Graphene, a two-dimensional carbon sheet,[1] has attracted great interest due to its unique properties.[2,3] To explore its practical applications, large-scale synthesis with controllable integration of individual graphene sheets is essential. To date, numerous approaches have been developed for graphene synthesis, including mechanical cleavage,[1] epitaxial growth,[4] and chemical vapor deposition.[5] All of those techniques are used to prepare flat graphene sheets on a substrate. Chemical exfoliation of graphite has been applied to prepare graphene oxide solutions and graphene-based composite materials.[6,7] Recently, tuning graphene shapes is attracting much attention.[8–16] Cheng and co-workers synthesized graphene foam using porous Ni foam as a template for the CVD growth of graphene, followed by etching away the Ni skeleton.[8] The graphene foam consists of an interconnected flexible network of graphene as the fast transport channel of charge carriers for high electrical conductivity. Ruoff et al. prepared porous graphene paper from microwave exfoliated graphene oxide by KOH activation.[9] The porous graphene, which has an ultra-high surface area and a high electrical conductivity, was exploited for supercapacitor cells, leading to high values of gravimetric capacitance and energy density. Feng, Müllen, and co-workers synthesized hierarchical macro- and meso-porous graphene frameworks (GFs).[10–12] The GFs exhibited excellent performance for electrochemical capacitive energy storage. Yu et al.[13] and Qu et al.[14] fabricated graphene tubes that could be selectively functionalized for desirable applications. Choi et al. synthesized macroporous graphene using polystyrene colloidal particles as sacrificial templates in graphene oxide suspension,[15] and the pore sizes can be tuned by controlling template particle size.[16] These important results represent a significant topic—tuning the properties of graphene sheets by controlling their shapes. However, it is still a challenge to synthesize three-dimensional graphene (3D) with a desirable shape.

Herein, we develop a novel strategy for the synthesis of a new type of graphene sheet with a 3D honeycomb-like structure by a simple reaction between Li2O and CO. Furthermore, these graphene sheets exhibited excellent catalytic performance as a counter electrode for dye-sensitized solar cells (DSSCs) with an energy conversion efficiency as high as 7.8%, which is comparable to that of an expensive platinum electrode.

Li2O is widely exploited as a promoter in catalysts to inhibit carbon formation.[17] However, this general principle is challenged by this work, in which Li2O is used to react with CO to form graphene-structured carbon [Eq. (1)]

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\text{Li}_2\text{O} + 2\text{CO} \rightarrow \text{C(graphene)} + \text{Li}_2\text{CO}_3
\] (1)

This strategy is supported by our thermodynamic calculations: The Gibbs free energy change is negative, indicating that this reaction is thermodynamically favorable (Figure S1 in the Supporting Information). The negative enthalpy change (\(\Delta H_{298} = -397.5 \text{kJ mol}^{-1}\)) suggests it is an energy-economic process. Furthermore, simultaneous formation of Li2CO3 with graphene can isolate the graphene sheets from each other to prevent graphite formation during the process. On the other hand, the Li2CO3 particles will also play a role in determining the locally curved shape of the graphene sheets. The feasibility of this novel approach was confirmed by following experiments.

1 mol of lithium oxide (Li2O) powder (from Aldrich) was treated with CO in a batch ceramic-tube reactor at an initial pressure of 35 psi and temperature of 550°C for 12, 24, or 48 h. The products were subjected to X-ray diffraction (XRD) measurements. As shown in Figure 1, diffraction peaks for Li2CO3 can be observed, confirming the reaction between Li2O and CO. The conversions of Li2O are 87, 90, and 92% for 12, 24, and 48 h, respectively. The average crystal size of Li2CO3 is 40 nm. The products were treated with hydrochloric acid to remove Li2O and Li2CO3, then washed with H2O, and dried at 80°C, the black powder was obtained and identified as carbon by elementary analysis. Surface areas are 151, 153, and 128 m² g⁻¹ for the carbon samples prepared with 12, 24, and 48 h, respectively. Their pore sizes are mostly in the range from 115 to 170 nm.

Field emission scanning electron microscopy (FESEM) was employed to evaluate the structure of the carbon powder.
As shown in Figure 2a and b, the graphene sheets are curved with thickness of about 2 nm, and connect to each other and form a 3D honeycomb-like structure. The cell size of graphene honeycombs lies in the range of 50–500 nm. The micro-structure of honeycomb cells was further evaluated by transmission electron microscopy (TEM). The TEM image showed the intrinsic wrinkles or corrugations of the cell sheets (Figure 2c). Furthermore, the curved shapes of honeycomb-structured graphene (HSG) were further supported by electron diffraction that shows poly-crystalline ring patterns (Figure 2d). Different from spot patterns of flat graphene sheets,

[18,19] ring diffraction patterns arise from scrolled or folded graphene sheets. [18] In addition, electron energy loss spectroscopy (EELS) was used to investigate the local structure of HSG sheets. As shown in Figure 3a and b, for all four selected locations, an intensive feature of sp\(^2\) bonded carbon atoms in the carbon K-edge region is seen: a peak at 285 eV corresponding to the 1s-\(\pi^*\) transition, and a peak at 291 eV associated with the 1s-\(\sigma^*\) transition. [20] However, clear differences in K-edge peaks at 532 eV (associated with oxygen groups) can be observed for different locations, namely, a large oxygen K-edge peak at 532 eV occurs at location 4, a small oxygen K-edge peak at locations 1 and 3, and no oxygen K-edge at location 2. This indicates that HSG sheets contain oxygen groups, which are heterogeneously distributed. The content of the sp\(^2\) and sp\(^3\) bonded carbon as well as oxygen groups was evaluated by X-ray photoelectron spectroscopy (XPS). As shown in Figure 3c–e, the deconvolution of the C 1s peak revealed three components centered at 284.9, 285.7, and 286.8 eV, which would be associated with sp\(^2\) carbon atoms, sp\(^3\) carbon atoms, and O-C-O groups. [22] The main component is sp\(^2\) bonded carbon (72.6–74.8%), whereas sp\(^3\) carbon (21.7–22.3%) and oxygen groups (3.5–5%) constitute a small part of graphene sheets. This is consistent with the energy dispersive spectroscopy (EDS) analysis that showed 94.6–97.5% carbon and 2.5–5.4% oxygen in HSG.
Furthermore, with increasing synthesis time for HSG, the content of sp² bonded C increases, whereas sp³ bonded C and the C–O groups decrease. Raman spectroscopy has been widely exploited to reveal the defect structure of carbon materials with characteristic peaks at approximately 1350 cm⁻¹ (D band corresponding to the breathing mode of aromatic rings with dangling bonds) and 1580 cm⁻¹ (G band associated with the bond stretching of sp² carbon pairs). The Raman spectra of HSG exhibit a clear G peak at around 1580 cm⁻¹, providing evidence of an sp² bonded carbon (Figure 4a). There is also a D peak with comparable intensity to the G peak, indicating structural defects caused by oxygen-functional groups. This is consistent with the XPS results (Figure 3c–e). Furthermore, sheet resistance of the 20 μm HSG film on bare glass is 3.4 kΩ/sq for HSG-12 h, 1.6 kΩ/sq for HSG-24 h, and 0.45 kΩ/sq for HSG-48 h (note: HSG-12, 24, or 48 h denotes HSG synthesized with reaction time of 12, 24, or 48 h). In contrast, CEG (graphene synthesized by chemical exfoliation of graphite) has a large sheet resistance (64 kΩ/sq). These results indicate that HSGs have a much higher conductivity than CEG. Therefore, the structural defects and the high conductivity of HSG offer unique opportunities for its applications related to energy conversion and storage.

The dye-sensitized solar cell (DSSC) is a third-generation photovoltaic device. As an important component in DSSCs, a counter electrode (CE) plays a role in the reduction of I₃⁻ to I⁻ for iodine-based electrolytes. An ideal CE material should have a small sheet resistance, high catalytic activity, and a low cost. Currently, platinum-loaded conducting glass is widely exploited as a CE for DSSCs. However, the high cost of platinum would limit its application. This problem has motivated the development of carbon-based CEs. Herein, we employed HSG without any conductive polymer as a CE for DSSCs. The photoelectrode of the DSSCs is N719 dye sensitized TiO₂ film on fluorine-doped tin oxide (FTO) glass plate, and the electrolyte is I₃⁻/I⁻ based liquid. The photovoltaic performance of the DSSCs is summarized in Table 1. The DSSC with HSG-12 h CE exhibited the best performance with the short-circuit current density (Jsc) of 27.2 mA cm⁻², open-circuit voltage (Voc) of 0.773 V, fill factor (FF) of 0.371, and power conversion efficiency (η) of 7.8% under illumination of AM1.5 simulated sunlight with power density of 100 mW cm⁻². This efficiency is 10-times higher than that (0.64%) of the DSSC with a CEG-based CE. Furthermore, it is even comparable to that (8%) of a Pt-based DSSC. However, when the synthesis time increased from 12 to 48 h, the efficiency of the DSSC with a HSG CE decreased from 7.8 to 6.3%. The relationship is further supported by incident photon to charge carrier efficiency (IPCE) spectra (Figure 4b). It is established that two critical factors (electrical conductivity and catalytic activity) determine CE performance for DSSCs, namely, the larger the conductivity and the catalytic activity, the higher the energy conversion efficiency.

Table 1: Photovoltaic performance and electrochemical characteristics of DSSCs.

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<tr>
<td>HSG-12 h</td>
<td>27.2</td>
<td>0.773</td>
<td>0.371</td>
<td>7.80</td>
<td>24</td>
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<tr>
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<td>0.774</td>
<td>0.325</td>
<td>6.53</td>
<td>25</td>
<td>35</td>
<td>265</td>
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<tr>
<td>HSG-48 h</td>
<td>26</td>
<td>0.773</td>
<td>0.314</td>
<td>6.30</td>
<td>24</td>
<td>45</td>
<td>310</td>
</tr>
<tr>
<td>CEG</td>
<td>6.48</td>
<td>0.785</td>
<td>0.127</td>
<td>0.64</td>
<td>27</td>
<td>2500</td>
<td>10'</td>
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[a] CE: counter electrode; HSG-12 h, HSG-24 h, and HSG-48 h: honeycomb-structured graphene synthesized for 12, 24, and 48 h; CEG: Graphene synthesized by chemical exfoliation of graphite.
efficiency is. However, when HSG synthesis time increased from 12 to 48 h, HSG conductivity increased (which is reflected by decrease in its sheet resistance from 3.4 to 0.45 kΩ/sq), whereas the efficiency of HSG-based DSSC decreased. This indicates that the decrease in efficiency with increasing HSG synthesis time is not due to the variation of HSG conductivity. It has been recognized that defects in graphene sheets are the active sites for the catalytic reduction of I$_3^-$ to I$^-$ at the CE.[90] Furthermore, it was suggested that the defects arising from nitrogen-doping could play a catalytic role.[31] Similarly, the existence of oxygen in HSG sheets could generate the defects as catalytic sites (Figure 3c–e). The XPS results showed that the increase in HSG synthesis time decreased the number of oxygen-containing groups, indicating a decrease in structural defects and thus the decrease in catalytic activity. Therefore, the decrease in catalytic activity with increasing HSG synthesis time would be responsible for the decrease in HSG-based DSSC efficiency. This notion is further supported by electrochemical impedance spectroscopy (EIS) measurements (Figure 4c). The EIS curves were fitted by equivalent circuit model with Z-view software (Figure 4c) and summarized in Table 1. The first semicircle corresponds to charge-transfer resistance (R$_ct$) at CE/electrolyte interface, which changes inversely with catalytic ability of CEs for the reduction of I$_3^-$ to I$^-$, while the semicircle in lower frequency region is attributed to Nernst diffusion process (Z$_N$).[32] As the three HSG counter electrodes have nearly the same value of R$_ct$, the effect of R$_ct$ on photovoltaic performance can be neglected. The value of R$_ct$ increases in the order of HSG-12 h (20 Ω) < HSG-24 h (35 Ω) < HSG-48 h (45 Ω), which is inverse to the order of electrocatalytic activity. Although HSG-12 h has the highest intrinsic sheet resistance, it exhibits the lowest R$_ct$ at the interface owing to it having the highest catalytic activity. Furthermore, the DSSC with a CEG has a very large R$_ct$ (2500 Ω), indicating its very low catalytic activity and thus explains why its power conversion efficiency is negligible.

Cyclic voltammetry (CV) curves were obtained for three HSG CEs, which show two pairs of oxidation and reduction peaks (Figure 4d). Since a DSSC CE mainly catalyzes the reduction of I$_3^-$ to I$^-$, which can be evaluated by the peak current density and the peak-to-peak separation ($E_{pp}$) of A$_{ox}$ and A$_{red}$ peaks, namely, the higher the peak current density and the lower the $E_{pp}$ value, the better the catalytic activity is.[33] The HSG-12 h CE showed the highest current density (1.644 mA cm$^{-2}$) and the lowest $E_{pp}$ (0.246 V) of the three electrodes (Figure 4d), indicating it has the best electrocatalytic activity. This further supports the results of J-V, IPCE, and EIS measurements. In summary, a novel approach, which is based on a simple reaction between Li$_2$O and CO, was exploited to synthesize 3D honeycomb-like structured graphene sheets. Furthermore, the dye-sensitized solar cell with the honeycomb-structured graphene counter electrode gave an energy conversion efficiency as high as 7.8%, which is even comparable to that of DSSCs with an expensive Pt counter electrode. In addition, the honeycomb-structured graphene is promising for applications in energy storage devices, such as batteries and supercapacitors.