ACS Partner Journal

ACCOUNTS
—of materials research—

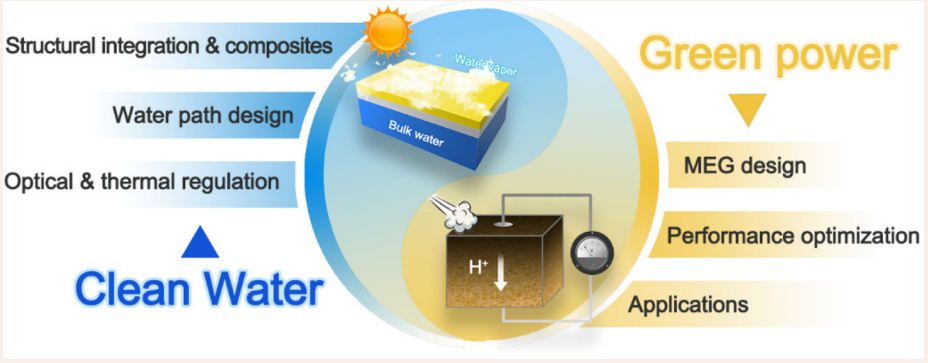
pubs.acs.org/amrcda Article

Graphene Oxide Assemblies for Sustainable Clean-Water Harvesting and Green-Electricity Generation

Yaxin Huang,[#] Chengzhi Wang,[#] Changxiang Shao, Boyu Wang, Nan Chen, Haibo Jin, Huhu Cheng, and Liangti Qu*

Cite This: *Acc. Mater. Res.* 2021, 2, 97−107 Read Online

ACCESS | Metrics & More | Article Recommendations



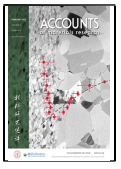
CONSPECTUS: The urgent problems of water scarcity and the energy crisis have given rise to the development of a range of sustainable technologies with the great advancement of nanotechnologies and advent of attractive nanomaterials. Graphene oxides (GO), a derivative of graphene with an atom-thin thickness and abundant oxygen-containing functional groups (such as −OH, −COOH), are water-soluble and can be assembled into a variety of structures (such as fiber, membrane, and foam) with great potential in environmental and energy-related fields. As a typical precursor of graphene, GO can be easily reduced to graphene by chemical or thermal treatments to demonstrate excellent photothermal properties as well as tunable thermal conduction, which is highly desirable for efficient solar-driven water evaporation. The intrinsic large specific area of GO nanosheets can provide enough sites for ions adsorption and its porous assemblies facilitate the transport of water. In addition, the abundant functional groups allow the spontaneous adsorption of water molecules from the ambient environment and give birth to movable ions (usually protons) under the solvation effect. Once a chemical gradient is formed on the component, a remarkable electricity is generated from the directional transport of protons. Thanks to the excellent chemical properties of GO nanosheets, a wide range of assemblies with 1D aligned fibers, 2D layered membranes and 3D porous foam can be easily fabricated by wet-spinning, solution-filtration, and freezing-drying methods. The various GO assemblies are able to exhibit abundant functions with remarkable weaving capability for GO fibers, superior flexibility for GO membranes, and exceptional adsorption capacity for GO foams. In light of all the advantages, GO and its assemblies are remarkably promising in the fields of sustainable development to meet the pressing challenges of water and energy crisis.

In this Account, we will discuss the progress of clean-water production and green-electricity generation technologies based on GO assemblies. The fundamental working mechanism, optimization strategies, and promising applications are explored with an emphasis on the materials development. We also discuss the functions of GO assemblies in the water and electricity generation process and present their limitations and possible solutions. Current challenges and promising directions for the development of clean-water production and green-electricity generation are also demonstrated for their realistic implementations. We anticipate that this Account would promote more efforts toward fundamental research on graphene functionalization and encourage a broad exploration on the application of graphene assemblies in clean-water production and electric power generation systems.

1. INTRODUCTION

Water scarcity and energy shortages are two seriously global problems that threaten the sustainable development of society. According to the report of World Economic Forum (WWF),[1] more than billions of the global population are suffering from water scarcity and electricity shortages, particularly for people

Received: November 3, 2020
Revised: December 30, 2020
Published: January 19, 2021

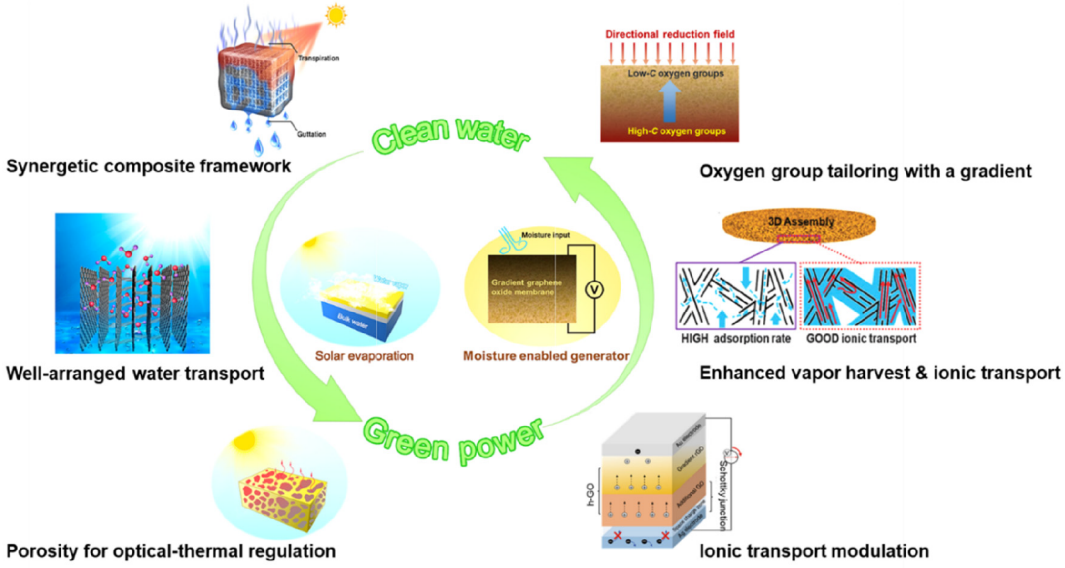


Downloaded via PURDUE UNIV on September 3, 2022 at 19:27:47 (UTC).
See https://pubs.acs.org/sharingguidelines for options on how to legitimately share published articles.

ACS Publications
© 2021 Accounts of Materials Research. Co-published by ShanghaiTech University and American Chemical Society. All rights reserved.

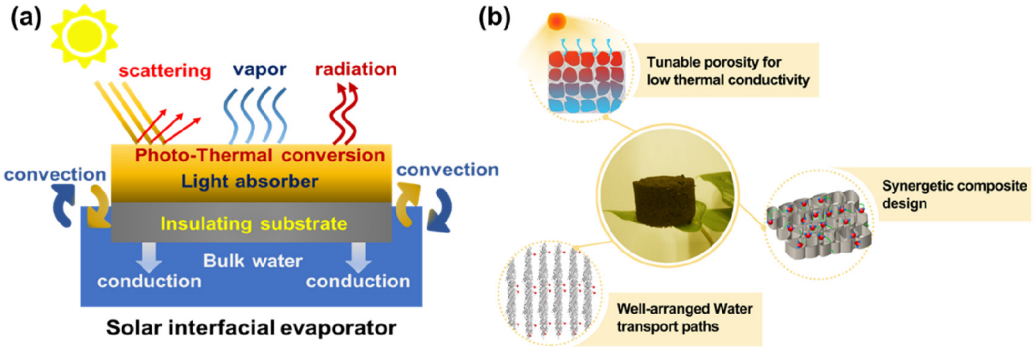
https://dx.doi.org/10.1021/accountsmr.0c00073
Acc. Mater. Res. 2021, 2, 97−107

Scheme 1. Rational Design of Various GO Assemblies with Strategies for SWE and MEG toward Improved Clean-Water Production and Power Output[a]



[a]Reproduced with permission from ref 7. Copyright 2017 American Chemical Society. Reproduced with permission from ref 15. Copyright 2019 Springer Nature. Reproduced with permission from ref 16. Copyright 2016 The Royal Society of Chemistry. Reproduced with permission from ref 17. Copyright 2018 Springer Natur.

Scheme 2. (a) Schematic of the Energy Diagram of a Floating Solar-Driven Water Evaporator and (b) the Typical Improvement Strategies of rGO Aerogels for Efficient Water Production under Solar Irradiation, Including Porosity Tuning, Sheet Arrangement, and Synergetic Composite Construction



living in poor countries and/or remote areas. The antiquated infrastructure and costly investment are crucial obstacles to conventional water purification and electricity generation technologies, such as membrane-based filtration[2] and centralized electric-grid technologies. With the development of nanotechnology, a range of advanced technologies, such as solar-driven water evaporation (SWE)[3] and moisture-enabled electricity generation (MEG)[4] technologies, have been developed to harvest clean water and green energy, which have attracted enormous interest due to their low cost, high performance, and versatility in a variety of scenes. In the SWE process, light adsorption, heat localization and water transport play an important role in the production efficiency. While the MEG process is mainly attributed to the moisture adsorption and asymmetrical ions transport. In this regard, functional materials with superior water affinity, excellent thermal and electrical properties are exceptionally attractive.

GO,[5] a derivative of graphene with ultrathin thickness, large specific surface area, and abundant functional groups can be easily assembled into different configurations, such as aligned fibers, layered membranes, and porous foams, showing great applications in environmental and energy-related fields.[6] Owing to its abundant chemical groups, GO assemblies show an admirable affinity. For example, porous GO foam is capable of extracting moisture from the ambient environment and the transport dynamics of water is extremely fast, particularly in aligned GO assemblies.[7] Chemical groups within GO assemblies could be ionized to release protons under the water solvation effect, exhibiting striking ionic properties.[8] Moreover, GO assemblies can be easily reduced into reduced graphene oxide (rGO) by thermal or chemical treatment, resulting in excellent thermal and optical properties.[9] Taking all the advantages into account, GO assemblies tend to be the perfect candidate for both SWE and MEG technologies. In addition, it has been reported that GO assemblies can be utilized to simultaneously harvest both clean water and green energy in a single system. Although there are some systematical reviews that survey either SWE[10] or MEG

https://dx.doi.org/10.1021/accountsmr.0c00073
Acc. Mater. Res. 2021, 2, 97−107

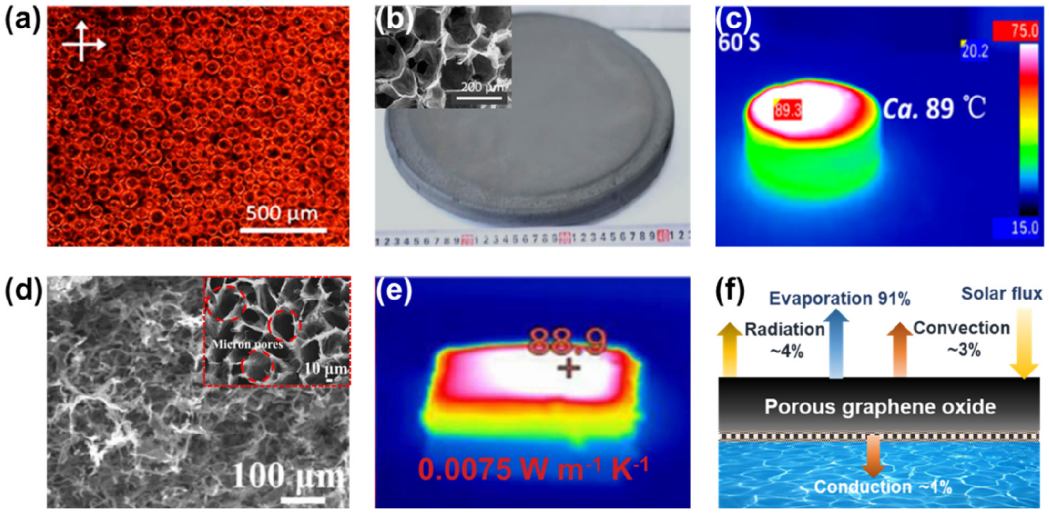


Figure 1. (a) Polarized-light optical microscopy image of surfactant-foamed GO suspension. (b) Photograph of the resulting rGO aerogel with intact micron pores (inset SEM image) after freezing and air drying. (c) Infrared image recording the quick solar-thermal conversion of rGO aerogel within 60 s under 1 sun irradiation. (d) SEM images of porous rGO aerogel by a laser reduction method. (e) Infrared image recording the temperature indicating a low thermal conductivity of 0.0075 W m^{-1} K^{-1}. (f) Balanced energy diagram with a high evaporation efficiency under 1 sun irradiation. (a)−(c) Reproduced with permission from ref 20. Copyright 2018 American Chemical Society. (d, e) Reproduced with permission from ref 21. Copyright 2018 Elsevier.

technologies,[11−14] there is still a lack of comprehensive discussion with GO assemblies in both environmental and energy-related areas.

In this Account, we will discuss the application of GO assemblies on both SWE and MEG technologies from a viewpoint of materials development and device mediation (Scheme 1). First, we discuss the fundamental principle of SWE process, including the light adsorption, thermal regulation and water transport path. Enhancement strategies related to the structural design of GO assemblies are also outlined. We then discuss the working mechanism of MEG, focusing on construction of ion gradient functional groups regulation and the moisture adsorption. The optimization approaches of MEG involving both structure engineering and interface mediation are addressed. Finally, existing challenges and promising solutions are illustrated in both fields.

2. SOLAR-DRIVEN WATER EVAPORATORS

SWE is an effective and sustainable way of generating clean water with both energy-saving and environmental merits.[18] A typical floating solar-driven water evaporator with a bilayer configuration consists of a solar absorber layer at the top and a thermal-insulating substrate at the bottom (Scheme 2a). The solar light shines on the solar absorber layer, while the brine water is pumped into the solar absorber layer and heated by the thermal energy converted from sunlight. Because the bottom insulating substrate has prevented thermal dissipation into bulk water, the brine water in the absorber layer evaporates efficiently into clean steam. Efficient water production on a SWE needs a high light absorption and a substantial reduction of heat losses. The area-specific net water evaporation rate m^* can be expressed as follows:[19]

$$m^* h_{fg} = \alpha q_{solar} - \varepsilon\sigma(T^4 - T_\infty^4) - h(T - T_\infty) - q_{water} \quad (1)$$

where h_{fg} is the latent heat of pure water, α the solar absorptance of the light absorber, q_{solar} the solar flux, ε the emittance of the absorbing surface, σ the Stefan−Boltzmann constant, h the convection heat transfer coefficient, T the temperature of the heat surface, T_∞ the temperature of surroundings, and q_{water} the heat flux of conduction and radiation to the bulk water. Accordingly, the evaporation efficiency η is defined as

$$\eta = \frac{m^* h_{fg}}{\alpha q_{solar}} \quad (2)$$

The basic principles for efficient utilization of solar energy should include: (1) The absorber has a high absorptance of solar light in a wide range of 250−2500 nm to provide enough heat for substantial water evaporation under ambient sunlight. (2) Low thermal emittance and conduction of the absorber are beneficial for reduced heat losses through irradiative and convective heat transfer to ambient surroundings and the excessive water. (3) The substrate has an extremely low thermal conduction to minimize the heat conduction from the absorber to the underlying bulk water. (4) Straight and reliable water transport paths are necessary for efficient water supply to the evaporation surface.

GO should be the idea absorber in SWE because of its wide-band absorption (>90%) and scalable fabrication of various assemblies with attractive properties.[13,14] The enhanced light absorption, high specific evaporation surface areas, low thermal conductivities and efficient water transport channels extremely promote the output performance of SWEs.[14] Porosity tuning, sheet arrangement and synergetic compounds have also been developed on GO assemblies. In this section, we will discuss the optimization strategies, device design for efficient water production based on GO assemblies (Scheme 2b).

2.1. Pore Structure Regulation for Desired Optical-Thermal Properties

According to the working mechanism of SWE, effective photothermal conversion and low thermal conduction are essential factors that determine the device's performance. rGO aerogel is promising due to the high solar absorption and low thermal conductivity from the highly porous structure.[13]

https://dx.doi.org/10.1021/accountsmr.0c00073
Acc. Mater. Res. 2021, 2, 97−107

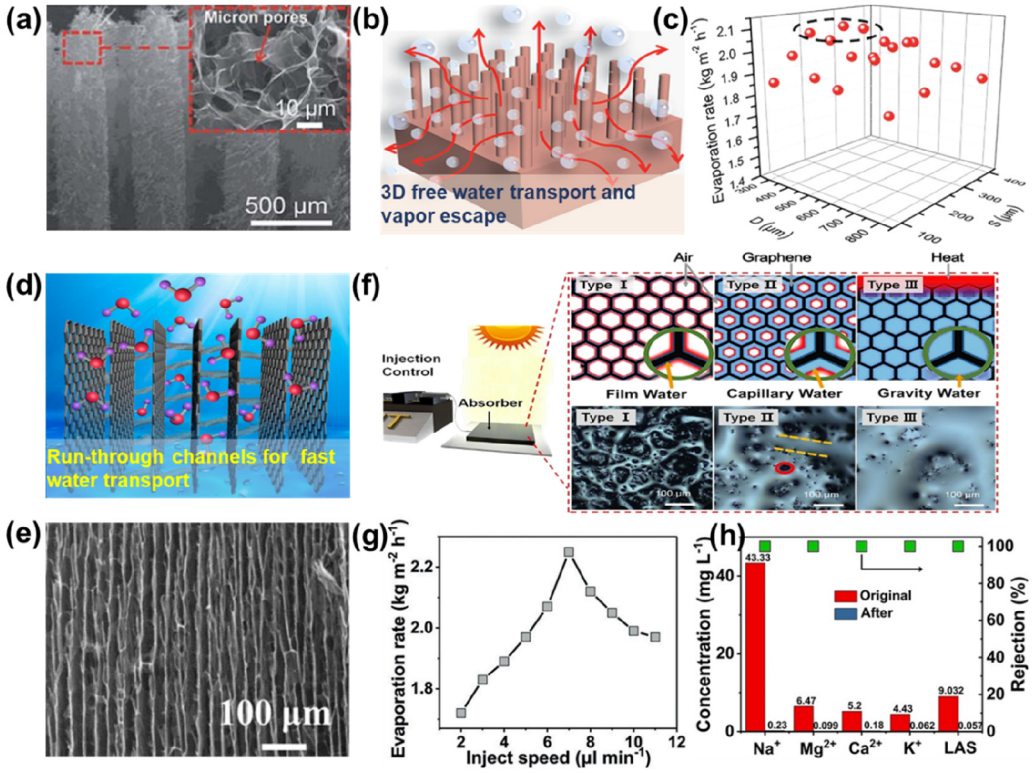


Figure 2. Vertically arranged rGO aerogels for efficient SWE under 1 sun solar irradiation. (a) SEM image of porous vertically aligned rGO pillar arrays with (b) 3D free water transport and vapor escape and (c) the evaporation rates under various pillar size settings. (d) Schematic and (e) SEM image of the vertically aligned rGO sheet membrane with favorable run-through channels for fast water transport. (f) Schematic of three types of water states within the rGO membrane controlled by an injection technique. (g) Relationship plot of the evaporation rate against the inject speed. (h) Ionic and pollutant rejection by the graphene membrane from the domestic swage. (a)−(c) Reproduced with permission from ref 23. Copyright 2018 Elsevier. (d, e) Reproduced with permission from ref 7. Copyright 2017 American Chemical Society. (f)−(h) Reproduced with permission from ref 26. Copyright 2019 Wiley-VCH.

However, the fabrication of rGO is severely hindered by undesired aggregation of pristine GO sheets and structure collapse after reduction. To address this problem, Yang et al.[20] developed surfactant-foaming sol−gel method via micro-bubbles as templates to achieve a large-scale rGO aerogel with intact porous structure (Figure 1a,b), which induced a quick solar-thermal conversion ability to reach a high surface temperature of ca. 89 °C under 1 sun irradiation (Figure 1c). In another way, Zhang et al.[21] synthesized highly porous rGO aerogels with abundant functional groups (Figure 1d) through a scalable and efficient laser reduction method. The as-synthesized rGO aerogels achieved a much low thermal conductivity of 0.0075 W m^{-1} K^{-1} with a surface temperature of nearly 90 °C under 1 sun irradiation (Figure 1e), enabling extremely low heat losses into bulk water and an efficient solar light utilization of 91% (Figure 1f). The high throughput of clean water at a rate of 1.78 kg m^{-2} h^{-1} under 1 sun irradiation was better than those of the GO-based composite aerogel[13] and the hierarchical graphene foam.[22]

2.2. Mediation of Water Transport Paths

Water transport from the underlying bulk water to the evaporation surface and subsequent release into the atmosphere are two basic processes for SWE.[18] Constructing a straight channel between the absorber layer and the substrate (or bulk water) can promote the water supply. For example, Zhang et al.[23] developed a vertically ordered rGO pillar array through laser processing technology (Figure 2a,b). A high evaporation rate of 2.10 kg m^{-2} h^{-1} with an efficiency of 95% was achieved under 1 sun irradiation (Figure 2c), which is much better than that of water evaporators with 1D or 2D water supply configurations.[24,25] Furthermore, a scalable freezing−drying technique was developed to create a long-range vertically aligned rGO foam.[7] The vertically arranged run-through channels with hydrophilic surface facilitate effective water supply and vapor release on the evaporation surface (Figure 2d,e). An average water evaporation rate of 1.62 kg m^{-2} h^{-1} with an efficiency of 86.5% was accomplished under 1 sun irradiation. On the basis of this achievement, Liang et al.[26] approached further enhancement with an efficiency of nearly 100% via an easy-to-operate inject control technique to manage water supply in a favorable capillary water state (Figure 2f), which not only ensured efficient water supply for evaporation but also effectively restricted the heat loss from the evaporating surface. In this way, a record rate of 2.4 kg m^{-2} h^{-1} was realized under 1 sun irradiation with high rejection of pollutants (Figure 2g,h), which is better than most carbon-based evaporators with the rate of less than 2.0 kg m^{-2} h^{-1}.[3,24,27]

2.3. GO Composites for Novel Solar-Driven Water Generators

While considerable progress has been made, emerging SWEs still struggle to meet the increasing demand and commercial requirements in various situations. In this regard, several novel concepts have been proposed to enhance the performance of SWEs. For example, nearly 100% solar-to-vapor transfer efficiency has been demonstrated in a 3D cylindrical structure

https://dx.doi.org/10.1021/accountsmr.0c00073
Acc. Mater. Res. 2021, 2, 97−107

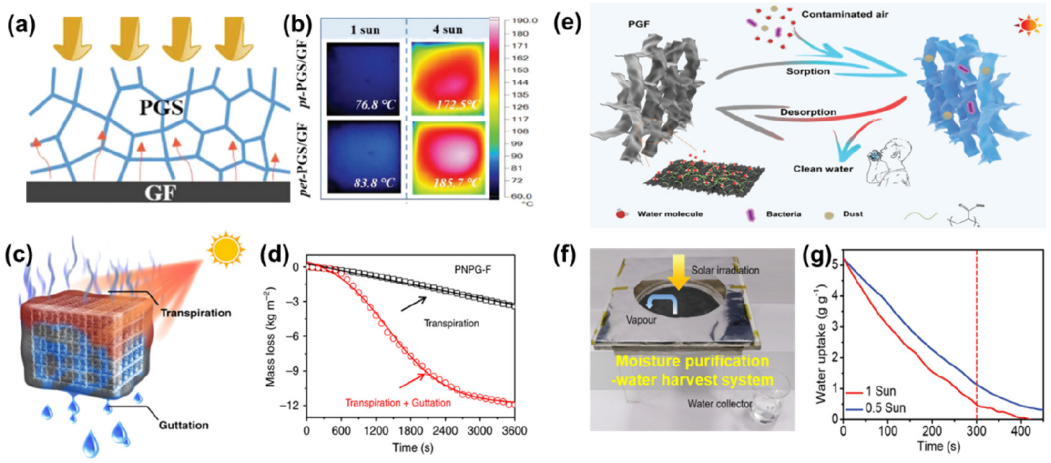
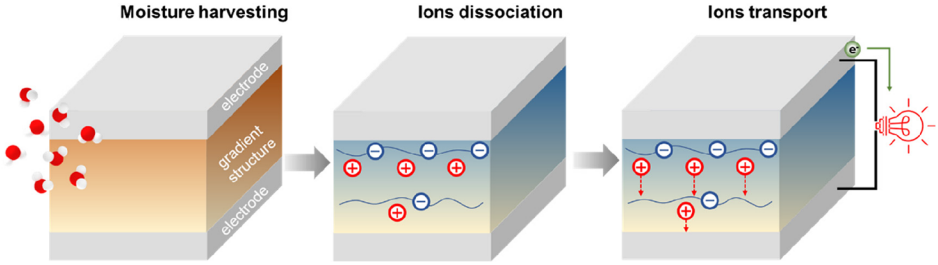


Figure 3. Synergistic GO composites for new-concept SWE. (a) Integrated porous graphene sponge/graphene foil structure with combined photothermal/electrothermal effects and (b) the much-enhanced surface heating effect compared with the sole photothermal effect. (c) rGO/PNIPAm composite frameworks with transpiration and guttation effects for clean-water production and (d) the water mass change under 1 sun irradiation. (e) Clean-water collection from contaminated air based on porous rGO/PAAS composites. (f) Lab-made moisture purification-water harvest system and (g) the clean-water-releasing plots under 1 sun and 0.5 sun irradiation. (a, b) Reproduced with permission from ref 30. Copyright 2018 Wiley-VCH. (c, d) Reproduced with permission from ref 15. Copyright 2019 Springer Nature. (e)−(g) Reproduced with permission from ref 31. Copyright 2020 Wiley-VCH.

Scheme 3. Schematic of the Mechanism of Moisture-Enabled Electricity Generation



by collecting thermal energy from the environment.[28,29] However, the evaporation rate was limited by the light absorption. A highly efficient photoelectro-thermal evaporator was further proposed by combining solar cells with porous graphene sponge (Figure 3a,b). The additional electrothermal effect increased the evaporation rates from 1.69 kg m^{-2} h^{-1} for pristine graphene sponge to 2.01 kg m^{-2} h^{-1} for the integrated system consisting of graphene foil and graphene sponge under 1 sun irradiation.[30]

Inspired by plant leaves with functions of transpiration during the day time and guttation at night, Geng et al.[15] made a high-efficiency sunlight-driven water purifier based on a thermal intelligent polymer/rGO composite (Figure 3c,d). The well-designed composite behaved with a reversible water suction and guttation property through the thermosensitive swelling/deswelling switch of poly(*N*-isopropylacrylamide) (PNIPAm) hydrogels near the lower critical solution temperature. On the basis of the excellent sunlight-to-heat conversion of the rGO-based component and the unique thermal responsive characteristic of PNIPAm, the purifier produced clean water at a high rate of 4.2 kg m^{-2} h^{-1} via the cooperation of transpiration and guttation under solar light. The performance is much higher than that of a hierarchically nanostructured gel based on poly(vinyl alcohol) and polypyrrole with a rate of 3.9 kg m^{-2} h^{-1}.[32] Yao et al.[31] proposed a newly moisture purification and water harvest system based on a rGO/sodium polyacrylate (PAAS) composite framework (Figure 3e−g), which can efficiently produce clean water from contaminated air under sunlight irradiation. The highly hygroscopic porous framework exhibited an ultrahigh equilibrium uptake of 5.20 g of water per gram at 100% relative humidity. The captured water can be conveniently released in hundreds of seconds with an impurity removal rate of 97% even under 0.5 sun irradiation. It can also collect more than 25 L kg^{-1} of clean water per day in a realistic outdoor condition, which is adequate to meet the needs of a few people for drinking water.

3. MOISTURE-ENABLED ELECTRICITY GENERATION

Thanks to the excellent water affinity and abundant chemical groups, GO assemblies can also be used to directly generate electricity by harvesting water from the ambient environment, which is designated as moisture-enabled electricity generation (MEG).[33,34] The basic mechanism of MEG is schematically shown in Scheme 3. In principle, water molecules are first adsorbed by the hygroscopic components, which allow the ionization of functional groups to produce movable ions, such as protons. Ions will directionally transport from the high-concentration region to the low-concentration region under the driving force of the ion concentration gradient, which is always resulted from the asymmetrical chemical structure or uneven distribution of moisture on the materials. This process leads to a significant built-in electrical field and generates considerable electrical output once connected to external

https://dx.doi.org/10.1021/accountsmr.0c00073
Acc. Mater. Res. 2021, 2, 97−107

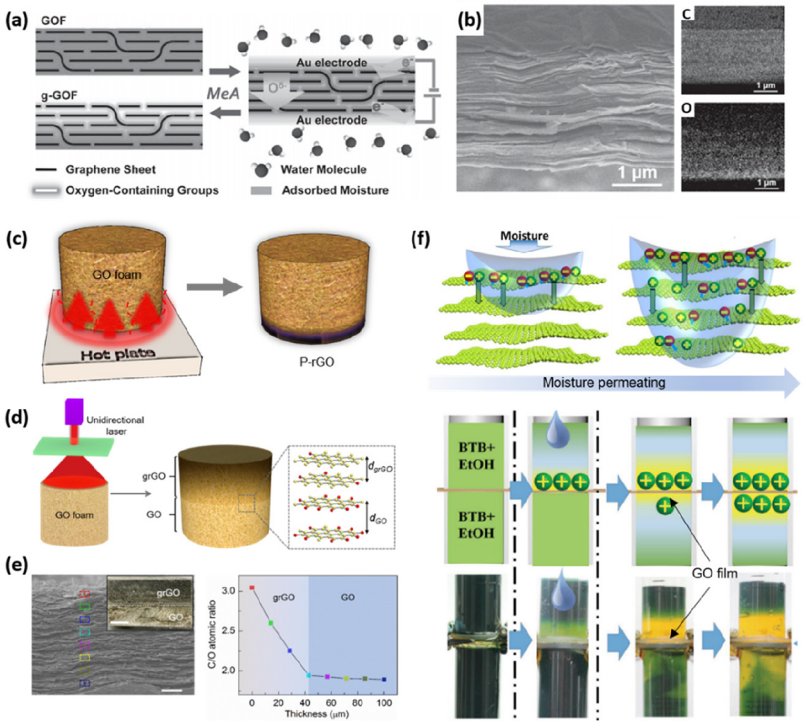


Figure 4. Typical methods to construct a gradient in GO assemblies. (a) Schematic illustration of the moisture-electric annealing process to fabricate the gradient GO membrane. (b) Cross-sectional SEM image and corresponding element mapping of carbon and oxygen. (c) Directional thermal reduction of the GO foam. (d) Construction of the heterogeneous GO foam through a unidirectional laser reduction method. (e) Cross-sectional morphology and C/O atomic ratios across the heterogeneous GO foam. (f) Asymmetrical moisture-enabled ion gradient in the GO membrane, as indicated by the evolution of color change. (a, b) Reproduced with permission from ref 4. Copyright 2015 Wiley-VCH. (c) Reproduced with permission from ref 35. Copyright 2018 Royal Society of Chemistry. (d, e) Reproduced with permission from ref 17. Copyright 2018 Springer Nature. (f) Reproduced with permission from refs 11 and 37. Copyrights 2018 Wiley-VCH and 2019 Royal Society of Chemistry.

circuits. The output performance depends remarkably on the harvesting of water molecules from the ambient environment and the formation of ion gradient through functional materials. In this section, we will mainly discuss GO assemblies-based MEG technologies, with a focus on the materials development, optimization strategies and applications in flexible electronics.

3.1. Tailoring Functional Groups for Constructing the Ion Gradient

According to the working mechanism of MEG, ion gradients contribute a critical role in the electric generation process. In general, there are mainly four methods to achieve a gradient structure on GO assemblies: electrochemical treatment,[4] directional thermal annealing,[35] selective laser reduction,[17] and asymmetrical moisturizing.[11] For example, Zhao et. al has developed a simple method to construct a gradient GO membrane by electrochemical treatment (Figure 4a). The GO membrane was first sandwiched by a couple of inert electrodes and placed in an enclosed container with high humidity to ensure homogeneous distribution of water. Then, a constant bias, which depends on the sample thickness, was applied to this membrane to cause electrochemical reactions. Oxygen-containing functional groups should undergo either oxidation or reduction at either side of the membrane, resulting in a chemical gradient within the membrane (Figure 4b). Apart from GO assemblies, other materials, such as polymers[36] can also establish a gradient structure through the electrochemical treatment, indicating the generality of this method. However, with the increase of sample size and thickness, it is difficult to form a homogeneous electric field within the sample, leading to a breakdown of materials. In this regard, laser irradiation[17] was employed on GO foams to selectively reduce the oxygen-containing functional groups, leading to an asymmetric structure. Alternatively, directional thermal treatment[35] is also effective in creating a gradient structure within porous GO foams, promising for large-scale construction of gradient GO assemblies with low cost and high efficiency (Figure 4c). It should be noted that the gradient structure in both thermal and laser treatment process is hierarchical with a gradient layer and an unreduced layer, as limited by the penetrating depth of thermal and laser (Figure 4d,e). Additionally, the gradient structure can also be manufactured in GO assemblies by controlling the applied moisture direction[11,37] to create asymmetrical transport of water (Figure 4f).

3.2. Regulating the Capacity for Moisture Harvesting

Owing to its large specific surface area and abundant chemical groups, GO can not only disperse well in water but also display excellent moisture-harvesting capabilities in its assemblies. In the electric generation process of MEG, moisture is able to trigger the dissociation of oxygen-containing functional groups (−OH, −COOH) under the solvation effect.[16] Therefore, increased moisture-harvesting capacity should result in higher output performance. For example, a GO membrane-based MEG[4] can deliver an output voltage of 35 mV under a relative humidity variation of 55%, whereas a porous GO foam-based device[16] could produce an output voltage of 260 mV, nearly 7 times that of the membrane counterpart. This is attributed to the enhanced ability of porous GO assemblies to harvest moisture from interconnected pores to accommodate enough

https://dx.doi.org/10.1021/accountsmr.0c00073
Acc. Mater. Res. 2021, 2, 97−107

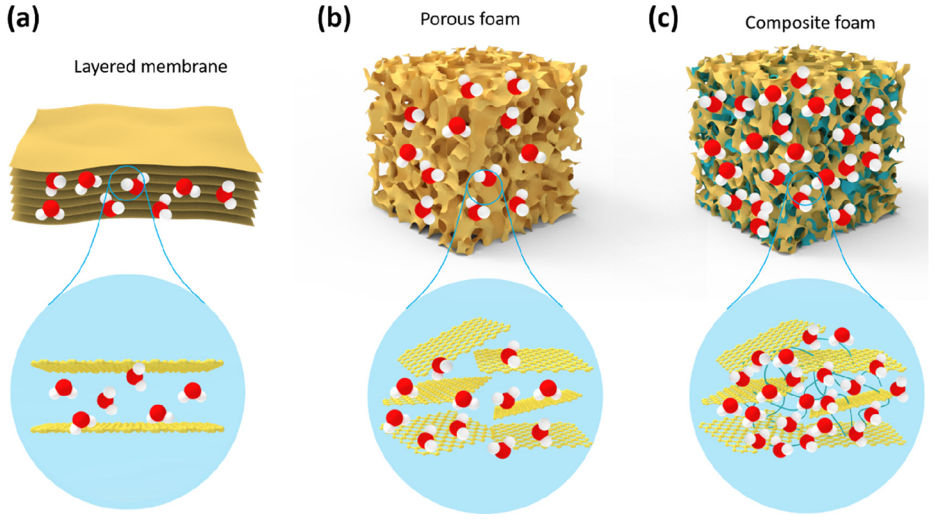


Figure 5. Regulation of moisture-harvesting capacity in GO assemblies. (a) Water molecules are in the confined space of layered GO membrane. (b) The porous structure in the GO foam is able to provide ample space for water molecule accommodation. (c) The incorporation of a hygroscopic polymer in the GO foam enables enhanced water molecule adsorption.

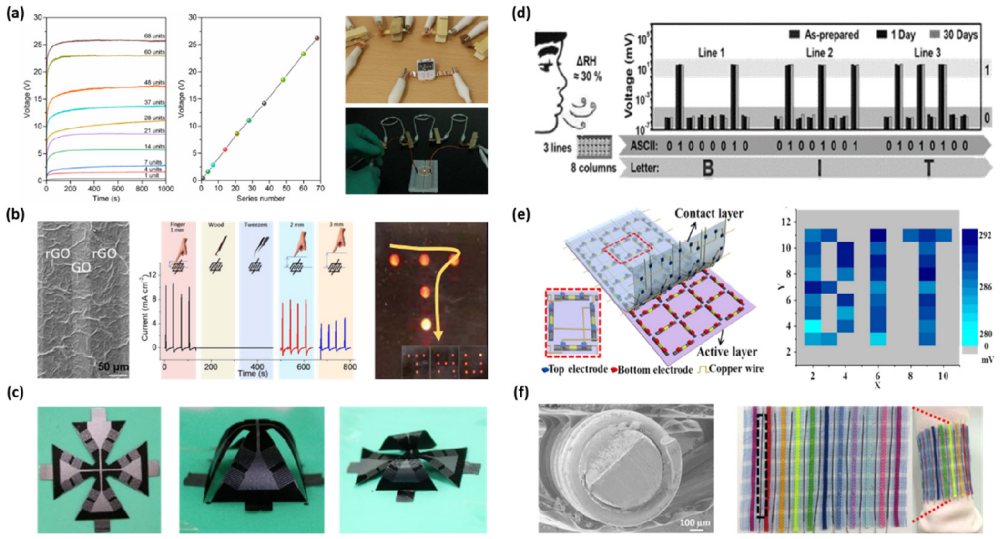


Figure 6. Applications of MEGs based on GO assemblies. (a) Voltage outputs of a porous GO-based MEG through device integration, capable of powering commercial LED and LCD. (b) SEM image of the interdigitated rGO/GO/rGO MEG units with characteristic electric response to specific objects at different positions and the application for a touchless interactive panel for writing the word "THU". (c) Deformable graphene MEGs manufactured by direct laser writing. (d) A 30-day reliable memory chip with 3 × 8 pixels based on gradient GO nanoribbons to read out the word "BIT" according to the ASCII. (e) Schematic of the wearable electronic label device based on GO fiber MEGs to express the word "BIT". (f) SEM image of a coaxial fiber-shaped MEG with a wearable feature. (a) Reproduced with permission from ref 38. Copyright 2019 Royal Society of Chemistry. (b) Reproduced with permission from ref 39. Copyright 2018 Elsevier. (c) Reproduced with permission from ref 33. Copyright 2019 Wiley-VCH. (d) Reproduced with permission from ref 34. Copyright 2017 Wiley-VCH. (e) Reproduced with permission from ref 40. Copyright 2017 Elsevier. (f) Reproduced with permission from ref 44. Copyright 2018 Elsevier.

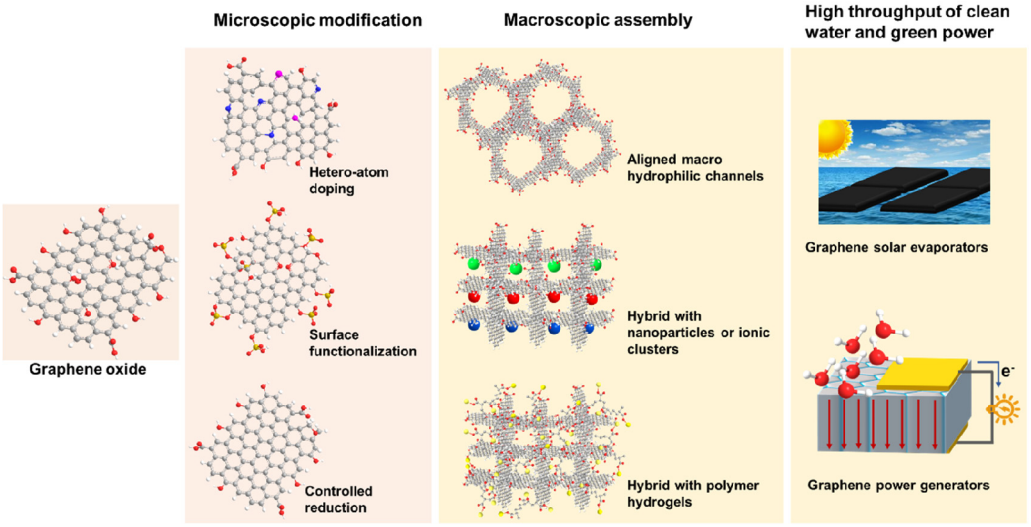
space and enormous sites for water molecules (Figure 5a,b). In addition, the moisture-harvesting capacity could be further improved by the addition of hygroscopic salts and/or polymers[38] to construct GO composite (Figure 5c). For example, the moisture-harvesting ability of GO/PAAS composite is almost 3 times higher than the pristine GO, leading to a substantial improvement in the output voltage of 0.8 V in MEG device.[38] However, the structure of GO assemblies is easily collapsed with higher moisture adsorption due to the enormous capillary force within GO nanosheets. Furthermore, the reversibility of ion transport within salt-doped GO assemblies is also a severe concern for the cycling performance of MEG.

3.3. Modulation of Ion Transport

Movable ions can be dissociated from the oxygen-containing functional groups in GO once triggered by water molecules. Since the large conjugated size of GO's backbone, the negatively charged ions are bound to the backbone of the GO sheet and can be immobilized, causing the movable species to be positively charged ions (typically protons). The transport of ions relies heavily on the channels within GO assemblies. For example, the transport of ions inside layered GO membranes shows advantageous kinetics in the horizontal direction compared to the perpendicular direction, because of the straightforward channels. Consequently, the planar MEG

https://dx.doi.org/10.1021/accountsmr.0c00073
Acc. Mater. Res. 2021, 2, 97−107

Scheme 4. Schematic of the Modification and Assembly of GO and Their Promising Application in Clean-Water Production and Green-Electric Generation Enabled by GO-Based SWEs and MEGs



device displays better output performance than the sandwiched counterpart.[39] However, the thickness of GO membrane is always limited to less than a dozen micrometers, and further arrangement of planar electrodes is also difficult to manufacture a planar device. The alternative is a fiber-based MEG,[40] consisting of a GO component and a couple of rGO electrodes, which is fabricated in a single GO fiber with monolithic structure. And the device shows prominent performance from its aligned channels and well-contacted interfaces. Moreover, in other aligned channels, such as polypyrrole nanowire arrays,[41] ions also exhibit excellent transport kinetics with favorable electrical performance. Another approach to promote the transport dynamics of ions in the sandwiched structure is to build connective pathways in the GO assemblies. Porous GO foams can provide adequate space for ion accommodation and interconnected morphology enables the transport of ions. The as-prepared MEG device[42] exhibits a 10-fold higher output voltage than the membrane-based MEG. Furthermore, the addition of conductive ionic species, such as salts or polymers, is capable of extremely enhancing the ionic conductivity of GO assemblies, while the reversibility should be further considered for the power generation process. Apart from the GO assemblies, the materials−electrode interface mediation also contributes a significant role in the transport kinetics of ions.[17] For example, a Schottky contact is enabled at the GO/electrode interface by means of Ag electrodes with lower work function. Consequently, the combination between electrons and ions is constrained by the charge space zone at the interface. The enhanced charge separation and ion transport therefore lead to a high output voltage approaching 1.5 V in a single MEG device.

3.4. Applications of Moisture-Enabled Electricity Generators

The output performance of MEG has been significantly improved over the last five years through the efforts of researchers.[6,10,12,43] The generated voltage and current density have reached an impressive level of 1.5 V and 0.1 mA cm^{-2}, respectively, which is high enough to run some electronics. For example, A porous GO-based MEG is able to generate an output voltage of more than 26 V through device integration, capable of powering commercial LED and LCD (Figure 6a).[38] In addition, MEG is generally a highly sensitive humidity sensor derived from the admirable sensing capacity of GO nanosheets to water molecules. For example, an interactive panel was built on the basis of a planar MEG with an interdigitated rGO/GO/rGO component, which can detect the features of exposed characters and even display hand-written words without touching the screen, such as the word "THU" (Figure 6b).[33] In addition, the membrane-based MEG shows a favorable flexibility and exceptional configuration capability with proper laser processing, to demonstrate excellent conformability from 2D to 3D space (Figure 6c).[39] Moreover, the electronic memory device has been successfully achieved with MEG by means of the superb humidity sensibility and the moisture-enabled switchable ion channels of GO nanoribbon.[34] A reliable 3 × 8 pixels MEG memory device was fabricated to demonstrate the ASCII transform term "BIT" (Figure 6d). Owing to the outstanding weaving ability of GO fiber, the fiber-based MEG can be integrated into masks[40] or other fabrics[44] (Figure 6e,f). For example, a coaxial fiber-shaped MEG was constructed of a couple of silver wires and GO fiber as electrodes and functional layer, respectively (Figure 6f).[44] It exhibited extraordinary shaping capabilities and could be easily incorporated into cloth fabrics to serve as a wearable power source.

4. SUMMARY AND PROSPECTS

GO assemblies with a variety of configurations from fibers, membranes to foams, are promising for high-performance SWEs and MEGs. The efficiency of over 95% with the water generation rates of 2.0−2.4 kg m^{-2} h^{-1} under 1 sun irradiation has been achieved by graphene-based SWEs owing to the molecular regulation of the GO assemblies with enhanced light adsorption, heat localization, and water transport. The output performance of MEG has growing over magnitudes from 30 mV to approaching 1.5 V in a single device by modulating the chemical groups and moisture adsorption capacity. The generated electricity can also be stored in commercial capacitors, for lighting bulbs, watches, and other electronic vehicles. GO fiber-based MEG can also be integrated into masks or fabrics to function as a humidity sensor for

https://dx.doi.org/10.1021/accountsmr.0c00073
Acc. Mater. Res. 2021, 2, 97−107

monitoring the body health. Despite the performance of GO assemblies-based water evaporators and electricity generators has boosted, there are still several challenges that should be addressed for further applications in real-world situations (Scheme 4).

First, the interactions between GO and water should be well understood from both experimental and theoretical perspectives, such as the adsorption dynamics, transport kinetics, and interfacial electric double layer, since the primary process during the water evaporation and electricity generation is strongly determined by the above-mentioned interactions. Advanced technologies and modeling algorithms with high resolution, such as liquid AFM, Raman spectrum, and machine-learning enhanced simulations, should be developed to provide deeper insight into the GO/water interactions. Second, the building blocks of GO assemblies can be further functionalized by chemical doping, molecular grafting, defect engineering, and compositing to accommodate more active sites for water adsorption. A hybrid hydrogel composed of GO and polymers has demonstrated excellent ability for water harvesting from the ambient atmosphere and can be applied to extensive conditions. Third, development of large-scale fabrication methods for the construction of GO and its assemblies in a highly effective way is extremely urgent, as the overall harvesting capacity of clean water and green electricity depends heavily on the size of device. Current methods to fabricate GO, such as chemical oxidation or electrochemical synthesis, are mainly based on massive quantities of polluting chemicals, extreme temperatures, and costly equipment and have only been implemented at the laboratory level. Green approaches are preferred to avoid additional pollution, ease energy consumption and reduce the cost of processing. Furthermore, the long-term stability of GO assemblies should also be well assessed, particularly under high humidity and extreme temperature conditions. Finally, the device structure should be further optimized to reduce interface resistance, facilitating the transport of water and mitigating the energy losses. Interface mediation with proper system design and excellent contact should be a promising solution to this problem.

Overall, GO assemblies-based water evaporation and electricity generation technologies have exhibited encouraging progress in the output performance. Mechanistic insight into interactions between GO and water is desirable to further enhance the performance through effective collaborations of experimenters and theorists. We anticipate that sustainable clean-water production and green-energy generation technologies will be employed in realistic settings to alleviate pressing environmental and energy-related issues around the world.

AUTHOR INFORMATION

Corresponding Author

Liangti Qu − *State Key Laboratory of Tribology, Department of Mechanical Engineering and Key Laboratory of Organic Optoelectronics & Molecular Engineering, Ministry of Education, Department of Chemistry, Tsinghua University, Beijing 100084, PR China; Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, Key Laboratory of Cluster Science, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, P. R. China;* orcid.org/0000-0002-0161-3816; Email: lqu@mail.tsinghua.edu.cn

Authors

Yaxin Huang − *State Key Laboratory of Tribology, Department of Mechanical Engineering, Tsinghua University, Beijing 100084, PR China*

Chengzhi Wang − *Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, Key Laboratory of Cluster Science, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, P. R. China*

Changxiang Shao − *Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, Key Laboratory of Cluster Science, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, P. R. China*

Boyu Wang − *Beijing Key Laboratory of Construction Tailorable Advanced Functional Materials and Green Applications, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, P. R. China*

Nan Chen − *Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, Key Laboratory of Cluster Science, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, P. R. China;* orcid.org/0000-0002-3105-4509

Haibo Jin − *Beijing Key Laboratory of Construction Tailorable Advanced Functional Materials and Green Applications, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, P. R. China*

Huhu Cheng − *State Key Laboratory of Tribology, Department of Mechanical Engineering and Key Laboratory of Organic Optoelectronics & Molecular Engineering, Ministry of Education, Department of Chemistry, Tsinghua University, Beijing 100084, PR China;* orcid.org/0000-0002-7626-1368

Complete contact information is available at: https://pubs.acs.org/10.1021/accountsmr.0c00073

Author Contributions

#Y. Huang and C. Wang contributed equally to this work.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

Biographies

Yaxin Huang is currently a Ph.D. student under the supervision of Prof. Liangti Qu at Tsinghua University. His research mainly focuses on energy conversion/storage devices related to graphene-based materials.

Chengzhi Wang received his Ph.D. degree in Materials Science & Engineering from Beijing Institute of Technology in 2019. He is currently working as a postdoctoral researcher in Beijing Institute of Technology focusing on energy devices.

Changxiang Shao received her bachelor's degree in environmental engineering from University of Jinan in 2015. She is currently a Ph.D. candidate at School of Chemistry and Chemical Engineering in Beijing Institute of Technology. Her research mainly focuses on graphene-based materials and applications on energy conversion/storage devices.

https://dx.doi.org/10.1021/accountsmr.0c00073
Acc. Mater. Res. 2021, 2, 97−107

Boyu Wang received his bachelor's degree in Materials Engineering from Northeastern University. He is currently a Ph.D. candidate at School of Materials Science & Engineering in Beijing Institute of Technology and working on thermoelectric materials and devices.

Nan Chen is currently a professor at the School of Chemistry and Chemical Engineering in Beijing Institute of Technology (China). He received his bachelor's degree from China Agricultural University and earned his Ph.D. from Institute of Chemistry, Chinese Academy of Sciences (ICCAS). His research interests lie in the development of new methods and strategies for fabrication of carbon-based functional materials for various applications.

Haibo Jin is currently a professor in Beijing Institute of Technology and his research activities mainly focus on electromagnetic functional materials, intelligent response materials, and energy devices.

Huhu Cheng received his Ph.D. degree in Chemistry from Beijing Institute of Technology in 2016. He is now an Assistant Professor in Tsinghua University focusing on advanced nanomaterials for energy conversion.

Liangti Qu received a Ph.D. in Chemistry from Tsinghua University (China) in 2004. He is now a Changjiang professor with research focusing on carbon-based/polymer-based advanced functional materials and energy-related devices.

■ ACKNOWLEDGMENTS

This work was supported by the financial support from the National Key R&D Program of China (2017YFB1104300, 2016YFA0200200), National Science Foundation of China (No. 22035005, 21674056, 52073159, 52022051, 22075165), NSFC-STINT (21911530143), and China Postdoctoral Science Foundation (2019M660474).

■ REFERENCES

(1) Mekonnen, Mesfin M.; Hoekstra, A. Y. Four Billion People Facing Severe Water Scarcity. *Sci. Adv.* **2016**, *2*, e1500323.
(2) Surwade, S. P.; Smirnov, S. N.; Vlassiouk, I. V.; Unocic, R. R.; Veith, G. M.; Dai, S.; Mahurin, S. M. Water Desalination Using Nanoporous Single-Layer Graphene. *Nat. Nanotechnol.* **2015**, *10* (5), 459−564.
(3) Ghasemi, H.; Ni, G.; Marconnet, A. M.; Loomis, J.; Yerci, S.; Miljkovic, N.; Chen, G. Solar Steam Generation by Heat Localization. *Nat. Commun.* **2014**, *5*, 4449.
(4) Zhao, F.; Cheng, H.; Zhang, Z.; Jiang, L.; Qu, L. Direct Power Generation from a Graphene Oxide Film under Moisture. *Adv. Mater.* **2015**, *27* (29), 4351−4357.
(5) Dikin, D. A.; Stankovich, S.; Zimney, E. J.; Piner, R. D.; Dommett, G. H.; Evmenenko, G.; Nguyen, S. T.; Ruoff, R. S. Preparation and Characterization of Graphene Oxide Paper. *Nature* **2007**, *448* (7152), 457−460.
(6) Cheng, H.; Huang, Y.; Shi, G.; Jiang, L.; Qu, L. Graphene-Based Functional Architectures: Sheets Regulation and Macrostructure Construction toward Actuators and Power Generators. *Acc. Chem. Res.* **2017**, *50* (7), 1663−1671.
(7) Zhang, P.; Li, J.; Lv, L.; Zhao, Y.; Qu, L. Vertically Aligned Graphene Sheets Membrane for Highly Efficient Solar Thermal Generation of Clean Water. *ACS Nano* **2017**, *11* (5), 5087−5093.
(8) Gao, W.; Singh, N.; Song, L.; Liu, Z.; Reddy, A. L.; Ci, L.; Vajtai, R.; Zhang, Q.; Wei, B.; Ajayan, P. M. Direct Laser Writing of Micro-Supercapacitors on Hydrated Graphite Oxide Films. *Nat. Nanotechnol.* **2011**, *6* (8), 496−500.
(9) Zhu, Y.; Murali, S.; Cai, W.; Li, X.; Suk, J. W.; Potts, J. R.; Ruoff, R. S. Graphene and Graphene Oxide: Synthesis, Properties, and Applications. *Adv. Mater.* **2010**, *22* (35), 3906−3924.
(10) Ye, M.; Zhang, Z.; Zhao, Y.; Qu, L. Graphene Platforms for Smart Energy Generation and Storage. *Joule* **2018**, *2* (2), 245−268.
(11) Xu, T.; Ding, X.; Shao, C.; Song, L.; Lin, T.; Gao, X.; Xue, J.; Zhang, Z.; Qu, L. Electric Power Generation through the Direct Interaction of Pristine Graphene-Oxide with Water Molecules. *Small* **2018**, *14* (14), 1704473.
(12) Bai, J.; Huang, Y.; Cheng, H.; Qu, L. Moist-Electric Generation. *Nanoscale* **2019**, *11* (48), 23083−23091.
(13) Hu, X.; Xu, W.; Zhou, L.; Tan, Y.; Wang, Y.; Zhu, S.; Zhu, J. Tailoring Graphene Oxide-Based Aerogels for Efficient Solar Steam Generation under One Sun. *Adv. Mater.* **2017**, *29* (5), 1604031.
(14) Shao, C.; Zhao, Y.; Qu, L. Tunable Graphene Systems for Water Desalination. *ChemNanoMat* **2020**, *6* (7), 1028−1048.
(15) Geng, H.; Xu, Q.; Wu, M.; Ma, H.; Zhang, P.; Gao, T.; Qu, L.; Ma, T.; Li, C. Plant Leaves Inspired Sunlight-Driven Purifier for High-Efficiency Clean Water Production. *Nat. Commun.* **2019**, *10* (1), 1512.
(16) Zhao, F.; Liang, Y.; Cheng, H.; Jiang, L.; Qu, L. Highly Efficient Moisture-Enabled Electricity Generation from Graphene Oxide Frameworks. *Energy Environ. Sci.* **2016**, *9* (3), 912−916.
(17) Huang, Y.; Cheng, H.; Yang, C.; Zhang, P.; Liao, Q.; Yao, H.; Shi, G.; Qu, L. Interface-Mediated Hygroelectric Generator with an Output Voltage Approaching 1.5 V. *Nat. Commun.* **2018**, *9* (1), 4166.
(18) Zhang, P.; Liao, Q.; Yao, H.; Huang, Y.; Cheng, H.; Qu, L. Direct Solar Steam Generation System for Clean Water Production. *Energy Storage Mater.* **2019**, *18*, 429−446.
(19) Ni, G.; Li, G.; Boriskina; Svetlana, V.; Li, H.; Yang, W.; Zhang, T.; Chen, G. Steam Generation Under One Sun Enabled by a Floating Structure with Thermal concentration. *Nat. Energy* **2016**, *1* (9), 16126.
(20) Yang, H.; Li, Z.; Lu, B.; Gao, J.; Jin, X.; Sun, G.; Zhang, G.; Zhang, P.; Qu, L. Reconstruction of Inherent Graphene Oxide Liquid Crystals for Large-Scale Fabrication of Structure-Intact Graphene Aerogel Bulk toward Practical Applications. *ACS Nano* **2018**, *12* (11), 11407−11416.
(21) Zhang, P.; Liao, Q.; Zhang, T.; Cheng, H.; Huang, Y.; Yang, C.; Li, C.; Jiang, L.; Qu, L. High Throughput of Clean Water Excluding Ions, Organic Media, and Bacteria from Defect-Abundant Graphene Aerogel under Sunlight. *Nano Energy* **2018**, *46*, 415−422.
(22) Ren, H.; Tang, M.; Guan, B.; Wang, K.; Yang, J.; Wang, F.; Wang, M.; Shan, J.; Chen, Z.; Wei, D.; Peng, H.; Liu, Z. Hierarchical Graphene Foam for Efficient Omnidirectional Solar-Thermal Energy Conversion. *Adv. Mater.* **2017**, *29* (38), 1702590.
(23) Zhang, P.; Liao, Q.; Yao, H.; Cheng, H.; Huang, Y.; Yang, C.; Jiang, L.; Qu, L. Three-Dimensional Water Evaporation on a Macroporous Vertically Aligned Graphene Pillar Array under One Sun. *J. Mater. Chem. A* **2018**, *6* (31), 15303−15309.
(24) Li, Y.; Gao, T.; Yang, Z.; Chen, C.; Kuang, Y.; Song, J.; Jia, C.; Hitz, E. M.; Yang, B.; Hu, L. Graphene Oxide-Based Evaporator with One-Dimensional Water Transport Enabling High-Efficiency Solar Desalination. *Nano Energy* **2017**, *41*, 201−209.
(25) Li, X.; Xu, W.; Tang, M.; Zhou, L.; Zhu, B.; Zhu, S.; Zhu, J. Graphene Oxide-Based Efficient and Scalable Solar Desalination Under One Sun with a Confined 2D Water Path. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113* (49), 13953−13958.
(26) Liang, H.; Liao, Q.; Chen, N.; Liang, Y.; Lv, G.; Zhang, P.; Lu, B.; Qu, L. Thermal Efficiency of Solar Steam Generation Approaching 100% through Capillary Water Transport. *Angew. Chem., Int. Ed.* **2019**, *58* (52), 19041−19046.
(27) Xu, N.; Hu, X.; Xu, W.; Li, X.; Zhou, L.; Zhu, S.; Zhu, J. Mushrooms as Efficient Solar Steam-Generation Devices. *Adv. Mater.* **2017**, *29* (28), 1606762.
(28) Li, X.; Li, J.; Lu, J.; Xu, N.; Chen, C.; Min, X.; Zhu, B.; Li, H.; Zhou, L.; Zhu, S.; Zhang, T.; Zhu, J. Enhancement of Interfacial Solar Vapor Generation by Environmental. *Energy. Joule* **2018**, *2* (7), 1331−1338.
(29) Shi, Y.; Li, R.; Jin, Y.; Zhuo, S.; Shi, L.; Chang, J.; Hong, S.; Ng, K.-C.; Wang, P. A 3D Photothermal Structure toward Improved Energy Efficiency in Solar Steam Generation. *Joule* **2018**, *2* (6), 1171−1186.

https://dx.doi.org/10.1021/accountsmr.0c00073
Acc. Mater. Res. 2021, 2, 97−107

(30) Cui, L.; Zhang, P.; Xiao, Y.; Liang, Y.; Liang, H.; Cheng, Z.; Qu, L. High Rate Production of Clean Water Based on the Combined Photo-Electro-Thermal Effect of Graphene Architecture. *Adv. Mater.* **2018**, *30* (22), 1706805.
(31) Yao, H.; Zhang, P.; Huang, Y.; Cheng, H.; Li, C.; Qu, L. Highly Efficient Clean Water Production from Contaminated Air with a Wide Humidity Range. *Adv. Mater.* **2020**, *32* (6), 1905875.
(32) Zhao, F.; Zhou, X.; Shi, Y.; Qian, X.; Alexander, M.; Zhao, X.; Mendez, S.; Yang, R.; Qu, L.; Yu, G. Highly Efficient Solar Vapour Generation via Hierarchically Nanostructured Gels. *Nat. Nanotechnol.* **2018**, *13* (6), 489−495.
(33) Yang, C.; Huang, Y.; Cheng, H.; Jiang, L.; Qu, L. Rollable, Stretchable, and Reconfigurable Graphene Hygroelectric Generators. *Adv. Mater.* **2019**, *31* (2), 1805705.
(34) Zhao, F.; Wang, L.; Zhao, Y.; Qu, L.; Dai, L. Graphene Oxide Nanoribbon Assembly toward Moisture-Powered Information Storage. *Adv. Mater.* **2017**, *29* (3), 1604972.
(35) Cheng, H.; Huang, Y.; Zhao, F.; Yang, C.; Zhang, P.; Jiang, L.; Shi, G.; Qu, L. Spontaneous Power Source in Ambient Air of a Well-Directionally Reduced Graphene Oxide Bulk. *Energy Environ. Sci.* **2018**, *11* (10), 2839−2845.
(36) Xue, J.; Zhao, F.; Hu, C.; Zhao, Y.; Luo, H.; Dai, L.; Qu, L. Vapor-Activated Power Generation on Conductive Polymer. *Adv. Funct. Mater.* **2016**, *26* (47), 8784−8792.
(37) Xu, T.; Ding, X.; Huang, Y.; Shao, C.; Song, L.; Gao, X.; Zhang, Z.; Qu, L. An Efficient Polymer Moist-Electric Generator. *Energy Environ. Sci.* **2019**, *12* (3), 972−978.
(38) Huang, Y. X.; Cheng, H. H.; Yang, C.; Yao, H. Z.; Li, C.; Qu, L. T. All-Region-Applicable, Continuous Power Supply of Graphene Oxide Composite. *Energy Environ. Sci.* **2019**, *12* (6), 1848−1856.
(39) Cheng, H.; Huang, Y.; Qu, L.; Cheng, Q.; Shi, G.; Jiang, L. Flexible In-Plane Graphene Oxide Moisture-Electric Converter for Touchless Interactive Panel. *Nano Energy* **2018**, *45*, 37−43.
(40) Liang, Y.; Zhao, F.; Cheng, Z.; Zhou, Q.; Shao, H.; Jiang, L.; Qu, L. Self-Powered Wearable Graphene Fiber for Information Expression. *Nano Energy* **2017**, *32*, 329−335.
(41) Nie, X.; Ji, B.; Chen, N.; Liang, Y.; Han, Q.; Qu, L. Gradient Doped Polymer Nanowire for Moistelectric Nanogenerator. *Nano Energy* **2018**, *46*, 297−304.
(42) Huang, Y.; Cheng, H.; Shi, G.; Qu, L. Highly Efficient Moisture-Triggered Nanogenerator Based on Graphene Quantum Dots. *ACS Appl. Mater. Interfaces* **2017**, *9* (44), 38170−38175.
(43) Xu, T.; Han, Q.; Cheng, Z.; Zhang, J.; Qu, L. Interactions between Graphene-Based Materials and Water Molecules toward Actuator and Electricity-Generator Applications. *Small Methods* **2018**, *2* (10), 1800108.
(44) Shao, C.; Gao, J.; Xu, T.; Ji, B.; Xiao, Y.; Gao, C.; Zhao, Y.; Qu, L. Wearable Fiberform Hygroelectric Generator. *Nano Energy* **2018**, *53*, 698−705.

https://dx.doi.org/10.1021/accountsmr.0c00073
Acc. Mater. Res. 2021, 2, 97−107