energy by power electronics, and also in pulsed power systems [7–9]. High-performance dielectric materials also have been utilized in various industrial applications such as computers, telecommunications, defense, and aerospace [10–12]. In general, the development of pulse power is in much demand, because of the requirement of much energy over a longer period and which further can release it quickly, thus increasing the available instantaneous power [13, 14]. The capacity of electrostatic energy relies upon induced electric field polarization of dielectric materials, which further need high strength of breakdown and high dielectric permittivity.

Previously, few researchers' reported that compared to available conventional ceramic-based dielectric materials, composites based on polymers were found to have better efficiency, good flexibility, minimal expense, and lightweight to become a standard material in the microelectronics industries [15, 16]. They observed that flexible polymer composites with a high dielectric constant are profoundly attractive, and this high dielectric constant of polymer nanocomposites is of great interest for various practical applications [17]. Similarly, over the past few decades' successful commercialization was made for organic light-emitting diodes (OLEDs) using organic electronics. One of the emerging device building blocks is organic field-effect transistors (OFETs) which have shown higher efficiency compared to amorphous silicon thin-film transistors [18], essentially utilizing the properties of flexible and printable materials. In recent years, applications of OFET in backplane displays [19], biosensors [20], and electronic devices were broadly investigated [21, 22]. Moreover, it is believed that in near future these types of materials with high synthetic tenability, multifunctional properties, and high interface sensitivity are most likely to expand the scope of technological development [23].

Additionally, other forms of nanodielectric materials are available which have been used for numerous industrial applications [24]. In the current instance, biaxially oriented polypropylene (BOPP) is broadly applied as a dielectric material for the storage of electrical energy, because of its low dielectric loss, high breakdown strength, and easy way of manufacturing. Recently, poly (vinylidene fluoride) (PVDF) and its copolymers were found to be the most prevalent dielectric material for the application of capacitors with high energy density [25]. Also, a great deal of effort has gone into creating PVDF-based polymers by mixing, blending, coating, spinning, and nanocomposite production. Among these methods, nanocomposites have demonstrated advantages for enhancing the impact of the inorganic nanofillers on the dielectric permittivity [26].

To develop such materials that are very flexible, those having a high dielectric constant, and are less expensive, efforts have been made to synthesize these materials using various synthetic techniques. There are several techniques available for the preparation of numerous forms of nanodielectric materials. Every synthetic strategy has advantages and disadvantages depending on the reaction time, particle size, thickness of the film, etc.

Keeping all the above in mind, in the present chapter, our prime focus is to discuss the novel and cost-effective synthetic routes of nanodielectric materials. There are several available methods for the preparation of materials with excellent dielectric properties. A schematic of available synthesis methods for nanodielectric materials synthesis are shown in Fig. 2.1.

2.2 Introduction to Various Synthetic Routes for Nanodielectric Materials Synthesis

It is vitally important to create and design materials for use in electronic applications. While examining the dielectric characteristics of nanodielectric, the production of the materials was frequently overlooked. The physical characteristics of the raw materials employed in the preparation process are what give rise to the physical characteristics of the composite material, it has been noted [27]. To achieve various properties and various forms of nanodielectric materials for a diverse range of applications, it is very important and essential to synthesize those materials with suitable techniques and under optimized conditions.

Fig. 2.1 Various synthetic techniques for nanodielectric materials synthesis

In recent years, highly cost-effective synthetic techniques have been adapted to create various forms of nanodielectric materials such as polymer-based, nanoparticle-based, and ceramic-based [28]. The enormous synthetic techniques for nanodielectric materials have attracted a lot of research interest, as they provide material with a high dielectric constant which is highly required for various applications. Recently, researchers have tried to overcome the difficulties associated with the development of nanodielectric with effective dielectric properties for devices and applications. Mostly, nanodielectric properties are observed in nanocomposites and ceramic materials [29]. In recent years, it has been found that in ceramics form nanostructures were obtained to large extent. Notably, it has been observed that nanocrystalline powder can be used as starting material for the synthesis of nanodielectric materials. The main focus was being made to synthesize nanostructure materials with dielectric property using novel concepts and approaches. There was various novel approached which has been utilized to obtain nanodielectric materials [30, 31]. The basic principle of materials nanodielectric mostly relies on its large internal surface area. In order to engineer these materials, one needs to select a specific aspect ratio, apply internal modifications, and change their morphology. Nanodielectric can also be fabricated using organic oxide materials. The traditional method for making dielectric materials with nanoparticles in them required combining polymer materials with nanoparticle precursors to create a composite dielectric material. Till date, various novel synthetic routes have been utilized to form highly effective nanodielectric materials for several industrial applications. The details of each synthetic techniques have been discussed in the later part of the chapter.

2.3 Sol–gel Technique for Nanodielectric Materials Synthesis

A sol–gel synthetic method is a bottom-up approach in which components of atomic dimensions are assembled to form nanomaterials [32]. The benefit of this technique is that particle size may be controlled. It is a method of wet chemical synthesis used to produce fibers, thin films, and powders of ceramic, dielectric, and glass materials [33–35]. A sol is a solid ion or particle suspension in a solvent, either colloidal or molecularly. When the solvent in the sol starts to evaporate and the particles left behind start to join up in a continuous network, a gel is created [36]. In this method, metal alkoxides and chlorides are typically utilized as precursors. During the synthesis technique, pH must be managed because this process is sensitive to it, and it will help to prevent precipitation and create a homogeneous gel.

The following steps occurred in the general sol–gel process (Fig. 2.2):

1. *Hydrolysis*—Metal precursors undergo hydrolysis by water in presence of catalysts such as HCl or ammonia.

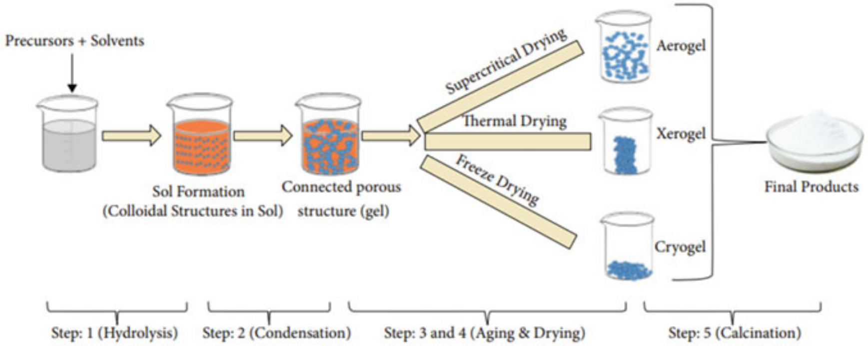
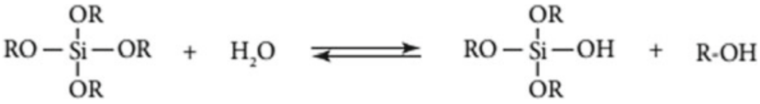


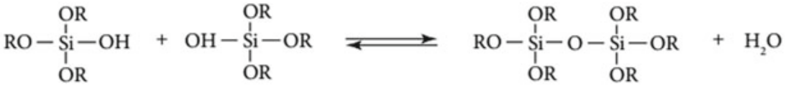
Fig. 2.2 Schematic diagram of different stages of the sol–gel process: from precursor to aerogel [1–5, 32]. Adapted with permission from ref. [32]. Open access under a CC BY 4.0 license. Copyright © 2021 Dmitry Bokov et al.



$$RO-\underset{OR}{\overset{OR}{Si}}-OR + H_2O \rightleftharpoons RO-\underset{OR}{\overset{OR}{Si}}-OH + R\text{-}OH$$

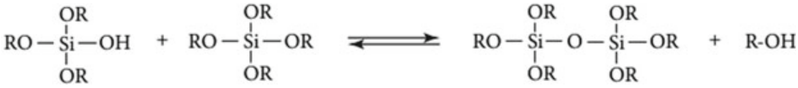
2. *Condensation*—Condensation reactions that either produce water or alcohol are used to polymerize siloxane to create bonds. Further, this results in the formation of monomers, dimers, cyclic trimers, and higher-order rings.

(a) Water condensation



$$RO-\underset{OR}{\overset{OR}{Si}}-OH + OH-\underset{OR}{\overset{OR}{Si}}-OR \rightleftharpoons RO-\underset{OR}{\overset{OR}{Si}}-O-\underset{OR}{\overset{OR}{Si}}-OR + H_2O$$

(b) Alcohol condensation



$$RO-\underset{OR}{\overset{OR}{Si}}-OH + RO-\underset{OR}{\overset{OR}{Si}}-OR \rightleftharpoons RO-\underset{OR}{\overset{OR}{Si}}-O-\underset{OR}{\overset{OR}{Si}}-OR + R\text{-}OH$$

3. *Growth of material*—The molecules start to aggregate with an increase in the number of siloxane bonds where they create a network, and when they dry, gel forms. The network contracts as the water and alcohol are driven away. The formation of spherical nanoparticles occurs at pH values greater than thee $\frac{H_2O}{Si}$ the ratio which ranges from 7 to 5.

High-purity and highly efficient nanodielectric materials can be prepared at room temperature using the sol–gel method. Nanodielectric materials with high efficiency have a wide range of applications in optical fibers and high-performance electrical insulation [32]. Dielectric materials are also used in semiconductor materials and capacitors which can store charge**.** Dielectric materials have applications in instrumental analysis. The instruments use dielectric material in diodes in the detectors and radiant power monitor devices.

Recently, in 2020, N. Murali and co-workers synthesized cobalt ferrite nanodielectric materials by utilizing the sol–gel method [37]. They have investigated the cobalt ferrite's magnetic, dielectric, and structural characteristics. They discovered that the magnetic and dielectric properties of nanomaterials are greatly influenced by several important factors, including particle size, crystallinity, composition, and site occupancy, and the earlier parameters can be effectively managed by adjusting the calcination temperature and calcination time. They have noticed that as the calcination temperature rises, the materials' coercivity diminishes. Additionally, they have researched $CoFe_2O_4$'s dielectric characteristics in the 100 to 5 MHz frequency range.

Many functional groups have been grafted onto metal oxide surfaces using the sol–gel procedures, and their dielectric properties have been further examined by a small number of researchers [38]. Dierkes and co-workers investigated how charge transfer of (PP)/(ethylene-octene) copolymer (EOC)/silica nanodielectrics was affected by 3 aminopropyltriethoxysilane (APTES) functionalized nano-silica [39]. They have incorporated APTES over the silica surface to generate an amine functional group which is responsible to modify the electronic properties and interfacial interaction on the silica-polymer surface. According to a few reports, it has been observed that surface modification can enhance the nucleation rate and crystallinity of the nanodielectrics. Most recently, in 2022, sol–gel technology was used by Ghamarpoor et al. to create silica nanoparticles based on vinyl [40]. They used the sol–gel technique to graft vinyltriethoxysilane (VTES) over silica for this purpose. The grafting was required to create strong interaction between the surface of the silica and nitrile rubber (NBR) Matrix.

A lot of interest has been paid to thin-film nanodielectric in addition to powder-based and polymer-based nanodielectric. Aoki et al. have reported the synthesis of HfO_2 nano-films using the sol–gel method ad further studied their dielectric properties. They stated that the sol–gel method and post-annealing can be used to create a high-quality metal oxide nano-film. In this thin-film manufacturing procedure, metal oxide precursors were first made to chemisorb on the silicon wafer in an organic solvent to create a homogeneous layer. Next, the alkoxide group was hydrolyzed. Later, the deposited film was annealed for a few cycles to get uniform nanodielectric thin film [41]. Similar to this, Jian et al. published in 2005 on the sol–gel produced $ZnFe_2O_4$–SiO_2 composite thin film's dielectric behavior [42].

A straightforward method called sol–gel can be utilized to create high-purity products with a high level of production efficiency. Using this method, optical components with complex shapes can be synthesized. The process can design and control chemical homogeneous composition. This technique can be used to create porous and rich materials with organic and polymeric properties, as well as thin layers of amorphous materials [43]. Precursors are highly reactive due to the solution-phase process. The structure of a material can be altered by modifying factors like pH, temperature, etc. This method is capable of sintering at low temperatures, typically between 200 and 600 °C. The sol–gel method is versatile as it can produce aerogels, xerogels, ceramic materials, nanopowders, nanorods, nanostructures thin films, etc. Apart from the merits, the sol–gel process has some demerits too. Nanoparticles (NPs), sometimes, get contacted during agglomeration. Processing time is a long, and large production of NPs is difficult. The use of toxic chemical solvents is harmful to both humans and the environment [44]. One of the major problems is the purification of NPs after the synthesis. Separation of the NPs from the solvent consumes a lot of time and generates toxic residues.

2.4 Hydrothermal Synthesis of Nanodielectric Material

In a hydrothermal method, nanoparticles are created through hydrolysis processes that take place at high temperatures and high vapor pressure [45]. In this process, materials are obtained by the crystallization of phases under high temperatures and pressure. The method can be used at room temperature and below critical pressure [46]. This technique is dependent on the solubility of minerals in hot, high-pressure water. Factors affecting the hydrothermal synthesis process are the initial pH of the solution, duration, temperature, and pressure in the autoclave. Typically, an autoclave is used to perform the hydrothermal technique [47]. In this process, a metal precursor solution is mixed in a hydrolyzing solution and kept at a high temperature for 10–24 h in an autoclave, then cooling it down to ambient temperature for crystallization. The resulting crystals are collected using filtration, washing, and drying. Large particle-size nanocrystals can be synthesized using the hydrothermal method which is useful to increase the dielectric constant of the material and hence increases dielectric properties of the synthesized materials. Nanomaterials synthesized using this method tend to withstand high frequencies and high temperatures and therefore can be used in semiconductor devices [48].

In recent years, many researchers have utilized the hydrothermal method for the synthesis of various forms of nanodielectric materials and also studied their dielectric properties for electronic applications. For example, the hydrothermal process was used to create silver nanowires that were then coated with a carbonaceous shell as shown in Fig. 2.3. The synthesis was carried out by using silver nitrate as a metal precursor, Cetyl trimethyl ammonium bromide (CTAB), and glucose [49]. Silver nanowire/manganese dioxide nanowire/poly(methyl methacrylate) (AgNW/MnO_2NW/PMMA) was synthesized, according to Zerrati et al. Here, they have utilized two types of synthetic techniques to get the final nanocomposite. For the synthesis of Ag, nanowires were synthesized via the hard-template technique, whereas the hydrothermal method was used for the synthesis of MnO_2 nanowires. They observed a high dielectric permittivity of 64 at 8.2 GHz was noted in the synthesized nanocomposite [50].

Similarly, hydrothermal synthesis in supercritical water has an advantage over the conventional method as the rate increases by 103 times under critical conditions. Supercritical water provides control of crystal phase, particle size, and morphology. Titanium dioxide NPs synthesized using this method have high crystallinity and high surface area due to which the dielectric properties of TiO_2 NPs are enhanced. For the synthesis, a slurry of titanium tetra propoxidein an aqueous medium was kept in a gold-tube reactor inside the autoclave. The synthesis is carried out at 400 °C at 25 MPa pressure for 24 h. This system is referred to as the batchwise system [51].

High-dielectric materials are used in diodes, solar cells, transistors, and gates. According to Ahmad et al., the hydrothermal process they used to create cubic ZrO_2 was far more stable at relatively high temperatures. Zirconia has potentially high dielectric properties due to which it has extensive use in gates. They discovered that solid zirconia NPs have a large surface area and function as p-type semiconductors. Additionally, they observed that the dielectric coefficient, which is influenced by the synthesis temperature, crystalline structure, and particle size, determines the band gap of these materials. For the synthesis, a solution of zirconium oxynitrate as a limiting reagent is prepared in NaOH and double distilled water. The solution was then put into a hydrothermal flask, and the precipitate was later cleaned and dried for 1.5 h at 110 °C before being ground [52].

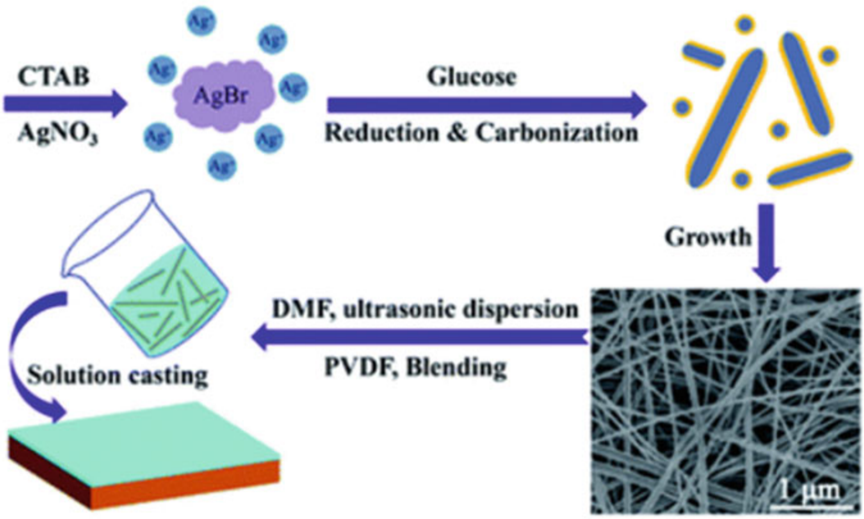


Fig. 2.3 Schematic diagram of the synthesis of Ag@Cnano cables [49]. Adapted with permission from ref [49] Copyright (2018) (Royal society of chemistry)

One of the advantages of the hydrothermal synthesis approach is its propensity to produce unstable or less stable materials at high temperatures. With this technique, one can produce large crystals with good purity. The method is easy and simple with a low cost of synthesis, but the initial setup cost is high [53]. The material's loss is minimal with a high product yield. Besides this, they have a few disadvantages which include longer reaction time, and it is difficulty to observe the crystals as they grow during the synthesis process inside the autoclave as the autoclave is fully equipped with Teflon.

2.5 Combustion Synthesis of Nanodielectric Materials

One of the most utilized processes for fabricating a variety of oxide materials is solution combustion synthesis (SCS). K.C. Patil and others invented and perfected this technique in India in the 1980s [54]. When urea and $Al(NO_3)_3$. $9H_2O$ were heated fast to a temperature of 500 °C in a muffle furnace (preheated), the first unintentional synthesis of α-alumina occurred. A large amount of white material that was recognized as α-Al_2O_3 was produced during the reaction, and the mixture foamed and burned with an incandescent flame. Concepts from propellant chemistry were applied to properly learn about the combustion reaction's high exothermic nature. The energy released during the reaction is at its highest, and there is no carbon residue left once the combustion is finished. To create pigments, phosphors, and catalysts, the host oxide matrix can be doped with the appropriate amount of metal ions. By using this technique, pink alumina was produced by adding an appropriate amount of chromium nitrate to the redox mixture of urea and aluminum nitrate, which uniformly doped the alumina matrix about 1% of Cr. Later, hydrazides were employed in place of urea to produce a wide range of oxides. Patil's group employed hydrazides such as malonic acid dihydrazide, oxalyldihydrazide, maleic hydrazide, and carbohydrazide [55]. Other researchers investigated various fuels, including glycine, alanine, hexamine, citric acid, etc.

Due to their high carrier mobilities, outstanding thermal stability, mechanical flexibility, and optical transparency, metal-oxide semiconductors and dielectrics, particularly in amorphous phases, constitute potential materials for next-generation electronics. The development of metal oxide films, particularly those for thin-film transistors, is widely performed via sol–gel processes. However, the necessary stages of sol–gel condensation, densification, and contamination removal are commonly needed for processing temperatures of > 500 °C, which are incompatible with affordable glasses and conventional flexible polymeric substrates. A unique variant of the SCS approach was recently developed by Marks and co-researchers at Northwestern University to fabricate thin-film transistors for next-generation electronics. To improve the preparation conditions and attributes of the synthesized films, many studies have already been published. We predict that, in addition to the production of electrical devices, combustion-based deposition techniques may have a significant impact on the creation of dielectric nanomaterials and electrochemical devices [56]. Controlling the type of combustion allowed for the modification of solid combustion product particle size, and by employing fuels that produce (i) the rate at which the fuel burns is slow, (ii) a decrease in exothermicity (making the reaction smolders instead of flam), and (iii) an increase in the number of gaseous products (H_2O, N_2, CO_2, etc., in which the heat is dissipated). Unlike volume combustion, linear combustion appears to produce oxide powders that are nanoscale in size. Additionally, it was found that metal acetates enhanced the synthesis of nanoscale oxides.

By using the solution combustion synthesis method, Kim et al. demonstrated a straightforward and relatively low-temperature (at 200 °C) synthesis technique for the construction of metal oxide thin-film transistors.In_2O_3, Zn-Sn–O, In-Zn–O, and In–Sn–O are materials used to create metal oxide thin-film transistors (ITO), and they incorporated NH_4NO_3 that had been dissolved in 2-methoxy ethanol with metal sources including $In(NO_3)_3$, $Zn(NO_3)_2$, and $SnCl_2$ to produce the precursor solution. To control the pH of the solution, they add ammonia solution, and precursor solutions were maintained for 72 h before film casting. Then, silicon wafers were spin-coated with solutions containing 0.05 M of total metal concentration, and they were heated for 30 min at 150–400 °C. Solution combustion synthesis-derived transistors with thin-film layers was found to be highly efficient with saturation mobility of 6.0 cm^2/V s. The authors claim that this property is far better than the mobility of amorphous silicon, which is now employed widely in large-area electronic applications (below 1 cm^2/Vs) [57]. The schematic of the device structure has been presented in Fig. 2.4.

Krengvirat and Sreekantan reported bismuth titanate ceramics which is considered as well knows nanodielectric material, using an intermediate fuel agent-assisted

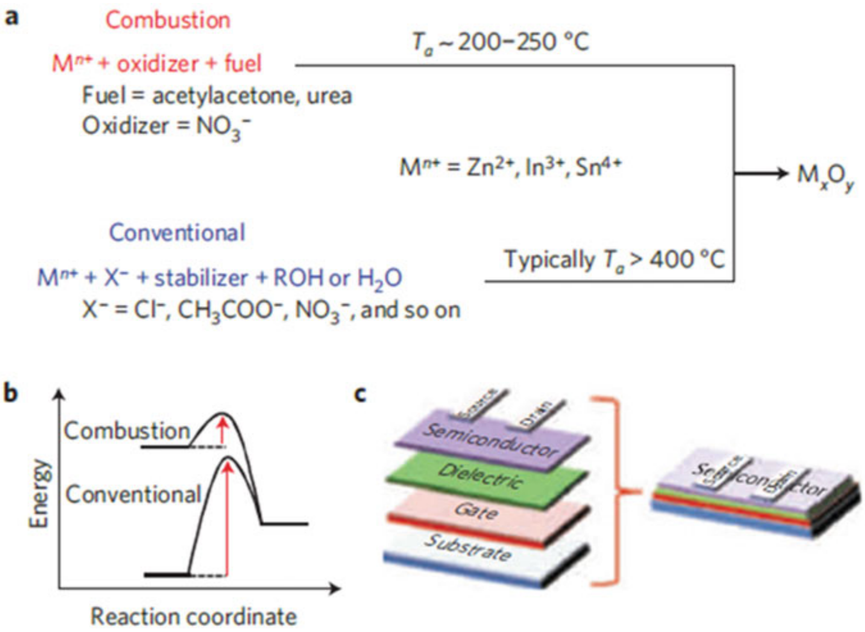


Fig. 2.4 Low-temperature solution-processing principles for metal oxides and fabricated device structures. **a** Depiction of the two different synthetic approaches. **b**, Energetics of combustion synthesis-based processes versus conventional processes. **c**, Top-contact bottom-gate TFT device structure used in this study [57]. Adapted with permission from ref. [57] Copyright (2018) (Springer Nature)

self-combustion synthesis (SCS) technique to replace praseodymium [58]. Similarly, Sekar et al. reported (Pb- BNb)O_3 (where B is Fe, Ni, Mg, or Zn), a lead-based niobate material based on two different combustion synthesis techniques. In the first combustion synthesis technique, they ignited the solutions of metal nitrates, NH_4NO_3, tetraformaltrisazine, and $Nb_2(C_2O_4)_5$ (Niobium oxalate) in a furnace (which is preheated) through a single-step fabrication approach. In the second combustion synthesis method, solution combustion was used in a two-step process to produce PbO (lead monoxide), $FeNbO_4$, $MgNb_2O_6$, $NiNb_2O_6$, and $ZnNb_2O_6$. They then combined PbO with metal niobates in the following stage, calcined the mixture, and the result was the desired lead-based ferroelectric ceramics. Microstructural investigations revealed that both synthesis methods create powders with good particle structures that can be sintered into compact samples with a relative density of around 97% [59]. They noticed that the ceramics created using the two-step synthesis process demonstrated higher dielectric properties in comparison with materials created using a single-stage synthesis strategy.

The solution combustion synthesis method's key benefits include: (i) the procedure is speedy and requires just basic equipment, (ii) since in this process redox reaction has exothermic nature, it can save energy by using the exothermicity; (iii) that method is allowing the modification in the composition of the product, structural modifications, also that method allows homogeneity as well as stoichiometry modifications of the product; (iv) that method allows to the formation of highly pure materials; (v) to create industrially usable materials, it enables incorporation of the necessary amount of impurity ions or dopants in the oxide hosts; (vi) that it allows metastable phases to be stabilized (γ-Fe_2O_3, anatase TiO_2, etc.); and apart from that (vii) it provides the fabrication of almost any size and shape of the obtained materials, for example, micron to nano size and spherical to hexagonal shape. Magnetic oxides, pigments, phosphors, high Tc cuprates, materials for solid oxide fuel cells, metal oxide catalysts, and durable materials are among the materials mentioned. (e.g., t-ZrO_2/Al_2O_3).

The solution combustion synthesis-derived powders are particularly efficient for removing pollutants from the environment. One-step combustion has been used to successfully deposit nano-sized crystalline ionic catalysts on ceramic cordierite honeycombs.

2.6 Electrospinning Method for Nanodielectric Material Synthesis

An electrostatically charged jet of molten polymer or a polymeric solution is used in the electrospinning (ES) technique to create continuous polymeric or inorganic fibers that can be anywhere between a few nanometers to a few micrometers in size. As depicted in Fig. 2.5, the procedure is carried out via a needle with a polymer solution streaming via it coupled to a grounded electrode for collecting and an HV DC generator [27].

The HV source is used to electrostatically charge a polymer solution, which then jets out of the needle tip as a hanging drop. The drop is distorted by the strong electric field between the grounded electrode and the needle until it becomes the shape of a Taylor cone. The thin fluid polymer jet is created and drawn in the direction of the metal collector when the charged drop experiences an electrostatic force that is greater than surface tension and exceeds a certain level of electric potential. The charged jet is then released. Objects are stretched and accelerated by the electric field and go through an instability process known as whipping instability; the spiral path taken by the fibers speeds up the stretching process, leading to fiber thinning as the solvent evaporates (or the melt polymer solidifies). During this instability process, fibers with diameters in the region of a few hundred nanometers are produced [60]. The jet's uneven motion results in the random deposition of fibers in the nonwoven nanoporous material type materials on the collector. Complex manufacturing procedures are required for the synthesis of high-quality nanocomposites. Electrospinning is now the most used technique in the field of electrical power engineering for creating nanodielectric materials based on polymers. The performance of composites depends on how evenly the fillers are distributed throughout the polymer. The two

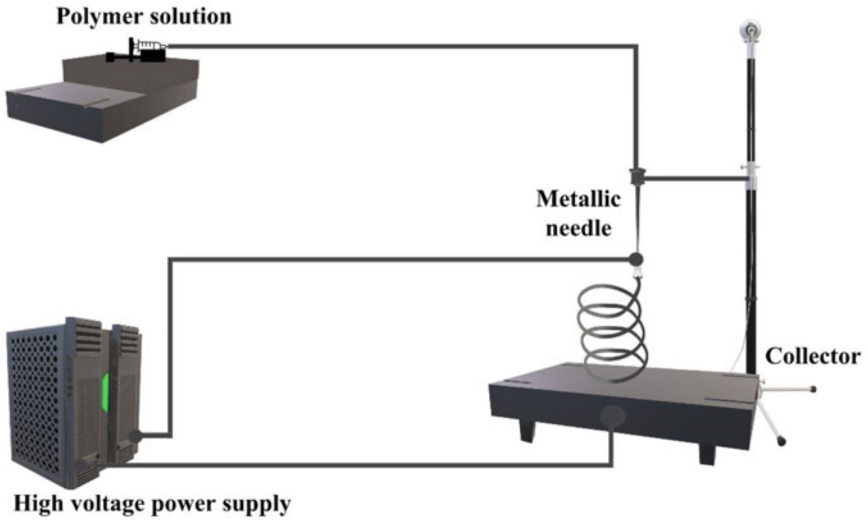


Fig. 2.5 Electrospinning apparatus

most common dispersion techniques utilized today are the solid-phase approach and the liquid-phase method. The solid-phase process, which is straightforward, simple to use, and convenient for large-scale production, under mechanical pressure, combined the matrix and fillers. However, the filler/matrix interface adhesion is poor, and the filler dispersion is not sufficiently uniform. The liquid-phase method, also known as the chemical method, has a higher interface adhesion and a far greater ability to spread fillers. For improving material characteristics, appropriate synthesis and preparation processes are also crucial in addition to material design and dispersion. In the electrospinning process, for instance, it is highly desirable for the development of composite qualities that the fibrous fillers can be layered sequentially along the direction of the fiber orientation to construct the network structure, retain the directional interconnection structure well, and produce no visible interface void or pore [61].

Li et al. reported a polymer-based nanodielectric material with high energy densities for electrical energy storage applications. They create uniform $BaTiO_3$ nanofibers (BT nfs) with a high aspect ratio, which are used as fillers in a poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) nanocomposite after being electrospun and surface-modified using poly(vinyl pyrrolidone). A straightforward solution-cast approach was used to create the nanocomposite films. They discovered that, compared to the polymer matrix and the nanocomposites with BT nfs, the dielectric constant and the energy density of the nanocomposites are significantly increased with a little loading of BT nfs [62]. Similarly, in 2017, Lin and co-workers prepared high-temperature resistance and high thermally stable core–shell barium titanate@silicon dioxide ($BT@SiO_2$) nanofibers with polyimide using the electrospinning technique as presented in Fig. 2.6. They have reported that the dielectric

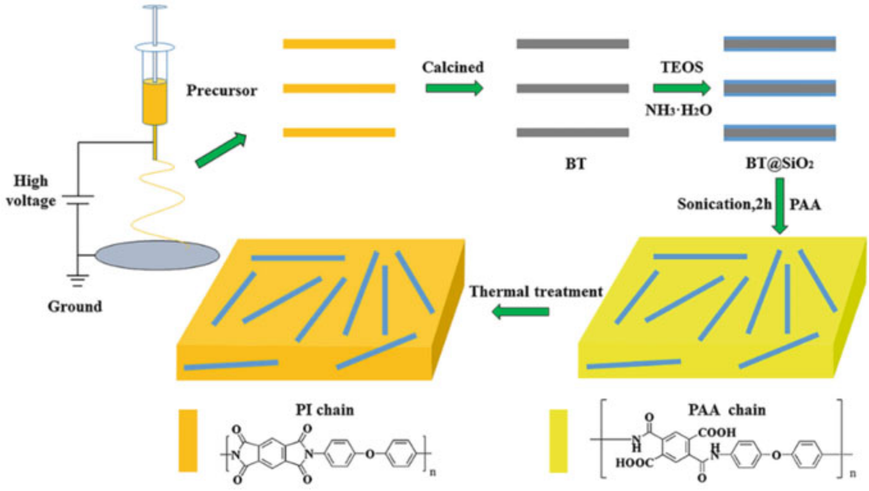


Fig. 2.6 Fabrication procedures of BT@SiO_2/PI nanocomposite films [63]. Adapted with permission from ref [63] Copyright (2017) (Elsevier)

permittivity of nanocomposite film increases significantly as the presence of thin SiO_2 layers was utilized to restrict the high dielectric loss from the nanofibers [63].

The ES method is thought to be straightforward, affordable, and useable in an industrial setting and creates extremely porous nanocomposite with excellent inorganic nanoparticle dispersion. For example, high-performance polymeric nanocomposite separators for Li-ion batteries could be made using ES. In another study, silicone rubber was mixed with nano-silica using the ES approach to lessen particle aggregation [64]. Nano-silica was electrospun into silicone fibers, which were then integrated into a silicone rubber matrix. Comparing ES to high-shear melt compounding, it has been demonstrated that a greater volume percentage of nano-silica may be disseminated more evenly into silicone rubber. In addition to this, a few limitations of the ES method include the use of toxic organic solvents, the difficulty to maintain uniform porosity of materials, and also, difficult to synthesize nanomaterials on large scale.

2.7 Intercalation Method for Nanodielectric Materials

Mostly, the intercalation method is used to synthesize polymer-based nanodielectric materials. PCNs, or polymer-clay nanocomposites, have received a lot of interest due to their exceptional properties, which include high dielectric properties, high thermal, and gas permeability, and pharmaceutical properties like optical, electrical, and mechanical at the nanoscaled level as compared to their pristine polymers. Dielectric properties of PCNs (acrylonitrile butadiene styrene and poly methyl methacrylate) with altering amounts (up to 10 wt%) of organically modified montmorillonite (OMMT) in the frequency range of 100 Hz^{-1} to MHz showed significant greater dielectric constant, and compared to pure polymers, exfoliated nanocomposites have greater dielectric loss values owing to the increased interfacial area between the clay layers and the polymer, which is driven by Maxwell–Wagner polarization. Pure polymers were shown to have higher dielectric constant and dielectric loss values in the same frequency range as intercalated nanocomposites, which is explained by the reduced mobility of polymer chains in the nanoscale pathways of OMMT [65].

These discoveries can be explained in terms of unique microstructures created in nanocomposite films after clay has completely laminated, exfoliated, and distributed in the polymer matrix with exfoliated polymer nanocomposites. The exfoliated OMMT and polymer matrix form a substantial interfacial area. In an applied electric field, different conductivities in the two phases lead to a significant interfacial or space charge polarization near the interface, due to trapped charges, and this phenomenon is known as Maxwell–Wagner polarization. As the OMMT content in exfoliated nanocomposites rises, the area at the interface between the polymers and OMMT expands, and as a result, the dielectric constant rises. Lower real and imaginary components of dielectric permittivity are displayed in intercalated nanocomposites than those displayed by the corresponding pristine polymers because the polymer chains are restricted between OMMT layers.

Polymer–clay nanocomposites (PCNs) are also known as organic–inorganic nanocomposites, and a suitable synthetic route can be utilized to control their useful properties [66]. The intercalation approach for the preparation of nanodielectric materials is most widely utilized for the preparation of PCNs; e.g., the clay, Nylon-6 hybrid was produced by the intercalation process and polymerization, and it is the prior nanocomposite developed by the Toyota group [67]. In general, the intercalation process is achieved by incorporating polymers within the layers of clay having dimensions in the range: from the thickness of a few nanometers to ~100 nm, length of 0.5 μm to as much as mm, and clay includes natural and synthetic clays, kaolinite, micas, and further layered inorganics [28] depending upon the exfoliated and intercalated hybrid techniques [28]. Moreover, when intercalate was requisite, organic materials were made to immerse within the layers of clay which further expands inside the component mixtures. Further, it is made to exfoliate the complete layers of clay materials that were distinct from one another but at the same time tied up inside the matrix of the organic component [66]. This strategy is a reversible technique that includes a collection of substances with layered structures. In PCN materials, three distinct phases occur from hydrogen bonding interactions between the clay intercalated/exfoliated at the nanoscale and the polymer (an organic substance) (an inorganic material). These steps are as follows:

(1) Microphase-separated composites, in which clay and polymer matrix are still incompatible,

(2) Intercalated clay assemblies, where polymer molecules infiltrate among clay galleries,
(3) Exfoliated structures, wherein the polymer matrix is filled with individual clay nanoplatelets [66].

Furthermore, intercalation or exfoliation is more feasible for a continuous in-line process than spherical inorganic nanodielectric, which can be produced in the lab more conveniently through a batch technique.

PEO is an etheric-linked simple chain polymer, contrary to PVA, which is a polymer with a backbone made of carbon chains and hydroxyl groups connected to carbons of methane. These polymer matrices composite (PMC) are frequently used in conjunction with montmorillonite clay for the development of organic–inorganic nanocomposite (NC) materials because they have a wide range of H-bond forming potential for the hydroxyl group (OH) of PVA monomer units and the ether oxygen of PEO monomer units. MMT clay is typically made up of linked silica and alumina sheets with an aspect ratio (length/width) of 100–1000 nm and a thickness of about 1 nm. To allow polar solvents and polymers to easily access the interlayer galleries, the cation quantity ratio can be changed depending on the source of the minerals, and its cation exchange mechanism can exhibit more hydrophilic organophilic MMT. This causes the exfoliation and intercalation of the polymer-layered silicate nanostructures.

In 2010, Sengwa et al. synthesized PEO-PVA blend-MMT clay nanocomposites using an intercalation process, and further, they presented the dielectric characteristics of the material in which their dielectric analysis showed that by incorporating 0.5–2 weight percent MMT clay into the PVA-PEO blend, the ϵ' value may be adjusted to be close to 1 [66]. As a result, the polymer-layered silicate nanostructures' end matrix is exfoliated and intercalated, enabling the use of these structures as low-dielectric constant nanodielectric with improved mechanical and thermal properties in low-frequency microelectronic technology. They created a PEO-PVA blend-MMT clay nanocomposite. In their research, they describe how they intercalated and exfoliated colloidally stable MMT clay in the suspension of the PVA-PEO blend matrix over a subsequent 24 h. Subsequently, adding clay hydrocolloids to 60 mm stainless steel rings, the PVA-PEO blend-MMT clay nanocomposite was cast and allowed to dry for a week at room temperature. Meanwhile, in the intercalation process, the miscibility of PVA and PEO is facilitated by the rise in polymer chain segmental motion relaxation time with increasing MMT clay concentration up to 2% by weight which is primarily due to intercalated and exfoliated nanostructures of MMT clay sheets allowing polymer chains to be connected by H-bonds.

Recently, exfoliated or Intercalated Montmorillonite (MMT)—PANI nanocomposites (PANC) using emulsion intercalation were reported by Hundekal et al. [68]. They have chosen to utilize a layered silicate known as natural montmorillonite (MMT) as a filler. With an increase in frequency, it is evident that the values of the dielectric constant and dielectric loss decrease. This drops significantly sharply after the onset frequency of the AC conductivity. All PANC nanocomposites' dielectric permittivity significantly increased at lower frequencies (less than 100 Hz), and this demonstrates that in this frequency range, the ionic conduction mechanism predominates.

For the PANI synthesized in this work, a high dielectric constant was observed, which is significantly greater than that stated in the literature [69, 70]. This might be a result of the PANI exhibiting nanocrystalline domains instead of microdomains simply because it was exposed to mechanical shear. They have observed that hyper-electronic polarization and a significant polar on delocalization may be contributing to the high dielectric response for the nanocrystalline PANC at a lower frequency (100 Hz–1 kHz). They have demonstrated that the use of swelling agents in combination with significant shear forces is the most efficient technique of exfoliation or intercalation, and the versatility of clay molecule orientation in the solid state offers a wider route for conduction in the composite.

In 2008, Akat and his co-workers reported a novel synthetic route for the preparation of PNCs which is considered efficient nanodielectric materials by employing a chain transfer agent that is intercalated in the process of traditional free radical polymerization [71]. This method of synthesis is extremely simple, and a facile quaternization procedure yields the interactive chain transfer agent from commercially accessible substances. Irrespective of the structure of the monomer, the above-mentioned technique can be used to polymerize free radicals from a variety of monomers since chain transfer events involving thiol groups are ubiquitous.

A few advantages associated with this technique are that it eliminates the need for various organic during the synthesis of nanocomposite materials. If the filler surface is transformed in such a way that the forces anchoring the particles or platelets together are very weak, the polymer can intercalate between the interlayers. Heat, radiation, diffusion of a suitable initiator, a catalyst, or organic initiator attached by cation exchange inside the interlayer can be used to start polymerization before the swelling phase. Apart from this, the synthesis process has some demerits which include the need for high temperatures but that is undesirable for polymer materials [72]. The desired monomer, when polymerized, was incapable of producing adequate shear stress to effectively exfoliate and achieve adequate dispersion of the nanoclay particles in the polymer matrix [73]. Also, it will work only for low viscous polymers [74].

2.8 Spray Pyrolysis of Nanodielectric Materials

Spray pyrolysis is a technique that produces thin films by simply misting a solution onto a heated surface, where a chemical product is produced when two or more components react. At the deposition temperature, the chemical reagents are chosen so that: other than the desired molecule, the byproducts are typically volatile. The technique has been used for a long time to create a transparent SnOx electrical conductor to glass and is advantageous for the deposition of oxides. Since Chamberlin & Skarman's pioneering work on CdS films for application in solar cells in 1966, there have been numerous investigations reported in this area [75].

A lot of effort has been made in the last several decades to synthesize $BaTiO_3$ powders that are nano-sized and have great phase purity and narrow particle size distribution. Sol–gel processing and co-precipitation of mixed metal oxalates are two examples of solution-based approaches that have been used to design various kinds of nanoparticles [76], including the hydrothermal approach [77]. Spray pyrolysis is being utilized reliably to develop ceramic particles that are between microns and submicron in size. Since it is an effective, continuous method that generates spherical particles with good phase purity and regulated size distributions [78]. Spray pyrolysis yields particles through the evaporation, pyrolysis, and crystallization of atomized liquid droplets [79]. Consequently, on a nanometer scale, all the components of a droplet are mixed homogeneously, and thus, the resulting particles exhibit remarkable phase purity and an outstanding stoichiometric composition for multicomponent oxides. The procedure has a limitation because there was not enough time for solute diffusion or particle densification, which results in a high rate of evaporation and the bulk of the synthesized particles having hollow and porous structures. To control particle morphology, extensive research has been done [80, 81]. A schematic representation of the spray pyrolysis method is presented in Fig. 2.7

Chemical spray deposition processes are categorized based on the type of reaction. As the solvent initially evaporates in process A, a droplet adheres to the surface, providing a solid residue that may still react after it dries [82]. In process B, the dry solid changes the surface because the solvent evaporates before the droplet reaches the surface, where the breakdown occurs. In process C, as the droplet gets closer

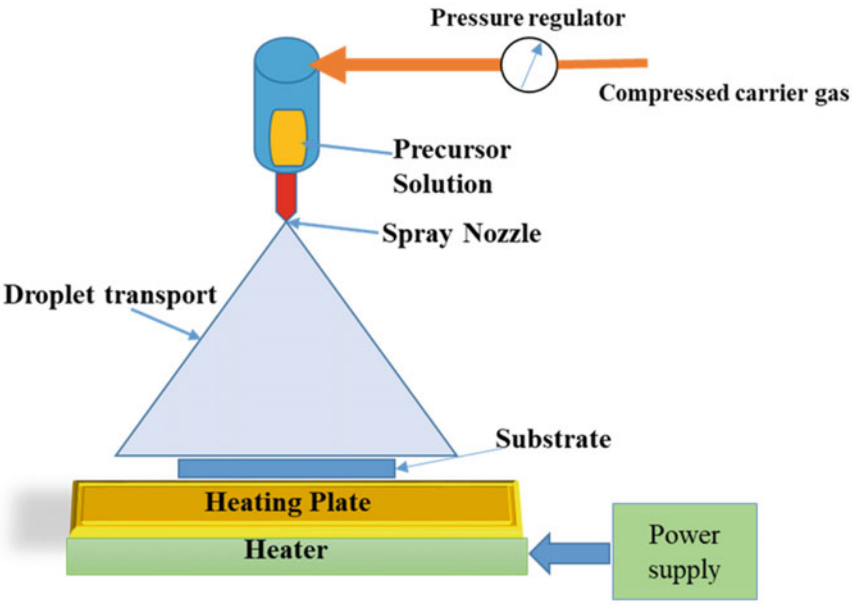


Fig. 2.7 Schematic diagram for spray pyrolysis system

to the substrate, the solvent evaporates; the solid melts and transforms into vapor, which then diffuses to the substrate, where it undergoes a heterogeneous process. (They refer to it as a genuine CVD technique.). In process D, a chemical reaction happens in the vapor phase at the maximum temperatures whenever the metallic compound evaporates before reaching the substrate [82]. The ideal temperature, solution concentration, carrier gas flow rate, droplet radius, nozzle-to-substrate distance, solution flow rate, and, for continuous processes, substrate motion are the key factors in all operations. The chemical makeup of the carrier gas and/or environment should be included in this list, as well as, most notably, the substrate temperature. Type A or Type B studies on spray pyrolysis depositions are the most frequent [82].

2.8.1 Types of Spray Pyrolysis Methods

Several attempts have been made to synthesize nanoparticles utilizing the spray pyrolysis technique, such as low-pressure spray pyrolysis [83], electrospray pyrolysis [84], and salt-assisted aerosol decomposition are reported [85]. Kang and Park introduced a novel aerosol method called the filter expansion aerosol generator (FEAG), and they reported that it can effectively produce nano-sized ZnO particles [78]. Another author, Xia et al. have also reported a novel spray pyrolysis synthesis method to efficiently fabricate nanoparticles, known as “salt-assisted spray pyrolysis” [85]. In addition to this, many researchers have utilized the spray pyrolysis technique for the preparation of highly efficient nanodielectric material and have presented their dielectric properties for various applications.

In 2012, Choi et al. prepared nanoscaled $Ba_{0.7}Sr_{0.3}TiO_3$ using spray pyrolysis, to create hollow, thin-walled particles for dielectric properties. In synthesis, strontium nitrate [$Sr(NO_3)_2$], titanium tetra-isopropoxide, and barium nitrate [$Ba(NO_3)_2$] are used as the precursors for the synthesis (TTIP). The hydrolyzed TTIP was peptized with a small amount of nitric acid [HNO_3] to create a clear solution, and ethylenediaminetetraacetic acid (EDTA) and citric acid were utilized as chelating agents as well as gas evolution additives to increase the hollowness of the particles of precursor. The concentrations of citric acid [$(CH_2CO_2H)_2$], EDTA, and metal components were set at 0.1 M. Precursor powders were processed via spray pyrolysis at 900 °C, and the air carrier gas flow rate was set at 40 L min^{-1}. Post-treatments after spray pyrolysis were carried out for 2 h in an environment of air at temperatures of 900, 1000, and 1100 °C. After being pelletized at 250 kg f cm^{-2} to a diameter of 10 mm, the powders were sintered for two hours at 1300 °C. Using the surfaces of the pellets as an electrode, the silver paste was applied to evaluate the dielectric characteristics. Figure 2.8 illustrates the equipment layout and the process of the nano-sized $Ba_{0.7}Sr_{0.3}TiO_3$ powders developed through spray pyrolysis [86].

Ko and co-workers have also reported on spray pyrolysis by applying the same procedure as described in Fig. 2.8 to create precursors of $BaTiO_3$ nanopowders with varying quantities of Ag. The pellet surfaces were coated with Ag paste to create

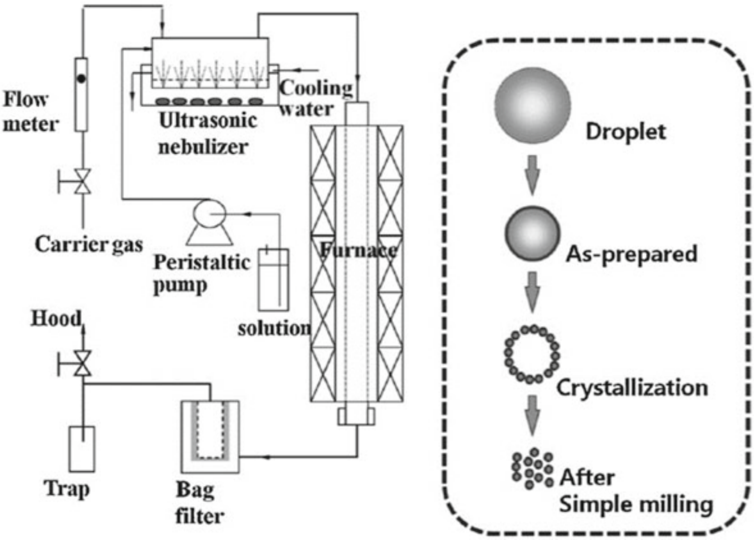


Fig. 2.8 Diagram illustrating the spray pyrolysis process and the method by which ceramic particles of nanoscale are formed [86]. Adapted with permission from ref. [86] Copyright (2012) (Elsevier)

an electrode, which was then used to create electrical contact. An LCR meter was utilized to measure the dielectric characteristics [87].

In another article, authors have reported spray pyrolysis fabrication of Al_2O_3, TiO_2, $Al_{2x-1}{\cdot}Ti_xO_y$, and ZnO nanodielectric materials. Aerosols comprising 50 mg/mL aluminum chloride ($AlCl_3$) and titanium dioxide solutions spray-coated at 420 °C onto commercially available indium tin oxide (ITO) coated glass (sheet resistivity Rs. 15 Ohms/) were applied using a pneumatic airbrush maintained at a vertical distance of around 30 cm (1:5). The spray coating of the precursors and blends' aerosols took place for 30 s, with a 20-s interruption to enable the vapors to settle. They have shown that after successful synthesis of the nanodielectric materials, they were spray-coated on ITO substrate to obtain an optimized thickness. Bottom-gate top-contact (BG-TC) transistors were developed using aluminum (Al) as source material for the manufacturing of thin-film transistors (TFTs) and the spray-coated glass/ITO/composite/ZnO stacks were used to thermally evaporate drain (S/D) electrodes with a shadow mask under a high vacuum. Device characterization was carried out at room temperature and under a high vacuum [88].

Similarly, Adamopoulos et al. reported the fabrication of a dielectric material zinc oxide (ZnO), ZrO_2, and Li-ZnO deposition through the spray pyrolysis process. They have presented transistor fabrication; ITO glass substrates were used to construct bottom-gate top-contact transistors. At a substrate temperature of around 400 °C, high-k ZrO_2 dielectric coatings were sprayed over ITO electrodes. Then, a layer of undoped/Li-doped ZnO with a thickness approximately of 35 nm was sprayed. Through a shadow mask and a high vacuum, aluminum source/drain electrodes successfully thermally evaporated (10^{-6} mbar) after the semiconducting films were deposited by using a spray pyrolysis process [89]. Jung et al. demonstrate the preparation of barium titanate nanodielectric material with tetragonal crystal structures by flame spray pyrolysis method. $BaCO_3$ and titanium tetra-isopropoxide (TTIP) were the substrate materials utilized in the fabrication of the barium titanate ($BaTiO_3$) powder. In the report, they observed that barium titanate powder synthesis via the spray pyrolysis method can function as an efficient dielectric material for various practical applications. Figure 2.9 depicts the flame spray pyrolysis apparatus schematic representation, and Fig. 2.10 represents the synthesis mechanism of the nanoscaled barium titanate ($BaTiO_3$) powders by flame spray pyrolysis process [90].

Spray pyrolysis thin-film coating of khaya gum biopolymer for electrical and dielectric properties was also reported. The primary source for the production of khaya gum was the exudates of the Senegalese khaya trees. Using an agate mortar and pestle, the collected gum was crushed into a powder and then sieved. The solution was then prepared by first refining the KG powder and then dissolving it in 20 ml of distilled water. After that, using a hot plate and spray pyrolysis, it was homogenized and sprayed onto the glass for four minutes at 200 °C and glass slides that had been coated with indium tin oxide (ITO). Aluminum (Al) having a thickness of 100 nm

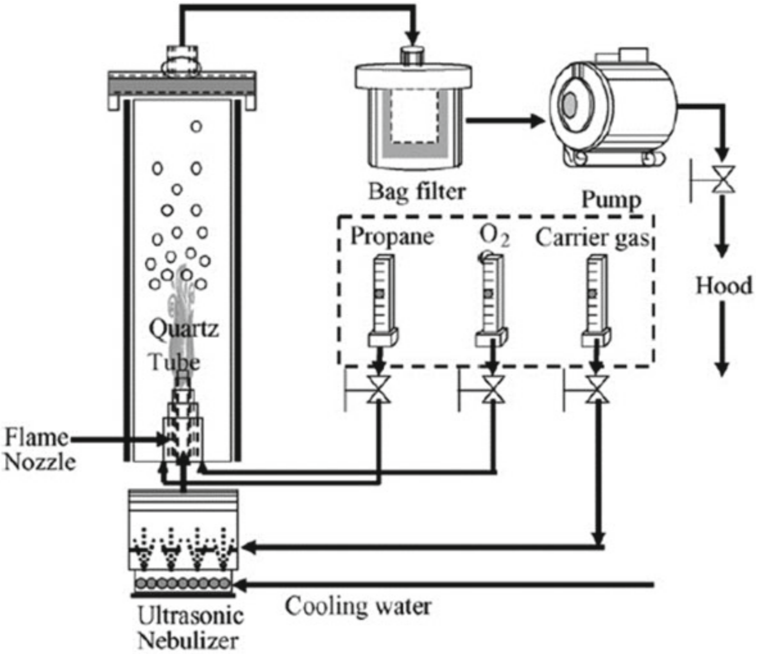


Fig. 2.9 Schematic diagram of flame spray pyrolysis [90]. Adapted with permission from ref. [90] Copyright (2008) (Elsevier)

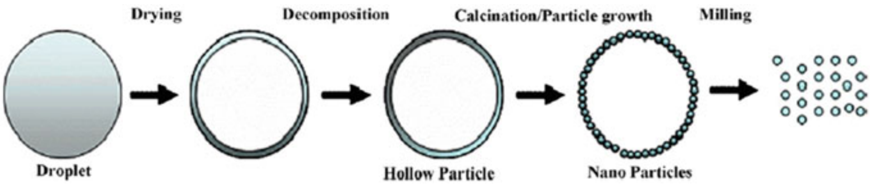


Fig. 2.10 Synthesis mechanism of the nano-sized $BaTiO_3$ powder by flame spray pyrolysis [90]. Adapted with permission from ref. [90] Copyright (2008) (Elsevier)

was thermally evaporated by a shadow mask with an area of 0.01 cm^2 to perform capacitance measurements. They calculated the capacitance values using several frequencies [91].

The following are some advantages of spray pyrolysis: (i) Open-air procedure; (ii) The opportunity to monitor the deposition technique (iii) Economical viable and ongoing operation; (iv) There is no requirement for high-quality regents as precursors; (v) Have higher production rate; (vi) High surface area allows crystal size to be controlled, and (vii) Compositional homogeneity present in fabricated materials. Spray pyrolysis has certain drawbacks also, including (i) a very poor yield produced from the powder materials; (ii) It is necessary to convert the sulfides into an oxide; and (iii) There are several difficulties with temperature optimization [92].

2.9 Reversible Addition-Fragmentation Transfer (RAFT) Process for Nanodielectric Materials

Due to their potential applications, such as in small electronic devices, capacitor materials, pulsed power systems, and power electronics for grid energy management, novel polymeric nanocomposite materials with improved dielectric characteristics are of great interest [93, 94]. Polymer nanodielectric materials synthesized by adding inorganic nanoparticles into polymer matrices have obtained significant attention because they promise the best characteristics of polymer and ceramic dielectrics and are among the most promising techniques for producing high-performance dielectrics [94]. The approach includes the incorporation of conductive polymer along with semiconductive fillers (such as carbon nanotubes and conductive polymers) and high-permittivity inorganic fillers (e.g., Barium titanate, i.e., $BaTiO_3$) or polymers with robust breakdown strength [95]. Ferroelectric polymers including PVDF-based homo- and copolymers and polyimides have been included in polymer nanocomposite matrices. The ceramic filler-based nanocomposites of conductive polymer (PNCs) can incorporate the features of polymers and ceramics and demonstrates a novel category of material that shows flexibility, easy processability, and of low cost [96]. Recently, significantly great approaches have been made toward the fabrication of core–shell nanoparticles, which involve the modification of nanoparticles incorporating polymer shells utilizing several synthetic methods (e.g., grafting from, grafting to, etc.). To develop single or multiple-component nanocomposite systems, most of the modified nanoparticles can be used.

To date, many polymer nanocomposites (PNCs) have been developed, However, certain challenging issues need to be addressed, e.g., homogenous nanoparticle dispersion, strengthening the adhesion of the polymeric particle interface, and optimizing dielectric loss. Consequently, several approaches have been used to deal with these challenges by altering the interface of PNCs through the addition of organic molecules to nanoparticles, along with coupling agents, phosphoric acids, surfactants, and others. However, these techniques still have constraints since surface modifications do not make a direct contribution to accomplishing the objective of enhanced dielectric properties. It has been established that the synthesis of core–shell structured dielectric of polymer nanocomposites (PNCs) via the "grafting from" technique is a promising strategy for this class of materials [97].

Tang and co-workers in 2013, developed a novel polymer nanocomposite using nanodielectric materials containing conjugated oligothiophene side chains. They depicted that the polymers synthesized by the RAFT method possess significant dielectric permittivity, which is comparable to poly (vinylidene fluoride) and significantly greater than most of the other polymers (such as 2–5 for polystyrene and polypropylene, etc.). Polyvinylidene fluoride (PVDF) in particular, polymers exhibit exceptional consistency over a wide frequency range, from 100 Hz to several MHz, with negligible dielectric loss (0.02). This functionality is due to fast-relaxing nano dipoles and significantly higher polarizable related to nanoscaled crystalline domains (<2 nm) incorporated into oligothiophene side groups. Using barium titanate ($BaTiO_3$, BT) nanoparticles and polymers containing oligothiophene, they soon created core–shell nanoparticles with a monolayered structure for use in dielectric polymer nanocomposites. Under controlled/living in situ surface-initiated RAFT polymerization, the oligothiophene-incorporating polymer was grafted from BT nanoparticles [98].

RAFT polymerization has become apparent as one of the best optimistic approaches due to its facile chemical experimental conditions, functional group tolerability, and versatility to a variety of vinyl monomers. In contrast to atom transfer radical polymerization (ATRP) and nitroxide-mediated polymerization, reversible addition-fragmentation transfer polymerization (NMP) relies on the degenerative chain transfer technique rather than the reversible termination of propagating radicals. A chain transfer agent (CTA) that contains thiocarbonylthio is often used by reversible addition-fragmentation transfer (RAFT) to accomplish its deactivation–activation equilibrium. The radical concentration is not significantly affected by the activation or deactivation process, an external initiator is required, and initiation proceeds as in a standard radical polymerization process. A typical RAFT polymerization involves the following four steps: initiation, addition-fragmentation, reinitiation, and equilibration. In the subsequent initiation step, the thiocarbonylthio molecule receives the propagating radical (Pn•).

(1) to generate intermediate radical
(2) followed by gradual fragmentation to generate another thiocarbonylthio group

(3) with a newly produced radical (R•)
(4) Thus, the radical (R•) may react with the newly formed thiocarbonyl group or with a monomer to produce a new propagating radical (Pm•), which can then start the polymerization process. After the subsequent consumption of the initially injected CTA, the degenerative chain transfer process between propagating (Pn or Pm) and dormant chains establish the "primary equilibrium" of activation–deactivation (i.e., the end of the "initialization period").

2.9.1 Merits and Demerits of the RAFT Method

It is believed that reversible addition-fragmentation chain transfer (RAFT) polymerization is a reliable method. Polymerization can be achieved in a wide diverse range of solvents, including water, at various temperatures, with a high functional group tolerance and without the need for metals. Majority of monomers susceptible to radical polymerization can be utilized to prepare confined copolymers or polydispersity polymers using this technique. It is feasible to enhance the conversion of RAFT polymerizations and attain economically viable polymerization rates. In heterogeneous media (emulsion, mini emulsion, and suspension), polymerizations can be carried out robustly. Monomers, solvents, and initiators are compatible with a diverse range of functionalities. Accessible and capable of exhibiting high purity are stars, microgel, blocks, supramolecular assemblies, hyperbranched structures, and other complex architectures. As of 2014, almost all monomer classes susceptible to radical polymerization are incorporated by the diverse range of RAFT agents that are commercially available. Besides this, the RAFT method also has some demerits, such as a specific RAFT agent is only appropriate for a specific set of monomers, and its synthesis often necessitates a multistep synthetic procedure followed by purification. Because the thioester moiety gradually breaks down to produce tiny sulfur compounds, RAFT agents can be unstable over extended periods, be highly colored, and have a pungent scent. For some applications, the resultant polymers presence of sulfur and color may also be undesirable; however, this can, to a certain extent, be eliminated using further chemical and physical purification techniques [99]. This remarkable versatility, however, cannot be attained without carefully considering the RAFT agent and reaction parameters. Inappropriate RAFT agent selection for the monomer(s) and/or reaction conditions is commonly responsible for reported RAFT polymerization challenges (retardation, ordinary than expected control). RAFT agents that perform effectively in one set of circumstances may not always be the best approach.

2.10 Self-assembly Process for Nanodielectric Materials

Organic, inorganic, and polymeric semiconductors that can be processed using a solution have been produced during the last 20 years as a result of factors like printability, the potential for large-area depositions, the ability to manufacture devices at a low cost, and compatibility with substrates that are versatile mechanically [100]. In addition to their mechanical adaptability and flexibility, hybrid materials offer the environmental, optical, and electrical resilience of inorganic materials. Several groups have combined hybrid materials made of self-assembled monolayers (SAMs) and ultrathin MO layers, such as those made of HfOx, AlOx, and ZrOx, to obtain extraordinarily low operating voltage OTFTs. Multi-layered organic–inorganic hybrid materials are necessary for potential and high-quality multilayers adopting the simplest and most reliable way in conventional thin-film transistors and other applications. High-quality hybrid films could be made using vapor-phase fabrication methods for organic/inorganic hybrid materials. However, they usually need high- or medium-vacuum deposition machinery (such as chemical/physical vapor deposition or atomic layer deposition), and it is not immediately clear how to incorporate them into large-volume coating techniques. By layer-by-layer solution-based deposition of precisely defined precursor molecules, a wide variety of functional materials can be produced with a high level of precision and structural control at the molecular level. A variety of such assembly's chemistry has been observed, frequently based on metal–ligand coordination or siloxane. One of these material systems is the family of silane-based nanodielectrics known as self-assembled nanodielectrics (SANDs), which has promising features for a variety of optoelectronic applications, including TFTs. Strong siloxane connections that alternate between organic and inorganic multilayers make up SANDs. Various self-assembly methods can be used to create high-performance multi-layered gate dielectrics for TFT applications [101]. Moreover, the functions of these dielectrics efficiently represent both organic and inorganic semiconductor devices and can be optimized by numerous self-assembled monolayers (SAMs) to boost the TFT efficiency even more.

In general, the molecular self-assembly method describes the spontaneous assembly of precursor molecules to produce nanostructured materials, which can be accompanied depending on their environments and the inherent characteristics of the molecules [102]. To modify the structures which emerge after the self-assembly method, we have to depend on the following deceptive approach: Firstly, the precursor molecule's framework can be utilized to modify the direction of intermolecular interactions, and secondly, carefully choosing the ambient temperature. The spontaneous assembling of molecules into well-defined, stable aggregates with non-covalent bonds at equilibrium conditions is referred to as molecular self-assembly. This method emerges as a novel approach in synthetic chemistry, having the potential of producing nonbiological assemblies having dimensions of 1 to 102 nm (with a molecular mass of 104 to 1010 Dalton's). The above process helps in synthesizing structures with comparable size to those which can be synthesized by microlithography and other methodology of microfabrication [103].

Thin-film transistors (TFTs) made from unusual materials have attracted interest recently because they can be used to make inexpensive electronic devices like printed RF-ID cards, sensors, and flexible electronic displays [104]. Strong capacitances and low processing temperatures (such as 200 °C) are provided by solution-processable self-assembled nanodielectrics (SANDs), which are composed of structurally distinct and substantial layers of alternately alternating inorganic oxide (such as ZrOx and HfOx) and organic (such as stilbazolium) layers. SANDs have produced outstanding device metrics when incorporated with a variety of semiconductors; they have never been incorporated into the most technologically sophisticated top-gate thin-film transistor architecture. Recently, solution-phase methods for the low-temperature development of highly efficient semiconductor films and dielectrics were synthesized by utilizing the self-assembly process of organic–inorganic hybrid nanodielectric (SANDs) films. The potential benefits are also limited by the diversity of the SAND structure, which can be modified to take into account both the organic and inorganic components in addition to the vast variety of suitable unconventional semiconductors.

Tobin J. Marks et al. demonstrated the development pathways of solution-processed zirconia self-assembled nanodielectric material (Zr-SAND) on template-stripped Al substrates. Based on the ultrasmooth (r.m.s. roughness 0.4 nm) nature of the resulting Zr-SAND on aluminum structures, template-stripped metal substrates show the same remarkable electronic uniformity (capacitance 700 nF cm^2 and leakage current < 1 Ma cm^{-2} at −2 MV cm^{-1}) and growth of multi-layered Zr-SAND on Si while demonstrating superior temperature and response toward the voltage capacitance. They reported that the synthesized nanodielectric material is essential to carry out comprehensive transport measurements in developing transistor technologies with SAND including for developing future technologies in flexible electronics or integrated circuits (ICs) [105].

The growth of Zr-SAND is shown schematically in which (a–d) layer-by-layer assembly of the zirconia self-assembled nanodielectric (Zr-SAND) multilayer structure is shown in the following Fig. 2.11. In a separate article, researchers utilized the solution-processed a-IGZO with the four-layer Hf-SAND to create top-gate thin-film transistors (TFTs), which exhibit exceptional bias stress stability and electron mobility (SAT = 19.4 and Vth = (10–100.83 V), subthreshold slopes (SS = 293 mV/dec), and gate leakage currents A. Structures for self-assembled nanodielectric (SAND) gate dielectrics [106].

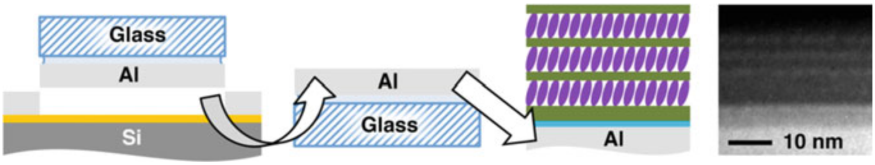


Fig. 2.11 Zirconia self-assembled nanodielectrics (Zr-SAND) solution-processed on aluminum substrates using template-stripped [106]. Adapted with permission from ref. [106] Copyright (2021) (American chemical society)

For the synthesis of nanostructures, solution-based self-assembly techniques have several advantages, such as the ability to control the characteristics of the nanostructures by altering the concentrations of constituent molecules, accessibility of this approach for effectively regulating the size and shape of nanostructures, and simple and economic viable experimental processes. The self-assembly technique yields silicate materials that are prone to aggregation. There are numerous significant challenges with the self-assembly technique because it is relatively a novel technique in nanotechnology. Unfortunately, it is difficult to handle self-assembly on a large scale, and to be extensively applied, we will need to ensure significantly high degrees of repeatability at these scales. The basic principles of atomistic and macroscale processes might differ dramatically from those of nanostructures, and the thermodynamic and kinetic mechanisms of self-assembly are poorly understood. In self-assembling systems, equilibrium time scale and kinetic rates are affected by concepts of thermal motion and capillary action that are less evident.

2.11 Conclusion and Perspectives of Every Synthesis Method for Nanodielectric Materials

Due to their widespread use in industry, particularly in telecommunication and electronic applications, nanodielectric materials. Moreover, different types of nanodielectric materials expand the possibility of realizing numerous significant applications. The nanoparticles have been produced using a variety of unique synthetic methods in order to achieve greater dielectric characteristics. In this chapter, we address alternative synthetic techniques for the creation of nanomaterials with greater dielectric characteristics while keeping the aforementioned in mind. Various synthetic routes have their own merits and demerits which have been well explained. Depending on the type of application of the nanomaterials, researchers have chosen the synthetic procedure, such as thin film, nanocomposite, polymer-based nanocomposite, and metal nanoparticle-based nanodielectric materials. In the sol–gel synthesis approach, nano-sized particles can be prepared with good stoichiometric control and ultrafine particles with narrow size distribution. Also, it takes short time for processing at a lower temperature. The hydrothermal method takes place in a closed system with high pressure and temperature. This process provides large-sized particles for various applications. To synthesize these film-based dielectric materials, spray pyrolysis method can be used, which provides limited size distribution of particles with a uniform coating. In the spray pyrolysis technique, a solution is made to spray on the heated substrate to create a thin film, which further can be used for various industrial applications. Polymer-based nanodielectric can be synthesized using the RAFT method. RAFT method includes the addition of inorganic fillers with high permittivities such as barium titanate, conductive or semiconductive fillers like carbon nanotubes, and other conductive polymers, to those polymers with high breakdown strength. The combustion method provides fast synthesis with the consumption of low energy and gives products with high purity. Control over particle size using the combustion method by choosing appropriate fuel that produces a slow burning rate and less exothermicity. Polymer-clay nanocomposite can be synthesized using the intercalation method. In the intercalation technique, the polymer was incorporated within the layers of clay having few nanometer dimensions. Polymer incorporation largely affected by the intercalated clay structure which is further responsible for the high electrical and dielectric properties of the nanocomposite. Silane-based nanodielectrics are referred to as self-assembled nanodielectrics (SANDs). In the SAMs technique, nanostructured materials were formed by spontaneous assembly of precursor molecules. This method provides a stable and structurally well-defined aggregate associated with non-covalent bonds. Nanofibers with higher dielectric properties can be synthesized by using electrospinning techniques. The electrospinning method is a comprehensive and simple method to get ultrafine fibers from various materials. The applicability of various synthetic routes has provided various challenges for the synthesis of nanomaterials with electronic properties. In the future, these synthetic routes can be further modified to produce other forms of nanodielectric for various industrial applications.

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