Review article

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Plasmon-enhanced solar vapor generation

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Abstract: Plasmonic nanostructures with strong light-matter interactions have been intensively explored in the past decades. The plasmonic photothermal effect has garnered significant research interest and triggered plenty of applications, such as photothermal therapy, photothermal imaging, and photocatalysis. Recently, plasmonic nanostructures are emerging as one of the most exciting candidates for solar vapor generation, inspiring the revival of solar-thermal-based water purification technologies. Here we present a review of state-of-the-art plasmonic-enhanced solar evaporation, including the theoretical background, various designs of plasmonic materials and structures, and their potential applications. The current challenges and future perspective are outlined as well.

Keywords: plasmonic nanostructures; broadband absorber; heat localization; photothermal; solar vapor generation; water purification.

1 Introduction

Plasmonic nanostructures have garnered tremendous attention from versatile research fields due to their unique capabilities to focus light into subwavelength volumes [1–6]. The basis of the well-known plasmonic effects [7, 8] is the high density of free electron gas (for noble metal ~10^{22} \text{ cm}^{-3}) and the induced intrinsic collective oscillation of electrons. When excited by electromagnetic waves, the interactions between the free electrons and incident photons result in various plasmonic excitations, such as surface plasmon polaritons (SPP) [9], localized surface plasmon (LSP) [10] and hybridized plasmonic modes [5, 10, 11].

So far plasmonic effects have been intensively explored for subwavelength light sources [12], on-chip wave guiding [13, 14], color filtering [15, 16], molecular sensing [17, 18], photocatalysis [19, 20] and photovoltaics [21, 22]. Among most of the applications above, the intrinsic plasmonic photothermal effects [23–26], which dissipate the harvested photon energy into ohmic loss via electron participated scattering processes [27], have long been considered as an inevitably parasitic effect. On the other hand, the plasmon-based photothermal effect has been playing crucial roles in various fields, such as photothermal therapy [28–31], medicine delivery [32, 33], photothermal imaging [34], and material synthesis and assembly [35].

Very recently, an emergent plasmonic photothermal effect, plasmon-enhanced solar vapor generation (SVG), has triggered a revived research interest on an ancient solar water purification technology [36–40]. SVG is a natural photothermal phenomenon that induces liquid-vapor phase change of water by solar energy. As an essential part of the water cycle, the interaction of the Sun and the Earth (with >70% area covered by ocean) is endlessly providing purified water from seawater. However, such natural SVG process is rather inefficient (energy transfer efficiency <20%) because of the low solar energy harvesting capability as well as severe thermal losses. Plasmonic materials are promising candidates for enabling highly efficient SVG, due to enhanced light-matter interactions and electromagnetic fields in a tiny volume, beneficial for minimizing optical and thermal losses.

The plasmonic photothermal utilizations can be understood as follows. Surface plasmons, firstly known as collective electron oscillations in close proximity of the metal-dielectric interface [10, 20], can either propagate along the interface (SPP shown in Figure 1A) or be localized near the curved surfaces of metal nanoparticles (NPs) (localized surface plasmon resonance [LSPR] shown in Figure 1B) [10]. As shown in Figure 1C, the excited surface plasmons can behave as strongly damped oscillators [23,
and decay via different interplay channels (electron-to-photon, electron-to-electron, and electron-to-phonon), most of which are dissipated in the form of thermal energy [23, 24, 26].

Therefore, several common features are related to plasmonic nanostructures for solar thermal utilizations like SVG. Firstly, they are highly absorptive with various optical transition processes for the high density of free electrons [26, 42]. For example, metal-based plasmonic materials can fully utilize both interband and intraband transitions of optical absorption with low radiation recombination because of the unique band structure [43]. Thus, very thin plasmonic materials can enable strong light absorption. Secondly, the absorption spectra of plasmonic materials can be flexibly manipulated [42, 44–47], which can possess versatile optical modes [48–50], beneficial for ideal spectral matching with solar irradiance. Thirdly, surface plasmons can generate a pronounced local field enhancement up to thousands of times with respect to the incident field [10, 43, 51]. The energy of incident light is transformed into the oscillation energy of electrons and condensed electromagnetic field, which is ultimately converted into heat (called light-induced heat concentration) [3, 4, 24].

Plasmonic nanostructures enabled SVG not only features the effective light absorption and local heating conversion, but also provides platforms for investigations on intriguing microscopic mechanisms of photothermal processes. Pioneer works by Halas and co-workers [37, 38, 52] suggested the physical pictures of vapor generation and dynamics based on micro-spectroscopy. When gold NPs are excited at the LSP wavelength, the thin water layer around the NPs is heated locally due to resonant light absorption and ultrafast heat conversion, reaching or even exceeding the boiling point and transforming into nanobubbles (which gather to form a vapor shell). As the light illuminates continuously, the vapor shell gradually grows or coalesces and the buoyancy increases, with steam bubbles ascending toward the water surface and escaping. Note that, in this configuration, the microbubbles wrapped around metal NPs play crucial roles in light-induced local heating effect, which serve as thermal barriers and further reduce the thermal dissipation towards the bulk water. Another explanation is the Kapitza resistance induced by the vibrational energy mismatch between water molecules adsorbed on metal surfaces and those in bulk water [53], preventing vibrational energy transfer from the nanostructures into the surrounding water and thus increasing the solar vapor efficiency.

Here we present a brief review of recent progresses in plasmon-enhanced solar evaporation [26, 49, 54–64].
Diverse materials and structural designs for tuning the efficiency and bandwidth of light absorption and field enhancement are firstly discussed. Subsequently, a few typical strategies of plasmon-enhanced SVG are demonstrated. We finally discuss the current challenges and prospects in the future, aiming at inspiring further investigations at both the fundamental and applications levels.

2 Tailoring of plasmonic properties for light absorption

Ideal photothermal utilization of SVG requires both broadband light absorption over the solar spectrum in the far field and light-induced heat localization in the near field. The development of plasmonics and metamaterials has revealed that the resonant frequency and intensity of plasmon excitations are strongly dependent on the intrinsic material properties [10, 65], including sizes [37, 66], shapes [48, 67], surrounding environment [10, 20, 68], and assembly profiles [20, 69]. Figure 2 summarizes some primary factors that can contribute to the tunability of absorption spectra [37, 69, 70] as well as the enhancement of localized electromagnetic fields [51, 65, 68].

Figure 2A–C shows representative structure-induced manipulation of the LSP resonant wavelength, which plays a crucial role in broadening the absorption bandwidth. Sizes of plasmonic NPs can lead to a resonant peak shift or a broadening of the absorption spectra [71, 72]. As shown in Figure 2A, Halas et al. reported that Au NPs with different diameters have different LSPR peak shifts [37]. On account of the damping and dephasing effects of surface oscillation, the broadening and absorptive dissipation of the surface plasmon are largely determined by the imaginary part of the dielectric constant [20, 73–75].

Light absorption in plasmonic NPs is also sensitive to the presence of adjacent NPs due to the plasmonic hybridization effect [69, 76–80]. When two metal NPs are adjacent to each other, their plasmon resonance modes will be coupled through near-field interactions, which can further lead to spectral splitting and plasmonic Fano resonance [76–80]. Hentschel et al. explored the extinction spectra of an isolated gold particle, gold monomer, gold hexamer, and gold heptamers with different interparticle gaps, as shown in Figure 2B [69]. Dipolar plasmon resonances were observed in the gold monomer and hexamer. In different heptamers, the transition from isolated to coupled modes is obvious when decreasing the interparticle gap. Specifically, when the interparticle gap distance is below 60 nm, a pronounced Fano resonance is formed with distinct resonance dips because of the destructive interference between the narrow subradiant mode and the broad superradiant mode.

Apart from plasmon hybridization, particle shape is another crucial aspect to tune the bandwidth of absorption [67, 70]. For example, Benjamin et al. calculated the absorption spectra of silver NPs (with the same size but various shapes) according to Mie theory (Figure 2C) [67]. It was clearly demonstrated that NPs with higher symmetry, such as spheres, cubes and triangular plates, have stronger absorption peaks. The plasmonic resonant wavelength varies from 400 to 800 nm, associated with the accumulation of surface charges at sharp corners also known as hot spots. On the contrary, the octahedron and the tetrahedron particles with lower symmetry have much broader but weaker absorption peaks with multiple resonances. Therefore, reducing the shape symmetry of plasmonic NPs is an effective method of broadening the spectra band.

In addition to efficient and tunable light absorption, the local electromagnetic field enhancement around metal/dielectric interface is another key factor influencing the photothermal effect [10, 43, 51], which is dependent on materials, geometries, and dielectric environment of the plasmonic structures (Figure 2D–F). To evaluate the enhancement of near-field effect that contributes to plasmonic photothermal processes, a dimensionless enhancement factor $E_F$ is widely employed for simplicity [65], which is defined as the square of the ratio of the maximal electric field amplitude in the vicinity of NPs ($E_{\text{max}}$) and the incident electric field ($E_0$) ($E_F = \left| E_{\text{max}} / E_0 \right|^2$). $E_F$ is highly dependent on types of plasmonic materials and particle geometry as well as dielectric response of environmental materials, etc.

The development of plasmonic field has evidenced several factors that play crucial roles in the tuning of $E_F$ [10, 20]. Guillaume Baffou et al. illustrated that, for a fixed dipolar sphere structure configuration, different metals show quite different near-field enhancement (Figure 2D) [65]. Noble plasmonic metals, such as gold, possess more pronounced near-field enhancement than Cu and Ta. Interestingly, some non-metal-based plasmonic materials were predicted with higher enhancement factor up to 28, mainly due to an even higher $|\varepsilon'/\varepsilon''|$ (the ratio of the real part and the imaginary part of the permittivity of the material).

Apart from the material choice of metals, different geometries of metal NPs can result in different field enhancements. Taking Au NPs for example, Figure 2E shows the calculated field enhancement difference induced by spheres (100 nm in diameter) and triangle
plates (100 nm in side length and 20 nm in height) excited by monochromatic light (785 nm). One may find that NPs with sharper corners (like triangles) can generate higher local field enhancement than isotropic smooth particles, similar to those observed in heterogeneous systems [10, 20, 43, 51]. In addition, larger field enhancement can be suggested by close packed particles assembled with decreasing intergaps (Figure 2E [b and c]).
Dielectric environment is a third parameter for manipulating both plasmonic resonant wavelength and field enhancement [10, 20, 68]. Zhao et al. calculated the field enhancement of bimetallic nanocore/shells (the inner gold core with a radius of 5 nm and the silver shell with a thickness of 15 nm) as a function of dielectric coating thickness as well as dielectric constant of surrounding [68]. As illustrated in Figure 2F, for an arbitrary NP with fixed geometry parameters, the field enhancement factor increases with the dielectric constant of the surrounding media $\epsilon$. When excited by incident electromagnetic field, free electrons on the surface of metal NPs induce polarization charges in the surrounding materials, which is highly adjustable by changing the dielectric constant of the surroundings. Therefore, increasing the amount of the induced polarization charges with an increased dielectric constant can enhance the dielectric screening of the Coulombic restoring force, beneficial for the electric field enhancement. On the other hand, the electric field decreases as the thickness increases for a fixed dielectric surrounding media. The nonmonotonic field enhancement as a function of thickness (especially for larger dielectric constant) can be ascribed to the synergetic contributions of dielectric constant and thickness.

Note that both the absorption bandwidth and localized electromagnetic field enhancement in Figure 2 can be flexibly tailored by materials and structure designs. Therefore, plasmonic nanostructures with fine chosen materials and well-defined structures can be ideal candidates for high-efficiency SVG by simultaneously tuning the absorption spectrum and field enhancement.

### 3 Plasmon-enhanced solar evaporation

The plasmonic materials-enabled solar evaporation process can be divided into three subprocesses: solar energy harvesting by plasmonic resonant absorption, light-to-heat conversion via electron relaxation, and heat transfer to water as latent heat via phonon scattering. In order to realize highly efficient solar evaporation, light absorption and light-to-heat conversion are two major processes most deeply investigated thus far, and the overall vapor generation efficiency can be expressed as the product of light absorption efficiency and light-to-heat conversion efficiency [81]:

$$\eta = \frac{AP_{\text{abs}}}{AP_{\text{solar}}} \frac{m h_{\text{LV}}}{AP_{\text{abs}}}$$  \ (1)

The first term on the right refers to the light absorption capability, where $AP_{\text{solar}}$ and $AP_{\text{abs}}$ refer to incident and absorbed solar power, respectively. The second term stands for light-to-heat conversion, $m$ and $h_{\text{LV}}$ being the mass of evaporated water and enthalpy change, respectively. Plasmonic materials interact strongly with the incident light at the resonant frequency, which greatly enhances the incident light absorption [26, 42]. However, the sunlight possesses not only low power density (1000 W/m$^2$ for ideal AM [air mass coefficient] 1.5 G solar illumination), but also a broad distribution in 280–4000 nm (~99% of which is in the range of 400–2500 nm) [82]. Therefore, it is necessary to artificially manipulate the absorption bandwidth so as to match the solar irradiance spectrum regime. In this part, we will discuss some recent representative efforts to enhance the light absorption and light-to-heat conversion efficiency with respect to the broadband characteristics of solar irradiance.

#### 3.1 Plasmon-enhanced absorption for solar evaporation

In order to improve the solar evaporation efficiency, the input solar energy should be effectively harvested by plasmonic nanostructures. Therefore, broadband plasmonic solar absorbers are highly desired. As overviewed above, surface plasmon resonances are strongly affected by material [10, 65], size [37, 66], shape [68, 67], surrounding environment [10, 20, 68] and assembling profiles [20, 69], resulting in efficient absorption in particular wavelength range. Noble metals such as Au and Ag have been extensively investigated in the field of solar energy conversion, due to their strong visible and infrared (IR) plasmonic responses [17, 83, 84], which are well matched with the solar spectrum. In the past few years, many other metals have attracted much attention in this field as well, such as Al, Cu, Mo, Co, Ni, Pt, Pb, Ti, W, and Te [50, 65, 85–87]. There have been significant efforts to achieve a broadband and efficient absorption through plasmonic hybridization between different building blocks [17, 42, 47, 52, 61].

In 2013, the Halas group reported the first plasmon-assisted solar evaporation, which has inspired the exciting development in the following 5 years [52]. As shown in Figure 3A, they dispersed SiO$_2$/Au NPs in water to enhance the evaporation process. These NPs possess a SiO$_2$ core of 120 nm in diameter and a gold nanoshell of 40 nm in thickness. The plasmons associated with the inner and outer surfaces of the shell mix and hybridize. They found that hybridization interaction is stronger for thinner shell layers, leading to a strongly red-shifted resonance.
for the “bright” plasmon at a wavelength determined by the thickness of the shell and the overall particle radius [27]. Because of plasmon hybridization, the plasmon resonance-induced absorption cross section is tuned to overlap with the solar spectrum (Figure 3B).

The past few years evidenced explosive developments of plasmonic solar evaporators with various broadband light harvesting structures. Marcin S. Zielinski et al. demonstrated a special technique to fabricate Ag/Au bimetallic hollow mesoporous plasmonic nanoshells as an efficient material for solar evaporation to produce vapor at high rates [89]. It was shown that for the 5 nm hollow Ag/Au alloy shells, the reported absorption peak was ~1280 nm. Although it is far from the irradiant peak of the solar spectrum (~500 nm for 5800 K blackbody irradiance), the utilized broadband region of the solar spectrum in the near-IR (NIR) regime was still enough to enhance the water vaporization efficiency, provided that the plasmonic nanostructures are carefully designed. The vapor generation kinetics is significantly improved due to the NP architecture, surface stabilization with a short PEG ligand, improved buoyancy, and material composition.

Apart from the core/shell structure, there are a couple of more idealized structures for polarization-independent broadband light absorption [59, 60, 85, 88]. Kyuyoung Bae et al. developed one large-area flexible thin-film black...
gold membrane consisting of self-aggregated metallic nanowire bundle arrays, which incorporated adiabatic nanofocusing to reach an average absorption of 91% at 400–2500 nm [88]. This membrane was fabricated by self-aggregation of collapsed nanowires after appropriate pore widening of the anodic aluminum oxide (AAO), then sputtered with gold film of 40 nm thickness. The unit of the nanowires structure was shaped like the star of David with a triangular cross section of each nanowire. Then these hexagonal units merge and align to a funnel-shaped bundle as shown in Figure 3C. Both the small taper angles and gradually changed nanogaps between the aggregated nanowires are proven as contributions to broadband absorption in the visible and NIR regions. Figure 3D shows their experimental measurement of total reflection, transmission, and absorption spectra for the black gold membrane on an aluminum tape.

Incorporation of other 3D porous matrices with plasmonic NPs also performs an appreciably enhanced solar absorption. Natural wood has attracted much attention of researchers owing to its naturally mesoporous and hierarchical structure [90–92]. Uniform deposition of plasmonic metal NPs (Pb, Au, and Ag) into the natural wood pores led to the preparation of plasmonic wood by the Hu group [59], which turned black as illustrated in Figure 3E. Ultimately, due to the plasmonic effect of the metal NPs and the waveguide effect of the wood microchannels, the plasmonic wood was reported to have a highly enhanced light absorption ability (~99%) over 200–2500 nm wavelength range (plotted in Figure 3F). In addition, because of the multiple scattering and the absorption of the special microstructures in the wood, the efficient absorption was angle-independent. As a result, the naturally hydrophilic plasmonic wood with numerous microchannels for water transport performed impressive high-efficiency solar evaporation.

Among various articles about plasmonic evaporators (utilizing plasmonic materials) reported thus far, the Zhu group reported a series of three-dimensional plasmonic NPs for solar evaporation in 2016, as illustrated in Figure 4B–D [98, 99]. By combining the plasmonic hybridization effect, porous substrate effect, the intrinsic self-limiting oxidation effect, and intrinsic aluminum absorption in the NIR region (~800 nm), the Al/AAO absorber enabled an efficient solar absorption up to 96.5% (Figure 4E), beneficial for highly efficient solar evaporation when combined with other advantages mentioned above.

Apart from the complex hybridization of different plasmonic resonant modes to increase the light absorption mentioned above, a novel broadband absorber made of self-assembled tellurium (Te) NPs with a wide size distribution was designed by the Yang group, combining both plasmonic-like and all-dielectric Mie-type resonances [87]. Perfect absorption (more than 85%) was achieved in the entire spectrum of solar radiation (300–2000 nm), derived from the unique optical duality of Te NPs. They discovered that the real part of permittivity of Te transforms from negative to positive at the UV-vis-NIR region, which endows Te NPs with optical duality. The Te NP gradually converts from a plasmonic-like material to a high-index all-dielectric material, as the size increases from 10 to 300 nm. Both the plasmonic-like and Mie-type resonances strongly extend and enhance optical absorption. It was the first reported material that can exhibit optical duality in the solar radiation region. Therefore, their findings demonstrated that the non-noble metal Te NPs could be a promising photonic material for solar energy absorption, and provided insight into perfect absorption assisted by various optical modes.
Figure 4: (A) Schematic of hybridized plasmonic structure to enhance solar absorption [60]; dependence of calculated normalized extinction cross-section of Al nanoparticles on (B) the particle number N, (C) on the thickness of the alumina oxidation layer t, and (D) on the substrate; and (E) experimental and simulated absorption of aluminum-based plasmonic absorbers. The normalized spectral solar irradiance density of air mass 1.5 global (AM 1.5 G) tilt solar spectrum is shown by the blue dashed line [85]. (A) Adapted by permission from Ref. [60]. Copyright 2016 American Association for the Advancement of Science. (B)–(E) Reprinted with permission from Ref. [85]. Copyright 2016 Nature Publishing Group.
3.2 Heat localization for solar evaporation

For the entire solar evaporation process, light absorption is merely the first step; light-to-heat conversion is the second most important issue. Heat localization is widely regarded as one of the most crucial components of high efficiency SVGs, which can be enabled by both material/structure design and system design for plasmon-based solar evaporators.

From the material/structure level, heat localization can be enabled by plasmonic near-field enhancement, called optical induced thermal concentration. Once the energy of the incident light converts to the oscillation energy of free electrons, there will be different passageways: electron-to-photon, electron-to-electron, and electron-to-phonon, respectively, as illustrated in Figure 5A. In the first 1–100 fs following Landau
damping, the thermal distribution of electron-hole pairs decays either through re-emission of photons or through carrier multiplication caused by electron-electron interactions. The hot carriers will redistribute their energy by electron-electron scattering processes on a time scale ranging from 100 fs to 1 ps. Finally, heat is transferred to the surroundings of the metallic structure on a longer time scale ranging from 100 ps to 10 ns, via thermal conduction [24]. As the enhanced electromagnetic field is localized, the generated heat is localized as well, which is beneficial for the evaporation of the liquid around the plasmonic materials.

To quantify the role of light-induced heat concentration of plasmonic materials to efficient photothermal conversion (solar evaporation), the dimensionless parameter Joule number $J_0 \left( J_0 = \frac{e\varepsilon}{\varepsilon_m} \left| E_m \right| E_0 \right)^2 \right)$ was introduced by Guillaume Baffou et al. [65]. This parameter contained the imaginary part of the permittivity of the material $(\varepsilon'' \varepsilon''')$, and a large value of $\varepsilon''$ is beneficial for the photothermal conversion. As they considered the relation $qV = \sigma_{abs} I (q$ being the heat source density within the material, and $I$ the light irradiance) the Joule parameter definition also had another equivalent expression: $J_0 = \frac{\lambda_{rel} \sigma_{abs}}{2nV}$, in which $\lambda_{rel}$ is about 1240 nm, $\sigma_{abs}$ is the absorption cross section of the NPs, and $V$ is the volume of the NP. They calculated the $J_0$ of some typical metals as plotted in Figure 5B–D. For a given material, $J_0$ is only related to the nature of the material, and therefore it offers a convenient reference tool for selecting the appropriate photothermal plasmonic materials. Among the most common plasmonic materials, gold is surprisingly not the largest; silver shows a much better potential for heat generation. In practice, however, silver NPs are highly prone to oxidation and aggregation under exposure to solar light. Another issue would be their application in the desalination process, where the presence of chloride anions would react with silver. Aluminum is also an ideal candidate for plasmonic photothermal applications due to its strong plasmon resonance in the UV range. However, the calculation might not be in accordance with experimental results because of the instability of metal surface similar for silver, as mentioned above [100–102]. What’s more, the ability of heat generation also strongly connects with the incident light and the geometry factors as illustrated in Figure 5E and F [25]. In order to achieve a visible heating effect, NPs of relatively large radius (>10 nm) should be used [23, 25].

In the past years, two types of material/structure-induced heat localization have emerged. The first one is plasmonic nanofluid under certain conditions (Figure 6A and B). For the typical bulk heating system where the NPs are dispersed in liquid, heat localization can be achieved by fine-tuning the particle concentration. As demonstrated Ref. [103], there are three distinct regimes for plasmonic nanofluid-based solar evaporation. At low concentration or small volumes (Regime I), NPs serve as absorbers instead of scatterers, and Beer-Lambert law works in this regime. Therefore, all scattered photons are lost from the beam, and light transmits through the solution. Because of the linear relationship between particle concentration and absorption efficiency, the linear dependence on particle concentration in the log scale profile is presented. For higher concentrations (or multiple scattering regime, Regime II) where scattering length is comparable to characteristic dimensions of the nanofluid, NPs serve as both scatterers and absorbers. In this case, multiple scattering plays a crucial role and increases the average path length of the photons, which increases the absorption coefficient and concentrates light into a smaller penetration depth. Furthermore, at extremely high NP concentration (Regime III), photon absorption is saturated, and part of the incident photon will be back scattered off the fluid surface (Figure 6B). Note that plasmonic nanofluid in both Regimes I and III will encounter tremendous heat loss due to large optical and thermal dissipation. Regime II can be regarded as an interfacial-like solar evaporation by heating an infinite volume of bulk water, which has inspired the second type of plasmonic structure-induced local heating systems.

Unlike the plasmonic nanofluid system, the second type is featured by integrated structures hosted by thin porous substrates [55, 60, 85]. Such solar evaporators are self-floating on air/water interfaces due to their hydrophobic surface and/or low density [39, 40, 54, 105]. Suppressed thermal dissipation is commonly suggested due to the reduced effective thermal conductivity. Figure 6C and D illustrates one of the representative integrated plasmonic evaporators with material/structure-induced heat localization [85]. By assembling the close-packed metal NPs in a highly porous substrate, the evaporator can integrate in one structure the interfacial effects of self-floating substrates, as well as the NP-induced near-field enhancement effects as in nanofluids (Figure 6C). This leads to a suppressed heat dissipation to bulk water and thus a distinct temperature difference between vapor and underneath water (Figure 6D). Note that the thermal conductance loss for the material/structure designed system is still distinct due to direct contact between plasmonic materials and bulk water, especially for low solar irradiance. Researchers have been attempting to further decrease thermal conductance loss by introducing thicker thermal insulating layers into the plasmonic absorbers.
such as porous membrane [61, 106], air-laid paper [54, 56], wood [59], and biofoam [57].

One of the representatives is the double-layer solar evaporators constructed with gold film/air-laid paper reported by the Deng group (Figure 6E), which can be regarded as a local heating design from the system level. Note that the average absorption efficiency of the gold film (with uniform gold particles of diameter $\sim 7.4 \pm 0.3$ nm) is $\sim 84\%$ in 400–800 nm and the solar thermal efficiency reaches 77.8% under 4.5 Sun illumination [104]. It indicates

Figure 6: Heat localization. (A) $\text{SiO}_2$/Au nanoparticles immersed in water and (B) three regimes of light propagation through the NPs colloid, depending on the NPs concentration [103]; (C) schematics of the self-floated solar evaporator based on the assembly Al nanoparticles on porous AAO membrane and (D) temperature changes of the steam and water over time (24°C ambient temperature and 48% humidity) [85]; (E) schematic illustration of the structure of air-laid paper-based gold nanoparticles (Au NPs) film evaporation system and (F) the simulated temperature distribution comparison of air-laid paper-based Au NPs film evaporation system with maximum temperature of 83°C and free-floating Au NP film with maximum temperature of 57°C [104]. (A) and (B) Reprinted with permission from Ref. [103]. Copyright 2014 American Chemical Society. (C) and (D) Reprinted with permission from Ref. [85]. Copyright 2016 Nature Publishing Group. (E) and (F) Reprinted with permission from Ref. [104].
that, apart from the explanations from the optical viewpoint as suggested in [104], the unique textile-like porous hydrophilic paper enhances light absorption and reduces thermal conductance with the bulk water at the same time, which may play a crucial role for the highly efficient evaporation.

4 Applications

As illustrated above, plasmonic nanostructures with rational designs can achieve efficient and broadband absorption and heat localization and therefore enable efficient solar evaporation (with over 80% energy conversion efficiency commonly achieved). The evaporation with solar energy as the only energy input and high energy conversion efficiency has formed the foundation to the exploitation of various applications. For example, Zhou et al. demonstrated the first plasmon-enhanced solar desalination device [60]. Their structure contains a nanoporous AAO membrane into which aluminum NPs are randomly dispersed. The as-prepared structure enabled a steam generation efficiency of 88.4% under 4 Sun illumination, and the produced clean water has salinity ~4 orders of magnitude lower than that of water sources. Ever since, there have been significant efforts to explore other choices of materials and designs of structures, to produce drinkable water with higher efficiency and lower cost.

Besides solar desalination, other practical functionalities can be integrated into the plasmonic structures. As an example, Chen et al. demonstrated an asymmetric plasmonic structure with dual functions, solar water purification, and pollution detection as illustrated in Figure 7A [107]. After the self-assembly of close-packed silver NPs into porous templates, the plasmonic structures showed different colors for the two sides. The dark porous side of the structure enabled efficient solar steam...
generation (with energy transfer efficiency ~80%), while the shiny metallic side could enable sensitive chemicals detection using the surface enhanced Raman scattering effect, realizing a detection limit down to $10^{-12}$ m. The dual functional structure could purify water and enable on-site pollution detection at the same time.

Another notable example is plasmonic structures designed by Gao Minmin et al. [19], which could enable water evaporation and fuel generation by water splitting. The structure took the form of a SiO$_2$ core embedded with Ag NPs and TiO$_2$ shells as depicted in Figure 7C. The TiO$_2$ shell coated by sol-gel method took in higher-energy photons for electron-hole pair generation, and the SiO$_2$/Ag core absorbs the lower energy photons for heat generation. Therefore, the integrated NPs offer both distillation production and clean fuel generation.

Solar steam of high temperature can enable various important applications beyond conventional low-temperature solar evaporation, such as sterilization, as plasmonic NPs can enable a fast responsive, high-temperature steam generation process. The pioneer work was conducted by the Halas group, where gold nanoshells were dispersed into water as shown in Figure 7D [58]. An equilibrium temperature of 140$^\circ$C could be readily accomplished, a fatal environment for multiple bacteria sources. A closed-loop autoclave and an open-loop disposal system were subsequently designed to sterilize medical equipment and treat domestic solid waste, both of which survived the test of *Geobacillus stearothermophilus* (Nos. 021314380140, 021314380150).

Note that, in most of the previously reported solar evaporation-based applications, heat (enthalpy) out of the solar steam is typically wasted to the environment. Recently, Li et al. reported a creative system which can store the generated latent heat enthalpy, even during night hours, providing an insightful initiative in the recycling of energy as demonstrated in Figure 7B [108]. Enthalpy recycling can be a promising direction for the optimization of vapor generation systems, to bridge the gap between solar steam generation and other heat-driven systems and energy-consuming fields.

**5 Summary and outlook**

In this review, we summarize various strategies for rational designs of plasmonic nanostructures for efficient solar evaporation, through enhanced light absorption and localized heating, and list out related potential applications. Despite tremendous progress, there are still issues and challenges that need to be addressed from both perspectives of fundamental understanding and practical applications. For example, it is still a challenge to precisely calibrate the temperature and thermal dynamics at nanoscale for the complicated photothermal processes. Moreover, the large-scale practical applications of desalination or water treatment call for not only more cost-effective materials and scalable processes, but also materials/structures with long-term chemical and physical stability. In addition, for high-temperature solar vapor applications, such as sterilization and electricity generation, it is urgent to develop spectrum-selective plasmonic absorbers with well-defined absorption spectra in both solar spectrum and mid-IR regime, in order to minimize heat losses of thermal radiation [109–111]. Actually, there is still a long way towards ideal plasmonic solar evaporators that possess simultaneous spectrum manipulation with optimized thermal and/or water transport system designs. Although further understandings and advancements are needed, the intrinsic advantages of plasmonic nanostructures with strong light-matter interactions and localized field make them promising candidates for solar evaporation and various other solar thermal applications.

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