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Heteroatom-Doped Flash Graphene

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methods, but they require reactive and harsh reagents. However, direct synthesis of various heteroatom-doped graphene in larger quantities and high purity through bottom-up methods remains challenging. Here, we report catalyst-free and solvent-free direct synthesis of graphene doped with various

heteroatoms in bulk via flash Joule heating (FJH). Seven types of heteroatom-doped flash graphene (FG) are synthesized through millisecond flashing, including single-element-doped FG (boron, nitrogen, oxygen, phosphorus, sulfur), two-elementco-doped FG (boron and nitrogen), as well as three-element-co-doped FG (boron, nitrogen, and sulfur). A variety of low-cost dopants, such as elements, oxides, and organic compounds are used. The graphene quality of heteroatom-doped FG is high, and similar to intrinsic FG, the material exhibits turbostraticity, increased interlayer spacing, and superior dispersibility. Electrochemical oxygen reduction reaction of different heteroatom-doped FG is tested, and sulfur-doped FG shows the best performance. Lithium metal battery tests demonstrate that nitrogen-doped FG exhibits a smaller nucleation overpotential compared to Cu or undoped FG. The electrical energy cost for the synthesis of heteroatom-doped FG synthesis is only 1.2 to 10.7 kJ g⁻¹, which could render the FJH method suitable for low-cost mass production of heteroatom-doped graphene.

KEYWORDS: flash Joule heating, direct synthesis, flash graphene, heteroatom-doping, catalyst-free

INTRODUCTION

Chemical functionalization of intrinsic nanomaterials has been widely used to tailor the local structures and electronic states, thereby greatly affecting the materials' optical, electrical, and mechanical properties.^{1–4} Traditional methods to achieve chemical modification involve the introduction of various heteroatoms,^{3,5} specific functional groups,^{1,6} or even other molecules⁷ into the intrinsic lattice. Heteroatom doping, which consists of substituting the original components with other elements, is the most basic yet highly effective modification.^{5,8} For graphene, many different dopants can be introduced, including nitrogen, sulfur, oxygen, boron, phosphorus, and some metal atoms.^{9–12} Heteroatom-doped graphene has demonstrated electrocatalytic properties,¹¹ superior performance in sensing applications,⁵ and stronger interactions with various polymers as well as single metal atoms.¹⁰

Previous research has focused on the chemical functionalization of preformed graphene lattice (post-treatment), including ball milling,⁵ thermal annealing of graphene oxide (GO),^{13,14} plasma treatment, and photochemical reactions.^{15,16} Ball milling and plasma methods are simple and scalable routes to synthesize heteroatom-doped graphene, but the doping is usually limited at the edges or other defects.^{5,15,16} Thermal annealing method not only needs GO as the precursor, which is synthesized under harsh oxidation, but also requires extended high temperature to partially recover the sp² carbon network.^{13,14} These top-down insertions into graphene usually cause irreversible degradation of graphene quality, and these procedures can be problematic since they result in inevitable impurities from the excessive supply of reactive agents such as KMnO₄ and BCl₃.^{1,5} Most bottom-up direct synthesis of heteroatom-doped graphene can be achieved by chemical vapor deposition (CVD)¹⁷ or synthetic organic strategies,¹⁸ but the products are limited to ultrasmall amounts, from μg - to mg-scales, and they often suffer from catalytic metal impurities such as Cr, Ti, and Ni. Furthermore, the types of heteroatomdoped graphene compositions achievable are often restricted by the vapor pressure or solubility of the precursors.⁵

heating

Doped flash graphene

Heteroatom source

 (M, MO_x, C_xH_yM)

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Therefore, the direct solid-phase synthesis of heteroatomdoped graphene in bulk quantities from amorphous carbon sources can potentially solve these dilemmas.

Here, we disclose a general synthetic route to heteroatomdoped graphene by ultrafast and all-solid-state catalyst-free flash Joule heating (FJH) method within 1 s. $^{19-23}$ It requires no solvent, no catalysts, and no water. A short electrical pulse of high energy density is passed through the solid precursors, which raises the sample temperature to >3500 K at >10⁵ K s⁻¹ followed by rapid cooling at $>10^4$ K s⁻¹. Seven types of important heteroatom-doped flash graphene (FG), including single-element-doped (B, N, O, P, S), two-element-co-doped (B, N), and three-element-co-doped (B, N, S) FG are produced by millisecond flashing with various low-cost sources, including elements, oxides, and organic compounds. This demonstrates the versatility of the FJH method. These dopants were selected since they can afford air-stable doped graphene products. Spectroscopic analysis indicates that heteroatom-doped FG has good graphene quality and modified electronic structure. Moreover, we demonstrate the precise control of size distribution at the nanoscale and the direct usage of heteroatom-doped FG without laborious purification procedures. The materials were studied for their dispersibility, and tested in electrochemical oxygen reduction reactions (ORR) and lithium metal battery (LMB) compositions. In addition, gram-scale synthesis of heteroatom-doped FG is explored to demonstrate the feasibility of scaling up its production.

RESULTS AND DISCUSSION

Direct Synthesis of Heteroatom-Doped Graphene by Flash Joule Heating. In a typical flash synthesis process, the powdery mixture of dopants and conductive carbon black is slightly compressed inside a thick-walled polymer tube between two well-fitted graphite spacers (Figure S1). The polymer tube can be made from Teflon, poly(1,4-phenylene sulfide), or polyacrylonitrile. The capacitor banks in the circuit are connected to graphite spacers and are used to provide electrothermal energy to the reactants in <1 s. Compared to fluffy copper wool-made electrodes used in our previous publications,¹⁹ thick-walled polymer tubes and well-fitted graphite spacers greatly decrease the loss of heteroatoms and facilitate the formation of the heteroatom-doped graphene. The detailed flash parameters are listed in Table 1. Different dopants can be used as precursors, including elements (M), oxides (MO_x) , and organic compounds (C_xH_vM) (Figure 1a). During a typical FJH synthesis process with a voltage of 110 V and a sample resistance of $\sim 1.0 \Omega$, the current passing through the sample reaches ~60 A within ~100 ms discharge time (Figure S2). Take nitrogen-doped FG (N-FG) as an example, the total amount of electrical energy is 6.6 kJ g^{-1} (Table S1). The temperature is measured by fitting the blackbody radiation spectra during the FJH process (Figure S3). The transient highest temperature reaches \sim 3500 K at \sim 2.0 \times 10⁵ K s⁻¹ and subsequent ultrafast cooling rate after \sim 55 ms is estimated as $\sim 1.8 \times 10^4$ K s⁻¹ (Figure 1b), which facilitates the formation of turbostratic structures with larger interlayer spacings.¹⁹ This ultrafast cooling does not permit AB-stacked graphene to occur, which facilitates dispersion in solvents as seen in the previous publications.^{7,19} The transient ultrahigh temperature volatilizes the heteroatom components and enhances the homogeneous reactions between these precursor vapors and the amorphous carbon source to form the doped graphitic

Table 1. Flash Parameters for Different Systems

	FG	N-FG		B-FG		O-FG
reactant	СВ	melamine + CB (75 wt %)		boric acid + CB (80 wt %)		sucrose + CB (60 wt %)
sample mass (mg)	30	40		40		40
sample resistance (Ω)	~0.7	~0.9		~2.0		~5.0
discharge voltage (V)	110	110		110		120
flash duration (ms)	100	100		100		200
flash repetitions	1 flash	1 flash		1 flash		3 flashes
total capacitance (mF)	60	60		60		60
chamber pressure	Ar (~1 atm)	Ar (~1	atm)	Ar (~1	atm)	Ar (~1 atm)
	P-FC	ì	S-	FG		B,N-FG
reactant	red phosphorus + CB (90 wt %)		PPS + CB bo (50 wt %)		boron (:melamine:CB 2:5:23) ^{<i>a</i>}
sample mass (mg)	25		40)		
sample resistance (Ω)	~1.5		~1.0		~3	3.0
discharge voltage (V)	120		120		11	0
flash duration (ms)	200		100		50	
flash repetitions	3 flashes		1 flash		1 f	lash
total capacitance (mF)	60		60 6		60	
chamber pressure	Ar (~1 atm)		Ar (~1 atm) A		Ar	(~1 atm)
	B,N,S-FG			N-FG-L1		N-FG-L2
reactant	boron:melamine:PPS:CB (3:4:12:12) ^a		:CB	melamine + CB (75 wt %)		melamine + CB (75 wt %)
sample mass (mg)	40			320		1000
sample resistance (Ω)	~1.3	~1.3		~1.0		~0.4
discharge voltage (V)	100			155		175
flash duration (ms)	50		200			VFD ^b
flash repetitions	1 flasl	1 flash		1 flash		1 flash
total capacitance (mF)	60			222		624
chamber	Ar (~	1 atm)		Ar (~1 a	ntm)	Air (~1 atm)

^aMass ratios are used here. ^bVFD means "variable frequency drive", which is a type of controller that drives an electric switch by varying the frequencies and durations of its power supply. Here, 10% duty cycle for 1s followed by 20% duty cycle for 5 s was used.

structure. Therefore, FJH process does not require the use of extra catalysts or excessive reactive agents, which avoids redundant postpurification procedures, such as dialysis.¹² In contrast, traditional post-treatment doping methods require (i) GO as the carbon source, (ii) gas- or solution-phase heteroatom sources, and (iii) long reaction time up to 12 h

pressure



Figure 1. Direct synthesis of heteroatom-doped graphene by flash Joule heating. (a) Schematics of the synthesis of heteroatom-doped turbostratic graphene via flash Joule heating. (b) The real time temperature measurement during direct FJH synthesis of doped flash graphene. (c) Representative temperature profile of common procedures for the post-treatment synthesis of doped AB-stacked graphene, such as that from GO plus solid or gaseous heteroatom sources. (d) Heteroatom ratios and (e) mass yields for different heteroatom-doped flash graphene.

(Figure 1c).^{1,5,13,14} The extended reaction time leads to the formation of heteroatom-doped AB-stacked graphene,¹ which is harder to exfoliate than turbostratic graphene.¹⁹

The as-synthesized FG can reach a heteroatom ratio up to 7.4% for a single type dopant²⁴ and a total heteroatom ratio >10% for multiple heteroatom codoping, including boron and nitrogen (B,N-FG) and boron, nitrogen, and sulfur (B,N,S-FG), demonstrating the broad applicability of the FJH process (Figure 1d). The FJH synthesis takes place in milliseconds within a thick-walled polymer tube with tightly fitting graphite spacers to minimize volatilization of the dopants. This enables a high mass conversion reaction yield up to 74% (Figure 1e).

Characterization of Nitrogen-Doped Flash Graphene. We first explore the nitrogen-doped graphene, since it has been reported to be an effective electrocatalyst.^{10,25} The incorporation of nitrogen into the honeycomb lattice of graphene can be diverse in its substitutional orientations, including pyridinic N, pyrrolic N, graphitic N, and nitrogen oxides (Figure 2a). These N-doped sites change the local symmetry along with electronic structure, and can behave as active sites for various electrochemical and electronic applications. Melamine ($C_3H_6N_6$) was our chosen dopant owing to its high nitrogen

ratio of ~67 wt %. The as-synthesized N-FG has good graphene quality with N doping. The average Raman spectrum is collected from 100 sampling points and the standard deviation is <5%, which reflects the high homogeneity of the N-FG (Figure 2b). High D peak (~1339 cm⁻¹, breathing mode of sp²-carbon atoms in rings), G peak (~1570 cm⁻¹ bonds stretching of all pairs of sp²-carbon atoms in rings), and 2D peak (~ 2672 cm⁻¹, second order zone boundary phonons in graphene)²⁴ can be observed simultaneously and the 2D/Gand D/G intensity ratios are ~0.84 and ~0.65, respectively, indicating abundant N-doped substitutional defect sites.^{26,27} In contrast, intrinsic FG has a low $I_D/I_G < 0.05$ and a high I_{2D}/I_G ~ 1.95 .¹⁹ The high-resolution Raman spectrum shows the existence of TS₁ (~1873 cm⁻¹) and TS₂ (~2018 cm⁻¹) peaks, and the absence of M peak (~1750 cm⁻¹) (Figure S4), substantiating the turbostratic oriented stacking of N-FG.^{19,28} High-resolution Auger spectroscopy enables quantification of the D-parameter, which measures the energy separation between maxima and minima in differentiated C KLL spectrum. The D-parameter of N-FG is 22.4 eV and is close to graphene (Figure S5).¹⁹ The X-ray diffraction (XRD) result reflects a downshift of the (002) peak relative to parent



Figure 2. Characterization of nitrogen-doped flash graphene. (a) Schematic of nitrogen-doped flash graphene. (b) Statistic Raman spectrum of the nitrogen-doped flash graphene. The black line and the gray shadow represent the average value and the standard deviation of 100 sampling points, respectively. (c) XRD result of nitrogen-doped flash graphene (Powder Diffraction File 89-8487, Graphite). (d) High-resolution N 1s spectrum of nitrogen-doped flash graphene. (e) Valence band XPS spectrum of nitrogen-doped flash graphene. (f) The SEM-determined sheet size distribution of nitrogen-doped flash graphene determined over 100 nanoparticles. (g) Characteristic SEM and (h) TEM images of nitrogen-doped flash graphene. (i) HAADF-STEM image and corresponding elemental mapping results of nitrogen-doped flash graphene. The scale bars are 20 nm.

graphene to ~25.9 degree, which indicates the expansion of interlayer spacing by $\sim 2.7\%$ (Figure 2c).⁷ The general (100) and (101) reflections cannot be observed, and the asymmetric shape of the (10) reflection, which has a pronounced tailing effect on the high Bragg angle side, can be seen. These results support the absence of an ordered stacking of basal planes, and the existence of turbostratic structure.^{19,29–31} Since the carbon source is carbon black, N-FG and the other heteroatom-doped FG belong to the nongraphitizable carbons.^{19,32} Unlike the graphitizable carbon (also known as soft carbons), which could be directly transformed into crystalline graphite when they were heated to the temperature up to 3000 °C, typical nongraphitizable carbons (also known as hard carbons) could not be thermally transformed into graphite at this temperature.^{33,34} Since graphite is the thermodynamically most stable form of carbon, our previous study found that the merging of graphene sheets and the formation of AB-stacked layers can happen if the flash duration is increased to several seconds.² The surface area of N-FG is 303 $m^2 g^{-1}$ with abundant pore sizes <10 nm (Figure S6). N-FG has two types of the pores, closed pores, and open pores. The term of closed and open depends on the location and size of the pores into which a

probe fluid (gas or liquid) can diffuse.^{35,36} The open porosity and the closed porosity are 0.54 and 0.11, respectively.

N doping is confirmed by X-ray photoelectron spectroscopy (XPS). The elemental ratio of N is \sim 5.4% (Figure S7), the majority of which is in the form of pyridinic N (\sim 398.7 eV) and pyrrolic N (~399.8 eV), with no indication of N-oxides (Figure 2d, Table S2). The ratio of pyridinic N and graphitic N reaches ~4.31.37 These pyridinic N atoms have unpaired electron spin density and exhibit strong interactions with some species, like metal atoms, which is useful in potential applications in electrocatalysts or metal electrodeposition.^{10,25} An appreciable valence band maximum (VBM) of -2.51 eV is measured for N-FG (Figure 2e). The N doping contents from 3 different batches are ~5.5%, 5.0%, and ~5.4%, which demonstrates the reliability of FJH method. Fourier transform infrared (FTIR) spectra of N-FG show the absence of melamine peaks and the signal of C—N and C=N stretching peaks in N-FG sample,⁵ confirming the nitrogen doping during FJH process (Figure S8).

The asymmetric broadening of the (002) diffraction peak reflects the nanosized feature of N-FG according to the Scherrer equation.²⁸ The average size of 100 graphene sheets is



Figure 3. Characterization of heteroatom-doped flash graphene. Characterization results, including Raman spectra (showing the average obtained spectra and standard deviations over 100 points), XRD spectra, XPS results (showing the elemental ratios and the bonding states), and the size distributions of (a) boron-doped flash graphene, (b) oxygen-doped flash graphene, (c) phosphorus-doped flash graphene, and (d) sulfur-doped flash graphene. The statistical Raman results are collected from 100 sampling points. High-resolution P 2p spectrum shows the splitting of each peak to $2p_{1/2}$ and $2p_{3/2}$ portions, which are denoted by the same color. The SEM-derived sheet size distribution results are obtained from at least 100 graphene sheets.

98.9 nm and the size distribution is narrow (Figure 2f), demonstrating the precise control of graphene flake size without obvious aggregation by FJH synthesis. The scanning electron microscopy (SEM) images show that N-FG is comprised of many nanocrystals (Figure 2g, Figure S9), and it is morphologically different from the undoped sheet-like FG, which usually has a lateral size up to several micrometers.^{19,28} Transmission electron microscopy (TEM) confirms the existence of nanoparticles and high-resolution TEM (HR-TEM) images show the presence of lattice fringes along with jagged structures (Figure 2h, Figure S10). Energy-dispersive spectroscopy (EDS) shows the existence of N-doping (Figure S11). Scanning TEM (STEM) and corresponding elemental mapping demonstrate the homogeneous distribution of the N doping by FJH synthesis (Figure 2i).

FJH Synthesis of Heteroatom-Doped Flash Graphene. The versatility of FJH synthesis is demonstrated and five distinct heteroatom-doped FG, including boron, nitrogen, oxygen, phosphorus, and sulfur-doped FG, are prepared (Figure 1a). The sealed polymer tubes prevent the dissipation of carbon and dopants, and a high mass conversion reaction yield (>70%) can be achieved as shown in Figure 1e. These heteroatoms have different atomic radii (50–100 pm)

compared to carbon (70 pm) (Figure S12). Therefore, there is some lattice mismatch in heteroatom-doped graphene, and the formation of substitutional solid solutions are limited to certain feasible ranges without the destruction of the graphitic structure. The electronegativities of these heteroatoms (2.0-(4.0) are distinct from that of carbon (2.5), and thus the intrinsic electronic structure of graphene can be modified by different heteroatom dopings.⁵ Owing to the ultrahigh electrothermal temperature (>3000 K) during the FJH process, a wide variety of dopants, such as elements (M), oxides (MO_x) , and organic compounds (C_xH_yM) can be used as precursors, regardless of their boiling points or conductivities. In contrast, post-treatment methods usually depend on the vapor pressure in the gas phase or the solubility in the solution phases.⁵ Thus, the FJH synthesis allows for the direct use of various solid dopants and enables the low-cost and mass production of heteroatom-doped graphene.

Boron forms bonding types similar to that of carbon, including graphitic B (BC₃), borinic B (C₂BO), and boronic B (CBO₂) patterns (Figure S12).⁹ The boron-doped FG (B-FG) has good graphitic structure with B doping. The average Raman spectrum indicates 2D/G and D/G intensity ratios are 0.26 and 0.91 (Figure 3a), which indicates the good graphene



Figure 4. Characterization of multiple heteroatoms codoped in flash graphene. (a) Raman spectrum of B, N codoped flash graphene. The black line and the gray shadow represent the average value and the standard deviation of 100 sampling points, respectively. The same applied to the Raman spectrum below. (b) XRD result of B, N codoped flash graphene. (c) TEM and (d) HR-TEM images of B, N codoped flash graphene. (e) STEM image and corresponding elemental distribution of B, N codoped flash graphene. (f) Raman spectrum of B, N, S codoped flash graphene. (g) XRD result of B, N, S codoped flash graphene. (h) TEM and (i) HR-TEM images of B, N, S codoped flash graphene. (j) STEM image and corresponding elemental distribution of B, N, S codoped flash graphene.

quality despite the simultaneous introduction of rich defects derived from B doping. Since the average 2D/G intensity ratio of the conductive carbon reactant is 0.06 (Figure S13), and the statistic median of doped graphene is 0.10 (Table S3), a threshold value of 0.10 is used to determine whether the site of interest is graphene. Therefore, the graphene yield of B-FG reaches 94% (Table S4). The interlayer spacing of the B-FG nanocrystals increases by 2.4% over that of commercial graphene (CG) and the average crystal size is 24.2 nm (Table S5 and Figure S14). Thermodynamic phase diagrams indicate covalent carbide B4C is the most stable state when icosahedral B12 is used as the dopant and the local concentration of boron reaches >9%.8 On the other hand, the H₃BO₃ precursor facilitates the formation of graphitic structures without the appearance of a carbide signal in the XRD spectrum (Figure 3a). The atomic concentration of boron in B-FG is ~1.8%.

Similarly, other pnictogens such as phosphorus, and chalcogens including oxygen and sulfur, can be doped into FG (Figure 3b-d, Figure S12). After heteroatom doping, the

graphitic structure is preserved, and the graphene content yields are 86-100% determined by Raman mapping (Table S4), while the mass yields are shown in Figure 1e. The heteroatom doping introduces abundant point defects and lowers the symmetry. Thus, a higher D peak ensues. Compared with intrinsic FG, with a low $I_D/I_G < 0.05$, these doped FGs have higher I_D/I_G of 0.65–0.91 (Table S4). The heteroatomdoped FGs exhibit expanded interlayer distance up to 2.7% over that of CG, and likewise have larger surface area reaching ~876 m² g⁻¹ (Figure S15) over that of CG (~200 m² g⁻¹) and FG (~300 m² g⁻¹).¹⁹ The doped FG nanocrystals have narrow flake size distributions and have abundant micropores as well as mesopores (Figure 3b-d, Figure S15-S16). The heteroatom contents are ~1.5% for P-FG, ~5.5% for O-FG, and ~1.6% for S-FG (Figure S17), which introduce VBM of -1.91to -2.68 eV as shown in the valence band XPS results (Figure S18).

Characterization of Multiple Heteroatoms Codoped in Flash Graphene. Dual doping and multiple doping can result in synergetic effects, which may lead to a stronger



Figure 5. Applications of heteroatom-doped flash graphene. (a) Various heteroatom-doped FG and commercial graphene (CG) dispersed in water/Pluronic (F-127) (1 wt %). (b) Dispersion efficiency of CG and heteroatom-doped FG. (c) The retention rate of different heteroatom-doped FG after recorded sedimentation times. (d) Oxygen reduction reaction (ORR) performance of different doped FG and intrinsic FG in 0.1 M KOH solution at 1600 rpm and (e) the corresponding Tafel plots. (f) The ORR polarization curves at different rotating rates of N-FG and (g) the corresponding K–L plots. (h) The voltage profile of Cu, FG, and N-FG during the Li metal electrodeposition. The testing condition is 0.1 mA cm⁻² with an areal capacity of 1.0 mAh cm⁻². (i) The nucleation overpotential of Cu, FG, and N-FG anodes in Li metal batteries at different current densities.

influence on charge density and spin density than a larger amount of single heteroatoms.^{11,38} These codoped heteroatoms with distinct chemical states can interact to provide active sites for enhancing electrocatalytic activity or introduce band structures along with local nanoscale effects. Likewise, since the entropy of mixing is higher when more distinct species are present, doping 2D materials with multiple types of heteroatoms is a viable strategy to obtain materials with high doping levels that would not be accessible with only a single dopant species. In this section, B,N-FG and B,N,S-FG are synthesized by an ultrafast and all-solid-state catalyst-free FJH method. As-synthesized B,N-FG has a good graphene structure (Figure 4a), and the graphene content yield reaches 89% (Table S4). Dual doping causes abundant point defects and a high average $I_{\rm D}/I_{\rm G}$ ~ 0.90 is obtained from 100 sampling points. The interlayer spacing of B,N-FG increases 2.6% (Figure 4b) compared to CG and the average particle size is 49.9 nm (Table S5, Figure S19). B,N-FG has a large surface area of 393 m² g⁻¹ and abundant micropores and mesopores (Figure S20). HR-TEM images show the presence of lattice fringes and wrinkled structures of doped FG nanoparticles (Figure 4c,d). The uniform distribution of B, C, and N in these nanoparticles is shown in Figure 4e. High resolution XPS

spectra indicate that the total amount of B and N is 10.4% (Figure S21), which is higher than the fraction achieved when using only N or B dopant atoms alone. Emerging bonding states between heteroatoms, B and N, can be found in B 1s and N 1s spectra (Figure S21), and B,N-FG has a large VBM -3.02 eV (Figure S22).

Similar results are found in B,N,S-FG. The graphene content yield and I_D/I_G are 87% and 0.83, respectively (Figure 4f, Table S4). The interlayer spacing of B,N,S-FG is 2.2% larger than CG (Figure 4g) and the average particle size is 76.0 nm (Figure 4h, Figure S19). These nanocrystals exhibit similar wrinkled structures and homogeneous elemental distribution of B, N, and S (Figure 4i,j). The total atomic content for these three types of heteroatoms is ~13.5% and additional bonding states between heteroatoms, B and N, can be observed (Figure S23). The VBM of B,N,S-FG is -2.54 eV (Figure S22).

Scaling up and Applications of Heteroatom-Doped Flash Graphene. Gram-scale N-FG (N-FG-L2) synthesis is demonstrated in this section, and the graphene quality along with properties of N-FG-L2 are similar to those of N-FG synthesized from the small batch. The graphene content yield and I_D/I_G of N-FG-L2 are 99% and 1.08, respectively (Table S4, Figure S24), which reflects the abundance of point defects

Since there are lone pair electrons in N, which provides strong binding energies with metal atoms such as Li, N-FG is used as an electrode material in a lithium metal battery.¹⁰ Compared to bare Cu electrode (54 mV), N-FG exhibits a smaller nucleation overpotential (11 mV) during the electrodeposition of metallic Li at 0.1 mA cm⁻² (Figure 5h), which indicates a smaller nucleation energy barrier for N-FG. A smaller energy barrier for nucleation facilitates the formation of more homogeneous nuclei and subsequent uniform metallic Li deposition.^{44,45} The nucleation overpotential for N-FG is smaller than that of FG (Figure 5i), because the binding energy of N-FG is stronger than in intrinsic FG. This result is consistent with a previous literature report.¹⁰

CONCLUSION

In conclusion, seven different heteroatom-doped FG, including single element doped N-FG, B-FG, O-FG, P-FG, S-FG, dual elements codoped B,N-FG, and multiple elements codoped B,N,S-FG, are directly synthesized by an ultrafast and all-solidstate catalyst-, solvent-, and water-free FJH method. Different low-cost dopants, including elements, oxides, and organic compounds can be used regardless of boiling point and conductivity. The as-synthesized doped FG has good graphene quality, turbostratic structure, and expanded interlayer spacing. Therefore, they are dispersible in water-Pluronic (F-127) (1 wt %) solution, and then form stable concentrated dispersions. Heteroatom doping modifies the electronic structures, which improves the performance of doped FG as electrocatalysts and electrochemical energy storage materials. The gram-scale synthesis of doped FG is also demonstrated to show the scalability of the FJH method to bulk quantities. The electrical energy cost for heteroatom-doped FG synthesis is only 1.2-10.7 kJ g^{-1} , which could render the FJH method suitable for low-cost and mass production of heteroatom-doped graphene. Since the intrinsic FG is currently being scaled to 1-ton per day production using an analogous FJH technology,⁴⁶ the protocol here should be easily translated to similar scales.

EXPERIMENTAL SECTION

Materials. Carbon black (CB, APS 10 nm, Black Pearls 2000) was purchased from Cabot Corporation. Melamine (M2659-1KG, 99%) was purchased from Millipore-Sigma. Boric acid (31768-453.6G, 99.9%) was purchased from Baker Analyzed Reagent. Sucrose (SX1075-1, 500G, ACS grade) was purchased from Millipore-Sigma. Red phosphorus (343242-5G, 99.99%) was purchased from Millipore-Sigma. Poly(1,4-phenylene sulfide) (PPS, 182354-100G, average Mn ~ 10 000) was purchased from Millipore-Sigma. Boron powder (11337-10G, amorphous, ~325 mesh) was purchased from Alfa Aesar. Graphite spacers and tungsten carbide cylinder rods (4 mm diameter) were used as the electrodes. Polytetrafluoroethylene tubes, poly(1,4-phenylene sulfide) tubes or polyacrylonitrile tubes (ID = 4 mm, OD = 25 mm, length = 6 cm) were used as the FJH reaction vessels. xGnP graphite nanoplatelets (xGnP-15, serial #: 5051209) were obtained from XG Sciences and were used as received for the comparison. Commercial graphene was obtained from Tianyuan Empire.

For the dispersion tests, the Pluronic (F-127, P2443-250G) was purchased from Millipore-Sigma. For the electrochemical tests, potassium hydroxide (KOH, 221473-500G, ACS grade) was purchased from Millipore-Sigma. For the battery tests, N-methyl pyrrolidone (NMP, >99.0%, 443778-500ML) was purchased from Millipore-Sigma. The milling ball (Yttrium stabilized ZrO₂, 99.5%, R = 5 \pm 0.3 mm) was purchased from MTI Corporation. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 99.95%, trace metals basis, 544094-25G) was purchased from Millipore-Sigma. Lithium

and local breaking of hexagonal symmetry. There is an asymmetrical (002) diffraction peak at ~26.0 degree, which indicates the expansion of interlayer distance by ~2.1%. The average size of N-FG-L2 is 41.2 nm (Figure S25) and the surface area is 573 m² g⁻¹. Pore size distribution of N-FG-L2 is similar to N-FG. The high-resolution N 1s spectrum shows the atomic ratio of N is ~3.1%, and pyridinic N and pyrrolic N are dominant, which have strong binding energies with metals and other electropositive species.¹⁰

Heteroatom-doped FG is dispersible in water-Pluronic (F-127) surfactant (1 wt %) solution and similar to intrinsic FG, they give highly concentrated dispersions reaching ~ 4 mg mL⁻¹ (Figure 5a, Figure S26).^{19,39} This result is distinct from CG, which shows little dispersibility in 1 wt % F-127 aqueous solution (Figure 5b, Figure S27). The dispersion efficiency measures the ratio between final dispersed concentration and initial concentration of graphene. The dispersion efficiencies of N-FG, B,N-FG and B,N,S-FG are ~8, ~17, and ~8 times higher than that of CG, respectively, which can be attributed to the turbostratic arrangement of heteroatom-doped FG allowing efficient exfoliation.¹⁹ The dispersion force needed for exfoliation is much lower than that need in conventional AB-stacked graphene obtained by graphite exfoliation. The dispersions show high temporal stability, and after 35 days, the retention rates of N-FG, B,N-FG and B,N,S-FG are 82%, 86%, and 69%, respectively (Figure 5c). In other organic solvents, such as N,N-dimethylformamide (DMF) and N-methyl-2pyrrolidone (NMP), N-FG also shows great dispersibility and the dispersion efficiencies of N-FG in DMF, and NMP solvents are \sim 40.4 and \sim 8.2 times higher than that of CG (Figure S28).³⁹

To demonstrate the applicability of heteroatom-doped FG as electrocatalysts, the electrochemical ORR performances of various doped FG are tested. The polarization curves of five different doped FG and intrinsic FG are shown in Figure 5d and Figure S29. S-FG shows the most superior ORR activity among the metal-free electrocatalysts. The potential at 0.2 mA cm^{-2} is 0.88 V and the Tafel slope is 74 mV dec⁻¹ (Figure 5e, Table S6). The saturated current density of S-FG at 1600 rpm reaches ~4.2 mA cm⁻². The electron transfer number $\binom{n}{n}$ is important to determine the final product of ORR and it can be estimated by the Koutecký–Levich equation (K-L equation).⁴⁰ The polarization curves of N-FG at different rotating rates and the corresponding K-L plots are shown in Figure 5f and g. And *n* is 2.3–2.7 for N-FG, which indicates H_2O_2 can be the major product. Heteroatom codoping results in distinct chemical states and synergistic effects. For B,N-FG, *n* is close to 4, which suggests H_2O is the major product (Figure S30). The stability tests of N-FG and B,N-FG show the increase of overpotentials and the decrease of current densities after 1000 cycles, which indicates the degradation of performance and might relate to the metastable structures (Figure S30). Since previous studies have shown that trace metals can also contribute to the electrochemical performance of the carbon materials, ^{4,41-43} we carried out ICP-MS to analyze the content of 14 different trace metals: Cr, Co, Fe, Mn, Ni, V, W, Pt, Mo, Ir, Pd, Au, Ti, and Ru, in the reactants and the products (Figures S31-34). The results show that the content of these metals from different samples are much lower than the values reported in the previous literature.41-43 Therefore, the reactants and flash reaction will cause minimal contamination of the products and little effect on the ORR.

nitrate (LiNO₃, 99.99%, trace metals basis, 229741-25G) was purchased from Millipore-Sigma. 1,2-dimethoxyethane (DME, anhydrous, 99.5% inhibitor-free, 259527-100ML) was purchased from Millipore-Sigma. 1,3-Dioxolane (DOL, anhydrous, 99.8%, ~75 ppm BHT as inhibitor, 271020-1L) was purchased from Millipore-Sigma. Poly(vinylidene fluoride) binder (PVDF, 121120-80G) was purchased from MTI Corporation. High conductive acetylene black (ABHC-01, 342431) was purchased from Soltex Corporation.

For the inductively coupled plasma mass spectrometry (ICP-MS) tests, HNO_3 (67–70 wt %, TraceMetal grade, Fisher Chemical), HCl (37 wt %, 99.99% trace metals basis, Millipore-Sigma), water (Millipore-Sigma, ACS reagent for ultratrace analysis), and all the standards (periodic table mixtures) were purchased from Millipore-Sigma.

Characterization. The reactant and flash products were characterized through scanning electron microscopy (SEM) using a FEI Helios NanoLab 660 DualBeam SEM at 5 kV with a working distance of 4 mm. TEM images were taken with a JEOL 2100F field emission gun transmission electron microscope at 200 kV. HR-TEM and HAADF-STEM images were taken with FEI Titan Themis S/ TEM instrument at 300 keV after accurate spherical aberration correction. X-ray photoelectron spectroscopy (XPS) data were collected with a PHI Quantera SXM Scanning X-ray Microprobe with a base pressure of 5×10^{-9} Torr. Survey spectra were recorded using 0.5 eV step sizes with a pass energy of 140 eV. Elemental spectra were recorded using 0.1 eV step sizes with a pass energy of 26 eV. All of the XPS spectra were corrected using the C 1s peaks (284.8 eV) as reference. X-ray diffraction (XRD) measurements were done by a Rigaku SmartLab Intelligent XRD system with filtered Cu K α radiation (λ = 1.5406 Å). Raman spectra were collected with a Renishaw Raman microscope using a 532 nm laser with a power of 5 mW. A 50× lens was used for local Raman spectra and Raman mapping. UV-vis (Shimadzu UV-3600 plus) was used to collect the spectra of the suspension of reactant and flash products. A Thermo Scientific Nicolet 6700 attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectrometer (Waltham, MA) was used to analyze the vibration and rotation modes in the reactant and the flash product.

FJH System. The circuit diagram and FJH reaction box were shown in Figure S1. A thick-walled polymer tube (ID = 4 mm, OD = 25 mm, length = 6 cm) was prepared in a machine shop and used to load the reactant powder. Graphite spacers (D = 4 mm, length = 5)mm) and tungsten carbide cylinder rods (D = 4 mm, length = 5 cm) were utilized as electrodes to compress the loaded powder. The graphite spacers were in contact with the samples and tungsten carbide cylinder rods were connected with the circuit. In this work, different precursors were used to prepare heteroatom doped FG. The reactants included a mixture of (1) CB, (2) melamine and CB, (3) boric acid and CB, (4) sucrose and CB, (5) red phosphorus and CB, (6) PPS and CB, (7) boron, melamine, and CB, and (8) boron, melamine, PPS, and CB. The electrical energy was provided by a capacitor bank in the circuit with a total capacitance of 60 mF. The capacitor bank was charged by a d.c. supply that could reach 400 V. The flash duration was controlled by an Arduino controller relay in the circuit acting as a high-speed switch. The reactant resistances for various reactants were different, and the flash conditions were changed to control the total input electrothermal energy. To scale up the N-FG, thick-walled polymer tube (ID = 8 mm, OD = 25 mm, length = 6 cm) and graphite spacers (D = 8 mm, length = 5 mm) were used for N-FG-L1. The quartz tube (ID = 16 mm, OD = 20 mm, length = 6 cm) and graphite spacers (D = 16 mm, length = 3 cm) were used for N-FG-L2. And the input electrothermal energy was calculated based on the energy densities in Table S1. The parameters are listed in Table 1. The weight ratios of various samples are optimized in Table 1. There are four factors for which we try to optimize the final conditions:

1. Homogeneous flash reactions. We control the resistance of the evenly mixed reactants between 0.4–5.0 Ω , and monitor the

current-time (I-t) curves to ensure a homogeneous flash reaction

- 2. The formation of turbostratic graphene. Raman and XRD are used to check the formation of turbostratic graphene to screen the condition.
- 3. The formation of bonds between sp^2 -C and heteroatom. Since the purpose is to prepare doped graphene, the possibility of bonds between sp^3 -C and heteroatom should be excluded. XPS is used to analyze the bonding states.
- 4. The contents of the heteroatom. XPS is used to analyze the contents of the heteroatom.

More safety notes and a circuit diagram of the FJH setup are in the Supporting Information and our previous publications.^{19,21} Caution! Ensure that all safety precautions are observed to mitigate electrocution. As a last measure, be sure to wear thick rubber gloves that extend to the elbows. After the FJH reaction, it is suggested to allow the apparatus to cool and vent for 3-5 min. And ensure that the capacitor bank has been separated from the system by a circuit breaker (not a toggle switch), and that the capacitor bank has been fully discharged.

Electrochemical Tests. Oxygen reduction reaction (ORR). The slurry was prepared by dispersing 2 mg heteroatom doped FG in 2 mL binder solution, which is 160 μ L of 5 wt % Nafion solution mixed in 2 mL water/ethanol (1:1, volume ratio). The slurry was sonicated for 30 min to form a homogeneous ink. A volume of 20 μ L of ink solution was loaded onto a glassy carbon electrode (5 mm in diameter) and dried in air at room temperature. The electrochemical measurements were carried out in a three-electrode configuration using a CHI 608D electrochemical workstation. A graphite rod and HgO/Hg (1 M KOH) electrode were used as the counter and reference electrodes, respectively. The electrolyte was 0.1 M KOH sparged with O₂ gas for O₂ saturation. CV was carried out with potential ranging from 1.2 to 0 V (vs RHE) for 10 cycles at a scan rate of 100 mV s⁻¹. LSV was carried out with potential ranging from 1.2 to 0 V (vs RHE) at a scan rate of 5 mV s⁻¹.

For the battery tests, the electrode was prepared by grinding the mixture of doped FG, and poly(vinyl difluoride) (PVDF) at a ratio of 0.9:0.1. A small amount (~3× of the total mass) of *N*-methyl pyrrolidone was used to form a homogeneous slurry. The slurries were formed by ball milling at 1500 rpm for 10 min. The current collector was Cu foil with a thickness of 10 μ m. The slurry was applied to the Cu foil by a doctor blade with a blade spacing of 100 μ m. The electrode was dried using a built-in heating cover placed on top of the electrode at 70 °C for 2 h and was then put in a vacuum oven overnight. The temperature and pressure of the vacuum oven were set at 70 °C and ~10 mmHg. The area of the cathode was ~2.0 cm². The electrolyte used was 1 M LiTFSI in a mixture of DME and DOL (V:V = 1:1) with 2% LiNO₃ as the additive. The volume of the electrolyte in each coin cell was 30 μ L.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.2c01136.

Safety instructions, TEM, SEM, and other images; XPS and Raman spectra; Additional graphs (PDF)

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Notes

The authors declare the following competing financial interest(s): Rice University owns intellectual property on flash graphene. Some of that intellectual property has been licensed to Universal Matter Inc. J.M.T. is a stockholder in Universal Matter, but he is not an officer, director, or employee. Conflicts of interest are mitigated through regular disclosures to and compliance with the Rice University Office of Sponsored Programs and Research Compliance. D.X.L. was employed by Rice University when this work was done. He is now employed by Universal Matter.

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