

SHANGHAI JIAO TONG UNIVERSITY

学士学位论文

BACHELOR'S THESIS



论文题目: <u>Study on the Application of</u> <u>Photo-Thermal Effect of Plasmonic</u> <u>Nanoparticle</u>

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等离激元纳米颗粒光热效应应用研究

摘要

当受到一定强度和波长的光照射时,等离激元纳米颗粒可产生表面等离激元,并高效 地将光能转化为热量。这一光热转化效应在诸如等离激元光热治疗,等离激元纳米焊接和 光热成像等领域有广泛的应用前景。尽管这一领域的科研投入不断增加,要直接利用等离 激元纳米颗粒产热还面临一些挑战。以通过蒸发利用热能的方法为例,之前提出的将纳米 颗粒分散在液体中的方法热损耗大,难以循环利用。在本论文中,使用无尘纸作基底承载 自组装的金纳米颗粒膜,制成纸基金纳米颗粒膜(PGF)。PGF表面对光进行宽谱吸收,热 传导与扩散小,其基底多孔亲水,因而能在 4kW/m² 的光强下,在气-液界面发生区域集中 加热,达到约 80°C的高温,并将光热转化效率提升到 87.1%。PGF 进行海水淡化实验的每 小时输出能力达到约 20L/m²,是现有工业模型的两倍左右。同时,因有报道称叶表面润湿 性可影响其上水蒸发速度,本课题以优化类似于 PGF 的现有双层膜蒸发系统为目的,研究 了亲疏水性对蒸发速度的调节作用。该部分实验制备出并选择性修饰了阳极氧化铝为基底 的金纳米颗粒膜(AANF)。相应实验结果揭示了基底润湿性对蒸发过程的决定性作用,并 为今后相似系统的设计提供了指导。在 AANF 实验中观察到的剧烈的气泡产生现象, 促成 了开发等离激元马达的想法。该部分实验制备了 PGF 筏和 PGF 船,可在激光推动下在液体 表面游动。在约 350mW/mm² 的激光功率下, PGF 船达到最高的运动速度约为 40mm/s。而 换用不同液体基底的进一步探究,则发现并证明了推动 PGF 筏的独特作用力: 与先前的光 热效应引发表面张力梯度机理不同,本 PGF 筏的推动力是气泡爆裂。此外,PGF 筏的运动 方向已被证明可控。

关键词: 光热转化,海水淡化,区域集热,等离激元纳米颗粒,等离激元马达,气泡爆 裂



ABSTRACT

When illuminated by light at certain wavelength and intensity, plasmonic nanoparticles can generate surface plasmon, and convert energy from light into heat efficiently. This photo-thermal effect has tremendous potentials in multitudinous domains like plasmonic photo-thermal therapy, plasmonic nanowelding, and photothermal imaging. Despite the ever-increasing research investigation, the intriguing idea of directly utilizing of heat converted by plasmonic nanoparticles still faces challenges. Take the common evaporation approach for example, previous system of dispersed nanoparticles in solution suffered from great heat loss and difficult for recycling. In this thesis, air-laid paper was used to support self-assembled gold nanoparticle film and form the bilayer paper-based gold nanoparticle film (PGF). Thanks to the broad-band light absorbing surface, reduced heat conduction and diffusion as well as hydrophilic porous substrate, PGF can generate localized heating at air-water interface with maximum temperature as high as ~ 80°C (light intensity was $4kW/m^2$), thus raising the light-heat efficiency to 87.1%. PGF is promising in desalination, with hourly output capability at ~ 20 L/m^2 , which is about two times that of present industrial model. Meanwhile, inspired by the report that wettability of leaves influenced water evaporation on them, investigation on controlling the evaporation speed by tuning hydrophilicity is set with a temptation to optimize the bilayer evaporation system like PGF. In this part, Anodic Aluminum Oxide-based AuNP films (AANFs) are fabricated and selectively modified. The result reveals the dominant role of the substrate's



wettability in evaporation and provides a guideline for future design of such system. Dramatic bubbling phenomena observed in experiments on AANFs led to the idea of developing plasmonic motor. In this part, PGF raft and boat are developed for laser-driven swimming on surface of liquids. The fasted moving velocity is achieved by PGF boat at about 40 mm/s, (under laser power of ~350 mW/mm²). Investigation with various liquid matrix also demonstrated the vapor bubble-burst propelling mechanism of the PGF raft, which is novel and different from previous photo-thermal effect induced surface tension gradient mechanism. In addition, the moving direction of PGF raft is proved to be controllable.

Key words: photo-thermal conversion, desalination, localized heating, plasmonic nanoparticle, plasmonic motor, bubble-burst



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Chapter One Introduction

1.1 Research Background on Surface Plasmon

1.1.1 Brief history on plasmonic materials

Plasmonic materials are matters that could generate the unique light responsive surface plasmon. Surface plasmons, though still quite a hot scientific topic, with related research and development being carried out worldwide currently, isn't that new to we mankind. Actually, as shown in **Figure 1.1**, the application of plasmonic effect can be date back to the Byzantine Empire as early as 4 century A.D., when colorful glasses were made as the stunning ornaments in windows of churches and cathedrals ([1], Pieter G. Kik and Mark L. Brongersma, 2007: 2). Another familiar common demonstration of the existence is the shining appearance of gold or silver artifacts' surface.



Figure 1.1 Plasmon resonances on the surface of metal nanoparticles embedded in



stained glass can produce remarkable color variations. (Credit: iStockphoto/Thinkstock. Read more at: <u>http://phys.org/news/2013-03-plasmonics-numerical-simulation-behavior-compo</u> <u>nent.html#jCp</u>)

However, it was surface plasmons' amazing physics other than aesthetic application that truly attracted scientists and engineers for over a century. As far as we know, the first scientific observation in this domain is done by Prof. Robert W. Wood in 1902; in his article named 'On a Remarkable Case of Uneven Distribution of Light in a Diffraction Grating Spectrum', he found that 'the singular anomalies were exhibited only when the direction of vibration (electric vector) was at right angles to the ruling', and assumed that 'polarization' could explain this singular behavior ([2], R. W. Wood, 1902: 270-271). Another important study was done by Maxwell Garnett in 1904, in his paper, by employing the Drude theory of metals and Lord Rayleigh's electromagnetic properties of small spheres, he discussed the optical properties of a medium containing minute metal spheres for both metal glasses and metallic films ([3], C. Maxwell Garnett, 1904: 385). And in 1908, Gustav Mie proposed the light scattering by spherical particles, which scientist also used in analyzing surface plasmons of nanoparticles (especially those with diameter around tens nanometers) today ([4], von Gustav Mie, 1908: 377). Nonetheless, it was half decade later, that the terminology 'plasmons' was first used on such physical phenomena. In 1956, David Pines attributed the energy loss of fast electrons passing through metals to collective oscillations of those electrons, and such oscillations was named with 'plasmons' in analogy with plasma oscillations in gas discharges ([5], David Pines, 1956: 184). And in the following year, Rufus Ritchie first described 'surface plasmons' theoretically, as he demonstrated the existence of the plasmon modes near the surface of metals ([6], R. H. Ritchie, 1957: 874). Along with coworkers, he then suggested surface plasmon resonances excited on the surface to explain the unique optical behavior of metal



gratings in 1958 ([7], R. H. Ritchie et al., 1958: 1530), which was originally observed by Wood.

Experiments were made available to broader range of scientists after the 1968 breakthrough by Andreas Otto, Erich Kretschmann and Heinz Raether, who together provided methods to excite surface plasmons on metal films with the help of prism ([8], A. Otto, 1968: 398).

It has been more than sixty years after Garnett's study on colorful metal doped glass, for scientists to figure out the properties of surface plasmons; while the following exploration on metal nanoparticles' optical properties was not been made until research by Uwe Kreibig and Peter Zacharias in the year 1970 ([9], U. Kreibig et al., 1970: 128). In their research, the term 'surface plasmons' was used to describe the optical response of gold and silver nanoparticles for the first time. In 1974, after the significance of coupling between the oscillating electrons and electromagnetic field was gradually accepted, Stephen Cunningham and coworkers introduced the 'surface plasmon-polarition (SPP)' ([10], S. L. Cunningham et al., 1974: 3342). In addition to these important findings, another breakthrough was made also in 1974, when Martin Fleischmann and his colleagues reported strong Raman scattering from pyridine molecules near roughened silver surfaces ([11], M. Fleischmann et al., 1974: 163). Now we understand that this is due to the presence of surface plasmons, and the Raman scattering is deemed as energy exchange process between photons and molecular vibrations, which is strengthened by the electromagnetic fields in the vicinity of the rough silver surface. Although such theories were not even hypothesized at that time, this study had opened up the field of Surface Enhanced Raman Scattering (SERS). Based on the aforementioned research on fundamentals of surface plasomons, studies focusing more on the daily life-related applications had surged in recent decades. According to Prof. Brongersma, the one who coined the notion of 'plasmonics',



plasmonics is the science and technology of metal-based optics and nanophotonics ([12], Rashid Zia et al., 2006: 20). This field was developed in face of technological challenges determined by the physical limits of technologies including optical lithography, optical data storage, and high density electronics manufacturing.

The following **Figure 1.2** and **Figure 1.3** reflects the growth of this field in terms of annual number of publications including the phrase 'surface plasmon' in the title, abstract or key words from 1955 to 2005 and from 2006 to 2015 respectively. (Note: the first image was reproduced from citation [1], while the later was drawn based on data provided on www.scopus.com) Since 1990, the publication on surface plasmons has doubled each five years. This surge was raised by novel properties being reported and studied, as well as the generation of multitudinous potential for applications, ranging from photonics to analytics, from catalytic to energy ([13], L. M. Liz-Marzan, 2014: 3820). The impetus was not kept after the year 2013. This stagnation may also be explained by considering the change of preference of terminology, that is, other terms like 'plasmonics' or 'nanoplasmonics' may well be used in some related publications without the words 'surface plasmon'. All in all, this statistic data also indicates the well-established status of research area of surface plasmon.





Figure 1.2 The growth of the field of metal nanophotonics is illustrated by the number of scientific articles published annually containing the phrase "surface plasmon" in either the title or abstract (based on data provided on www.sciencedirect.com). Credit: [1], Mark L. Brongersma, 2007: 2)



Figure 1.3 The annual number of scientific publications containing the phrase "surface plasmon" in either the title, abstract or keywords. (based on data provided on www.scopus.com)

1.1.2 Basic concept and coverage of nanoplasmonics

According to Liz-Marzan, the nanoplasmonics was defined as 'the coherent oscillation of conduction electrons in metals (and other free-electron materials) in response to incoming light' ([13], L. M. Liz-Marzan et al., 2014: 3820). The physical field enhancement and coupling of plasmonic structures render them rich spectral responses as well as opportunities to function as chemical and biological sensors ([14], J. N. Anker et al., 2008: 442), as a result, they also works in domains like plasmon-assisted



laser welding ([15], Erik C. Garnett et al., 2012: 242), nonlinear plasmonic waveguide manipulating light ([16], Shuofeng Lan et al., 2015: 807), and plasmon-enhanced spectroscopies, i.e. the Tip Enhanced Raman Scattering ([17], R. Zhang, 2013: 82). When surface plasmons decay, they can generate energetic electrons as 'hot electrons', which is the basis of plasmon-based photodetectors ([18], Long Ju et al., 2011: 630), plasmon enhanced solar energy harvesting and conversion ([19], Ran Long et al., 2015: 2425), and coupling of plasmonics to chemical reactions ([20], Ran Long, Yu Li, Li Song, and Yujie Xiong, 2015: 3873) with high selectivity in an energy efficient way. And **Figure 1.4** shows the subfields of the domain nanoplasmonics.



Figure 1.4 Schematic representation of various subfields that are currently studied within the field of nanoplasmonics. From the inner to outer sides are (1) the fundamentals, including the materials, theoretical background, characterization, and fabrication, (2) the properties of hybrid plasmonic nanostructures, (3) the applications in optics and optoelectronics, and (4) the applications closely related to our daily life. (Credit: [13], L. M. Liz-Marzan et al., 2014: 3821)

The abundance in performance and applications of plasmonic materials mainly comes



from four properties, including: a) enhanced electromagnetic field, which result in strong interaction with light (scattering and absorption), b) efficient photo-thermal conversion, generating localized joule heat rapidly due in the decay of electron oscillation, c) sensitivity to environment change and the geometry of nanoparticle, which means modification on its composition and geometry could provide various sensors; d) generation of energetic electron, also called 'hot electron', contributing in both photodetector as well as solar energy harvesting by assisting photovoltaic process. As shown in **Figure 1.5**, some current typical applications in both research and daily-life are listed below, indicating the broad coverage of plasmonic materials, including areas like optoelectronic, photonics, chemistry, spectroscopy, biomedicine, energy, as well as materials.



Figure 1.5 Main properties of plasmonic materials and examples of corresponding applications (the inner circle properties are: enhanced electromagnetic filed, efficient photo-thermal conversion, energetic electron generation and sensitivity



to environment and geometry; the out circle of applications are plasmon-enhanced spectroscopies, light manipulation & concentration, plasmonic-based photodetector, plasmoni-assisted laser welding, photo-thermal therapy, phtocatalytic/photovoltaic, plasmonic coupled chemistry reactions, plasmon-assisted photoacoustic imaging, and chemical and biological sensors. Please be noted the relationship between the properties are not simply one to one)

Besides such richness in applications, new matters other than noble metals had been found to showing surface plasmon resonance behavior, including Aluminum ([21], M. W. Knight, 2014: 834), graphene ([22], Jianing Chen, 2012: 77) and metal/semiconductor hybrids ([23], Wenhua Li, 2013: 7098).

1.2 The photo-thermal effect of plasmonic materials

1.2.1 Physics of plasmonic heating

The photo-thermal conversion occurs when the plasmonic nanoparticles are illuminated by incident light at their plasmonic resonance (note: usually when semi-wavelength comparable to the particle's size, e.g., the diameter for spherical nanoparticles). As shown in **Figure 1.6**, electrons of the nanoparticle are excited to move coherently in a cloud, generating oscillation of electric field that resonate with the electric field of the incident light, and will generate joule heat. ([24], K. A. Willets and P. Van Duyne et al., 2007:269)





Figure 1.6 Schematic diagrams illustrating a localized surface plasmon on metal nanosphere (Credit: [24], K. A. Willets and Van Duyne et al., 2007: 269)

According to Guillaume Baffou and Romain Quidant, the generated heat of a given NP could be theoretically calculated with two methods ([25], G. Baffou et al., 2012: 172-173). For geometries with absorption cross-section known, the heat power Q could be estimated by equation 1-1:

$$Q = \sigma_{abs}I \tag{1-1}$$

Where σ_{abs} is the absorption cross section of the particle, and *I* is the irradiance of incident light (power per unit surface). In addition, the absorption cross section is mainly determined by the nanoparticle's morphology. As for more complex morphologies, for which no simple analytical expression is available, calculation should be done via equation 1-2 and 1-3:

$$Q = \int_{V} q(\mathbf{r}) \, d^3 r \tag{1-2}$$

$$q(\mathbf{r}) = \frac{\omega}{2} \operatorname{Im}(\varepsilon(\omega)) \varepsilon_0 |\mathbf{E}(\mathbf{r})|^2$$
(1-3)

Where in equation 1-2, V is the volume of the nanoparticle, q(r) the heat power density, and in equation 1-3, ω is the frequency of the light, and E(r) the inner electric field amplitude.

1.2.2 Applications of plasmonic heating



As a source of heat with the precision nanoscale, the plasmonic nanoparticles has long been a fundamental tool for researchers in various fields. With the advantages like chemistry stability, convenience in synthesis and modification as well as the tunable resonance peak from visible to near infrared (NIR), which is suitable for biomedical occasion as NIR could well penetrate tissues, gold nanoparticles are the major materials utilized in this area ([25], G. Baffou et al., 2012: 178).

To begin with, the application attracted most researchers and engineers is the plasmonic photo-thermal therapy. In this domain, plasmonic nano-agent is excited to generate local hyperthermia to selectively kill cells and cure disease. For example, Shunhao Wang and coworkers has utilized plasmonic copper sulfide ($Cu_{2-x}S$) nanocrystals in photo-thermal therapy, they gained deeper insight of not only the photo-thermal but also photodynamic properties, based on experiments on both cultured melanoma cells and a murine melanoma model. In addition to the heat mechanism, they reported high levels of reactive oxygen species generation when intrinsic NIR induced photodynamic activity occurred ([26], Shunhao Wang, 2015: 1788). Similar to the therapy application, nano-surgery using plasmonic heating in transfection of individual cells is also a promising technique ([25], G. Baffou et al., 2012: 180).

Besides, delivery of nano-agent like drugs is intensively studied for their potential in combining multiple functions in a single nanovehicle. In this area, plasmonic heating are also taken as a photo-thermal control of the release of load. In 2012, Croissant and colleagues developed nanovalves on mesoporous silica nanoparticles (MSNs), with a gold nanoparticle core that enabling remotely triggering of plasmonic heating and thus release the agent ([27], J. Croissant & J. I. Zink, 2012: 7628). With the help of laser irradiation, they demonstrated that instead of bulk temperature raise, the local internal heat generation is the key for release mechanism. In addition, diagnostic applications have also been exploited with plasmonic heating's potential in generating signals



within cells. Jing Lin has developed a gold vesicles (GVs), which is capable of encapsulating photosensitizer Ce6 within itself, and promising in NIR fluorescence/thermal/photoacoustic imaging ([28], Jing Lin et al., 2013: 5320).



Figure 1.7 Optical nanowelding set-up (a) and scanning electron microscope (SEM) images before (b) and after (c) illumination (Credit: [15], Erik C. Garnett et al., 2012: 242)

Furthermore, plasmonic heating has found its applications beyond biomedical diagnostic and therapeutic domain. As shown in **Figure 1.7**, Erik C. Garnett and co-workers has demonstrated a light-induced selective plasmonic nanowelding technique via light of tungsten–halogen lamp, to assemble silver nanowires into large interconnected networks. The power density they used was about 30W/cm², with illumination for 10s to 120s. Which is relatively convenient, compared to former techniques which need laser illumination to trigger plasmonic heating. They also reported this process's dependence on both the light power density and the spacing between the wires. This work had opened up possibilities for using plasmonic heating in simple and large-scale processing of devices and circuits, like solar cell, light-emitting diode (LED) and touch-screen display ([15], Erik C. Garnett et al., 2012: 242).

1.2.3 Research background of plasmonic heating for energy usage



Despite the attraction of the photo-thermal effect of plasmonic materials, photo-thermal effect specially for energy application is relatively less investigated. As shown in **Table 1.1**, from the year 2007 to 2015, in the field of plasmonic heating, publications in energy field only took part as little as about 1 to 5 percentage. These data revealed that attention to plasmonic heating as an energy source is too less, especially when considering its potentials.

Table 1.1 Numbers of Publication with phrase 'surface plasmon' and 'heating' or'thermal', and those belong to energy field (Data source: www.scopus.com)

Year	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015
Total Number	114	104	151	197	203	225	271	283	353	357	349
Energy' field Number	0	0	2	10	10	6	13	12	17	10	9
Percentage %	-	-	1.32	5.08	4.93	2.67	4.8	4.24	4.82	2.8	2.58

In the early stage of researching on nanoplasmon as heat source, theoretical and experiment investigations had been carried out. Halas group from Rice university ([29], Zheyu Fang et al., 2013: 1736) and Richardson group from Ohio University has investigated the evaporation process of vicinity water around plasmonic nanoparticles under the radiation of laser or solar light, their detailed research works ([30], Andrew J. Green et al., 2013, 4142) did have accumulated both experimental evidences ([31], Oara Neumann et al., 2012: 42) and theoretical insight of this physical phenomena.





Figure 1.8 Schematic of nanoparticle-enabled solar steam generation: initially, light is absorbed by nanoparticles, raising their surface temperature above the boiling point of the fluid. The nanoparticles surface serves as boiling nucleation site. Vapor is formed around the nanoparticle surface, and the complex moves to the liquid-air interface, where the steam is released. New liquid is replenished at the hot nanoparticle surface, and the process is repeated. (Credit: [31], Oara Neumann et al., 2012: 43)

Their research, however, were limited in the system. As shown in **Figure 1.8**, the dispersed nanoparticles in water is the system under investigation. Considering the final purpose of heat output, such system has little potential in industry promotion for the following reasons: 1) In microscale, distance traveled by the newly generated bubble to the water surface is too long, during which the bubbles will inevitably get into touch with the cool liquid and condensed back to liquid with its temperature dropping down; 2) In macroscale, the evenly dispersed nanoparticles in the liquid, instead of localized heating after light illumination, heat up the liquid in a whole, leading to great heat loss from radiation and convection (to air surrounding the container); 3) The transportability is poor, owning to the weak stability of nanoparticles in aqueous liquid,



they could not be applied in different aqueous systems.

Based on the aforementioned exploration in research, this study was aiming at developing method to utilize plasmonic heating as a heat source by direct evaporation. The major challenge is to raise the total energy efficiency, with focus on reducing heat loss in forms of heat conduction and hot fluid convection.

Chapter Two Materials and methods

2.1 Synthesis of gold nanoparticles

In this study, two kinds of bilayer films, namely the paper-based gold nanoparticle film (PGF) and aluminum anodic gold nanoparticle film (AANF) both utilized gold nanoparticles as light absorbing layer. While 10 nm gold nanoparticles were used in PGF, 50 nm and 100 nm ones were used in AANF, because of the relative large pore size (~20nm, as shown in **Figure 2.7** in part 2.3) of aluminum anodic oxide (AAO) substrate.

2.1.1 Synthesis of ~10 nm gold nanoparticles

To synthesis aqueous gold nanoparticles solution, we used citrate reducing method ([32], K. R. Brown et al., 2000: 306). This protocol will give as-synthesized gold



nanoparticles stability as the Dimethyl acetyl acetone will be produced by citrate. To begin with, powder of gold (III) chloride tetrahydrate (49~50% Au basis; Aladin) was dissolved by DI water (NANOpure, Millipore Water Purification System; 18.2 M Ω) first into 1 wt.% to reduce waste, as the extra amount of solution would be added in further seed-growth process to synthesis nanoparticles with larger diameter. Then the solution is further diluted in a 100 mL flask to a concentration at 1 mmol/L, which was bring to boil by heating in the oil bath. Immediately after it started boiling, 5 mL of as-prepared sodium citrate (38.8 mmol/L, dissolved from trisodium citrate dehydrate, 99% Aladin) was added altogether, with vigorous stirring (~1000 rpm) and continuous heating in oil bath. The solution now would first change from pale yellow to blueish dark gray, and then generally turned into deep purple and burgundy, the color changing process usually continued for about several minutes to ten minutes. When the burgundy color is stable, the flask was transferred to another heating & stirring plate, on which the stirring is continued while the heating is stop to let the solution cool down in air. This cooling down and aging process would last for at least 20 minutes to render a good monodispersity to the as-synthesized nanoparticles while the stirring would prevent the nanoparticles from aggregating together. As shown in **Figure 2.1**, the nanoparticles were spherical and uniform in size, with an average diameter of 17.4 nm and a standard error at 0.3 nm.



Figure 2.1 (a) SEM images of 10-nm AuNPs obtained (b) Size distribution of Au NPs (based on 100 counts; NP diameter = 17.4 ± 0.3 nm)



2.1.2 Synthesis of ~100 nm gold nanoparticles

While the 10 nm gold nanoparticles solution was ready to be utilized to synthesis PGF without further treatment, it was necessary to grow them to obtain 50 nm or 100 nm nanospheres for the fabrication of AANFs. In the following stepwise NH₂OH-seeding method, the stock solutions of 10 nm gold nanoparticles in the first process was utilized as seeds. As the name of method shows, hydroxylamine hydrochloride was used as reducing agent. The synthesis process did not require heating, but vigorous stirring was stilled needed. After diluting the seed solution 4 times to 100 mL volume with a specific concentration in a 250 mL flask, 1.25 mL of reducing agent (0.2 M) was added with stirring, and 1.5 mL the aforementioned 1 wt.% gold chloride tetrahydrate solution was added drop by drop. During the addition of droplets, the solution's color changed from light purple to deep red with brown-tint. The first growth process usually cost about 10 to 15 minutes and when the color did not change, about 18 nm gold nanoparticles solution was obtained. By repeating a similar process with the newly synthesized 18 nm solution while adjusting the diluting times, the amount of reducing agent and chloroauric acid solution, containing gold nanoparticles with even larger size was produced. Similar procedure was utilized in further steps of synthesizing 50 nm and 100 nm gold nanoparticles solution. Figure 2.2 shows the as-synthesized ~100 nm gold nanoparticles, with NP diameter = 101.8 ± 10.9 nm.





Figure 2.2 (a) SEM and (b) TEM images of 100-nm Au nanoparticles obtained via published method. (c) Size distribution of Au nanoparticles (based on 220 counts; NP diameter = 101.8 ± 10.9 nm)

2.2 Preparation of paper-based gold nanoparticle film (PGF)

2.2.1 Fabrication process of PGF

The Paper-based gold nanoparticle film (PGF), was prepared as shown in **Figure 2.3** ([33], Y. Liu, S. Yu, R. Feng et al., 2015: 2768). First, a piece of air-laid paper (45% polyester, 55% cellulose) was cropped into a round shape that matches the inner size (about 4 cm in diameter, typically) of the bottom of a beaker (50 mL, typically). To be noted, the two surfaces of the air-laid paper is not exactly the same, one is relatively rough while another is fluffier with short and fine fibers at top, and according to our test, the fluffy surface is more suitable to be the up surface (see discussion in part 3.2). Next, about 5 mL of the as-synthesized 10 nm gold nanoparticle solution (see part 2.1) was



diluted 4 times with purified water carefully in the container, and then the beaker was placed in a desiccator with atmosphere of formic acid (by put some used and diluted formic acid in a small container in the desiccator previously). After about 48 hours undisturbed *storage*, shiny but thin film of gold nanoparticles could be observed on the top of the solution's surface, while the originally light purple liquid now becoming nearly transparent with a little tint of red. The floating layer of gold nanoparticle is formed by self-assembly, as the charge of nanoparticles were neutralized by that of the molecule of acid, which diffused in the solution during the static time.



Figure 2.3 Schematic illustration of method to fabricate paper-based Au NP film (PGF) ([33], Y. Liu, S. Yu, R. Feng et al., 2015: 2768)

This self-assembled gold nanoparticle film, though free-standing, is not robust enough and vulnerable to even very weak mechanical impact. Therefore, the following step is done with great caution. A syringe (typically 10 mL or 20mL) was probed carefully into the solution, without disturbing the fragile film, and the clear solution was removed gradually. When nearly all liquid was drawn, the gold film would deposit on the air-laid paper. Interestingly, the color of the gold nanoparticle film would turn from gold into dark purple at the end. This is a result of the aggregation of nanoparticles on the fibers of paper. Then, the paper was removed from the container and placed in a drying oven at about 50 °C to 60 °C.

2.2.2 Appearance and absorption property of PGF



The as fabricated paper-based bilayer film appeared to be dark purple, as shown in **Figure 2.4**. Similar to the stable performance of this film, its appearance did not change even after many runs of evaporation experiments. The microstructure of the PGF is shown in the SEM image **Figure 2.5**, on those fibers, pieces of gold nanoparticle films can be found scattering around, which also explains the dark color of the film. The PGF's wettability is not homogeneous, the bottom is hydrophilic, as endowed by the air-laid paper, while the top is relatively not hydrophilic and even a little hydrophobic, due to the presence of the hydrophobic gold nanoparticles.



Figure 2.4 (a) SEM image and appearance of free-floating AuNP. (b) Appearance of as-synthesized and dried PGF ([33], Y. Liu, S. Yu, R. Feng et al., 2015: 2768)



Figure 2.5 SEM image of the PGF paper: (a) scattered gold nanoparticle films on the air-laid paper fiber, scale bar: 1 μ m; (b) disordered fiber structure of the air-laid paper scale bar: 10 μ m



The optical property of the PGF is shown in **Figure 2.6**, which is discussed in part 3.3 in detail.



Figure 2.6 (a) Absorption spectra of the paper-based AuNP film and free-floating AuNP film; (b) reflectance spectra of the paper-based AuNP film and free-floating AuNP film ([33], Y. Liu, S. Yu, R. Feng et al., 2015: 2768)

2.3 Preparation of Aluminum anodic oxide (AAO)-based gold (Au) nanoparticle film (AANF)

2.3.1 Preparation for fabrication of AANF

The Aluminum anodic oxide (AAO)-based gold (Au) nanoparticle film (AANF) are made by a vacuum filtration process ([34], S. Yu, Y. Zhang, H. Duan et al., 2015: 13600). After getting the 50 nm solutions or 100 nm solutions as described in part 2.3, they are not ready to use as their concentration is too small. Therefore, these solutions were stored in jars undisturbed for at least a week to let the precipitation occurs completely. By carefully removing about 90 % of the nearly clear solution from the top with the help of syringe, concentrated solution of 50 nm and 100 nm solutions are obtained and no further treatment were done before filtration process.



The AAO nanopore film is purchased from Whatman company, its pore-size is about 24 nm and 185 nm at each surfaces respectively. Microstructure of its two surfaces and cross section (vertical to the surface) shown in **Figure 2.7** below. Based on the account of 50 pores each, the porosity of two surfaces are 12.4 % and 39.4 % respectively.



Figure 2.7 Microstructure of the Aluminum Anodic Oxide (AAO) film: (a) up surface with pore size at about 24 nm and porosity at 12.4 %, scale bar: 500 nm; (b) bottom surface with pore size at about 185 nm and porosity at 39.4 %, scale bar: 1 μ m; (c) cross-section of the channels vertical to the surface, branching of single channel into two could be seen, scale bar: 2 μ m; (d) cross-section of the channels near the up surface, branching of single channel into about four ones could be seen, scale bar: 2 μ m ([34], S. Yu, Y. Zhang, H. Duan et al., 2015: 13600)

To protect the ceramic AAO film during filtration, as well as to get a gold film with good quality, that is, more smooth and free from cracks, we have built a customer-designed filtration suite. This suite comprised of a 20 mL volume tube with



wide rim at top and thick lip with frosted glass surface, matching the supporting part with frosted glass surface and a white sand core. After clipping tightly together by the adjustable clamp, the two parts can form a funnel similar to the Buchner funnel. And then, installment of a flask at bottom and linking to the vacuum pump by rubber tubes (after first connecting to two U-tubes for drying) were made to set the whole system of vacuum filtration.

2.3.2 Fabrication and chemical modification process of AANF

In a typical vacuum filtration process, a piece of AAO film was first treated with newly-made aqua regia. By immersing the film for a few seconds in aqua regia and washing it with pure water immediately, the pre-treatment is done. Next, the film is put on the sand core with the small pore-sized surface as up surface. To seal the AAO film between the tube and the sand core, purified water was deliberately dropped at the rim of the film before topping the tube and clipping the clamp (The suite is made to matching the diameter of the AAO film). After tightening the clamp by screwing the adjusting bolt, about 3 or 6 mL of the gold nanoparticle solution were added into the tube on AAO film. Next, vacuum pump is activated and the solutions would gradually permeate the nano-pored film and after about 30 seconds, all the liquids were collected in the flask and a layer of yellow film could be seen formed on AAO film. Then the vacuum pump was turning down and the as-fabricated AANF was peeled off the sand core part with the help of rubber suction bulb (blowing air gently from the bottom). Next, the AANF was put into oven at about 60 °C, to dry it completely, after which golden luster of the AANF could be observed and the two layers of the film is tightly attached. At last, the as-fabricated films were stored up for following experiments.

The fresh made AANF was dried in oven overnight and stored for further chemical modification. To explore the evaporation performance of AANF with different surface



wettability, we designed and fabricated the following series: 1) hydrophilic AAO membrane (HLA) alone; 2) hydrophobic AAO membrane (HBA) alone; 3) hydrophilic AuNP film sitting on hydrophilic AAO membrane (HLN-HLA); 4) hydrophobic AuNP film sitting on hydrophilic AAO membrane (HBN-HLA); 5) hydrophilic AuNP film sitting on hydrophobic AAO membrane (HLN-HBA); 6) hydrophobic AuNP film sitting on hydrophobic AAO membrane (HBN-HBA); 6) hydrophobic AuNP film sitting on hydrophobic AAO membrane (HBN-HBA). The hydrophilic and hydrophobic treatment was simple and straightforward. AAO membrane intrinsically has many hydroxyl groups on the surface that make it hydrophilic.



Figure 2.8 Schematic of preparation of AAO-based AuNP film (AANF), including the filtration and chemical modification ([34], S. Yu, Y. Zhang, H. Duan et al., 2015: 13600)

As shown in **Figure 2.8**, to make it hydrophobic, we placed AANF in a desiccator filled with 1H, 1H, 2H, 2H -perfluorooctyltri-chlorosilane (97%, Alfa Aesar) vapor under a negative pressure for about 20 minutes to make the surface of AAO membrane hydrophobic. To modify the AuNP film with controlled hydrophobicity, AANF was incubated in the mixture of alkyl thiol and acetone solution with a volume ratio V(thiol):V(acetone) = 1:49 for 3 hours. The hydrophilic surface of AuNP film was



achieved by incubating AANF in the presence of 2 wt.% N-acetyl-L-cysteine acetone solution.

The as-prepared AANF's appearance is shown in **Figure 2.9** (**a**), and the scanning electron microscopy (SEM) image shows the two-dimensional arrangement of AuNPs within the metallic film (**Figure 2.9** (**b**)).



Figure 2.9 (a) Optical image of AANF, diameter: ~2 cm; (b) front view SEM image of AANF (scale bar: 500 nm) ([34], S. Yu, Y. Zhang, H. Duan et al., 2015: 13600)

2.4 Fabrication of PGF swimmers

There are two types of swimmers fabricated in this research, both based on the paper-based gold nanoparticle films (see part 2.2 for fabrication details). The two swimmers are different in configuration, and were named PGF raft and cone-shaped PGF boat accordingly.

2.4.1 Fabrication of PGF raft

The raft comprised of a piece of PGF, with two stripes of commercial polypropylene foam attached at bottom as floating supporters. As shown in part 3.2, the PGF is



efficient at converting solar energy into thermal one, and thus enabling localized heating and evaporation at the water surface. As shown in the SEM image (**Figure 2.5**), the \sim 12 nm spherical nanoparticles formed pieces of films on the fibers of the air-laid paper (polyester and cellulose). In order to make it move faster, the PGF was cropped into a shape with square body (10mm X10mm) and semicircular head (5mm in radius), the appearance was shown in **Figure 2.10**. In addition, the stripes were set in parallel position; and they were cut to be 10 mm long with a 1 mm X 1 mm cross area. Similar rafts were also made for the direction control exploration experiments, the most successful one (in easiness of controlling) is a swallow-shaped one with right-angle triangular as head and a V-shaped tail.



Figure 2.10 Typical PGF raft appearance with bottom up at left (scale unit: centimeter), white colored stripe is made of polystyrene foam, while the deep purple paper is PGF as fabricated by method in part 2.2

2.4.2 Fabrication of cone-shaped PGF boat

As for the cone-shaped PGF boat, it could be regard as an optimism of the raft. As can be seen in **Figure 2.11**. A transparent pipet tip was first cut from the top to be about 10 mm long as the shell of boat; next, a piece of triangular-shaped PGF was put into this



cone-shaped tube by rolling it and attached to the shell's inner wall, as the light absorber and in another word, "engine". After that, a piece of parafilm is stretched to seal the large end of the shell, to form a hollow space as "vapor chamber", now that the small tip end was the mere path for mass exchange.



Figure 2.11 Typical dry cone-shaped PGF boat appearance (scale unit: centimeter), the sealing material at the left end (large end) is stretched parafilm

In addition, very fine fibers of the PGF were deliberately remained out of the small end, thus capillary force can be used to draw water or other liquid in. As a result, PGF is permeated by liquid when the boat was put on liquid, although it could maintain floating during the whole experiment process. This is mainly accounted for by the fact that the vapor chamber was always partially filled with air. In fact, PDMS was also used as sealing materials at the large end. However, due to the poor thermal stability of this polymer, this fabrication method would cause linkage after heating for a few times, and thus was discarded in the end. There was one thing to be noted: the side of PGF matters, when the surface with more amount of gold nanoparticles faced out, the localized heating would be more great and the same went with the locomotion performance.

2.5 Experiment set-up of localized evaporation



The set-up for the evaporation experiments for the two kinds of bilayer films are similar, but not exactly same (as shown in **Figure 2.12**). The difference mainly came from the different size of the film.



Figure 2.12 Experimental setup for characterizing the evaporation process. The PGF or AANF was floating onto the water in a 50 mL beaker full of water. A focalized solar beam from a solar simulator illumined perpendicularly onto the film. A PC was connected to the electronic balance to record weight loss ([33], Y. Liu, S. Yu, R. Feng et al., 2015: 2768)

As for PGF, the weight loss of the water during the solar-driven evaporation process is measured by an electronic balance with four decimal precision (FR124CN, Ohaus Instrument, Shanghai). A piece of PGF with 40 mm diameter was put on the surface of water, which was contained by a 50 mL beaker. The light source was a solar simulator (Newport 94023A), whose light beam was focalized via a panel of Fresnel lens (Shenzhen Salens Technology Co., Ltd). To be noted, the focalized light was illuminating perpendicularly onto the floating PGF. The evaporation weight-time value



was recorded by a PC connected to the electronic balance. In addition, for free-standing AuNP film and air-laid paper, evaporation rates were obtained in a similar way, except that free-standing AuNP film or air-laid paper was used rather than PGF.

For the desalination applications setup, 3.5 wt.% sodium chloride aqueous solution was used to alternate sea water. The NaCl solution was obtained by dissolving sodium chloride (\geq 99.5%, Shanghai Lingfeng Chemical Reagent Co., Ltd) in distilled water. As mentioned before, the PGF was free-floating at the surface of solution. In this comparison experiment, we used black aluminum foil at the bottom of the beaker, as light absorber to simulate industrial desalination using solar still or parabolic trough. And for more fair comparison, PGF attaching at the beaker bottom is also done. It should be noted that, the light was focused to a power density of 2.5 W/cm², and the relative position of the absorbing film to the lens is the same to ensure the similar light distribution. For all of the three different evaporating systems, the hourly outputs were measured by dividing the weight change in an hour with the area.

In the case of AANF. A 10 mL beaker full of purified water (NANOpure, Millipore Water Purification System; 18.2 M Ω) was placed on the same balance. A piece of AANF, with the similar diameter of the beaker (20 mm in diameter), was floating on the surface of water. Then, a Xenon lamp (JYANG HID 922, Ju Jing Yang Electronics Co., Ltd.) with the power density of ~3.2 kW/m² was set up to illuminate vertically upon the floating AANF, which will generated localized heat within the AANF. To gain deeper insight of the evaporation mechanism as well as the impact of surface wettability on this process, week light (~3.2 kW/m²) and strong light (~14.3 kW/m²) comparison experiments were also carried out, where the light intensity is reduced by transparent plastic panel and increased by focalizing via Fresnel lens respectively.

2.6 Experiment set-up of light-driven motion of PGF swimmer



As illustrated in **Figure 2.13**, the experiment set-up to record the motion on liquid surface is not complex. As for the power source, a laser generating beam with the wavelength at 532 nm was used, whose diameter of the light spot is about 2 mm, which is suitable for the size of the raft or boat (both about 10 mm in length). A glassware containing hundreds of milliliter of the liquid matrix, which may be water, alcohols or aqueous SDS solution was put on a height adjustable lift, which is covered with two layers of blank air-laid paper to reduce reflection from the metallic surface of the lift. Via reflecting the laser beam with the angle manually adjustable mirror, which has a degree of freedom of two, the light would be shot on the PGF raft or the transparent shell. As a result, localized heating from plasmonic effect was produced, and the swimmer was propelled.

As for the recording method, an optical digital video and an IR camera (FLIR, T620) were used simultaneously. The former camera is put in vertical position overlooking the container and the liquid surface, while the IR one is put in a tilted position from the same side with laser source, in prevention of direct laser incidence into the camera lens. Meanwhile, by constant control the mirror's angle by hand, the laser beam was easily controlled to keep up with the movement of the swimmer, which made it viable to trace the boat's locomotion as well as generating unstop force by maintaining the light on the near-tail part of the PGF swimmer.




Figure 2.13 Setup for experiment on light-driven PGF raft/boat movement. IR stands for infrared camera, while DV means digital video, the PC is used to monitor and assist recording; the liquid in container is changeable from water, alcohols, glycols and SDS solutions

In sake of experiment safety, high screens were set around the set-up devices, to block laser from shooting around in the laboratory. The cameras are connected to a personal computer outside the screen, to better monitor the experiment phenomena in a safe environment, as observation in the screen by eyes is limited by the red laser goggle. At the same time of the movement, the real-time temperature pattern of the swimmer as well as the liquid surface was captured by IR camera, which was later synchronized with the motion of PGF-boat recorded by the digital camera.

2.7 Infrared image record and analysis methods

In order to measure the temperature distribution of both the bilayer PGF and AANF



during solar-driven evaporation process, as well as to monitor the time-dependent thermal flow pattern of both the PGF raft and capsuled PGF swimmer, IR images were taken at fixed time interval, and IR videos were recorded during the moving of swimmers. In this study, we utilized a model T620 IR camera, manufactured by FLIR company. Its maximum dissolution is 480*680 (pixels), with a fasted recording rate at 30 frames per second; the temperature scale of a pixel is (-40 °C to 160 °C or 100 °C to 600 °C). The camera is assisted by a FLIR analysis software, rendering the flexibility to adjust parameters including emissivity, distance, air temperature, reflectance temperature and etc. both during and post recording. One thing to be noted as for the swimmer experiment set-up: to protect the camera from direct shot of laser light, it was fixed on tripod with an angle of depression from the same side of the laser source to the pool.

The emissivity of samples was calibrated by using a reference surface as ideal black body. First, floatable carbon film was made by dissolving carbon black in ethanol and pasting on the same supportive layer as the sample film. Next, the carbon film and the sample were put on hot water with a temperature of 90 °C, which will ensure that the two films are at the same temperature in a few minutes. Then, IR image were taken to get the two films' temperature at the same time, when the exact temperature was recorded by a pre-calibrated thermal couple (with probe at the water surface). At last, by reading the temperature of the films and comparing in the IR analyzing software suite, the exact emissivity was obtained thus the temperature measurement of the sample, especially, the AANF, should be more reliable.

2.8 Other instruments for characterization

All chemicals were obtained from commercial sources and used without further purification. Transmission electron microscopy (TEM) samples were prepared by



pipetting one drop of solution onto a 3-mm-diameter copper grid coated with carbon film. The excess solution was removed from grid with a piece of filter paper. TEM was conducted on a JEOL JEM-2010 instrument operated at 200 kV and the images were collected using a Gatan CCD image system. Scanning electron microscopy (SEM) samples were prepared by transferring Au thin films onto clean Si wafers. The Si-wafers was modified with fluorosilane using methods reported in the literature. ([35], D. Qin, Y. Xia, & G. M. Whitesides, 2010: 491) The Si wafers were firstly washed by acetone, ethanol, and distilled water, respectively, in ultrasonic bath for 10 min. After drying in air completely, the wafers would be further cleaned in the Plasmon Cleaning (PDC-32G, HARRICK PLASMA) to remove trace amount of organic impurities and rinsed thoroughly. Next, the as-cleaned Si wafers were placed in a desiccator filled with 1H,1H,2H,2H-perfluorooctyltrichlorosilane (97%, Alfa Aesar) vapor under a negative pressure for about 50 min, which was aimed to make Si wafers surface hydrophobic. SEM instrument (Quanta 250 from FEI, 20 kV) equipped with Energy dispersive spectroscopy (EDS) (Oxford Instruments, 80 mm2 detector). UV-Vis Spectra were collectedon UV-Vis spectrometer (Ocean Optics, Model: HR2000+CG). Reflectance and transmittance were measured by UV/VIS/NIR Spectrometer (PerkinElmer Lambda 750S) equipped with 60 mm integration sphere.

As for contact angle measurement, a high-speed camera (X-Stream XS-4, IDT, US) recorded the process of dropping 2 μ L water droplet on the AuNP film by a pipette. The contact angles were obtained through the analysis of the recorded optical images before, during and after the evaporation processes. In addition, images analysis (including contact angle measurement, SEM size distribution statistic, as well as size and position of swimmers in the picture) was carried out with the help of the software Image J.

Chapter Three Solar-driven localized evaporation via bilayer



plasmonic films

3.1 Research background of solar-driven evaporation system

Solar enabled evaporation is a frequently employed solar energy harvesting technology in modern power plants, chemical plants and seawater desalination plants ([36], M. Elimelech et al., 2011: 712; [37], G. N. Tiwari et al., 2003: 367; [38], M. Gupta et al., 2010: 1228). Multiple technological advances such as optimizing mechanical system and improvement of facilities have been implemented to increase the thermal efficiency of evaporator and lower equipment cost for the evaporation process ([39], E. Cartlidge, 2011: 922; [40], H. Ghasemi et al., 2014: 4449; [41], M. A. Shannon et al., 2008: 301). The process, however, still costs the world thermal power market billions of dollars to maintain these high technological facilities every year ([39], E. Cartlidge, 2011: 922; [41], M. A. Shannon et al., 2008: 301).

Meanwhile, plasmonic heating enabled solar energy harvesting is one of promising efficient technology to utilize renewable solar energy source ([42], I. C. Karagiannis et al., 2008: 448; [43], S. Quoilin et al., 2011: 955; [44], S. A. El-Agouz et al., 2014: 276). As introduced in chapter one, plasmonic heating, also known as thermoplasmonics, is induced by illuminating plasmonic nanostructures under light. Recently, it has opened up an emerging area of critical interest due to its wide range of applications such as photo-thermal therapeutics, thermo-enhanced catalysis, delivery agents and thermal storage ([25], G. Baffou et al., 2012: 178-184).

As a result, exploration of utilizing plasmonic heating to harvest solar energy directly has been exploited during recent years' surge of research on nanoplasmonics, Halas and her coworkers previously reported that aqueous solution containing



light-absorbing gold nanoparticles (AuNPs) exposed to sunlight can induce plasmonic heating, resulting in relatively efficient evaporation ([31], Oara Neumann et al., 2012: 42; [45], Oara Neumann et al., 2013: 11677). In their study the AuNPs served as localized heaters and dispersed throughout the solution. The vapor bubbles were generated inside the solution and travelled to the water-air interface to release the steam trapped inside the bubbles. The heat transfers from the travelling vapor bubbles to the bulk water intrinsically limited the efficiency of the evaporation process.



Figure 3.1 Comparison of evaporation through the heating of the evaporative surface (a) and the heating of particles dispersed in the solution (b) (Credit: [46], Zhenhui Wang et al., 2014: 3233)

In order to dealing with such limit on efficiency, we had demonstrated that free-floating hydrophobic gold nanoparticles (AuNPs) films can serve as light-to-heat converter in solar steam generation system, and relatively high evaporation efficiency (i.e. the ratio of the energy used for the vaporization of the liquid to the total energy input) can be obtained by localizing heat at the surface. **Figure 3.1** reproduced from



this previous work shows the improvements of the free-floating film system compared to the solution-based system ([46], Zhenhui Wang et al., 2014: 3233).

Nonetheless, the fragility of AuNP film make it hard to be practically used. What was worse, three main challenges impede the industrial application of such thin-film based evaporation approach: 1) scale-up of AuNP films in a large evaporation system. The as-prepared AuNP film is fragile and hard to be transferred among various large evaporation system; 2) reusability of the AuNP film. The fragility of the film also makes it impossible to recycle the assembled films; 3) heat loss to the non-evaporative portion of the liquid due to thermal diffusion ([47], G. Langer et al., 1997: 1510). As shown in that previous work, even though the free-floating AuNP film enables the reduction of heat loss occurs in the dispersed aqueous AuNP solution, the thermal diffusion from the heated AuNP film to non-evaporative portion of liquid is inevitable ([46], Zhenhui Wang, et al., 2014: 3233).

To address these challenges, we still took the approach to exam the biological evaporation systems for inspiration. In skins, the biological tissues support the evaporation system (sweat pores, sweat glands, and blood vessels) and provide the mechanical stability. The low thermal conductivity of these tissues (~0.3 W/m K) also help reduce the heat transfer from the evaporative skin surface to the internal biological parts ([48], G. E. Miller, 2012: 937). Another inspiration came from close examination of natural leaf transpiration. It was reported that hydrophobic surface of desert plant leaves impedes the water evaporation to prevent water loss; while the spreading water on the hydrophilic surface of rainforest plant leaves evaporate rapidly to reduce the growth of micro-organisms ([49], K. Koch & W. Barthlott, 2009: 1487). Learning from leaf transpiration, surface wettability controlled by structural morphologies and chemical groups is critical to the proper functioning of solid surfaces.



Therefore, nanoporous AAO membrane has been introduced not only to provide mechanically stability and good thermal insulation for AuNP film but also to promote the flexibility of the structural and chemical modification. Because AAO membrane has drawn much attention in a wide range of chemical and biological areas, especially chemical separation, catalysis, biosensor and drug delivery, due to its superior transport and selectivity properties ([50], S. B. Lee et al., 2002: 2198; [51], W. Shi et al., 2008: 801; [52], Z. Zeng et al., 2012: 4138; [53], A. Santos, 2013: 25).

In addition, Tunable property across different application situation is one of the most important criteria to evaluate the applicability of bio-inspired man-made functional materials. We expected that evaporation rate could be well tuned by the chemical modified AANF, which may behave like a "water gate" controlling the water vapor flux. With the knowledge about hydrophilic and hydrophobic behavior of AAO-based film, we would gain deeper understanding of evaporation mechanism of such system, and it can potentially offer us an opportunity to design the evaporation application where tuning the evaporation rate is required.

3.2 Evaporation Performance of PGF

3.2.1 Comparison between PGF and free-floating AuNP

The primary feature of the evaporation performance of PGF paper was the generation of hot zone, which was restricted spatially at the vicinity of the film ([33], Y. Liu, S. Yu, R. Feng et al., 2015: 2768). As a result, the energy in light was highly efficiently converted into enthalpy of vapor. The IR images in **Figure 3.2** clearly shows this localized heating property by comparison. Before the evaporation (light off) the air-laid paper and PGF had similar temperature distribution across the surface about 26 °C;



however, after the illumination by simulated solar light at 4.3 kW/m² has been shone on the PGF for 900 seconds, the heated area were at different temperature. As for PGF, the IR images demonstrated a central maximum temperature at about 80 °C, while the air-laid paper's highest temperature was around 40 °C. Considering the similar thermal conductivity of the two films, the very presence of gold nanoparticles layer is the main reason of the localized heating, as it would naturally induce plasmonic heating.



Figure 3.2 The surface temperature distribution and maximum temperature (annotated) of a, b) air-laid paper, c, d) paper-based AuNP film (PGF) and e, f) free-floating AuNP film before (a, c, e) and after (b, d, f) solar illumination for 15 minutes at 4 kW/m², which was monitored by an IR camera ([33], Y. Liu, S. Yu, R. Feng et al., 2015: 2768)

The performance of free-standing AuNP film was compared with the PGF's, together with that of the air-laid paper and water as reference, see **Figure 3.3**.





Figure 3.3 Evaporation weight change of PGF, free-floating AuNP film, water natural evaporation and air-laid paper under solar power density of 4 kW/m² ([33], Y. Liu, S. Yu, R. Feng et al., 2015: 2768)

In order to quantify such differences of the thermal performance, the equation was first proposed by Chen and coworkers for calculation of thermal efficiency (η_{th}), and in other words, the light-heat conversion efficiency ([40], H. Ghasemi et al., 2014: 4449).

$$\eta_{th} = \frac{\dot{m}h_{LV}}{I} \tag{3-1}$$

Where \dot{m} is the mass flux (evaporation rate per unit evaporative surface area), h_{LV} is the total enthalpy of liquid-vapor phase change (sensible heat plus phase-change enthalpy), and I is the power density of solar illumination. The calculation result showed that the light-heat conversion efficiency of the PGF and AuNP film were 87.1% and 51.2 %, respectively. This values matched those evaporation rate of the AuNP film and PGF (the former is about 61 % of the later). This result demonstrated the contribution of the supportive paper layer in the evaporation system. This good performance in could be explained by analogy with a biological system, human skin, which sweats in a way that could quickly cool down the body temperature. As introduced in part 3.1, the efficient heat conversion into water vapor during sweating, is enabled by the heat insulation and mechanical stable skin tissue underneath. And the



air-laid paper in PGF also played a similar key role in raising the evaporation rate and efficiency.

3.2.2 Properties of PGF

Besides good heat insulation that enhanced the PGF's localization of heating (note: AuNP film without air-laid paper reached maximum temperature at 68 °C as shown in **Figure 3.2**), there were some other properties that was worth mentioning, including broad-band absorption, good reusability, potential for large-scale production.



Figure 3.4 Optical image of large-scale PGF with diameter of 18 cm ([33], Y. Liu, S. Yu, R. Feng et al., 2015: 2768)

Figure 3.4 shows the lab level capability of PGF at large-scale, which was sized about 18 cm in diameter. Considering the straightforward and simple synthesis and fabrication steps introduced in part 2.1 and 2.2, industrial scale manufacturing is quite promising. To demonstrate the reusability, a PGF sample was tested under light intensity of around 4 kW/m², for about 30 cycles, each one continued for 15 minutes. After each test cycle, the PGF was wet and was thus dried thoroughly in the drying oven at a temperature of about 60 °C. In **Figure 3.5** (a), the total weight loss each cycle was depictured, along with three lines representing for the maximum value, minimum



and average weight of the evaporated water; and in **Figure 3.5** (**b**), each point stands for a weight loss value each cycle, and after 30 times of test, the value did not change much from the average of 1.25 g, which demonstrated the stability of the PGF film in evaporation performance. As for the light-absorption property, please see part 3.3 for more details.



Figure 3.5 (a) The maximum, minimum and average evaporation experimental data of PGF as a function of weight change vs time. (b) Every point represents the total weight change after 15 minutes' illumination in each cycle. It has an average of 1.25 g ([33], Y. Liu, S. Yu, R. Feng et al., 2015: 2768)

3.2.3 Analysis on PGF's advantages

The reasons for PGF's high evaporation efficiency could be summarized as: 1) good light absorption property of reduced flection and structure-induced scattering of the air-laid paper; 2) reduced heat loss from low thermal conductivity; 3) large evaporation area due to the rough microstructure.

Firstly, as shown in the inset in **Figure 2.4** (**a**), the free-standing AuNP film is so shiny that most solar light would be reflected backward instead of being absorbed and used in evaporation. While the PGF appeared to be dark in color, and as shown in **Figure 2.6**,



the absorption of this film is as high as 90 %, while the reflectance is only about 7 %, those value of the frees-standing AuNP film is 65 % and 10 %, respectively. This data demonstrated the excellent light absorption property of PGF. The polymer fibers of the air-laid paper increased the surface roughness, which in turn enabled a 3D microstructure with would scatter and trap the incident light. As a result, the shiny metallic gold film did not exist any longer after it was deposited on the air-laid paper. Instead, the dark purple PGF shows a board band absorption of solar light as seen in **Figure 2.4 (b)**.

Secondly, the air-laid paper has low thermal conductivity, which reduced heat loss to the bulk liquid, which part was not contributive to evaporation. Although the dry air-laid paper was demonstrated to has low thermal conductivity in previous study ([54], F. Dominguez-Munoz, et al., 2010: 2159), wet PGF's thermal conductivity was not known before. Therefore, we used IR camera to measure the temperature difference in vertical direction of and wet overlapped PGF, while temperature at one side maintained by cool plate and the other heated to a stable status. The result shew that the wet air-laid paper and PGF has conductivity at 0.48 W/m · K and 0.49 W/m · K, respectively, which were lower than that of pure water (0.0056 W/m · K). In addition, the microstructures also impeded the convection of liquid. Combining the lowerd conductivity and reduced convection, the diffusion of heat into bulk water was greatly limited in PGF, and such reduction in waste means a higher efficiency in evaporation.

Thirdly, as shown in **Figure 2.2** (b), the fibrous microstructure of air-laid paper also enlarged the evaporative surface and further increased the evaporation rate. Keeping in mind that both the free-standing AuNP film and the AuNP film on the air-laid paper (PGF) have the similar structures generated by self-assembly; however, thanks to the microstructures exist at the surface of the air-laid paper, the AuNP films on the air-laid paper have extra micro-scale roughness. To our expect, the measured micro-scale



roughness of the PGF and free-standing AuNP film were about 5.8 and about 1.00017, respectively. In addition, fibers in the air-laid paper have generated multitudinous pores in micro and nano scale. This pores would interconnect to form channels, which made the liquid flow more easily by capillary force, which replenished the evaporation constantly.

3.3 Desalination application of PGF

In industrial domain, the solar driven evaporation has long been utilized as a sustainable and green solution for applications like solar still desalination. In fact, solar energy is currently used to desalinate seawater to obtain purified water in many regions all around the globe. In this industry, the increasing of efficiency of evaporation process not only means higher production and lower operation cost, but also means the capability to support more clean drinking water for people facing diminishing water supplies. However, limitation owning to low productivity has impede the process of this field, where scientists has been put lot of research work, which mainly focused on the design of the desalination system. Nonetheless, the PGF could provide a novel solution to this problem, that is, increase the productivity by enhancing the efficiency of the light to heat conversion.

As for the experimental demonstration on simulated desalination, setup method, as well as key value of parameters could be found in previous part 2.5. To estimate the desalination output efficiency (E), the following formula is used:

$$\boldsymbol{E} = \frac{\boldsymbol{Q} \times \boldsymbol{L}}{\boldsymbol{G} \times \boldsymbol{A}} \tag{3-2}$$

Where Q is output of distilled water measured in liter per square meter, G is solar irradiation, L is the latent heat of vaporization of water (= 2.26 MJ/kg), A is aperture area of the still. After this calculation, the desalination output efficiency via the floating PGF was about 56 %, which is quite higher than that of the black aluminum absorption



layer one; even the PGF stick to bottom one shew higher efficiency than the black Aluminum one. These values were visualized in **Figure 3.6**. Knowing that the typical commercially-applied solar stills have efficiencies of around 30 to 40 percent, the PGF's potential in increasing desalination production was demonstrated.



Figure 3.6 Comparison of hourly outputs of the saline solution with PGF floating at liquid/air interface, PGF sitting at the bottom and black aluminum foil sitting at the bottom as the light absorption layer ([33], Y. Liu, S. Yu, R. Feng et al., 2015: 2768)

3.4. The Evaporation Performance of AANF

To achieve higher evaporation efficiency and enhance the mechanical stability of plasmonic heating system, we have successfully fabricated hydrophilic paper-based gold nanoparticle films (PGF) by taking inspiration from how human skin reduces heat transfer and promotes sweat evaporation (part 3.2 & 3.3). We note that: i) coupling hydrophobic AuNP film with hydrophilic paper substrate leads to substantial change in evaporation rate; ii) wettability of surface could influence evaporation rate of water on it, while two reported high-performance evaporation film systems did not share the same wettability at top layer ([40], H. Ghasemi et al., 2014: 4449; [46], Zhenhui Wang



et al., 2014: 3233). Therefore, we were prompted to study how and to what extent wettability of a floating film plays a key role in controlling the speed of water evaporation.

To mimic the hydrophilic and hydrophobic evaporation surface in biological system (part 3.1), we performed chemical hydrophilization or hydrophobization on top and bottom layer of anodic aluminum oxide (AAO)-based gold nanoparticle film (AANF) (Check details in part 2.3) ([34], S. Yu, Y. Zhang, H. Duan et al., 2015: 13600).

3.4.1 Evaporation of AANFs with different wettability



Figure 3.7 Evaporation weight change of HLN-HLA, HBN-HLA, HLN-HBA, HBN-HBA, HLA and HBA as a fi=unction of time under Xenon lamp with power density of ~3.2 kW/m² ([34], S. Yu, Y. Zhang, H. Duan et al., 2015: 13600)

Figure 3.7 listed the weight change of water of different surface chemistry modified AANF, which we concluded following findings: 1) evaporation of the AAO film alone is not influenced by modification, as HLA and HBA had almost the same evaporation speed; 2) all the AANFs achieved higher evaporation rates than HLA or HBA alone



because of the induced plasmonic heating; 3) comparing AANF with the same AAO base, varying wettability of AuNP film does not affect the evaporation rate of AANFs; 4) when HLA and HBA were used to support the same AuNP film, the differences in evaporation rate between HLA and HBA was apparent (i.e. the evaporation rate of HLN-HLA or HBN-HLA achieved the highest evaporation rate (0.180 mg/s), which is about 23 % higher than that of HLN-HBA or HBN-HBA).



Figure 3.8 Contact angle measurements of HLN-HLA, HBN-HLA, HLN-HBA, HBN-HBA, HLA and HBA during water evaporation process. Right side shows the optical images of water droplets on different surfaces ([34], S. Yu, Y. Zhang, H. Duan et al., 2015: 13600)

To further verify the role of wettability during evaporation, we also carried out measurements of surface contact angle (**Figure 3.8**). For measurement details, please check part 2.8. **Figure 3.8** shows that the contact angles of all six samples were relatively similar, which indicates that chemical modification was still effective during water evaporation.

3.4.2 Evaporation performance of AANF under strong light illumination



Further experiments on AANF's evaporation performance under strong light intensity was carried out with the help of a Fresnel lens (Shenzhen Salens Technology Co., Ltd) to focus the Xenon light upon the surface of AANF (light power density is ~14.3 kW/m²), while other parameters of the setup were kept the same as mentioned in part 2.5. As shown in **Figure 3.9** (a), the evaporation rate could reach as high as ~1.1 mg/s, which was about 6 times higher than that under weak light condition. When it came to hydrophobic AAO-based AANFs, however, we observed that the film quickly turned into golden shiny at the center spot and was ruptured after about 12-minute illumination (**Figure 3.9** (c)).



Figure 3.9 (a) Evaporation weight change of HLN-HLA, HBN-HLA, HLA and HBA as a function of time under Xenon lamp with power density of ~14.3 kW/m²; optical images and IR images of HLN-HLA (b) and ruptured HBN-HBA (c); (d, e) SEM images of HBN-HBA after exposed to Xenon lamp with power density of ~14.3 kW/m² ([34], S. Yu, Y. Zhang, H. Duan et al., 2015: 13600)



This scorching process of AuNP film also showed extreme higher surface temperature than that of the hydrophilic AAO-based AANFs (**Figure 3.9 (b**)). Close examination via SEM (details in 2.8) revealed that the AuNPs in the shiny ruptured area were fused together (**Figure 3.9 (d**)), while those at the normal part with darker color remained as discrete particles (**Figure 3.9 (e**)). According to the work by Peng et al., the temperature of fusing of AuNPs should be higher than 200 °C ([55], Q. Yu et al., 2011: 3868) which means that the local temperature of central ruptured AuNP film was actually higher than 160 °C observed in **Figure 3.9 (c**) due to the intensively localized plasmonic heating ([29], Zheyu Fang et al., 2013: 1736). Please be noted that the highest temperature detectable by the IR camera is 160 °C, as mentioned in part 2.7. Besides the influence on plasmonic effect, the scorched AuNPs further limited the vapor escaping rate and thus resulting to the pressure accumulation and the rupture of the film. As for the hydrophilic AAO-based AANFs, they kept their shape and not even slightly color change was observed, even though illuminated from the same strong light for 30 minutes.

To quantitatively evaluate the evaporation performance of AANFs, we calculate the difference in form of relative evaporation rate (ΔR_r) to quantify the difference in evaporation rate between hydrophilic and hydrophobic AAO-based AANFs under specific incident light intensity (Equation 3-3 and 3-4):

$$R_r^L = \frac{R_{AANF(L)}}{R_{HLA}}$$
 and $R_r^B = \frac{R_{AANF(B)}}{R_{HLB}}$ (3-3)

$$\Delta R_r = R_r^L - R_r^B \tag{3-4}$$

where $R_{AANF(L)}$ and $R_{AANF(B)}$ are the evaporation rates of hydrophilic and hydrophobic AAO-based AANFs, respectively; R_{HLA} and R_{HBA} are the evaporation rates of the bare hydrophilic and hydrophobic AAO membrane, respectively; R_r^L and R_r^B are the relative evaporation rate ratio of hydrophilic AAO-based AANF to hydrophilic AAO and hydrophobic AAO-based AANF to hydrophobic AAO, respectively; ΔR_r is the difference between relative evaporation rates.



As a result, the output value has taken the benchmark into consideration. The calculated ΔR_r under different incident light intensity is shown in Figure 3.10 ($\Delta R_r = 0.39$, intensity = ~3.2 kW/m²; $\Delta R_r = 2.23$, intensity = ~14.3 kW/m²), which shows that plasmonic nanoparticle film can differentiate the evaporation rates of hydrophilic and hydrophobic AAO during solar light driven evaporation. In addition, the difference can be amplified when the incident light intensity increases. (Note: because of the relatively large fluctuation in evaporation during the first minute as the evaporation process became stable, only evaporation rates between the 1st and 12th minute were used in Figure 3.10)



Power density:~3.2kW/m²; ΔR_{r} =0.152/0.076-0.121/0.075=0.39 Power density:~14.3kW/m²; ΔR_{r} =1.072/0.114-0.868/0.121=2.23

Figure 3.10 Evaporation rates of HBN-HLA and HBN-HBA illuminated under different power density of ~3.2 kW/m² (a) and ~14.3 kW/m² (b). The calculations of the difference between relative evaporation rate (ΔR_r) are shown under the plots ([34], S. Yu, Y. Zhang, H. Duan et al., 2015: 13600)

Taking advantage of the flexibility to control the chain length of alkyl thiols, we also tailored the organic tether group attached to the AuNP film surface. In this investigation, thiols with different carbon chain lengths had been used in AuNP film modification, and evaporation performance of a series of HBN-HLA was then studied. Different thiols could potentially change the optical absorption performance of the AuNPs and result in the difference in heat localization and evaporation ([56], S. K. Ghosh, 2004:



13963). Thiols with 4, 8, 12, 16 carbon atoms in the straight aliphatic chain were attached to the top AuNP layer using the same experimental procedure as described in part 2.3. **Figure 3.11** shows that the evaporation performances of these systems were almost the same, indicating that the alkyl chain length does not affect evaporation rate.



Figure 3.11 (a) Schematic of AuNP films sitting on the AAO membrane modified with different alkyl chains (C4, C8, 12, C16); (b) Evaporation weight change of AANF as a function of time ([34], S. Yu, Y. Zhang, H. Duan et al., 2015: 13600)

3.5 Influence of wettability of AANF on evaporation

To gain deeper insight in the AANF evaporation process, we further observed the morphologies of nano-porous AAO membranes via SEM (details in part 2.8) and then proposed a possible mechanism of evaporation of these AAO-based film. **Figure 2.7 (a, b)** depicted top and back view of AAO membrane, respectively. A typical cross-sectional (**Figure 2.7 (c, d**)) of the AAO membrane shows the separated, cylindrical branched nano-channels in AAO membrane. Vertical to the surface, there are numerous small parallel branches that connect the large and small nano-channels. As shown in **Figure 3.12**, when AAOs are placed on the surface of water, water was draw by capillary force from bottom to the top of nano-channels within HLA, while for HBA, due to the water repelling nature of the hydrophobic surface, water remains at the



bottom of HBA.



Figure 3.12 Schematics of evaporation process of HLA, HBA and AANFs under weak (~3.2 kW/m²) or strong (~14.3 kW/m²) light illumination (not drawn to scale) ([34], S. Yu, Y. Zhang, H. Duan et al., 2015: 13600)

The top evaporation areas of HLA and HBA, however, are almost the same, which is consistent with our experiments on HLA and HBA, which exhibited similar evaporation rate during the light-driven process (**Figure 3.7 and 3.9 (a)**). The evaporation mechanism of AAO membranes covered with AuNP films, however, was different. When AANF is exposed to simulated solar light radiation, the surface temperature of AuNP film will first be raised owning to the highly efficient light-to-heat conversion ([57], H. H. Richardson et al., 2009: 1139). Such increase in temperature inevitably accelerates the rate of water evaporation. Therefore, the rapid water replenishment from the bottom of AAO to the top helps cool down the heated thin film in the case of hydrophilic AAO (**Figure 3.9 (b**)). For hydrophobic AAO, the



surface temperature of AuNP film will keep increasing and the volume of accumulated hot vapor will substantially expand. Eventually the pressure exceeds the mechanical strength of AuNP film, leading to rupture observed in hydrophobic AAO-based AANF under strong light illumination (**Figure 3.9** (c)).

Interestingly, during water evaporation, periodic bubble formation, growth and departure cycles under hydrophobic AAO-based AANF's bottom were observed. The cycle length of such process would vary with the incident light intensity. Please be noted that small bubbles also formed under the hydrophilic AAO-based AANFs, we did not observe periodic bubble departure during the whole process of evaporation (at least 30 minutes). As shown in **Figure 3.13**, under weak light (~3.2 kW/m²) illumination, small bubbles formed and merged under hydrophobic AAO-based AANFs and the cycle of bubble formation, growth and departure were in the time scale of several minutes. In contrast with weak light, under strong light (~14.3 kW/m²) illumination, huge bubbles (~one or two centimeters in diameter) formed and the cycle length of was reduced to the time scale of ~10 seconds. These bubbles formed under hydrophobic AAO-based AANFs acted as insulating layer, which led to smaller temperature rise at the water surface and lower evaporation rate than those of hydrophilic AAO-based AANFs (**Figure 3.10**).



Weak light (~3.2 kW/m²)Hydrophilic AAO-based AANFImage: Strain S

6 minutes

10 minutes

Figure 3.13 (a) Optical images of hydrophilic AAO-based AANFs exposed to weak light illumination with the power density of ~3.2 kW/m². A few small bubbles formed beneath hydrophilic AAO substrate after several-minute illumination. However, no bubble departure was observed during the evaporation process ([34], S. Yu, Y. Zhang, H. Duan et al., 2015: 13600)



Strong light (~14.3 kW/m²) Hydrophilic AAO-based AANF



5 minutes

7.5 minutes

Figure 3.13 (b) Optical images of hydrophilic AAO-based AANFs exposed to strong light illumination with the power density of ~14.3 kW/m². Compared to the weak light illumination, more small bubbles formed beneath hydrophilic AAO substrate after several-minute illumination. However, no bubble departure was observed during the evaporation process ([34], S. Yu, Y. Zhang, H. Duan et al., 2015: 13600)



Weak light (~3.2 kW/m²) Hydrophobic AAO-based AANF



4 minutes



Figure 3.13 (c) Optical images of hydrophobic AAO-based AANFs exposed to weak light illumination with the power density of ~3.2 kW/m². Bubbles formed beneath hydrophobic AAO substrate after several-minute illumination. Bubbles gradually grew up and departed from the substrate. The cycle of bubbles formation, growth and departure is usually in the time scale of several minutes under weak light illumination ([34], S. Yu, Y. Zhang, H. Duan et al., 2015: 13600)





2 minutes 56 seconds

2 minutes 57 seconds

Figure 3.13 (d) Optical images of hydrophobic AAO-based AANFs exposed to strong light illumination with the power density of ~14.3 kW/m². Bubbles formed beneath hydrophobic AAO substrate within two-minute illumination. Bubbles progressively grew up and exploded. The cycle of bubbles nucleation, growth and explosion is usually in the time scale of ~10s of seconds under strong light illumination ([34], S. Yu, Y. Zhang, H. Duan et al., 2015: 13600)



To sum up, we investigated the plasmonic heating induced evaporation performance by tailoring the wettability of both the top light-to-heat conversion layer and the bottom supporting layer. Through systematic variation of the surface chemistry and different combination of surface wettability of the AuNP films supported by AAO membranes, both the evaporation performance and the top surface wettability were recorded during the evaporation process under both weak and strong light illumination. The wettability of the top surfaces did not play a key role in controlling the evaporation performance, which clarified the reported performances of localized water vapor generation systems with hydrophilic top ([40], H. Ghasemi et al., 2014: 4449) or hydrophobic top ([46], Zhenhui Wang et al., 2014: 3233). The wettability of the bottom surfaces, however, controlled the performance of such localized steam generation systems: hydrophilic supporting layers resulted in better and more stable performance than the hydrophobic supporting layers. The bubbles formed under hydrophobic AAO membrane acted as an insulting layer that limited both the heat and mass transport, which resulted in the decreased evaporation performance of the system. The use of hydrophobic supporting layers led to the undesired heat accumulation and even generated film rupture under strong light illumination. The findings in this part provide new insight of roles played by the surface chemistry for the localized water vapor generation system, which will help expand the design guideline for the use of such systems in power generation, autoclave, and desalination.

3.6 Summary of bilayer plasmonic film for solar-driven evaporation

In this chapter, inspired by natural evaporation system (human skin and plant leaf), two bilayer film capable of localized plasmonic heating were developed for the application of solar-driven evaporation, respectively.



The first one is paper-based gold nanoparticle film (PGF) ([33], Y. Liu, S. Yu, R. Feng et al., 2015: 2768). A common and low cost material was used as the support of self-assembled AuNP film to fabricate the bioinspired reusable evaporation system. Such system enables the application of plasmonic heating to desalination, fractionation and sterilization at large scale. Compared to conventional evaporation process, PGF generates localized plasmonic heating only at the surface of solution while the bulk liquid still remains low temperature. The PGF maintains high evaporation efficiency even it is cycled for multiple times. Another advantage of the PGF is that its fabrication procedure is simple, could be easily scaled up to large-scale production and the process do not require complex equipment. Furthermore, the PGF can be integrated with many existing commercial desalination systems, resulting in high productivity with minimum extra installation costs.

The second film is aluminum anodic oxide (AAO)-based Au nanoparticle film (AANF) ([34], S. Yu, Y. Zhang, H. Duan et al., 2015: 13600). This part demonstrates that, in the absence of AuNP film, water evaporates through hydrophilic AAO membranes at rates similar to hydrophobic ones under the same light illumination. However, in the presence of AuNP film, water evaporation through hydrophobic AAO membranes significantly lags behind hydrophilic ones. In other words, AuNP films act as "evaporation rate amplifier", which differentiate the water evaporation rates through hydrophilic and hydrophobic AAO membrane and amplify the difference. In this part, we present that this evaporation rate differential resolution can be achieved as high as ~34% when increasing the intensity of incident light. Nevertheless, varying the wettability of AuNP film has no direct effect on the evaporation rate in terms of our experimental results. We also provide mechanistic insights into a simple heat transfer model to fully understand the reason why AuNP film enhanced the differential evaporation rate across AAO membranes with different wettability.



Chapter Four Light-driven locomotion of plasmonic film-based

swimmer

4.1 Research background of micro/small motors

During the solar-driven evaporation experiments on Aluminum Anodic Oxide (AAO) –based Au Nanoparticle Films (AANFs), furious bubbling was observed under hydrophobic AAO-based samples (part 3.5, **Figure 3.13** (**d**)). Herein, we came up with the idea of using photo-thermal conversion of plasmonic materials for movement at water-air interface.

In fact, such concept of self-powered small motors or machines, which ranges from nanoscale, microscale to macroscale (millimeter) in size, has attracted attention from researchers around the world, owning to its promising potential as building blocks for device applications in sensing, delivery, actuating, electricity generation and environmental remediation. Various kinds of the small motors moving in or on liquids have been developed, in which different energy sources including chemical potential difference, Marangoni effect, acoustic wave, and even electric field were utilized ([58], W. Gao & J. Wang, 2014: 3170). The motors could be categorized into two major genres by their power source, that is, self-powered and external field triggered.

For the self-powered type of small motors, two main methods are chemicals releasing, and catalytic reactions with matrix. For example, Jin and co-workers has developed a membrane system utilizing the vapor-driven Marangoni propulsion. In this work, the fuel, ethanol or pentane, could be carried on board of the nanostructured super-hydrophobic and super-oleophobic aerogel membrane. The slow but continuous



release of fuel into water and immediately evaporation could generate significant surface tension to push the membrane forward. In addition, they demonstrated the tunable velocity feature by using different solvents varying in vapor pressure ([59], H. Jin et al., 2012: 2526). For instance, Matsui's group, developed a peptide assembly-driven Metal-Organic Framework (MOF) motors, which in nature uses the surface tension gradient generated motion. Based on the emittance of peptides at the water-MOF interface, which would self-assemble to reorganize the hydrophobic building block and generating a large surface tension gradient, the motion toward high surface tension side is realized. What's more, their motion can be used to generate electric power by adding on magnetic field and guiding the motion trajectory into a circular one ([60], Y. Ikezoe et al., 2015: 288).

Despite the delicacy achieved by the aforementioned design of motors, they have at least one of the following three intrinsic disadvantages: consumable fuel, uncontrollable moving direction, dependence on chemical matrix that is rare present in nature.

As for the external field activated motor, all kinds of physical field including electric (both static and dynamic), magnetic, electromagnetic, mechanical (acoustic), as well as thermal fields were exploited to either control or propel the locomotion of small motors.

J. Zhang and co-workers, has developed a liquid metal-based motor, which could adapt its shape according to the environment, which is similar to mollusk like living organism, herein, their swimmer was named a biomimetic liquid metal mollusk, with the ability to reach narrow spaces like channels. The special feature of this liquid metal swimmer is it could be remedied by electric field under the exposure of the field even when the propulsion is hindered ([61], J. Zhang et al., 2015: 2648). Fre'chet's group, have



utilized thermal field to induce surface gradient to power small object on water. To realize remote control, they fabricated (vertically aligned carbon nanotube forests) VANT as light absorber as well as heat generator. As shown in Figure 4.1, the asymmetrically heated object could move quite fast (~ 20 mm/s) on water surface. In addition, by addition of tiny amount of SDS, they reported that the surface tension quenching effect induced by the surfactant impeded the movement, and they came to conclusion that it was surface tension that drove their boat ([62], David Okawa et al., 2009: 5396-5397).



Figure 4.1 Light-based control of VANT-PDMS objects on water. When illuminated, as in (a), the retarding surface tension force diminishes and the object is pulled forward. Alternatively, when the back-left side is heated (b), an asymmetry of forces is created, resulting in forward and right turning propulsion. Such selective irradiation can be used to produce and remotely control motion. Optical images (c-d) of a VANT-PDMS composite in a water filled trough show the linear propulsion described in (a). The VANTPDMS object is briefly irradiated at



time zero with focused near-IR light (450 mW) just right of center on the back, absorbing face of the object. The laser source is roughly 13 cm away, with the beam nearly grazing the surface of the water and the focus set to coincide with the absorbing face of the object. Credit: [62], David Okawa et al., 2009: 5396)

As demonstrated in part 1.2, plasmonic heating is an ideal heat source for applications in the nano/micro area. nevertheless, motors powered by plasmonic materials was quite uncommon at present. The pioneering work done by X. Zhang's group is inspiring in the aspect of the viability of plasmonic as a converting way in the step for energy to transform from solar one to mechanical one. By using a nanoscale plasmonic structure, they achieved rotational force under illumination with linearly polarized light, which result in rotation of a 4,000 times larger silica transparent microdisk shell. Their work, however, is done in a micro-scale (~2 micro meter in size) ([63], M. Liu, 2010: 570).

Actually, a macroscale motors based on plasmonic photo-thermal conversion has not been created before, therefore, this research would generate another new branch of the photo-thermal application of the plasmonic nanoparticles.

4.2 Swimming performance of PGF raft

4.2.1 Motion on water and surfactant solution

Firstly, learning from Fre'chet's work ([62], David Okawa et al., 2009: 5396), we investigated the surfactant's influence on the motion. **Figure 4.2** shows the maximum velocities of the light driven locomotion of PGF-rafts on water and sodium dodecyl sulfate (SDS) solution with concentration ranging from 6 g to 30 g per 100 g water. When low concentration surfactant was added, the speed of raft was reduced, which seemed to agree with Frechet's work. As shown in the set-up in part 2.6, the PGF-raft is



illuminated at one edge of the PGF, as a result, it moved forward due to asymmetric surface tension gradient, caused by heating at focused point.



Figure 4.2 Moving velocities of PGF raft on water and SDS aqueous solutions with different concentration (6-30 g /100 g water). The quenching effect of surfactant on the moving agrees with previous report, while further increasing of velocity with SDS concentration indicates other propelling mechanism

Surprisingly, as shown in **Figure 4.2**, with the further increase of SDS concentration, the mode of motion evolved from a smoothly continuous slow mode to a pulsed but fast one. Considering the fact that surface tension of liquid is similar regardless of further addition of SDS (as the CMC of SDS aqueous solution is about 0.24 g/100 g water), the explanation that the movement of raft is mainly driven by surface tension gradient from localized heating and temperature gradient is invalid, especially for SDS solution concentration ranging from 6 g to 30 g per 100 g water. Herein, we assume that the motion of PGF raft in high concentration SDS solution is not only propelled by temperature gradient induced surface tension gradient, there must be another driving force for the raft.





Figure 4.3 (a, b) the IR images of moving PGF boat on 30 g SDS aqueous solution under laser (power density: 353.5mW/mm²) and the corresponding linear temperature distribution; (c, d) IR images and corresponding linear temperature distribution of PGF boat on water surface when illuminated by laser with the same power density; (e, f) IR images and corresponding linear temperature distribution of paper boat on water surface when illuminated by laser with the same power density;

To investigate the driving force of the PGF raft in high concentration SDS solution, we analyzed the temperature distribution over time, with the help of IR images. **Figure 4.3** shows the IR images of moving PGF raft and paper raft on the surface of different liquids. When illuminated at power density of ~350 mW/mm², localized hot region was



observed. The sizes of this area were different. For the PGF raft on 30 g SDS solution, that area was about 113.04mm²; while that of the air-laid paper raft (fabrication similar to that of PGF raft, as in part 2.4) on 30 g SDS solution was only 12.6mm², which is a magnitude smaller. The measured maximum temperatures were 91°C, 84°C, and 40°C respectively for PGF raft on 30 g SDS solution, PGF raft on water and air-laid paper raft on 30 g SDS solution. As described in part 3.2, this difference was induced by the highly-efficient photo-thermal conversion of the PGF raft, and the localized heating effect at the liquid-air interface.

Figure 4.3 (b, d) clearly demonstrated the temperature distribution along the moving direction of raft in Figure 4.3 (a), 4.3 (c) respectively. Unlike the thermal gradient shown in Figure 4.3 (d), temperature curve in Figure 4.3 (b) did not decrease monotonically, and two peaks (α and β), with value about 10 °C higher than surrounding water presented. This thermal pattern means that when raft was moving on high concentration SDS solutions (24 g-30 g), heated waves traveled backwards on the liquid surface from the laser-shot hot zone. This accounted for the main propulsive force in higher concentration SDS solutions. While in water, heat diffused from the hot spot to vicinity bulk water in all directions, resulting in surface tension gradient, though small, that drove the raft.

4.2.2 Analysis on propelling mechanism of PGF raft

During experiments, we noticed water droplets were ejected into air, especially when laser beam was shot on some shining point of PGF (where Au nanoparticles may aggregate). With a closer examination of the optical video we found tiny bubbles thrown into water fiercely from the heated spot repeatedly, as shown in **Figure 4.4**, which we think was initiated by bubble burst.





Figure 4.4 Screen-shots of optical video showing bubbles from PGF raft in solution (24 g/100 g water): (a) PGF raft was attracted at the glass container wall, with rear part facing the camera, the red circle denotes a wave of tiny air bubbles pushed downwards by bubble burst, while the blue circle denotes previously pushed bubbles floating upwards, the large bubbles pre-existed before small ones, they were actually air bubbles attached to the glass wall in solution; (b) when PGF raft is moving on the solution surface, where the green circle denoted a newly generated bubble, which then moved fast to the left (backward direction to the moving direction); (note: the shiny light is actually green laser, the color incorrectness was due to both strong intensity and the pink dye used in solution for better visual effect)

Combining evidences from both thermal images and optical video, we concluded that it was bubbles that propelled the PGF raft, on high concentration SDS solutions. As far as we were concerned, various investigations on the bubbles generated by plasmonic heating have been done ([29], Zheyu Fang et al., 2013: 1736), and the content of the bubbles could be air or vapor. According to G. Baffou and co-workers' work on microbubbles, if the bubbles were filled with air, they could last at least a few seconds, even without continuous heating after formation ([64], G. Baffou, et al., 2014: 4890).


While the vapor ones well cease to exist once the heat source was cut. Considering their short life time (<30 ms), the burst bubbles are made of vapor, instead of air.

In microscale, the rough fabric structure of raft provided sites for bubble nucleation, lowering bubble formation energy threshold. In addition, the presence of SDS molecules decreased the surface tension of liquid, made the bubble growth easier ([65], Q. Xu, 2009: 208). However, when surfactant concentration is low (<6 g per 100 g water), it was preferred for small bubbles to be formed. As a result, the presence of low concentration SDS retards the motion of PGF raft instead of promoting it (**Figure 4.2**).

With the increase of the concentration of SDS in solution, even though surface tension was the same, bubbles were more stabilized ([65], Q. Xu, 2009: 209). As a result, the thermal vapor bubble explosion was thus postponed, which means higher level of energy accumulated during the extra growth and or generation time of bubbles, when continuous plasmonic heating excited by laser illumination breaks the thermal balance. Upon explosion, the accumulated high pressure in vapor bubble pushes heated waves into bulk liquid. According to Peng's work, the heated waves (**Figure 4.3 (a**)) were a mixture of vapor and liquid. ([66], Xiaofeng Peng, 2010: 65) In addition, the vapor release process is similar to the fog-like jet-flow.

4.2.3 Verification of bubble-burst propelling mechanism

In order to extend the application of our boat as well as verify the bubble-burst propelling mechanism, we performed experiments on various liquids including ethanol (ethyl alcohol), i-propanol, n-propanol, n-butanol, and ethyl glycol. The results of the velocity are shown in **Figure 4.5** (a). Similar pattern occurs in the SDS experiments, (e. g., impulsive, fast motion) have been observed in all liquids except



ethylene glycol.



Figure 4.5 (a) PGF raft's velocities when moving on different liquids including: ethyl alcohol, n-propanol, i-propanol, n-butanol, ethyl glycol; (b) linear temperature distribution at the axis of moving raft on different liquids including: ethyl alcohol, i-propanol, n-butanol, ethyl glycol. (Note: (i) the temperature peaks presented at the rear part of raft, while lines' left parts were at front direction, indicating the temperature of the boat, and the right ones were at back direction, indicating the water's temperature gradient; (ii) peak position difference was deliberately set to avoid overlap)

	•		5 0	,		
Physical Property	Unit	Water	Ethyl Alcoho	n-Propanol	n-Butabol	Ethyl Glycol
Boiling Point	°C	100	78.3	97.8	117.73	197.3
Density	g/cm^3	1	0.7851	0.8038	0.81	1.115
Thermal Conductivity	mW/(m·K)	609	171	152.3	167	165.87
Heat Capacity	kJ/(kg·K)	4.182	2.44	2.348	2.372	2.47
Thermal Diffusivity	mm^2/s	0.1456	0.0893	0.0807	0.0869	0.0602
Surface Tension	mN/m	72.75	21.97	23.7	24.7	46.49
Viscosity	mPa∙s	1.005	1.074	1.938	3	16.1

 Table 4.1 Physical Properties of Liquids Used as Matrix for Locomotion (Credit:

 http://www.engineeringtoolbox.com)

IR data (shown in Figure 4.5 (b) explained this difference. Considering the emissivity



calibration not done for this data, ethanol and two propanol were all boiled, as the maximum temperature at the laser spot reached levels only about 10 °C lower than their boiling points. This data also matched phenomena that bubbles burst were observed on the ethanol and i-propanol. As for the high-boiling point ethylene glycol (~166°C, as seen in Table 4.1), its moving pattern was relatively slow and steady, as shown in **Figure 4.5 (a)**, which is distinguishable from that of ethanol and propanol.

As for the slow but impulsive motion of n-butanol, it is possible that boiling point was not reached, as the measured maximum temperature in **Figure 4.5 (b) is 20** °C lower than the value in **Table 4.1** (This difference is similar in the case of water, as seen in **Figure 4.3 (d)**, and water is not heated to boiling, either). Please be noted that, the thermal diffusivity is calculated by equation 4-1, with values obtained from http://www.engineeringtoolbox.com.

$$\boldsymbol{\alpha} = \frac{k}{C\boldsymbol{p}\cdot\boldsymbol{\rho}} \tag{4-1}$$

Where α is thermal diffusivity, k the thermal conductivity, Cp is the heat capacity, while ρ is the density. This not reaching boiling point could be explained by the thermal properties of the alcohols: all the alcohols under investigation presented similar thermal diffusivity (varied from 0.080 to 0.089 mm²/s), which means the level of heat accumulated near the bubble generation site should be similar, considering the same power input by laser; in addition, heat capacity of these alcohols are similar, so that the temperature induced by the similar amount of accumulated heat were quite similar, too.

Another possible reason for low performance of butanol is viscosity (3 mPa s), which is quite higher than that of ethanol or propanols (1.0~1.9 mPa s), because the viscosity played an important role as the drag force in the movement.

The different performance on ethylene glycol and n-butanol further confirmed the effect of bubble burst in driving the boat. Meanwhile, the ethanol and propanols have



similar surface tension (ranged from 21 to 25, see **Table 4.1**), which means similar driving force other than the bubble burst (that is, thermally induced surface tension gradient) should be similar.

4.3 Direction controlled motion of PGF raft

The raft could be made into various shapes due to the flexible property of the PGF. We developed some different boats with special shapes for controllable movement. When laser light was shot near the bottom of "swallow tail" of the boat, the boat moved in straight line. The structure with special geometry of the "swallow tail" restrained the heating waves. As for rotational motion, we designed the other side of boat as triangle. The boat would be swerved to other direction as long as laser light was located at edge of triangle. The trajectories of controllable movement of boat are illustrated in the **Figure 4.6**. Furthermore, as the motion of boat was regulated by the laser light, it is possible to achieve remote control on the boat through the position of laser light spot.



Figure 4.6 Direction controlled motion of PGF raft on surface of pure ethanol, left case moved in a clockwise direction, while the right one anti-clockwise, the



direction is controlled by the laser spot position. (Note: (i) the time interval was 2 seconds, and the trajectory is drawn by overlapping images in the software Photoshop; (ii) the light spots denote the starting point of motion)

4.4 Light-driven motion of PGF boat

Despite the advantage of highly-efficient photo-thermal conversion and controllable fast movement, the total energy conversion from light to kinetic energy remained low-efficient. Most of vapor generated by localized heating did not form bubbles and floated upward into air. Only small part of the vapor diffused into water in form of vapor bubble.

Therefore, we fabricated a cone-shaped PGF boat, the preparation details can be found in part 2.6. When the laser light was orientated at the PGF boat (motor), water in the chamber was heated up and vapor was generated within a second. The phase transformation in chamber contributed to dramatic pressure accumulation, which was released periodically with burst of hot, compressed mixture of water and vapor from the tip end and propelled the boat forward. During the heating and ejection process, the PGF fibers kept drawing water in the chamber, guaranteed a continuous evaporation and propulsion. Furthermore, the boat shell reduced the drag on different liquids, improving the applicability in various environment.

To our expectation, the PGF boat outperformed the PGF raft. The velocities in different solutions are improved apparently, which is shown in **Figure 4.7 (b)**. The temperature distribution pattern of the PGF boat is distinctly different from that of PGF raft on water (See **Figure 4.7 (c)**). The high temperature ejection visualizes trajectory of capsuled-PGF boat in IR images. In the capsuled boat, PGF was entirely heated up not only because of its smaller size but also because that vapor chamber



was there to limit heat conduction to bulk water. Moreover, when heated vapor was ejected out, the propelling force was more focused by being more linear with the boat's axis; while bubble burst force that driving the raft was not focused enough, which was marked by heated waves in temperature pattern as discussed before.

Thanks to the ability to reduce waste heating and focus force for propulsion, the cne-shaped PGF boat even performed beyond our expectation. While the PGF raft was moving slowly in water and low concentration SDS solution (<6 g), the boat could move quite fast on both water and those low surface tension gradient surface.



Figure 4.7 (a) schematic of the model of the cone-shaped PGF boat, the white end is boat's front covered by stretched parafilm, the cone shell is made of common 1 mL pipette tip, PGF paper (dark colored) was attached at the inner wall of the



shell; (b) the PGF boat outperformed the PGF raft in mobility on SDS solution, the concentration of solution was denoted in the lable; (c) the IR image of moving PGF boat, the tail like heated waves were ejected from the boat end

4.5 Summary of plasmonic heating-powered swimmers

In despite of the background that plasmonic heating is widely researched for its applications in biomedical domain, like photo-thermal therapy and drug delivery, studies focused on the possibility in direct solar energy harvest (other than assisting photovoltaic process) is rare. Meanwhile, self-powered or light powered small motors have shown great potential in areas like environmental remediation, sensor, and electricity generation. As a result, we carried out work on fabricating the plasmonic photo-thermal swimmer. Based on the PGF film introduced in chapter 3, we developed two types of light-driven plasmonic swimmers in this chapter (PGF raft, and PGF boat). respectively. When illuminated by laser beam, the raft could generate plasmonic heating at the spot point, this asymmetric thermal stimuli not only induced surface tension gradient due to Marangoni effect, but also enabled bubble generations and burst, which was demonstrated to be the major driving force for the boat. To verify the main propelling force, experiments of light-driven locomotion were carried out on different liquids, including water, physically similar alcohols, ethylene glycol, and SDS aqueous solution with different concentration ($6 \sim 30 \text{ g}/100 \text{ g}$ water), By comparing the moving modes and thermal patterns of different liquids, the bubble burst mechanism for powering the PGF raft was established. In addition, with the flexibility to tailor its shape, moving direction of PGF raft could be controlled by the incident light (straight line and circle). However, the energy conversion efficiency is found to be low as heated waves could diffuse unlimitedly. Therefore, to increase the total kinetic energy converted, the cone-shaped PGF boat was developed as an optimization design of the PGF raft. This Boat, by confining vapor in the tip-shell made vapor chamber, reduced



heat loss to the bulk water, and accumulated pressure to generate fast and continuous ejection of hot vapor waves backwards. In fact, his PGF boat moved faster than the PGF raft, and its surprising ability to move fast on water surface also revealed the potential of plasmonic heating in small motor application, which is not receiving enough attention currently.

Chapter Five Conclusion

5.1 Summary

In recent decades, Plamonic materials have raised surge in research and development for their multitudinous potential in areas including nanophotonic, optoelectronic, photocatalytic, photovoltaic, spectroscopy, sensing, biomedical, energy and environment. Among all these application possibilities, utilizing the highly-efficient photo-thermal conversion of nanoplasmonic materials in heating is relative less focused. When it comes to the usage in solar-driven evaporation, where plasmonic materials were used as light absorber for desalination, power generation and sterilization, previous theoretical studies done by scientists like Halas ([31], Oara Neumann et al., 2012: 42) and Richardson ([57], H. H. Richardson, 2009: 1139) had proved the viability of this concept, and paved the way for developing solar-driven evaporation system.

Nonetheless, their solution based system with dispersed plasmonic nanoparticles, though ideal as a model for fundamental research, is not practicable for real-life application. This was because not only the intrinsic heat loss when generated vapor travel through cool liquid upward to surface, but also the great cost of materials, which is expensive noble metals. In endeavor to deal with these problems, our group fabricated free-floating AuNP film by self-assembly of gold nanoparticles. This film



was demonstrated to be more efficient in evaporation thus more cost-effective in previous work. However, such film is limited for industrial application owning to its fragility and still large amount of heat loss into underlying water. In addition, when it comes to practicable materials, expectations on not only the mechanical strength, but also the stability under cycling usage and the manufacturing convenience are the common prerequisite. These requirements became the challenges facing the evaporation system we aimed to develop.

Encountering with these challenges, we were searching solutions in nature. Enlightened by natural evaporation system as human skin, where enough mechanical support is provided by the tissue underlying surface, and thermal insulation is evolved for a fast energy conversion for better cooling, we have fabricated the paper-based gold nanoparticle film (PGF) ([33], Y. Liu, S. Yu, R. Feng et al., 2015: 2768). Under the following abstract guideline: the evaporation should be supported by materials with good thermal insulation and water-permeable, we have taken air-laid paper as the supportive layer and formed the successful bilayer evaporation film. The PGF's features are: i) fibrous microstructure enabled multi-scattering at surface for better light absorption; ii) good thermal insulation due to the reduced heat conduction as well as heat convection; iii) hydrophilic substrate along with capillary force enabled by porous structure to ensure continuous water supply. As for the aforementioned challenges, PGF also have good solutions: i) proved convenient to be fabricate in large-scale; ii) demonstrated endurance under many times of reuse; iii) readiness to install in existing evaporation system like desalination basin without assistive equipment.

Despite the high level efficiency achieved by the bilayer PGF film, another scientifically interesting aspect was found in face of the disagreement on the wettability of such double-layered solar-driven evaporation, because Gang Chen's group ([40], H. Ghasemi et al., 2014: 4449) reported a hydrophilic top layered carbon-based



evaporation system that could generate solar steam in an efficient manner, while the top layer of PGF, that is, the self-assembled AuNP film is hydrophobic.

In a temptation to optimize the PGF film, as well as to understand the influence of wettability on this evaporation system, we once again learned from nature in our film design. It is reported that, water on the hydrophilic leaves in rainforest plants evaporate faster ([49], K. Koch & W. Barthlott, 2009: 1487), in prevention of growth of microbes on it. Inspired by this phenomenon, we assume that the hydrophilicity has an influential role in controlling the evaporation rate of film system. This time, Anodic Aluminum Oxide (AAO) film was utilized, considering its convenience for chemical modification on surface ([34], S. Yu, Y. Zhang, H. Duan et al., 2015: 13600).

As a result, we fabricated the AAO-based AuNP films (AANFs), and modified both the top layer and bottom one's wettability, making them hydrophilic or hydrophobic, independently. By comparing the evaporation rate to the reference substrate, we came to the conclusion that the top layer's wettability has no effect on the evaporation system, while the bottom layer is dominant in tuning the evaporation efficiency. Closer examination by conducting evaporation experiments with focused strong light has revealed the mechanism behind. The reason why hydrophobic-AAO based film evaporate slow is that air bubbles were formed within and even under the hydrophobic substrate, which insulate heat conduction to the evaporative water surface and impede the upward vapor transportation; while the hydrophilic-AAO supported films are not vulnerable to this problem as their evaporation occurs above the AAO film.

In the AANF evaporation experiments with strong light, we have witnessed the fierce periodical bubble formation and burst, which indicating the potential for plasmonic heating in powering kinetic movement. At the same time, we also noticed that plasmonic heating-based small motors have not been reported yet. Therefore, we



devised the plan to fabricate a plasmonic materials-based swimmer, whose locomotion could be remoted triggered and controlled by light.

Consequently, we developed two kinds of swimmers, the plastic foam floated PGF raft, and the pipette tip capsuled cone-shaped PGF boat, with the latter as an optimized design for the former. The PGF raft, is responsive to laser illumination at a power density of 350 mW/mm². In fact, it could move in a speed of several millimeters per seconds on water surface (self-length was about 10 mm). We also changed the liquid matrix to perform the swimming. Once again, we were led by disagreement of phenomenon with previous publication. According to Frechet's work ([62], David Okawa et al., 2009: 5396), the photo-thermal conversion induced surface tension gradient shall be diminished with the addition of surfactant, while our data showed that further increase of surfactant concentration raised the moving velocity instead of reducing it. What was more, the swimming pattern evolved from a slow but continuous one to a fast but impulsive one, when the SDS's concentration was as high as 24 g/100g water. These phenomena indicated another driving force for our raft. After careful examination of the recorded optical video along with the infrared one, we found interesting temperature distribution pattern that influenced the movement, which finally lead to the unique finding of bubble-burst propulsion mechanism. To verify our finding, we also performed experiments on selected liquids including ethylene alcohol, i-propanol, n-propanol, n-butanol as well as ethylene glycol. Fortunately, results of these comparison experiments confirmed our hypothesis. What's more, by tailoring the shape of the PGF raft, direction controlled movement was also realized.

Nevertheless, as the heated vapor and liquid would release or diffuse in all directions, the total energy converted into kinetic energy by our PGF raft is limited. To take good use of the localized heating generated by laser illumination on PGF, we fabricated the second swimmer, the PGF boat. To our expectation, it outperformed the PGF raft on



various liquid. In addition, the PGF boat could move fast on water surface, which is promising for further application.

5.2 Prospect

In this study, the (PGF) is demonstrate to be promising in desalination, after comparing with the present commercial system in a simulated desalination experiment. Therefore, it is expected that PGF could be one day used in real-life industrial production of fresh water, or power generation. However, some technical problems should be overcome before the application. i) the laboratory level synthesis is not suitable for large scale manufacturing, in terms of both cost and complexity of procedure; ii) the erosion and toxicity from the sea-water environment; iii) salt crystallization on the top surface of the PGF that will block the light and reduce productivity.

As for the AANF, investigation on the impact of surface chemistry on its evaporation performance has provided a design guideline for future development of solar-driven evaporation system. However, this guideline is doubtable, as the substrate under investigation was limited to AAO. The could narrow the applicability of the mechanism, considering the unique branched nano-channel structure of AAO film. Therefore, for a better understanding of the evaporation process occurs in such solar-driven bilayer evaporation system, further study on different substrate and light-absorbing plasmonic materials and the coupling effect between them is needed.

When it comes to the PGF swimmers, they have proved the feasibility of using plasmonic materials to drive locomotion. However, this part lacks of enough scientific insight, where mechanism analyzing is ideal and static (ignoring the influence of temperature variance on physical properties of matrix) and not cross-examined. The next step of this research topic should firstly focus on the analysis on forces on the



swimmer during moving, which would generate stronger prove on the bubble-burst mechanism.

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