Synthesis of Few-Layer Graphene Sheets from Waste Expanded Polystyrene by Dense Fe Cluster Catalysis

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ABSTRACT: Graphene sheets have a vast number of potential applications due to their excellent properties. However, poor quality and harsh preparation conditions restrict their application. Here, few-layer graphene (FLG) sheet powder with high quality has been synthesized from waste expanded polystyrene (EPS) at low temperature by dense Fe cluster catalysis. The micron-sized FLG sheets comprising about three layers show high crystallinity and good electrical conductivity that are comparable to those of the shear-exfoliated graphene nanoplatelets. More than 70% carbon yield of FLG sheets from cheap EPS and their safe, controllable synthesis conditions make it easy to expand production. The catalytic formation mechanism of FLG sheets is studied.

1. INTRODUCTION

Graphene, as a monolayer of carbon atoms organized in a two-dimensional, atomic-thick honeycomb lattice by sp²-hybridized C–C bonds, has zero band gap, high carrier concentration (electrons or holes, \(10^{13} \text{ cm}^{-2}\)), high electron mobility (1.5 \(\times\) \(10^6\) \(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\)), high thermal conductivity, half-integer quantum Hall effect, low absorbance (about 2.3%), nonlinear optical effects, high Young’s modulus (1060 GPa), and high breaking strength (42 N m\(^{-1}\)). These exceptional properties give rise to a great number of applications in electronics, optoelectronics, sensors, thermal management, energy generation and storage, anticorrosion paints, seawater desalination, sensors, thermal management, energy generation and storage, anticorrosion paints, seawater desalination, etc. Graphene consists of 10 or fewer layers is absolutely imperative and remains a challenge.

The production methods of graphene sheets mainly focused on the liquid-phase exfoliation (LPE) of graphite\(^\text{1,10}\) and chemical vapor deposition (CVD)\(^\text{1,10}\). The LPE of graphite was used to produce suspensions or slurries of the graphene platelets by overcoming the van der Waals forces between graphene layers in a solvent by the energy input.\(^\text{1,5}\) Nevertheless, a survey of the commercially available products revealed that less than 10% of the materials in most of the products consisted of 10 or fewer layers. None of the products contained over 50% of such graphene.\(^\text{11}\) Besides the rather poor quality, the harsh separation procedure of the materials and solvents or additives in the product limited their applications.\(^\text{12}\) The CVD technique as a bottom-up approach was employed to grow a large-area continuous graphene film in applications of touch panels and displays,\(^\text{12}\) however, it had limited success due to the extended defects and void, which jeopardized the structural stability of the film and damaged its excellent physical properties.\(^\text{1}\) The CVD growth of multilayer graphene on a metal substrate was uncontrollable.\(^\text{1}\) The reduced graphene oxide (rGO) (around 23% of oxygen content) or GO (usually 45% of oxygen content) were prepared via oxidation of graphite and subsequent exfoliation and/or reduction.\(^\text{11,17}\) However, the rGO and GO were amorphous materials due to the high density of structural defects and showed poor electrical and thermal conductivities when compared to those of crystalline graphene.\(^\text{11,17}\) Furthermore, their manufacturing processes suffered safety hazards from the oxidizing agents.\(^\text{15,16}\) Therefore, the development of a safe, controllable method for the synthesis of micron-sized crystalline graphene materials with a high content of graphene consisting of 10 or fewer layers is absolutely imperative and remains a challenge.

Expanded polystyrene (EPS) (about 15.4 million tons annually produced in the world)\(^\text{18}\) as the most difficultly biodegradable thermoplastic mostly turned into “white pollution” due to its one-off usage and a low recycling rate (10–30%), leading to serious damage to the marine ecology and wastage of resources.\(^\text{19–23}\) EPS as an aromatic linear polymer material possesses excellent chemical and thermal stabilities and is a good carbon precursor with 92.4% carbon content. Our purpose is to turn waste EPS into useful carbon-based material such as few-layer graphene (FLG).

In this communication, we have developed a novel, safe, and controllable method to synthesize micron-sized FLG sheets from waste EPS. Here, few-layer graphene (FLG) sheet powder with high quality has been synthesized from waste expanded polystyrene (EPS) at low temperature by dense Fe cluster catalysis.

Supporting Information

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using waste EPS as a precursor. Especially, micropores were constructed in waste EPS using a simple two-step cross-linking strategy, followed by in situ loading of small-sized catalysts and subsequent carbonization. Compared with the reported methods, the powder product has a high content of crystalline FLG sheets and can be obtained at a low temperature of 700 °C due to the dense Fe cluster catalysis. The yield of over 70% from waste EPS is beneficial for scaling up the production of FLG sheets, which provides an effective way for the recycling of waste EPS.

2. RESULTS AND DISCUSSION

The high cross-linking of EPS is necessary to resolve the complete decomposition of linear PS at high temperatures and obtain a carbon product. Uniform loading of small-sized transition-metal catalysts needs to be achieved in a precursor
for the low-temperature preparation of graphitic flake due to its “dissolution—precipitation” formation mechanism on the surface of transition metal. Therefore, the preparation process of FLG sheets from waste EPS is well-designed (Scheme 1 and Figure S1). First, a pre-cross-linking strategy using glacial acetic acid (HAc) as solvent is adopted to prepare a low cross-linked EPS to prevent EPS from dissolving in 1,2-dichloroethane (DCE) and maintain its framework during the subsequent hyper-cross-linking reaction. Afterward, the cross-linking density of the pre-cross-linked EPS is sharply increased by the hyper-cross-linking reaction using FeCl3 as a cross-linker and solvent, in favor of achieving a high carbon yield. Meanwhile, a large number of micropores are constructed in the interior of the PS framework. FeCl3 is reduced into FeCl2 and uniformly loaded by the HRTEM characterization (Figure 1g) and the selected area electron diffraction (SAED) pattern with a typical hexagonal structure (Figure 3c,d), the high crystallinity of the FLG sheets prepared at 700, 800, and 900 °C (Figure S2), which should be attributed to the formation of more dangling bands due to the cracking of the larger FLG sheets at higher temperatures (Figure S3). Crystal boundaries (bright lines) existing in large FLG sheets of G4-3-8 (Figure S3c,d) shrink and crack with the increase of temperature so that the smaller, isolated FLG sheets start to form in G4-3-8 (Figure S3c,d). After the temperature rises up to 900 °C, the FLG sheets mostly demonstrate isolated and more dangling bands from the edge of FLG sheets (Figure 1a,b).

The XPS spectra of G4-3-9 are shown in Figure 2a,b. The XPS C 1s core-level spectrum reveals the characteristic signals of crystalline carbon of FLG sheets with a carbon content of 96.5 atom % (Figure 2a). Fitting results show that FLG sheets mainly include sp2-hybridized C–C bonds, which is confirmed by the C 1s peak at 284.6 eV (Figure 2b). Their thermal stability is investigated by the TG and DSC curves in an air flow (Figure 2c). The FLG sheets demonstrate excellent resistance to thermal oxidation with little mass loss until about 560 °C due to high crystallinity, which is superior to that of reported graphene oxide, and is comparable to graphene nanoplatelets prepared by ball milling or sonication.

FLG sheets were also successfully prepared at lower temperatures (Figure 3a,b,e,f). Their high crystallinity is proved by the HRTEM characterizations (Figure 3c,g), the SAED pattern with clear diffraction rings (Figure 3d,h), sharp and strong (002) diffraction peaks (Figure 1c) and low I_d/I_G values (Figure 1d). Although the XRD patterns indicate similar crystallinity of the FLG sheets prepared at 700, 800, and 900 °C (Figure 1c), the I_d/I_G values increase with the rise of temperature (Figure S2), which should be attributed to the formation of more dangling bands due to the cracking of the FLG sheets at higher temperatures (Figure S3). Crystal boundaries (bright lines) existing in large FLG sheets of G4-3-7 (Figure S3a,b) shrink and crack with the increase of temperature so that the smaller, isolated FLG sheets start to form in G4-3-8 (Figure S3c,d). After the temperature rises up to 900 °C, the FLG sheets mostly demonstrate isolated and more dangling bands from the edge of FLG sheets (Figure 1a,b).

The carbonization process of G4-3Fe, i.e., FeCl3-loaded hyper-cross-linked EPS was monitored by the TG and DSC curves to find out the formation of the FLG sheets (Figures 2d, 3a,b,e,f).
and S4). The mass loss of about 15% between 200 and 600 °C should be attributed to the pyrolysis of the hyper-cross-linked EPS and the reduction of FeCl₂. This is validated by the formation of graphitized carbon and amorphous carbon due to the coexistence of sharp and broad diffraction peaks indexed with the (002) plane of graphite shown in the XRD pattern of G4-3-6 obtained at 600 °C (Figure 1c), which is confirmed by the 2D band and the high I_D/I_G value of the Raman spectrum (Figure 1d). A rapid mass loss of about 20% with an obvious endothermic peak between 600 and 700 °C is ascribed to the sublimation of residual FeCl₂. Meanwhile, amorphous carbon is further catalytically graphitized (Figure 1c,d). A large endothermic peak without a mass change appears between 700 and 1000 °C, corresponding to the increase of crystallinity of the FLG sheets. This is testified by similar XRD results despite the size decrease of the FLG sheets with the increase of temperature (Figures 1a–c and S3).

Figure 4. (a) SEM image of the G4-3-6 prepared at 600 °C. (b) SEM image and (c–e) elemental mapping of Cl, C, and Fe corresponding to the pink rectangle area in (b). (f) EDS and (g) XRD pattern of G4-3Fe demonstrating that FeCl₃ was reduced to FeCl₂ or FeCl₂·2H₂O, which is uniformly distributed in the micropores of the hyper-cross-linked EPS. (h) SEM image and (i–j) elemental mapping of C and Fe corresponding to the pink rectangle area in (h). (k) EDS and (l) XRD pattern of G4-3-9Fe showing that FeCl₂ or FeCl₂·2H₂O was reduced to Fe clusters, which were evenly distributed in the matrix of FLG sheets.

Scheme 2. Schematic Representation of the Formation Mechanism of FLG Sheets by Concerted Catalysis of Dense Fe Cluster Array

Endnote: (a) FeCl₂-loaded hyper-cross-linked EPS, (b) Fe cluster-loaded FLG sheets, and (c) FLG sheets.
The formation mechanism of FLG sheets from EPS was clarified based on the well-accepted dissolution–precipitation mechanism of graphitic flake growth on metallic Fe (Figure 4b–l and Scheme 2). In general, Fe was incorporated into C to form Fe₃C at around 600 °C[21] and Fe₃C was decomposed into α-Fe and carbon atoms, precipitating as graphitic sheets with the increase of temperature (above 800 °C).[21] The decomposition temperature of Fe₃C usually decreased with the reduction of the size. As a result, the nanosized Fe₃C decomposed at 600 °C, showing a high graphitization catalytic activity of the nanosized Fe particles.[29] The uniformly loaded small-sized FeCl₂ particles in the micropores of hyper-cross-linked EPS constructed an arranged array (Figures 4b–g and S4 and Scheme 2a) and were reduced to Fe cluster array below 600 °C during the carbonization process (Figure 4h–j,l and Scheme 2b). The freshly formed graphene domain on Fe clusters (about 0.3–1.0 nm deriving from HRTEM image in Scheme 2) had highly active edges, which absorbed adjacent carbon atoms so that the small graphene domain grew up with the increase of temperature and growth time.[30] The dense Fe cluster array coordinately catalyzed neighboring graphene domains connected with each other to form continuous graphene sheets.[30] The high crystallinity of G4-3-6 confirmed the high catalytic activity of Fe cluster array at 600 °C(Figure 1c,d).[29] The 1.2 nm thickness of FLG sheets composed of about three-layer graphene was ascribed to the small size of Fe clusters. At a high temperature of 900 °C, the noncrystalline boundary between the FLG sheets was inclined to crack due to the ordered arrangement of disordered carbon atoms.

The formation of dense Fe cluster array determines the production of FLG sheets. G4-10-9 has a smooth surface of graphene sheets and a high crystallinity because the high loading of FeCl₂ results in the formation and concerted catalysis of dense Fe cluster array (Figures S5a,b and S6). On the contrary, the dense Fe cluster array could not form due to the low loading of FeCl₂ in the precursor so that G4-0.6-9 shows a fragmented shape, rough surface (Figure S5c,d), and low crystallinity, which are confirmed by a high I₀/I₇ value and a weak 2D band (Figure S6).

High cross-linked density and microporous structure of EPS are critical to form a dense Fe cluster array and achieve high carbon yield that contributes to the large-scale synthesis of FLG sheets. Preparation of highly cross-linked and microporous EPS by hyper-cross-linking reaction must avoid the dissolution of the EPS in DCE and maintain a close distance between PS chains. The pre-cross-linking reaction using HAc as solvent and FDA as cross-linker is an effective solution strategy (Scheme 3). The original microcellular and walls of the EPS are maintained despite a small deformation by the pre-cross-linking reaction of 4 h (Figure 5a). The occurrence of Friedel–Crafts alkylation is demonstrated by the increase of the relative intensity of the peak at 2851 cm⁻¹ attributed to the symmetric stretching vibration of −CH₃− and the decrease of the relative intensity of the peaks at 3026 and 3060 cm⁻¹ ascribed to the stretching vibration of the =C−H on the benzene ring (Figure 5c), compared with the Fourier transform infrared spectroscopy (FT-IR) spectrum of standard PS.[31] The constructed −CH₃− cross-linking bridges between the benzene rings support resistance to dissolution of pre-cross-linked EPS in DCE. After the hyper-cross-linking reaction for 3 h, disappearance of the characteristic peaks of the monosubstituted benzene ring between 1667 and 2000 cm⁻¹ indicates that the monosubstituted benzene rings almost entirely convert into poly-substituted benzene rings (Figure 5c,d),[32] i.e., G4-3 has a high cross-linking density, which agrees with the high carbon yield of over 70% from EPS. The thickness of the PS wall greatly increases due to the expansion of spacing between the PS chains caused by swelling, resulting in the production of a large number of micropores (Figure 5b).
in which FeCl₂ particles can be uniformly loaded. Anyhow, the obtained carbon products with or without pre-cross-linking (Figure S7) indicate that pre-cross-linking is vital to obtain FLG sheets with high crystallinity.

The high electrical conductivity of the FLG sheets was investigated by the open circuit consisting of two pieces of close copper tapes equipped with a multimeter. Their electrical conductivity is close to that of shear-exfoliated graphene nanoplates (Figure 6a–d), which is confirmed by the Nyquist plots of G4-3-9 and shear-exfoliated graphene (Figure 6e,f). This should be ascribed to the high crystallinity of FLG sheets that is comparable to that of the shear-exfoliated graphene nanoplates. The capacitance performance of FLG sheets reflects their structure (Figure 6g–h). The cyclic voltammetry (CV) curves with a quasi-rectangular shape at different scan rates even at 200 mV s⁻¹ (Figure 6g) demonstrate a double-layer capacitance characteristic and a small equivalent series resistance (ESR) with a rapid ion response, which is confirmed by the Nyquist plot with no semicircle in the high-frequency region (Figure 6e). Minimum ESR facilitates ion diffusion into pore channels. The fast transmission of ions is further confirmed by the chronopotentiometry (CP) curves with symmetrical triangles and without distinct voltage drop (IR) related to resistance even at 5.0 A g⁻¹ (Figure 6h) and is related to large holes from curved shape of isolated FLG sheets, which exist as powder, which agrees with the SEM results.

3. CONCLUSIONS

We have successfully developed a novel, safe, and controllable method to prepare micron-sized FLG sheets with high crystallinity using waste EPS as a precursor. The products have a high content of crystalline FLG sheets that can be obtained at a low temperature of 700 °C and are composed of three-layer graphene due to concerted catalysis of a dense Fe cluster array. Their electrical conductivity is comparable to that of shear-exfoliated graphene nanoplatelets due to high crystallinity. The FLG sheets exist as powder, which can extend their applications. The yield of over 70% from waste EPS is beneficial to the scale-up of the production of FLG sheets, which provides an effective way for the recycling of waste EPS.

4. EXPERIMENTAL SECTION

4.1. Materials. Chemically pure FeCl₂, 1,2-dichloroethane (DCE), and glacial acetic acid (HAc) were ordered from National Pharmaceutical Group Chemical Reagent Co., Ltd., China. Analytically pure formaldehyde dimethylacetal (FDA) was bought from Shanghai Aladdin Biochemical Technology Co., Ltd., China.

4.2. Preparation of FLG Sheets. The wasted EPS as a precursor was broken up into small particles, which were washed by deionized water and dried in an oven at 60 °C. In a typical synthesis process, 0.3 g of clean EPS particles were blended with 10 g of FeCl₂. The mixture was added into a solution of HAc (40 mL) and FDA (5.6 mL) at 80 °C for pre-cross-linking of EPS under vigorous stirring. Four hours later, pre-cross-linking EPS particles (labeled as G4) were obtained by leaching, washing, and drying at 60 °C. After that, G4 was swelled in DCE (40 mL) at 60 °C for 1 h under vigorous stirring, forming a suspension. The addition of FeCl₂ (3 g) into the suspension was regarded as the starting of a hyper-cross-linking reaction. After reaction for 16 h, FeCl₂ was reduced to FeCl₃, which was loaded in interior micropores of hyper-cross-linked EPS by the evaporation of DCE at 60 °C. The obtained FeCl₂-loaded hyper-cross-linked EPS was signed as G4-3Fe. Subsequently, G4-3Fe was heated up to 900 °C at 2 °C min⁻¹ and held for 2 h in a nitrogen flow in a quartz tubular furnace and the obtained product was marked as G4-3-9Fe. Finally, the FLG sheets (tagged as G4-3-9) were prepared after removing the Fe-containing salts in G4-3-9Fe by 2 M HCl. Besides, G4-3-6, G4-3-7, and G4-3-8 were, respectively, synthesized by carbonization at 600, 700, and 800 °C to study the catalytic activity of Fe clusters and the catalytic formation mechanism of FLG sheets.

To investigate the effect of pre-cross-linking on the formation of the FLG sheets, the G0-3-9 without pre-cross-linking and G2-3-8 and G2-3-9 with the pre-cross-linking of 2 h were, respectively, prepared. In addition, G4-3 was fabricated by removing FeCl₂ in G4-3Fe.

4.3. Characterization. The morphology and structure of graphene sheets were investigated by an FEI Quanta 200 field emission scanning electron microscope (FESEM) and an FEI TECNAI G2 F20 transmission electron microscope (TEM). X-ray diffraction (XRD) spectra were recorded on a Y-2000 X-ray diffractometer with a Cu Kα radiation ($\lambda$ = 0.15406 nm, 40 kV, 40 mA). Raman spectra were obtained on a Renishaw
microscope system RM 2000 with laser excitation of 532 nm, and peak fitting was performed by OriginLab. X-ray photoelectron spectroscopy (XPS) was carried out on an AXIS Supra photoelectron spectrometer, and peak fitting was performed by CasaXPS. Fourier transform infrared (FT-IR) spectra were tested on a TENSOR 27 FT-IR spectrometer. The thermal stability of FLG sheets in the air and the carbonization process of FeCl2-loaded hyper-cross-linked EPS in nitrogen flow were monitored at a heating rate of 10 °C min−1 using a TGA/DSC 1 synchronous thermal analysis produced by METTLER TOLEDO. The thickness of FLG sheets was investigated by an FM-Nanoview 1000 atomic force microscope (AFM).

The capacitance performance of the FLG sheets was evaluated in an aqueous 2.0 M KOH solution on a CHI 660D electrochemical workstation with a standard three-electrode system using nickel foam as the working electrode with mass loading of >1 mg, Hg/HgO electrode as the reference electrode, and Pt foil as the counter electrode.24 A round sheet test electrode was fabricated by pressing a stainless steel wire current collector with a round sheet test electrode was fabricated by pressing a stainless steel wire current collector with a film of 80 wt % G4-3-9 (about 1.1 mg), 10 wt % acetylene black, and 10 wt % poly(tetrafluoroethylene) (PTFE) mixture. Cyclic voltammetry (CV) curves were obtained at different scan rates and voltage range of −0.5−0 V. The chronopotentiometry (CP) curves were obtained at various current densities within the same voltage range.

The electrical conductivity of the FLG sheets and shear-exfoliated graphene nanoplates were studied by electrochemical impedance spectroscopy (EIS) using a glassy carbon electrode (Φ = 5 mm) as the working electrode. Twenty microliters of the ink from dispersed G4-3-9 (1 mg) or shear-exfoliated graphene nanoplates (1 mg) and naphthol (5 μL) in ethanol (1 mL) was respectively dropped into the working electrode and dried at room temperature. The Nyquist plots of the G4-3-9 and shear-exfoliated graphene nanoplates were measured in an aqueous solution of 2 M KOH within 0.1 Hz to 100 kHz frequency range at the open-circuit voltage of the AC amplitude of 5 mV at room temperature. The electrical conductivity of the samples was also investigated by the designed open circuit consisting of two pieces of copper tape at a distance of tens of microns on an insulated glass slide and two electrodes of the multimeter. Five microliters of the as-prepared 2 mg mL−1 suspension of FLG sheets or shear-exfoliated graphene nanoplates and ethanol was added dropwise to the crack between close copper tapes and dried at room temperature. The resistance of the samples was measured after setting the meter to the ohm scale.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03743.

Digital images, SEM images, and TEM images of the reference samples; fitted I_R/I_Q values (PDF)

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Notes

The authors declare no competing financial interest.

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