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Metamaterials for optical and MW applications

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**Final Report** 

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#### **1.0 SUMMARY**

In this report, we developed smart optical metamaterials which integrate solid mechanics with transformation optics to realize variable-index macroscale optical devices with inhomogeneous gradient index distribution. We employed transparent compressible silica aerogels to redistribute the desired index distribution by compressing with 3D-printed pressing molds. Based on self-aggregated nanowire structures, we achieved ultrabroadband perfect absorbers in the range from 0.3 to  $17\mu$ m by versatile metal coatings. These large area few µm-thick films are used to get highly efficient solar steam generation and desalinations. Nanoporous structures are used to achieve high performance sensors with plasmonic behaviors. By using plasmonic metamasks, the image resolution is enhanced for the photolithography in the far field.



#### **2.0 INTRODUCTION**

Figure 1. A schematic of the applications of thermoplasmonics.

Thermoplasmonics is a new research field that utilizes the thermal energy from an absorption by plasmonic resonance. The plasmonic resonance absorption occurs in metal or metaldielectric structures which have sharp absorption peak caused by localized surface plasmon between metal and dielectric interactions. The absorption wavelength range and position can be tuned as target applications by controlling the shape and composition of the thermoplasmonic structures. Numerous researches are making progress for the application of thermoplasmonic in diverse fields such as medical and imaging. In this research, we will develop the thermophotovoltaic reactors and radiative cooling system to maximize thermoplasmonic effect.



Figure 2. A schematic concept of thermophotovotaics using the optimization of selective emitters.

Metamaterials, made of artificial atoms with metals and dielectrics, can be engineered to have ultimate material properties that have not been found in nature, such as negative refractive index, perfect absorbers, blackbody, selective emitter, cloaking or superlensing, so on. By choosing appropriate materials of intrinsic properties (specific metals or dielectrics), design of shapes (unit cell patterns), and some periodicity (crystal lattice structure), we can engineer desirable material properties that cannot be naturally available.

The plasmonic resonance absorption in metal or metal-dielectric structures can be changed by structural parameters. The frequency selective thermoplasmonic structure using dielectric or metal-dielectric nanowires can easily control the absorption wavelength range and position. In this research, we develop the thermoplasmonic structures which have different resonant spectrum range for solar vapor generation, thermophotovoltaic (TPV), and radiative cooling system. This novel thermoplasmonic structure can be achieved from nanowires fabricated by commercializable large-scale fabrication processes. While the same basic fabrication method is used for the nanowires, its optical properties easily change by applying small changes, such as the metal deposition. As the optical properties change easily, various applications become possible.



Figure 3. A fuel based micro thermophotovoltaic system.

A design for a mm-scale 10 W TPV propane-powered micro-reactor developed. A key component in this device is the selective emitter made with tantalum PhC. The typical efficiency of the device ranges from 0.5% to 2.2%, depending on whether all key design elements are included. In all cases, the system requires a silicon MEMS reactor for catalytic combustion of fuels such as propane and butane, and a GaInAsSb photovoltaic diode for efficient conversion of above-gap photons into electricity. An additional design element for improved performance is a 1D PhC emitter grown on the surface of the MEMS reactor to suppress mid-IR radiation. Finally, a low-power maximum power-point tracker can be added to ensure the maximum power is always generated under varying conditions. With some relatively small tweaks to the existing 2.2% design, it has been predicted that an efficiency of 5.3% could be achieved. Furthermore, if one raises the operating temperature to 1,200 K, efficiencies as high as 21.7% would theoretically be achievable.



Figure 4. A solar based thermophotovoltaic system.

Solar thermophotovoltaics can be seen as an alternative to solar photovoltaics and solar thermal power generation. In terms of device architecture and operating principle, solar TPV is identical to the combustion TPV except that the emitter is heated by the sun light instead of burning chemical fuel. One of the unique challenges of solar TPV is designing the suitable solar absorber, and optimizing it to work in tandem with the TPV selective emitter and diode.

Selectivity is needed because there is a tradeoff between absorbing sunlight and re-radiating infrared radiation, which fundamentally derives from Kirchoff's law. Optimal design for selective solar absorbers has been discussed extensively in previous literature.

However, the maximum efficiency of the TPV back end will increase with temperature. This implies that for a given solar concentration, there will be an optimal operating temperature and TPV bandgap where the product of these two components is at a maximum. Due to experimental constraints, previously built solar TPV systems, have diverged substantially from these values. It is reported that 2% efficient operation is observed at relatively modest concentrations and temperatures using germanium indirect bandgap photovoltaic cells. Replacing those solar cells with a higher-performance III-V TPV cell such as GaSb would by itself roughly double the expected efficiency. Other desirable changes would come from PhC-based designs for more wavelength-sensitive selective solar absorbers, selective emitters, and filters for photon recycling. Combining all those elements and optimizing yields a theoretical prediction of 44% using a tandem junction for 100 sun concentration at 1,000 K, and up to 50.8% efficiency for a single junction under 46,200 suns at 2,360 K. Overall, the photonic design approach is predicted to yield up to an order of magnitude enhancement in the performance of these systems. Furthermore, these projected efficiencies exceed the Shockley-Queisser limit for single-junction photovoltaic cells under equal solar concentrations.

One of the most recent reports describes a 3.2% efficiency in a device that combines carbon nanotube absorber and PhC emitter for optimal performance. The device construction and operating principle are shown the figures below. Briefly the sun light is illuminated on the absorber made of carbon nanotubes. The heat is then emitted on the emitter side which is composed of a 1D PhC. The thermal radiation emitted from the PhC surface drives the InGaAsSb PV cell for electricity generation. This device with 3.2% efficiency represents the current state-of-the-art, highlighting the challenge of spectral engineering and thermal management. The current proposal will address these challenges by developing a novel plasmonic PhC structure, as described earlier.



Figure 5. The absorption cross section of the gold nanoshells.

In recent studies, metal nanoparticles or carbon based materials have been widely used for

photo-thermal light harvesting because these materials are highly light absorptive. Metal nanoparticles has tunable characteristic in their absorption spectrum by controlling the size of the particles or using metal-dielectric shell structure. Thus, the absorption cross section can be tuned to overlap the solar spectral irradiance, which makes efficient light harvesting from the sun. (Neumann et al., *ACS Nano* 7(1) 42-49(2013))



Figure 6. Solar steam generation with a structure of carbon foam.

Carbon based materials are almost blackbody which shows >97% absorptivity in the solar spectrum (250-2250nm). H. Ghasemi et al.(2014) have reported that they achieved solar thermal efficiency up to 85% by using graphite/carbon foam double layer.

In this research, we investigated the heat generation from photo-thermal effect of the metamaterials and metasurface coatings. Photo-thermal effect refers to a phenomenon that light energy is converted into thermal energy by the photo-excitation of materials. By using a specially designed metamaterial, which confines the light in a few micro meter thick, heat energy converted from the light is also highly localized in a small volume.

Although metal nanoparticles or carbon based materials are high performance photo-thermal materials, they have some weaknesses for the practical use. The solar thermal conversion efficiency of the metal nanoparticles was only 24% in the study of Neumann et al. Also, low melting point (~1000 $^{\circ}$ C) of the metal nanoparticles hinders their use for devices working at high temperature. Carbon based materials are fragile to use in harsh environment such as windy desert. These approaches use rigid bulk materials which are not easily feasible or flexible in real applications.

To overcome those disadvantages, we develop high efficiency, mechanically strong photothermal materials, flexible thin film membranes by using metamaterials and metasurface coatings.

#### 3.0 METHODS, ASSUMPTIONS, AND PROCEDURES

#### 3.1 Smart metamaterials

By integrating solid mechanics and transformation optics, we develop metamaterials whose properties change the property correspondingly with the elastic deformation. We consider a porous material with the volume fraction parameter of dielectric  $(f_d)$ , the effective permittivity ( $\varepsilon_{eff}$ ) is given as  $\varepsilon_{eff} = \varepsilon_d f_d + \varepsilon_a f_a$  from the effective medium theory.

If we compress the material, the deformed effective permittivity is changing to  $\varepsilon'_{\text{eff}} = \varepsilon_{\text{d}} f'_{\text{d}} + \varepsilon_{\text{a}} f'_{\text{a}}$ . By the relationship of  $f'_{\text{d}} = f_{\text{d}} \frac{A}{A'} = f_{\text{d}}/J$ , the effective permittivity ratio becomes as.



Figure 7. Coordinate transformation for the elastic deformation.

In the limiting case of  $\varepsilon_d \gg \varepsilon_a$ , it approximateds as.

$$\frac{\varepsilon'_{\rm eff}}{\varepsilon_{\rm eff}} \approx \frac{1}{J} \propto \frac{A}{A'}$$

This is the same relationship for carpet cloaking derived by Prof. Pendry as following.

$$\varepsilon' = \frac{\varepsilon}{|\mathsf{G}|}$$

With this theoretical method, we develop smart metamaterials for self-adjustable metamaterials which change their properties appropriately for the mechanical deformation.

#### 3.2 Self-aggregated nanowire structures

Based on our previous/ongoing research (following list), we can make structures for highly efficient light absorbers.

- Integrating biomimetic moth-eye structure with antireflective nano-island
- Resonant light leakage using whispering gallery modes of nanosphere crystals
- Plasmonic nanofocusings made by randomly self-aggreagated metallic nanowire bundles
- Metal insulator metal nano-gap plasmons



Figure 8. A schematic for the self-aggregated nanowire fabrication.

To increase the resistance to heat or wear, we are going to introduce alumina nanowire bundles for our metasurface coating. We use thin film membranes which can be the alternative of metal nanoparticles. Noble metal is high performance materials for plasmonic matematerials, however, low melting point of noble metal makes them unstable under strong light illumination. We will also search for better candidates to able to improve thermal properties for realistic applications.



Figure 9. The schematic for the self-aggregated alumina nanowire structures

Using Finite Difference Time Domain (FDTD) or Finite Elements Methods (FEM), such as Lumerical or Comsol, we are able to design metamaterials or metasurfaces, in the regime of visible light wavelength.

In the optical regime, we use reflection/transmission spectroscopy system with an integrating sphere, which enables us to measure specular and diffuse reflection/ transmission/ absorption with variable incidence angles for surface textured structures.



Figure 10. The images of nanowire structures.

For the measurement of photo-thermal effect of our metamaterials and metasurface coatings, we use light source, light concentrator with mirror and lens, IR camera, high precision electronic scale etc.

For the fabrication of the designed structures, we use photolithography, nano-imprinting, and self-assembly methods of anodized aluminum oxides (AAO), block copolymer, or colloidal nanosphere lithography, in addition to FIB milling, e-beam lithography.

Year	Research plan
1	Structure design of photothermal energy conversion metamaterials, metasurface coatings, Sample fabrication
2	Measurement of photothermal conversion effect by steam generation experiment / Analysis of Optical, thermal properties of the sample(experimental, theoretical- FDTD,FEM)
3	Optimization of structure for maximizing solar thermal efficiency (final goal: >50%)

Table 1. Research plan

#### 4.0 RESULTS AND DISCUSSION

Our methods can be applied to following research advances.

Smart optical metamaterials, which integrate solid mechanics with transformation optics, are useful for macroscopic optical devices and components with inhomogeneous gradient index distributions. They can be used for photonic applications, lenses, waveguides, or possibly optical cloakings in the future.

Perfect absorbers, which have almost 100% absorptions in visible, IR regimes, are useful for absorber part of solar thermophotovoltaic devices. This material can be applied to the conventional solar power generation system to reduce the expenses of the ground rent, light concentrators such as mirror array, and so on.

Our photo-thermal metamaterial can be used for de-icing of the surface. By coating the metasurface on any large structure, heat is generated by solar illumination and ice on the surface melts or it prevents icing on the surface. This is applicable to aircraft surface, wind turbine blade, large construction structures or buildings, and so on.

Plasmonics can be used to develop high performance sensors and high resolution photomask in the lithography. We use plasmonic device phenomena to enhance the sensitivity or the resolution in various environments.

#### 4.1 Smart optical metamaterials

4.1.1 Scalable variable-index elaso-optic metamaterials



Figure 11. Concept of the elasto-optic metamaterials with aerogels and 3D-printed pressing molds.

Controlling the propagation of natural light through bulk optics components is a important requirement in recent photonics applications. By introducing metamaterials, gradient index materials or photonic crystals, there are many efforts to realize macroscopic optical components with controllable beam propagation. Since commonly used nanofabrication techniques are prohibitively expensive and time-consuming, optical metamaterials have been demonstrated almost exclusively on microscopic scales within thin planar waveguides. Macroscopically large, yet mass-producible at a consumer-affordable price, optical metamaterials would therefore open up new opportunities in the photonics markets. We use metamaterials to realize inhomogeneous gradient index materials by combining solid mechanics and transformation optics.

We experimentally demonstrate macroscale (~50 mm) transformation-optics Wave Bender and a Luneburg lens in the broadband wavelengths at 473 nm, 523 nm, 589 nm, and 650 nm, using a novel class of elasto-optic metamaterials combining optics and solid mechanics. By mechanical deformation, we achieve the required graded refractive index profiles through compression ratio distribution.(Fig. 11a) We employ an elasto-optic metamaterial, specifically, a compressible, transparent, mesoscopically-homogeneous aerogel with a nanoporous (~60 nm) structure with a Poisson's ratio of 0.12 and the refractive index of 1.074.(Fig. 11b) It can compress from the initial porosity 84% to nearly zero in maximum, leading to stresstunable refractive index varying in a wide range from 1.078 to 1.43. As we deform the homogeneous aerogel chunks by pressing our designed molds, we end up with the desired compression ratio and gradient refractive index distribution on the top surface region for the Wave Bender and the Luneburg lens (Fig. 11c, 11d).



Figure 12. The mechanical and optical properties of aerogels.

The areas of our two proof-of-concept demonstrators, the Wave Bender and the Luneburg lens, are 293 mm<sup>2</sup> and 1,884 mm<sup>2</sup> across the visible spectrum, respectively. (Fig. 11e, 11f) The vertical thickness of working devices (~1 mm) is determined by the maximally compressed region. This shows that wide-spectrum natural light propagation can be controlled in the metamaterial volume as large as  $10^{13}\lambda^3$  (e.g. >  $10^5\lambda \times 10^5\lambda \times 10^3\lambda$ ) without any extra light-coupling components.

Our elasto-optic concept enables industrial applications of optical metamaterials in general, and transformation optics in particular, for example, adaptive lenses for advanced miniaturized cameras, machine vision, lidar-based technologies, energy harvesting, and so on.

#### 4.1.2 Meta-lens design with smart transformation optics

The ability to design and fabricate transformation optics device with a commercial 3D printing technology has long been tantalizing. In previously proposed transformation devices, the metamaterial properties require large range of permittivity. Such devices demand

dielectric material with high value of permittivity which cannot be made of 3D printing material.

Smart transformation optics, which we propose in this study, not only design transformation optical device but also reduce the maximum value of required permittivity using intuitive stretching method as shown in Fig. 13. We develop a method based on smart transformation optics to decrease the range of electric permittivity required to manufacture transformation optics devices. We illustrate the design procedure with two types of collimator meta-lens designs, which we call warping space collimator meta-lens and half fisheye collimator meta-lens. We experimentally demonstrated two types of lens manufactured by 3D printer in the microwave regime.



Figure 13. Intuitive design process of metalens



Figure 14. Two metalens samples manufactured by 3D printer and 2D microwave scanning apparatus.

#### 4.1.3 Related Publications

Dongheok Shin, Junhyun Kim, Changwook Kim, Kyuyoung Bae, Seunghwa Baek, Gumin Kang, Yaroslav Urzhumov, David R. Smith and Kyoungsik Kim, "Scalable variable-index elasto-optic metamaterials for macroscopic optical components and devices", Nature Communications 8, 16090 (2017)

Junhyun Kim, Dongheok Shin, Seungjae Choi, Do-Sik Yoo, Ilsung Seo, and Kyoungsik Kim, "Meta-lens design with low permittivity dielectric materials through smart transformation optics", Applied Physics Letters 107(10): 101906 (2015)

#### 4.2 Applications of perfect absorbers

Since sunlight is one of the clean and sustainable energy resources on the planet, extensive studies have been conducted on the solar energy conversion into electricity through photovoltaic (PV) devices. However, single-junction PV device cannot break the theoretical efficiency limit caused by sub-bandgap transmission and heat dissipation loss in semiconductors which is known as the Shockley-Queisser limit. Solar thermal conversion approaches can be an alternative way to exceed this limit and to utilize solar light more efficiently than PV devices. Recently, spectrally or thermally engineered metamaterials have attracted considerable attention because of their excellent physical properties. There are extensive research progresses in the photothermal and thermoplasmonic metamaterials including their promising applications in solar thermophotovoltaics, radiative cooling, and solar desalination.

#### 4.2.1 Noble metal-coated perfect absorbers for solar steam generation

To enable efficient steam generation under solar irradiation, the localized resonant surface plasmon heating has been realized by using metallic nanoshells or nanoparticles, which have inherently narrow absorption bandwidth. For efficient light-to-heat conversion from a wider solar spectrum, we employ adiabatic nanofocusing structures of surface plasmons to attain both polarization-independent ultrabroadband light absorption and high plasmon dissipation loss.

By employing an efficient self-assembly approach, we demonstrate a large scale flexible thin film black gold membranes, which exhibit adiabatic nanofocusing of surface plasmons. (Fig. 15: a inset) Our self-aggregated metallic nanowire bundles have random 3D patterns similar to mountain ridges and valleys, which have the cross sections of microscale funnel shapes. (Fig. 15: a) It is a multiscale structure of a very wide range of metallic nanoscale gaps from zero to hundreds of nm over few micron depth and microscale funnel structures, leading to the unltrabroadband absorption of the membrane. (Fig. 15: b-c) The small taper angle and

varying nanogaps between aggregated nanowires are responsible for the broadband absorption of 91% in the wavelength range of 400 nm to 2,500 nm. The 3  $\mu$ m funnel structure yields the ultrabroadband absorption (reflection <7%) from 2.5  $\mu$ m to 17  $\mu$ m.



Figure 15. The structure and optical properties of the gold-coated self-aggregated nanowire structures.



Figure 16. The energy conversion efficiencies for solar steam generation

Using this film, we efficiently generate solar vapour with solar thermal conversion efficiency up to 57% at light illumination of 20 kW m<sup>-2</sup>. (Fig. 16) This membrane is attached on a micropore tape then floats on the water surface. On the membrane, the vapourized bubbles escape directly into air while hydrophilicity of the membrane continuously provides underlying water to the surface through pores. The heat localization on the surface minimizes the thermal energy losses into bulk water, thus enhances the efficiency of solar vapour generation in comparison with nanoparticles.

This ultrabroadband absorber membrane in the visible to midinfrared region opens new approaches for solar energy harvesting and thermoplasmonics applications.

#### 4.2.2 Versatile metal coated perfect absorbers

For solar-thermal type of energy conversion systems, broadband light absorbers have been enthusiastically researched. As well as high absorptance, thermal durability is essential for the light absorbers to operate at the high working temperature. Refractory materials such as tungsten (W), molybdenum (Mo), Tantalum (Ta), and titanium nitride (TiN), have been exploited because of their high melting point, however, their weakness in thermal oxidation has been overlooked in many previous studies. Noble metal based plasmonic light absorbers are stable, but the high cost is a big obstacle to commercialization of the plasmonic devices.



Figure 17. The optical properties of aluminum, tungsten, TiN coated self-aggregated nanowire structures.

$$\alpha_s = \frac{\int_{0.3\mu m}^{2.5\mu m} [1 - R(\theta, \lambda)] I_s(\lambda) d\lambda}{\int_{0.3\mu m}^{2.5\mu m} I_s(\lambda) d\lambda}$$

Annealing	Solar absorptance ( $\alpha_s$ )				
Temperature (°C)	Al	W	TiN		
unannealed	0.85	0.88	0.84		
200	0.87	0.91	0.83		
300	0.85	0.85	0.81		
400	0.83	0.38	0.55		
500	0.79	0.29	0.14		

Table 2. Solar absorptance of metals (W, Al, TiN) versus annealing temperatures.

We developed a light absorber with broadband, high absorption based on a multiscale funnel structure of self-collapsed nanowire bundle arrays. The structure is fabricated by a simple and cost-effective wet etching process of anodic aluminum oxide (AAO), followed by metal coating. The funnel structure shows high solar absorptance of ~ 0.9 in 300 to 2500 nm wavelength regime, with a wide selection of earth-abundant coating material such as Al, W, and TiN. By using numerical simulation, it is demonstrated that ultra-broadband, high absorption of the funnel structure is induced from plasmonic nanofocusing and index matching effect, and the absorption band can be controlled by changing the degree of collapse, i.e. the angle between nanowire bundles.



Figure 18. XRD results for various absorbers.

To test the resistance to thermal oxidation, we annealed the funnel structures coated with Al, W, and TiN in the air. Interestingly, Al coated structure shows the best performance in thermal durability, even though Al has the lower melting point compared to the W or TiN. Al

shows a slow oxidation due to the dense oxide film at the surface, while W or TiN has unstable oxide film with high oxidation rate. After annealing at 400 °C, W or TiN coated absorber shows solar absorptance of 0.23 and 0.27, while Al coated absorber shows solar absorptance of 0.82, as shown in Fig. 17. By using XRD diffraction pattern data of Fig. 18, we confirmed the formation of WO<sub>3</sub> and TiO<sub>2</sub>, as a result of the oxidation of W and TiN, respectively. These results can be applied to various solar-energy conversion systems, especially for devices with mid- to high- working temperature.

#### 4.2.3 Three-dimensional solar evaporator for efficient steam generation

Water is an essential requirement for sustaining life on earth; however, owing to population and environmental factors, a sufficient supply of freshwater is often not available. Desalination plants are increasingly being needed to satisfy this demand. However, such desalination plants are currently very costly to run, both in terms of monetary and energy terms. Desalination technology using sunlight in combination with the advancements in nanotechnology have shown great promise as a cheap, environmentally friendly and efficient method for desalination to satisfy the future demands for freshwater.

We use the flower Amorphophallus titanum and the solar chimney structure as inspirations for a new design of 3D solar evaporator. Here, an array of evaporators is arranged in a cluster to maximise the solar thermal efficiency and also produce an updraft so that vapour saturated air produced near the active surface of the evaporator can be replenished by dry air. This arrangement achieves a solar thermal efficiency, after subtracting the dark evaporation rate, of 132.8%, which indicates an excellent enhancement of the solar thermal efficiency by the engineered thermally-driven updraft.

#### 4.2.4 Related Publications

Kyuyoung Bae, Gumin Kang, Suehyun K. Cho, Wounjhang Park, Kyoungsik Kim, and Willie J. Padilla, "Flexible thin film black gold membranes with ultrabroadband plasmonic nanofocusing for efficient solar vapour generation", Nature Communications, 6, 10103 (2015)

Dongheok Shin, Gumin Kang, Prince Gupta, Sawaswati Behera, Hyungsuk Lee, Augustine M. Urbas, Wounjhang Park, and Kyoungsik Kim, "Thermoplasmonic and Photothermal Metamaterials for Solar Energy Applications", Advanced Optical Materials 6 (18) 1800317 (2018)

Yunha Ryu, Changwook Kim, Junmo Ahn, Augustine M. Urbas, Wounjhang Park, and Kyoungsik Kim, "Material-Versatile Ultrabroadband Light Absorber with Self-Aggregated Multiscale Funnel Structures", ACS Applied Materials & Interfaces 10 (35), 29884-29892 (2018)

Dongheok Shin, Changwook Kim, Yunha Ryu, Augustine M. Urbas, Wounjhang Park and Kyoungsik Kim, "High-efficiency solar vapour generation with 3D wet structure boosted by solar-induced updraft", To be submitted.

Changwook Kim, Yunha Ryu, Dongheok Shin, Augustine M. Urbas, and Kyoungsik Kim, "Metal-versatile hierarchical nanostructures with aerogel insulator for efficient solar steam generation", To be submitted.

Saraswati Behera, Changwook Kim, and Kyoungsik Kim, "Solar desalination based on graphen-oxide plasmonics with AAO haze nanowire structures", To be submitted.

Saraswati Behera, Jonghyuk Im, and Kyoungsik Kim, "SERS Enhancement and Fluorescence Quenching in Graphene Oxides by Self-aggregated AAO Nanowire Bundles", To be submitted.

#### 4.3 Plasmonics for sensing

4.3.1 Nano-porous silica aerogels for SERS enhancement

It has long been a noteworthy study to easily fabricate large area substrates for greatly amplified surface enhanced Raman spectroscopy (SERS).

In this study, we proposed a large-scale low-cost template with high Raman signal based on ultralow refractive index (n~1.08) silica aerogels.(Fig. 19a) By depositing 30 nm and 60 nm thick silver and gold layer on this nanoporous and ultralow index aerogel template, we got Raman signal enhancement of benzenethiol up to  $7.86 \times 10^7$  at 633nm excitation.(Fig. 19b) Lots of metallic nanogaps, formed by metal deposition on the nanoporous structure of the aerogel substrate, concentrate optical fields, resulting in Raman-active hot spots.(Fig. 19c) In addition, ultralow index (n~1.08) of the aerogel pushes the electric field into the target analyte side, thus enable us to have 60.3 times higher than the incident light.(Fig. 19d) Using finite-difference time-domain (FDTD) simulation, we theoretically compared Raman signals with the same geometry on various substrates, such as aerogel, glass, silicon.(Fig. 19e)



Figure 19. The SERS enhancement with a large-scale nanoporous silica aerogel template.

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#### 4.3.2 Colorimetric index sensing by AAO nanotemplate



Figure 20..Colorimetric sensing with AAO MIM samples.

Recent advancements in nanotechnology have enabled versatile optical sensors that can measure a broad range of chemical or biomolecular analytes in environmental and Internetof-Things applications. Here, we present a highly versatile and low-cost large-area refractive index sensor capable of refractometric and colorimetric sensing by using a plasmon-coupled hybrid nanotemplate of anodic aluminum oxide with deposited gold nanosurface. The plasmon-coupled nanotemplate greatly enhances sensitivity and figure-of-merit up to 346 nm/RIU and 27.7, respectively, owing to coupled mode of a Fabry-Perot microcavity and plasmonic nanosurface. (Here RIU stands for refractive index unit of analyte.) Linear peak shift in the entire visible spectrum is observed in the range of refractive index from 1.0 to 1.7.



Figure 21. The sensitivity of AAO MIM sensors.

Taking the advantage of the proposed large scale feature with sensitive color change by

simple infiltration of the analyte, we examined visually recognizable sensing characteristics by analyzing CIELab 1931 color map and found out that ~ 0.006 RIU change could be perceptually recognized with our sensor. In addition, we investigated the thickness and annealing effect of the nanotemplates to understand the changes in the Fabry-Perot mode and plasmonic resonance condition of the gold nanosurface for further optimization.

#### 4.3.3 Porous metallic nanocone arrays with block copolymer

The substrate for surface enhanced Raman spectroscopy (SERS) requires highly amplified Raman signal as well as cost-effective simple fabrication. In this work, we present a facile method of fabricating SERS substrate by combining solvent-assisted nanoimprint lithography and selective etching of block copolymer (PS-b-PMMA) film. As a result, highly porous metallic nanocone arrays are formed with dense electromagnetic hotspots. The block copolymer film could be molded under atmospheric pressure and at temperature below the glass transition less than half an hour. Our simple time-saving large-area patterning method allows SERS templates with more than  $3.5 \times 10^6$  enhancement factor on average at 532 nm excitation compared to normal Raman spectra from glass substrate. We also examined theoretically how the porous Ag-coated nanocone structure forms dense electromagnetic hot spots by finite-difference time-domain simulation.

The facile method, which we propose in this study, is quite versatile so that other conventional SERS substrates can be morphed into more porous structure to enhance SERS signal further.

#### 4.3.4 Related Publications

Changwook Kim, Seunghwa Baek, Yunha Ryu, Yeonhong Kim, Dongheok Shin, Chang-Won Lee, Wounjhang Park, Augustine M. Urbas, Gumin Kang and Kyoungsik Kim, "Large-scale nanoporous metal-coated silica aerogels for high SERS effect improvement", Scientific Reports 8, 15144 (2018).

Yunha Ryu, Gumin Kang, Chang-Won Lee, and Kyoungsik Kim, "Porous metallic nanocone arrays for high-density SERS hot spots via solvent-assisted nanoimprint lithography of block copolymer", RSC Advances 5(93): 76085-76091 (2015)

Kyuyoung Bae, Jungmin Lee, Gumin Kang, Do-Sik Yoo, Chang-Won Lee and Kyoungsik Kim, "Refractometric and colorimetric index sensing by a plasmon-coupled hybrid AAO nanotemplate", RSC Advances, 5 (125), 103052-103059 (2015)

#### 4.4 Plasmonics for superlensing

There have been numerous efforts for resolution enhancement of photolithography to overcome of the diffraction-limited optical systems. Increasing numerical aperture with immersion fluid and extreme ultraviolet light source are currently under active development in VLSI technologies. These techniques have not yet fully implemented, though, especially for large-area applications such as television displays because photomasks in contact with photoresist suffer from short lifetime.

In this study, we demonstrate resolution enhancement by a plamonic metamask in the proximity regime where Fresnel diffraction dominateds. The transverse magnetic component of the diffracted wave from the photomask (Fig. 22a), which reduces the pattern visibility and lowers resolution, was successfully controlled by coupling with the anti-symmetric mode of the excited surface-plasmon.(Fig. 22b)



Figure 22. Resolution enhanced photolithography in the far field with plasmonic metamask.

We obtained persistent fine patterning photoresist surface up to  $15\mu$ m far from the mask surface for  $3\mu$ m pitch slits owing to conserved field visibility propagating from near-field to the proximity regime. (Fig. 22c above) Also, we achieved the fine pattern  $30\mu$ m separate distance, between photoresist to photomask, for  $5\mu$ m pitch slit.(Fig. 22c below) We confirmed that the sharp-edge patterning can indeed be possible with a wafer-scale photomask in the proximity photolithography regime. Our plasmonic metamask method permits cost-saving ultra-large-scale high-density display fabrication by keeping longer photomask lifetime and by allowing enough tolerance for the distance between photomask and photoresist.

#### 4.4.1 Related Publications

Seunghwa Baek, Gumin Kang, Min Kang, Chang-Won Lee, and Kyoungsik Kim, "Resolution enhancement using plasmonic metamask for wafer-scale photolithography in the

far field", Scientific Reports 6:30476 DOI: 10.1038/srep30476 (2016)

#### **5.0 CONCLUSIONS**

Metamaterials, made of artificial atoms with metals and dielectrics, can be engineered to have ultimate material properties that have not been found in nature. In this study, we invented scalable variable-index elasto-optic metamaterials to realize macroscopic optical devices, such as a wave bender or a Luneburg lens as large as  $855 mm^2 \times 1 mm$ . We use plasmonic device phenomena to enhance the sensitivity of optical sensors or the resolution of photolithography in various environments. We also investigated heat generation from the photo-thermal effect of the metamaterials. By using a specially designed metamaterial, heat energy converted from the light can be highly localized in few micro meter thick. We use varying metals or alumina to increase heat and wear resistance of our metamaterial device in extreme environment such as high temperature or windy dust. Our device can be applied to solar steam generation, solar thermophotovoltaic devices, de-icing of the surfaces and so on.

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#### **APPENDIX A – PUBLICATIONS AND PRESENTATIONS**

Yunha Ryu, Gumin Kang, Chang-Won Lee, and Kyoungsik Kim, "Porous metallic nanocone arrays for high-density SERS hot spots via solvent-assisted nanoimprint lithography of block copolymer", RSC Advances 5(93): 76085-76091 (2015)

Kyuyoung Bae, Jungmin Lee, Gumin Kang, Do-Sik Yoo, Chang-Won Lee and Kyoungsik Kim, "Refractometric and colorimetric index sensing by a plasmon-coupled hybrid AAO nanotemplate", RSC Advances, 5 (125), 103052-103059 (2015)

Junhyun Kim, Dongheok Shin, Seungjae Choi, Do-Sik Yoo, Ilsung Seo, and Kyoungsik Kim, "Meta-lens design with low permittivity dielectric materials through smart transformation optics", Applied Physics Letters 107(10): 101906 (2015)

Kyuyoung Bae, Gumin Kang, Suehyun K. Cho, Wounjhang Park, Kyoungsik Kim, and Willie J. Padilla, "Flexible thin film black gold membranes with ultrabroadband plasmonic nanofocusing for efficient solar vapour generation", Nature Communications, 6, 10103 (2015)

Seunghwa Baek, Gumin Kang, Min Kang, Chang-Won Lee and Kyoungsik Kim, "Resolution enhancement using plasmonic metamask for wafer-scale photolithography in the far field", Scientific Reports 6:30476 DOI: 10.1038/srep30476 (2016)

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Changwook Kim, Seunghwa Baek, Yunha Ryu, Yeonhong Kim, Dongheok Shin, Chang-Won Lee, Wounjhang Park, Augustine M. Urbas, Gumin Kang and Kyoungsik Kim, "Large-scale nanoporous metal-coated silica aerogels for high SERS effect improvement", Scientific Reports 8, 15144 (2018).

Changwook Kim, Yunha Ryu, Dongheok Shin, Augustine M. Urbas, and Kyoungsik Kim, "Metal-versatile hierarchical nanostructures with aerogel insulator for efficient solar steam generation", to be submitted.

Dongheok Shin, Changwook Kim, Yunha Ryu, Augustine M. Urbas, Wounjhang Park and Kyoungsik Kim, "High-efficiency solar vapour generation with 3D wet structure boosted by solar-induced updraft", to be submitted.

Saraswati Behera, Changwook Kim, and Kyoungsik Kim, "Solar desalination based on graphen-oxide plasmonics with AAO haze nanowire structures" to be submitted.

Saraswati Behera, Jonghyuk Im, and Kyoungsik Kim, "SERS Enhancement and Fluorescence Quenching in Graphene Oxides by Self-aggregated AAO Nanowire Bundles", to be submitted.

#### ABSTRACTS



#### ARTICLE

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Flexible thin-film black gold membranes with ultrabroadband plasmonic nanofocusing for efficient solar vapour generation

Kyuyoung Bae<sup>1,\*</sup>, Gumin Kang<sup>1,\*</sup>, Suehyun K. Cho<sup>2</sup>, Wounjhang Park<sup>2</sup>, Kyoungsik Kim<sup>1</sup> & Willie J. Padilla<sup>3</sup>

Solar steam generation has been achieved by surface plasmon heating with metallic nanoshells or nanoparticles, which have inherently narrow absorption bandwidth. For efficient light-to-heat conversion from a wider solar spectrum, we employ adiabatic plasmonic nanofocusing to attain both polarization-independent ultrabroadband light absorption and high plasmon dissipation loss. Here we demonstrate large area, flexible thin-film black gold membranes, which have multiscale structures of varying metallic nanoscale gaps (0-200 nm) as well as microscale funnel structures. The adiabatic nanofocusing of self-aggregated metallic nanowire bundle arrays produces average absorption of 91% at 400-2,500 nm and the microscale funnel structures lead to average reflection of 7% at 2.5-17  $\mu$ m. This membrane allows heat localization within the few micrometre-thick layer and continuous water provision through micropores. We efficiently generate water vapour with solar thermal conversion efficiency up to 57% at 20 kW m<sup>-2</sup>. This new structure has a variety of applications in solar energy harvesting, thermoplasmonics and related technologies.

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#### Meta-lens design with low permittivity dielectric materials through smart transformation optics

Junhyun Kim, 1,a) Dongheok Shin, 1,a) Seungjae Choi, 1 Do-Sik Yoo, 2 Ilsung Seo, 3 and Kyoungsik Kim<sup>1,</sup> School of Mechanical Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 120-749, South Korea <sup>2</sup>School of Electronic and Electrical Engineering, Hongik University, 94 Wausan-Ro, Mapo-Gu, Seoul 121-791, South Korea <sup>3</sup>Agency for Defense Development, 4-4 Yuseong, P.O. Box 35, Daejeon 305-600, South Korea (Received 10 July 2015; accepted 31 August 2015; published online 11 September 2015)

We report here a design method based on smart transformation optics (STO) to control the range of the permittivity values of the materials required to manufacture transformation optics devices. In particular, we show that it is possible to reduce the maximum electric permittivity value required to realize a STO device with certain functionality by means of a simple conceptual elastic stretching process. We illustrate the design procedure with two types of collimator meta-lens designs, which we call warping space collimator meta-lens and half fisheye collimator meta-lens, respectively. We provide design examples of these two types of lenses with the help of COMSOL Multiphysics software. These two design examples are fabricated with commonly available dielectric materials by means of 3D printing technology. For the functional verification of these two collimator lenses, we provide measurement results obtained with transverse electric waves of frequency range 7-13GHz. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4930842]



### RSC Advances



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# a plasmon-coupled hybrid AAO nanotemplate<sup>†</sup>

highlighted as the demand for environmental and Internet-of-Things (IoT) applications increases. In this work, we demonstrate a large-area refractive index sensor capable of refractometric and colorimetric sensing with a plasmon-coupled hybrid nanotemplate of anodic aluminum oxide (AAO). The nanotemplate enhances the figure-of-merit and sensitivity due to the coupled mode of the Fabry-Perot microcavity and metallic nanosurfaces. The increased mode confinement and interaction between AAO pores and analytes show highly modulated reflection spectra, which enable a refractive index sensitivity up to 348 nm per RIU and a figure-of-merit value up to 27.7. Also, the vivid color change induced from infiltrated analytes allows a colorimetric sensing performance up to RIU/ $\Delta E \sim 0.006$  according to CIELab 1931 analysis. The key features of our device are simultaneous applications to superb dual (refractometric and colorimetric) sensing schemes by the plasmon-coupled hybrid AAO nanotemplate.

#### **RSC** Advances

#### PAPER

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#### Porous metallic nanocone arrays for high-density SERS hot spots via solvent-assisted nanoimprint lithography of block copolymer\*

L SOCIETY HEMISTRY

View Article Online

Yunha Ryu,<sup>a</sup> Gumin Kang,<sup>a</sup> Chang-Won Lee\*<sup>b</sup> and Kyoungsik Kim\*<sup>a</sup>

Porous nanostructures have been enthusiastically investigated for SERS application thanks to the internal nanogaps or protrusions acting as effective electromagnetic hotspots. In this work, we report a facile fabrication method of highly porous metallic nanocone arrays for SERS application by integrating solvent-assisted nanoimprint lithography and selective etching of block copolymer (PS-b-PMMA) film. By taking advantage of the solvent-assisted nanoimprint, we easily mould the block copolymer film under atmospheric pressure and moderate temperature below the glass transition temperature in a short time. Then, the PMMA domain of the patterned block copolymer film was selectively etched to make porous structures to form dense nanogaps and protrusions. After Ag deposition, the fabricated structure exhibited a maximum enhancement factor (EF) up to  ${\sim}3.5$   ${\times}$  10<sup>6</sup>. In comparison to Ag coated "solid" nanocone arrays, the EF of "porous" nanocone arrays is maximum  ${\sim}8.9$  times enhanced, which demonstrates the effectiveness of the internal nanogaps and protrusions as plasmonic hot spots. Our fabrication method is very time-saying and cost-effective with good SERS enhancement and also can be easily applied to conventional SERS substrates or other applications that utilize porous structures

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# Scientific **reports**

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## **OPEN** Resolution enhancement using plasmonic metamask for wafer-scale photolithography in the far field

Seunghwa Baek<sup>1</sup>, Gumin Kang<sup>1</sup>, Min Kang<sup>2</sup>, Chang-Won Lee<sup>3</sup> & Kyoungsik Kim<sup>1</sup>

Resolution enhancement in far-field photolithography is demonstrated using a plasmonic metamask in the proximity regime, in which Fresnel diffraction is dominant. The transverse magnetic component of the diffracted wave from the photomask, which reduces the pattern visibility and lowers the resolution, was successfully controlled by coupling with the anti-symmetric mode of the excited surface plasmon. We obtained a consistently finely-patterned photoresist surface at a distance of up to 15 µm from the mask surface for 3-µm-pitch slits because of conserved field visibility when propagating from the nearfield to the proximity regime. We confirmed that sharp edge patterning is indeed possible when using a wafer-scale photomask in the proximity photolithography regime. Our plasmonic metamask method produces cost savings for ultra-large-scale high-density display fabrication by maintaining longer photomask lifetimes and by allowing sufficient tolerance for the distance between the photomask and the photoresist.



#### ARTICLE

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OPEN

# Scalable variable-index elasto-optic metamaterials for macroscopic optical components and devices

Dongheok Shin<sup>1</sup>, Junhyun Kim<sup>1</sup>, Changwook Kim<sup>1</sup>, Kyuyoung Bae<sup>1</sup>, Seunghwa Baek<sup>1</sup>, Gumin Kang<sup>1,†</sup>, Yaroslav Urzhumov<sup>2</sup>, David R. Smith<sup>2</sup> & Kyoungsik Kim<sup>1</sup>

Optical metamaterials with an artificial subwavelength structure offer new approaches to implement advanced optical devices. However, some of the biggest challenges associated with the development of metamaterials in the visible spectrum are the high costs and slow production speeds of the nanofabrication processes. Here, we demonstrate a macroscale (>35 mm) transformation-optics wave bender (293 mm<sup>2</sup>) and Luneburg lens (855 mm<sup>2</sup>) in the broadband white-light visible wavelength range using the concept of elasto-optic metamaterials that combines optics and solid mechanics. Our metamaterials consist of mesoscopically homogeneous chunks of bulk aerogels with superior, broadband optical transparency across the visible spectrum and an adjustable, stress-tuneable refractive index ranging from 1.43 down to nearly the free space index (~1.074). The experimental results show that broadband light can be controlled and redirected in a volume of  $>10^5\lambda \times 10^5\lambda \times 10^3\lambda$ , which enables natural light to be processed directly by metamaterial-based optical devices without any additional coupling components.

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#### REVIEW

Solar Thermal Conversion



### Thermoplasmonic and Photothermal Metamaterials for Solar Energy Applications

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Sunlight is one of the Earth's clean and sustainable natural energy resources, and extensive studies are conducted on the conversion of solar energy into electricity using photovoltaic (PV) devices. However, single-junction PV devices cannot break the theoretical efficiency limit known as the Shockley-Queisser limit that is caused by the sub-bandgap transmission and heat dissipation losses in semiconductors. Solar thermal conversion approaches may provide an alternative way to exceed this limit and enable more efficient use of solar light than that in PV devices. Recently, spectrally or thermally engineered metamaterials have attracted considerable attention for solar energy applications because of their excellent physical properties. The recent research progress in the development of these photothermal and thermoplasmonic metamaterials, along with their promising applications in solar thermophotovoltaics, radiative cooling, and solar desalination, is discussed. lower than the bandgap of the semiconductor used cannot generate electronhole pairs and, thus, cannot contribute to power generation. Light with energy that is higher than the bandgap generates electron-hole pairs, but any excess energy above the bandgap is simply dissipated as heat, and this causes a drop in efficiency. In other words, the maximum achievable conversion efficiency of any PV device is limited by sub-bandgap photon losses and thermal relaxation losses in the semiconductor; this limit is known as the Shockley-Queisser (SQ) limit.[1] While considerable efforts have been made to exceed this thermodynamic limit using multijunction solar cells, these structures suffer from several drawbacks, including



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#### Material-Versatile Ultrabroadband Light Absorber with Self-Aggregated Multiscale Funnel Structures

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#### Supporting Information

ABSTRACT: Broadband light absorbers are essential components for a variety of applications, including energy harvesting and optoelectronic devices. Thus, the development of a versatile absorbing structure that is applicable in various operating environments is required. In this study, a materialversatile ultrabroadband absorber consisting of metal-coated self-aggregated Al<sub>2</sub>O<sub>3</sub> nanowire bundles with multiscale funnel structures is fabricated. A high absorptance of ~0.9 over the AM 1.5G spectrum (300-2500 nm) is realized for absorbers with a range of metal coatings including Al W and titanium



with a range of metal coatings, including Al, W, and titanium nitride (TiN). We demonstrate that the plasmonic nanofocusing and index-matching effects of the funnel structure result in strong ultrabroadband absorption for the various metal coatings, even though the coating materials have different optical properties. As an example of applicability in an operating environment, in the evaluation of the thermal-oxidation resistance, the Al-coated solar absorber exhibits superior performance to those coated with refractory materials such as W and TiN because of the protective alumina layer formed on the Al surface.

KEYWORDS: broadband absorber, material-versatile, funnel structure, nanowire bundles, thermal-oxidation resistance

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## **OPEN** Large-scale nanoporous metalcoated silica aerogels for high SERS effect improvement

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We investigate the optical properties and surface-enhanced Raman scattering (SER5) characteristics of metal-coated silica aerogels. Silica aerogels were fabricated by easily scalable sol-gel and supercritical drying processes. Metallic nan ogaps were formed on the top surface of the nano porous silica network by controlling the thickness of the metal layer. The optimized metallic nanogap structure enabled strong confinement of light inside the gaps, which is a suitable property for SERS effect. We experimentally evaluated the SERS enhancement factor with the use of benzenethiol as a probe molecule. The enhancement factor reached 7.9 × 107 when molecules were ad sorbed on the surface of the 30 nm silver-coated aerogel. We also theoretically investigated the electric field distribution dependence on the structural geometry and substrate indices. On the basis of FDTD simulations, we concluded that the electric field was highly amplified in the vicinity of the target analyte owing to a combination of the aerogel's ultralow refractive index and the high-density metallic nanogaps. The aerogel substrate with metallic nanogaps shows great potential for use as an inexpensive, highly sensitive SERS platform to detect environmental and biological target molecules.

Metal-versatile hierarchical nanostructures with aerogel insulator for efficient solar steam generation

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#### Abstract

Metallic nanostructure-based solar absorbers are widely used for solar steam generation because of their controllable range of absorption wavelength and various applications. Metal-versatile solar absorber which is not limited to noble metal is essential for low-cost production. Here we designed efficient solar steam generation platforms using black Ni, Au films as a solar absorber which includes Ni or Au deposited self-aggregated alumina nanowire structures. We also analyzed both high solar absorptance of the Ni deposited nanowire structures (~0.85) and Au deposited nanowire structures (~0.88) by comparing electric field distributions from FDTD simulation and dielectric functions of Ni and Au. In addition, we improved solar steam generation efficiency by heat localization using aerogel as a thermal insulator and PVA sponge as a water supplier. The efficiencies of solar steam generation platforms using black Ni, Au films under 5 kWm-2 illumination were 83.8 % and 78.3 %, respectively.

Keywords: Solar steam generation, metal-versatile, self-aggregated alumina nanowires, Aerogel thermal insulator, Heat localization

High-efficiency solar vapour generation with 3D wet structure boosted by solar-induced updraft

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#### ABSTRACT

A sunlight-based desalination process is the most environmentally friendly and economical method of obtaining increasingly scarce freshwater on the planet. We implement a threedimensional (3D) solar evaporator with higher efficiency than a conventional twodimensional (2D) structure. The 2D solar evaporator and the 3D evaporator have the same area of incident solar energy, but the 3D evaporator, which has an increased evaporation surface area by extending into three dimensions, shows a much better evaporation efficiency than the 2D evaporator. Our 3D solar evaporator was constructed to completely absorb broadband sunlight in a carbon-coated poly(vinyl alcohol) (PVA) foam that can also supply a sufficient amount of water to the vertical area because of the excellent water absorption and wicking capability. When the 3D solar evaporators are assembled into an array, they suffer reduced efficiency from the mutual exposure to water-vapour-saturated air from adjacent units. We propose bio-inspired arrangements of the 3D solar evaporators that can achieve maximum efficiency in a given area. Motivated by the convection flower (Amorphophallus titanum) and solar chimney structures, these clustering arrangements generate an up-draft airflow owing to a solar-induced temperature difference in the vertical air column. Using these structures, we demonstrate 3D solar evaporator clusters with a solar thermal efficiency of more than 133% for a one sun condition.

Solar steam generation and desalination using graphene oxides coated AAO plasmonic haze nanowire structures embeded with Au nano particles as efficient broadband absorbers

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#### Abstract

Solar steam generation is the most promicing cost effective solar energy harvesting technology to address the global clean and desalinated water deficiency. In this work, we present a plasmonic photothermal composite scheme based on graphene oxides for broadband solar absorption and efficient solar steam generation. The plasmonic composite is based on 5 nm Au nano particles deposited over a mixture of graphene oxide and reduced graphene oxide coated over the annodized aluminum oxide (AAO) haze nanowire structures transferred to micropore tape. Graphene oxides enable broadband absorption, photothermal effect and the presence of 5 nm Au nano particles reduces the defects in graphene oxides and enhances plasmonic photothermal effect through the localized hostspots and can be able to reach the smallest nanogap region in the nanowire structures. AAO haze structures over micropore tape provide maximum optical density of states or interaction volume through multiple nanogaps for plasmonic heat localization and porocity for water channelization. It is observed from optical characterizations that GO/Au and rGO/Au composite have enhanced the absorption in haze nanostructures to more than 90% due to strong plasmonic localization of electromagnetic field. FESEM and image J analysis reveals the surface morphology of GO, rGO, rGO/Au and composite haze substrates consisting of nano wire bundles of 20 - 26 nm widths, 5 - 10 micrometers of axial length and inclined at an angle of 5 - 6 degree arranged in microscale funnels of approximately 1 µm inter-funnel spacing.

Key words: Plasmonics; photothermal effect, graphene oxide; reduced graphene oxide; broadband absorption, solar steam generation, solar desalination

SERS Enhancement and Fluorescence Quenching in Graphene Oxides by Self-aggregated AAO Nanowire Bundles

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ABSTRACT: Graphene oxides are biocompatible 2D functional carbon components. We have studied the effect of anodized aluminum oxide (AAO) based self-aggregated nanowire bundles over Raman signal enhancement from graphene oxides in the presence of Au nano particles. The underlying nanostructure increases the optical density of states in graphene oxides through maximum interaction volume for electromagnetic wave which is important for the Raman signal enhancement. GO, rGO and Au nanospheres are deposited over the 3D haze substrate through drop casting technique. It is observed experimentally that GO/Au and rGO/Au composite have enhanced the absorption in these nanostructures to more than 90% due to strong localization of electromagnetic field through plasmonic photothermal effect. FESEM and image J analysis reveals the surface morphology of GO, GO/Au, rGO, rGO/Au and composite nanostructures. Raman characterization studies reveal the signal enhancement up to eight folds in the fabricated SERS substrate and its application as an efficient fluorescence quencher for dye molecules. FDTD simulation study presents an enhancement to the local field in the studied substrate up to a factor of  $3.3 \times 10^3$  at 532 nm that is even more in higher wavelengths. The studied biocompatible sample can be used as a SERS substrate for biomolecular sensing.