ESTUDO DE MATERIAIS DE BAIXO CUSTO PARA A MELHORIA DA DESSALINIZAÇÃO SOLAR DE ÁGUA DO MAR

STUDY OF LOW COST MATERIALS FOR THE ENHANCEMENT OF SOLAR SEAWATER DESALINATION

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RESUMO

A evaporação de água altamente eficiente sob iluminação solar é de importância fundamental para o desempenho de destiladores de dessalinização de água do mar. A eficiência da geração de vapor térmico aumenta acentuadamente através do isolamento térmico das camadas da superfície da água irradiada da água subjacente a granel. Estudos recentes mostraram que o uso de nanomateriais com propriedades da superfície plasmática leva a aumentos de eficiência térmica adicionais. Apresentamos resultados experimentais de experiências in situ de evaporação de água realizadas em condições ambientais normais. O uso de estruturas flutuantes em camadas em sanduíche (SLS), pode aumentar as taxas de evaporação da água de até 43% quando comparadas às taxas obtidas para superfícies de água simples com um volume exposto à luz subjacente. A importância do transporte de água para a superfície SLS exposta à luz e, portanto, o design SLS é crucial, como demonstramos com um conjunto adicional de experiências. A eficiência de evaporação aumenta quando as camadas de pó impregnadas com água de fortes absorventes de luz estão presentes na superfície SLS iluminada. Os resultados comparativos obtidos com camadas de pó úmido de grafite e compostos de rocha ígnea mostram que, nas mesmas condições experimentais, a taxa de evaporação da água pode ser aumentada em até 470% em comparação com as superfícies de água descoberta.

ABSTRACT

Highly efficient water evaporation under solar illumination is of key importance for the performance of seawater desalination stills. Thermal vapor generation efficiency increases markedly through thermal insulation of the irradiated water surface layers from the underlying bulk water. Recent studies have shown that the use of nanomaterials with plasmonic surface properties lead to additional thermal efficiency boosts. We present experimental results of in situ water evaporation experiments performed under normal ambient conditions. The use of floating sandwich-layered structures (SLS), can increment water evaporation rates of up to 43% when compared to the rates obtained for plain water surfaces with an underlying light-exposed bulk. The importance of water transport to the light-exposed SLS surface, and hence the SLS design is crucial, as we demonstrate with an additional set of experiments. Evaporation efficiency increases when water impregnated powder layers of strong light absorbers are present at the illuminated SLS surface. Comparative results obtained with wet powder layers of graphite and igneous rock compounds show that, under same experimental conditions, the water evaporation rate can be boosted by as much as 470% compared to bare water surfaces.

Keywords: *Desalination, Nanomaterials, Evaporation, Solar Stills, Igneous Rock, Graphite*

INTRODUCTION

Water is key to sustainable development. Water resources, and the range of services they provide, underpin poverty reduction, economic growth and environmental sustainability. From food and energy security to human and environmental health, water contributes to improvements in social wellbeing and inclusive growth, affecting the livelihoods of billions (UN-WWAP, 2015).

About 97% of the earth's water is salt water in the oceans and only 3% (about 35 million km³) is fresh water contained in the poles (in the form of ice), ground water, lakes and rivers, which supply most of human and animal needs (Fig.1). Many of these freshwater systems are directly threatened by human population growth, agriculture, industrialization, and contamination. They also stand to be further affected by anthropogenic climate change (NASA Climate Change Webpage, 2017), (Haddeland *et al.*, 2014) which has the potential to disrupt patterns of water availability that have motivated human decisions with long-term implications, such as city locations, urban structure, reservoir placement, and water system design (Bates *et al.*, 2008).

Figure 1. Surface water distribution on planet Earth. Freshwater represents less than 3% of the planet's total water resource. Nearly 70% of the fresh water is frozen in glaciers, permanent snow and permafrost. Thirty percent of all fresh water is underground, most of it in deep, hard-to-reach aquifers. Lakes and rivers together contain just a little more than 0.25% of all fresh water, or less than 0.01% of the total water (Gleick, 1993).

Presently, over one-third of the world's

population lives in water-stressed countries and by 2025, this figure is predicted to rise to nearly two-thirds (Service, 2006). Water scarcity is one of the most serious global challenges of our time, despite of being one of the most abundant resources on earth, covering three-fourths of the planet's surface. Even regions traditionally considered water-rich have difficulty providing sufficient fresh water (Supply *et al.*, 2011). Pollution and rising costs associated with treating and distributing new sources of water are among the largest issues facing water planners (UNESCO, 2012).

The only methods to increase water supply beyond what is available from the hydrological cycle are desalination and water reuse (Shannon *et al.*, 2008). Of these, seawater desalination offers a seemingly unlimited, steady supply of high-quality water, without impairing natural freshwater ecosystems. Desalination of brackish groundwater is also an option to augment water supply for inland regions; however, the management of brines from inland desalination plants represents a major challenge.

The major desalination technologies currently in use are based on membrane separation, e.g. via reverse osmosis (RO) and thermal distillation (multistage flash and effect distillation), with RO accounting for over 50% of the world's installed capacity (Zotalis *et al.*, 2014)(Zhou and Tol, 2005).

Conventional thermal desalination processes are inefficient in their use of energy and suffer particularly from corrosion, as well as scaling that also affects RO. Even where fuel is readily available and low-cost, high capital and operational costs limit adoption. Therefore, the market share of large conventional thermal desalination plants will probably decline (Shannon *et al.*, 2008), (S. P. Chaurasia, Sushant Upadhyaya *et al.*, 2011). In a mid-term future, massive seawater desalination through thermal processes could be achieved by using the heat energy stored in the earth crust - is sufficient to cover our present energy needs for approximately 50 million years. The technology to harvest this enormous energy source, for example through Enhanced Geothermal Systems (EGS) is technically feasible, but still needs to be developed (Idaho National Laboratory, 2006).

For family and very small community systems in remote locations, especially in the developing world, solar seawater distillation, i.e. freshwater generation with solar stills, has great

potential in coastal areas with limited access to other energy sources than (Bourouni, Chaibi and Tadriss, 2001)(Fath, 1998).

Solar seawater distillation

Solar powered fresh water production has been used since ancient times. Phoenician sailors (1500 BC–500 BC) which travelled along the Mediterranean Sea were already making use of the solar thermal radiation to convert seawater into fresh drinking water. The classic Greece philosopher Aristotle described the water cycle in nature and remarked that when salt water turns into vapor and the vapor condenses, it does so in the form of fresh water (Ross, LL.D. and Smith, 1931). Since its introduction by Arab alchemists in 1551 (Ferrario, 2007) distillation technology has been applied to fresh water production over centuries. The number of today's existing different solar still designs is overwhelming (Dsilva Winfred Rufuss *et al.*, 2016), (Kalogirou, 2005). One of the major drawbacks of such systems is its limited freshwater production capacity, which according to literature exhibit a desalination capacity, generally below 0.6 l of freshwater per hour and m^2 of sun-exposed area, at an irradiance of 1 KWh^{-1} . (Sivakumar and Ganapathy Sundaram, 2013).

Recently however, new material approaches driven by the emergence and proliferation of Nanoscience and Nanotechnologies have brought up a significant potential for efficiency improvements of solar stills. As depicted schematically in Fig 2, nano-improvement areas for solar stills are manifold: nanomaterials can markedly optimize thermal insulation (reduction of heat losses (Roco, Mirkin and Hersam, 2010), (Nikita Aigner, 2011), improve water pre-treatment and post-treatment, optimize water condensation (Yoon *et al.*, 2012), (Chen *et al.*, 2016) and improve solar light harvesting with advanced optical materials (McClean-Iltén and Zerulla, 2016).

A major breakthrough in light induced water evaporation research with nanomaterials has been achieved by the recent discovery that evaporation efficiency can be significantly enhanced by the use of plasmonic nano material surfaces.

Figure 2. Schematic presentation of conventional solar still, showing potential areas for nano-improved efficiency gains

In this work, we focus on this latter discovery, by developing new approaches for enhanced light-induced evaporation at thermally insulated wet material layers with extraordinary light absorption properties. This approach targets one of the main reasons for the observed limitations of conventional solar still desalination capacity where only a small fraction of the incident solar light is converted into the necessary translational energy of water molecules needed for the phase change.

In classical thermodynamic approaches (Ni *et al.*, 2016), the water evaporation rate per unit area generated by the ambient solar flux are calculated as (Eq. 1).

$$\text{(Eq. 1)}$$

Where m is the mass flux or water evaporation rate [Kgs^{-1}], A is the surface area of the water facing the sun [m^2], q_{solar} is the solar flux measure in [Wm^{-2}] and h_{fg} is latent heat of evaporation of water used in widespread literature (Datt, 2011), with a value of 2.260 MJkg^{-1}

(Eq. 1) leads to a maximum water evaporation rate of $4.4 \times 10^{-4} \text{ kgm}^{-2}\text{s}^{-1}$, or $1.58 \text{ kgm}^{-2}\text{h}^{-1}$, for a water surface of 1 m^2 that is exposed to a solar flux of 1000 Wm^{-2} (1 sun), for an ideal system with no heat losses and with a solar vapor generation efficiency η_{thermal} of 100%.

is defined in literature as:

(Eq. 2)

In real systems however, heat losses however do occur. Water evaporation is a surface process and only water molecules at the thin water-air interface can be driven into vapor phase through their kinetic energy state. Heating of the bulk water transfers energy to water molecules which do not directly participate in the evaporation process, inducing changes in their vibrational states and/or relaxing attractive forces between these bulk molecules. Other heat loss contributions include convection losses to the gas phase, as well radiation losses at gas/liquid and liquid/solid interfaces (see Fig 3). These heat losses reduce solar vapor generation efficiencies for sun exposed water surfaces significantly, leading to low $\eta_{thermal}$ values (below 40%) at solar fluxes $q_{solar} = 1000 \text{ Wm}^{-2}$ (Bae *et al.*, 2015), (Morciano *et al.*, 2017).

Figure 3. Solar energy dissipation of irradiated water surface. Left: Energy losses of irradiated bare water surface. Right: Energy dissipation on water-impregnated SLS layer. Reduction of conductive and radiation heat losses result into a noticeable gain of energy available for inducing phase changes, resulting in a boost of solar vapor generation efficiency $\eta_{thermal}$. Figure adapted from (Ni *et al.*, 2016)

The reduction of conductive heat losses to the bulk water can be experimentally achieved through isolation of the bulk water layers from sun radiation, for instance by floating structures of porous, water-absorbing materials as shown in Fig. 4. which significantly reduce the thickness of the sun-exposed water layer and insulate bulk water from the hot water regions at the surface (Neumann *et al.*, 2013).

If the sun-exposed area of the floating is

covered with light absorbing materials, heat energy can be localized close to the water surface and can induce energy localized non-equilibrium phase changes, generating steam while the surrounding medium remains cold (Boriskina, Ghasemi and Chen, 2013). As a result, solar vapor generation efficiency can be significantly increased.

MATERIALS AND METHODS

Seawater evaporation experiments were performed under laboratory conditions: 21°C regulated by air conditioning system, 930 hPa ambient pressure and 65% relative humidity. A 3D printed water container (75x75x50mm) with a square surface area of $5,6 \times 10^{-3} \text{ m}^2$ (Muñoz *et al.*, 2016) was filled with 250 ml of seawater obtained from the Pacific Ocean coast of El Salvador (Xanadú, La Libertad). A floating SLS structure, consisting of floater, water-absorbing material (paper tissue) and finely ground light-absorbing material (see fig. 4) was placed on top of the water surface.

Figure 4. Schematic view of evaporation cell used for evaporation experiments. Left: Section of evaporation cell with floating Sandwich Layer Structure (SLS). The SLS consists of a Polyurethane floater covered with water absorbing paper (gray). The top surface of the paper is covered with thin layers of light absorbing materials investigated in this study. Right: SLS side view. Water transport occurs by capillary action from the container to the SLS surface, wetting the light absorbing, evaporation enhancing material

The top of the floating SLS, *i.e.* the wet light-absorbing material surface, was exposed to the light emitted by a 100W LED source (Unbranded, Luminous Intensity: 8000-9000lm, eBay), placed 12 cm above the evaporation surface. Mass losses of the water container were

measured with an OHAUS scale with 0.01 g precision (Fig. 5). Measurements of the surface temperature of the light-absorbing materials were performed with a portable FLUKE 62 MAX infrared thermometer.

Figure 5. Schematic view of experimental set-up for weight loss measurements. Seawater in the container is irradiated with a 100W LED source, causing evaporation and thus mass loss of the water container. The corresponding weight loss transients of the container are recorded with a precision scale. The setup includes a cover, designed to avoid illumination of the scale and to protect the evaporation surface from convective airflows generated by laboratory air conditioning system and the LED-cooling fan.

The LED irradiation source used in the in situ experiments has an active cooling system, consisting of a heat sink blown by a fan. In order to avoid precision losses of the weight loss measurements the experiment was enclosed in a wind-insulating dark chamber with a glass-covered square opening on top. In order to avoid temperature gradients in the underlying balance, the opening was positioned at the distance at allowed the light from the LED source to travel through the glass surface and illuminate solely the entire surface of the floating sandwich-structure top layer (Fig. 6).

All evaporation experiments were performed during a time period of one hour, during which weight loss and temperature were recorded at 5 minute intervals.

Figure 6. Experiment of seawater evaporation, inside there is a 75x75x50mm container, Water is irradiated with a 100W LED light source. Weight loss induced by water evaporation and SLS surface temperature are measured at 5-minute intervals for a duration 1 hour.

RESULTS AND DISCUSSION

Previous studies (Christoph, Hernández, Muñoz, & Ventura, 2016) have shown that the evaporation rate of light-exposed bare seawater surfaces (without SLS), measured under the prevailing temperature, pressure, humidity conditions and the radiation intensity described in the experimental section, are in the order of $0.126 \text{ Kg m}^{-2} \text{ h}^{-1}$.

In a second set of experiments, performed under identical experimental conditions, of bare water impregnated SLS surfaces, i.e. without the presence of light-absorbing material layers, water mass loss due to evaporation was measured for different types of cellulose based water absorbing tissues (see Fig. 7)

The results of these experiments clearly show a SLS-induced increase of the water mass loss, even at absence of light absorbing material layers at the light exposed surface. This effect is

attributed to heat insulation of the floating structures, which losses to the underling water in the container. We also observe marked differences between the used paper types, i.e. commercial bond paper (Hammermill, Fore Multipurpose®) and paper towel tissues (Aurora®). Significantly higher evaporation was observed for the paper tissue, demonstrating the important role of fluid transport from the underlying water bulk to the SLS surface for obtaining optimized solar vapor generation efficiencies (Canbazoglu *et al.*, 2016), (Ito *et al.*, 2015).

Figure 7. Seawater evaporation mass losses (evaporation rates) expressed in evaporated water per square meter and hour, obtained, at same experimental conditions for a bare water surface (a), and at the surfaces two different water-absorbing materials of the SLS layer (b) and (c). The results show that the introduction of an isolated floating structure lead to a significant enhancement of water evaporation, due to the reduction of heated losses to the underlying water bulk. Different water evaporation rates observed for the dissimilar water absorbers also indicates the importance of fluid transport through capillary action from the bulk water in the container to the SLS surface

A third set of in-situ experiments was performed with top SLS layer consisting of different light-absorbing materials, including graphite powders used in previous studies (Christoph *et al.*, 2016) and finely ground magnetic powder extracted from crushed igneous rocks and finely ground beach sand (Costa del Sol, El Salvador). Particle diameters of these materials, measured by optical microscopy, were in the order of 5-10 microns.

Figure 8. Infrared reflection spectra of igneous rock powders with very similar bulk-rock compositions (Carli, Serventi and Sgavetti, 2014)

The results for these experiments are depicted in Fig. 8. We report the following findings:

- Graphite layers enhance water evaporation by a factor of two to three, when compared to bare water surfaces. This findings is in good agreement with our previous studies (Christoph *et al.*, 2016).
- SLS top layers of igneous rock powder components increase water evaporation rates by 120%, when compared to the rates obtained with graphite powders. We attribute this effect to the broader IR absorption band of the used magnetic powder shown in Fig. 8.
- We observe good correlation between the measured evaporation rates and the corresponding surface temperature of the irradiated SLS surface. High surface temperatures translate to high evaporation rates. This observation is consistent with basic thermodynamic considerations, i.e. the fact that at increasing temperature larger numbers of water molecules have sufficient kinetic energy to overcome the attractive forces prevailing in the liquid phase. Other explanations of our observation with magnetic particles, such as the presence of localized hot spots induced by surface plasmons need further experimental confirmation.
- For the case of the magnetic particles, we

also observed that the time needed to reach the maximum temperature of the irradiated surface is markedly lower than for the case of graphitic materials.

Figure 9. Comparative graph of evaporation rates and maximum SLS surface temperatures obtained with different light absorbing SLS top layers. The data shows good correlation between the measured evaporation rate, and the maximum surface temperatures of the top layer achieved during 1 hour of irradiation.

Figure 10. Comparative results of water evaporation experiments, where mass loss rates were measured at different light intensities at uncovered seawater surfaces, and SLS surfaces with graphite and igneous rock powder components. The relative mass loss increase is highest for graphite, whilst igneous rock powder components show the largest mass loss rate was measured for igneous rock powder components.

CONCLUSIONS

Light induced water evaporation can be significantly increased when using thermally insulated wet powder layers.

In situ experiments performed with floating SLS structures showed that igneous rock powder components doubles the light induced water mass loss measured at graphite powder surfaces, representing a fivefold increase of the corresponding values obtained for uncovered bulk water.

We did not observe enhanced with increasing light concentrations. We conclude that this might be due to the relatively large average particle sizes as well considerable fluctuation of their sizes and shapes. Additional experimental evidence is needed to support this assumption.

It must be underlined that the nature of the heat transfer between the nanoparticle and vapor/liquid phases of water at the nanoscale (i.e., diffusive or ballistic), the mechanism of vapor phase nucleation, their influence of pressure field on heat transfer, the growth kinetics of vapor phase, vapor-induced particle buoyancy, fluctuations of absorbed energy due to

Fig. 10 shows the result of a fourth set of *in situ* experiments, where evaporation measurements were performed at different light concentrations, by varying the distances of the LED lamp relative to the SLS top surface. Comparative mass loss measurements were performed at lamp distances of 12 cm and 6 cm. Assuming that light intensity at half distance is approximately 4-fold, the corresponding mass loss increase should be at least the same, assuming that $\eta_{thermal}$ remains unchanged. Our results however show that at double light intensity the mass loss increases only by a factor of 2.0 (water and igneous rock powder components) and 2.7 for the case of graphite powder.

Results from other authors, obtained at irradiated plasmonic materials, including Au and Ag nanoparticles and graphene, report an increase of $\eta_{thermal}$ with increasing light concentration, which is attributed to the presence of surface plasmons. Our results, obtained with micron sized powder grains do not indicate such finding, suggesting no plasmonic activity, and it remains to be confirmed whether nanoparticles of the igneous rock powder components used in our experiments would prove to show said effect.

formation of vapor phase and radiation between the phases are among the topics that needs to be explored to gain a better understanding of water evaporation at irradiated surfaces (Boriskina, Ghasemi and Chen, 2013).

As a next step, quantitative experiments will be performed under in vivo conditions. SLS enhanced solar distillers with light capturing areas in the order of square meter are planned to be placed in coastal regions of El Salvador and monitored via IoT technology (Villanueva, Bausells and Brugger, 2016).

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