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The role of micro-nano pores in interfacial photothermal evaporation systems – a review

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HIGHLIGHTS

• Enhancing light absorption, heat conversion, water and vapor transmission of micro-nano pores in interfacial photothermal evaporation system (IPES).
• Systemic review of classification and roles of micro-nano pores in IPES.
• Applications of IPES with pores.
• Shortcomings and optimization directions of IPES.
ABSTRACT

Access to clean water is one of the global grand challenges. Using solar energy to evaporate seawater is a potential approach to mitigate the shortage of fresh water. Interfacial photothermal evaporation systems (IPES) employing micro-nano pores demonstrate enhanced light absorption, heat conversion, water and vapor transportation. The basic principles and mechanisms of this photothermal evaporation process is presented followed by a review of potential materials with micro-nano pores such as natural biological and artificial materials. The review identifies several shortcomings in the present knowledge on the effects of the pores on evaporation such as how the morphology of pores, aperture and distribution, material wettability, and porosity affect evaporation. To assume that all pores contain water is inconsistent with the real conditions. Furthermore, assuming that the porous characteristics alone affect the vapor flow rate or thermal distribution is misleading as the water and vapor flow field and the temperature field are coupled. A reliable unified measurement and calculation method is also missing making comparison of results difficult, e.g. some studies have used empirical data for the enthalpy of water evaporation, which would be inconsistent with the actual conditions. To measure the steam temperature accurately is difficult as steam quickly cools down after escaping to air. The micro-nano porous materials need to be stable over a long time and in particular salt accumulation need to be addressed. Exploring above issues further would be very helpful to improve the performance of photothermal evaporation with micro-nano pores.

Keywords: Solar thermal utilization; Interfacial photothermal evaporation; Pore structure; Micro-nano scale

1. Introduction

Clean water is a key resource for the whole society. However, along the rapid industrial development and the population growth, the shortage of clean water has become one of the most important threats to sustainable development [1-2]. According to the U.N. World Water Report, two-third of the world population will face water scarcity by 2025 [3]. To meet the demand for clean water, different technologies to obtain clean water has been explored such as thermal distillation, electrodialysis, and reverse osmosis [4-7]. In thermal distillation a thermal source is used to heat up a brine or polluted water to generate steam, enabling to separate water and impurities due to different boiling points, and then condensing the steam into potable clean water. However, thermal distillation is often based on fossil-fuel use such as coal or petroleum with high emissions. A clean and pollution-free desalination technology has become a necessary requirement for water scarcity [8-9].

Using solar energy for photothermal evaporation would be a modern cleantech approach to produce potable water [10-11]. Traditional photothermal evaporation systems employ large concentrating solar collectors (heliostats, parabolic troughs and Fresnel lenses) to focus incident solar radiation (< 1kW/m²) to raise the temperature needed to evaporate seawater [12]. However, this technology option is still uneconomic. Another type of solar distillation is to use non-concentrating solar radiation coupled to efficient water evaporation. Fig. 1 illustrates such development: in (a) [13-15] and (b) [16-17] the photothermal materials are fixed at the bottom or dispersed in the water body.
respectively, whereas in (c), the photothermal material floats on the surface of the water body, also called interfacial heating [18-20]. Compared to the two first structural settings, interfacial heating can constrain the sunlight to the surface of a thin water layer rather than heating the entire water body, thus greatly reducing the heat losses and improving the photothermal utilization efficiency. This type of photothermal evaporation system can be used for seawater desalination, heavy metal removal and steam sterilization.

![Fig. 1. Photothermal evaporation systems](image)

In the Interfacial photothermal evaporation system (IPES), the photothermal material is used to absorb the sunlight and evaporate the water, for which reason the photothermal conversion efficiency is one of the key factors affecting the practical application of the system. The photothermal effect can be observed in various materials, such as plasma metals [21], semiconductors [22], carbonaceous materials [23-24] and polymers [25-26]. All of these rely on three conversion principles: plasma resonance, a electron-hole generation and relaxation, and thermal vibration of the molecule. Local plasmon resonance on the surface of metal nanoparticles leads to an increase in near-field intensity, which in turn gives rise to local heating around the nanoparticles [27-28]. For the electron-hole mechanism, when the incident light energy is similar to the band gap energy of the semiconductor material, an electron-hole pair will be generated and adjusted to the edge of the band inside the semiconductor materials. Finally, the excess photon energy can be released in the form of thermal energy through the thermalization process [29]. Carbon materials or polymer materials can exhibit excellent light absorption capacity due to their black appearance, and they convert light energy into heat through lattice vibration or phonon scattering [30-31].

By comparing the micrographs of the above-mentioned photothermal materials, microscopic pores are found in these materials, but of different size, shape and distribution. Compared to other porous materials not in the micro-nano range, photothermal micro-nano porous materials significantly
differ in their behavior linked to light absorption, heat conversion, water or vapor transport due to their nanometer to micrometer size. The solar radiation spectrum covers the light in the range from 300 nm to 2500 nm (ultraviolet light in the 300-400 nm accounts for about 3% of the total solar energy, the visible light band 400-700 nm about 45% of the total energy, and the infrared band 700-2500 nm 52% of the total [32]). The absorption effect of the photothermal material in the different wavelengths is directly linked to the size of the pores, which could be adjusted. Also, abundant micro-nano pores greatly increase the specific surface area of the photothermal material and the heat exchange area between the material and the water. Furthermore, the increasing bubble activation nucleation in the micro-nano gap brings about an increase of bubbles that exchange heat [33]. At the same time, the micro-scale structure can reduce the detachment resistance of bubbles [34]. The above factors greatly promote the formation and detachment of bubbles, and hence improve the heat transfer coefficient of the material [35]. Therefore, proper micro-nano materials can optimize the heat conversion effect by increasing the heat transfer area and coefficient, which is difficult to achieve with ordinary structural materials. Finally, the micro-nano structure can also improve the wetting characteristics of the material [36-37]. Its well-developed micro gaps act as numerous vapor transmission channels. In summary, compared with an ordinary photothermal material, sunlight can be scattered and absorbed in these porous structures and water near the top interface is heated [38]. In other words, micro-nano pore photothermal materials greatly enhances light absorption, heat conversion, water and vapor transportation due to the micro-nano pores, thus making these materials highly potential for IPES.

Previous studies have shown that the micro-nano porous structure promotes light absorption, heat conversion and water vapor transport of IPES to varying degree. However, most of the previous literature have seldom systematically summarized the specific influence of micro-nano pores on the interfacial photothermal evaporation. Therefore, comparing and summarizing the role of micro-nano pores in IPES, which is the subject of this review, will contribute to the further development of photothermal evaporation.

In this review, we will focus on the latest developments in photothermal evaporation with micro-nano porous structures. Firstly, the photothermal evaporation process is briefly introduced and the performance evaluation method based on micro-nano pore structures is discussed. After comparing natural biological and artificially constructed micro-nano pores in detail, we explain how the pores affect the light absorption, heat conversion and distribution, water and vapor transportation. Then the applications of IPES with pores are summarized including desalination, heavy metal recycling and sterilization. Finally, an outlook is presented based on the literature reviewed, in particular on the optimization of micro-nano pores to enhance their potential in IPES.

2. Basic considerations on the evaporation process using micro-nano pores

2.1 Principle of photothermal evaporation process

The photothermal evaporation based on a photothermal material with micro-nano pores involves a phase transition between gas and liquid, i.e. the water absorbs heat when changing from liquid to gas. In micro-nano pores, a large number of bubbles form, grow, and escape all the time. The interfacial photothermal evaporation can be summarized in the following steps [39]: (1) The incident light is
absorbed through the light trapping structure of the tiny pits on the photothermal material’s surface; (2) then the microporous skeleton in the photothermal material converts the light into heat energy, which can quickly be transferred to the thin water layer in the adjacent pores by thermal convection; (3) the temperature of the thin water layer rises and begins to generate small bubbles; (4) as the photothermal material continuously absorbs sunlight and heats the water in the nearby pores, the amount of bubbles gradually increase and they finally escape into the air and condense into water. During this process, the impurities in the water are slowly retained in the photothermal material. Above steps complete the generation of purified water. Three crucial elements in this process can be identified: light absorption, heat conversion, water and vapor transmission [40]. The unique pores in the photothermal materials can provide strong light absorption, efficient heat conversion and sufficient vapor transmission.

2.2 Performance evaluation

For comparing the effects of different materials in IPES, it is very important to define a proper photothermal utilization efficiency for evaluating the system performance, e.g. the share of incident total solar energy used for heating and evaporating water [40-42]:

$$\eta = \frac{\dot{m} h_{LV}}{C_{opt} P}$$  \hspace{1cm} (1)

where $\eta$ is the photothermal utilization efficiency, $\dot{m}$ is the evaporation rate of water, $h_{LV}$ is the evaporation enthalpy of water including both of the latent and sensible heat, $C_{opt}$ is the optical concentration, and $P$ is the solar radiation for one standard sun. $h_{LV}$ includes the sum of the sensible and latent heat of water, which can usually be calculated as $h_{LV} = C \times \Delta T + \Delta h_{vap}$. $C$ is the specific heat capacity of water, which can be regarded as a constant, and $\Delta T$ is the difference between the steam temperature and the initial temperature of water. $\Delta h_{vap}$ is the latent heat of water, which depends on the steam temperature of the water. One difficulty in calculating the photothermal utilization efficiency lies in calculating $h_{LV}$, the evaporation enthalpy, which is directly related to the heat loss distribution of IPES [40]:

$$\dot{m} h_{LV} = Aa q_{solar} - A \epsilon \sigma (T^4 - T_w^4) - Ah(T - T_\infty) - Ah(T - T_\infty) - A q_{water}$$  \hspace{1cm} (2)

where $A$ is the surface area of the photothermal material facing the sun, $\alpha$ is the solar absorptance, $q_{solar}$ is the incident solar heat flux density, $\epsilon$ is the emittance of the photothermal material, $\sigma$ is the Boltzmann constant, $T$ is the steam temperature, $T_\infty$ is the ambient temperature, $h$ is the convective heat transfer coefficient between IPES and the surrounding environment, and $q_{water}$ is the heat flux density to water body including convection and heat conduction. From this energy balance formula, there are several measures to maximize the evaporation enthalpy and the photothermal utilization efficiency of IPES: increasing the solar absorptance of photothermal materials as much as possible [43], reducing the convection and radiant heat loss of IPES facing the environment or the convection and heat conduction losses facing water body [44-45]. These are also potential directions to optimize IPES now.

There are different ways to determine the evaporation enthalpy of micro-nano pores such as
empirical data, a combination of empirical data and formulas, and experimental measurements. For example, in the early studies [46-49] a fixed value \( h_{LV} = 2260 \text{ kJ kg}^{-1} \) have been used ignoring the actual different temperature of water. Later combination of empirical data with formulas has been applied, e.g. Li et al. [50] and Wu [51] used a special empirical formula for estimating \( \Delta h_{vap} \) and \( h_{LV} \):

\[
\Delta h_{vap} = 1.91846 \times 10^6 [T / (T - 33.91)]^2 \text{ J kg}^{-1}
\]  

Sun Yat-sen University [52] used an empirical data table to obtain the latent heat data vs. steam temperature, which was then added to the sensible heat of water. Their calculation showed that compared to using the empirical value \( h_{LV} = 2260 \text{ kJ kg}^{-1} \), the difference in \( \eta \) was between 2.7%-6.1%, which represented a notable error between the different calculation methods. By assuming that under the same ambient temperature and pressure, the product of the evaporation rate and enthalpy of water is equal to the product of the evaporation rate and enthalpy of water in pores, Papavassiliou [53] were able to quickly estimate the latent heat of water in photothermal materials compared to the relative data of pure water. Furthermore, the latent heat of water in different photothermal materials can be measured by utilizing differential scanning calorimetry (DSC) [39]. In summary, there is no unified standard available for calculating \( h_{LV} \), which makes it difficult to compare different materials and research results. In addition, the above methods are all based on macroscopic properties in a macroscopic environment. However, the water in the micro-nano pores is obviously different from the water in macro-conditions. When using macro concepts for calculating micro-nano parameters errors will be induced. Therefore, future research should better address microscopic methods to determine the \( h_{LV} \) and the efficiency of photothermal utilization.

Desalination capacity is another key indicator for examining the evaporation performance. Desalination capacity refers to the ability of the IEPS to remove various ions, organics and bacteria from water sources (rivers, lakes, coasts, industrial wastewater, etc.), which is especially critical when producing fresh water for drinking [54]. In micro-nano pores, salt water absorbs heat and generates bubbles to obtain pure water, while impurities such as salt will remain on the surface of the pores and will block the water transmission path [55]. Furthermore, after several cycles of desalination by photothermal evaporation, the salt on the porous surface will be dissolved and accumulated repeatedly, which also means that the problem of salt accumulation in different pore structures needs attention. In actual operation, to determine whether the desalination ability meets the relevant standards, it can be measured by comparing it with the ion concentration in the water before and after evaporation. For example, Zhu et al. [56] designed a three-dimensional porous membrane with aluminum nanoparticles to perform photothermal evaporation. They pointed out that the sodium ion concentration was greatly reduced by four orders of magnitude compared to before evaporation, and it met the salinity standards defined by the World Health Organization (WHO) and the US Environmental Protection Agency (EPA).

Finally, as an important factor in the practical application of water treatment [57], durability indicates whether the system can maintain the water evaporation rate, photothermal utilization efficiency and desalination capacity after long-term use [58]. Durability can be determined by comparing the cycle data of repeated photothermal evaporation experiments. Excellent durability requires that the system is cost-effective for long-term cycles and can minimize the replacement cost,
which will be particularly beneficial in actual application [59].

3. Classification of micro-nano pores in the IPES

3.1 Micro-nano pores in natural organisms

Nature offers different kinds of organisms with special micro structures which would benefit in better managing the energy needed for their survival. For example, plants have multi-level channels to continuously transport water and nutrients from roots, stems to branches. In addition, cellulose-based plants have low thermal conductivity and excellent hydrophilicity. Therefore, with their special micro-nano porous structure and material properties, plants could be a potential choice for a photothermal evaporation system. The design of organisms and their bionic structures could also be relevant to designing interfacial photothermal evaporation.

3.1.1 Micro-nano pores based on wood

Wood is one of the most abundant renewable resources on the earth, which has high mechanical strength, good processability, low price, and promising market development [60-62]. Trees absorb water, ions and other nutrients from the soil through many vertically arranged microchannels that are connected by nano-scale spiral and pit-shaped micro channels [63]. Therefore, the trees have countless multi-level microscopic channels. Biomass-based amorphous carbon can be obtained through simple carbonization and other treatment methods [64]. The biocarbon materials have different micro-nano porous structures depending on the source and synthesis conditions.

From the SEM image of carbonized wood (Fig. 2a-2d), Xue et al. [65] observed that wood has two kinds of near-round pores with different sizes parallel to the growth direction. The larger pores with a diameter of 50-100 μm were evenly surrounded by the smaller pores with a diameter of a few microns. Both of these two different microchannels could pump water from the bottom to the top and helped to capture incident light. It was worth noting that the flame treatment deposited a layer of nanoparticles with a diameter of about 30 nm on the inner wall of the microchannel, which was quite effective for improving the light absorption of the material on the surface. In order to carbonize the wooden block, a 500°C hot plate was pressed against the cross section of a wooden block [66]. From the microtopography of the carbonized zone, the authors [66] indicated that there were concave pores with a diameter of about 2 μm which were perpendicular to the growth direction of the tree. These concave pores facilitated the lateral transport of water between adjacent channels. Since it was found that wood had a variety of microporous structures in three-dimensional space, Hu et al. reversed the tree design, meaning that the growth direction of the wood block was carbonized and used it as light absorption surface. This design could not only use the large pore channels as an excellent thermal barrier, but could also facilitate future scalable production [67]. Different types of trees have different microscopic structures. For example, the pores of Chinese fir are perpendicular to the growth direction were uniform in size and armore regularly arranged [68].

Chen et al. [69] studied a convenient and effective aluminophosphate treatment on wood (Wood@AIP). Brushing this acid solution on the wood surface promoted wood carbonization and accelerated the formation of carbon layers. As shown in the Fig. 2e-2f, there are well-defined multiple pores conducive to absorbing sunlight and steam escaping. In addition, wood can be alkalized to obtain a porous three-dimensional carbon foam in order to get unique interconnected channels and rough
surfaces [70]. The above methods of directly or partially carbonizing and alkalizing wood can retain natural rich micro-nano pores. This seamlessly integrated porous structure makes the photothermal absorption layer and water transport layer of IPES closely connected to ensure the stability of the system. However, other common IPES often require additional connection components between the photothermal absorption and the water delivery layer, which inevitably reduces the application stability of the system.

In addition to simple carbonization of wooden blocks, various studies have also utilized wood as substrates and have sprayed graphite (Fig. 2g-2h) [71], graphene oxide [72], carbon nanotubes [73-74] and ionic metal nanoparticles such as Pd, Au, Ag, etc. in the pores of the wooden block (Fig. 2i-j) [75]. These additional deposits can provide high photothermal absorption, and the untreated wood underneath can also act as a thermal insulator to prevent thermal energy from being transferred to the environment. These studies employed regular vertical large channels and horizontal small concave pores in wood.

![Fig. 2. IPES based on natural biological micro-nano pores. (a-d) Top and cross-sectional views of carbonized wood, enlarged SEM images of the inner pores and deposited carbon nanoparticles of carbonized wood [65]. (e-f) Schematics image showing the fabrication and SEM image of cross section of uncoated wood and Wood@AlP [69]. (g-h) Schematic of the graphite-coated wood, SEM image of mesoporous wood and schematic showing the solar steam generation mechanism of the graphite-coated wood [71]. (i-j) Natural woods decorated with various metal nanoparticles, SEM images showing the mesoporous structure of plasmonic wood with numerous open and aligned microchannels and Pd nanoparticles with a diameter of about 5 nm [75]. Adapted with permission from Refs. [65, 69, 71, 75].](image-url)
3.1.2 Micro-nano pores based on other organisms

Other organisms also have special porous structures. Bamboo has a special fiber structure. Wang et al. [76] coated bamboo fibers with reduced graphene oxide (rGO) and agar. SEM showed that the bamboo fibers had bundled fibers with a diameter of 3 mm, and the pores between the fibers were filled with a complex 2D structure composed of rGO and agar. The IPES had better water transportability due to the hydrophilicity of bamboo.

Carbonized white radish had a highly developed honeycomb structure whose size ranged from 50-100 μm in Fig. 3a-3b [77]. These tightly packed pores provided abundant interconnected channels for rapid water circulation. Wilson et al. [78] used Indian citrus peels to dry and pulverize for carbonization, and coated this highly porous carbon powder with a mesoporous structure on the polyvinyl alcohol (PVA) sponge. This IPES achieved a photothermal efficiency of 90.88% of under 1 Sun radiation.

Maize straws have low-tortuosity water microchannels, which can transport water from the soil at the bottom to a height of tens of meters and then perform excellent water distribution work. Inspired by this special agricultural waste, Xu et al. [79] used polypyrrole (PPy) to make simple chemical modification of maize straws and obtained photothermal material with honeycomb-shaped hexagonal pores (Fig. 3c-3d). The average diameter of the tangent circles of these hexagons was about 100 μm (ranging from 20 to 200 μm), and the thickness of the solid cell wall used for transportation and storage was about 0.3 μm. This perfect masterpiece of nature played a vital role in rapid and uniform water delivery when evaporating water. The eggshell membrane is a natural semi-permeable membrane with a thickness of only a few tens of micrometers, which has a uniform porous structure conducive to vapor transmission. Lou et al. [80] carried out three treatments on the ultra-thin eggshell membrane such as carbonization, reduction of graphene oxide and growth of carbon nanotubes, and found that the roughness, thickness and average pore diameter of the eggshell membrane changed to varying degrees (Fig. 3e-3f). They concluded that the growth of carbon nanotubes on the porous eggshell membrane skeleton had a graded aperture distribution that would also strongly affect the formation of water transportation channels. As a kind of organism with a porosity of up to 90%, a mushroom has an umbrella-shaped pileus, a thick context and a small stipe [81]. The porous structure of three different areas is quite different (Fig. 3g). The increased surface roughness of the carbonized pileus could be conducive to light absorption. The carbonized content had evenly arranged pores with an average diameter of 3.6 μm, which could serve as an effective channel for steam to escape. The carbonized stipe was composed of thick and long fiber channels arranged in parallel along the growth direction, which could provide ideal water transmission from bottom to the top. Therefore, proper cooperation of different micro-nano structures in different parts of the mushroom can bring an ideal photothermal evaporation effect.

Natural nano-cellulose foams have attracted extensive interest due to their nano-size, excellent mechanical properties, sustainability and biodegradability [82-88]. Interestingly, they also exhibit excellent hydrophilicity, low thermal conductivity and rich graded pores, which can ensure sufficient water transport, and good thermal management to achieve effective solar evaporation. Jiang [89] designed a double-layer aerogel structure, in which natural cellulose nanofibrils (CNF) were used as basic components to achieve sustainability and biodegradability while carbon nanotubes (CNT) were
designed to achieve effective solar energy utilization. In this special design, the cellulose nanogel met the requirement of water transportation and thermal insulation due to its highly porous structure (99.4% porosity). In addition, carbon black nanoparticles can also be sprayed on the surface of cellulose to achieve effective photothermal evaporation [90].

By analyzing and studying the microscopic porous structures in different biological materials, further design and optimization of materials and systems for photothermal evaporation could be enhanced.

![Fig. 3. Micro-nano structure of other organisms. (a-b) White radish and their SEM images [77]. (c-d) Polymerization process and morphologies of the polypyrrole-modified maize straw [79]. (e-f) Top and cross-sectional SEM images of ultra-thin eggshell membranes treated with carbonization, reduced graphene oxide, and growth of carbon nanotube [80]. (g) Schematic diagram of carbonized mushrooms and the SEM images of its umbrella-shaped pileus, context and stipe [81]. Adapted with permission from Refs. [77, 79, 80].]

3.2 Artificial micro-nano pores

Efficient porous materials can also be obtained through artificial construction, and optimizing the shape and size of pores by changing the synthesis technology. Common artificially constructed porous materials include nano-metals, carbon materials, macromolecule polymers and semiconductors.

3.2.1 Nano metals
As an example of nano-metals, Wang et al. [91] prepared plasmon membranes by depositing Au-nanoparticles with an average diameter of 11.3 nm on a filter membrane (Fig. 4a-4b). Compared with the arrangement of pure water, nanoparticles dispersed in the water body, and the plasmon membrane at the bottom of the water, the water evaporation of the plasmon membrane on the water surface reduced the mass the most. This also proved superior thermal restriction by interfacial heating. Bae [92] used collapsed alumina nanowires to produce a flexible black gold film with plasma heating. Fig. 4c-4d show that a self-aggregating metal nanowire could randomly assemble micro funnels like ridges and valleys. Due to these nano-scale gaps from zero to hundreds of nanometers and micron-scale funnel structures, the blackfilm achieved ultra-wideband absorption of sunlight. In addition, aluminum nanoparticles can be self-assembled into a 3D porous membrane to make efficient light-to-heat conversion. This honeycomb-like porous structure with a size of about 300 nm can provide paths for efficient water supply and continuous steam flow [56]. Nano-metallic photothermal materials can also be obtained by depositing Ni nanoparticles on Al anodized plates [93]. Deng et al. [94] designed copper foam with a three-dimensional porous structure as a photothermal material. Fig. 4e-4g show that the surface of the copper foam had a needle-shaped nanostructure, which absorbs 95% of the incident sunlight.

![Diagram](image)

**Fig. 4.** Artificial porous structure. (a-b) SEM images of Au plasmonic membranes at different scales, 2D and 3D AFM images of Au plasmonic membranes [91]. (c-d) Schematic diagram and SEM image of the aluminum oxide nanowires with micro-funnels like ridges and valleys [92]. (e-f) Schematic process for preparing copper foam with different surface wettability, photograph of untreated copper foam and treated hydrophilic copper foam and SEM images of treated hydrophilic copper at different scales [94]. Adapted with permission from Refs. [91, 92, 94].
3.2.2 Carbon materials

Black carbon material is a wide-band solar absorption material. Different carbon materials such as flake graphite, carbon nanotubes and graphene also exhibit different microstructures. Zhang et al. [95] attached activated carbon powder to cotton fabric as a photothermal material, which achieved a water evaporation rate of 1.95 kg m\(^{-2}\) h\(^{-1}\) under one sun. The arrangement of CNT on qualitative filter paper by Miao et al. [96] also realized 84.6% photothermal utilization efficiency under 1 Sun.

Ghasemi et al. [97] synthesized a two-layer structure of exfoliated graphite layer supported by a carbon foam layer. The bottom carbon foam with smaller pores transported liquid, while the top graphite layer with larger pores was conductive to steam. The combination of such a hydrophilic network of pores with different diameters could effectively assist light absorption and continuous transmission of water and vapor.

In addition, porous graphene materials have mesoscopic porosity, lower specific heat and thermal conductivity. As illustrated in Fig. 5a, Ito et al. showed that the growth temperature of chemical vapor deposition (CVD) and the N-doping conditions affected the average aperture and surface of porous graphene [41]. Liu [98] proposed a layered graphene foam (hG foam) as a broadband omnidirectional sunlight absorber through CVD. This graphene foam owned a multi-level microporous structure that resulted in multiple internal light reflections and promoted light absorption.

Graphene oxide is one of the most important derivatives of graphene. It has good dispersibility and enables designing of the microstructure [99]. Xia [100] used a combination of halloysite (Hal) nanotubes (HNT) and graphene oxide (GO) to form efficient photothermal materials, which showed high porosity, excellent absorbance and good thermal insulation performance (thermal conductivity 0.162 Wm\(^{-1}\)K\(^{-1}\)). Graphene oxide-based aerogel RGO-SA-CNT had a dense porous structure and defects on the reduced graphene oxide RGO sheet (Fig. 5b) yielding in excellent thermal insulation properties, fast steam escape rate and sufficient liquid supply channels [101]. Similar porous graphene aerogels [102-104] have been used to generate steam. These prepared graphene aerogels have micrometer-sized pores, which can be used as water transmission channels and are consistent with the necessary conditions for efficient light-to-heat conversion.

However, the graphene required for these aerogels is expensive and this limits its large-scale application. In order to reduce the demand of graphene, Storer [105] utilized straw-derived cellulose fibers and sodium alginate as the bone support for the 3D photothermal aerogel, which finally reduced the amount of rGO by 43.5%. The integration of straw fiber and rGO significantly improved the flexibility and mechanical stability of graphene aerogels.

Assembling different types of carbon materials can also bring excellent results. Hong et al. [106] sprayed a carbon composite material of GO and CNT on the skeleton structure of the porous cellulose filter (Fig. 5c). Its periodic concavity pattern effectively captured diffuse reflection light and reduced the convection and radiation heat loss, thereby improving steam generation efficiency.
3.2.3 Polymers

Some commercial sponge polymers such as PVA, polyurethane (PU) and melamine have rich open-cell structures and skeletons similar to staggered tree roots. Based on these special structures, sponges are used as substrates and combined with photothermal materials to achieve photothermal evaporation. Tanemura et al. investigated PVA dyed with nano-inks (Fig. 6a-6b) and found that its disordered, open macroporous structure with a certain roughness greatly accelerated water and vapor evaporation [107]. Yu et al. studied polyvinyl alcohol/graphene oxide (PVA/rGO) showing that due to mixing of rGO and internal capillary channels, the PVA/rGO hydrogel achieved 98% solar absorption and high water evaporation rate of 2.5 kg m⁻²h⁻¹ [108]. Similarly, a nanostructured gel material (HNG), in which epolypyrrole (PPy) was linked into a PVA grid, had wide pores with a diameter of about 150 μm [39]. These pores formed multi-stage micro-channels with a width from a few microns to ten microns, including internal gaps and micro-channels, helping continuous generation of steam at a high rate. Papavassilion et al. [53] calcined melamine in air to obtain a carbonized sponge (AMS). As shown in Fig. 6c-6d, this porous material significantly reduced in size after calcination, but its shape remained unchanged. Reduced graphene oxide/polyurethane foam (rGO/PU) (Fig. 6e-6f) had also been prepared for photothermal evaporation [109]. Interconnected pores of rGO/PU serve as transport paths for water.
to the surface of the rGO/PU foam, but also as thermal insulation. Li et al. [110] added PPy to the recompressed melamine foam to obtain a large double-layer polymer photothermal material. The SEM image showed that this material had a network structure with a size of 100-200 μm where PPy coating caused a rough surface inside. Wu et al. [111] used carbonized and oxidized polyacrylonitrile to prepare a porous carbon film through electrospinning technology. This carbon film had a highly porous structure and long-distance continuous fibers can support water transport through each layer, and the air between each layer reduced heat loss between the layers.

In addition, the polymer photothermal material can also be composed of holes of different sizes. Zhao et al. [112] imitated the hydrophobicity of lotus leaves and the porous structure of lotus root, and then designed a bionic evaporator based on truss-like resorcinol-formaldehyde resin (TRR). Hydrophilic macropores modified by polydopamine (PDA) could quickly transport water, while the upper hydrophobic layer modified by perfluorodecyltriethoxysilane (PFDTs) prevented water transport and salt accumulation. The IPES skeleton contained 3D interconnected truss-shaped large pores and parallel lotus-shaped mesopores, which helped ventilation and reduced thermal conductivity. Yu et al. [113] designed vertically oriented porous membranes (VOPMs) with a hydrophobic upper layer and hydrophilic lower layer based on a commercial polyvinylidene fluoride (PVDF) membrane (Fig. 6g-6i). The vertical pores remained open and not clogged during modification. And the material had a light absorption of up to 97% and the evaporation rate of water under one solar condition was up to 1.08 kg m⁻² h⁻¹.

Fig. 6. IPES based on polymers. (a-b) SEM images of PVA and PVA sponge dyed with nano ink [107]. (c-d) Photograph and SEM images with different magnification of the as-prepared AMS and AMS [59]. (e-f) SEM images of PU and rGO/PU [109]. (g-i) Digital photos and SEM images of nascent VOPM, PPy-coated VOPM and Janus VOPM [113]. Adapted with permission from Refs. [107, 59, 109, 113].
3.2.4 Semiconductors

Many metal oxides and chalcogens have been used in photothermal evaporation such as MoS$_2$ [114], Ti$_2$O$_3$ [115] and Cu$_7$S$_4$ [116]. For example, CuS nanocage served as a photothermal absorption material in CuS nanocage-agar-cotton, and the agar with a 3D hydrophilic pore network was an ideal candidate to support active photothermal materials [117]. Micron-level uneven pores between the CuS nanocage surrounded by the agar could be identified (Fig. 7a-b). Zheng et al. [118] combined Au plasma particles and carbon dots on the basis of Bi$_2$MoO$_6$ to obtain a nanocomposite with higher light-to-heat conversion efficiency (Fig. 7c). By wrapping Au plasma particles inside the Bi$_2$MoO$_6$ sphere and stacking 2D carbon nanosheets outside the sphere, coral-like Au@Bi$_2$MoO$_6$-CDs heterostructure was synthesized for the first time. The addition of Au and carbon dots effectively inhibited the recombination of electron-hole pairs, thereby enhancing the photothermal performance of Bi$_2$MoO$_6$. This 3D composite structure had a synergistic and efficient effect in broadband light-to-heat conversion, which was attributed to the multiple internal reflections of light from the 3D cavity and ribbon coral structure on the spherical shell.

Fig. 7. IPES based on semiconductors. (a-b) SEM image of the co-existence of cotton fibers, agarose and CuS nanocages and Eement mappings (C, O, Cu and S), SEM images of the CuS nanocages bound by agarose [117]. (c) SEM and mapping images and of Au@Bi$_2$MoO$_6$-CDs composites [118]. Adapted with permission from Refs. [117, 118].

In natural biological or artificial materials, micro-nano-scale pores can be regularly arranged to form cross-sized pores, honeycomb-type uniform dense pores, or disordered tree-shaped pores, which in turn can provide sufficient water and vapor channels, promote light trapping, and enhance heat conversion at different levels.

4. Role of the micro-nano pores in the IPES

Porous structures with micro-nano scale has increasingly been used for photothermal evaporation. However, there is very little information about how the pores affect the critical functionalities. Next, a summary of detailed experimental and simulation results of porous structures in the IPES is provided.
4.1 Light absorption

In 3D porous materials, light absorption is usually affected by the porous structure such as multiple scattering and internal reflection of light [119]. Zhao et al. [39] briefly explored the relationship between the aperture and light absorption. PPy was linked into PVA to obtain a gel material (HNG). The nanostructure of HNG was controlled by adjusting the mass ratio of PVA and water. The aperture of HNG1 to HNG4 expanded from a few microns to 10-20 μm as the water content increased. However, the UV-Vis-NIR spectroscopy measurement showed that all of the HNGs exhibited excellent absorption characteristics over the entire spectrum. Only the absorbance of HNGs in the ultraviolet and visible regions in the 250-570 nm range was inversely proportional to the aperture. Zhu et al. [66] investigated the fundamental factors of the high absorbance of carbonized wood blocks through optical modeling the simplified square wood structure (Fig. 8a). By changing the angle of the incident light and the aperture, it was indicated that when the angle and wavelength of light was 10° and 550 nm, respectively, the absorbance of pore diameters with > 100 nm exceeded 80%. They concluded that a large aperture was more favorable to light absorption, especially when the aperture exceeded 30 μm, which was mainly due to the fact that under this condition the incident light would be captured and penetrated deeper until it was fully absorbed.

In order to explore how the pore accumulation affect the absorbance of the material, Fang et al. [120] used COMSOL simulation model to simulate the optical performance of carbonized rice husk. He constructed three models with crossed hollow spheres to study the influence of different pore layers on transmittance (Fig. 8b). The simulation results proved that as the ball layer increased, the number of sunlight that escaped from the bottom also showed a significant decrease due to the continuous reflection and absorption of light. The number of spheres increased mainly affected the transmittance of the bottom, and the cross-pore structure indeed enhanced the light absorption of the absorber.

![Fig. 8. Light absorption simulation of micro-nano pores. (a) Optical model of simplified wooden blocks to calculate absorbance [66]. (b) Ray tracing of three models with crossed hollow spheres [120]. Adapted with permission from Refs. [66, 120].](image)

4.2 Heat conversion and distribution

An important process after the porous material have absorbed sunlight is to convert the light into heat, i.e. to generate thermal energy and to heat up the water. Using differential scanning calorimetry experiments, researchers [39] claimed that the latent heat of water in HNGs gel materials gradually
increased and continued to be less than the latent heat value of pure water as the water content of HNGs gel materials increased. They explained this phenomenon with the water cluster theory and also proved it through experiments and thermodynamic analysis. The water cluster theory assumes that when water molecules were confined in the molecular grid, water was more likely to leave the polymer network in the form of small clusters instead of a single molecule, so the enthalpy of water evaporation became smaller. According to their conclusions, the smaller the aperture within a certain range, the smaller the latent heat of water in the pores, i.e., a material with a smaller aperture could evaporate more water. However, this idea is not unambiguously supported by the evaporation rate of water in their experiments. Similarly, Tang et al. [121] conducted a photothermal evaporation experiment by adjusting the hydrophilicity of charred wood surface and the height of the wood. The results of differential scanning calorimetry showed that the latent heat of water in wood (1769 kJ kg⁻¹) was much lower than that of pure water (2444 kJ kg⁻¹). This was because the water in the wood was kept in micron-sized capillaries where capillary water moved unrestrictedly and had more space to escape.

When the incident light hits the photothermal evaporation system, it is important that the thermal energy is effectively confined in the evaporative surface of the water body rather than heating the entire water body, in other words, it is necessary to achieve thermal localization. Therefore, heat conduction, heat convection, or heat radiation loss to the surrounding environment should be minimized. Guo et al. [122] introduced a solar absorber derived from renewable biomass konjac glucomannan (KGM) and iron-based metal organic framework (Fe-MOF) into the PVA network to form a cost-effective hybrid hydrogel evaporator (HHE). They used COMSOL to simulate the temperature distribution of the entire device to clearly demonstrate the advanced thermal management capabilities of this hybrid hydrogel (Fig. 9a). Compared with non-interfacial heating, the interfacial heating heated near the evaporation surface reducing unnecessary heat loss exhibiting a stronger thermal restriction effect. Three-dimensional simulation of the temperature distribution of mixed hydrophobic porous copper foam (Fig. 9b) showed local heating of the copper foam, while the rest of the evaporation system remained unheated [94]. After 30 minutes of 1 Sun exposure, the temperature of the copper foam reached 100 °C, indicating that the evaporator could produce steam smoothly.

To illustrate the thermal field distribution in the porous structure, Tang et al. [121] used ANSYS Fluent to simulate the steady-state temperature distribution of charred wood. As shown in the Fig. 9c-9d, the surface temperature was much higher than the bottom temperature, and the temperature around small-sized channels was much higher than that of large-sized channels. The simulation results confirmed that the heat was confined to the surface of the 3D solar evaporator. Zhao et al. simulated the temperature in the internal gaps, microchannels, and molecular grids of the HNG gel material when fully saturated with solar radiation [39]. The steady state value of the highest temperature of the HNG in the polymer grid reached 315 K and it occurred on the surface of the polymer grid. The simulated value was quite close to experimental results, confirming that the HNG gel material included an effective thermal constraint.
Fig. 9. (a) COMSOL simulation of the temperature distribution of pure PVA hydrogel with absorber uniformly distributed and HHE, showing a clear heat localization effect after introducing KGM and localizing absorber [122]. (b) Three-dimensional thermal distribution map of porous copper foam [94]. (c-d) Model of longitudinal section of the charred wood and theoretical simulation of temperature distribution [121]. Adapted with permission from Refs. [122, 94, 121].

4.3 Water and vapor transport

To better understand how water is transmitted through a porous structure, Hu et al. [66] constructed a 3D physical model of carbonized wood blocks (by SOLIDWORKS) and performed CFD simulations and experimental tests on a near-real wooden block unit built on the basis of real data of the microchannel and walls from SEM pictures. The unit was completely filled with water by capillary forces. Therefore, the fluid area in this CFD simulation was split into three parts: a water film above the wooden board (25 μm in height), a water area covering the timber structure (200 μm in height) and a large amount of water (50 μm in height) under the board body. The simulation results (Fig. 10a) indicated that the water transport process through the wood block unit included the following steps: (1) the water first passed into the large diameter microchannel from below the wood block; (2) then the water raised through the microchannel and reached the top wooden surface; and finally, (3) a thin water film was formed on the surface of the wooden block and the water flow became slow after evaporation. The simulation demonstrated that the effective capillary size to drive the water by evaporation depends on the size of the microchannel. The end trachea fiber hindered water transmission. Surprisingly, the small pits distributed on the inner wall of the microchannel did not affect the transmission of water.

They also reversed the design of the carbonized wood block, i.e. the growth side of the carbonized wood block was used as the light absorption surface. Through the flow simulation (Fig. 10b), it was
found that the horizontal micro pores of the wood could indeed sufficiently transmit water, and the vertical micro pits (about 2 µm in diameter) on the side walls could effectively adjust the flow [67]. Similar simulations showed that in the reverse design of the wooden block microstructure (Fig. 10c), the flow of water driven through the capillary pores was effective and could quickly replenish the evaporated water on the top of the wood [71].

A two-phase hybrid model has also been used to simulate water transport in the internal water gap, microchannels and molecular grid in HNG that was fully saturated under solar radiation [39]. 2D mapping of the water flow velocity showed that the water transport through the internal gap reduced the water loss on the surface, which mainly supported the water transport from the bottom to the surface. At the same time, uniform water diffusion on the evaporation surface was mainly assisted by the microchannels. Tang et al. [121] used ANSYS Fluent's two-phase mixed model to simulate the water transport process of charred wood. The simulated longitudinal profile showed that water could pass through the microchannel at an average speed of 1.1 µm·s\(^{-1}\) to offset the loss of surface water (Fig. 10d). The transportation was mainly supported by microchannels and a large number of pores.

In addition, adjusting the porosity to change the water delivery rate is also an important part. Liu et al. [122] designed a two-layer biomass system with carbon particles on the top and a thin film of wood chips on the bottom. The experimental results showed that the porosity significantly affected the water transport in the wood film. The positive effect of the water diffusivity increase and the negative effect of the thermal conductivity increase in the film determined that a porosity of 0.52 was the best choice to improve the photothermal utilization efficiency of the double-layer biomass system.

From the above analysis, the performance of IPES can be significantly improved by exploring the light absorption, heat conversion and distribution, and water vapor transmission of IPES by micro-nano pores.

![Fig. 10. Simulation of water transport in micro-nano pores. (a) CFD simulation of water velocity profile on the cross section of the wooden block [66]. (b) Reverse design simulation of carbonized wood blocks and water velocity distribution of micro-nano units of reverse-designed carbonized wood blocks [67]. (c) Water velocity distribution through mesopores in reverse design of carbonized wood blocks [71]. (d) Model of longitudinal section of the charred wood and theoretical simulation of water transport [121]. Adapted with permission from Refs. [66, 67, 71, 121].](image-url)
5. Application of IPES with micro-nano pores

IPES can use solar evaporation to treat the water source, thereby separating the treated water source from impurities. This water purification process can be used to desalinate seawater to obtain clean water, and also to collect heavy metals remaining in the water body after evaporation. The high temperature steam in the evaporation process also plays a special role in the field of sterilization.

5.1 Desalination

Zhu et al. [56] used a three-dimensional porous membrane self-assembled by Al nanoparticles to treat simulated seawater with different salinities, namely the Baltic Sea (0.8wt% salinity), the average salinity of the world ocean (3.5 wt% salinity), and the Red Sea (4 wt% salinity) and the Dead Sea (10 wt% salinity) water. Observed by inductively coupled plasma spectroscopy (ICP-OES), the concentration of Na-ions was significantly lower than the concentration before the desalination process (four orders of magnitude), which was lower than the salinity level defined by the WHO and the United States EPA standards. Similarly, experiments on real seawater samples from the Bohai Sea in China found that the concentrations of all five major ions (Na\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), K\(^+\) and B\(^{3+}\)) present in sea water were significantly reduced. In order to further explore the practical feasibility of aerogels made of straw-derived cellulose fibers and RGO (RGO–SA–cellulose aerogel), Storer et al. [105] measured the salinity of steam under one sun radiation. He found that the concentration of four main ions (K\(^+\), Ca\(^{2+}\), Na\(^+\) and Mg\(^{2+}\) in the generated steam) was far below the standard of the WHO for drinking water (Fig. 11a). In 15 test cycles for 2 days, the average evaporation rate of water reached 2.0±0.2kgm\(^{-2}\)h\(^{-1}\) (Fig. 11b).

Xu et al. [79] utilized polypyrrole-modified maize straw (PMS) to evaporate seawater with an average salinity of 2.6% by recording mass changes under outdoor light (Fig. 11c-11g). After distillation, the concentrations of the five main elements (Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\) and B\(^{3+}\)) in the seawater were all lower than 1 mg⋅L\(^{-1}\), and their declines were all over 98%. The concentration of elements in distilled water was far below the WHO standard (1000 mg⋅L\(^{-1}\)). It is worth noting that it could effectively remove the toxic pollutant B\(^{3+}\) in seawater, which was difficult to capture by conventional reverse osmosis technology.
Fig. 11. Desalination of IPES with micro-nano pores. (a-b) Ion concentrations in the original seawater and condensed steam collected during evaporation and cycle evaporation performance of RGO–SA–cellulose aerogel under 1 sun irradiation [105]. (c-g) Outdoor water production of PMS, evaporation test of the planar system and PMS system in the outdoor condition, the mass change of purified water, comparison of the outdoor water production of the previous reports under 1 sun, concentration of ions in seawater and purified water [79]. Adapted with permission from Refs. [105, 79].

5.2 Heavy metal recycling

When dealing with polluted water with valuable heavy metal ions, heavy metal recovery has obvious economic significance. Zhu et al. [123] used an umbrella-shaped graphene film to treat the heavy metal solutions including CuSO$_4$$\cdot$5H$_2$O and HAuCl$_4$$\cdot$4H$_2$O, which were commonly found in wastewater from the electroplating industry. After 5 h of evaporation, Au was deposited on the surface of IPES and recovered (Fig. 12a). They expected that similar methods could be used to recover other heavy metal ions (such as Pt$^{4+}$, Cr$^{2+}$, Ni$^{2+}$, etc.). Liu et al. [124] used PU sponges impregnated with rGO and Ag nanowires to treat simulated electroplating wastewater. As shown in the Fig. 12b, the initial concentrations of Pb$^2^+$, Cu$^{2+}$ and Cd$^{2+}$ were all 1500 mg l$^{-1}$, and the concentration of heavy metal ions in collected evaporated water was less than 0.1 mg l$^{-1}$, which meets China's current drinking water standards for residents (GB5749-2006).
5.3 Sterilization

In order to prove the sterilization performance of high-temperature steam in interfacial heating, Zhang et al. [125] used a rGO/polytetrafluoroethylene composite film as a photothermal material to generate heat energy. When the intensity of the solar simulator was 2.2 Wcm$^{-2}$, the steam temperature reached at least 121°C after about 40 minutes and killed most of the bacteria. In order to prove the thermal stability of the composite film, it was exposed to concentrated sunlight with a power density of 2.56Wcm$^{-2}$. The film was able to generate steam above 132°C and showed excellent sterilization performance after only 5 minutes. Even after 15 cycles, the performance of the composite membrane remains at the same level. The sterilization cost of this device was significantly lower than that of commercial autoclaves due to using renewable solar energy. Therefore, the high-temperature steam generated by interface heating is a potential cost-effective sterilization way.

6. Conclusions

Major progress has been made in the field of interfacial photothermal evaporation in recent years. The literature review indicates that the pores of the material play an important role in light absorption, heat conversion, water and vapor transmission. This review first discussed the basic principles of the photothermal evaporation process in porous materials followed by an analysis of potential materials with micro-nano pores such as natural biological and artificial materials. The review also discussed the influence of the micro-nano pores on light absorption, heat conversion, water and vapor transportation. The application of IPES based on micro-nano pores in seawater desalination, heavy metal recovery and sterilization was briefly introduced.

Though the literature included several innovative approaches to photothermal evaporation, the state-of-the-art of the field still is in an exploratory phase dominated by material selection and laboratory experiments. A coherent explanation of the mechanisms of dynamics, heat and mass transfer is still incomplete. For example, it is not yet fully clear how the microscopic morphology of pores, aperture and distribution, material wettability, and porosity affect photothermal evaporation. The actual thermal and humid environment in pores, in which both liquid water and vapor coexist, is complex. Current research typically assumes that all pores contain water, which is not consistent with the real conditions. The characteristics of the pores affect water and vapor transportation, and change the...
various physical properties of materials such as thermal conductivity and specific volume, which affect the distribution and utilization of thermal energy in the porous structure. Therefore, the water and vapor flow field and the temperature field are coupled with each other, for which reason it would be erroneous to assume that the porous characteristics alone affect the vapor flow rate or thermal distribution. Exploring these mechanisms further would be very helpful to improve the performance of photothermal evaporation with micro-nano pores.

The literature review also found that there is no reliable unified measurement and calculation method for photothermal evaporation systems, which makes it difficult to compare research results. For example, some studies used as default empirical data for the enthalpy of water evaporation, which would be inconsistent with the actual conditions. Also, how to measure the steam temperature accurately is a major challenge for the experiments, as there may be large deviations when measuring the steam temperature since the steam will quickly cool down after escaping into air.

Concerning interfacial photothermal evaporation for practical applications, several other issues need to be addressed. The micro-nano porous materials need to show long-term stability to maintain a stable performance. Especially the problem of salt accumulation after several cycles may be a major issue. Such technical challenges will directly affect the system replacement cost of IPES and its commercial viability.

**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**References**


