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Wang, Mei-xian; Liu, Qi; Li, Zhe-Fei; Sun, Hong-fang; Stach, Eric A.; and Xie, Jian, "Structural Modification of Graphene Sheets to Create a Dense Network of Defect Sites" (2013). *Birck and NCN Publications*. Paper 1400.  
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Structural Modification of Graphene Sheets to Create a Dense Network of Defect Sites

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Supporting Information

ABSTRACT: Pt/graphene composites were synthesized by loading platinum nanoparticles onto graphene and etched at 1000 °C in a hydrogen atmosphere. This results in the formation of a dense array of nanostructured defect sites in the graphene, including trenches, nanoribbons, islands, and holes. These defect sites result in an increase in the number of unsaturated carbon atoms and, consequently, enhance the interaction of the CO2 molecules with the etched graphene. This leads to a high capacity for storing CO2; 1 g of the etched samples can store up to 76.3 cm3 of CO2 at 273 K under ambient pressure.

SECTION: Surfaces, Interfaces, Porous Materials, and Catalysis

Graphene is a single atomic layer of sp2-bonded carbon atoms arranged in a honeycomb crystal structure and can be viewed as an individual atomic plane of the graphite structure.1 It is the basic building block of the allotropes of carbon and can be stacked to form 3D graphite, rolled to form 1D nanotubes, and wrapped to form 0D fullerenes.2 Long-range π-conjugation in graphene yields extraordinary thermal, mechanical, and electrical properties, and thus, graphene has been the subject of extensive theoretical and experimental investigation.3 A single-atom-thick graphene sheet has a theoretical specific surface area of 2630 m2/g, which makes graphene an ideal candidate for gas adsorption.4 However, like carbon nanotubes, graphene is ineffective in this role as the binding strength of gas molecules on its surface is weak.5 In graphene, each carbon atom uses three of its four valence band (2s, 2p) electrons (which occupy the sp2 orbit) to form covalent bonds with the neighboring carbon atoms in the same plane. Each carbon atom in the graphene contributes its fourth p electron to form a delocalized electron system. The carbon atoms in the graphene plane are saturated carbon atoms, with the three sp2 electrons forming three covalent bonds and the fourth p electron forming a π bond. Thus, these carbons atoms are relatively inert and are not prone to form a strong van der Waals interaction with the gas molecules. Several studies have shown that the binding strength of gas molecules, such as molecular hydrogen, can be substantially enhanced by doping alkali or transition metals on the graphene sheets.6–13 This is because significant charge transfer from the metal to the graphene substrate occurs, which results in an increased interaction between the gas molecules and the graphene.

Graphene can be made by several methods, including manual exfoliation of the top surface of small mesas of pyrolytic graphite,14,15 chemical vapor deposition on a metal surface,16 and epitaxial growth on an electrically insulated surface such as SiC.17 However, large-scale applications of graphene require simple and cost-effective methods. Hence, the exfoliation of graphite oxides followed by chemical reduction is still the primary route to make graphene.18 In this study, multilayer graphene sheets were produced from graphene oxide and used as a support for Pt nanoparticles. The Pt/graphene sheet composites were heat treated at 1000 °C in a hydrogen atmosphere to create vacancy sites within the graphene sheet. Atomic-scale observations of this reaction process were made in situ with an environmental transmission electron microscope and showed that this reaction is very effective at creating substantial numbers of defect sites. The resulting materials were investigated for use as the absorbent for carbon dioxide physisorption. Results show that in the heat-treated composites, carbon dioxide adsorption was increased 2-fold in comparison to that in the non-heat-treated composites, with a measured uptake of 76.3 cm3 of CO2 per gram. This indicates that the...
defect sites created by the Pt nanoparticle etching enhance the interaction of the gas molecules with the graphene. Graphene is generally quite inert when exposed to gases such as oxygen and hydrogen at room temperature. At high temperatures, oxygen exposure can cause preferential etching at defect sites because the carbon atoms at the defect sites are reactive (this is because the p electrons of these carbon atoms may not be involved in the conjugated electron system). In a hydrogen atmosphere, the carbon atoms in the graphene bulk remain inert even at high temperatures. However, carbon atoms near defect sites of a graphene sheet become very active when a reactive metal is on or nearby these atoms. At high temperatures, one would expect Pt nanoparticles to etch graphene through the catalytic hydrogenation of carbon, where carbon atoms on the graphene dissociate on the surface of Pt nanoparticles and then react with H2 at the Pt nanoparticle surface to form methane. This process is shown schematically in Figure 1.

The mechanism of etching of graphene by Pt nanoparticles at elevated temperature was studied in situ using high-resolution environmental transmission electron microscopy (Cs-corrected Titan 80/300 ETEM). Graphene sheets were loaded with 20 wt % of Pt nanoparticles and subsequently placed onto a lacey carbon TEM grid. The samples were heated to 1000 °C, and hydrogen gas was slowly introduced into the TEM objective lens and equilibrated at a pressure of approximately 50 mTorr. As the Pt nanoparticles began to etch the graphene, the process was imaged continuously through the use of a high-frame-rate camera (see Supporting Information Movies S1 and S2). Image sequences extracted from these two movies are presented as Figure 2. Initially, the Pt nanoparticles were static after the hydrogen gas was introduced. In Figure 2a–c, the Pt nanoparticles began to react with the carbon atoms (presumably at defect sites) and the hydrogen gas to produce methane. Only those carbon atoms that were in direct contact with these Pt nanoparticles were able to participate in this Pt-catalyzed hydrogenation reaction. Once the process was initiated, the conversion process was able to continue as there was an abundance of defect sites created continuously following the onset of the etching process, leading to a self-sustaining reaction. In this case, a straight trench was etched through the graphene sheet (Figure 2a–c). In other cases, the etching process did not follow a straight line but rather followed a more tortuous pathway (Figure 2d–f). During the graphene etching process, the Pt nanoparticles were observed to maintain a crystallographic relationship with the graphene sheet at all times, as is particularly evident in the movies (Supporting Information, Movies S1 and S2). These observations are consistent with prior work and indicate clearly that the interaction between the Pt and the graphene at elevated temperature can create a variety of in-plane nanostructures in the graphene. The result of these interactions is the formation of nanoscale trenches, ribbons, and islands and thus a dense network of edge sites. XPS analysis (Supporting Information, Figure S1 and Table S1) supports our hypothesis that Pt etching increased the number of edge sites. The C==C sp² peak of Pt–graphene sheets appears at about 283.5 eV, which is...
lower than the 284.2 typically observed in graphene. The decrease in binding energy might be caused by an interaction between the graphene and the Pt nanoparticles.\textsuperscript{26} After H\textsubscript{2} etching of Pt–graphene sheets, the C=C sp\textsuperscript{2} peak shifts to a higher binding energy of about 284.1 eV. This shift is believed to be related to the formation of defective sp\textsuperscript{2} carbon atoms.\textsuperscript{27}

Figure 3. Comparison of the morphology of the original graphene and the Pt nanoparticle/graphene composites after the etching process. (a) Multilayer graphene sheets with many folds. (b) Pt nanoparticle/graphene composites after etching at 1000 °C; the formation of different graphene nanostructures within the sheets, including nanoribbons and islands, is apparent.

Figure 4. N\textsubscript{2} adsorption isotherms and CO\textsubscript{2} capture properties of graphene composites. (a) The N\textsubscript{2} isotherms for graphene, Pt/graphene, and Pt/graphene at 1000 °C and 77 K. P/P\textsubscript{0}, relative pressure; STP, standard temperature and pressure. (b) Enlarged plot of N\textsubscript{2} isotherms for Pt/graphene and Pt/graphene at 1000 °C and 77 K. (c) The CO\textsubscript{2} adsorption isotherms for graphene, Pt/graphene, and Pt/graphene at 1000 °C and 273 K; filled and open symbols represent adsorption and desorption branches, respectively. (d) CO\textsubscript{2} adsorption enthalpy calculated for graphene, Pt/graphene, and Pt/graphene at 1000 °C.
Another possible cause of this shift is the loss of interaction between the Pt and the graphene sheets. During the process of H₂ etching, those carbon atoms that have a strong interaction with the Pt nanoparticles were etched away, resulting in the shift toward higher binding energy.

Our real-time observations indicate that the heat treatment process creates an abundance of defect sites, in the form of embedded nanostructures of trenches, ribbons, and islands in the multilayer graphene sheets (see Figures 2 and 3b). The resulting materials are anisotropic, having different properties both in-plane and out-of-plane. Importantly, the carbon atoms along the edges of the resulting trenches, ribbons, and islands are likely to be unsaturated, with one of the electrons in the sp² orbitals not forming a covalent bond with the other carbon atoms. The resulting material provides an important platform for a wide variety of applications, including in catalysis, biomedical science, polymer science, and energy science. This is because these unsaturated carbons allow graphene to be functionalized by chemically grafting other compounds or groups to the surface of the graphene sheet. As a result, these functionalized graphenes can be used, for example, in drug delivery or as sensors, catalysts, sorbents, and so forth. Without such features, it is impossible to chemically graft compounds or groups onto graphene. These unsaturated carbons also promote the establishment of weak bonding between graphene and other species. One such application is gas adsorption. Of particular interest is the adsorption of carbon dioxide, which we explore as an example below. Our premise is that the p₂ electrons and one sp² electron of these unsaturated carbon atoms near defect sites will be available for bonding and will more readily form bonds with CO₂ molecules, which could in turn result in a significant improvement in CO₂ adsorption.

To investigate this premise, we have performed gas adsorption measurements. The nitrogen adsorption isotherms of graphene, the as-deposited Pt/graphene, and the etched Pt/graphene composites (Figure 4a and b) exhibit a type-I adsorption curve at low relative pressures (<0.4) and an H4 hysteresis loop (slit-like pores) at relative pressures between 0.5 and 1.0, consistent with the presence of micropores, mesopores, and some macropores in these samples. Similarly shaped isotherms were also observed in the work of Ma et al.18 The BET surface areas of the graphene, the as-deposited Pt/graphene, and the etched Pt/graphene composites were 573, 333.1, and 396.7 m²/g, respectively (Table S2, Supporting Information). After loading with the Pt nanoparticles, the BET surface area of the graphene was reduced; this might be due to the blocking of existing pores by the Pt nanoparticles. The surface area of the Pt/graphene composites increased slightly after the hydrogen treatment, consistent with the observed increase in surface defect sites, as shown in Figure 3. The isotherms for CO₂ adsorption at 273 K for the graphene, the as-deposited Pt/graphene, and the etched Pt/graphene composites (Figure 4c) traced a type-I adsorption curve at 760 Torr.29

On all three samples, the CO₂ adsorption showed good reversibility, suggesting that the adsorption is mainly controlled by physisorption. The curves did not reach saturation. The graphene samples showed a CO₂ adsorption amount of about 35 cm³ of CO₂ per gram at 273 K at ambient pressure, which is similar to values reported in the literature.30 The etched Pt/graphene composite was able to store up to 76.3 cm³ of CO₂ per gram, which is significantly higher than that of the as-deposited Pt/graphene sample. The uptake value of CO₂ at 273 K for the etched Pt/graphene composite increased by 103.4 and 233.4% in comparison with the graphene and Pt/graphene samples, respectively. Yaghi’s group has performed extensive work on the preparation of zeolitic imidazolate frameworks (ZIFs) and the investigation of ZIFs as sorbents for carbon dioxide storage.31 The maximum uptake value of CO₂ for ZIFs (ZIF-69) was found to be 69 cm³/g at around 273 K at ambient pressure, a value that is smaller than that of the etched Pt/graphene composite reported here under similar conditions. The CO₂ adsorption enthalpy of graphene, Pt/graphene, and Pt/graphene at 1000 °C was calculated and is shown in Figure 4d. The values of the BET surface area, the CO₂ uptake (mass-based and surface area normalized), and the CO₂ adsorption enthalpy are listed in Table S2 (Supporting Information) for the different sorbents. For gas physisorption, the main factors that affect gas uptake are (1) the interaction between the gas molecules and the sorbent surface (i.e., the active sites) and (2) the surface area of the sorbent. The surface area of ZIF-69 was 950 m²/g, while the surface area of the etched Pt/graphene composite was only 396.7 m²/g. The CO₂ uptake normalized by the sorbent surface area (second row in Table S2, Supporting Information), which excludes the surface area effect on the CO₂ uptake, showed that the etched Pt/graphene composite achieved a 164.4% and a 179.7% increase in CO₂ uptake in comparison with that of the ZIF-69 and the as-deposited Pt/graphene, respectively. These data reveal two key points; the Pt nanoparticles do not play a major role in promoting the CO₂ uptake on graphene (from the marginally increased CO₂ uptake, 0.066 versus 0.069 cm³/m² = graphene versus as-deposited Pt/graphene), but the structures formed as a result of the heat treatment do. Thus, the high CO₂ storage capacity of the etched Pt/graphene composite is probably a result of the strong interaction between the CO₂ molecules and defect sites formed by etching the Pt/graphene composites. Returning to the prior discussion, it is suggested that the interaction of CO₂ molecules with the carbon atoms on the defect sites of the graphene surface was enhanced as the result of a combination of the increased number of carbon atoms with unsaturated sp² orbitals and the free p₂ electrons at the defect sites. Consequently, the increase of defect sites in Pt/graphene composites etched at 1000 °C results in a higher CO₂ uptake. This combined effect is further supported by the CO₂ adsorption enthalpy (a direct indicator of the interaction between gas molecule and the sorbent surface), which increased from 20 to 26.3 kJ/mol, after the Pt/graphene was heat treated (Table S2, Supporting Information). This increase in adsorption enthalpy suggests a stronger physisorption of CO₂ on etched Pt/graphene composites than that on graphene and Pt/graphene.32

In summary, in situ TEM was used to study the Pt nanoparticle etching of graphene sheets and revealed that numerous vacancy sites are formed by this process. The etching of the graphene by platinum nanoparticles can produce a dense array of nanostructured features and edge sites in the graphene, which, in turn, generates many unsaturated carbon atoms. The resulting graphene is ideally suited to a wide range of applications. These samples were investigated as a sorbent for CO₂ physisorption and showed significant increases in CO₂ uptake. The unsaturated carbon atoms produced from the Pt-enhanced etching of graphene enhance the interaction of the CO₂ molecules with the graphene sheets, resulting in the observed enhanced CO₂ uptake. This work indicates a new approach to exploit graphene nanostructures and provides a new avenue for graphene applications.
ASSOCIATED CONTENT

Supporting Information
Description of experimental methods, XPS data, and CO₂ adsorption data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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ACKNOWLEDGMENTS

This work was partially supported by the multidisciplinary Undergraduate Research Initiative (MURI) of Indiana University–Purdue University Indianapolis (IUPUI). This research was also carried out in part at the Center for Functional Nanomaterials of Brookhaven National Laboratory (US-DOE Contract DE-AC02-98CH10886).

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