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## Low temperature solvothermal synthesis of crumpled carbon nanosheets

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### Abstract

Crumpled carbon nanosheets have been successfully synthesized via a catalyst-free solvothermal route at very low temperatures (60–100 °C), using tetrachloromethane as the carbon source and potassium as the reductant. The X-ray powder diffraction pattern indicates that the products are hexagonal graphite. Transmission and scanning electron microscopy show that the thickness of crumpled carbon nanosheets ranges from 3 to 8 nm. Raman spectroscopy supports the existence of graphitized carbon at the nanoscale. BET experiments show that carbon nanosheets have a large surface area. Compared with previous methods to prepare graphite nanosheets, such a low reaction temperature has attractive advantages.

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**Keywords:** A. Graphitic carbon; B. Hydrothermal treatment; C. Transmission electron microscopy; D. Surface areas

### 1. Introduction

Carbon sheets a few nanometers thick (nanosheets) may have potential applications, such as serving as catalyst supports [1,2], electrode materials for lithium-ion batteries [3], and electronic conduct fillers for preparing conducting polymer composites [4–6], because of their remarkable surface area as well as special characteristics of flexibility and elasticity, high thermal resistance, high chemical stability and light weight [7]. In addition, such quasi-two-dimensional nanostructured materials may serve as the building blocks for other promising carbon materials. For instance, nanotube-like carbon nanoscrolls have been formed from exfoliated graphite nanosheets via a scrolling mechanism [8], carbon nanohorns are a new type of horn-shaped aggregate of single-walled graphene sheets [9], and carbon nanowalls could be in nature regarded as well-separated graphene sheets vertically growing on the substrates [10].

In some early studies [11–13], carbon nanosheets were produced with low yields, accompanying other carbon allotropes such as carbon nanotubes. Recently, petal-like carbon nanosheets were produced in macroscopic quantity by an arc-discharge reaction [14], and expanded graphite (EG) nanosheets were produced from various graphite intercalation compounds (GIC) submitted to a brutal thermal shock [15–18]. Moreover, well-separated graphene sheets on substrates, i.e. carbon nanowalls, were synthesized by a microwave plasma enhanced chemical vapor deposition method and by a hot filament chemical vapor deposition method [10,19–22]. These synthetic methods, however, required high temperature, complicated instruments or metal catalysts. Herein, we report the high-yield synthesis of crumpled carbon nanosheets with thickness less than 10 nm from carbon tetrachloride under low temperature and catalyst-free conditions. The reaction was carried out by a solvothermal route that had been widely used for the preparation of various carbon nanostructures, such as diamond [23], carbon nanotubes [24–28], carbon nanorods [25], carbon nanobelts [27] and hollow carbon spheres [28,29]. The carbon nanosheets synthesized by this proposed method have a high surface area.

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## 2. Experimental

A solvothermal route was employed in the synthesis as described below. About 25 ml of tetrachloromethane was placed in a 30 ml Teflon-lined autoclave. Then 1.8 g metallic potassium was cut into flakes and rapidly added to the autoclave under the protection of  $N_2$  atmosphere. The autoclave was sealed and quickly heated to the desired temperature (typically 60 °C within 60 min), where it was maintained for 10 h before it was cooled to room temperature naturally. The products, dark precipitates, were filtered out and washed with toluene, absolute ethanol and water in sequence, and were then dried in a vacuum at 60 °C for 4 h.

X-Ray powder diffraction (XRD) patterns were carried out using  $Cu K\alpha$  radiation. Field-emission scanning electron microscopy (FE-SEM) images were taken at an accelerating voltage of 10 kV. Raman spectra were recorded using a confocal microprobe Raman system (Dilor Labram I) with the excitation line of 632.8 nm from an internal He–Ne laser. Specific surface areas were measured by a nitrogen adsorption technique at liquid nitrogen temperature.

## 3. Results and discussion

Fig. 1a shows a typical XRD pattern of the as-prepared final products. A broad diffraction peak at about 26.20° can be indexed as the (002) diffraction of hexagonal graphite (JCPDS no. 04-0221). The broad peak at about 43.1° could be due to the overlap of broad (100) and (101) diffraction peaks which are expected to occur at 42.22° and 44.39°, respectively. The thickness of the graphitic products along the [001] direction (i.e. the average crystallite size along the [001] direction) is

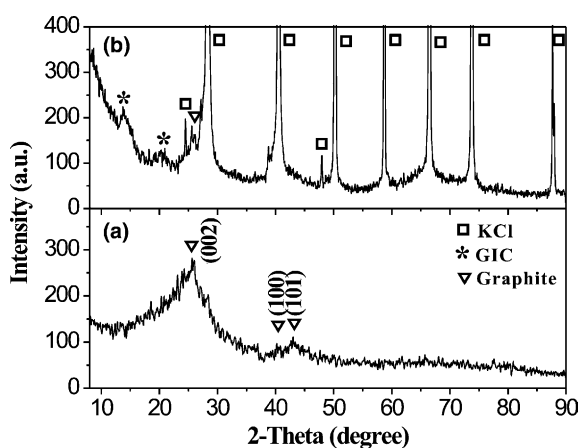


Fig. 1. XRD patterns of the products with various treatments: (a) the as-prepared final products washed with solvents; (b) the raw products without any post-treatments. In the figure, the diffraction peaks of carbon nanosheets are marked as  $\nabla$ , potassium GIC as  $*$ , and KCl as  $\square$ .

about 4.5 nm estimated from the half-peak width of the (002) reflection peak using the Scherrer equation. This indicates that graphitization is not complete and the degree of long-range order of these nanostructures is lower than that of bulk graphite [30]. The interlayer spacing is calculated to be 0.339 nm from the position of (002) reflection peak, slightly larger than that of bulk hexagonal graphite (0.335 nm). In order to obtain some further information about the formation mechanism, the raw products without any post-treatment were checked by XRD as shown in Fig. 1b. Compared with that of the final products, the XRD pattern of the raw products has only a very weak peak at about 26°. However, besides the strong diffraction peaks of KCl, two broad peaks at about 14° and 20° appear. The two broad peaks might correspond to (004) and (101) diffractions of the potassium-GIC (K-GIC),  $KC_8$  (JCPDS no. 04-0221). It should be pointed out that the angles of the two broad peaks are lower than those of the standard  $KC_8$  (16.5° and 21.1°, respectively), which implies that the interlayer distance of the K-GIC in the raw products is larger. After washing, the K-GIC changed to graphite, resulting in an increase of the intensity of the graphite characteristic peak at 26° and disappearance of the diffraction peaks of K-GIC.

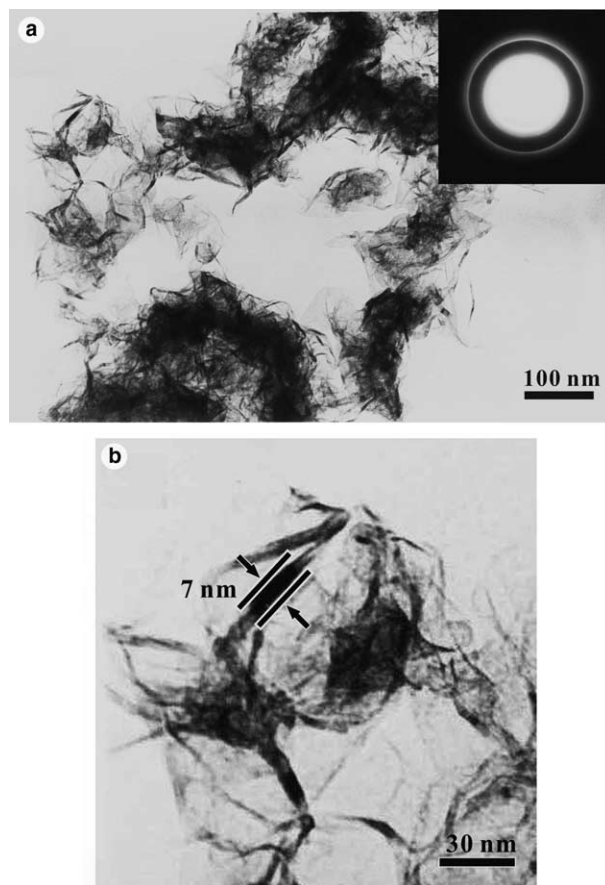


Fig. 2. (a) TEM image of as-prepared carbon nanosheets; (b) partially enlarged detail of (a).

Fig. 2 shows the morphology of the as-prepared products. As shown in the TEM of Fig. 2a, the products are nanosheets interlaced like a cluster of crumpled paper. The diffraction rings in the electron diffraction (ED) pattern (inset of Fig. 2a) indicate that the as-prepared nanosheets are polycrystalline, which is in good agreement with the XRD pattern. These nanosheets are usually several hundred nanometers wide, but they are so thin that they seem to be transparent for electron beams except some folded parts. According to a partially enlarged detail of the folded parts of carbon nanosheets (Fig. 2b), their thickness is about several nanometers, which is much thinner than the EG nano-

Table 1  
Thickness and specific surface area for as-prepared carbon sheets and other carbon materials

Carbon material	Ref.	Thickness (nm)	$A_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )
Natural graphite	[34]	–	1.7–6.0
Expanded graphite	[31]	>20	40–60
Carbon nanowalls	[10,19]	<10	–
As-prepared carbon sheets		<10	97.2

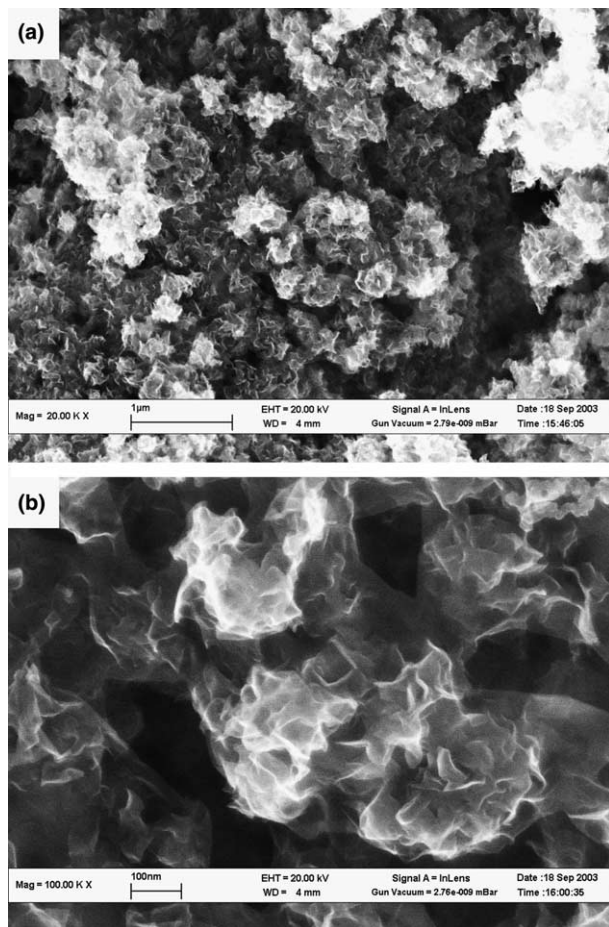


Fig. 3. (a) FE-SEM image of carbon nanosheets crumpled like a flower; (b) high-magnification SEM image of the carbon nanosheets.

sheets [31] but similar to that of carbon nanowalls [10,19] (Table 1).

More vivid image of carbon nanosheets was observed by FE-SEM. It can be seen that the products consist of a large number of nanosheets with the shape of flowers (Fig. 3a). A high-magnification image (Fig. 3b) indicates that they have sharp edges and many folds. Unlike well-separated carbon nanowalls [10], the as-prepared carbon sheets are interlaced each other.

Fig. 4a is the HRTEM image of a separated carbon nanosheets. Fig. 4b was taken from the small area of a folded part of the separated nanosheet indicated by the arrow in Fig. 4a. It can be seen from the HRTEM image that the thickness of the nanosheets ranges from 3 to 8 nm, which is similar to the petal-like graphite nanosheets produced by hydrogen arc discharge [14]. In addition, from the inset of Fig. 4b, lattice fringes can be distinctly observed with an interlayer spacing of about

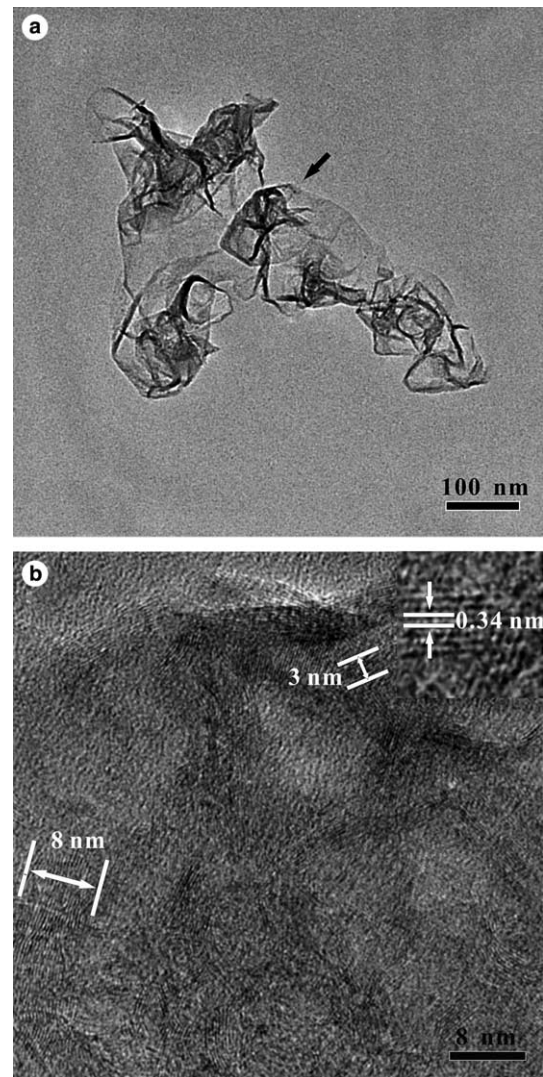


Fig. 4. (a) TEM image of a separated carbon nanosheets, (b) HRTEM image enlarged from the folded part as marked by arrow in (a).

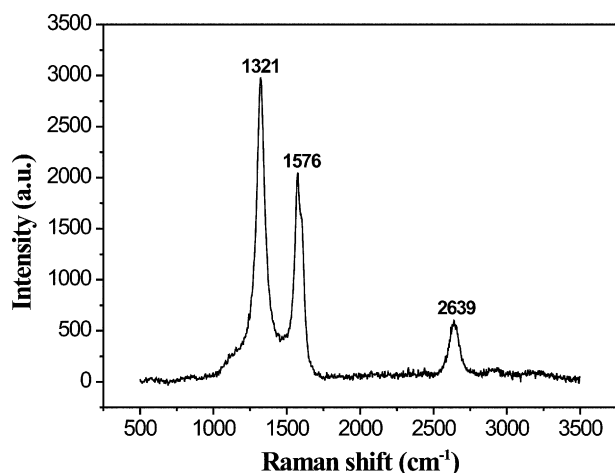


Fig. 5. Raman spectrum of the as-prepared carbon nanosheets.

0.34 nm, consistent with the XRD measurement. The folding of the nanosheets in different parts increases the stress in them, which might be the reason that the interlayer spacing is slightly larger than that for bulk graphite.

The Raman spectrum may provide more convictive information about the crystallography and morphology of the as-prepared material [32]. Fig. 5 shows that it has two strong peaks at 1576 and 1321  $\text{cm}^{-1}$  and a weak peak at 2639  $\text{cm}^{-1}$ . The peak at around 1321  $\text{cm}^{-1}$  is the D-band associated with vibrations of carbon atoms with dangling bonds in plane terminations of the disordered graphite, and the peak at 2639  $\text{cm}^{-1}$  is an overtone of the disorder mode ( $2 \times \text{D}$ ). The peak at 1576  $\text{cm}^{-1}$  (G-band) is attributed to the vibration of  $\text{sp}^2$ -bonded carbon atoms in a two-dimensional hexagonal lattice [26,27]. Moreover, the D-band peak is stronger than the G-band peak and their intensity ratio is about 1.5, unambiguously suggesting the carbon nanosheets are long-range disordered graphitized carbon.

In view of their thickness and the morphology, the as-prepared carbon nanosheets should have large specific surface area and BET measurements gave values up to 97.2  $\text{m}^2\text{g}^{-1}$ . This is tens of times that of natural graphite and much higher than that of ordinary EG sheets as shown in Table 1. It has been hypothesized that the surface area of an individual graphite sheet would be up to 2630  $\text{m}^2\text{g}^{-1}$ , assuming that both sides of the sheet are accessible [8,33]. The measured value of specific surface area of as-prepared carbon nanosheets corresponds to about 1/27 of the potential surface area. This signifies that their average thickness is about 9 nm, which is a little thicker than the value estimated by TEM observations and XRD measurements. The discrepancy between the calculated value and that observed might be ascribed to two factors. First, in addition to nanosheets, the products synthesized in this work contain a small quantity of nanoparticles (<10%), which can lower the value of the specific surface area. Second, folding of the

nanosheets, results in a decrease of the surface area. Table 1 summarizes the thickness and the specific surface area of various carbon sheets. Compared with other carbon materials, the specific surface area of as-prepared products is relatively high.

To investigate the effect of experimental conditions on the formation of the carbon nanosheets, a series of experiments were carried out at different experimental conditions. The results indicated that the reaction temperature and reductant were critical factors in the formation. The optimum reaction temperature was from 60 to 100  $^{\circ}\text{C}$ , and the percentage of carbon nanosheets in the final product was more than 90% according to SEM and TEM observations. When the reaction temperature was lower than 60  $^{\circ}\text{C}$ , the reaction hardly proceeded, and when it was over 120  $^{\circ}\text{C}$ , the reactions took place too rapidly and destroyed the reaction chamber.

The reductant is another key factor in the transformation of tetrachloromethane to nanoscale carbon materials at such low temperature range (60–100  $^{\circ}\text{C}$ ). To the best of our knowledge, although carbon nanotubes, carbon nanorods, carbon nanobelts and hollow carbon spheres have been synthesized by analogous methods, there is no report of carbon nanosheets synthesized by a solvothermal method in such a low temperature range. In the previous studies [24–29], sodium, magnesium,  $\text{NaNH}_2$  and potassium acted as the reductant in the solvothermal routes. However, the reducibility of metallic potassium was found to be much stronger than metallic sodium and the other reductants mentioned, and therefore tetrachloromethane is more easily dechlorinated by potassium at low temperature. In our study, if using sodium as reductant instead of potassium, the reaction hardly took place below 160  $^{\circ}\text{C}$ .

Although the autoclave was kept at a low temperature in our experiments, the local temperature, especially at the interface between the potassium and the tetrachloromethane, could be much higher during the reactions because of its exothermicity. Therefore, the formation of carbon nanosheets would be a very complicated process. As the as-prepared carbon nanosheets are built from the hexagonal lattice of  $\text{sp}^2$  carbon while the reactant tetrachloromethane is an  $\text{sp}^3$  structure, the possible mechanism could follow the mechanism that has been proposed for the transformation from a  $\text{sp}^3$ -hybridized carbon source (tetrachloromethane, tetrachloroethylene, etc.) to  $\text{sp}^2$ -hybridized carbon nanostructured materials (nanotubes, hollow spheres, etc.) [25,28]. Tetrachloromethane is first reduced by metallic potassium to dichlorocarbene and further forms free  $\text{—C=C—}$  through a series of dechlorinating and bonding processes. The freshly formed free  $\text{—C=C—}$  may assemble into two-dimension hexagonal carbon clusters, then into a graphitic sheet and finally into K-GIC. Different from the situations where some transition metal nanoparticles were used as catalysts [24,25,28], the ultimate products in

the present study, where no catalyst was employed, were carbon nanosheets rather than carbon nanotubes. It should be pointed out that the same product can be obtained if we put a glass beaker into the Teflon-lined autoclave as the container which avoids a possible catalytic reaction in the presence of Teflon. However, it is unclear at the present time whether the pre-formed K-GIC presents some catalytic properties to the further growth of the carbon nanosheets.

#### 4. Conclusions

Crumpled carbon nanosheets have been successfully synthesized via a catalyst-free solvothermal route in a very low temperature range (60–100 °C). The as-prepared carbon nanosheets have a large specific surface area. The material should find potential applications in many areas as a catalyst support of other functional materials.

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