Chapter 1
The Past, Present, and Potential Future of Dielectric Nanomaterials

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Abstract Dielectric nanomaterials with a relatively high dielectric loss tangent are used in various fields such are transformers, solar cells, transistors, capacitors, energy storage devices, microwave, and nanophotonic applications. An abundance of bonded surface charges is present on the surface of these nanomaterials that change their functional properties. Dielectric nanomaterials help to improve the dispersion of nanomaterials by applying them as thin film layers or as composites. These dielectric nanomaterials provide less space charge and a lower electric field by forming a multilayer composite and extending the life of electronic devices and electric motors. In this chapter, the past, present, and potential future of dielectric nanomaterials and their surface modification with polymers or several composites such are nanodielectric of metals and metal oxides including their characteristics are highlighted. The importance of dielectric nanomaterials and flexible nanocomposite materials with their wide range of applications for energy storage, electronics, sensors, and their potential deliverables as futuristic devices are presented along with their future scope.

Keywords Dielectric nanomaterials · Flexible dielectric nanocomposites · Energy · Electronics · Sensors

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1.1 Introduction of Dielectric Nanomaterials and Their Origin

Interest in dielectric devices grew in the early 1990s with the discovery that certain thin elastomeric films, such as silicon films, can withstand large electrical stresses and generate large mechanical forces. It is interesting to take a look at the past, present, and potential current developments, current challenges, and future advances in dielectric nanomaterials related to the properties of dielectric nanomaterials [1].

A number of commercial products based on dielectric nanomaterials technology have already reached the market. This effect lags far behind other transducer technologies such as electromagnetism, but the history and potential of the technology are linked to antennas, loudspeakers, microphones (which convert waves into sound signals), and thermometers. It continues to expand from transponders, wireless communications, echo scanning, electromagnetic sensors, and energy storage. Polymer-based nanocomposites are usually chosen for energy storage devices because of their dielectric properties that enhance device performance [2]. Solid–liquid and gaseous dielectric nanomaterials are used along with metal dopants for various applications, whose properties vary with respect to their corresponding applications have made strides in the field of nanodielectrics with advances in the synthesis methodology to modify the structure of chemical nanomaterials applied in electronic applications. The combination of chemical constituents of nanocomposites brings out the dielectric characteristics.

The challenges exist with the use of nanoparticles as they are prone to agglomeration, and there are issues with regard to stability and viscosity in addition to polymer matrices. This results in the need to carry out surface modification of nanoparticles with organic dyes or other organic or electromagnetic nanomaterials and is presented in Fig. 1.1. Changes to the surface of the nanomaterials are a viable method to alter the dielectric properties of nanoparticles with polymers, improving their energy storage and capacity behavior over a long history [3]. This has led to the development of nanodielectrics properties with a wide range of materials and nanocomposites that have reactive flexibility of each dielectric nanocomposite. These nanocomposites also come with challenges, unique properties, advantages, and limitations.

The dielectric behavior of the nanocomposites selected in this chapter includes a wide variety of metals, widely used in energy storage, solar cells, batteries, and many other applications. Modification of dielectric nanoparticles results in changes to the interfacial structure that bring about the reduction in the interfacial force between particles, and the performance of dielectric nanocomposites is degraded. The interfacial charge density provides a stimulus effect on the dielectric properties of the modified nanocomposites [4]. The interfacial location of cationic groups and electron-withdrawing functional groups may reduce the overall dielectric loss and improve the dielectric breakdown strength. Ceramics, plastics, mica, glass, distilled water, dry air, vacuum, nitrogen, and helium are among the natural sources of dielectric nanomaterials. This would lead to a better evaluation of all types of dielectric

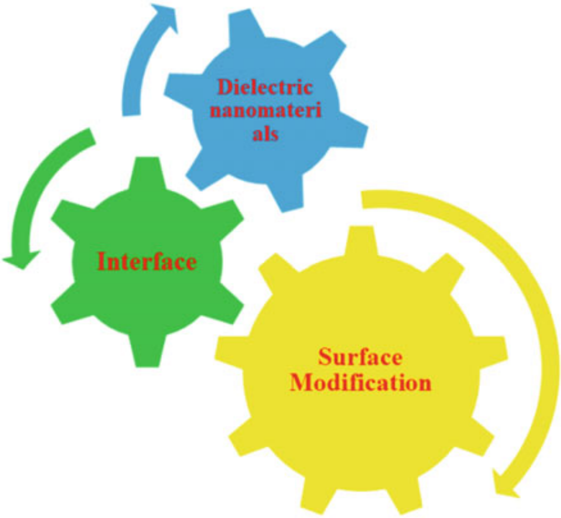

Fig. 1.1 Overview of nanodielectric materials

nanomaterials, and a better understanding of their long-term impact, stability, and potential for global energy storage and human health can be explored [5].

Normally, the dielectric constant of nanoparticles generally increases, and changes can be attributed to the interface relationship between the metal nanoparticles and polymer, which can improve the homogeneity of the composites. High dielectric parameters make it suitable for applications such as conductive paints and sensors. Polymer matrix dielectric non-materials were introduced in the twenty-first century. The rapid growth of life sciences and electrochemistry is impacted by the introduction of carbon-based materials, semiconducting metal oxides, hydroxyapatite (chemical constituent present in natural bone), and many dielectric nanomaterials [6]. Non-dielectric materials of the past have fueled innovation in portable electronics manufacturing and electrical insulation. With their high thermal conductivity, dielectric nanomaterials have found their way into almost all fields, resulting in higher energy storage compared to nanomaterials with polymer matrix dielectric nanomaterials [7]. Their potential applications of nanomaterials-based dielectrics are given in Fig. 1.2.

Their multiferroic properties at room temperature make them ideal candidates for future potential applications in memory devices. These devices are required from scientific calculators to supercomputers with varying sizes and speeds. Life science research is one of the future developments of dielectric nanomaterials involved in the molecules that will lead to upcoming areas of application of nanotechnology-based devices. Although the above dielectric parameters can be used for past and present nanomaterials applications and devices, and the future potential of nanodielectric nanomaterials has differences mainly in the parameters involved in interfacial effects of molecular ordering. The disadvantage of currently used insulating composites is the disintegration of electrical properties [8, 9].

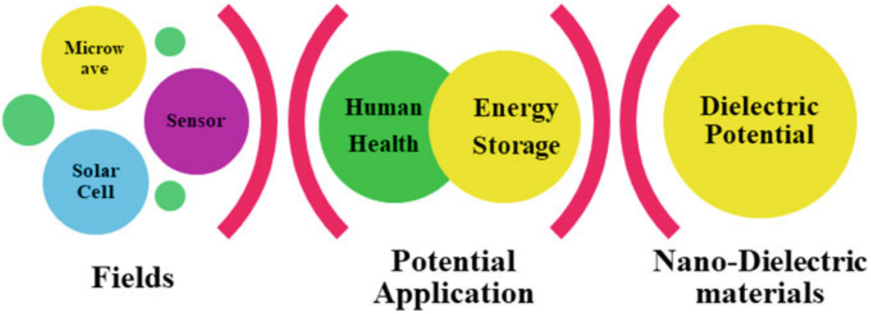

Fig. 1.2 Potential applications of nanodielectric materials

The shortcomings of the present applications offer us the scope for further modifications or the addition of metals to nanoparticles that are required to improve the strength of current dielectric nanodevices. Polymers act as fillers, and the interactions between fillers and nanomaterials impact the physico-chemical and mechanical properties of the polymers paving the way for future improvements in dielectric and electrical insulation. Polymer nanocomposites properties are further modified with inorganic fillers to bring out significant changes in dielectric properties widely used as energy storage materials [10].

1.2 Properties of Dielectric Nanomaterials and Their Applications in the Present Scenario

Dielectric nanomaterials exhibit properties that are required for the fabrication of highly flexible materials. Flexible polymer matrix nanodielectrics have been used in emerging or developing international research fields as it offers scientists the opportunity to present different perspectives, methods, and results [11]. It is presently applied to energy systems, life sciences, medical technology, robotics, machine learning, a host of biomedical devices like artificial skin and dresses with sensors, and electrical isolation among several others. Polydopamine (PDA) is used as a surface adhesive material in combination with polymers, semiconductor materials, inorganic ceramics, and rare metals [12]. Next, the PDA modifiers are commonly applied with nanomaterials, changing the dielectric nature with the use of small molecules like organosilanes, phosphonic acids, dopamine, and carboxylic acids. These characteristic primary organic molecules or nanomaterials prevent aggregation. The leakage current and dielectric damage of these nanomaterial-based devices can be brought down. Further, the dielectric breakdown property is enhanced by the modified surface of the metal oxide which presents an electron-withdrawing functional group with an electropositive phenyl configuration at the interface. After dopamine surface modification, the nanofiller dispersion and its dielectrics in the nanocomposites have enhanced their performance. Surface modification has led to the development of cost-effective methods to improve dielectric devices.

The properties of the nanoparticles present in nanomaterials are affected by the changes in interface charge density which in turn impacts the performance of dielectric composites. Dielectric nanomaterials and their composites are attractive for applications in dielectric capacitors as the carbon-based energy and fuel resources are being over-exploited for energy requirements, and its pollution levels have harmed the environment depriving us of clean air. Renewable energy technologies based on solar, wind, biofuel, geothermal, and tidal power are the leading alternatives to replace carbon-based energy resources [13]. A major challenge for renewable energy today is achieving efficient conversion and storage. The dielectric of capacitors with surface-modified nanomaterial brings about a change in the levels of dispersion due to flexible dielectric nanomaterials. Dielectric nanoparticles with relatively high dissipation factors are chosen due to the abundance of bound surface charges present on their surfaces. The dielectric properties of the fabricated nanocomposites are evaluated by recording the capacitance of the surface-modified nanocomposites as a function of frequency to determine the real (ε') and imaginary (ε") components of the complex permittivity [14].

Dielectrics are non-metallic substances with high resistivity, insulation resistance, and negative temperature coefficient of resistance. Other hands it is a non-conducting substance that retains an electric charge, and it has free electrons for current to flow. In the presence of an electric field, no charge flows through the material. The charge shifts slightly from its average equilibrium position due to dielectric polarization in the presence of an electric field. Further polarization results in the flow of positive charges toward the field, while negative charges move in the reverse way of the field. This property brings about changes in the internal electric field leading to the enhanced capacity to accumulate electrons inside materials, and this property result enhances the energy storage applications [15].

The dielectric properties of nanomaterials have changed in their fundamental molecular properties that are capable of imminent electron migration even though the energy gap is very large for dielectric nanomaterials. This in turn brings about a change in polarization when it is subjected to a peripheral electric field. Further, a negative temperature coefficient of resistance is obtained that could increase the conductivity, the resistivity of the semiconductor material decreases with increasing temperature, and the insulation resistance is high which allows objects of a certain size on the surface of metal plate. Being a poor insulator and an excellent conductor of electricity, it retains a large amount of charge for a long period. Dielectric nanomaterials have high resistivity, and the electrostatic force between electrons and nuclei is very strong. Electrical breakdown is observed with these materials as a disadvantage with these insulating materials. Finally, it is the mechanism of nanometric interfacial and molecular ordering processes that triggers the electrical breakdown in these insulating materials which need to be studied. To overcome the drawbacks, the present applications need some more changes or addition to enhance the current nanodielectric devices' strength [16].

Hydrogels synthesized by polymerization using dielectric nanomaterials as dopants are excellent candidates for 3D cell models due to their biocompatible structures. Further, it provides useful properties for biosensors and tunable drug delivery applications. Electronic device applications are based on the light intensity, chemical structure, and dielectric characterization of dyes—methylene-blue (MB), rhodamine-B (RB), and MB/RB dyes along with $NiFe_2O_4$ nanoparticle-based hydrogels as a function of frequency and bias, viscosity, and zigzag motion have approximately equal parts of the same absorbing medium absorbing equal parts of incident light in terms of suitability for biocompatibility for biosensor based applications. Hydrogels doped with organic dyes exhibit low adsorption coefficients such as MB, RB, and MB/RB, whereas dielectric nanoparticles exhibit high adsorption coefficients as a result of the dipole, Fermi direct distribution, which increases electron transfer [17]. Hydrogels doped with $NiFe_2O_4$ nanoparticles, the small size and high ratio of emitted photons to absorbed photons offer new scope for biomedical imaging of cancer and other target molecules in-vivo in the human body.

Organic dyes have been incorporated into hydrogels framed works to detect the membrane biology of the cells and image them with doped nanoparticles. These materials should have increased dielectric capacity on the application of electrical potential that results in partial ionization at elevated temperatures for applications in e-cars, e-bikes, space, and high-temperature furnaces industry. Polymers incorporated with dielectric nanomaterials show superior results of excellent power density and excellent rate capabilities. Power density indicates how quickly a device can deliver energy than batteries such as magnesium, lithium, and zinc ion batteries. One of the major problems of today's scenario in aircraft engines is that it requires some form of cooling to prevent engine damage. Normally, these cooling devices break down resulting in degradation of the critical electronic-based control systems due to disabling of cooling systems. Here, there is a requirement for materials that can withstand temperatures of up to 250 °C for power electronics and heat sources which causes damage to electronics systems [18]. Therefore, polymer matrix nanoparticles provide excellent cooling even under a high electric field which is a property to be incorporated in dielectric capacitors to withstand all weather conditions. The various types of dielectric nanomaterials currently being used along with their potential applications are summarized in Table 1.1.

1.3 Nanodielectric of Metals

The metal and polymer composites are solid-based dielectric nanomaterials that show extremely improved properties with respect to surface structure, the interaction between particles, and the size of nanomaterials. Nanodielectric metals are commonly expensive to manufacture as it involves the use of a large magnetic spin moment and strong ferromagnetic coupling due to high Curie temperature. Metals are solids, and they can have anisotropic behavior where nanodielectric metals have

Table 1.1 Types of dielectric nanomaterials currently being used along with their potential applications

Types of dielectric nanomaterials	Dielectric constant value at kHz	Application
Pure PVC	3.2	High thermal conductivity metal industry
Metal nanoparticles	1.2	Energy, sensors, and superconductors
Polydopamine	3.2	Energy, solar cell, and biomedical
Metals	1.3	Energy, sensors, biomedical
Hydrogels	1.5	Biomedical, drug delivery, and 3D cells models
Metal oxides	1.5	Energy, sensors, and biomedical
Polymer nanocomposites	3.2	High-voltage cables
Carbon-based nanocomposites	2.8	Solar, wind, biofuel, geothermal, and tidal power
Organic nanocomposites	2.5	Membrane biology and thermal barrier coating industry

large magnetocrystalline anisotropy which means it does not have the extrinsic property of metals which has ferromagnetic behavior and is not dependent on the particle size and structure, but the quantum of energy required for magnetization in each direction is high. The crystal lattice angles dictate these directions, as it is essential that the orbital motion of electrons coupled to the electric field of the crystal would provide the first-order contribution to the magnetocrystalline anisotropy. Studies have reported that gold, germanium, zinc, and some other metal nanoparticles have shown that the dielectric behavior changes contribute the device applications [5, 19]. These nanodielectric properties could be applied to interdisciplinary sciences involving chemistry, biology, physics, and materials science to fabricate these devices.

1.3.1 Gold

Gold has characteristics of high tensile strength which is responsible for developing uniform coatings with polymer matrix, and the obtained surface structures are ideal for the required applications. Trace levels of gold are used to cure the disease in medicinal applications so that it can kill or destroy the harmful cells present in the human body. The smaller levels of gold are well tolerated by the human body. Gold nanoparticles present in the composite with the polymer matrix are suitable materials for health care, cosmetics, tissue engineering, and most importantly medical diagnostics and sensors applications. Gold plays a vital application on both sides of electrochemical-based devices as well as in the process involving biomedical aspects of drug delivery systems [20]. The reason this gold is an ideal material for many applications is due to its enormous dielectric property of gold nanoparticles and its antibacterial activity that favors the development of smart drug delivery systems. Gold-containing nanoparticles have high dielectric constant and dielectric loss which enhances the dielectric properties when compared to the pure polymeric matrix [21].

The vibrant optical property of nanomaterials enhances the device application and also has strong catalytic properties for all types of industrial applications. The presence of gold in the composite with polymer matrix enhances the dielectric constant due to the composition of polymer materials as they act as conductive fillers. This type of high-energy storage material is more needful for the future to replace the need for deficiency of nonrenewable sources. Society needs storage devices to store more energy for the future with high dielectric permittivity (ε’) at the low applied voltage, and this can be developed with gold nanoparticles [4].

The polymers used have different chemical compositions, and these changes affect the dielectric constant of nanomaterials; for example, the copolymer which is formed with two different monomers react together to form more flexible properties. Already gold has more tensile strength compared with the transition elements present in the periodic table and also as a composite with copolymers it enhances more flexible properties that interconnect with the conductive fillers to produce more efficient energy-stored capacitors.

1.3.2 Metal Oxides

Zinc oxide is a transition metal oxide with the formula of ZnO which is commonly used for several applications from plastics to rechargeable batteries as ZnO nanostructures can be used as anode materials in lithium-ion batteries. Materials with low frequency and temperature dependence are well suited for the fabrication of devices. Nano copper (II) oxide (CuO) has a superior dielectric constant and is independent of the temperature of the device. M-type hexagonal ferrite with the chemical formula $\mathrm{M\,Fe_{12}O_{19}}$ (M = Ba, Sr, Pb) has excellent oxidation resistance, high magnetic material resistance behavior to variations in the magnetic field, and has the magnetic field strength capacity to demagnetize a completely magnetized material [22]. These nano oxides have the ability to provide information about the remanence and magnetic energy of the products. These characteristics of dielectric nanomaterials can be used as sensors, radar adsorptive materials, and several others. The rare earth metal doped in glass matrix results in enriching the optical properties. The silicon solar cell shows a high refractive index due to the plasmonic effect of gold and silver nanoparticles which are the reason for the rare earth metal growth on the glass matrix. This kind of material is widely used in ultrafast device response [22].

1.4 Applications of Dielectric Nanomaterials in Energy, Electronics, and Sensors

The wide range of applications of nanodielectrics is illustrated in Fig. 1.2, and this technology has been applied in many areas. The prominent areas are space charge suppression, charge storage, partial discharge (PD) resistance, high thermal conductivity, and the biomedical field which lead to the significant role of nanodielectrics in sectors like energy (supercapacitors and batteries), electronics, and sensors. The most prominent applications of nanodielectrics are as follows:

1.4.1 High Voltage Direct Current (HVDC) Cable

Nanodielectrics possess excellent dielectric properties and can moderate the internally developed electric field. In the case of conventional dielectrics, the space charge accumulation can destroy the distribution of the electric field and thereby degrading the polymer chain gradually. The polymer-nanoparticle composite (PNC) is a revolutionary material system that prohibits space charge accumulation and has been proven as a boon to researchers in this field. Many researchers have explored different PNCs. The incorporation of poly(stearyl methacrylate)-grafted SiO_2 into crosslinked polyethylene (XLPE) was studied by Zhang et al. [23] and showed the efficient suppression of space charge that led to limit the distortion in the internal field by 10.6% at room temperature over a broad externally applied DC field ranging from 30 to 100 kV/mm. Chu et al. [24] have used carbon-doped TiO_2 nanofibers in P(VDF-HFP) nanocomposites and studied their dielectric and energy storage properties. The incorporation of MgO nanoparticles in the MgO/low-density polyethylene (LDPE) nanodielectrics resulted in the enhancement of the average trap depth that led to space charge accumulation near the electrodes [25]. Ganea et al. [26] reported the effect of incorporating TiO_2 nanoparticles in bis-imidazolium salt with two cyanobiphenyl groups and dodecyl sulfate counterion (BIC). They have showed the conductivity enhancement with an increase in temperature and doping concentration at a constant frequency as shown in Fig. 1.3a–c. Besides, the characteristic relaxation time was found to decrease with an increase in the TiO_2 nanoparticles' concentration. The effect of the coupling agent was studied by Wang et al. [27] on the electrical properties of Al_2O_3/LDPE nanodielectrics and observed that the modified Al_2O_3 exhibits better space charge suppression than that of pristine one. Chen et al. [28] explained the charge dynamics in nanodielectric materials using deep trap formation by introducing nanoparticles in the material. In another work, space charge characteristics of polypropylene (PP)-based nanodielectrics were investigated by Zhou et al. [29] for its application as a recyclable insulating material for HVDC cable (Fig. 1.3).

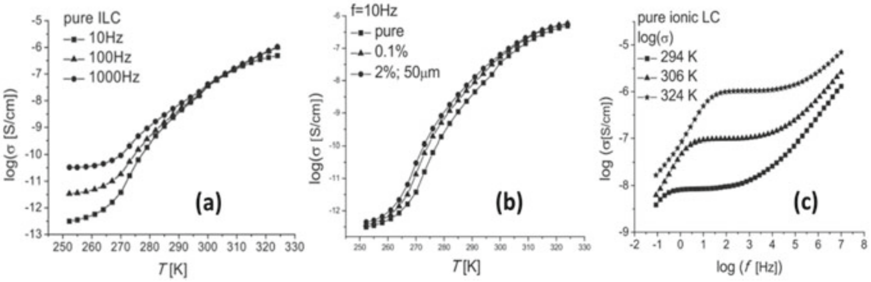

Fig. 1.3 **a** Temperature dependency of the electric conductivity σ' for BIC, **b** Electric conductivity versus temperature at a fixed frequency, $f = 10$ Hz, for the samples: BIC, BIC-01, and BIC-2, and **c** Conductivity spectra at $T = 296$ K, $T = 306$ K, and $T = 324$ K for BIC. Adapted with permission from ref. [26], Copyright: Elsevier, 2020

1.4.2 Nanodielectrics for Energy Storage Applications

Capacitors are the main energy storage components in electrical and electronic circuits as well as sensors [30]. These are of various types, viz. thin film, ceramic (film and laminated), electrolytic (aluminum and titanium), and the most sought supercapacitors type. Among these, the largest are supercapacitors and electrolytic which are manufactured by many manufacturers like Panasonic, Kemet, Murata, Vishay, etc. [31]. The energy storage capacitors seek huge applications in defense for transportation through vehicles, aircraft, and ships. For significant improvement of proficiency of energy storage in the capacitor, the dielectric material is required to possess high energy density [32]. Capacitors are highly required in power circuits for conditioning. It provides a constant current flow in the electrical circuit by regularizing the fluctuations in the current. The capacitors are more important for the circuits which are used for a wide range of temperature and frequency [33]. Energy-storing capacitors are highly important in power electronic circuitries, AC, and DC filters. Huai et al. [34] analyzed the importance of electrolytic and PNC film capacitors in DC-link filters for their high energy density, current, and voltage regulation efficiency, reliability, and stability provided to the circuit. Nanodielectric materials possess high dielectric constant and exhibit high breakdown field strength, hence are an important part of capacitors. The nanodielectrics are advantageous in enhancing the storage density of capacitors and supporting the miniaturization of the capacitor. The excellent dielectric breakdown properties, anti-aging properties, temperature, frequency independence, and reliability are some of the issues that need to be explored in the near future [35].

1.4.3 High Thermal Conductivity of Nanodielectrics

Nanodielectrics with high thermal conductivity are highly required for electrical as well as electronic circuits and systems. For applications employing high-voltage fields, the dissipation due to leakage current is enormous when the conducting voltage is enhanced. Particularly, for miniaturized devices, the compactness of the device will lead to more generation of heat in integrated circuitries.

Most of the literature on nanodielectrics focuses only on the thermal conductivity of the material. However, thermal expansion and breakdown strength studies are equally important and play a key role in the microelectronic packaging of integrated circuits. High thermal conductivity can be achieved by incorporating nano-sized fillers in polymer host matrices [36]. These fillers can create thermally conductive pathways like whiskers and filaments in the host matrix and modify the thermal resistance at the contacts [37].

There are various fillers that have been used to enhance the thermal conductivity of dielectric materials. As mentioned in an earlier section, these are classified as metal nanoparticles like Ag, Cu [38] inorganic nanoparticles like Si_3N_4, BN, AlN, SiC, MgO, SiO_2, and Al_2O_3) [39–41], and carbon-based materials [42, 43]. Sengwa et al. [39] reported a comparative study of different metal oxides fillers like Al_2O_3, SnO_2, TiO_2, and ZnO) in PVDF blended with poly (ethylene oxide) (PEO) for their dielectric properties and concluded that the incorporation of Al_2O_3 nanoparticles significantly improved the dielectric permittivity of the PNC as shown in Fig. 1.4. Boron nitride nanosheets (BNNSs) have also been proven to be a great influencer in improving the thermal conductivity of PNCs and explored by Seyhan et al. [44] and Sun et al. [45]. Additionally, the thermal conductivity of the polymer was reported to be highly dependent on the geometric distribution of the BNNSs in the host in the former case, whereas Ag nanoparticles were also used in the latter case to reduce the interfacial thermal resistance between two adjacent BNNSs. In another report, Hong et al. [46] suggested a different approach for enhancing the thermal conductivity and mechanical stretching of the PNC by incorporating a 3D hexagonal BN network in the polymer. Graphite was used as a filler for synthesizing nanodielectric PNC by Zhang et al. [47].

1.4.4 Nanodielectrics for Rotating Machines

The rotating machine systems include electric motors and generators. Nanodielectrics play a crucial role here too to restrain partial discharge (PD) to occur. Rotating machines are highly useful to run many appliances, smaller equipment, machines, etc. And PD may accelerate the degradation of polymer sequences and can cause major breakdowns of appliances or machines particularly for high-voltage devices. In high-voltage machines like pellet on and other electrostatic accelerators, homogeneous

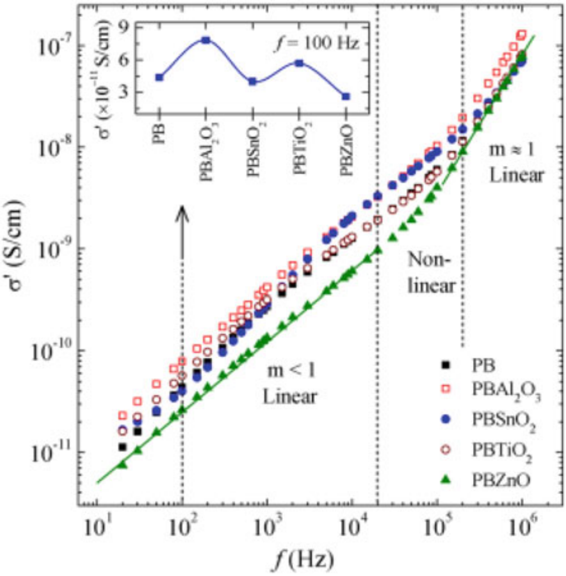

Fig. 1.4 Thermal conductivity spectra of the 75PVDF/25PEO blend (PB) film and the 75PVDF/25PEO–5 wt% nanofillers-based different PNC films (PBAl$_2$O$_3$, PBSnO$_2$, PBTiO$_2$, and PBZnO), at 27 °C. The solid lines drawn on the conductivity spectrum of PBZnO film represent linear fits of the low-frequency data as well as high-frequency data. Inset shows the comparative plot of thermal conductivity at 100 Hz for different PNC films. Adapted with permission from ref. [39], Copyright: Elsevier, 2020

distribution of electric field is hard to realize, and hence, there are high chances for surface corona discharge thereby breakdown down the machine.

An investigation on the property of PD resistance in nanodielectrics is highly desirable to understand the quality and its performance for prolonged high-voltage applications. There are three key parameters that decide the efficiency of a nanodielectrics material. These are PD current, erosion depth, and surface roughness. Here, again the incorporation of nanofillers like fumed silica (SiO_2) in XLPE [48] and silicate in polyamide [49] can be a boon to strengthen the bonding by resisting energetic charges moving in the polymer. This way, it is possible to shield the polymer and enhance the life of the equipment.

1.4.5 Nanodielectrics for Modulation and Sensing

In a recent breakthrough work, Tan et al. [50] reported the induction of dynamically controllable quasi-bound state in the continuum (QBIC) with ultrahigh quality factor in a symmetric metallic metal surface at terahertz (THz) frequencies using a nanodielectric or semiconductor layer, having thickness 1000 times less than the resonant wavelength (λ/1000), Additionally, the germanium nanostrips work as microchannels for their promising application as BIC-based refractive index sensor. The nanostrips provide 200% transmission intensity modulation when subjected to photoexcitation with very fast recovery (~ps). The sensitivity of the refractive index sensor was reported as −24.5 GHz/RIU with a 500-nm-thick superstrate as depicted in Fig. 1.5a–c.

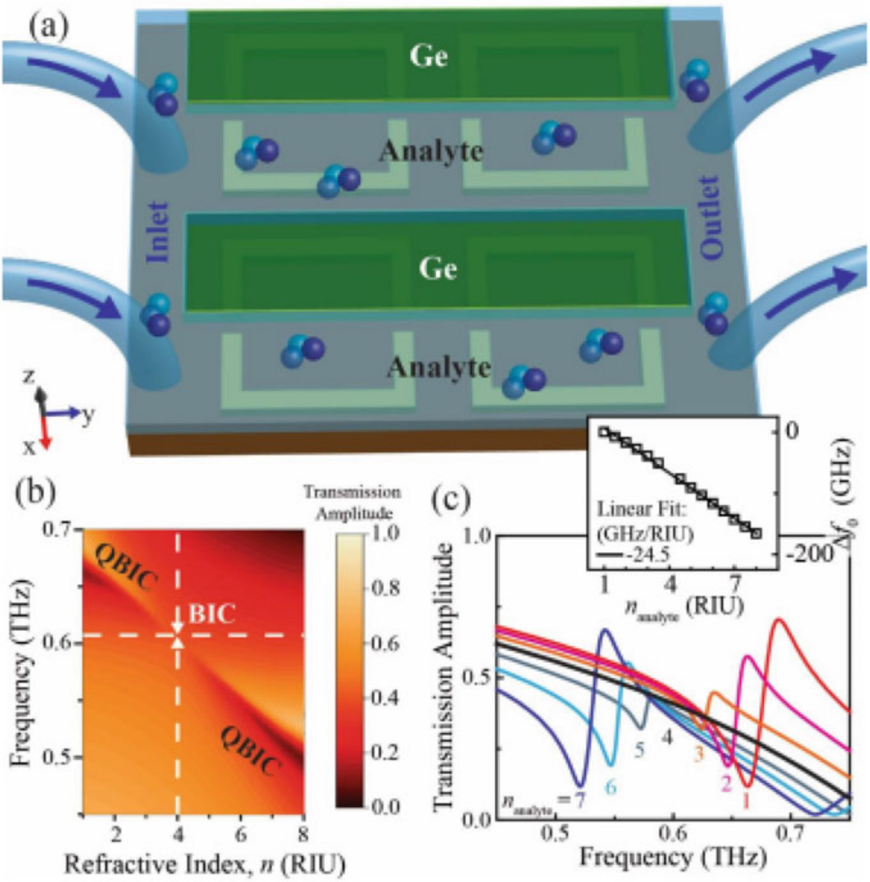

Fig. 1.5 Terahertz refractive index BIC sensor. **a** Illustration of the device with analyte flowing through the Ge strip microchannels. **b** Simulated transmission amplitude spectra showing the collapse and revival of the BIC resonance mode with changing the refractive index of an analyte placed in microchannels separated by the Ge strips of the device of Fig. 1.2a. The refractive index of Ge is 4 (vertical dashed line), and the calculated BIC resonance (from COMSOL) is at 0.61 THz (horizontal dashed line). **c** Transmission amplitude spectra of the QBIC resonance for a superstrate thickness (Ge strip and analyte) of $h = 500$ nm and different refractive indices of the analyte. The inset shows the frequency spectral shift as a function of the analyte refractive index. The device sensitivity in terms of frequency shift per refractive index unit is obtained from the slope through a linear fit. Adopted with permission from ref. [50], Copyright 2021

1.4.6 Advanced Applications of Dielectric Nanomaterials in Various Fields

The solid dielectric material such as ceramic substances has proven superior dielectric properties which is the major requirement for the development of supercapacitor applications. These solid materials should have characteristics of definite shape and structure. Solid dielectric nanomaterials depend on the distance between two grains and their size followed by the bonding between particles. Ferromagnetic substances doped into ceramic materials enhance the performance of supercapacitors. Chromium nanoparticles incorporated into the crystalline structure of superconducting (CuTl)-1223 matrix to obtain (Cr)x/(CuTl)-1223 superconductor composites are an example of supercapacitor application [51].

The dielectric nature of nanocomposites enables us to deploy them in energy storage applications as capacitors. The common factors which affect the energy storage levels and its discharge properties in nanocomposite materials are an accumulation of nanofillers and phase separation in the composites as this leads to the two constituent phases which are separated apart. This leads us to concentrate on improving the energy conversion rate of dielectric nanocomposites to influence the potential to enrich them to be incorporated as capacitive devices. Silanes have been the best candidates as modifiers with the only setback being its hydrolytic stability that restricts its development. The other candidate available is phosphonates which contain phosphorus and are also an insurmountable weakness in its detrimental properties that affect our environment. To overcome these challenges, there is a need for surface modifiers such are low-molecular-weight carboxylic acids and catechol which are present in dopamine and polydopamine and can be explored as surface modifiers. This surface modification focuses on silanes, phosphonates, and dopamine as chemical agents to modify the surfaces of metal oxide dielectric nanomaterials. Chemical modification of nanomaterials brings about a change in the functioning capacity of dielectric properties which include breakdown strength, energy density, and dielectric constant of the nanocomposites. The dielectric calculations of these nanomaterials depend on the frequency and temperature applied to the system as it fluctuates, and the parameters which affect the dielectric materials include conductance (G), capacitance (c), tangent loss (tanδ), and complex dielectric constant ($\varepsilon r'' = \varepsilon' r - i\varepsilon'' r$) varies. These parameters can be calculated by using an impedance analyzer. If temperature increases, the $\varepsilon r''$ are also increases as most energy is lost from the sample, but it is inversely proportional to the frequency given to the system.

Specific polymer matrices are used to potentially determine the final performance for optimizing nanocomposites and the properties of dielectric nanomaterials which are responsible for the various applications and the ways to overcome them have to be explored [51]. Dielectric-polymer nanocomposites are most suitable, but the choice of chemical reactions or chemical reagents used to functionalize these nanomaterials in the polymeric matrix determines the potential performance in various applications. Surface modification techniques have been widely used to modify nanomaterials for dialectics, but there is scope for further research in this field.

Several classifications have been used to classify dielectric nanomaterials as they differ in their dimensions, breakdown strength, surface area, composition, porosity, nature of ceramic inorganic materials, negative temperature coefficient of resistance, high insulating resistance, and polarization. MgxCa (0.90-x)Zn0.10Fe_2O_4 nanoparticle is an example of a surface-modified system for microwave applications [52]. Permittivity and dissipation factor, loss tangent, and dielectric constant are the properties that need to be evaluated to test the suitability of nanomaterials for microwave application. These properties indicate the role of metal nanoparticles on the dielectric properties of the developed nanocomposites. The presence of polymer matrix helps to clarify the applicability of metals/microelectronics industry such as transistors, capacitors and resistors, solid-state devices like solar cells, semiconductor laser, electrochemical sensing, and electricity resistance.

Parallel plate capacitors can only store a limited amount of energy before dielectric breakdown occurs. Because of the setting of the electric field in between two parallel plates are connected across the battery by external charge. This is used to measure the dielectric properties of materials; on the other hand, the impedance analyzer was used to measure the dielectric loss with respect to changes in frequency. It explained that dielectric loss is the energy loss that occurs when heating a dielectric material with a varying electric field or AC circuit alternately charges and discharges every half cycle. Dielectric nanomaterial especially gold has higher dielectric loss with polymer matrix concerning all frequency ranges from impedance analyzer. The dielectric loss of nanomaterials is directly proportional to the polarization resulting in a higher dielectric constant, and dielectric loss can be attributed to the maximum polarization of dipoles at low and high frequencies. The dipole polarization is minimal and the dielectric constant and Dielectric loss is reduced. The dielectric loss can be calculated by using the below formulae

$$\varepsilon * (\omega) = \varepsilon(\omega) - \mathrm{i}\varepsilon'(\omega)$$

where ε is a real number (permittivity), and ε′ is an imaginary number (dielectric loss) Part of the dielectric constant of a material.

1.5 Flexible Dielectric Nanocomposites

Flexible polymer-based nanocomposites (PNCs) have attracted researchers for frontier research on flexible electronics, sensors, and energy devices. Flexible matrix provides the folding and bending opportunity to device foldable electronics [40, 53–56], fabrication of sensors [50], energy devices [54–59], electromagnetic shielding [60], etc.

As far as flexible energy harvesters are concerned, Kar et al. [59] devised a highly efficient self-cleaning piezoelectric nanogenerator (PSNG) based on 2D SnO_2 nanosheet and PVDF polymer nanocomposite. The schematic representation of the fabrication process of PSNG is depicted in Fig. 1.6a–e. They adopted a simple

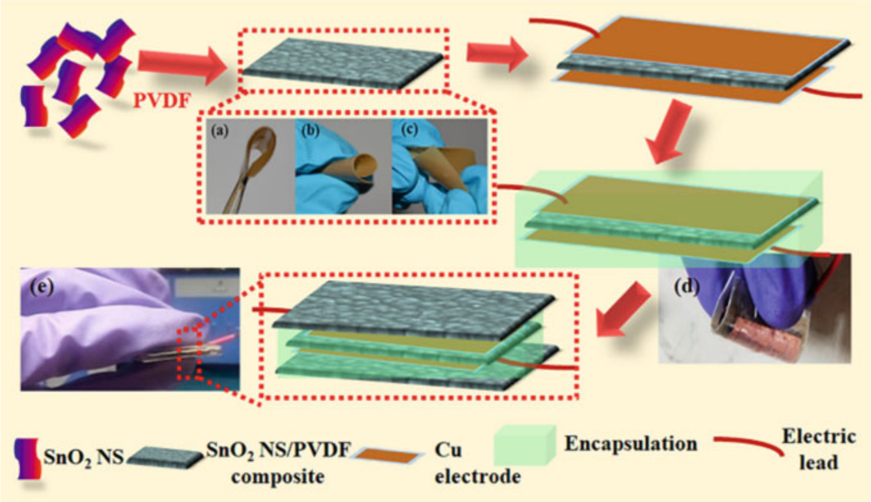

Fig. 1.6 Schematic representation of the process of fabrication for PSNG, Images show **a** bending, **b** rolling, and **c** twisting of the sample S-5.0. Digital images of PSNG **d** before and **e** after covering with SnO$_2$ NS/PVDF. Adopted with permission from ref. [59], Copyright: Elsevier, 2019

approach of hydrothermal to prepare 2D SnO$_2$ nanosheets and their composites with PVDF in different concentrations of SnO$_2$ were synthesized using the facile solution casting method in thickness $\sim 100 \pm 5$ μm. So formed self-standing PNC films are easy to bend, fold, twist, and roll as shown in Fig. 1.6a–c.

A summary of this entire work is schematically represented in Fig. 1.7a. The PSNG is capable of energy generation (illumination of LED panel) by body movement, sound energy of the string of a guitar, air blowing, and the self-cleaning property of 2D SnO$_2$ nanosheet-PVDF nanocomposites. Figure 1.7b shows the real-time applications of this PSNG under bio-mechanical pressures, particularly with human body movements like tapping by finger, twisting by the wrist, pressure by heel and toe, etc. The PSNG is capable and efficient to illuminate a panel of 85 blue and yellow LEDs directly and instantly without any capacitor or storage through a rectifier circuit connection using gentle imparting of human fingers. Other ways to generate power are depicted in Fig. 1.7c–f. The power generation using this PSNG was investigated under air blowing by an air-blower (Fig. 1.7g) and sound using a speaker of 3W (Fig. 1.7h).

Polymer-based flexible nanodielectrics are immensely beneficial for biomedical and futuristic robotics as well. The electroactive polymers (EAPs) exhibit a change in shape or size if subjected to an external bias. Advanced robotics find numerous applications of these EAPs as artificial skin to the human-like robots. EAPs are preferred owing to their fantastic dielectric properties, flexibility, robustness, lightweight, faster response as well as economic [61].

Numerous efforts have been carried out to realize this futuristic and revolutionary research. Particularly, capacitive type sensors are extremely useful for different

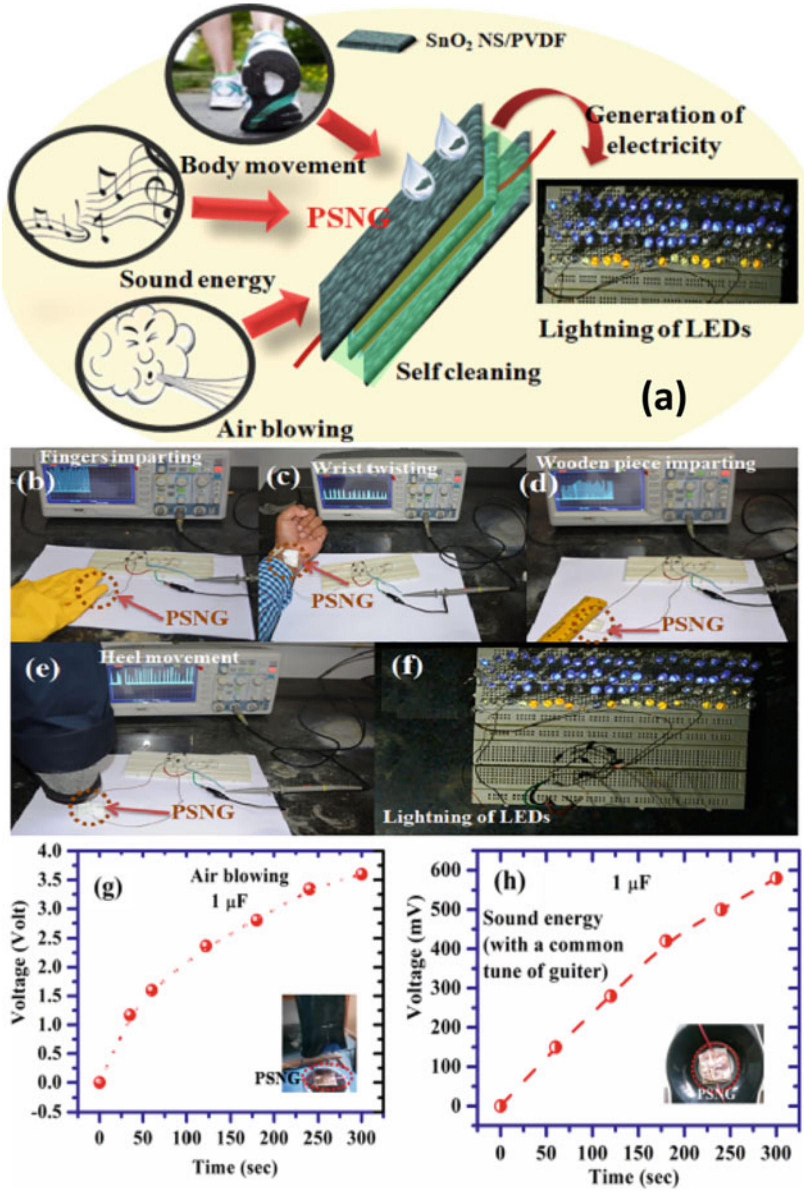

Fig. 1.7 **a** Schematic representation of the function of the flexible and self-cleaning energy harvester. Digital images of piezoelectric power generation (rectified output voltage) by PSNG due to **b** fingers imparting, **c** wrist twisting, **d** wooden piece imparting, **e** heel pressure. **f** Digital image of instant illumination of 85 numbers of commercial LEDs by simple finger imparting onto the upper surface of PSNG. Charging capacitor (1μF) by power generated from the PSNG via **g** air blowing, and **h** sound (a common tune of guitar) from a speaker using a full wave rectifier. Capacitor voltage reached around 3.5 V for air blowing of250s duration. Adopted with permission from ref. [59], Copyright: Elsevier, 2019

biomedical applications owing to their low power consumption, environment friendliness, and sustainability in adverse conditions. Their promising applications are health monitoring can be done by wearable sensors, electronic skin (e-skin) for artificial intelligent appliances, etc. [62]. Dielectric elastomers (DE) are a special class of EPAs, which are designed by sandwiching a thin and soft layer of polymer between two compliant electrodes and are extremely promising for making muscles of human-like robots. In this row, simulations of human facial expressions on the artificial skin were experimented with by Kwak et al. [63]. Additionally, the electromechanical properties of Des are extensively useful as touch sensors and functional sensors as well as the interconnects for the artificial outer skin of the robot to the circuits inside [64]. In other work, multi-walled CNTs were used as fillers in DEs to prepare nanocomposite. Further, their electrical and shape properties were examined, and it was observed that less power is required with better deformation properties.

1.5.1 Challenges with Present Dielectric Nanomaterials and Future Perspectives

The challenge with these types of dielectric nanomaterials is the separation of conductive particles of porous ferrite or dielectric nanomaterials samples, the value of the dielectric parameter shows a very small change, and it should obey Koop's phenomenology and Maxwell–Wagner polarization ease to show that the dielectric dispersion pattern was also elucidated by Maxwell–Wagner polarization, following Koop's phenomenology. It states that conductive particle shows the separation of the porous ferrite or dielectric nanomaterials. Nanocomposites sample allow very small changes in the numbers of the dielectric properties which are breakdown value, dielectric loss tangent and permittivity, resistance, and conductance which result from band gap variation due to grain boundary. Maximum electrical permittivity values arise due to the presence of thin grain boundaries to keep away Koop's hypothesis and the Maxwell–Wagner model of interfacial polarization. The connection between frequency and AC conductivity is explained with Koop's theory for different nanodielectric materials. Here, grain boundaries that possess increased resistance at low frequencies result in maintaining constant conductivity. The rise in AC conductivity values occurs in the high-frequency region where higher conductivity of the grains when compared to the grain boundaries of the corresponding dielectric spectrum is dominated by polarization processes that start from the grain boundaries of ferrite and dielectric nanoparticles. The thickness of the grain boundaries determines the performance of the dielectric constant as they are inversely proportional. The Maxwell–Wagner model at low frequencies is widely used to define grain boundary polarization standardized materials. Johnsher's power law is applied to heterogeneous disordered nanodielectric solid materials or multiphase materials built up with interfaces and defects which are responsible for the electrical properties of ferrites. Koop's theory has been also used to explain the correlation between AC conductivity and frequency for different ferrites.

Integrating the sensor scattering property of silicon nanoparticles and the electrons present inside the atom shows a magnetic dipole due to its spinning nature around the nuclei of silicon nanoparticles to escape thermal forfeiture. Anapole mode is an anon-emitting radio rays source that exists when electric and circulating dipole is present on the surface of an imaginary torus along the plane (toroidal dipole) suitable for refractometric sensors. The nanoparticles which have large dipole show a high dielectric constant. Refractometric sensors are currently used in the field of food and cell membrane application in the biomedical field. Organic dye-doped and nanoparticles including Fe and Ni combination particles doped in hydrogel exist with high dielectric constant values respective to their frequency range by impedance hence proved by using Koops theory and Maxwell–Wagner approach.

In general, Maxwell–Wagner polarization reduces the efficiency of nanomaterials. To avoid polarization, the cyclability of the connections of the lithium-ion batteries should be improved. Rare-earth metal doping of $LiR_xMn_{2-x}O_4$ nanoparticles improved their structural stability and increased their dielectric constant for memory devices. The dielectric barrier discharge method (DBD) is diverse from another synthesis of C_3N_4-Mn_3O_4 nanoparticles nonthermal plasma formed in between the two electrodes separated on the application of AC potential. DBDs include the ionization of the surrounding air followed by an H_2S gas atmosphere, producing a variety of reactive species for gas detection in sensors. Reducing the size of the nanoparticles increases the surface area resulting in increased sensitivity and faster responses in both response time and recovery time.

Dielectric nanomaterials have created an impact on the currently manufactured devices for dielectric applications from health care to communications engineering. This has paved the way for the future generation of novel smart technologies for harnessing nonrenewable energy resources from sensors to microelectronic devices as given below in Fig. 1.8.

1.6 Conclusions

Nanomaterials have significantly enhanced the properties of dielectric devices, and it is currently applied across all industries and in device manufacturing. The twenty-first century is the move toward protecting our natural fossil resources and living in a green environment free of pollution. The demonstration of e-vehicles as a challenge to the present carbon-based fuels had increased our dependence on nanodielectric materials for developing smart sensors and fast charging tools. Renewable energy resources have to be optimally used to build a sustainable future for our people on earth in the coming decades where the requirement of reusable materials for batteries, better storage capacity, and monitoring their performance remotely with sensor and artificial intelligence technologies would be the next challenge. Nanodielectrics are now in the forefront of frontier technologies which scientists are working up to technical

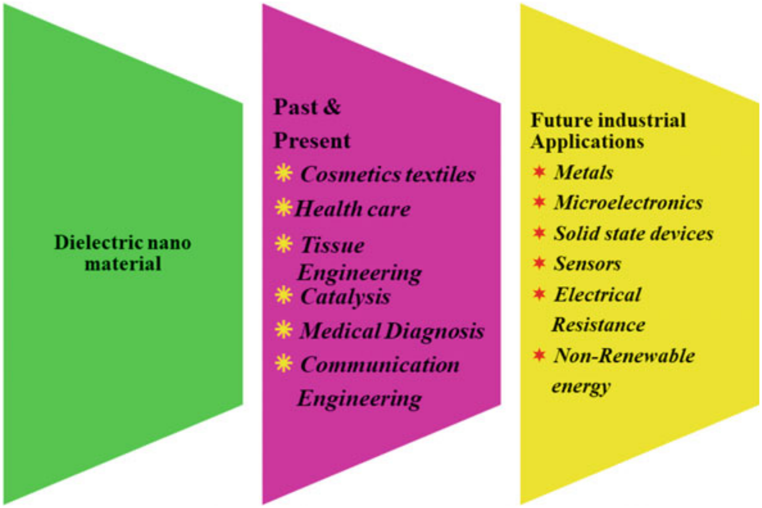

Fig. 1.8 **a** Schematic representation of past, present, and future applications of dielectric nanomaterial

produce products and devices using flexible polymer-matrixes, doped metal semiconducting oxides, and hybrid nanomaterials. The advancement in the development of nanomaterials for dielectric applications would further lead to the development of a sustainable economy by harnessing of nature through green energy routes and containing pollution.

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