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A novel bottom-up solvothermal synthesis of carbon nanosheets

Wentai Wang, Sandip Chakrabarti, Zhigang Chen,
Zifeng Yan, Moses O. Tade, Jin Zou and Qin Li*

We report a bottom-up one-step solvothermal synthesis of thin layered carbon nanosheets as a highly effective adsorption material.

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PAPER

A novel bottom-up solvothermal synthesis of carbon nanosheets†

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Wentai Wang,^{ab} Sandip Chakrabarti,^c Zhigang Chen,^d Zifeng Yan,^b Moses O. Tade,^e Jin Zou^{df} and Qin Li^{*a}Received 8th September 2013
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We report a bottom-up one-step solvothermal synthesis of thin layered carbon nanosheets (CNSs) by dehydrating glycerol with concentrated sulfuric acid in the presence of melamine. In this synthesis, melamine plays a critical role in the formation of the thin-layered CNS. This CNS was found to be a highly effective adsorption material: its adsorption of methylene blue (MB) is considerably faster than GO with a maximum adsorption capacity of MB at 585 mg g⁻¹, comparable to most of the other carbon based nanomaterials.

Introduction

Carbon nanosheets (CNSs) are two-dimensional (2D) carbon nanostructures consisting of free-standing carbon-containing sheets with graphene as the most distinguished member possessing extraordinary electrical and mechanical properties.^{1,2} The 2D sheet structure also provides an enormous accessible surface area, facilitating adsorption,^{3,4} catalytic reactions,^{5,6} sensing,^{7,8} *etc.* These unique features and versatile applications have stimulated intense research on developing simple and low cost methods for large-scale synthesis of graphene and graphene-like materials.

Both top-down and bottom-up approaches have been extensively employed to synthesize CNSs. In top-down methods, CNSs are obtained from a larger carbon structure, typically graphite. For graphene synthesis, one typical top-down method is exfoliation, including mechanical exfoliation,¹ sonication or microwave assisted exfoliation,^{9–11} chemical oxidative exfoliation,^{12–14} chemical intercalation^{15,16} and thermal exfoliation.¹⁷ Though chemical exfoliation offers a scalable and effective production avenue, the harsh chemicals involved in the processes are not favorable. Among the bottom-up methods,

chemical vapor deposition (CVD) of various carbon-containing molecules is the most established route, which generally produces high quality, large area layered carbon structures,^{18–20} but is often costly. Developing simple chemical methods to build atomic-layered carbon structures from carbon-containing molecules is highly desirable in large-scale synthesis. Though significant improvements have been made in exclusive 2D polymerization from carbon precursors,^{21–25} various challenges in producing large quantity and high quality remain. Most of these bottom-up syntheses involve employing metal reduction reagents to assist layered formation of graphene, which is often associated with high cost and impurity issues. To synthesize CNSs entirely from organic matter, formation of removable separation layers between the carbon nanosheets has been demonstrated to be a successful strategy by Antonietti and coworkers²⁶ and Zhao *et al.*²⁷

Herein we report a bottom-up one-step solvothermal synthesis of thin layered CNSs from common, inexpensive chemical reagents, namely glycerol, concentrated sulfuric acid and melamine. In this synthesis we found that melamine plays a critical role in the formation of a layered sheet structure. Moreover, our process has several advantages such as high yield, low cost, and short time of processing. Furthermore, we found that the CNS is a highly effective adsorption material: its adsorption of methylene blue (MB) is considerably faster than GO, with a maximum adsorption capacity of MB as high as 585 mg g⁻¹.

Experimental section

Materials

Glycerol, melamine and graphite powder were purchased from Sigma-Aldrich. Concentrated sulfuric acid (98%) was purchased from Alfa Aesar. Methylene blue (MB) was supplied by Chem-Supply. All chemicals were used as received without any further purification.

^aQueensland Micro- and Nanotechnology Centre, Griffith University Nathan Campus, Brisbane, Australia. E-mail: qin.li@griffith.edu.au; Fax: +61 7 555 28226; Tel: +61 7 3735 7514

^bState Key Laboratory of Heavy Oil Processing Key Laboratory of CNPC, China University of Petroleum, Qingdao, China

^cAmity Institute of Nanotechnology, Amity University Uttar Pradesh, Noida, India

^dMaterials Engineering, the University of Queensland, St Lucia, QLD 4072, Australia

^eDepartment of Chemical Engineering, Curtin University, Bentley, WA 6845, Australia

^fCentre for Microscopy and Microanalysis, The University of Queensland, St Lucia, QLD 4072, Australia

† Electronic supplementary information (ESI) available: FESEM, FTIR spectra, atomic percentages, XPS spectra of CNSs, TGA results, dynamic adsorption and removal efficiency of MB, and pseudo-second-order kinetic, linear isotherm plots of Freundlich and Langmuir models. See DOI: 10.1039/c3ta13593d

Synthesis of CNSs

A typical experimental procedure is as follows: 0.5 g of melamine and 10 mL of glycerol were mixed together and stirred until melamine was totally dissolved in glycerol, followed by addition of 10 mL of 98% sulfuric acid under vigorous stirring. The mixture was then transferred into a 50 mL PTFE (polytetrafluoroethylene) inner vessel of an autoclave and placed into an oven at 180 °C for 4 h. This step was recognized as pre-carbonization of a carbon precursor and the product was named as CNS. The obtained black solid product was then washed with Milli-Q water and ethanol three times to remove the impurities for measurement and application tests. The as-synthesized CNSs were then calcinated at 800 °C for 2 h at a heating rate of 10 °C min⁻¹ under argon gas protection for further carbonization. The final product was named as CNS-800.

Characterization

Morphology. Field Emission Scanning Electron Microscopy (FESEM) images were captured through a Zeiss Neon 40EsB. A High Resolution Transmission Electron Microscopy (HRTEM) image was obtained on a JEOL JEM2100 LaB6 TEM. X-ray diffraction (XRD) measurement was taken on a Bruker D8 Advance Diffractometer (Cu K α radiation, 2° 2 θ per min). Atomic force microscopy (AFM) analysis was carried out on a Dimension 3000 with tapping mode to obtain the morphology of the samples.

Chemical composition. FT-IR spectra were collected on a Perkin-Elmer Spectrum 100 with a resolution of 4 cm⁻¹ in transmission mode at room temperature. A baseline correction was applied after measurement. Raman spectral data were collected on an Olympus BX40 using 514 nm laser excitation. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra Photoelectron Spectrometer which uses Al K α (1253.6 eV) X-rays. Curve fitting and background subtraction were performed using Casa XPS version 2.2.73 software. Thermogravimetric analysis (TGA) was performed by heating the samples in an argon flow at a rate of 25 mL min⁻¹ using a Perkin-Elmer Diamond TG/DTA thermal analyzer at a heating rate of 10 °C min⁻¹.

Adsorption experiments

A MB dye adsorption experiment was performed by using the as-synthesized CNS as an adsorbent. MB solutions of different concentrations were prepared. 40 mg of adsorbent were added into 50 mL of MB solution, which was then subjected to 300 rpm stirring at room temperature. 3–4 mL MB solution was withdrawn at a certain time interval and filtered with a 0.45 μ m syringe filter to separate the MB solution and the adsorbent. The collected MB solution was diluted 10 times before the absorption measurement using a Varian Cary 300 Bio UV-Visible Spectrometer at 663 nm.

The equilibrium concentration (C_e) of MB was calculated according to the calibration curve of MB. The equilibrium adsorption capacity (q_e) and removal efficiency of MB was calculated by the following equations:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

$$\text{Removal\%} = \left(1 - \frac{C_e}{C_0}\right) \times 100\% \quad (2)$$

where C_0 is the initial concentration of MB; V is the volume of the added solution; and W is the mass of the adsorbent.

Results and discussion

Morphology and structure of CNSs

The raw product after solvothermal synthesis, CNS, appears as a fluffy block of carbon, and it was easy to be broken into powder after washing by water and ethanol. The calcinated product, CNS-800, sustained the block morphology with strong mechanical strength, and its volume is about 1/3 of the original as-synthesized CNS block. Fig. 1 shows the XRD patterns of the as-synthesized CNS and CNS after calcination (CNS-800). No diffraction peak is observed on the CNS (before calcination), indicating its amorphous nature, while diffraction peaks of carbon appeared at around 24.3° (002) and 43° (100) in CNS-800 that was treated at 800 °C in argon for 2 h. These two bands are rather broad, indicating highly disordered but mainly sp²-hybridized carbon.²⁸ The (002) peak of the calcinated CNS-800 suggests a layered 2D carbon structure with a basal spacing in the range of 3.5 to 3.8 Å.

The morphology of the as-prepared CNS and calcinated CNS-800 was examined by FESEM, HRTEM and AFM, respectively, as shown in Fig. 2. The optical images of the CNS block, washed CNS powder and CNS-800 block are shown in Fig. 2A, B and C, respectively. Fig. 2D shows the FESEM image of the CNS which reveals that the as-synthesized carbon material is of a fluffy morphology with thin layers forming bubble-like pockets on the surface. The formation of bubbles is most likely due to the trapped gas that was released in the solvothermal process. It has been observed during SEM imaging that the bubbles expanded and burst due to electron irradiation, as illustrated in Fig. 1S in the ESI.† Fig. 2E provides a close-up view of the crumbled thin-

Fig. 1 XRD patterns of the CNS and CNS-800.

Fig. 2 Optical images of the CNS block (A), washed CNS powder (B) and CNS-800 block (C); (D) shows the FESEM image of the CNS showing a bubble-like layer structure; (E) shows the close-up FESEM image of the thin-sheets-like morphology of the CNS; (F) shows the FESEM image of CNS-800; HRTEM images of CNS (G) and CNS-800 (H) show a layer structure; the insets show corresponding SAED patterns; (I) AFM image of the CNS, below: height profile of CNS thickness following the line on the image.

sheet morphology of the CNS. The HRTEM image shown in Fig. 2G further confirms the layered morphology of the as-synthesized CNS, with the selected area electron diffraction (SAED) suggesting its amorphous nature. With the calcinated sample, the thin-layered morphology remains as shown by the FESEM in Fig. 2F and HRTEM in Fig. 2H and the carbon shows a slight degree of ordering as captured by the inset SAED pattern as shown in Fig. 2H, which is consistent with the broad peaks observed by XRD. The thickness of the multilayer CNS ranges from 1 to 5 nm according to the AFM characterization shown in Fig. 2I.

Fig. 2S in the ESI† displays the FT-IR spectra of the CNS after washing with DI water and ethanol and CNS-800 in comparison with the raw materials melamine and glycerol. In the CNS, the absorption peak from 3000–3400 cm^{-1} is related to –OH groups, while the peaks at 1700 cm^{-1} corresponding to carbonyl C=O confirm the formation of the –COOH group. The fingerprints of triazine²⁹ between 1400 cm^{-1} and 1600 cm^{-1} appeared in both melamine and CNS samples which suggest that the triazine rings originated from melamine are incorporated into the CNS. The calcinated CNS-800 does not show sharp peaks, indicating the decomposition of functional groups in the sample, e.g. the hydroxyl and carbonyl groups. One of the triazine characteristic

peaks can be observed at 1450 cm^{-1} , though the majority of its fingerprints may be covered by the broad peak after calcination.

Both Raman spectra of the CNS and CNS-800 in Fig. 3 show the G band at 1588 cm^{-1} arising from the first order scattering of the E_{2g} phonon of sp^2 C atoms, an indication of graphitic carbon,³⁰ and the D band at 1370 cm^{-1} arising from a breathing mode of k -point photons of A_{1g} symmetry, reflecting the presence of disorders and the edges and boundaries of amorphous carbon domains.³¹ The ratio of the intensities of the D–G peak, I_D/I_G , increased from 0.61 to 0.95 after calcination, implying a significant decrease of the size of in-plane sp^2 domains and an increase of disorder.³² It was noted that after calcination the volume of CNS-800 shrank to almost 1/3 of the as-prepared CNS. The drastic volume shrinkage upon calcination suggests a degree of collapse of the original layered structures, hence a decrease of in-plane sp^2 domain size. The increase of disorder can also be attributed to the defects generated by the decomposition of oxygen-containing groups during pyrolysis.

XPS measurements were carried out to reveal more details on the chemical bonding states before and after calcination. As shown in Fig. 4A, the XPS survey spectra over a wide range of binding energies (0–1200 eV) for both of CNS and CNS-800 show a predominant narrow C 1s peak at 284.5 eV, O 1s peak at

Fig. 3 Raman spectra of the CNS and CNS-800 using 514 nm laser excitation.

Fig. 4 (A) Survey XPS spectra of CNS and CNS-800; C 1s spectra of CNS and CNS-800; N 1s spectra of CNS and CNS-800.

531.5 eV and N 1s peak at 400.5 eV. In addition, an S 2p peak is also observed at 167.5 eV. The percentages of these atoms are enlisted in Table 1S in the ESI,[†] where a >50% reduction in oxygen content after calcination can be observed, which is attributed to the decomposition of oxygen-containing groups, consistent with the FT-IR interpretation.

The high resolution C 1s and N 1s peaks of CNS and CNS-800 are presented in Fig. 4 for comparison. The C 1s peak of the CNS can be fitted into seven peaks, corresponding to C=C (284.1 eV), C-C (284.6 eV), sp² C-NH₂ (285.6 eV),³³ C-O/C=N (286.2 eV), C-N (287.2 eV), O-C=O (288.8 eV)³⁰ and π-π* shake-up satellite of the sp² band (290.9 eV).³⁴ The C 1s peak of CNS-800 was divided into six peaks, corresponding to C=C (284.1 eV), C-C (284.5 eV), C-O/C=N (286.2 eV), C-N (287.2 eV), C=O (288.3 eV)^{35,36} and π-π* shake-up satellite of the sp² band (290.9 eV). The existence of a sp² C-NH₂ bond in the as-synthesized CNS suggests that there may be melamine that is not incorporated into the main framework of the sheets, and it may exist between the layers and facilitate the formation of the sheet structure, similar to the function of carbon nitride (g-C₃N₄) in other reports.²⁶ It was observed that sp² C-NH₂ and O-C=O peaks disappeared after calcination, confirming the deammoniation of the adsorbed melamine³⁷ and decomposition of -COOH at high temperature. Analysis of N 1S peaks reveals that there are three kinds of nitrogen bonds in CNS-800, namely, pyridinic-N (398.5 eV), pyrrolic-N (399.8 eV) and graphitic-N (401.2 eV), while there are only two types of nitrogen bonds in the CNS, namely pyridinic-N (398.5 eV) and in-plane pyrrolic-N (399.8 eV). This difference shows that graphitic-N was generated upon calcination. The XPS results are in agreement with FT-IR data, revealing the existence of sp² carbon and triazine structures that constitute the 2D structure in the carbon nanosheets. The S atoms and some of the O atoms are most likely originated from the H₂SO₄ and adsorbed SO₂ gas, a byproduct of the reaction, as well as the adsorbed H₂O molecules. The amount of gas adsorbed in the as-synthesized CNS is shown in the TGA results (ESI, Fig. 4S[†]), where an 18% weight loss when the temperature was below 120 °C under argon is observed.

It was also noted that graphitization of the CNS through pyrolyzing at 800 °C caused a certain degree of conductivity, with a resistance of 56 Ω measured using a typical multimeter. As a reference, we applied the same measurement method to reduced GO (rGO),³⁸ which has a resistance of 55 Ω, as shown in Fig. 5S.[†] The comparable conductivity between CNS-800 and the rGO film further confirms their structural similarity.

Although the exact reaction mechanism is still under investigation, it appears that the introduction of melamine into the reactants is crucial for forming layered CNSs. The reaction without addition of melamine did not result in the CNS but in coke-like carbonaceous blocks as shown in Fig. 6SA.[†] In other words, melamine has played an important role as the planar structure template or nucleates. The effect of the amount of melamine (with 10 mL glycerol and 10 mL H₂SO₄) was evaluated. As revealed by the FESEM images shown in Fig. 6S[†] when the melamine amount was reduced to 0.25 g or increased to 1 g, a large amount of carbon spheres was produced accompanied by some thin sheets. In the tested system, melamine : glycerol : H₂SO₄ set at 0.5 g : 10 mL : 10 mL yields the best outcome, with the majority as thin sheets accompanied by some carbon spheres. It appears that the SO₂ and H₂O gas produced in the reaction also facilitates the separation between the layers. It is worth noting that the amount of added sulfuric acid is also

important to the formation of layered structures. With the same reactants but only one drop of concentrated sulfuric acid, we have previously successfully synthesized highly fluorescent N-doped carbon nanodots.²⁹

Adsorption performance of CNSs

It was found that the as-prepared CNS showed more efficient adsorption properties compared to the calcinated CNS-800. Therefore, the adsorption of MB from aqueous solutions using the as-prepared CNS was investigated in comparison with GO obtained by Hummer's method.¹² After mixing 40 mg of CNS and 50 mL of MB solution, the colour of the MB solution changed from deep blue to light blue or colourless depending on the initial concentration of MB solution.

Fig. 5A shows the adsorption kinetics of MB on the CNS and GO with a 150 mg L⁻¹ MB initial concentration. It can be observed that the adsorption of MB on the CNS increased rapidly within the first 30 min before slowing down and reaching equilibrium. The CNS shows much faster adsorption dynamics than GO, as depicted by the rising curves in Fig. 5A. The adsorption of MB on the CNS and GO achieved an equilibrium after 200 min and 300 min, respectively. It should be noted that one of the acknowledged advantages of GO as an adsorbent is its fast kinetics compared to most other adsorbents owing to the thin sheet structure.^{30,39} This faster adsorption kinetics of the CNS could make it a very attractive adsorbent over other carbon-based MB adsorbents including GO.

The amounts of MB adsorbed on the CNS and GO at equilibrium were almost the same (332.7 mg g⁻¹ and 336.3 mg g⁻¹, respectively) at an initial MB concentration of 150 mg L⁻¹. This similar adsorption capacity between the CNS and GO suggests that the two materials may have a similar specific surface area. The faster adsorption kinetics of the CNS may be primarily attributed to the expanded layer interspace, providing more porous structures and better molecular access, as well as surface charge. In addition, when the MB initial concentration is less than 90 mg L⁻¹, the CNS can achieve more than 98% removal efficiency in less than 150 min (as shown in Fig. 7SB†), more effective than GO, activated carbon³⁷ and graphene sheet materials.⁴⁰

The CNS adsorption of MB was found to be highly sensitive to pH; as exhibited in Fig. 5B, the adsorption capacity of MB significantly increases with the pH. The equilibrium capacity of

MB can reach up to 585 mg g⁻¹ at a pH of 11.5, which might be caused by the charge effect.

The adsorption kinetics of the CNS fits well using the pseudo-second-order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \quad (3)$$

where q_e and q_t are the amounts of solute adsorbed (mg g⁻¹) at equilibrium and time t (min), respectively; k_2 is the rate constant of the pseudo-second-order adsorption (mg g⁻¹ min⁻¹). The linear plot of the pseudo-second-order model is shown in Fig. 8S,† whereas Table 1 summarizes the kinetic constants obtained by linear fitting. The adsorption of MB on both the CNS and GO follows the pseudo-second-order kinetics, which implies a surface chemistry dominated adsorption behavior. The calculated $q_{e,cal}$ value for the CNS, 341.3 mg g⁻¹, is very close to the experimental $q_{e,exp}$ value, 332.7 mg g⁻¹. The calculated value of k_2 , 2.68×10^{-4} mg g⁻¹ min⁻¹, is faster than that of GO by almost an order of magnitude (k_2 , 3.87×10^{-5} mg g⁻¹ min⁻¹).

The adsorption isotherm data of the CNS were fitted to both the Freundlich model (eqn (4)) and the Langmuir model (eqn (5))

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (5)$$

where K_F is the Freundlich constant and $1/n$ is the heterogeneity factor; K_L is the Langmuir adsorption constant (L mg⁻¹) related to the energy of adsorption, and q_m (mg g⁻¹) is the maximum adsorption capacity. The fitting curves are presented in Fig. 9S† and the parameters are summarized in Table 2, respectively.

As judged by the correlation coefficient R^2 in Table 2, the Langmuir isotherm is a better fit to the experimental data, suggesting that the adsorption of MB on the CNS is a monolayer adsorption. The maximum adsorption capacity q_m derived from the Langmuir model, 327.9 mg g⁻¹, is very close to the experimental data, 332.7 mg g⁻¹.

Table 1 Parameters of pseudo-second-order kinetics for MB adsorption on the CNS and GO

Adsorbent	$q_{e,exp}$ (mg g ⁻¹)	$q_{e,cal}$ (mg g ⁻¹)	k_2 (g (mg g ⁻¹ min ⁻¹) ⁻¹)	R^2
CNS	332.7	341.3	2.68×10^{-4}	0.9995
GO	336.3	386.1	3.87×10^{-5}	0.9817

Table 2 Langmuir and Freundlich isotherm parameters for MB adsorption on the CNS

Dye	Freundlich isotherm			Langmuir isotherm		
	K_F	$1/n$	R^2	q_m (mg g ⁻¹)	K_L (L mg ⁻¹)	R^2
MB	195.66	0.1804	0.8252	327.9	2.85	0.9992

Fig. 5 (A) Adsorption kinetics of MB on the CNS and GO (in 150 mg L⁻¹ MB solution at room temperature, pH = 7); (B) effect of pH value of MB solution upon adsorption of MB on the CNS (in 150 mg L⁻¹ MB solution at room temperature).

Overall, the as-synthesized CNS showed a comparable adsorption capacity to most of the other carbon based nanomaterials, such as GO/GO sponges^{39,41,42} and activated carbon.^{43,44} More importantly, the CNS in this study has a very fast adsorption dynamics, surpassing GO.

Conclusions

We have developed a novel and simple bottom-up synthesis method to produce thin-layered CNSs by dehydrating glycerol with sulfuric acid in the presence of a certain amount of melamine. It is highly interesting that in this facile solvothermal synthesis, melamine played a critical role as a structure-directing agent in the formation of a layered carbonaceous material, in addition to its N-doping function. This molecule-based structure-directing approach sheds new light on 2D nanocarbon synthesis. Furthermore, the resultant CNS possesses excellent adsorption properties of organic dyes. Its highest adsorption capacity of MB reaches 585 mg g⁻¹, comparable to most of the other carbon based nanomaterials, such as GO/GO sponges and activated carbon. More distinctively, the CNS shows very fast adsorption kinetics, which can be described by the pseudo-second-order kinetic model with its kinetic rate almost an order of magnitude faster than that of GO.

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