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Fabrication of holey graphene: Catalytic oxidation by metalloporphyrin–based covalent organic framework immobilized on highly ordered pyrolytic graphite

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Abstract

We report a facile chemical method for fabricating holey graphene by catalytic oxidation of highly ordered pyrolytic graphite (HOPG) using an Fe(III) porphyrin complex-based covalent organic framework (COF) as a bifunctional surface catalyst–template. We demonstrate regular hole formation after oxidation with H_2O_2 and NaOCl , COF removal, and HOPG exfoliation.

Graphical Abstract

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Arrays of holes are patterned on highly ordered pyrolytic graphite (HOPG) by catalytic oxidation using an Fe(III) porphyrin covalent organic framework surface catalyst–template and $\text{H}_2\text{O}_2/\text{NaOCl}$. The oxidation localizes in the vicinity of Fe(III) ions immobilized on the surface of HOPG, facilitating hole formation near the metal catalytic center and generating patterned holes. Subsequent exfoliation conveniently provides multiple holey graphene sheets.

Keywords

covalent organic framework; holey grapheme; catalytic oxidation; nanopatterning; surface catalyst

Porous graphene substrates (i.e., holey graphene,^[1] graphene nanomesh,^[2] graphene foam^[3]) have been fabricated for modification of the intrinsic zero energy bandgap of semimetallic graphene,^[2a,4] and recently have shown great promise as gas separation membranes with good mechanical properties^[5] Various fabrication methods using graphene oxide as a precursor have been reported including chemical (e.g., KOH activation^[6] and HNO_3 oxidation^[7]) and physical etching (e.g., photoelectron beam, oxygen plasma, and ion irradiation).^[2c,8] Related holey graphene (i.e., holey reduced graphene oxide) has been prepared by enzymatic and photocatalytic oxidation.^[1b,1d,9] Direct perforation of graphene precursors requires deposition on solid templates before patterning holes.^[2a,9a] These

preparation methods involve multiple oxidation and reduction steps, require high-cost nanolithography equipment, and are time-consuming.

Our strategy for developing a new type of nanopatterning employs a bifunctional metallated covalent organic framework (COF) which serves as a surface catalyst and a master template for creating holes on graphite that is subsequently exfoliated into multiple patterned graphene sheets. This copy–print process eliminates the need of preparing graphene–template superlattices on a solid support, and ultimately allows for scalable production of patterned graphene. The metallated COF is immobilized onto the graphite surface and provides a polymeric network of metal–ligand catalyst^[9d], thereby maintaining the catalytic center and reactive site for oxidation at the interface between the catalyst and the substrate. Once the catalytic oxidation is complete, the COF layer is chemically removed and then the patterned graphite is exfoliated. In the nanopatterning for fabricating holey graphene, COFs provide unique advantages: (i) The regular arrangement of the repeating catalytic centers enables precise localization of chemical reactions, (ii) the periodicity (the center-to-center distance between two neighboring holes) can be conveniently controlled by reticular synthesis with different spacers or linkers, (iii) COFs can be directly grown on graphite, simplifying the cumbersome pre-patterning step for template deposition, and (iv) COF ligands can prevent aggregation of metal ions resulting from metal leaching and Fe(III) dimerization initiated by hydrolysis in aqueous environments,^[10] and thus generate relatively uniform hole sizes in contrast to metal and metal oxide nanoparticles.

Inspired by the studies of peroxidase-catalyzed oxidative biodegradation of carbon nanomaterials^[11] and the use of synthetic Fe(III) porphyrin catalysts for oxidation of polycyclic aromatic hydrocarbons (PAHs),^[12] we develop an oxidative method of patterning holes on the basal plane of graphite using a synthetic Fe(III) porphyrin COF as a catalyst–template. Porous graphene is prepared on the highly ordered pyrolytic graphite (HOPG) surface in the presence of H₂O₂ and NaOCl oxidants (Figure 1).

The metalloporphyrin COF (Fe-DhaTph-COF) was synthesized following the previously reported procedure.^[13] Iron(III)-tetrakis(4-aminophenyl)porphyrin chloride (Fe-TAP-Cl) was prepared with iron(II) chloride tetrahydrate (FeCl₂·4H₂O) and 5,10,15,20-tetrakis(4-aminophenyl)porphyrin (Figure S1).^[14] To grow the metallated COF (Fe(III)-DhaTph-COF) directly on graphite, condensation of Fe-TAP-Cl and 2,3- dihydroxybenzene-1,4- dicarbaldehyde was performed at 120 °C in a convection oven. The polymerization was also attempted in a gas-tight vessel under atmospheric conditions at 90 °C as described in the literature,^[15] but there was no sign of COF formation. Instead, a flame-sealed pyrex tube was used, in which about 5–8 pieces of mechanically cleaved HOPG (0.5 mm × 0.5 mm) flakes were immersed in the reaction mixture before the flame seal. After 6 d of condensation *in vacuo* under the solvothermal condition, Fe-DhaTph-COF-deposited HOPG flakes were collected. A black powder of Fe-DhaTph-COF was collected from the same reaction batch for further characterization (see Figure S2 and S3). Fe-DhaTph-COF catalyst was also prepared by complexation of Fe(III) with already synthesized DhaTph-COF in a separate post-polymerization step. Then a solution of DhaTph-COF coordinated with Fe(III) was deposited on HOPG by either dipcoating or drop-casting and dried at 50 °C. The

morphological characteristics of the different deposition methods were analyzed by AFM (Figure S5a–d).

As demonstrated in peroxidase-catalyzed oxidation of carbon nanomaterials where an oxidant such as H_2O_2 converts Fe(III) into a reactive intermediate species Fe(IV)=O^{+} and produces hydroxyl radical,^[11a,11b,16] we hypothesize that synthetic Fe(III) -porphyrin catalysts would oxidize graphite in a similar fashion. To perform the oxidative patterning of the COF-deposited HOPG, each sample was placed in 0.5 mL of acetonitrile in a 1-dram vial. The oxidative condition was adjusted based on the Fe(III) -catalyzed oxidation of benzene and polycyclic aromatic hydrocarbons (PAHs).^[12] The use of co-oxidants $\text{H}_2\text{O}_2/\text{NaOCl}$ with a synthetic porphyrin catalyst is unprecedented although their noncatalytic oxidation of organic substrates has been reported.^[17] Nonetheless, we sought to examine if the role of hypochlorite (OCl^-) formed in situ in the peroxidase-catalytic cycle of the oxidation of carbon nanomaterials could be also applicable to the COF-catalytic system. The catalytic cycle of Fe(III) was activated by addition of H_2O_2 every 4 h. The co-oxidant system was tested by addition of NaOCl 2 h after the H_2O_2 -activation. Upon addition of NaOCl , it immediately reacted with extra H_2O_2 remaining in the solution, resulting in vigorous formation of oxygen gas that can initiate singlet oxygen-mediated oxidation.^[17]

After the metallated COF was removed from the HOPG surface, the morphology of HOPG was analyzed by transmission electron microscopy (TEM) and atomic force microscopy (AFM). The pristine HOPG sheets exfoliated with H_3PO_4 ^[18] do not exhibit significant defects (Figure 2, panels a, c, and e). In contrast, the HOPG samples treated with oxidants ($\text{H}_2\text{O}_2/\text{NaOCl}$) at 65 °C clearly show dense holes on the surface. As shown in the TEM image (Figure 2b), catalytic oxidation on the Fe-DhaTph-COF deposited graphite resulted in the formation of continuous hole arrays of 4–50 nm in diameter, consistent with holes of 8–40 nm found in the AFM image (Figure 2d). This pattern suggests that the Fe(III) ions coordinated to the COF were anchored to the graphite surface and facilitated oxidative degradation. Based on the pore size of DhaTph-COF (ca. 2.3 nm) reported in the previous study,^[13] the hypothetical hole periodicity can be roughly estimated by measuring the distance between Fe-DhaTph-COF catalytic centers. The average hole periodicity of 8.3 nm and the average neck width (the smallest edge-to-edge distance between two neighboring holes) of 2.0 nm measured on TEM images were larger than the periodicity of Fe(III) catalytic center (i.e., the distance between porphyrin rings). The elongated pattern suggests that defect formation laterally propagated over the nearby graphitic surface. When a pH 5.0 acetate buffer solution was mixed with acetonitrile (1:1, v/v) to see if increasing formation of HOCl accelerates oxidation,^[19] samples exhibited relatively large, random holes (Figure S6a–c and S6e).

The hole nanoarrays were also created by H_2O_2 -activated oxidation (Figure S6d and S6f), but a larger amount of oxidant was required to generate a significant holey structure than the co-oxidant system. The co-oxidant system is efficient for a short-term treatment probably because hypochlorite can induce reactive singlet oxygen-mediated oxidation by insertion of peroxy groups (O—O) on the graphitic carbons without a catalyst. Once sp^2 carbons are substituted with the oxygen-containing groups, bond cleavage of C—C can undergo readily.^[17a] As hypochlorite can serve solely as an effective oxidant under non-catalytic conditions,

we conducted a control reaction with only hypochlorite (OCl^-). However, no repeating holey structure was observed, suggesting that the Fe-DhaTph-COF catalyst was critical to generating site-selectivity for patterning.

To successfully realize the copy-print concept in the fabrication of multiple holey graphene sheets, defect formation needs to propagate vertically and create regular nanochannel arrays through several graphitic layers. AFM height analysis after COF removal reveals that the vertical channel propagated from the top surface is about 1–3 nm (Figure S8). Some large holes indicate that the oxidation process may have laterally expanded the defect area, or sonication during exfoliation may have caused several neighboring holes to collapse and form large holes. In addition, the COF catalyst should not be disintegrated under the oxidative condition and protect the metal-catalytic centers, thereby maximizing catalytic activity and engineering site-selective patterning. The morphology of Fe-DhaTph-COF deposited on HOPG after oxidation/before COF removal shows that much of the COF catalyst remained intact under the oxidative condition (Figure S9a).

Exfoliation of the pristine HOPG sample was not greatly effective. After an extensive amount of time of sonication (6 h) and stirring in DMF (2 d) at room temperature, the pristine HOPG sample afforded stacked graphene sheets of 2–4 nm in height (Figure 2e). Oxidized samples were easily exfoliated by sonication in 10–30 min, depending on the extent of oxidation applied to a sample. The height of patterned samples was <3 nm (Figure S8c), and a few 2- or 3-layers (<1 nm in height) of patterned graphene were observed (Figure 2f). Longer sonication times (>total 1 h) were attempted, but reduced the lateral size of graphene sheets, which may not be ideal for achieving high surface-volume-ratios.

We analyzed changes in the functional group of HOPG before and after oxidation using diffuse-reflectance infrared Fourier transform spectrometry (DRIFTS) analysis. The spectra of patterned HOPG and freshly cleaved HOPG samples are almost identical (Figure 3a). Generally, IR absorption spectra for HOPG and graphite samples are featureless, but the overall band profile of mechanically cleaved HOPG appears close to those of graphene and graphene oxide.^[20] The patterned HOPG shows a new peak at 1705 cm^{-1} , which can be attributed to C=O stretching modes due to oxidation.^[21] Raman spectroscopy was utilized to quantify the number of newly formed sp^3 defects relative to pristine sp^2 graphitic carbons and characterize the defect type (Figure 3b). The average $I_{\text{D}}/I_{\text{G}}$ value of the samples treated with $\text{H}_2\text{O}_2/\text{NaOCl}$ is 0.31 whereas only a residual peak (1331 cm^{-1}) is shown in the pristine HOPG spectrum. The peak width (fwhm) of D' band at $1607\text{--}1635\text{ cm}^{-1}$, indicative of the formation of vacancy-like defects, appears far more pronounced than those of other samples. To investigate the effect of deposition method, the average $I_{\text{D}}/I_{\text{G}}$ values are compared (Table S1). The direct growth method has slightly higher $I_{\text{D}}/I_{\text{G}}$ values than drop-casting for both H_2O_2 and $\text{H}_2\text{O}_2/\text{NaOCl}$ systems. Based on Raman spectroscopic data, both deposition methods were effective in oxidatively patterning graphite. Under the same oxidative treatment catalyzed by Fe-DhaTph-COF, X-ray photoelectron spectroscopy (XPS) confirms the presence of carboxylate OC=O ^[22] or carbonyl C=O ^[23] (C1s: 288.7 and O1s: 533.4 eV) and C—O (C1s: 285.9 and O1s: 532.1 eV) in a flake sample (Figure 3c and d).^[24] Approximately 82% of the carbon atoms were graphitic carbons (C=C) intact after

oxidation. The details of quantitative information are described in the Supporting information.

Powder X-ray diffraction (PXRD) was undertaken to correlate synthesized Fe-DhaTph-COF with earlier reports.^[13] Comparison of DhaTph-COF with and without Fe can be found in Supporting information(S2). Computational efforts correlating Fe-N distances to d-spacing from PXRD data can also be found in Supporting information (S13, Table S2).

In summary, we demonstrated a facile chemical patterning method of utilizing an Fe(III) porphyrin COF as a surface catalyst and a template. The fabricated few-layer graphene sheets exhibited holey structures after treatment with H₂O₂ or H₂O₂/NaOCl. However, the size and shape of holes varied depending on the oxidative condition and the proximity to the catalytic site. The use of low-cost, ubiquitous iron as a catalyst with H₂O₂ and NaOCl can potentially advance green chemistry, in that this oxidative condition is also applicable in the design of synthetic reagents and industrial production that eliminates high energy consumption. The copy-print concept of oxidative patterning and exfoliation will allow for facile processing and scalable production of patterned holey graphene. Future studies will focus on tuning the oxidative condition to achieve precise, uniform patterning and the controlled 2D hole morphology.

Experimental Section

Deposition of Fe-DhaTph-COF.

A direct growth procedure of Fe-DhaTph-COF on HOPG was described in the synthesis of Fe-DhaTph-COF section (Supporting Information). A solution of Fe-DhaTph-COF in post-polymerization process was prepared in DMF (1 mg/1 mL). Mechanically cleaved HOPG flakes were sequentially rinsed with DI H₂O, ethanol, and hexanes and dried in a petri dish on a hot plate for 24 h at 50 °C. About 100 µL of the solution was drop-cast on a HOPG flakes on a glass slide and dried at 100 °C. The dip-coating method was performed on clean HOPG flakes that were completely immersed in the COF solution with tweezers and were stored for about 12 h. Then the flakes were dried in the same fashion.

Addition of oxidants.

A dried Fe-DhaTph-COF on HOPG flake was placed in a 1-dram vial containing 0.2 mL of acetonitrile or a mixture of acetonitrile: pH 5.0 buffer (1:1, v/v). 20 µL of a H₂O₂ solution 30% (w/w) was added, followed by gentle shaking for 30 s. The same amount H₂O₂ solution was replenished at every 4 h (20 µL per addition). When NaOCl was employed as a co-oxidant, 20 µL of a NaOCl solution (available chlorine 10–15 %) was added after 2 h of the H₂O₂ addition. The capped vial was placed in a sand bath at 65 °C. When the oxidative patterning was completed, the COF on HOPG was removed by the wash cycle of NaOH (5 M solution), HCl (7 M solution), NaOH (1 M solution), DI water, and acetone. The sample was stored in each different solution of the acid and the base over 12 h with occasional stirring.

Exfoliation of patterned HOPG flakes.

An oxidized HOPG flake was transferred to a 1-dram vial containing 2 mL of DMF. After bath sonication for 10–30 min, the exfoliated HOPG suspended in DMF was collected in a new 1-dram vial. After DMF was dried *in vacuo*, concentrated phosphoric acid (0.5 mL) was mixed with the HOPG. The mixture was ground with a glass rod and heated in air at 125 °C for about 12 h. The acid treated HOPG in fresh DMF (2 mL) was bath sonicated for about 30 min and stirred in DMF (6 mL) at room temperature.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

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Figure 1. Illustration of fabricating holey graphene with Fe-DhaTph-COF catalyst deposited on HOPG and exfoliation of the patterned bulk graphite.

Figure 2.

Micrographs of TEM (a)–(b) and noncontact mode AFM amplitude (c)–(d) and height (e)–(f). (a) and (c) Pristine HOPG. (b) and (d) Patterned HOPG with Fe-DhaTph-COF and $\text{H}_2\text{O}_2/\text{NaOCl}$ (80 μL /80 μL). Mean hole size in (d) is $159 \pm 153 \text{ nm}^2$. (e) Exfoliated pristine HOPG (Height: 2.9 nm). (f) Exfoliated sample of oxidized HOPG with Fe-DhaTph-COF and $\text{H}_2\text{O}_2/\text{NaOCl}$ (Height: 0.73 nm).

Figure 3.

(a) DRIFTS spectra of HOPG samples before and after oxidation. (b) Raman spectra of the patterned HOPG sample (Fe-DhaTph-COF in the presence of $\text{H}_2\text{O}_2/\text{NaOCl}$, total addition of 80 $\mu\text{L}/80 \mu\text{L}$) shows distinct D and D' bands. Each of the spectra was normalized to the G peak for ease of comparison. (c) C1s and (d) O1s high resolution XPS spectra after oxidative patterning with Fe-DhaTph-COF.