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# STRATEGIES FOR IMPROVING PHOTOTHERMAL CONVERSION CAPABILITIES IN HYDROGEL POLYMER MATERIALS FOR SOLAR VAPOR GENERATION

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***ABSTRACT:*** Solar evaporation is a promising technology that has garnered attention due to the renewable nature of the sun as an energy source, which can facilitate the sustainable advancement of human society. This technology relies on easily obtainable water sources and uncomplicated structures, while also benefiting from significant enhancements in conversion efficiency through the utilization of advanced photothermal materials and effective thermal management techniques. This review provides a brief summary of recent research conducted on hydrogel polymers utilized in solar vapor generation. The primary goal of this review is to explore multiple strategies aimed at optimizing light absorption, hence enhancing the overall efficiency of the design. We present the photothermal management in hydrogel polymer with proper solar absorber selection, tuning the thermal conductivity via porosity of hydrogel and the incorporation of a layered structural design that leads to a greater photothermal conversion efficiency.

***KEYWORDS:*** *Hydrogels, polymer,solar vapor generation*

## 1. INTRODUCTION

Water is a fundamental component necessary for the sustenance of life and crucial for the existence of all living beings. Water resources are considered valuable assets due to their significance in sustaining various aspects of human life and the environment. Consequently, the practice of water conservation is imperative, given the prevalent occurrence of water crises on a global scale. According to the United Nation Development Programme, a significant proportion of the global population, exceeding 40%, currently experiences the adverse effects of water shortages. This figure is of great concern and is projected to escalate further in tandem with the anticipated rise in temperatures. It is predicted a minimum of 25% of the global population is predicted to encounter recurring water scarcity by the year 2050. The escalation in population pressure, shifting water consumption patterns, and the impact of climate change are expected to heighten the challenge of sustaining appropriate levels of water use.[1] The predominant proportion of water present on the Earth's surface, amounting to more than 96%, is composed of saline water found in the oceans. Freshwater resources, encompassing precipitation and subsequent flow into various hydrological systems, including streams, rivers, lakes, and groundwater, play a vital role in meeting the daily water requirements for human sustenance.[2] Therefore, desalination has become the predominant way to overcome the water crisis, and is the main source of drinkable water. Desalination is a procedure that involves the

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division of saline water into two distinct components: freshwater, characterized by a reduced concentration of dissolved salts, and brine concentrate, which exhibits a significantly higher concentration of dissolved salts compared to the original feed water.[3] However, the process of water desalination is characterized by high costs, complex technology and a significant demand for energy.[4] Due to this complexity researcher has been came up with a simple preparation, low-cost, non-toxic, and mechanically strong approached which is through the process of desalination by utilizing a three-dimensional network of hydrogel polymer materials. Hydrogel is a three-dimensional cross-linked hydrophilic polymer network, that may expand and deflate reversibly in water and retain huge amounts of liquid. [5] Polymeric networks with strong water absorption and pollutant immobilization capacities are the most promising hydrogels for water purification. Hydrogels polymer possess a remarkable capacity to effectively sequester and retain various pollutants present in water through the process of adsorption. Because of that hydrogel has been studied based on its available functional groups, which expected to remove the contaminant via adsorption for water purification [6] In order to further enhance the efficacy of hydrogel polymer for the purpose of generating clean water, researchers have introduced an innovative and economically viable technology for desalinating seawater. This technology incorporates a solar vapor generation (SVG) system, which combines the utilization of solar energy and water, both of which are abundant resources. SVG can directly transfer heat to facilitate evaporation is an effective method of collecting solar energy and purifying water.[7] The SVG system utilizes hydrogel networks to convert seawater into potable water. The device successfully harnesses solar energy and enhances the efficiency of freshwater conversion and overall device performance. In essence, SVG and hydrogel function similarly to the natural convection of water bodies, such as seas or rivers. Natural convection is a process of heat and mass transport in which a water body absorbs heat from solar radiation. The primary focus of SVG design revolves around two key aspects, namely the system structure and the evaporation surface. The system's architecture relies on the presence of an insulating layer positioned at the bottom of the hydrogel, as well as the photothermal material's capacity to effectively absorb incident light. The evaporation efficiency of the merged SVG with hydrogel polymers ranges from 60 to 94%, which is equivalent to 1-3 kg $m^{-2}\ h^{-1}$ under 1 sun irradiation.[8] As solar radiation is the only source of power for vapour generation, a variety of materials, such as ultra-black absorbers, plasmonic nanoparticles, and thermal-concentrating ceramics, have been employed to improve the conversion efficiency.[9-11] Nonetheless, inefficient utilization of converted heat presents an additional obstacle from these materials such as water heating, parasitic thermal loss, and water evaporation. Also, poor solar absorption and large heat losses due to the placement of the light absorber at the bottom of the water source severely limit the practical application of traditional solar evaporation approaches, which typically deliver a low photothermal conversion efficiency of 30%-45%.[12] Additionally, black inorganic semiconductors like $Cu_7\ S_4$ nanocrystals, TiOx nanoparticles, etc., have been studied as a potential new class of solar-thermal absorbers because of their low cost and low toxicity.[13-14] However, their practicality is limited by the difficulties of producing large-scale samples. Efforts have been made to improve photothermal efficiency by increasing light absorption and minimizing heat loss by combining materials to create a microporous structure with dispersed pores. The recent development of interfacial solar evaporation systems that position the light absorber at the water-air interface has made it possible to heat only the air-liquid interface as opposed to the bulk water, resulting in a significant increase in photothermal efficiency.[15] Typical components of a double-layered interfacial solar evaporation system include a light absorber, substrate, bulk water reservoir, incident light, and condensate. The light absorber absorbs incident light and converts it to heat. In parallel, water is absorbed by the substrate and transported to the evaporative surface via

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capillary forces and interconnected water pathways. The generated heat raises the water's temperature on the evaporative surface, which powers the continuous evaporation process with an unlimited water supply. Nonetheless, a portion of the generated heat is always lost to the surrounding environment via conduction to bulk water and air, radiation to air, and convection to bulk water, resulting in a less-than-perfect evaporation efficiency. The ratio of the thermal energy contained in the generated vapor to the incoming solar flux can be used to calculate the evaporation efficiency.[16]

$$\eta = \frac{\dot{m}\, h_{LV}}{P_{in}} \qquad (1)$$

where, ṁ is denotes as the mass flux, $h_{LV}$is the total enthalpy of liquid vapor transformation, and $P_{in}$ is the rate of solar energy incident. The marking point as an ideal number to achieve highly efficient SVG is $1 kW m^{-2}$ (typically ~50% to higher than 80%) under 1 sun or even weaker natural daylight.

In this short review, we provide insights to a few strategies for tuning the light absorption in particular emphasis on hydrogel polymer materials with solar absorbers in enhancing the thermal efficiency of SVG design for high water transport.

## 2. MECHANISM OF PHOTOTHERMAL EFFECT FOR POLYMER BASED MATERIALS IN SOLAR VAPOR GENERATION

In solar evaporation devices, photothermal materials and thermal-insulating and water-transporting materials are essential components. These materials' properties largely determine the efficacy of solar evaporation. For solar absorber design, strong light absorption across the entire solar spectrum range of 0.3 to 2.5 μm, as well as high light-to-heat conversion efficiency, are of equal importance, whereas for substrate material design, thermal insulation and water transport properties are desired. There are three types of photothermal mechanisms involved in SVG plasmonic localized heating, electron-hole generation and relaxation, and thermal vibration of molecules as illustrated in Fig.1. In general, one type of photothermal material uses a single mechanism to convert light to heat. In some instances, however in a specific photothermal material, one or more of these photothermal mechanisms can convert light into heat. Here, the emphasis is on polymeric materials with a photothermal mechanism based on the thermal vibration of molecules. Under irradiation, the photothermal effect has been observed in organic materials (such as polymers) [17] that convert incident light into thermal energy. A photothermal process is a direct conversion of solar light that can achieve the highest possible energy conversion efficiency in comparison to other solar energy utilization technologies.

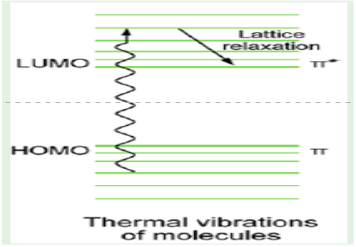


Fig.1. Thermal vibration of molecules of the photothermal effect [18]

When incident light energy matches the electronic transition energies in molecules, loosely held electrons can be excited from the ground state to higher-energy orbitals. Under irradiation, for instance, the electron can transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The photoexcited electrons then return to

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their ground state via electron-vibration coupling, causing molecules to generate heat. Due to their abundant conjugated π bonds, which can facilitate electron excitation from π to π* orbitals even with low irradiation energy, carbonaceous and certain polymeric materials (typically black polymers) [18] with strong light absorption can convert solar energy into thermal energy through the thermal vibration mechanism. In addition, the energy disparity between the LUMO and HOMO can become lower as the number of π bonds rises. Polymers have utility in solar evaporation applications due to their high light absorption across a broad spectrum of wavelengths, relatively low cost, and stability as solar absorbers for high-efficiency solar evaporation, such as polypyrrole (PPy) [8], PEGDA-polyaniline (PANi) [19], polyvinyl alcohol (PVA), and chitosan/PPy[20] have recently been utilized. However, their selection is more limited if compared to carbon materials. Polymers, particularly polymer hydrogels, possess a number of advantageous properties, such as the ability to bind with water to facilitate evaporation.

## 3. STRATEGIES TO INFLUENCE THE THERMAL BEHAVIOR IN HYDROGELS POLYMER FOR HIGH EFFICIENCY IN SOLAR VAPOR GENERATION

Water evaporation and thermal insulation are commonly regarded as two fundamental roles that the substrate must accomplish. Efficient water transport and evaporation need the presence of both excellent wetting qualities and continuous routes. Enhanced thermal insulation can be achieved through the utilization of materials with low heat conductivity and porous architectures. The pore structure has a significant role in facilitating water transport and thermal insulation. It is important to find a balance between effective water transport, which necessitates water-filled holes, and thermal insulation, which requires air-filled pores. Hydrogel materials, characterized by their hydrophilic nature, porous structure, and thermal insulation properties, have been extensively studied in accordance with established criteria. The objective of these investigations is to enhance water transport capabilities and optimize heat management, hence rendering hydrogels suitable as substrates for solar evaporation. PVA and chitosan hydrogels demonstrate remarkable hydrophilicity, low thermal conductivity, and ample hierarchical porosity, hence ensuring adequate water transport/evaporation and appropriate heat management capabilities for solar evaporation. [20] For the occurrence of evaporation at the interface between liquid and vapor, the material must possess certain properties based on the principle of heat localization. These properties include a high capacity for absorbing solar radiation in the volumetric range, low thermal conductivity, the ability to float on the liquid surface, and the capability for continuous or rapid fluid transport to the liquid-vapor interface. A considerable body of research has been dedicated to the advancement of hydrogel materials in conjunction with photothermal materials, mostly from a theoretical perspective. In the context of thermal structure design, the fundamental ideas revolve around the minimization of heat loss and the optimization of heat concentration on the evaporative surface. This section will examine a few main strategies employed in material and structural engineering to enhance the evaporation performance.

### 3.1. Photothermal materials

Materials employed as light absorbers must have the crucial attribute of strong absorption in the solar spectrum for solar heat localization, allowing the hydrogel to be integrated with the SVG system. The chosen material must be efficient in absorbing light across the full range of the solar spectrum, which is roughly 300 nm to 2500 nm, as illustrated in Fig. 2 [21] When photothermal material incorporated to other polymer material it may resulted with improvement across solar spectral irradiation wavelength due to the chemical interaction

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between two materials. In an investigation examining the influence of polyaniline (PANi) on chitosan, the study successfully observed the structural, conductivity, and dielectric properties of chitosan [22]. The protonation of chitosan material was achieved through the acid-induced protonic doping effect of PANi within the chitosan structure, as depicted in Fig. 3. Fig 4 illustrates the depiction of the protonation process involving two forms of polyaniline (PANi), respectively emeraldine base (EB) and emeraldine salt (ES). Basically, emeraldine is considered to be a comparatively more stable form of PANi, which may occur in two distinct forms: emeraldine base (neutral), characterized by its insulating properties, and emeraldine salt, which exhibits conductivity due to the protonation of its imine nitrogen through the process of doping with acids.[23] When acid is introduced to the PANi, protons (H+) from the acid start to attached to the nitrogen-hydrogen (NH bonds) in the polymer chains. This protonation makes the nitrogen atom to become positively charge, which is known as polaronic sites. It acts as a carrier in the polymer, it can accept and donate electrons which allowing the movement of electric charge within the materials, i.e., the movement of proton along the NH bonds or called electron hopping. Through this additional charge carrier via protonic doping, it furthered increase the electrical conductivity of chitosan with incorporation of PANi. The result of the PANi doping in chitosan can be seen in Fig. 5 where the incorporation resulted with 551 nm peak in visible range of solar spectral due to the polaron formation. This optical energy is due to the Pi-to-Pi star transition from the valence band to the conduction band at 389 nm due to the common doped state of PANi.

Table 1: Proposed hydrogel polymer with photothermal materials for SVG applications

| **Hydrogel type and Photothermal Material** | **Structure Design** | **Evaporation Rate** | **Evaporation Efficiency, %** | **Advantages for SVG applications** | **Reference** |
|---|---|---|---|---|---|
| Pegda hydrogel and Polyaniline | Cellulose-wrapped EPE foam with 2D water supply via capillary force | 1.40 $kg\ m^{-1}h^{-1}$ under 1 sun illumination | 91.5 | Strong light absorption, layered structures design, 2D water transport | Yin et al. (2018) |
| PVA hydrogel and Polypyrrole | Buoyancy by tuning density and porosity by the molecular mesh | 3.2 $kg\ m^{-1}h^{-1}$ under 1 sun illumination | 94 | Direct contact with water, improving water diffusion without layered, facile synthesis | Zhao et al. (2018) |
| Chitosan hydrogel Carbon dots | Buoyancy via porous network | 1.4 $kg\ m^{-1}h^{-1}$ under 1 sun illumination | 89 | Broadband absorption, lightweight | Singh et al. (2019) |
| PVA, Chitosan hydrogel with Polypyrrole | Buoyancy by tuning density and porosity by the molecular mesh | 3.6 $kg\ m^{-1}h^{-1}$ under 1 sun illumination | 92 | Water transport rate efficiency via porosity, facile synthesis, temperature management via porosity | X. Zhao et al. (2019) |
| Chitosan hydrogel with Molybdenum Carbide/Carbon-Based | Buoyancy by tuning density and porosity by the molecular mesh | 2.19 $kg\ m^{-1}h^{-1}$ under 1 sun illumination | 96.15 | Broadband absorption, facile synthesis | Yu et al. (2020) |
| PVA, chitosan hydrogel with CNP | PVC foam and cotton wipe | 2.28 $kg\ m^{-1}h^{-1}$ under 1 sun illumination | 66.7 | Broadband absorption, layered structure, 2D water transport | Zhu et al. (2022) |

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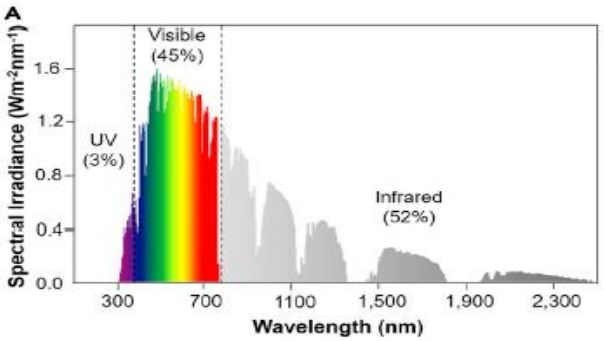


Fig.2. Solar spectral irradiation across a wavelength range of 300 nm to 2.5 mm [21]

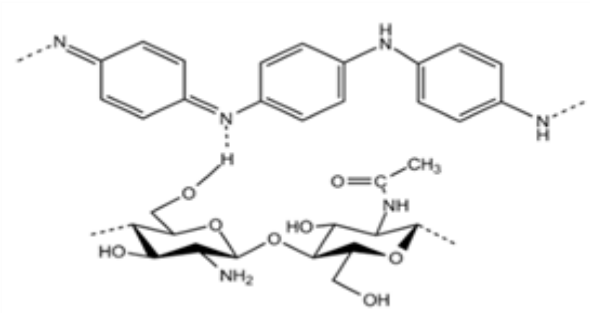


Fig.3. Schematic for PANi-chitosan interaction [22]

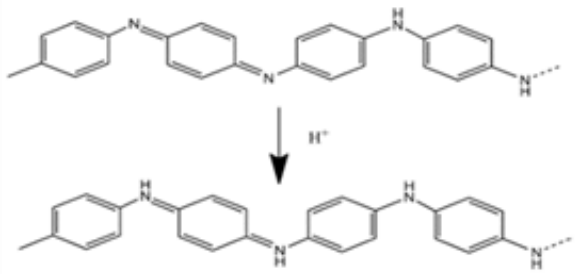


Fig.4. Protonation of emeraldine base to emeraldine salt upon acid introduction [22]

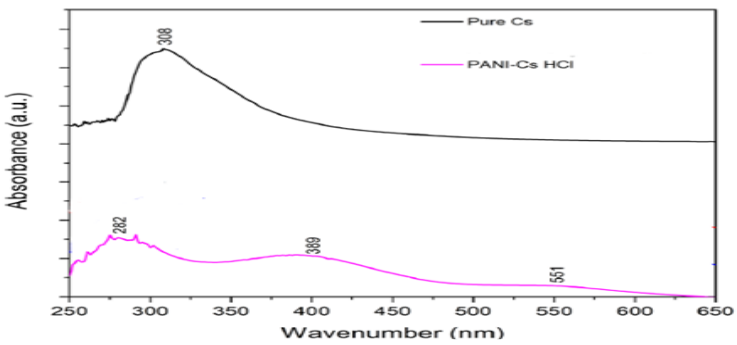


Fig.5. UV-VIS absorbance spectra of chitosan and PANi-chitosan sample with acid dopant [22]

Furthermore, when photothermal materials are added to the other material, it will produce a significant difference in physical observation. The observation of Fig.6 reveals the investigation of the integration of PANi into a hydrogel composed of poly (ethylene glycol) diacrylate (PEGDA). The hydrogel exhibits a noticeable visual transformation, transitioning

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from a transparent state with invisible porous to a darkened appearance with rich in porosity upon the inclusion of PANi. This change of color is due to the absorption of molecular or delocalization Pi electron in conductive PANi.[19] Based on this discovery, it can be inferred that the integration of a solar absorber into a hydrogel polymer enhances the mechanical stability of the hydrogel. This is evident from the presence of a well-developed macroporous structure in the hydrogel containing PANi. The hydrogel's porous structure is recognized for its robustness, resembling that of a sponge. Also, this characteristic allows for efficient water absorption, hence potentially enhancing the water transport rate in SVG.[24] The combination of these materials also showing a high light absorption in visible range as shown in Table 2, as hydrogel with rough and porous surface naturally traps light, which cuts down on repeated scattering and reflection. PEGDA-PANi hydrogel also recorded a high SVG efficiency of 91.5% with 1.40 $kg\,m^{-1}h^{-1}$ water transport, under 1 sun illumination making it a suitable candidate for SVG design.

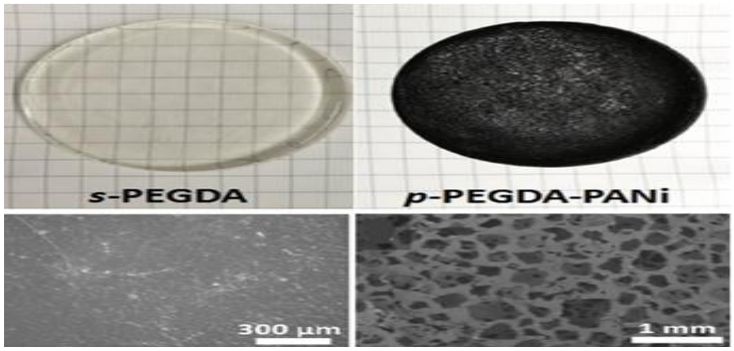


Fig. 6. Representative of hydrogel with and without the incorporation of solar absorber [19]

Table 2: Proportion of light absorption in different spectral regions of solid-PEGDA and PEGDA-PANi [19]

| Sample | Total absorption | UV (< 400 nm) | Visible (400-700 nm) | NIR (700-2500 nm) |
|---|---|---|---|---|
| **Solar Spectrum** | 100% | 5.40% | 54.7% | 39.90% |
| **s-PEGDA** | 32.61% | 4.25% | 17.29% | 11.07% |
| **PEGDA-PANi** | 98.48% | 5.22% | 54.02% | 39.24% |

### 3.2. Tuning density of hydrophilic polymer

Tuning density refers to quantifying chemical connections that connect polymer chains, subsequently influencing thermal vibration. Typically, an increase in density results in a hydrogel that exhibits greater stiffness due to a decrease in chain mobility, leading to a reduction in thermal vibration. The work conducted by Zhao et al. [8] demonstrates that altering the ratio of polymer density has a discernible impact on the structural characteristics of hydrogels as shown in Fig.7, where the hydrogel porosity changes with different amount of ratio. The efficiency of localized heating on the hydrogel surface is dependent upon the size and shape of the hydrogel. When the hydrogel polymer porosity does not have homogenous porosity, it will interfere with the temperature distribution on the hydrogel surface. The ineffective localization of the hydrogel surface has the potential to decrease the thermal

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conductivity of the material, resulting in reduced heat loss to the bulk water and its surrounding environment. X.Zhao et al. [20] improved their hydrogel by changing the ratio of their hydrophilic polymer of PVA and chitosan with water content, which resulted with altered internal gaps within the hydrogel as depicted in Fig.8. The internal gaps within hydrogel may efficiently transport water to the hydrogel surface in timely manner.[24] However, the hydrophilic polymer of PVA/chitosan with highest concentration resulted in the highest saturated water content, as depicted in Fig.9. This highest amount of water saturation with the highest concentration of hydrophilic polymer results in a higher demand for energy during the process of water heating, thereby diminishing the part of usable energy that can be utilized for water vaporization. Although the enthalpy of vaporization is relatively low, the presence of a high level of saturated water content hinders energy utilization and restricts the rate of SVG. In essence, the reason the hydrogel with the highest concentration does not have the highest evaporation rate is due to the continual presence of highly saturated water within the polymer networks, which keeps the internal gaps moistened and heats the water instead. Therefore, from this observation it can be inferred that achieving a balance between the volume and concentration of hydrophilic polymer is essential for increasing the rate of water evaporation. It can be seen in Fig. 10 by tuning the density of hydrophilic polymer, resulted with localize heating in the middle of hydrogel surface, and the bulk water temperature remain low and stabilize within 1 hour period, as an indicator of efficient temperature distribution within the hydrogel network.

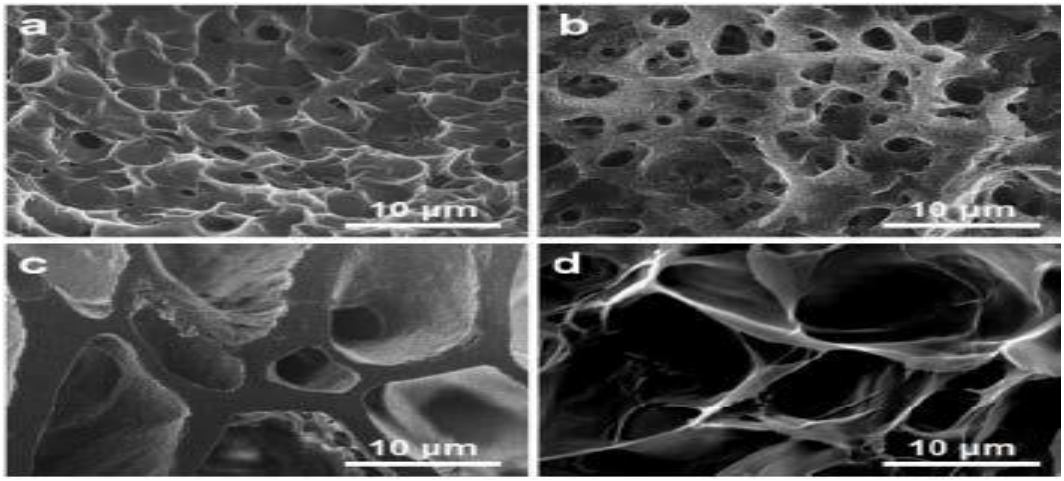


Fig. 7. Porous structure different shape with different ratio of PVA and ppy[8]

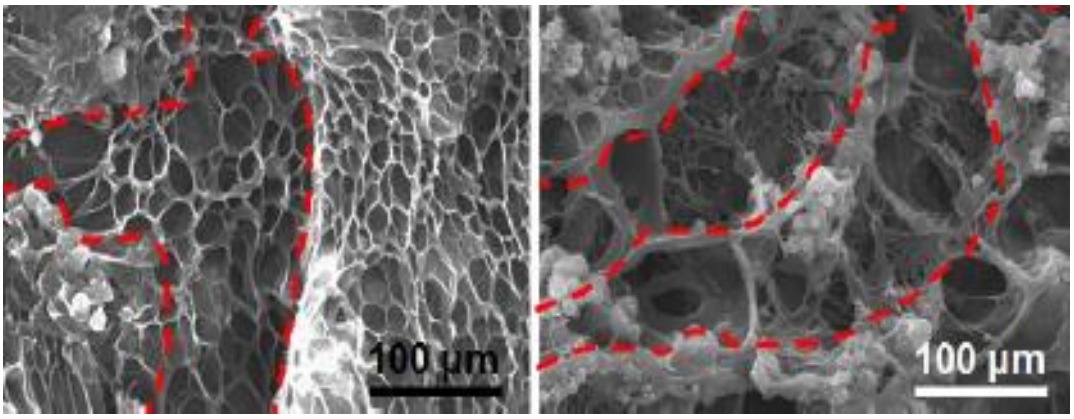


Fig. 8. Internal gaps within hydrogel after tuning the density of hydrophilic polymer [20]

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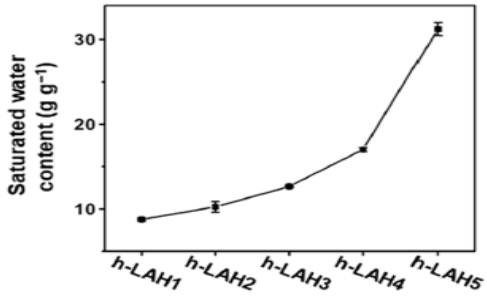


Fig. 9. Saturated water content with different concentration of hydrophilic polymer [20]

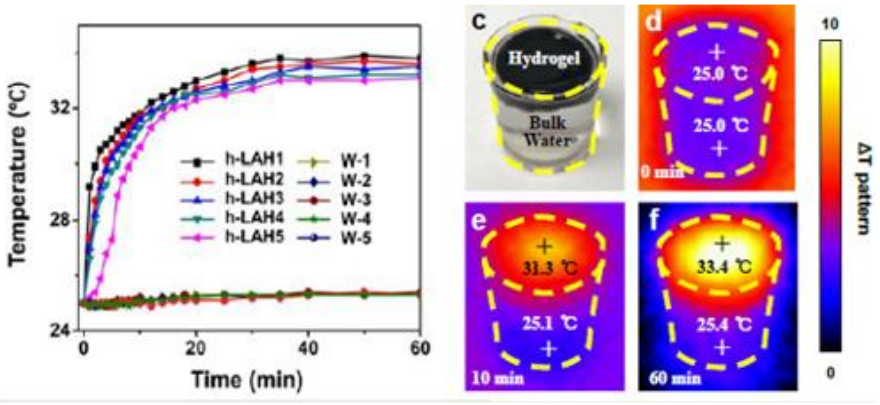


Fig.10. Low temperature to the bulk water and effective localize heating at the hydrogel surface [20]

### 3.3 Thermal conduction via structural design

Hydrogel is known to have higher density than water, therefore, in new SVG design it is necessary for the hydrogel to be able to float in water surface as opposed to traditional evaporation design where the absorber is immersed in the water.[8] Hence, in order to enable the hydrogel's buoyancy, researchers proposed the integration of an insulator material to regulate the heat conductivity of the SVG design. This approach also serves to provide structural support for the hydrogel, which functions as a light absorber and is positioned atop the structural design. As demonstrate in Fig. 11, Yin et al. [19] proposed a design that consist of the cellulose-wrapped expanded polyethylene (EPE) foam, which serves as thermal insulation and also as water supply between the hydrogel and the bulk water. By placing EPE foam around the hydrogel material, it acts as a thermal barrier, minimizing heat transfer to the surroundings and maintaining a higher temperature within the system. This insulation helps improve the overall energy efficiency of the system by reducing heat losses during the vapor generation process that resulted with 91.5% solar thermal efficiency. Another simple design proposed by Zhu et al. [15] as illustrated in Fig. 12, where the design is composed of polyvinyl chloride (PVC) foam as heat insulation in the bottom layer and then a cotton wipe is act as water pipe between hydrogel and bulk water, which the water will be transfer from PVC surrounded to the cotton and then absorbed by the hydrogel, this design resulted with 66.7% solar thermal efficiency.

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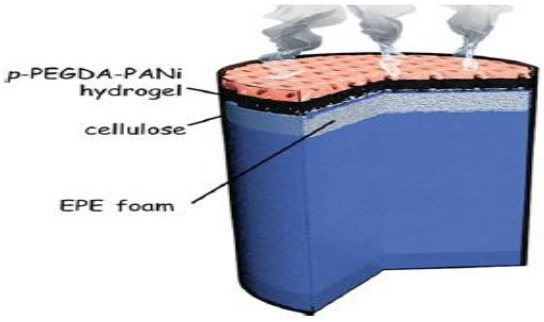


Fig. 11. Structural design using EPE foam and Cellulose with hydrogel [19]

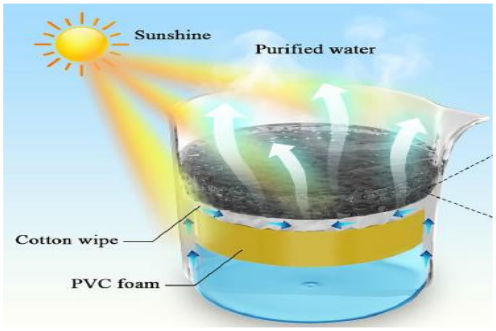


Fig. 12. Structural design using PVC foam and cotton wipe with hydrogel [15]

## 4. CONCLUSION

This review article has provided a brief summary of a few strategies in hydrogel polymer with SVG. It discusses three primary strategies that have significantly enhanced the efficiency of SVGs through the utilization of hydrogel polymers. These strategies include the careful selection of solar absorber materials, the optimization of hydrophilic polymer properties to improve temperature management, and the incorporation of hydrogel into the SVG design. Hydrogel polymer possess a significant benefit in terms of water purification and water transport. The optimization of light absorption strategies to enhance the compatibility between SVG and hydrogel materials, resulting in improved water delivery and solar energy utilization efficiency, holds significant promise for future societal benefits. These approaches are characterized by their simplicity, cost-effectiveness, and ability to achieve higher water rates. As a result, the integration of these two technologies facilitates the effective utilization of solar energy, presenting a feasible and enduring solution to mitigate the challenge of limited energy resources. Furthermore, the intricate nature of hydrogel polymers allows them to serve as a medium for harnessing solar energy. Additionally, they can function as an external control mechanism for manipulating temperature, particularly when combined with various unexplored materials. Notably, the morphology of hydrogel polymers exhibits promising characteristics that undergo changes when impregnated with others emerging polymer materials, photothermal materials, and different methods of producing the hydrogels. Through the process of further integration with diverse other materials and new structural designs, the functionalized hydrogel polymer that exhibits synergistic properties demonstrates the potential to perform many functions tailored to water transport and water purification applications.

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