SMART MATERIALS: APPLICATION IN FUTURISTIC TECHNOLOGY

Abstract

Stimuli-responsive materials have been able to fascinate researchers owing to their unique responsive behaviour towards external stimuli and hence have seen immense applicability in digital technology, sensors and biomedical applications. The external stimuli induce changes in their internal physiochemical properties and facilitate improved heat/photo stability, enhancing detection sensitivity, accuracy and biocompatibility. In this aspect, another class of intelligent materials that has gained momentum are the shape memory polymers (SMP), shape memory alloys (SMA), and their composites. This emerging class material shows the unique property of shape memory effect (SME) which enables it to serve in challenging applications like medical, sensors, robotics, and in aerospace designs and more. These materials in term have also opened the door to smart clothing, as it made the integration of chemical sensors into textiles possible. Thus, here we have discussed the unique features of these smart materials and their advancement in various fields at current times.

Keywords: Smart materials, stimuli responsive, chromogenic, SMP, SMPC

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I. INTRODUCTION

In recent times extensive advancements in industrial processes and technologies have necessitate improvised designing in terms of smart composite materials and manufacturing processes. The call for modern structures has caused high demand for performance, high strength and light weight materials [1]. One of the prime causes of shifting towards smart materials is the alarming increase in carbon footprint, which in turn has led the urge to switch over to alternate technologies and approaches. A critical class included in smart materials is the stimuli− responsive materials. These materials are triggered by various external stimuli such as photons, temperature, electromagnetic field, water, pH, and more, and accordingly they can adjust various responses in terms of changing color, their shape from the coded auxiliary shape to the original shape etc. Thus their autonomous behavior and stimuli responsiveness makes them basis for the development of various futuristic technologies [85-87].

In the group of advanced materials shape memory polymers (SMP) is the forerunner attributed to its stimuli responsive behavior because of their properties like higher recoverable strains , low density, multiple modes of activation, quick and uncomplicated processing , and tailorable properties [85]. The various mechanical and optical−electrical properties can be further enhanced by fabricating fillers into the polymer matrix of SMP, to form the shape memory polymer composites (SMPC). SMPC has found its application in state-of-the-art technologies such as aerospace, space, medical, biomimetics of nature, and robotics. These materials have been able to boost shape memory properties, and improvised stimuli responsiveness. Lately, huge investments have been made in both the research and industrial sectors to provide ingenious wearable devices and technologies in healthcare and environmental parameters [2-6]. Real-time monitoring of specific physiological parameters has seen increased desirability and the current implanting devices significant drawbacks in terms of biocompatibility and thus the demand for wearable sensors [7].

In a nutshell, the vast applicability and advantageousness of the smart materials has made them an intriguing research subject matter. Here we have discussed certain prominent classes of these materials to provide an overview about their behavioral mechanism and applications.

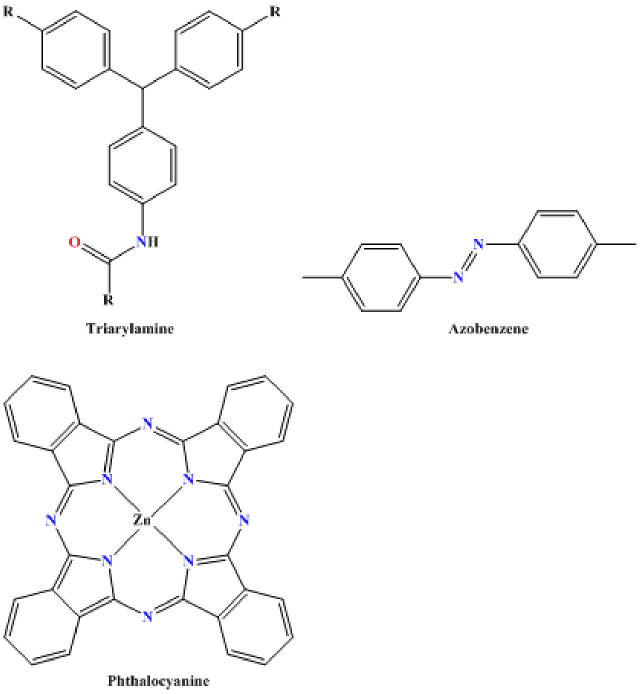
II. STIMULI RESPONSIVE SMART MATERIALS

In the latest decades polymer based materials have found applications in sensors and digital technology [8]. However, due to its non-renewable and disinclined nature towards environmental changes and there developed an urge for tailoring the innate properties of polymers by external stimuli. 'Stimuli' phenomenon has become ubiquitous in current technology due to its ability of enhancing the detection sensitivity and biomimicry behavior for clinical testing [9]. Moreover, stimuli-responsive polymers exhibit vivid applications such as memory devices, drug delivery and chromogenic materials etc [10].

1. **Photoresponsive Smart Materials:** The responsive materials wherein light acts as external stimuli, inducing changes in its electronic properties are termed as photoresponsive materials. Light exhibits triggering of dynamic photo switching due to its ability to generate photo induced radicals. Moreover, processes like photo isomerization/polymerization have also been utilized to achieve such responsive

behavior. Photoresponsive behavior is also observed in various host-guest redox active materials, leading to designing of molecular machines. Thus, intensive research has been going on for better utilization of the properties of light and thus uses it in further development of photoresponsive materials [11, 12].

Feringa et. al., designed a model in which the photoisomerization in bulky alkene derivatives is utilized to imitate the working of ATP synthase enzyme [13]. Harada et. al., developed photoresponsive hydrogels and xerogels, which exhibited bending in direction of light source [14]. Fragouli et. al., designed a spiropyran doped with silk fibroin poly-(ethylene oxide) nanofibers which exhibited photochromism and thus was able to detect acid vapor and metal ion [15]. Hong et. al., reported the photoinduced proton transfer under blue light irradiation for non-photoresponsive molecules [16].



Triarylamine

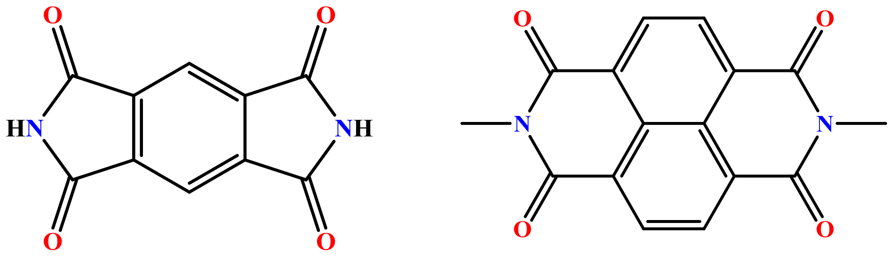
Azobenzene

Phthalocyanine

Figure 1: Compounds Exhibiting Light-responsive Behavior **[17-19]**

2. **Voltage Responsive Smart Materials:** The electro-active compounds sensitive to voltage as external stimuli, producing redox switches by depicting variable color changes in each state can be defined under voltage responsive smart materials. Voltage responsive redox active materials are generally advantageous due to its quick response time, diverse colors, and ease of operability. These highly sophisticated materials have found their utility in detection of toxic gases and vapors in air and in development of self-healing supramolecular polymers [20, 21].

Aida et. al., reported interconversion of supramolecular nanotubes to nanorings via redox-mediated pathway which was facilitated by pyridyl arms with dangling ferrocene moeity [22]. Harada et. al., designed a supramolecular complex exhibiting self healing properties by using poly (acrylic acid) modified cyclodextrins (pAA-CDs) and ferrocene (pAA-Fc) [23].

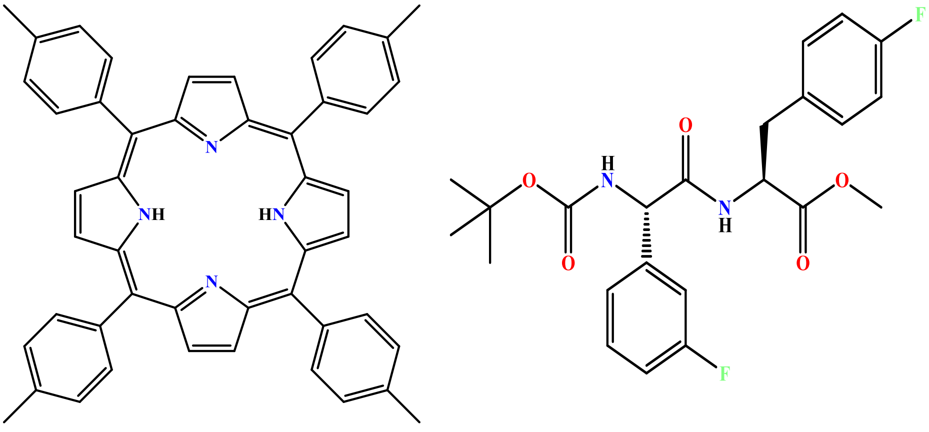


Perylene diimide **Naphthalene diimide**

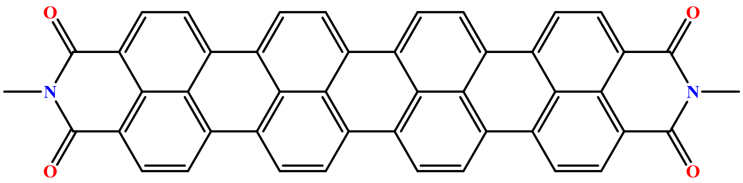
Figure 2: Compounds Exhibiting Voltage Responsive Behavior **[24]**

3. **Frequency responsive Smart materials:** Responsive materials where the physico-chemical properties can be modulated by frequency are known as frequency responsive smart materials. These materials have found their importance in sensor technology due to their efficient selectivity and sensitivity. The vibrational and radio frequency variations are able to induce changes in their physiochemical properties, conformation and binding kinetics towards ligand and hence are being utilized in processes of differentiating the air pollutants. To add to the benefit, these materials are of great practical applicability as they are highly economical, gives constant output and high synthetic feasibility [25].

   Guo et. al., reported ultrasound induced effects on β-lactoglobulin, which resulted in surfacial hydrophobicity and changes in content of free sulfhydryl groups [26]. Potyrailo et. al., designed batteryless radio frequency identification (RFID) sensors to analyze food quality [27].



Porphyrins **Aromatic fluorinated peptides**

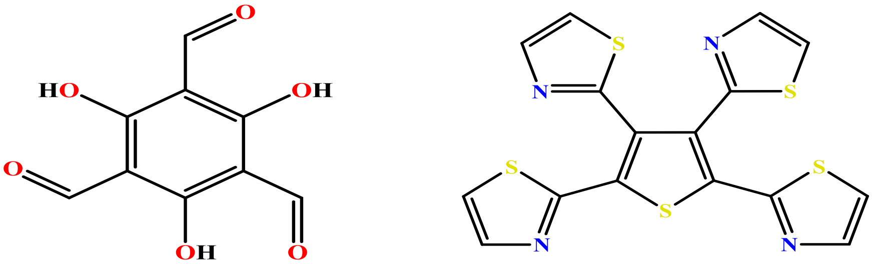


Quaterrylenediimide

Figure 3: Compounds Exhibiting Frequency Responsive Behavior **[28, 29]**

4. **Stress/Strain/Pressure responsive Smart materials:** Materials, in which mechanical forces can be exploited as another significant external stimulus, promoting selective chemical transformations are regarded as stress/strain/pressure responsive materials. In this regard, mechanochromic compounds are thought of as excellent for designing materials which can identify critical stress/strain as well as recording changes in mechanical properties. These materials have found their applications in devising optical memory devices and forensic imaging [30].

   Yam et. al., explained pressure responsive behavior in benzophosphole alkynyl gold (I) complexes with/without thiadiazole group comprising of methyl/phenyl moieties showcasing a range of colors from yellow to orange to red [31]. Yamaguchi et. al., reported the stress responsive fluorophore, tetrathiazolylthiophene systems. The photoluminisence studies of crystalline showed that upon grinding, the yellow color of the crystal changes to green. This behavior is reversible as recrystallization of the green powder yields yellow crystal. [32].

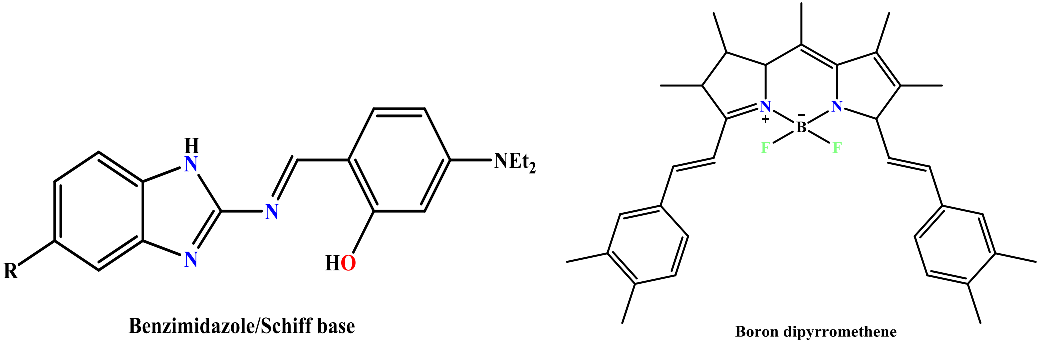


Triformylphloroglucinol

Tetrathiazolylthiophene

Figure 4: Compounds Exhibiting Stress/Strain/Pressure Responsive Behavior **[32, 33]**

5. **Chemical responsive Smart materials:** The materials showing responsiveness in case of change in chemical parameters like that of pH, heat are termed as chemical responsive smart materials. In this regard, pH activated stimuli responsive systems include the covalent organic polymers, supramolecular hydrogels, which are mostly used in target drug delivery and also to develop wound (pH) sensors [33]. Liu et al., synthesized THPP-BAE-PEG COPs is used to enclose doxorubicin (DOX-an anticancer drug) to study the drug delivery behavior with different DOX amount [34]. Huang et. al., devised utilization of the thermoresponsive feature of peptide based supramolecular assemblies by tailoring the host-guest interactions, thus enabling their usage in photodynamic therapy [35].



Benzimidazole/Schiff base

Boron dipyrromethene

Figure 5: Compounds Exhibiting Chemical Responsive Behavior [36, 37]

III. CHROMOGENIC SMART MATERIALS

Chemically, the term “chromogenic” refers to the phenomenon in which a material matrix can demonstrate reversible color change. These materials are stimulated by diverse external stimuli making them a integral part of smart materials. Their vivid applicability in the field of sensors/indicators is due to its ability of differentiate changes in the surroundings or the system to which it is integrated making them an eminent choice for smart materials [38].

1. **Photochromic Materials:** Materials that show reversible light induced color change either going from colorless to colorful or switching between two different colors are known as photochromic materials. This feat is achieved due to reversible change from a thermodynamically stable state to a metastable state induced by radiation energy [39].

2. **Thermochromic Materials:** Materials in which the shift in chemical equilibrium between two molecular conformations or different crystalline phases, leads to change in color are termed as thermochromic materials. They mainly consist of two categories: liquid crystalline or conjugated polymers and polymers with thermochromic agents (inorganic dye/pigments and conjugated polymers) [40].

3. **Electrochromic Materials:** Electro-active materials changing and bleaching colors when exposed to electrochemical stimuli, such as the redox process, are called electrochromic materials. One of the main mechanisms followed by these materials is oxidation-reduction [41].

4. **Ionochromic Materials:** Materials which shows color switchability (from colorless to colored or vice-versa) induced by ionic species are called ionochromic materials. This behavior is mainly attributed to the interaction between ionochromic compound and anions. However, ionochromic processes can follow various mechanisms as: 1. halochromism (change in acidic or alkaline pH); 2. acidochromism (stimulated by acid); 3. metallochromism (due to the formation of colored metal complexes with chelating ligand) [42].

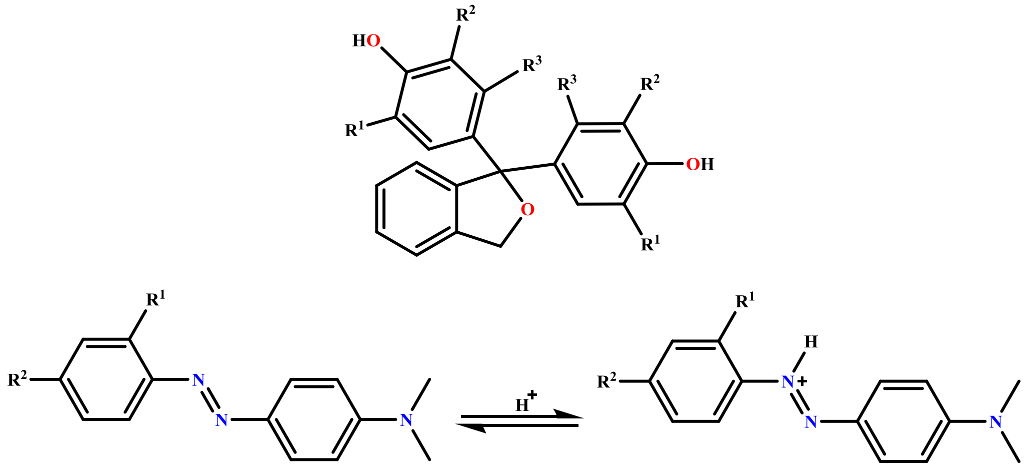
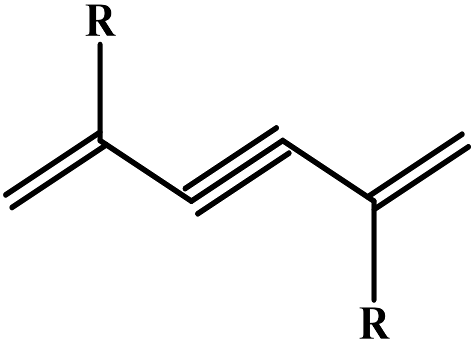


Figure 6: Representation of Ionochromic Nature of Phthaleins and Sulfophthaleins azo dyes

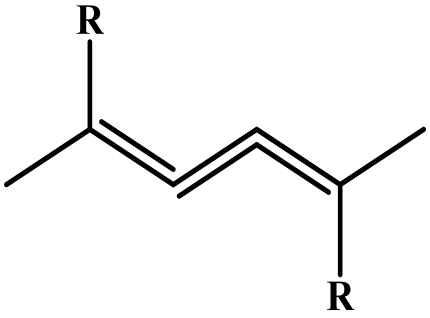
5. **Mechanochromic Materials:** The systems that exhibits color changes when subjected to mechanical stimuli, owing to change in the transmitted and emitted wavelengths are called mechanochromic materials. However, this process can sometimes also be based on the emission intensity [43]. Mechanochromism can be broadly categorized into two groups based on mechanical stimuli applied: Piezochromism (based on pressure stimuli; conjugated polymeric materials are often seen showing this behavior) and Tribochromism (induced by friction or grinding; include spiropyran, spirooxazine etc. exhibiting strong color) [44].

6. **Solvatochromic Materials:** Materials that display solvent induced color changes are known as solvatochromic materials. It can be divided into two classes depending on dipole moment discrepency between the ground and excited states of the chromophore: Negative solvatochromism (increasing solvent polarity leads to hypsochromic or blue shift) and Positive solvatochromism (increasing solvent polarity leads to bathochromic or red shift) [45].

7. **Biochromic Materials:** A material that changes color when exposed to biological or biochemical stimuli is called to biochromic materials. This kind of chromogenic systems has been long utilized for visual detection of enzymes and reactions and detecting pathogenic microbes [46].



Acetylenic



Butatrienic

Figure 7: Resonance Structure of Polydiacetylene (PDA) Backbone (enabling it to show biochromism)

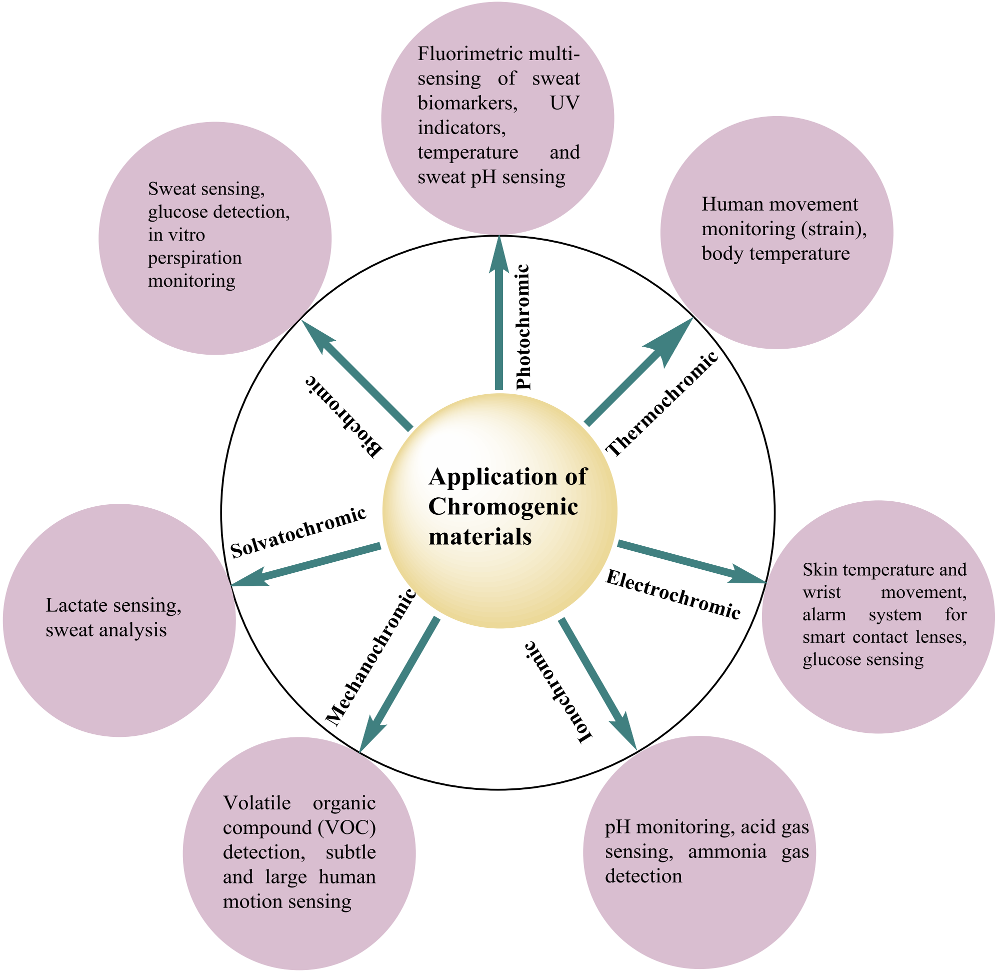


Figure 8: Application of Chromogenic materials

IV. SMART MATERIALS: SHAPE MEMORY POLYMERIC MATERIALS AND COMPOSITES

Shape Memory Materials (SMM) is the class of phase-changing material capable of altering their original shape into transient shapes, when the medium is changed and again reboot to its primary one. These materials are broadly divided into four categories:

- Shape Memory Alloys (SMA): high strength, stiffness, and resistance but has limited (~8%) elasticity and strength to weight ratio.
- Shape Memory Ceramics (SMCr): render good hardness and tencile strength.
- Shape Memory Polymer (SMP): furnishes large elasticity (~ 400%) and are provoked by many stimuli.
- Shape Memory Composites (SMC): they have both high elasticity and good strength unlike SMP.

The programming of such smart materials is quantifiable in terms of mainly two properties: Shape Fixity Ratio (the ability of SMP material to embrace the applied mechanical deformation) and Shape Recovery Ratio (the SMP material’s ability to reclaim its original shape) [47, 48]. These two essential characteristic is responsible for the establishment of shape memory effect (SME).

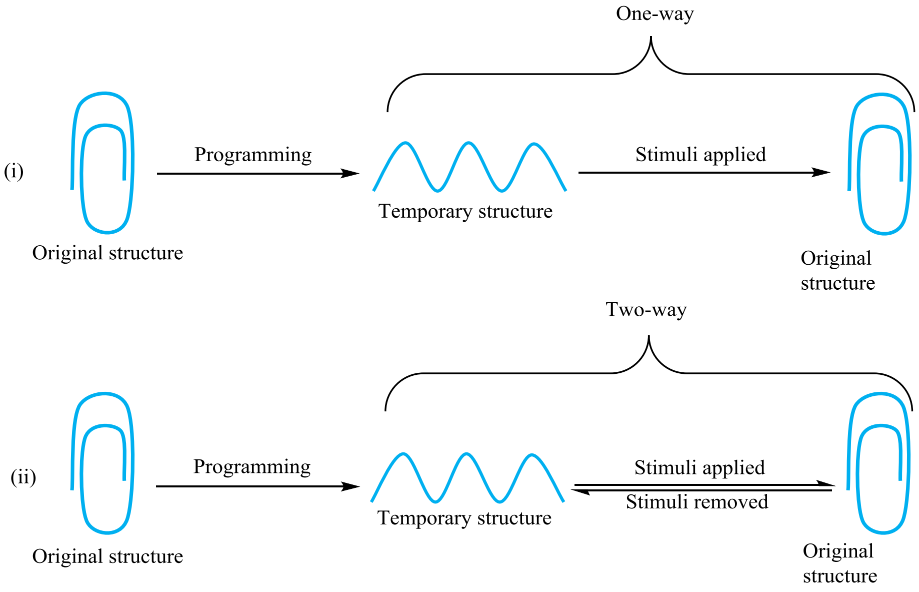


Figure 9: Shape Memory Effects: (I) One-Way Action (Reprogramming Required) (Ii) Two-Way Action (Reverisible, Thus Reprogramming Not Required) .

1. **Shape Memory Polymer (SMP):** Shape Memory Polymer (SMP) was first put into light in the year 1984 in the United States as a category of polymers that can retain to its primary shape after distortion due to an external factor. This very feature of the polymeric material of being able to restore to its prior shape even after being stimulated for a change in shape is called Shape Memory Effect (SME) [49-52]. The construction of such materials is based on glass transition, melting point, triple point, reversible bond transitions such as covalent bonds and supramolecular interactions etc [53-59]. Generally, SMP possess dual phases: 1. Stable grid (accountable for retaining the original shape). This phase can be attained by introducing crystalline phases, interpenetrating networks, or chemical crosslinks. 2. Phase two (reverts the temporary shape into original) [60].

2. **Shape Memory Polymer Composites (SMPC):** This material class also possesses shape recoverable property, but it is more advantageous owing to the additional features like low density, light weight, varying glass transition temperature, ease of production, low cost, high shape recoverability, biodegradability, and high reliability [61-64]. Even with all these added benefits lower mechanical properties like strength, lower recovery stress seems to be its drawbacks. But these drawbacks can be overcome by addition of various reinforcement filler materials (like fibers, carbon black, carbon nanotubes (CNT), and Kevlar, extra additives like photoinducers and curing agents. Thus, SMPC can be regarded as an arrangement of primary matrix material (SMP) and reinforcement fillers (composite), enhancing the mechanical, thermal, and electrical properties [65].

- **Actuation Mechanism for SMPC**
  - **Thermal Actuation:** exhibits a temperature-induced SME.
  - **Electroactuation:** exhibited by electroresponsive conductive filler material such as carbon nanotubes (CNT), magnetic nanoparticulates, carbon fillers, nanoclay in SMPC.
  - **Light Actuation:** SME shown due to activation by light in presence of photochromic reinforcement fillers.
  - **Magnetic Actuation:** SME induced by changing peripheral magnetic field. To attain magnetoresponsive SMPC, an arrangement of SMP matrixes and magnetic filler, specifically Ni, FeO3, and Fe3O4 nanoparticles are used.
  - **Other Actuation Modes:** Other stimuli that can induce SME behaviour include hydroresponsive, chemoresponsive, and solvent responsive SMPC [85].

V. APPLICATIONS

1. **Smart Materials in Healthcare Technology:** Halochromic Dyes: Halochromic dye is a color changing indicator, activated by visible wavelength. It can be easily intergraded into fabrics and also be associated with an optical-electronic circuit, enabling it to act as a pH sensor. The optical sensor utilizing such indicator dye can be used for both detection and quantitative measurement of an analyte by producing a visual (e.g., colorimetric) change [66].

   Wound (pH) Sensors: Normal skin pH ranges from 4–6, but when the skin barrier is compromised it changes to alkaline (pH = 9). A highly acidic pH could be indicative of bacterial infection. Thus the devising method for monitoring bacterial behavior during the healing process is important as bacterial infection is a big cause to deal with [67].

   Cui et al. has designed many such devices to monitor varying pH of wounds, such as electrochemical pH sensors, ion-sensitive field effect transistors so on. Halochromic natural dyes such as anthocyanins and alizarin also have shown medical uses, due to its larger pH response range and more distinguishible color changes [68].

2. **Aeronautics and Space Era:** The ceaselessly advancing world of strategic aerospace defense and astronomy has been a major hub of applications of SMPC material application. The origami and compliant mechanisms with SMP and SMPC has helped in developing foldable and deployable bulky structures and also encourage conception of numerous categories of unfurling structures [69, 70]. The structures in which have found the wide usage of SMPC are: deployable solar arrays and booms, morphing wings and skins, SMPC hinge for deployable structures, and expandable space habitats. The advantage of having excellent maneuverability, performance, and controllability added to the light weight feature are the reasons as to why these morphing structures are the prime focus for the designing of energy efficient aircraft designs and spacecraft structures.

3. **Wearable Electronics:** The sol–gel technique is an ecofriendly technique that has been utilized for textile surface fabrication by means of introduction of various functionalities, such as UV protection, antibacterial coatings, hydrophobicity, bio-molecule immobilization, fire resistance, and self-cleaning by deposition of sol–gel coatings on a

textile substrate [71-76]. This technique also has proved to enhance the physical characteristics, chemical stability while preserving natural properties of the fibers [77].

GPTMS has been able to grab attention for its dual functionality (epoxy and methoxy silane) and its applicability in the designing many functional cross-breed textile materials by implanting dyes or functional organic/inorganic moieties in the sol–gel matrix; leading the way for development of wearable sensors [78-80]. Wang et al. have developed a wearable electrochemical organophosphorus biosensor. The carbon nanotubes (CNTs) integrated cotton fibers has been designed for its potential use in photoplethysmography (PPG) [81].

4. **Biomimectic Era:** SMPC materials has also found its wide application in biomimectics in which it is utilized to imitate structural and anatomical behavior of plants like the opening and closing movement of flowers, movement of leaves towards the sun ; basic animal movements such as the flapping of bird wings etc [82].

   Li et al. designed thermoactuated multiresponsive flying bird model with a graphene-based nanomatrix coating. The designed model demonstrated shape memory effect, which in turn inspired 4D reprogramming investigations such as robotics equipped with advanced artificial intelligence and bioprinting [83].

5. **Medical Era:** SMPC materials have also got promising application in devising medical instruments; such devices are self-rolling stents, dynamic switches etc. The thoughtful incorporation of such materials can help us to develop resolutions to life-threatening issues like cerebrovascular and cardiovascular diseases [83].

   Kashyap et al. produced a radio-opaque, heat-driven self-expanding and porous ink structure by thawing NaCl (for porosity), W (for radiopacity), and SMPU (for shape memory), which could find its applicability in tackling medical problems such as vascular blood choking [84].

VI. CONCLUSION

In summary, here we have demonstrated the various smart materials stimulated by different external stimuli like light, voltage, pressure, frequency and pH which lead to change in molecular conformations, opto-electronic properties, crystalline/amorphous phases; sol-gel conversions, twisting chirality, and mixed valence species generation triggered by change in intrinsic properties. This responsive behavior in turn helps in the designing of actuators, molecular machines, biomimitic systems and artificial muscles etc. However, there are still various scopes of improvement in terms of long term stability, biocompatibility and detection sensitivity for accuracy of devices. The SMP and SMPCs also have proved to be valuable asset in designing new and efficient technologies especially in the field of aeronautics and space. These classes of materials are the best suitable candidate in terms of 4D printing. Further, work can be done on enhancing its properties by reinforcement fillers and also product sustainability [85-87].

In addition, smart materials have also ventured into the domain of wearable healthcare technologies over the recent years. Even though there are many obstacles, these materials have shown a promising future in terms of wearable sensors. The harmonious amalgamation of these subsystems in the construct of wearable sensors and the cooperation among medical professionals, engineers and scientists can lead to a greater advancement in this field as well as cause high commercial success.

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