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PAPER

Low-temperature rapid synthesis of high-quality pristine or boron-doped graphene *via* Wurtz-type reductive coupling reaction†Xujie Lü,<sup>ab</sup> Jianjun Wu,<sup>ab</sup> Tianquan Lin,<sup>ab</sup> Dongyun Wan,<sup>a</sup> Fuqiang Huang,<sup>\*a</sup> Xiaoming Xie<sup>c</sup> and Mianheng Jiang<sup>c</sup>

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High-quality graphene nanosheets are prepared *via* a rapid Wurtz-type reductive coupling (WRC) reaction without the assistance of any transition metal catalysts. This method involves a nearly stoichiometric reaction of tetrachloromethane (CCl<sub>4</sub>) and potassium (K) at 150–210 °C for as short as 10 min, which possesses great advantages compared with the solvothermal method. The layer number of the as-prepared graphene is mainly less than five. The formation mechanism of graphene is proposed, which comprises of three steps, stripping off the chlorines from CCl<sub>4</sub> by the highly reductive K, the coupling and assembly of –C=C– and the layer growth of hexagonal carbon clusters to form graphene. Many important factors determining the quality of graphene, such as the residual chlorines, the reaction temperature and the reductant, are discussed in detail. The low residual chlorine in the reaction favors the improvement of the graphene quality. Furthermore, controllable boron doping can be easily realized by adding an appropriate amount of BBr<sub>3</sub>. The developed method provides a cost-effective route to prepare high-quality pristine or doped graphene for mass production.

## 1. Introduction

Graphene, with a two-dimensional (2D) structure consisting of sp<sup>2</sup>-bonded carbon atoms, has attracted tremendous attention from both fundamental research and promising applications in recent years due to its unique structural and physical properties.<sup>1</sup> Graphene holds great promise for many applications, such as nano-electronics,<sup>2,3</sup> sensors,<sup>4,5</sup> nano-composites,<sup>6,7</sup> batteries,<sup>8</sup> super capacitors and hydrogen storage.<sup>9</sup> Since pristine graphene is a zero-band-gap semiconductor and its density of states (DOS) at the Dirac point equal to zero, which serves a great obstacle for applications.<sup>10,11</sup> The electronic structure of graphene is necessary to be tuned by electron or hole doping to further induce novel physicochemical properties and greatly expand the application range.<sup>12</sup> Although great progresses have been made

on the preparation of graphene, large-scale production of high-quality graphene at low-cost remains to be highly challenging.

Graphene synthesis methods can be generally classified into two groups, top-down and bottom-up. The top-down approach involves the transformation of carbon materials into separated graphene sheets by chemical or physical treatment, including exfoliation from bulk graphite, thermal splitting of silicon carbide (SiC) granules,<sup>13</sup> unzipping of carbon nanotubes,<sup>14,15</sup> *etc.* The chemical exfoliation is a suitable method for mass production of graphene, however, the obtained graphene has poor electrical conductivity owing to many defects formed during the vigorous exfoliation and reduction processes.<sup>16</sup> The bottom-up route realizes graphene growth from carbonaceous precursors, such as chemical vapor deposition on transition metal substrates<sup>16,17</sup> and epitaxial growth on single-crystal silicon carbide or ruthenium.<sup>18,19</sup> While the presence of the substrates usually degrades the electronic properties of the products and further limit the applications.

A solvothermal reaction is a promising approach to prepare high-quality and freestanding graphene in a supercritical reaction environment with the presence of the reductant of alkali metal and an organic solvent (e.g. sodium and ethanol,<sup>17</sup> potassium and tetrachloromethane<sup>20</sup>). However, such an approach does not always ensure the formation of graphene, as evidenced by the formation of various reported carbon products.<sup>21,22</sup> Therefore, it is highly desirable to develop a rapid and cost-effective approach to the mass production of high-quality and freestanding graphene.

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† Electronic supplementary information (ESI) available: Estimate of reaction enthalpy, TEM image and Raman spectrum of graphene nanosheets prepared in 10 min at 210 °C, the crystallinity of graphene variation with the CCl<sub>4</sub> volume, and XPS characterizations of pristine and boron-doped graphene samples. See DOI: 10.1039/c1jm11184a

In the present study, a Wurtz-type reductive coupling (WRC) reaction is proposed as a new bottom-up method for the rapid preparation of high-quality pristine and boron-doped graphene. The nearly stoichiometric reaction of tetrachloromethane ( $\text{CCl}_4$ ) and potassium (K) for the WRC reaction is different from the solvothermal reaction where a supercritical environment is needed. Following this method, graphene nanosheets can be obtained at 150–210 °C in as short as 10 min. A formation mechanism of graphene is proposed and key parameters determining the quality of the products are investigated in detail. Boron doping can be easily achieved by adding a boron source (*e.g.*  $\text{BBr}_3$ ) into the reaction system. The process is free of transition metal catalysts (Cu, Ni, *etc.*). The proposed approach is a rapid and cost-effective method for the volume preparation of freestanding graphene with low defects.

## 2. Experimental

### 2.1 Sample synthesis

All the chemicals were purchased commercially (analytical grade) without further purification. In a typical synthesis of pristine graphene nanosheets (PG), 3.0 ml of tetrachloromethane ( $\text{CCl}_4$ ) was placed into a 50 ml Teflon-lined stainless steel autoclave, and then 1.0 g of metallic potassium (K) was rapidly added to the autoclave in an Ar-filled dry glove box. The autoclave sealed in the glove box was kept at 150–210 °C in an oven for 10–30 min, and then cooled down to room temperature. The resultant product was dispersed in acetone under stirring to remove the remaining  $\text{CCl}_4$ . After filtering, the product was further washed with deionized water, and dried in a vacuum oven at 100 °C for 12 h for further characterization. The preparation of the boron-doped graphene sample followed a similar procedure, except that boron tribromide ( $\text{BBr}_3$ , 52, 104 and 156  $\mu\text{L}$ ) was first dissolved in the  $\text{CCl}_4$  (3.0 mL).

### 2.2 Characterizations

A JEOL JSM-6700F scanning electron microscope (SEM) was used to investigate the morphologies of the graphene nanosheets. For field-emission transmission electron microscopy (TEM) observation, the samples were dispersed in ethanol by ultrasonic treatment and dropped on carbon–copper grids. TEM as well as high-resolution transmission electron microscopy (HRTEM) images were collected by using a JEOL JEM 2100F microscope working at 200 kV. Atomic force microscopy (AFM) topography images were recorded using a Seiko SPI 3800 N probe station. Raman spectroscopy was performed on an inVia Renishaw Raman microscope using green laser excitation ( $\lambda = 514.5 \text{ nm}$ ). X-ray photoelectron spectroscopy (XPS) was carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg K $\alpha$  radiation ( $h\nu = 1253.6 \text{ eV}$ ). The crystal structure analysis of the samples were performed by X-ray diffraction (XRD Bruker D8 ADVANCE) with a monochromatized source of Cu K $\alpha$ 1 radiation ( $\lambda = 0.15405 \text{ nm}$ ) at 1.6 kW (40 kV, 40 mA).

## 3. Results and discussion

### 3.1 Morphologies of pristine graphene

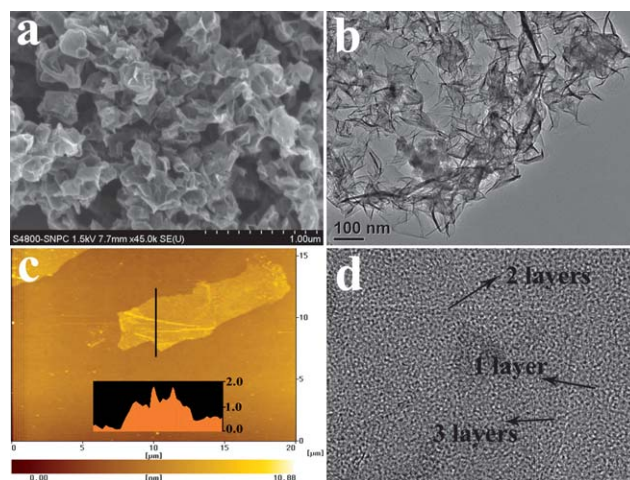
The typical SEM, TEM and AFM images of the pristine graphene (PG) sample, prepared at 210 °C for 30 min using 3 mL

of  $\text{CCl}_4$  and 1 g of K, are displayed in Fig. 1. Before ultrasonic dispersion, the sample consists of flower-like nanosheets and some stacked flakes (SEM, Fig. 1a). Folded graphene layers were observed in many samples, and the sheet edges tended to scroll and fold slightly (TEM, Fig. 1b). The TEM images can be used to identify the layer number of graphene (Fig. 1d).<sup>23,24</sup> After sonication for 40 min in ethanol, mono-layered graphene sheets with a topographic height of about 0.7 nm were observed by atomic force microscopy (AFM, Fig. 1c), consistent with the previously reported value of mono-layered graphene.<sup>25</sup> The typical number of layers was determined to be less than five with mono-layered graphene approximated to be 19% by statistical analysis. The frequency counts of different layers are shown in Fig. 2.

### 3.2 Raman spectroscopy analysis

Fig. 3a shows the Raman spectra of the graphene nanosheets prepared at 150, 180 and 210 °C with the Raman spectrum of graphite for reference. Three dominant peaks at about 1350, 1580 and 2690  $\text{cm}^{-1}$  are observed in all prepared samples, which are commonly referred to as the D, G and 2D band, respectively. As reported, The D band is ascribed to the breathing modes of  $\text{sp}^2$  atoms in rings and is usually associated with defects,<sup>26</sup> which may come from the grain boundaries, edges and ripples of the nanosheets. The 2D peak is located at 2684–2698  $\text{cm}^{-1}$  for samples prepared *via* the WRC method, which are much lower than 2725  $\text{cm}^{-1}$  for graphite, indicating few-layer graphene nanosheets were successfully prepared in all cases.<sup>26,27</sup>

Raman scattering properties of graphene provide useful information about its crystallinity and the number of layers.<sup>27,28</sup> The intensity ratio of the D to G band ( $I_D/I_G$ , defined as the integrated areas ratio) is used to evaluate the defect content of the graphene. As shown in Fig. 3b, with an increase in reaction temperature, the value of  $I_D/I_G$  decreases from 0.95 at 150 °C to 0.86 at 180 °C, and further to 0.70 at 210 °C. This implies that a higher reaction temperature favors defect repair, such as the elimination of the carbon nanohorns and amorphous carbon species. It is worth noting that the  $I_D/I_G$  values of the prepared



**Fig. 1** (a) SEM, (b) TEM, (c) AFM and (d) HRTEM images of the pristine graphene (PG) sample.

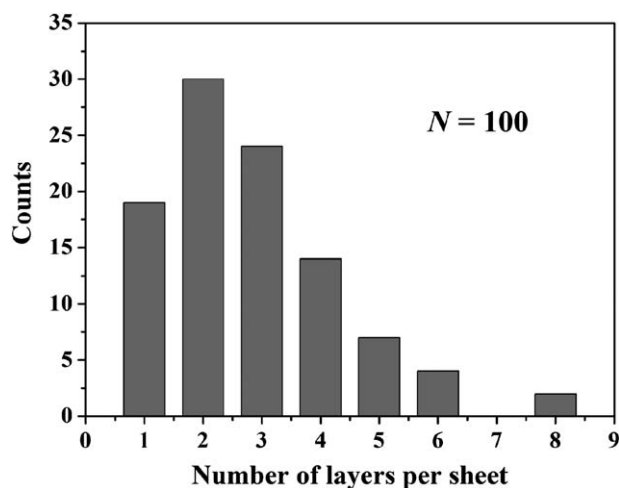


Fig. 2 Statistical analysis of the layer number of the graphene nanosheets (with a total number of 100).

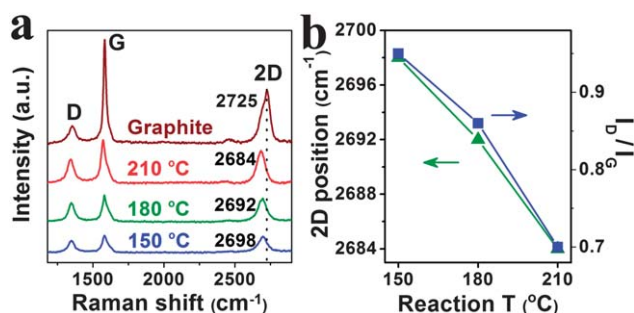


Fig. 3 (a) Raman spectra of graphene nanosheets prepared at different reaction temperature, with graphite provided as a reference. (b) The position of the 2D band and the intensity ratio of the D to G band ( $I_D/I_G$ ) as functions of reaction temperatures.

graphene nanosheets are lower than that of most chemical reduced graphene in previous reports,<sup>29</sup> demonstrating that the WRC route is advantageous compared with other chemical methods for the preparation of high-quality graphene.

The 2D band is a second-order two-phonon mode and its shape, as well as position, is used to determine the layer number of the graphene sheets.<sup>30</sup> With an increase in reaction temperature, the 2D peak position shifts to a lower value (*i.e.* 2698, 2692 and 2684 cm<sup>-1</sup> for 150, 180 and 210 °C respectively, see Fig. 3), which indicates a decrease in the layer number of the graphene nanosheets.<sup>27,31</sup> Furthermore, the layer number of the graphene can be estimated from the full width at half-maximum (FWHM) of the 2D peak, using the equation of  $\text{FWHM (2D)} = (88 - 45/n)$  [cm<sup>-1</sup>], where  $n$  is the number of layers.<sup>32</sup> It was calculated that the average number of layers are 3.3 (150 °C), 3.0 (180 °C) and 2.5 (210 °C).

### 3.3 Reaction mechanism

Stripping off the halogens from halides has been a trick commonly used by chemists to synthesize a great variety of new molecules. The Wurtz-type reaction is a typical example of a halogen stripping reaction. By stripping off the halogens, metals, metal silicides and carbon-related materials can be

obtained using metal halides, silicon halides and carbon halides.<sup>21,33</sup> The nano-structured carbon materials can be prepared by stripping off the halogens from halocarbons when powerful “halogen-scavengers” are employed. The present synthetic route of graphene is based on stripping off Cl from CCl<sub>4</sub> using K. A proposed mechanism for graphene growth is illustrated in Fig. 4.

Considering the graphene nanosheets are built from the hexagonal lattice of sp<sup>2</sup>-carbon while the reactant of CCl<sub>4</sub> is a sp<sup>3</sup> structure, the transformation from carbon sp<sup>3</sup> to sp<sup>2</sup> should have occurred. During the reaction, CCl<sub>4</sub> is first converted to dichlorocarbene *via* stripping off the chlorines by metallic K, and further couples to form tetrachloroethylene (Cl<sub>2</sub>C=CCl<sub>2</sub>).<sup>21</sup> Cl<sub>2</sub>C=CCl<sub>2</sub> species can continuously be dechlorinated to turn into -C=C-. Subsequently, the freshly formed -C=C- readily couple together and assemble into two-dimension hexagonal carbon clusters,<sup>34</sup> and then grow to be sp<sup>2</sup>-structural graphene nanosheets. The final products in the present study where no catalyst was used, were graphene nanosheets rather than carbon nanotubes, which is different from the situations using transition metal nanoparticles as catalysts.<sup>21,34</sup> In order to avoid a possible catalytic reaction in the presence of Teflon, a glass beaker was put into the Teflon-lined reactor as the container, and the same product was obtained.

It should be noted that the WRC reaction is different from the solvothermal reaction which needs an excessive amount of CCl<sub>4</sub> to form a supercritical reaction environment. The present WRC process can be a nearly stoichiometric reaction of CCl<sub>4</sub> and K. Experimentally, a near-stoichiometric ratio of CCl<sub>4</sub> (1.5 ml) and K (2.0 g) were reacted in a Teflon-lined reactor, and the high-quality graphene nanosheets were obtained at 210 °C for 10 min, as shown in Fig. S1†. The preparation of high-quality graphene at such a low temperature in a very short time provides a rapid synthesis method with low energy consumption. On the other hand, we have conducted the experiments with excessive amounts of K, which resulted in violent reactions and damage to the reactor. The residual K could cause a fire when the reactor is opened in air and therefore a slight excess of CCl<sub>4</sub> was used in the reaction for safety reasons.

### 3.4 Key factors determining the graphene quality

The stripping-off ability of Cl from the carbon halides is closely related with the following coupling and assembly process

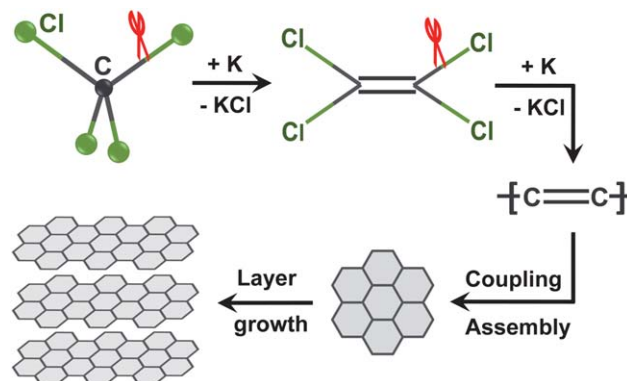


Fig. 4 Schematic illustration of the formation mechanism of graphene.



of  $\text{--C=C--}$ . It stimulates us to pay more attention to the effect of the residual Cl during the transformation of the  $\text{sp}^3$  carbon resource to the  $\text{sp}^2$  graphene networks. As shown in Fig. S2†, the crystallinity, determined by the FWHM of the C (001) peak, decreases as the volume of  $\text{CCl}_4$  increases in the reaction system. Meanwhile, the corresponding TEM images shown in Fig. 5 indicate that too much residual Cl would hinder the coupling process, suppress the formation of the final  $\text{sp}^2$  network, and thus lead to a lower crystallinity of graphene with a large amount of defects with some unidentified carbon products. The nearly stoichiometric  $\text{CCl}_4$  and K in the WRC reaction may be the key reason for the formation of single-phase graphene. To the contrary, the large amount of  $\text{CCl}_4$  in the solvothermal reaction brings a low yield of graphene and various carbon products due to the large amount of terminators of chlorine atoms.

The reaction temperature plays a vital role in the formation process. A higher reaction temperature makes a greater contribution to the recovery of the graphene structures by eliminating the carbon nanohorns and amorphous carbon species. The quality of graphene increases with the reaction temperature increasing from 150 to 210 °C, as shown in Fig. 3b. The optimum temperature is 210 °C, and the yield of PG is approximately 0.12 g per 1 g K. When the reaction temperature

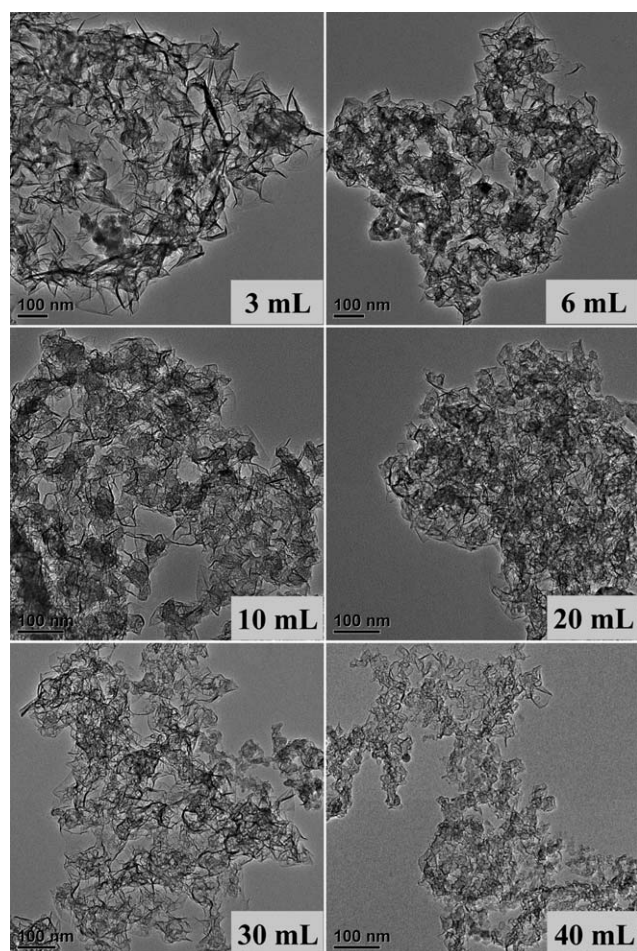
was lower than 150 °C, the reaction hardly proceeded, whilst when it was above 210 °C, the reactions took place too fiercely and the reaction container was destroyed.

The reductant (halogen-scavengers) is another key factor in the transformation of  $\text{CCl}_4$  to graphene at such a low temperature range. In previous studies,<sup>21,33</sup> sodium, magnesium,  $\text{NaNH}_2$  and potassium were used as the reductant to prepare carbon-related materials by solvothermal routes. Metallic K possesses a much stronger reducibility than other reductants mentioned above, and therefore,  $\text{CCl}_4$  is more easily dechlorinated by K at low temperature, and higher quality of graphene can be prepared. Using Na as the reductant, the reaction hardly took place below 200 °C due to the 10% enthalpy reduction for Na instead of K. (see the reaction enthalpy in the ESI for details†).

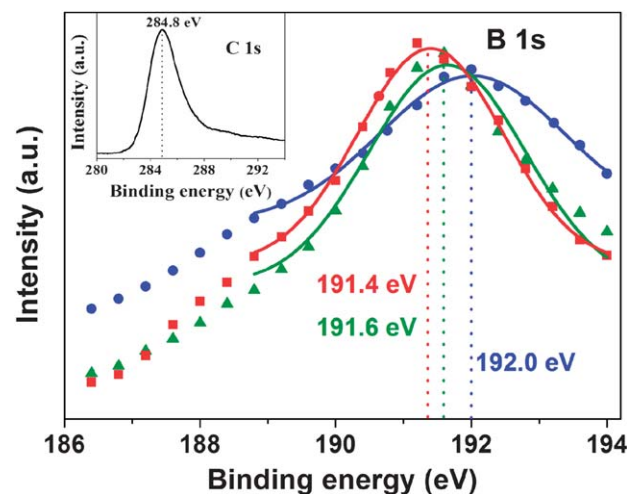
### 3.5 Boron-doping of graphene

It is important that the WRC strategy can be applied to graphene doping with other elements (*e.g.* B) by selecting suitable element sources. In this study, boron tribromide ( $\text{BBr}_3$ ) was used as the boron source, and the B-doped graphene was successfully prepared *via* this rapid and low-temperature synthetic route. As shown in the X-ray photoemission spectroscopy (XPS) in Fig. 6, the BG nanosheets have a binding energy peak (B 1s) of  $\sim 192.0$  eV while the C 1s peak is located at 284.8 eV (inset of Fig. 6). The higher binding energy of BG, compared with that of pure boron (188 eV), indicates that the boron atoms are bonded to the carbon atoms in the  $\text{sp}^2$  carbon network.<sup>35</sup> The content of boron was determined to be 1.02 at.% based on the XPS results for the sample using 52  $\mu\text{L}$  of  $\text{BBr}_3$ . It is worth mentioning that the doping content of B can be easily tuned by adjusting the amount of  $\text{BBr}_3$  added. As listed in table S1 of the ESI†, the B contents were detected to be 1.02 at.% (52  $\mu\text{L}$   $\text{BBr}_3$ ), 1.90 at.% (104  $\mu\text{L}$ ), and 2.56 at.% (156  $\mu\text{L}$ ), respectively.

As mentioned in the introduction, doping is an effective way of tuning the electronic structure of graphene and further improving its physicochemical properties. In our case, boron doping brings more holes to the valence band of graphene, and



**Fig. 5** TEM images of the graphene nanosheets prepared using different amounts of  $\text{CCl}_4$ .



**Fig. 6** The B 1s XPS spectra of B-doped graphene with B contents of 1.02 at.% (●), 1.90 at.% (▲) and 2.56 at.% (■); inset shows the C 1s XPS spectrum.

increases the carrier concentration of BG, thus enhanced its conductivity. Experimentally, the electrical conductivities of PG and BG were measured using electrochemical impedance spectra (EIS), and the corresponding Nyquist plots were shown in Fig. S3†. A smaller semicircle for BG than PG was observed, indicating a better conductivity of BG. The lower impedance of the BG sample probably indicates its increased DOS value near the Fermi level.

## 4. Conclusions

In summary, a rapid and low-temperature preparation method, based on a Wurtz-type reductive coupling (WRC) process, was proposed to prepare high-quality and freestanding graphene from the nearly stoichiometric reaction of  $\text{CCl}_4$  and K. By this method, the high-quality graphene nanosheets can be prepared in 10 min at 210 °C. The layer number of the as-prepared graphene can be controlled at typically less than five. The formation mechanism was proposed and the reaction process was fully discussed based on the following three steps: stripping-off, coupling and assembly, and layer growth. The influencing factors of the reaction and the optimization of the synthesis technology are investigated in detail. The less residual Cl content, higher reaction temperature and more reactive reductant result in higher quality of final graphene nanosheets. Boron-doped graphene was prepared by adding  $\text{BBr}_3$  to the system, and the concentration of boron can be easily controlled by adjusting the volume of  $\text{BBr}_3$ . By employing the proposed WRC method, the high-quality graphene can be obtained under a very mild condition (at 150–210 °C for 10–30 min) with cheap equipment and easy operation, and the entire formation process is free of transition metal catalysts. This cost-effective and highly reproducible approach can be used to produce large quantities of graphene for various advanced applications, including photovoltaic devices, energy storage devices, nanoelectronics, sensors, absorption media, etc.

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