Precise CO₂ Reduction for Bilayer Graphene

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ABSTRACT: It is of great significance to explore unique and diverse chemical pathways to convert CO₂ into high-value-added products. Bilayer graphene (BLG), with a tunable twist angle and band structure, holds tremendous promise in both fundamental physics and next-generation high-performance devices. However, the π-conjugation and precise two-atom thickness are hindering the selective pathway, through an uncontrolled CO₂ reduction and perplexing growth mechanism. Here, we developed a chemical vapor deposition method to catalytically convert CO₂ into a high-quality BLG single crystal with a room temperature mobility of 2346 cm² V⁻¹ s⁻¹. In a finely controlled growth window, the CO₂ molecule works as both the carbon source and the oxygen etchant, helping to precisely define the BLG nucleus and set a record growth rate of 300 μm h⁻¹.

INTRODUCTION

The CO₂ reduction reaction (CO₂RR) is involved in hydrodeoxygenation (HDO), C–C coupling, and aromatization processes. This reaction has received much attention for its significance in recycling CO₂ into value-added chemical feedstock and exploring unique reaction pathways for transforming and utilizing CO₂. Armed with state-of-the-art electrochemistry, photochemistry, and thermocatalysis, CO₂ can be converted into C₁ (methanol, formic acid), C₂ (ethylene, ethanol), and C₂+ products (propanol, aromatics). Bilayer graphene (BLG), with a tunable band gap and bizarre phenomena at a magic stacking angle, holds tremendous promise for next-generation electronic and twistronics devices under 3 nm. However, the selective pathway from CO₂ to a BLG single crystal has never been activated, due to the difficulty in precisely splitting the inert C=O bond and the perplexing growth mechanism. In addition, in the conventional chemical vapor deposition (CVD) system, once the first graphene layer fully covers the copper surface, nucleation of the second layer becomes restricted, significantly suppressing the BLG’s growth. Reducing CO₂ molecules into a high-quality BLG single crystal would broaden the understanding of CO₂ reduction and simultaneously harvest a precious electronic material.

With both carbon (C) and oxygen (O) atoms, carbon dioxide (CO₂) is a greener and safer C source in graphene growth compared with conventional CH₄. After stripping O from CO₂ in a controllable manner, the active C fragments can participate in building π-conjugated graphene. On the other hand, the residual O atom has been widely reported to be beneficial to BLG growth. In previous studies, using a tandem catalytic CVD method, single-layer graphene (SLG) with a single crystal structure can be synthesized from CO₂ feedstock. Our group also demonstrated a tandem electrochemical-CVD system to efficiently convert CO₂ into an SLG film, providing a way for tunable CO₂ transformation. Nevertheless, there is no BLG reported in these works, due to inappropriate oxygen content caused by uncontrolled CO₂ reduction. A moderate amount of O can remove the undesirable carbon and open the carbon diffusion channel for BLG nucleation. By introducing O-rich copper and oxygen-containing molecules such as ethanol, both the quality and growth rate of BLG were improved.

Here, we demonstrate a catalytic strategy in CVD systems to precisely reduce CO₂ into BLG single crystals by finely tuning the growth window. With CO₂ providing both carbon as the BLG growth feedstock and oxygen as an etching reagent, we can realize the growth of large BLG single crystals with unprecedented swift kinetics. We also measure the electrical transport properties based on BLG single crystals; the mobility can reach 2346 cm² V⁻¹ s⁻¹ at room temperature.

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RESULTS AND DISCUSSION

The BLG single crystal is grown by a CVD method in a home-built tube furnace equipped with dual heating zones as shown in Figure 1. Given that the CO$_2$ molecule is too inert by itself to be converted into graphene, 1.5 sccm CO$_2$ is preliminarily activated with 200 sccm H$_2$ to produce more reactive carbon species in the first heating zone. This zone is equipped with commercial catalyst Ni/Al$_2$O$_3$ and operated at an optimal temperature of 300 °C. Components of the gas mixture are quantitatively analyzed in a following tail gas chromatography (GC) setup. The activated feed gas further flows into the second heating zone with a temperature of 1055 °C and is converted into a BLG single crystal on a polished copper foil substrate.

The as-prepared BLG single crystals can be directly observed under optical microscopy (Figure 2a). Specifically, many hexagonal crystals were stacked on top of a uniform SLG film. Their thickness and stacking mode were determined using Raman spectroscopy according to their full width at half maximum (FWHM) of the 2D peak and the intensity ratio between the 2D peak and G peak ($I_{2D}/I_G$). For a typical hexagonal graphene crystal, the Raman mapping of FWHM and $I_{2D}/I_G$ at different regions shows even intensity, indicating that the whole hexagonal crystal has a uniform thickness and stacking mode (Figure 2b,c). Corresponding values of FWHM of the 2D peak and $I_{2D}/I_G$ are ∼53−54 cm$^{-1}$ and 0.7−0.8, respectively, consistent with characteristics of AB-stacked BLG (Figure 2d). While in areas not covered by the hexagonal crystals, the counterparts are ∼30−35 cm$^{-1}$ and 1.2−1.5, respectively, manifesting an SLG signature. It is worth noting that although the graphene is grown in an etching CO$_2$ atmosphere, we did not observe any D peaks in both the single-layer and bilayer region. A small amount of CO$_2$ was reported to selectively remove amorphous carbon without compromising the lattice of graphene. BLG is also known to display a higher etching resistance and a slower etching rate than SLG. Thus, we did not observe any obvious defect in our BLG samples. Besides, the $I_{2D}/I_G$ mapping of a BLG single crystal shows minimum variation, with a ratio close to 0 (Figure S1), suggesting an intact atomic arrangement with negligible defects. The BLG single crystals produced from CO$_2$ display an average lateral size of ∼200 μm, with an optimized value of ∼220 μm (Figure 2e and Figure S2).

Detailed structure information on a BLG single crystal was further studied by transmission electron microscopy (TEM). The edge of the graphene under TEM observation displays a clear bilayer structure (Figure 2f). The crystal lattice adjacent to the edge exhibits a periodical hexagonal symmetry, whose lattice pattern is in good agreement with that of graphene (Figure 2g). A high crystal quality in most regions of BLG is evidenced by an orderly lattice arrangement with nearly no defects, correlating with the D peak absence in Raman spectra. Stacking mode and crystal orientation of the BLG can be clearly measured by selected area electron diffraction (SAED). In ∼73% of the BLG regions, the intensities of the diffraction spots at (1100) and (0110) facets are about half of those at (2110) and (1120) facets, strongly supporting the AB-stacked BLG structure (Figure 2h and Figure S3). We also observed ∼27% BLGs with 30° twisted angles (Figure S4), a ratio in agreement with the Raman spectra. Specifically, we analyzed Raman signals of 100 randomly selected single crystals. AB-stacked BLG is the dominated bilayer product in our system, accounting for ∼72% of the total number of the BLG single crystals based on Raman spectra statistics, while the remaining ∼28% are mostly 30°-twisted BLG single crystals. We can also observe sharp edges of the BLG domains through optical microscopic images. The AB-stacked BLG domains account for ∼75%, and the rest are mostly 30°-twisted angles (Figures S5 and S6). It had been reported that the orientation of the second graphene layer can be affected by the environment of graphene growth, such as the variation in gas flow and distinct interface energy between the adlayer graphene and graphene/
Cu steps. According to theoretical calculations, AB-stacked and 30° are the top two stable structures in twisted BLG, which is consistent with our experimental observations in Figures S3, S5, and S6.

In addition, SAED results at several different spots spreading across a large area (20 × 30 µm²) show that all of the diffraction patterns can be overlapped very well, indicating a single crystal structure nature of the BLG with identical crystalline orientations (Figure S7).

To understand the kinetic process of BLG growth from CO₂, we monitored the graphene growth with different time duration under the same condition (Figure 3a–d, Figure S8). We found that the adlayer graphene formed on the hexagonal SLG islands in the first 10 min (Figure S5). Within 40 min of growth, the SLG islands merged into a fully covered SLG film, while the adlayer graphene gradually grew into a larger single crystal with a size up to 220 µm. By measuring the domain size with the growth time, the rate of the first layer growth was calculated to be 1200 µm h⁻¹ (Figure 3e). Although slower than the first layer, the growth rate of the adlayer still reaches 300 µm h⁻¹ (Figure 3f). To the best of our knowledge, it is the highest growth rate of BLG single crystals among reported works (Figure S9 and Table S1). As the reaction continued, the BLG single crystals gradually transformed into multilayer graphene (MLG; Figure S10). At 20 min, the number ratio of BLG’s nucleus to MLG’s nucleus (N_{BLG}/N_{MLG}) reaches 50; the amount of BLG nuclei can still be dominant at 40 min with N_{BLG}/N_{MLG} also being 8 (Figure S9).

Figure 2. Structure of the BLG single crystal. (a) Optical image of a typical AB-stacked BLG single crystal on a 300 nm SiO₂/Si substrate (scale bar: 50 µm). Raman mapping of (b) the FWHM of the 2D peak and (c) the I_{2D}/I_{G} of the BLG single crystal in panel a (scale bar: 50 µm). (d) Raman spectra measured at Area 1 and Area 2 in panel a. (e) Size distribution of the as-prepared BLG single crystals. (f) HRTEM image of the AB-stacked BLG’s edge (scale bar: 5 nm). (g) AB-stacked BLG lattice extracted from the white dash-line box in panel f after the inverse Fourier function transformation (IFFT) treatment (scale bar: 1 nm). (h) SAED pattern of a typical AB-stacked BLG and the corresponding intensity profile of the diffraction spots along (2110), (1100), (0110), and (1120).
After 40 min, the density of MLG nuclei kept increasing, while both the density of the BLG’s nuclei and the $N_{BLG}/N_{MLG}$ continuously declined (Figure 3g). At 40 min, the size and the density of the BLG single crystal reach the optimal values.

![Figure 3. Kinetics of BLG single crystal growth.](image)

![Figure 4. Growth mechanism of the BLG single crystal.](image)
measuring the area of BLG single crystals, the coverage of BLG single crystals on the surface of SLG reaches ~65% after 40 min of growth (Figure S12). The catalytic transformation of CO2 into graphene in our system involves many chemical processes such as deoxidation and hydrogenation.1 In order to further reveal the mechanism of BLG growth, we analyzed the tail gas with GC equipped with a hydrogen flame ionization detector (FID) and thermal conductance detector (TCD). A typical tail gas indicated H2 (97.9%), CH4 (0.6%), CO (0.08%), CO2 (0.04%), and H2O (1.3%) in our growth system (Figure S13). Among these gases, CH4 is the most common carbon source broadly reported in graphene growth.41,42,43 No graphene was grown, and no CH4 was detected in the tail gas when we fed CO2 and H2 into a tube furnace without Ni/Al2O3 activation (Figures S14 and S15). Therefore, CH4 in situ formed from CO2 hydrogenation is most likely the effective carbon source in our experiment as well. In addition, in the case of only CH4 and H2 (1.5:200) fed into our system, only the SLG film was found with no BLG nucleus (Figure S16), indicating that the oxygen atoms originating from the inlet CO2 are also necessary for the BLG growth (the CO2 hydrogenation mechanism can be found in the Materials and Methods section). To ensure that there is no oxygen introduced to the copper foil, Cu foil could also be annealed in a H2 atmosphere instead of O2. Under this condition, BLG single crystals can still be grown as shown in Figure S17, indicating that the possible oxygen in copper foil does not play a significant role in BLG growth.

In our experiment, we observed an enhanced D peak in the Raman spectrum after treating the SLG film with pure CO2 at the growth conditions (Figure S18). This indicates an increase in the number of defects. While SLG was annealed in a pure H2 atmosphere, its Raman spectrum changed little (Figure S19), suggesting a much weaker etching capability of H2 compared to CO2. Meanwhile, it has been reported that H2 tends to etch the edge of graphene,40 while CO2 can attack both the edge and surface.41.42 Given that all of the nuclei of adlayer are located within the first graphene layer, we believe that BLG’s nucleation originates from CO2 etching rather than H2 etching.

During the growth, we found that the growth windows for BLG and MLG are quite close to each other. In order to optimize the system growth pressure (P) for the favored BLG growth, we kept the CO2/H2 ratio at 1.5:200 and studied the BLG growth under different pressures ranging from 800 to 1600 Pa (Figure 4a-d, Figures S20 and S21). We found that the optimal P is ~1100–1200 Pa, under which conditions the BLG coverage reached its highest value while the nucleation density of MLG was still relatively low (Figure 4e). A similar optimal P can be derived under a series of BLG growth experiments performed under different CO2/H2 ratios (1:200 and 2:200) (Figures S22-S25).

Both etching (O atoms) and growing (CH4) components coexist in our system, which impose opposite effects on graphene formation. To rationalize this competitive relationship, we thereby define a relative concentration ratio of [O]/[CH4], where [O] is determined by inlet CO2 content and system pressure P, and [CH4] is controlled by the conversion yield from CO2 to CH4 with catalyst Ni/Al2O3. A tail gas analysis reveals that the [O]/[CH4] presents a negative correlation with the P (Figure 4f). A higher P favors a smaller [O]/[CH4] ratio, corresponding to a higher conversion yield of CO2 to CH4. In Figure 4g, the MLG density reduced monotonically against [O]/[CH4]. By contrast, the nucleation of BLG follows a “volcano” curve versus the relative ratio, with an optimal BLG growth window located at a [O]/[CH4] ratio of 2.3–2.6 (Figure 4h). Therefore, the growth pressure P plays the most important role in the conversion of CO2 to BLG. Based on our results, we propose a possible role of CO2 in our BLG growth (Figure 4i). Composed of O and C atoms, CO2 can simultaneously serve as an etching gas and carbon source for graphene growth. First, the oxygen atoms provided by CO2 create defects on SLG, which break the SLG self-limiting growth and host the nucleation sites for BLG. It was reported that such defects with a low energy barrier could serve as the BLG nucleation centers.1,12,13,36 Around the defect, Cu–O and C–O bonds can promote decomposition of CH4 and nucleation of the second graphene layer. Therefore, the CH4 produced from CO2 can be deposited on the defect sites to form the second layer. Furthermore, a moderate amount of oxygen atoms inhibit the further growth of MLG, giving rise to a high selectivity toward BLG.

It has been reported that BLG, with weaker temperature-dependent scattering than SLG, exhibits a higher mobility (µ).43 In order to evaluate the mobility of BLG, we fabricated a back-gate field effect transistor (FET) device based on our BLG single crystals, with the schematic diagram shown in Figure 4a. A graphene channel was constructed based on the BLG sample. Au/Ti electrodes work as the source and drain and the silicon wafer works as the bottom-gate. Figure 5b is the optical image of the back-gate FET device. Calculated from the transfer characteristic data in Figure 5c,44 the µ is ~2.346 cm2 V−1 s−1 at room temperature. The value is comparable to those of CVD-grown BLG using CH4 as the carbon source.36,45,46

CONCLUSIONS

In conclusion, we have successfully developed a unique catalytic strategy to precisely convert CO2 into a high-quality graphene.
BLG single crystal with large size, swift growth rate, and high electronic performance. Facilitated by oxygen atoms originating from CO$_2$, the growth rate of BLG is accelerated to $\sim$300 $\mu$m h$^{-1}$, the fastest kinetics reported to the best of our knowledge. An appropriate concentration of etching oxygen atoms not only creates the precise nucleation centers for BLG but also inhibits the MLG formation. Through this finely tuned precise reduction of CO$_2$, larger BLG can be grown more quickly and reliably, boosting the development for next-generation electronic and twistronic devices.

**MATERIALS AND METHODS**

**Graphene Preparation.** BLG Single Crystal Growth from CO$_2$. A piece of 30 $\mu$m thick Cu foil was first electrochemically polished in a polishing solution composed of 25 mL of H$_2$O and 75 mL of H$_3$PO$_4$ under 5 V and 2 A for 30 s on both sides. After being washed with deionized water and dried under N$_2$ flow, the polished Cu foil was placed in the second heating zone of the CVD system; the commercial catalyst Ni/Al$_2$O$_3$ (Sichuan Shutai Co. Ltd.) was loaded in the upstream side of the Cu foil. To prevent impurities from depositing on the copper foil, the space between the catalyst and the copper foil was filled with quartz wool. When the CVD system was pumped to 20 mTorr for 30 min, the Cu foil was put into the heating zone of a furnace. To deplete carbon impurities, Cu foil was annealed in an O$_2$ atmosphere with a partial pressure of $\sim$5 mTorr for 10 min. Before that, the catalyst was heated at 300 °C in the first heating zone until the pressure remained stable. The reaction was then carried out at 1055 °C with 200 sccm H$_2$ and 1–2 sccm CO$_2$ under 800–1600 Pa for 5–120 min. After growth, the Cu foil was cooled to room temperature under 100 sccm H$_2$ for 30 min.

**SLG Growth from CH$_4$.** A piece of 30 $\mu$m thick polished Cu foil was placed in a quartz tube of our CVD system. When the CVD system was pumped to 20 mTorr for 30 min, the Cu foil was put into the heating zone of the furnace, and then the Cu foil was annealed in an O$_2$ atmosphere with a partial pressure of $\sim$5 mTorr for 10 min. Then, the reaction was carried out at 1055 °C with 200 sccm H$_2$ and 1.5 sccm CH$_4$ under 1200 Pa for 40 min. After growth, the Cu foil was cooled to room temperature under 100 sccm H$_2$ for 30 min.

**Graphene Transfer to Wafer from Cu Foil.** The graphene/Cu samples were coated with 2 drops of 6% PMMA solution (poly(methyl methacrylate), M$_w$ 50 000, in anisole) by spin-coating, and then, the samples were etched by 0.5 mol L$^{-1}$ hydrochloric acid for 5 min and 0.1 mol L$^{-1}$ BOE solution (8 g of ammonium fluoride in 2 mL of hydrofluoric acid and 12 mL of deionized water). After the etching process, the PMMA-coated graphene samples were cleaned by deionized water and then transferred to a TEM grid and heated at 85 °C for 10 min. Finally, PMMA was dissolved by hot acetone.

**Graphene Transfer to TEM Grid from Cu Foil.** The graphene/Cu samples were coated with 2 drops of 6% PMMA solution (M$_w$ 50 000) by spin-coating; after the copper was etched, the PMMA-coated graphene samples were cleaned by deionized water and then transferred to a TEM grid and heated at 85 °C for 10 min. Finally, PMMA was dissolved by hot acetone.

**Structural Characterization.** The as-prepared BLG single crystal, transferred onto a 300 nm SiO$_2$/Si substrate, was characterized by Raman spectroscopy and optical microscopy (LabRAM HR, 514 nm laser wavelength). The graphene samples were peeled from the SiO$_2$/Si substrate for further TEM characterization (HT7700 EXALENS, 120 kV; and TECNAI G2 F20 S-TWIN, 200 kV) and SEM characterization (NOVA NANOSEM 450, 5 kV). The electrical transport properties were measured by a KEYSIGHT probe station (B1500A) equipped with a PICO probe (ST-20-S).

**Growth Mechanism Studies.** CO$_2$ Hydrogenation Mechanism. The CO$_2$ hydrogenation includes two processes, as shown below:

\[
\begin{align*}
\text{CO}_2 + \text{H}_2 & = \text{CO} + \text{H}_2\text{O} \\
\text{CO}_2 + 4\text{H}_2 & = \text{CH}_4 + 2\text{H}_2\text{O}
\end{align*}
\]

The mathematical derivation of the relative oxygen ratio $([\text{O}]/[\text{CH}_4])$ is presented as follows:

\[
\frac{[\text{O}]}{[\text{CH}_4]} = \frac{2 \times [\text{CO}_2]_{n_0}}{[\text{CH}_4]} = \frac{2 \times (P_{\text{CO}_2} + P_{\text{CO}} + P_{\text{CH}_4})}{P_{\text{CH}_4}}
\]

$[\text{CO}_2]_{n_0}$ is the initial concentration of inlet CO$_2$ into the CVD system. The total concentration of oxygen atoms, existing as CO$_2$, CO, and H$_2$O in the system, is determined by the inlet CO$_2$ concentration and pressure as eqs 1 and 2 show.

**Collection and Analysis of Intermediate Gases.** A pipe was connected at the back of the CVD system before the reaction. During the BLG growth process, we collected 500 $\mu$L of the tail gas from the CVD system by a sampler and injected the mixture into a GC equipped with a TCD and FID for further analysis.

**Process of Etching Graphene by CO$_2$.** A piece of SLG/Cu foil was prepared based on the synthesis method of SLG. When the CVD system was pumped to 20 mTorr, the SLG sample was put into the heating zone of a furnace. Then, the etching process was performed at 900 °C with 1.5 sccm CO$_2$ under 262 mTorr for 1 min. After the process, the sample was cooled to room temperature under 1.5 sccm CO$_2$.

**Process of Etching Graphene by H$_2$.** When the system was pumped to 20 mTorr, the SLG sample was put into the heating zone of a furnace. The SLG was annealed at 900 °C with 200 sccm H$_2$ under 110 Pa for 1 min. After the etching process, the sample was cooled to room temperature under 200 sccm H$_2$.

**FET Device Based on BLG Single Crystals.** Fabrication of the FET Device. The BLG single crystal grown on copper was transferred to a SiO$_2$/Si substrate with the PMMA-assisted method. A photoreist was spin-coated on the surface of the BLG sample which was then baked at 170 °C for 3 min. A graphene channel with a width of 5 $\mu$m was preserved. Other regions were exposed by electron beam lithography (EBL), and the photoreist was washed away by the developer solution. Unwanted graphene regions were etched away by O$_3$ plasma. The sample was covered again by the photoreist. A pattern of
source and drain electrodes were exposed by EBL and the photoresist was washed away, followed by the deposition of 15 nm Ti and 70 nm Au on the pattern by physical vapor deposition (PVD). After being cleaned by acetone, the back-gate FET device based on the BLG single crystal was fabricated.

**Calculation of Mobility of the FET Device.** The calculation is based on eqs 4 and 5.

\[
\mu = \frac{dI_d}{dV_g} \times \frac{L}{W C_i V_d}
\]

(4)

Here, \(dI_d/dV_g\) is 2.6979 × 10^{-5}, the channel length \(L\) is 5 \(\mu m\), the channel width \(W\) is 5 \(\mu m\), \(V_d\) is 1 V, and the capacitance between the channel and the gate per unit area \(C_i\) is 1.15 × 10^{-4} F m^{-2}.

\[
C_i = \frac{\varepsilon_0 \varepsilon_r d}{d}
\]

(5)

Here, \(\varepsilon_0\) is 3.9, \(\varepsilon_r\) is 8.85 × 10^{-12}, and \(d\) is 300 nm.

**Safety Statement.** **Caution!** Hydrofluoric acid solution is extremely corrosive. It must be handled very carefully in the hood. Face masks, safety goggles, and double nitrile gloves are needed when using this reagent.

**Caution!** Hydrogen is classified as a GHS Flammable Gas, Category 1. Safety goggles are mandatory, and the hydrogen alarm next to the CVD system needs to be activated during the graphene growth process.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscentsci.1c01578.

Additional information regarding optical, Raman, SEM, and TEM characterizations; statistics of the BLG stacking mode; SAED overlaps; GC analysis; and a literature summary (PDF)

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**Author Contributions**

P.G., C.T., Q.L., and Z.S. conceived the project, analyzed the data, and wrote the paper. P.G. and C.T. conducted the growth and transfer of BLG single crystals and ran the optical microscopy, Raman microscopy, SEM, and TEM tests. P.G. analyzed the gas products. P.G., B.W., and H.Z. fabricated the FET devices and calculated the mobility. T.X. drew the schematic illustration. Z.S. and Q.L. supervised all research phases and revised the paper. All authors read and commented on the paper.

**Author Contributions**

∥P.G. and C.T. contributed equally.

**Notes**

The authors declare no competing financial interest.

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