**Foamlike 3D Graphene Coatings for Cooling Systems Involving Phase Change**

Abdolali K. Sadaghiani,† Ahmad Reza Motezakker,† Sibel Kasap,‡ Ismet I. Kaya,†‡,§ and Ali Koşar*†,‡,§

†Faculty of Engineering and Natural Sciences, ‡Sabanci University Nanotechnology and Application Center (SUNUM), and §Center of Excellence for Functional Surfaces and Interfaces for Nanodiagnostics (EFSUN), Sabanci University, Tuzla 34956, Istanbul, Turkey

3 Supporting Information

**ABSTRACT:** Boiling is an efficient heat-transfer mechanism because of the utilization of latent heat of vaporization and has the potential to be used for cooling high-power electronic devices. Surface enhancement is one of the widely used techniques for heat-transfer augmentation in boiling systems. Here, an experimental investigation was conducted on chemical vapor deposition-grown three-dimensional (3D) foamlike graphene-coated silicon surfaces to investigate the effect of pore structures on pool boiling heat transfer and corresponding heat-transfer enhancement mechanisms. 3D graphene-coated samples with four graphene thicknesses were utilized along with a plain surface to investigate boiling heat-transfer characteristics and enhancement mechanisms. A high-speed camera was used to provide a deeper understanding of the bubble dynamics upon departure of emerging bubbles and visualize vapor columns in different boiling regimes. On the basis of the obtained results, in addition to interfacial evaporation, mechanical resonance of the 3D structure had also a considerable effect on vapor column formation. The results indicated that there is an optimum thickness, which exhibits the best performance in terms of boiling heat transfer.

**INTRODUCTION**

Because of the recent trend of miniaturization of electronic devices, thermal management of such devices is obligatory and yet challenging. There are many cooling methods such as spray cooling¹,² and passive cooling techniques³⁻⁵ involving phase change phenomena. Among phase change (liquid⁻vapor) phenomena, boiling is a widely used phenomenon in the industry.⁶ Owing to a large amount of heat dissipation and achievable high heat-transfer coefficients, it is one of the most effective heat-transfer mechanisms for cooling high-power microelectronic devices.⁷⁻⁹ A typical boiling phenomenon (shown in Figure 1) starts with single-phase natural convection. As the wall heat flux increases, bubbles start to form. They grow and eventually depart from the heated surface. The process of bubble formation and departure is associated with partial nucleate boiling. The nucleation process in partial nucleate boiling strongly depends on the surface morphology. As the rate of bubble nucleation increases with the applied heat flux, more bubbles coalesce, forming vapor columns. In the so-called developed nucleate boiling region, heat transfer from the heated surface is enhanced up to a point, where the formation of vapor columns and blankets eventually reduces the heat transfer by acting as an isolating layer between the heated surface and the liquid. This point is called critical heat flux (CHF), which is the limit for systems involving boiling phenomena. Beyond CHF, a permanent vapor blanket appears on the heated surface, and the surface temperature dramatically increases, leading to the device burnout.

Both heat-transfer coefficient and CHF are affected by surface properties such as surface roughness, wettability, and porosity. Accordingly, pool boiling heat transfer has been...
enhanced using micro–nanostructures, coated particles, and nanowires. Graphene is a new material and has received much attention because of its unique properties and interesting capabilities. Graphene consisting of sp²-hybridized carbon atoms in two-dimensional hexagonal lattice has been a promising alternative for many fields owing to its high thermal and electrical conductivity, noteworthy optical transmittance, superior chemical stability, and high flexibility. Although graphene has these unique properties, its preparation typically results in cracks, wrinkling, defects, and mechanical problems when integrated into three-dimensional (3D) applications. To overcome this drawback, graphene has been prepared in 3D forms such as aerogels, foams, and sponges during the last decade. These forms have low mass density, large surface area, good mechanical stability, and high thermal and electrical conductivity. Besides energy, sensing, detecting, tissue engineering, and environmental applications, 3D graphene frameworks also have a potential in heat-transfer enhancement because of their high thermal conductivity and porosity.

3D graphene foam has been prepared using two main approaches: self-assembly method and temple-assisted chemical vapor deposition (CVD) method. In the self-assembly method, reduced graphene oxide (rGO) is used as a precursor and prepared by the oxidation of natural graphite powder with the use of strong chemical oxidants such as HNO₃, KMNO₄, and H₂SO₄. Because of the ability of preparation in large quantities and abundant surface functional groups, rGO has been extensively used as a precursor for producing 3D graphene and graphene-based composites. Although rGO has these advantages, it is poorly conductive because of the surface defects and oxygen-containing groups, which are introduced during the oxidation process of graphite. The use of chemical oxidants also introduces some disadvantages such as toxicity, corrosiveness, and the possibility of noncarbon impurities in rGO. In addition, the hydrophobic rGO sheets are easy to aggregate and restack because of the partial removal of hydrophilic functional groups after the reduction of GO. Therefore, both of these shortcomings limit the performance of 3D graphene structures.

The CVD method has been considered as an alternative method to overcome these drawbacks. In this method, 3D graphene foams are produced onto a porous metal substrate using a carbon precursor with hydrogen at a high temperature under vacuum conditions. With this method, more controlled and uniform morphologies and structures can be obtained. In addition, obtained graphene foams exhibit a continuous and interconnected graphene 3D network with each other without any breaks and copying and inheriting the interconnected 3D scaffold structure of the porous metal substrate templates. This structure provides desired properties such as outstanding thermal conductivity and large specific surface area (SSA), thereby making 3D graphene foams a strong alternative for high heat flux cooling systems.

The effect of graphene coatings on boiling heat transfer has been investigated in a number of studies. Most of them focused on the graphene layer coating and resulting deposition of graphene suspensions on a heated surface. For example, investigated CHF enhancement in a graphene oxide (GO) colloidal suspension. In their experiments, nucleate boiling was performed on a surface coating, which formed as a resulting deposition of GO colloids. It was reported that the thickness of the deposited layer was approximately proportional to the observed increase in CHF. Using the graphene/GO suspensions in water, Park et al. examined the effect of nanosheet deposition on CHF. They concluded that the nanosheet porous structure formation (because of its own self-assembly characteristic) resulted in critical instability wavelength alteration, which eventually enhanced CHF. 3D foamlike rGO was used by Ahn et al. to prevent heater failure during boiling. They showed that because of the excellent thermal conductivity, the graphene-coated layer prohibited preparation of hot spots, resulting in CHF enhancement.

Seo et al. examined pool boiling heat transfer on nanoporous graphene-layered-deposited surfaces, which were prepared by the rapid thermal annealing method. Enhancement in CHF was explained by high porosity and permeability of graphene coating and subsequent effects of these parameters on hydrodynamic and capillary pumping limits. Jaikumar et al. investigated the effect of graphene and GO coatings on pool boiling enhancement. They transferred the mixture of graphene and GO to copper plain samples by the dip coating method. They reported enhancements of 42 and 47% for CHF and heat-transfer coefficient, respectively. They also showed that the pool boiling performance was notably impeded by the increase in coating thickness of graphene and the GO layer. Afterward, Jaikumar et al. presented the combined effect of GO and porous copper particles on pool boiling enhancement. Rapid nucleation activity, high wettability as a result of roughness augmentation, and wicking-enabled dendritic structures were mentioned as the contributing mechanisms for CHF and HTC enhancements.

RESULTS AND DISCUSSION

In this study, 3D graphene foams were grown on porous nickel foams with a thickness of 1.6 mm and pore sizes ranging from 60 to 700 μm. (≥95% porosity, 99.99% purity, Alantum Advanced Technology Materials (Dalian) Co. Ltd.) by the CVD method in a horizontal furnace system. The CVD growth procedure and conditions are presented in Supporting Information Note S1. To obtain graphene foams without nickel scaffold, nickel foams were etched in 1 M FeCl₃ solution for 24 h. After the nickel foams were completely etched, graphene foams were cleaned with deionized water/HCl mixed solutions until FeCl₃ residues were completely gone. At the last step, the samples were transferred onto the SiO₂/Si substrate with 2 × 2 cm² and then dried at 80 °C for 30 min in an oven to enable the adhesion of the graphene foams on the substrate. The Brunauer–Emmett–Teller surface area measurement technique (Micromeritics ASAP 2020) was used to measure the SSA of graphene foams. The samples were degassed using flowing N₂ at 200 °C for 24 h before the measurements. The characterization of 3D graphene foams was performed by the X-ray diffraction (XRD, Bruker AXS ADVANCE), Raman (Renishaw inVia Reflex), and scanning electron microscopy (SEM, Zeiss Gemini 1530) techniques.
structures of the samples were determined by XRD patterns, which were obtained at ambient temperature over $2\theta$ values within the range of $20^\circ$–$80^\circ$ under Cu Kα X-ray radiation ($\lambda_{Cu} = 1.5406$ Å). The Raman spectra were collected in the wavelength of $100$–$3200$ cm$^{-1}$ under $532$ nm excitation at $2$ μm spot size to identify the graphene morphology. The scanning electron microscope operated at $20$ kV was used to observe the 3D structures of graphene foams. Table 1 shows the graphene thicknesses for each sample.

### Table 1. Sample Characterization

| sample no. | SSA (m$^2$/g) | graphene thickness (nm) | water contact angle measurement (deg) |
|------------|---------------|-------------------------|--------------------------------------|
| #1         | 550           | 8                       | 123 ± 1                              |
| #2         | 350           | 13                      | 124 ± 1                              |
| #3         | 150           | 29                      | 125 ± 1                              |
| #4         | 80            | 55                      | 128 ± 1                              |

*a SSA, graphene thickness, and water contact angle measurements of each sample.

The 3D networks are identified via the SEM technique, as shown in Figure 2, for sample #4. The SEM image of the interconnected 3D nickel foam structure with a smooth surface is shown in Figure 2a. After CVD growth, graphene layers cover the nickel foam surface (Figure 2b). Single-layer graphene flakes and multilayer graphene flakes are represented as SLG and MLG on the SEM image, respectively. Figure 2c displays the SEM images of graphene foams without a nickel foam template. It can be seen from SEM images that graphene foams copied the interconnected 3D structure of nickel foam templates. Because the graphene foam is extremely thin, wrinkles occur on the graphene surface during the etching process. The pore size of the graphene foam was calculated as between $70$ and $400$ μm, and the thickness of the branch width was found to be about $70$ μm. The detailed information about sample characterization is presented in Supporting Information Note S2.

It is known that only cavities within a specific size range can be activated during the nucleation process. The size range depends on several factors such as liquid superheat, implying that a sufficient liquid superheat is required for bubble growth from a nucleus. Figure 3 presents the bubble nucleation process from a single cavity and within porous medium. As can be seen, bubble nucleation from surfaces with only discrete cavities strongly depends on the individual cavity radius and its surrounding fluid temperature, which causes different bubble departure diameters on such surfaces (Figure 3a). For surfaces with porous coatings, as demonstrated in Figure 3b, the cavities are connected with a mesh structure. By providing interconnected paths for liquid and vapor phases, the pore network increases the interaction among nucleation sites and the surrounding fluid.

Pool boiling experiments were conducted under atmospheric pressure using deionized water as the working fluid. A detailed description of the experimental setup, procedure, and uncertainty analysis is presented in Supporting Information Note S3. Heat-transfer mechanisms and forces acting on the individual bubbles in the partial nucleate boiling region [wall superheat lower than $\sim 15$ (K)] and vapor columns in the developed nucleate boiling region [wall superheat higher than $\sim 15$ (K)] are different from each other. It should be noted that the difference between the wall and saturation temperatures is defined as wall superheat ($\Delta T_{sup}$).

**Figure 2.** Obtained SEM images for (a) nickel foam, (b) GF/nickel foam, (c) GF (sample #4), and (d) contact angle goniometer image (sample #3).

**Figure 3.** Bubble nucleation from surfaces with (a) discrete cavity structure and (b) pore network. The porous medium directly affects the nucleation process by providing interconnected paths for vapor and liquid transport.
The onset of partial nucleate boiling is identified with individual bubbles growing and departing from the heated surface. According to the obtained wall superheats shown in Figure 4a, at a fixed wall heat flux (up to ∼30 (kW/m²)), graphene coatings have a considerable effect on the wall superheat (ΔT_{sup} < 15 (K)). Because of high thermal conductivity of graphene coatings, bubbles nucleate not only at the bottom of coating but also within the porous medium. The heat-transfer coefficients are shown in Figure 4b. As expected, promising heat-transfer enhancement can be observed for graphene coatings. The heat-transfer enhancement at partial nucleate boiling (ΔT_{sup} < 15 K) increases with graphene thickness such that the maximum heat-transfer enhancement for coatings with graphene thicknesses of 55, 29, 13, and 8 nm are ∼56, ∼33, ∼23, and ∼12%, respectively.

To have an understanding about the bubble departure diameter at partial nucleate boiling, a model was developed based on the bubble growth force, buoyancy force, inertia forces, lift force, and surface tension force. Figure 5a shows the forces acting on a departed bubble from a pore. The buoyancy and lift forces tend to detach the bubble from the surface, while other forces keep it attached. The force balance equation is obtained as

\[ F_{\text{buoyancy}} + F_{\text{lift}} - (F_{\text{growth}} + F_{\text{surface tension}} + F_{\text{inertia}}) = 0 \]  

(1)

The expressions of the forces acting on the bubble are used to analyze the effect of graphene coating on the bubble upon the departure point (Supporting Information Note S4). The heat transfer from the superheated liquid into the bubble is considered to be a transient conduction process (Figure 5b). Within the porous medium, heat transfer from the superheated liquid is much more than the uncoated sample. Taking into account that at a partial nucleate boiling region bubble nucleation strongly depends on the liquid superheat, the 3D graphene foam acts as a conductive network, providing the required liquid temperature for the onset of the nucleation process. The time required for the liquid to attain this superheat is called the waiting period. Heat transfer from the superheated liquid into the bubble is considered to be a transient conduction process. The graphene network reduces the waiting period, thereby offering enhanced conduction heat transfer within the porous medium and consequently enhanced pool boiling heat transfer. This accelerates the nucleation process and results in lower bubble growth force, as shown in Figure 5a. Consequently, graphene coating reduces the bubble departure diameter. Bubble departure diameter decreases simultaneously with a decrease in departure frequency, which enhances cooling of the surface.

Furthermore, using visual images bubble departure diameter and frequencies are measured in the experiments. A detailed procedure for bubble departure diameter and frequency calculation is presented in a previous study. The obtained bubble departure diameters and frequencies are presented in Figure 5c,d. According to the obtained results, in the partial nucleate boiling region, the bubble departure frequency increases with graphene thickness, indicating the enhancing effect of coating on surface cooling. Comparing the trends in obtained results shown in Figure 5c,d, it can be seen that the differences between departure frequency and bubble departure diameter for graphene-coated surfaces are much smaller than for bare silicon surfaces. One of the main reasons for such a trend on coated surfaces is attributed to the combination of active nucleation sites on porous surfaces.
Although higher heat-transfer coefficients are obtained for all graphene-coated samples compared to bare silicon surface (as shown in Figure 4), 3D graphene-coated surfaces exhibit different trends for the partial boiling ($\Delta T < 15$ K) and developed boiling ($\Delta T < 15$ K) regions. In the partial nucleate boiling region, the heat-transfer coefficient increases with graphene thickness. For the developed boiling region, the heat-transfer coefficient increases as the graphene thickness decreases down to 13 nm, beyond which the obtained heat-transfer coefficients are lower than the ones of the 13 nm thick sample. There are several factors causing the different heat-transfer behaviors of 3D foamlike graphene coatings such as disconnected pores, vapor column size, graphene interface evaporation, and mechanical resonance of the 3D structure.

SEM images indicate that as graphene thickness decreases, the number of disconnected rods increases in the 3D branch (Supporting Information Note S5), which implies that the pore sizes increase with the decrease in graphene thickness. One reason for heat-transfer deterioration in the 8 nm thick sample is bubble trapping in the porous structure. At high heat fluxes, the maximum pore size is large enough to trap the bubbles and vapor blanket inside, which acts as the insulator and deteriorates the heat-transfer performance of the samples (Table 1).

The other factor affecting the heat-transfer mechanism in the developed nucleate boiling region is the formation of vapor column within the 3D graphene structure. As the wall heat flux increases, individual bubbles form vapor layers within the coating, which influences the developed nucleate boiling region. Figure 6a shows the departure bubbles at the heat flux of 100 W/cm$^2$ (for sample #3). The schematic of the vapor column within the porous medium is shown in Figure 6b. Visualization studies reveal different vapor column formation on graphene-coated samples, indicating the effect of graphene thickness. As shown in Figure 6d, the coating with 55 nm thick graphene structures generates smaller bubbles but more vapor columns compared to the 8 nm thick graphene coating. According to the obtained results, it is found that the vapor column size increases as the graphene thickness decreases.

The forces acting on the vapor column in the porous medium can be determined by Bond ($Bo = \Delta \rho g a^3/\sigma$) and capillary ($Ca = \frac{a^4 \eta}{\sigma k}$) (nondimensional) numbers. Here, $\Delta \rho$, $g$, $a$, $\sigma$, $\eta$, $u$, and $k$ are density difference between vapor and water (kg·m$^{-3}$), gravity acceleration constant (m·s$^{-2}$), the characteristic length (e.g., pore radius), water–vapor surface tension (N·m$^{-1}$), dynamic viscosity (N·s·m$^{-2}$), mean fluid velocity (m·s$^{-1}$), and porous medium permeability, respectively. Because of lower density, the resulting balance inside the porous medium forces the vapor phase to form vapor columns in the saturated medium (fully developed nucleate boiling). Graphene coatings with different pore sizes have different Bond and capillary numbers such that coating with a higher graphene coating thickness has denser and smaller pore sizes meaning lower Bond number but higher capillary number for the corresponding coating, which leads to smaller vapor column formation.
The vapor column growth can also be analyzed based on the thermal resistance network model proposed by Ha and Graham, which suggests that the heat transfer occurs by evaporation at the interface. The other reason for higher heat-transfer coefficient corresponding to 3D coatings with thinner graphene coatings is that the evaporation in the larger interface area per volume enhances the heat-transfer performance of such coatings. As expected, at high heat fluxes, the graphene coating raises the bubble departure frequency.

Weak van der Waals forces between graphene layers enable graphene layers to slide easily and give flexibility to the structure. The resulting mechanical resonance due to the bubble nucleation effect within the porous medium and reaction force of the departed bubble on the coating surface alters boiling characteristics in foamlike graphene coatings. Observed different bubble departure angles and bubble coalescence shapes on coated surfaces with different graphene thicknesses could be attributed to the mechanical resonance for the 3D structure (Supporting Information Note S6).

This study presents pool boiling experiments conducted on CVD-grown 3D foamlike graphene-coated surfaces to show the effect of graphene coating thickness on the pool boiling heat-transfer performance. According to the obtained results, the 3D structure of the coating has a significant effect on pool boiling heat-transfer mechanisms. Effects such as pore shape and mechanical resonance of the 3D structure are possible reasons for different bubble behaviors in developed nucleate boiling. Furthermore, there exists an optimum thickness of 3D graphene coatings, where the highest performance was achieved. This is mainly due to the trapped bubbles inside the porous medium for thick configurations, which affect the bubble dynamics involving bubble departure diameter and frequency. The results reveal that the facile method of producing 3D foamlike graphene coatings implemented in this study can be used as an effective alternative for boiling heat-transfer enhancement.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b02040.

Preparation of 3D foamlike graphene coating by the CVD method, XRD spectrum and SEM images of the 3D graphene foam, experimental setup and procedure details, force expressions, SEM images of graphene-coated Ni foams, and effect of graphene coating on bubble departure (PDF)

**AUTHOR INFORMATION**

*Corresponding Author*

E-mail: kosara@sabanciuniv.edu (A.K.)
2007 chemical vapor deposition; SEM, scanning electron microscopy on surface-coating enhancement of pool boiling heat transfer. Thermophys. Eng. Clarendon Press, 1994.

■ ABBREVIATIONS

BET, Brunauer–Emmett–Teller; CHF, critical heat flux; CVD, chemical vapor deposition; SEM, scanning electron microscopy

■ REFERENCES

(1) Incropera, F. P. Liquid Cooling of Electronic Devices by Single-Phase Convection; Wiley-Interscience, 1999; Vol. 3.
(2) Kim, J. Spray cooling heat transfer: the state of the art. Int. J. Heat Fluid Flow 2007, 28, 753–767.
(3) Zhou, D.; Zhao, C. Y.; Tian, Y. Review on thermal energy storage with phase change materials (PCMs) in building applications. Appl. Energy 2012, 92, 593–605.
(4) Kandasamy, R.; Wang, X.-Q.; Mujumdar, A. S. Transient cooling of electronics using phase change material (PCM)-based heat sinks. Appl. Therm. Eng. 2008, 28, 1047–1057.
(5) Sadaghiani, A. K.; Saadi, N. S.; Parapari, S. S.; Karabacak, T.; Keskinos, M.; Koşar, A. Boiling heat transfer performance enhancement using micro and nano structured surfaces for high heat flux electronics cooling systems. Appl. Therm. Eng. 2017, 127, 484–498.
(6) Collier, J. G.; Thome, J. R. Convective Boiling and Condensation; Clarendon Press; New York, 1994.
(7) Nikolayev, V.; Chatkin, D.; Garrabos, Y.; Béysens, D. Experimental evidence of the vapor recoil mechanism in the boiling crisis. Phys. Rev. Lett. 2006, 97, 184503.
(8) Şişman, Y.; Sadaghiani, A. K.; Khedir, K. R.; Brozak, M.; Karabacak, T.; Koşar, A. Subcooled Flow Boiling Over Micro-structured Plates In Rectangular Minichannels. Nanoscale Microscale Thermophys. Eng. 2016, 20, 173–190.
(9) Motezzahi, A. R.; Sadaghiani, A. K.; Akkoc, Y.; Parapari, S. S.; Góźdź, D.; Koşar, A. Surface modifications for phase change cooling applications via crenarchaeon Sulfolobus solfataricus P2 bio-coatings. Sci. Rep. 2017, 7, 17891.
(10) Dhullon, N. S.; Buongiorno, J.; Varanasi, K. K. Critical heat flux maxima during boiling crisis on textured surfaces. Nat. Commun. 2015, 6, 8247.
(11) Zou, A.; Maroo, S. C. Critical height of micro/nano structures for pool boiling heat transfer enhancement. Appl. Phys. Lett. 2013, 103, 221602.
(12) Sarangi, S.; Weibel, J. A.; Girimella, S. V. Effect of particle size on surface-coating enhancement of pool boiling heat transfer. Int. J. Heat Mass Transfer 2015, 81, 103–113.
(13) Hsu, C.-C.; Chen, P.-H. Surface wettability effects on critical heat flux of boiling heat transfer using nanoparticle coatings. Int. J. Heat Mass Transfer 2012, 55, 3713–3719.
(14) Yao, Z.; Lu, Y.-W.; Kandlikar, S. G. Fabrication of nanowires on orthogonal surfaces of microchannels and their effect on pool boiling. J. Micromech. Microeng. 2012, 22, 115005.
(15) Chen, R.; Lu, M.-C.; Srinivasan, V.; Wang, Z.; Cho, H. H.; Majumdar, A. Nanowires for enhanced boiling heat transfer. Nano Lett. 2009, 9, 548–553.
(16) Novoselov, K. S.; Jiang, D.; Schedin, F.; Booth, T. J.; Khotkevich, V. Y.; Moreo, S. V.; Geim, A. K. Two-dimensional atomic crystals. Proc. Natl. Acad. Sci. U.S.A. 2005, 102, 10451–10453.
(17) Neto, A. H. C.; Guinea, F.; Peres, N. M. R.; Novoselov, K. S.; Geim, A. K. The electronic properties of graphene. Rev. Mod. Phys. 2009, 81, 109.
(18) Scarp, F.; Adhikari, S.; Panahi, A. S. Effective elastic mechanical properties of single layer graphene sheets. Nanotechnology 2009, 20, 065709.
(19) Bonaccorsi, F.; Sun, Z.; Hasan, T.; Ferrari, A. Graphene photonics and optoelectronics. Nat. Photonics 2010, 4, 611–622.
(20) Yavari, F.; Chen, Z.; Thomas, A. V.; Ren, W.; Cheng, H.-M.; Koratkar, N. High sensitivity gas detection using a macroscopic three-dimensional graphene foam network. Sci. Rep. 2011, 1, 166.
(21) Fang, Q.; Shen, Y.; Chen, B. Synthesis, decoration and properties of three-dimensional graphene-based macrostructures: a review. Chem. Eng. J. 2015, 264, 753–771.
(22) Mao, S.; Lu, G.; Chen, J. Three-dimensional graphene-based composites for energy applications. Nanoscale 2015, 7, 6924–6943.
(23) Zhang, L.; Shi, G. Preparation of highly conductive graphene hydrogels for fabricating supercapacitors with high rate capability. J. Phys. Chem. C 2011, 115, 17206–17212.
(24) Xue, Y.; Yu, D.; Dai, L.; Wang, R.; Li, D.; Roy, A.; Lu, F.; Chen, H.; Liu, Y.; Qu, J. Three-dimensional N-doped graphene foam as a metal-free catalyst for oxygen reduction reaction. Phys. Chem. Chem. Phys. 2013, 15, 12220–12226.
(25) Lee, J.-S.; Ahn, H.-J.; Yoon, J.-C.; Jiang, J.-H. Three-dimensional nano-foam of few-layer graphene grown by CVD for DSSC. Phys. Chem. Chem. Phys. 2012, 14, 7938–7943.
(26) Zhang, X.; Sui, Z.; Xu, B.; Yue, S.; Luo, Y.; Zhan, W.; Liu, B. Mechanically strong and highly conductive graphene aerogel and its use as electrodes for electrochemical power sources. J. Mater. Chem. 2011, 21, 6494–6497.
(27) Yong, Y.-C.; Dong, X.-C.; Chan-Park, M. B.; Song, H.; Chen, P. Macroporous and monolithic anode based on polyaniline hybridized three-dimensional graphene for high-performance microbial fuel cells. ACS Nano 2012, 6, 2394–2400.
(28) Cao, X.; Shi, Y.; Shi, W.; Lu, G.; Huang, X.; Yan, Q.; Zhang, Q.; Zhang, H. Preparation of novel 3D graphene networks for supercapacitor applications. Small 2011, 7, 3163–3168.
(29) Pettes, M. T.; Ji, H.; Ruoff, R. S.; Shi, L. Thermal transport in three-dimensional foam architectures of few-layer graphene and ultrathin graphite. Nano Lett. 2012, 12, 2959–2964.
(30) Lin, H.; Xu, S.; Wang, X.; Mei, N. Significantly reduced thermal diffusivity of free-standing two-layer graphene in graphene foam. Nanotechnology 2013, 24, 415706.
(31) Nguyen, D. D.; Tai, N.-H.; Lee, S.-B.; Kuo, W.-S. Super-hydrophobic and superoleophilic properties of graphene-based sponges fabricated using a facile dip coating method. Energy Environ. Sci. 2012, 5, 7908–7912.
(32) Dong, X.; Cao, Y.; Wang, J.; Chan-Park, M. B.; Wang, L.; Huang, W.; Chen, P. Hybrid structure of zinc oxide nanorods and three dimensional graphene foam for supercapacitor and electrochemical sensor applications. RSC Adv. 2012, 2, 4364–4369.
(33) Li, C.; Shi, G. Three-dimensional graphene architectures. Nanoscale 2012, 4, 5549–5553.
(34) Jiang, L.; Fan, Z. Design of advanced porous graphene materials: from graphene nanomesh to 3D architectures. Nanoscale 2014, 6, 1922–1945.
(35) Huang, X.; Yin, Z.; Wu, S.; Qi, X.; He, Q.; Zhang, Q.; Yan, Q.; Boey, F.; Zhang, H. Graphene-based materials: synthesis, characterization, properties, and applications. Small 2011, 7, 1876–1902.
(36) Nardecchia, S.; Carriazo, D.; Ferrer, M. L.; Gutiérrez, M. C.; del Monte, F. Three dimensional macroporous architectures and aerogels built of carbon nanotubes and/or graphene: synthesis and applications. Chem. Soc. Rev. 2013, 42, 794–830.

(37) Dreyer, D. R.; Park, S.; Bielawski, C. W.; Ruoff, R. S. The chemistry of graphene oxide. Chem. Soc. Rev. 2010, 39, 228–240.

(38) Park, S.; Ruoff, R. S. Chemical methods for the production of graphenes. Nat. Nanotechnol. 2009, 4, 217–224.

(39) Xu, Y.; Shi, G. Assembly of chemically modified graphene: methods and applications. J. Mater. Chem. 2011, 21, 3311–3323.

(40) Huang, X.; Qi, X.; Boey, F.; Zhang, H. Graphene-based composites. Chem. Soc. Rev. 2012, 41, 666–686.

(41) Compton, O. C.; Nguyen, S. T. Graphene oxide, highly reduced graphene oxide, and graphene: versatile building blocks for carbon-based materials. Small 2010, 6, 711–723.

(42) Dong, X.; Su, C.-Y.; Zhang, W.; Zhao, J.; Ling, Q.; Huang, W.; Chen, P.; Li, L.-J. Ultra-large single-layer graphene obtained from solution chemical reduction and its electrical properties. Phys. Chem. Chem. Phys. 2010, 12, 2164–2169.

(43) Gómez-Navarro, C.; Meyer, J. C.; Sundaram, R. S.; Chuvilin, A.; Kurash, S.; Burghard, M.; Kern, K.; Kaiser, U. Atomic structure of reduced graphene oxide. Nano Lett. 2010, 10, 1144–1148.

(44) Li, D.; Müller, M. B.; Gilje, S.; Kaner, R. B.; Wallace, G. G. Processable aqueous dispersions of graphene nanosheets. Nat. Nanotechnol. 2008, 3, 101–105.

(45) Cote, L. J.; Kim, F.; Huang, J. Langmuir– Blodgett assembly of graphite oxide single layers. J. Am. Chem. Soc. 2008, 131, 1043–1049.

(46) Luo, J.; Cote, L. J.; Tung, V. C.; Tan, A. T. L.; Goins, P. E.; Wu, J.; Huang, J. Graphene oxide nanocollods. J. Am. Chem. Soc. 2010, 132, 17667–17669.

(47) Chen, Z.; Ren, W.; Gao, L.; Li, B.; Pei, S.; Cheng, H.-M. Three-dimensional flexible and conductive interconnected graphene networks grown by chemical vapour deposition. Nat. Mater. 2011, 10, 424–428.

(48) Dong, X.; Wang, X.; Wang, L.; Song, H.; Zhang, H.; Huang, W.; Chen, P. 3D graphene foam as a monolithic and macroporous carbon electrode for electrochemical sensing. ACS Appl. Mater. Interfaces 2012, 4, 3129–3133.

(49) Bi, H.; Huang, F.; Liang, J.; Tang, Y.; Lü, X.; Xie, X.; Jiang, M. Large-scale preparation of highly conductive three dimensional graphene and its applications in CdTe solar cells. J. Mater. Chem. 2011, 21, 17366–17370.

(50) Ji, H.; Zhang, L.; Pettes, M. T.; Li, H.; Chen, S.; Shi, L.; Piner, R.; Ruoff, R. S. Ultrathin graphite foam: a three-dimensional conductive network for battery electrodes. Nano Lett. 2012, 12, 2446–2451.

(51) Ning, G.; Fan, Z.; Wang, G.; Gao, J.; Qian, W.; Wei, F. Graphene nanosheets as high surface area and its application in supercapacitor electrodes. Chem. Commun. 2011, 47, 9876–9878.

(52) Chen, G.; Liu, Y.; Liu, F.; Zhang, X. Fabrication of three-dimensional graphene foam with high electrical conductivity and large adsorption capability. Appl. Surf. Sci. 2014, 311, 808–815.

(53) Dai, X.; Huang, X.; Yang, F.; Li, X.; Sighler, J.; Yang, Y.; Li, C. Enhanced nucleate boiling on horizontal hydrophobic-hydrophilic carbon nanotube coatings. Appl. Phys. Lett. 2013, 102, 161605.

(54) Yu, Q.; Lian, J.; Siriponglertr, S.; Li, H.; Chen, Y. P.; Pei, S.-S. Graphene segregated on Ni surfaces and transferred to insulators. Appl. Phys. Lett. 2008, 93, 113103.

(55) Kim, J. M.; Kim, T.; Kim, J.; Kim, M. H.; Ahn, H. S. Effect of a graphene oxide coating layer on critical heat flux enhancement under pool boiling. Int. J. Heat Mass Transfer 2014, 77, 919–927.

(56) Park, S. D.; Lee, S. W.; Kang, S.; Bang, I. C.; Kim, J. H.; Shin, H. S.; Lee, D. W.; Lee, D. W. Effects of nanoluids containing graphene/graphene-oxide nanosheets on critical heat flux. Appl. Phys. Lett. 2010, 97, 023103.

(57) Ahn, H. S.; Kim, J. M.; Park, C.; Jang, J.-W.; Lee, J. S.; Kim, H.; Kaviani, M.; Kim, M. H. A novel role of three dimensional graphene foam to prevent heater failure during boiling. Sci. Rep. 2013, 3, 1960.